Visible Light Photocatalytic MoO₃-Based Nanomaterials Synthesis, the Effect of Polymer Coatings on Their Photocatalytic Activity and Dissolution, and Their Applications in Water Treatment

by

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DEDICATION

I dedicate this work to my mother, Penelope, who encouraged and supported me throughout my studies, and was always there to motivate and help me wherever possible. Thank you for raising me to love and appreciate science and for inspiring me to never stop learning.

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ABSTRACT

Water reuse is becoming increasingly important as water sources are being depleted or becoming progressively contaminated. Photocatalytic metal oxide semiconductors such as MoO₃ have shown much promise in water decontamination as they can generate reactive oxygen species (ROS) that degrade pollutants. MOO_3 is an environmentally friendly, low-cost, visible light photocatalyst that has gained much popularity in research due to its effectiveness. Furthermore, MoO₃ morphology and surface chemistry are easily controlled during synthesis. In this work, MoO₃-based photocatalysts were studied to determine their efficacy in water treatment and to discover methods to improve their properties. MoO₃ photocatalytic activity was shown to improve as the number of oxygen vacancies was increased. Even though MoO₃ photocatalysts demonstrated high contaminant removal, their stability in water is poor. High dissolution was observed in a wide pH range and particle aggregation was elevated in the presence of inorganic and organic compounds, resulting in diminished photocatalytic activity. However, material dissolution was significantly reduced in the presence of inorganic and organic matter, indicating that coatings may be beneficial in improving the utility of the photocatalyst for water treatment.

Hence, conductive polymers such as polypyrrole (PPy) and polyaniline (PANI) were studied as coatings for magnetic MoO₃ to determine their effect on material dissolution and photocatalytic activity. In addition, to provide insight on the effects of the base nanomaterial on the polymerization of PPy and PANI, the polymerization kinetics of PPy and PANI on two different base MoO₃ nanomaterials were investigated. It was determined that a higher amount of oxygen vacancies in the MoO₃ base nanomaterials resulted in smaller polymer chains and faster polymerization on top of the nanomaterials. In addition, both coatings significantly reduced material dissolution while improving photocatalytic activity. A magnetic core was also added to the base material to facilitate photocatalyst removal from water. The PANI-coated magnetic MoO₃ was further studied, demonstrating high tetracycline degradation by ROS produced via the oxidation of water by photogenerated holes on the surface of

PANI after electron excitation using visible light. This work demonstrates that use of conductive polymer coatings is an excellent method in improving photocatalytic properties of nanomaterials.

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CHAPTER 1 – INTRODUCTION

In part adapted from "Nano-based Absorbent and Photocatalyst Use for Pharmaceutical Contaminant Removal During Indirect Potable Water Reuse" by S. Fanourakis, J. Peña-Bahamonde, P. Bandara, and D. Rodrigues^[1]

1. THE IMPORTANCE OF DECONTAMINATING WATER

Potable water can be considered the most important human need. However, human activities have introduced dangerous contaminants in water systems requiring a multibarrier treatment approach to purify water for potable use. From the Ganges River Basin in India to the surface water in Milan, contaminants such as pharmaceuticals and personal care products have been detected.^[2–10] These contaminants are difficult to remove and can cause harm not only to humans but to wildlife and local ecosystems as well. Pharmaceuticals, personal care products, persistent organic pollutants, methanesulfonic acids, artificial sweeteners, transformation products, and engineered nanomaterials have all been identified as current contaminants of emerging concern (CECs).^[11–14] Emerging pharmaceutical contaminants (EPCs) are of particular concern due to their potential adverse effects to humans and the ecosystem (Table 1.1). For instance, EPCs such as antibiotics can give rise to antibiotic resistant bacteria, which can cause irreparable harm to humans and the ecosystem.

Although detection of alarming concentrations of EPCs in wastewater streams has been a major concern for years, the true fate of some EPCs continues to be understudied. With the currently available information, it can be clearly seen that EPCs bioaccumulate in animal and plant tissues and often persist in the

environment.^[15,16] For example, antibiotic presence in water and related ecosystems is

already leading to an increase in antibiotic resistant bacteria.^[10,17]

EPC class	EPC examples	EPC function	Harmful effects
Analgesic	acetaminophen, phenazopyridine, non- steroidal anti-inflammatory drugs (NSAID) such as diclofenac, ibuprofen, naproxen	Pain relief, NSAIDs also reduce inflammation	Ibuprofen could interfere with cardiac benefits of aspirin ^[18] ; analgesics can cause negative developmental effects ^[19] ; diclofenac can be bioaccumulated. ^[20]
Antibiotics	tetracycline, ciprofloxacin, ofloxacin, sulfonamides (ex. sulfadiazine), amoxicillin, cefixime, metronidazole, trimethoprim	Kill or inhibit bacterial growth	Antibiotics have been shown to create antibiotic resistant bacteria (tetracycline resistant enterococci, antibiotic resistant <i>Escherichia coli</i>) and can negatively affect plant growth. ^[21] Sulfonamides are found to be associated with birth defects. ^[22]
Anticoagulant	warfarin	Disrupt blood clotting factor synthesis or function to avert formation of blood clots	Warfarin, after prolonged exposure, could lead to severe bleeding due to its prolonged inhibition of vitamin K. ^[23]
Anticonvulsant	carbamazepine	Treat epileptic seizures	Could cause cancer ^[19,24] and negatively affect reproduction and development. ^[19]
Antidiabetic	metformin, insulin, pramlintide, acarbose, chlorpropamide	Lower glucose levels in the blood	Antidiabetics, such as metformin, can act as an endocrine disruptor, and is not easily degradable and is highly mobile in the environment. ^[25]
Antihistamine	diphenhydramine	Block histamine action to treat allergic reactions	Diphenhydramine has been shown to cause acute and chronic toxicity to a variety of aquatic organisms. ^[26]
Antipsychotic	loxapine, olanzapine, risperidone, chlorpromazine, clozapine	Treat psychosis and other emotional or mental health conditions	Olanzapine, risperidone, chlorpromazine, clozapine are shown to be persistent, bioaccumulative, and toxic to human health and the ecosystem. ^[15,27] They are up-taken from hospital effluent contaminated soil and bioaccumulate in plant tissues. ^[16]
Antipyretic	antipyrine, NSAIDs	Lower fever	Antipyrine is toxic to the mucosa and lungs and can cause organ damage ^[28]
Beta-blocker	metoprolol, propranolol	Lower blood pressure	Can be toxic on organisms in aquatic environments and shows more toxicity to phytoplankton and zooplankton ^[29]
Fibrate	gemfibrozil	Lower blood triglyceride levels	Developmental side effects and carcinogenic in rodents ^[19] , toxic to aquatic organisms ^[29]
X-ray contrast agent	iopromide, diatrizoic acid	Enhance visibility of internal organs or structures for diagnostic X-rays	While x-ray contrast agents are generally non- toxic, ^[30] they persist in the environment and chlorination has been shown to cause mutagenicity and acute toxicity of iopromide ^[31]

Table 1.1. EPCs, examples, and their effects

More alarming is the amount of these contaminants ending up in effluent streams as a result of their continuous usage in the treatment of various diseases. As such, the existence of EPCs in water sources is a globally important issue requiring increased attention on how non-target organisms are affected and how EPCs can be removed from potable water.

2. BRIEF BACKGROUND ON WATER REUSE AND RECLAMATION

Due to the multiple concerns surrounding the decline of freshwater resources and increasing water demand, water reclamation and reuse projects are widely popularizing all around the world.^[32–34] With CEC detection in freshwater sources and revelations about CEC harm on human health and safety, potable water treatment facilities require careful design of additional steps to ensure water is safe for consumption.^[35–37] Conventionally, harmful contaminants are removed from wastewater with a multiple barrier approach.^[35,37,38] Primary and secondary treatment techniques are well established and capable in removing dissolved organic matter as well as larger particles (suspended particles and biodegradable solids are removed via physical and biological means, respectively).^[34,39] In the case of CECs, many stable and non-biodegradable compounds can survive these steps requiring further treatment.^[38,40]

The next treatment step is determined by different water reuse downstream approaches, which can be categorized as unplanned, direct, and indirect. The unplanned potable reuse water cycle is the simplest, where treated water is released to a natural water system after the primary and secondary treatment steps.^[34,38,39] Both direct and indirect potable reuse plants contain a tertiary (advanced) treatment step before being released from the plant. This step can include one or more of the following processes: membrane filtration, carbon adsorption, ion exchange, chlorination, and advanced oxidation processes (AOPs), such as ozone and UV radiation.^[38,39,41] Selection of the appropriate combination of tertiary operations in a water treatment plant is important as contaminants that are not removed by primary and secondary processes, such as CECs, are often removed with advanced processes.^[41,42] However, even these energy-intensive methods may not fully decontaminate water from CECs and may result in the generation of harmful byproducts.^[43,44]

While direct potable reuse water plants feed treated water from the tertiary step to the distribution system located before a drinking water treatment plant, indirect potable reuse plants purposely release it to a natural water source such as a surface water reservoir, river, sea, or groundwater aquifer^[34,38,39,45] (Figure 1.1). Direct potable water reuse is a common practice in areas with few source waters and high demands. Indirect potable reuse plant operation is plausible only when there is an adequate natural system downstream. The effluent from the treatment plant is expected to be held in the environmental buffer for a specified retention time where the water can be treated by natural processes such as direct photolysis, adsorption, filtration through natural media, and natural microbiota.^[45–47] Certain CECs can travel through the water subsurface for up to 60 days, therefore, a longer time in the buffer may reduce CEC concentrations in the source water making it cleaner for the subsequent drinking water treatment step.^[48,49] However, communities with limited natural recharge opportunities may be unable to accommodate long lag times between the discharge and reuse steps.^[46] The possibility of artificial recharge systems resembling natural buffers has been raised as a method overcoming such limitations.^[46,50]

It is important to note that uncertainties related to removal and potential hazards of unremoved contaminants can account for a considerably larger proportion of the associated risk of maintaining the plant.^[51] In terms of cost, indirect potable water treatment can cost more than the direct potable treatment mainly due to the environmental buffer used along with the indirect potable reuse plant. Although, the cost of water treatment after the environmental buffer is less for the indirect potable reuse plants as they receive much cleaner source water making it easier to treat. Furthermore, inclusion of reverse osmosis or other advanced treatment techniques increases treatment plant cost, however, currently, these techniques are the most successful in removing most pharmaceutical contaminants.^[46,52,53] Therefore, application of novel low-cost EPC removal techniques can have a clear effect on reduced water purification costs, and development of such techniques can potentially guarantee the complete removal of EPCs.



Figure 1.1. Representation of indirect potable water treatment for CECs. Contaminants such as pharmaceuticals, microorganisms, and harmful ions can be present in water.

3. THE PHOTOCATALYTIC PROCESS

Photocatalysis is a photoreactive process by which irradiation of a

photocatalyst (material capable of photocatalysis) initiates catalytic reactions. In the

absence of light, the reaction sites of the photocatalysts are typically inactive. Thus,

photocatalysts – semiconducting materials, typically metal oxides, such as titanium oxide and zinc oxide – rely on their ability to absorb light and generate reactive oxygen species, which are responsible for the degradation of pollutants.^[54,55] Composites consisting of metal doped semiconductors, as well as adsorbent materials combined with semiconductor materials can be used for photocatalytic processes.

As Figure 1.2 depicts, once light hits the surface of the photocatalyst, if the light is equivalent to or greater than the material's bandgap, electrons in the material's valence band (VB) can be excited and jump to the conduction band (CB), creating an electron-hole pair. The generated electron-hole pair is responsible for the subsequent redox reactions that generate reactive oxygen species (ROS), which react with pollutants, ultimately yielding water and carbon dioxide. The generation of ROS can be a complex process, dependent not only on the properties of the photocatalyst but also on the chemistry of the solution.^[56] The pH of the solution, for instance, can have an extensive influence on redox reactions involved in ROS production. For example, the properties of superoxide radicals $(\cdot O_2^{-})$ change depending on the acidity of the solution.^[56] In more acidic solutions protonation of $\cdot O_2^-$ occurs, which alters $\cdot O_2^$ reactivity towards organic substances.^[56] Additionally, the one-electron and twoelectron redox potentials are highly depended on pH, changing which ROS form and persist in solution.^[56] The type of ROS present can play a significant role in the ability of the photocatalyst to degrade contaminants (discussed in Section 4).



Figure 1.2. Potential redox reactions leading to the formation of reactive oxygen species in the photocatalysis process

The basis for photocatalysis is the generation of electron-hole pairs via the ability of the material to absorb light. Thus, material characteristics that promote light absorption and electron excitation are beneficial. For example, surface defects can help increase light adsorption by lowering the bandgap of the material, reducing electron-hole recombination via the introduction of defect traps, and promoting electron transfer to the surface.^[57] A lower bandgap has the potential to both increase and reduce photocatalytic efficiency. While, with a lower bandgap, electron excitation can be achieved with lower frequency light, enabling visible light absorption, the lower bandgap can also lead to an increase in electron-hole recombination, reducing

photocatalytic efficiency.^[58] Regardless, controlling the bandgap of the material is essential in increasing photocatalytic efficiency.

Material defects can be achieved via alterations to the surface morphology, or introduction of dopants. Modifications in the synthesis of the photocatalyst (pH, temperature, reagents, etc.) can change particle size and introduce morphological defects, which can change the adsorptive properties of the photocatalyst, or they can alter the bandgap of the material due to the introduction of oxygen vacancies in the structure of the material.^[58] Doping utilized to reduce the bandgap of the material and reduce recombination of the photogenerated electrons and holes, can also be effective.^[59,60] Doping can result in the introduction of trap states or formation of a heterojunction can reduce electron-hole recombination, increasing the chance of them taking part in the photocatalytic process.^[61]

4. PHOTOCATALYSTS IN WATER TREATMENT

Photocatalysis is one of the most widely studied water purification methods due to its effectiveness and potential scalability. Photocatalytic materials have been of particular interest due to their ability to both remove and degrade contaminants, which can lead to a sustainable and environmentally friendly solution for water treatment. Due to the popularity of such materials in research, literature presenting photocatalysts for the removal of pharmaceuticals have been published in recent years (Table 1.2).^[62– 65]

EPC Class	EPC	Material	Reaction Source	[EPC] (ppm)	Removal	Reaction rate, k (10 ³ /min)	Ref
		BaTiO ₃ /TiO ₂ composite	UV-Visible, 200- 800 nm, 500 W	10	82.76	9.215	[66]
		WO ₃ /TiO ₂ /SiO ₂ composite	UV-Visible, 200- 800 nm, 500 W	10	88	11.67	[67]
		graphene/titanium dioxide nanotubes	UV, 14 W	5	-	24.8	[68]
	Acetaminophen	ZnO/Sepiolite	UV		85	3.12	
		ZnO/Fe ₃ O ₄ -Sepiolite	<320 nm, 450	10	55	1.32	[69]
		ZnO/SiO ₂ -Sepiolite	W/m^2		20	0.66	
		Carbon doped TiO ₂	440-490 nm, 5 W	15.12	94	5.03	[70]
		TiO ₂ /montmorillonite	UVA with ozonation, 8 W	5	50.12	-	[71]
	Acetaminophen (paracetamol	magnetic ZnFe- CLDH/RGO composites	Solar light (>300nm), 500 W	5	95	7.37	[72]
	specifically)	TiO ₂ , TiO ₂ /cellulosic fiber	200-280 nm, 11 W	40.06	-	10.2	[73]
	Diclofenac (NSAID)	Ag ₃ PO ₄ /TiO ₂ nano- tube arrays	Simulated sunlight, 350 W	-	100	-	[74]
esic		g-C ₃ N ₄ /BiVO ₄ photoanode	Visible light, >420 nm	10	30.1	3.23	[75]
Analg		C-TiO ₂	Visible light, >400 nm, 150 W	0.050	100	33.4	[76]
		PVDF membrane with TiO ₂	Low-pressure UV, 254 nm, 40 W	0.2-0.4	Too fast for analysis		[77]
		C doped TiO ₂ coated on zeolites	Solar, 300-400 nm (65 W/m ²), 400- 570 nm (1,844 W/m ²)	0.1	>95	-	[78]
		TiO ₂	Solar light, 19° 19' 42" S and 146° 45' 36" E, sunny days between July and September	250	100	9.5	[79]
	Diclofenac sodium (NSAID)	Co ₃ O ₄ -g-C ₃ N ₄	Visible light, >420 nm, 300 W	10	20	4.69	[80]
		BiOCl nanosheets	UV, ~400 W	10	-	280	[81]
	Ibuprofen (NSAID)	g- C ₃ N ₄ /TiO ₂ /Fe ₃ O ₄ @Si O ₂ heterojunction	Visible light, 64 W	2	98	-	[82]
		Zn-Fe mixed metal oxides	Solar light, >300 nm, 500 W	250-1000	95.7	15.84	[83]
			High pressure UV, 160 W		81	8.98	
		1102-2.7% rGO SOFs	Low pressure UV, 39W	5	41 18	3.32 1.33	[84]
			Visible, 40 W				

Table 1.2. Material used in EPC removal a	and associated removal conditions
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*Continued in next page

EPC Class	EPC	Material	Reaction Source	[EPC] (ppm)	Removal	Reaction rate, k (10 ³ /min)	Ref
		TiO ₂ (in reactor with UV-LEDs)	UV <382 nm, 40 W	213	100	24	[85]
		TiO ₂ rutile nanorods	UV-Visible, 60 W	10	80	-	[86]
	н	ZnO/Sep	UV		100	6.39	
	(NSAID)	ZnO/Fe ₃ O ₄ -Sep	<320 nm, 450	10	95	4.58	[69]
	(NSAID)	ZnO/SiO ₂ -Sep	W/m ²		80	2.84	
2		POM-γ-Fe ₂ O ₃ /SrCO ₃	Solar light, N = 36° 18' 41.6", E = 59° 31' 54.2"	10	-	-	[87]
Ilges		ZnO				11.0	
Ane		TiO ₂	UV, 365 nm, 6 W	4.5	-	6.00	[88]
		$2ZnO-TiO_2$				7.64	
	Naproxen	T:O2	Solar light, 19° 19' 42" S and 146° 45'	250	06	0.2	[79]
		1102	between July and September	230	90	9.2	[,,]
	Phenazopyridine	TiO ₂ -P25 nanoparticles in photoreactor	UV-C, 254 nm, up to 13 W	10	100	-	[89]
					70	0.17	
esic retic	.	ZnO/Sep	UV	10	70	2.16	[69]
nalg tipy	Antipyrine	ZnO/Fe_3O_4 -Sep	<320 nm, 450 W/m^2	10	50	1.23	[07]
An		Zn0/S10 ₂ -Sep	w/m		50	1.27	
		ZrO2/Fe ₃ O ₄	Sunlight $30 \times 10^3 \pm$	20	66	4.32	[00]
	4-chlorophenol	ZrO2/Fe ₃ O ₄ /Chitosan	100 lx	20	88.56	8.74	[90]
	Cefixime	nano N- TiO ₂ /graphene oxide/titan grid sheets	Visible, 7.45 W/m2	5	29 w/o ozone	9.9 w/ ozone	[91]
	Cefixime		UV-Vis, <365 nm				1021
otic	trihydrate	nano α-Fe ₂ O ₃ /ZnO	(4 W), 480 nm (60 W)	10.11	99.1	-	[92]
Antib	Ciprofloxacin	mesoporous carbon (GMC)-TiO ₂ nanocomposite	UV, 254 nm, 14 W	15	100	-	[93]
	- 1	TiO ₂ /montmorillonite	UVA with ozonation, 8 W	5	80.58	-	[71]
		Bi ₂ WO ₆ nanocuboids	Visible, 400-520	10	80	8.7	
	Levofloxacin			15	69	-	[94]
			iiii, 100 W	20	60	-	
	Metronidazole	SnO ₂ - ZnO/clinoptilolite	Maximum at 435.8 nm, 35 W	2	-	13.0	[95]
		ZnO/NiO	Maximum at 435.8 nm, 35 W	2	-	16.6	[96]
		TiO ₂ /montmorillonite	UVA with ozonation, 8 W	25	64.60	-	[71]

Table 1.2 Continued Material used in EPC remova	val and associated removal condition
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EPC Class	EPC	Material	Reaction Source	[EPC] (ppm)	Removal	Reaction rate, k (10³/min)	Ref
	Oxytetracycline	Graphene/TiO ₂ /ZSM- 5 composites	Visible light, 300 W	10	-	40	[97]
		Cobalt promoted TiO ₂ /GO	Solar/visible, 300W	10	>75	27.2	[98]
	Penicillin G (PENG)	Ti ³⁺ self-doped TiO ₂ (r-TiO ₂) nano- catalyst	Full spectrum sunlight, 35 W	100	98.7	-	[99]
	Sulfadiazine	TiO ₂ GAC-TiO ₂	UV-C, 28 W	1	91.8 100	20 92	[100]
		Zeolite coated with TiO ₂ (TiO ₂ /ZEO)	UV, 265 nm, 20 W	10	93.31	21.2	[101]
	Sulfamethoxazole	TiO ₂ -rGO SOFs	High pressure UV, 160 W	5	-	12.6	[84]
	Sunamethoxazoie	PVDF membrane with 25 ppm TiO ₂	Low-pressure UV, 254 nm, 40 W	0.2-0.4	Too fast f	or analysis	[77]
ntibiotic	Sulfathiazole	Lu ₃ Al ₅ O ₁₂ :Ce Nanoparticles/ZnO nanostructures	UV-Vis, 350-800 nm, 1 kW	25 5	100	-	[102]
Ar	Tetracycline	TiO ₂ (P25)	UV, 254 nm, 9 W	10	-	21.9	[103]
		AgInS ₂ /SnIn ₄ S ₈ heterojunction	Visible light, >420 nm, 300 W	10	77.17	-	[104]
		FeNi3@SiO2@TiO2	UV, 254 nm, 18 W	10	100	25	[105]
		Ag/AgIn ₅ S ₈	UV, 254 nm, 9 W	10	95.3	23	[103]
		CuInS ₂ /Bi ₂ WO ₆ heterojunction	Visible light, >420 nm, 300 W	10	-	17.6	[106]
		MWCNT/TiO ₂	UV, 240 nm, 12 W	10	100	64.2	[107]
	Trimethoprim	PVDF membrane with TiO ₂	Low-pressure UV, 254 nm, 40 W	0.2-0.4	-	28	[77]
Penicillin antibiotic	Ampicillin	WO ₃ /ZrO ₂ Ru/WO ₃ /ZrO ₂	Solar light, 150 W	10	96 100	13 17.3	[108]
Synthetic antibiotic	Norfloxacin	Ag ₃ PO ₄ /BiVO ₄ electrode	Visible, >420 nm, 300 W	5	100	26.3	[109]
Anticoagulant	Warfarin	PVDF membrane with TiO ₂	Low-pressure UV, 254 nm, 40 W	0.2-0.4	-	34	[77]
ulsant	Carbamazepine	BiOCl microspheres	Visible, >420 nm, 350 W	2.5	70	93.5	[110]
Anticonv		TiO2-rGO SOFs	High pressure UV, 160 W	5	-	4.3	[84]

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EPC Class	EPC	Material	Reaction Source	[EPC] (ppm)	Removal	Reaction rate, k (10³/min)	Ref
t		C-TiO ₂	Visible light, >400 nm, 150 W	0.050	100	34.8	[76]
Anticonvulsan		PVDF membrane with TiO ₂	Low-pressure UV, 254 nm, 40 W	0.2-0.4	-	39	[77]
	Carbamazepine	C doped TiO ₂ coated on zeolites	Solar, 300-400 nm (65 W/m ²), 400- 570 nm (1,844 W/m ²)	0.1	>95	-	[78]
Antihistamine	Diphenhydramine	ZnO/Fe ₂ O ₃ /Zeolite TiO ₂ /Fe ₂ O ₃ /Zeolite	UV, 254 nm, 6 W	100	100 95	-	[111]
Antipsychotic	Loxapine	TiO2, SrTiO3	Solar spectrum, 280 – 800 nm, 750 W m2	10	99.77	-	[112]
Beta-blocker	Metoprolol	PVDF membrane with TiO ₂	Low-pressure UV, 254 nm, 40 W	0.2-0.4	-	48	[77]
Fibrate	Gemfibrozil	PVDF membrane with TiO ₂	Low-pressure UV, 254 nm, 40 W	0.2-0.4	-	43	[77]
trast	Iopromide	PVDF membrane with TiO ₂	Low-pressure UV, 254 nm, 40 W	0.2 0.4	Too fast f	or analysis	[77]
X-ray con agent	Diatrizoic acid	C doped TiO ₂ coated on zeolites	Solar, 300-400 nm (65 W/m ²), 400- 570 nm (1,844 W/m ²)	0.1	>95	-	[78]
N/A	Pharmaceutical wastewater	octahedral CdS/SnIn4S8 nano- heterojunction	Visible, >420 nm, 300 W	35% minerali- zation efficiency			[113]
	Pharmaceutical wastewater (antibiotics, anti- inflammatory)	Fe-TiO ₂	Solar light, 30.3398° N, 76.3869° E, October- November from 10 am to 4 pm, 788 W/m2 average intensity	83 COD removal			[114]
	Pharmaceutical wastewater	CuInS ₂ /Bi ₂ WO ₆ heterojunction	Visible light, >420 nm, 300 W	53.7 COD removal			[106]
	Pharmaceutical wastewater	MWCNT/TiO ₂	UV, 240 nm, 12 W	84.9 COD removal			[107]

 Table 1.2 Continued Material used in EPC removal and associated removal conditions

The method by which photocatalysts degrade EPCs can be complex. Briefly, the electron is responsible for the reduction of dissolved oxygen to form the superoxide anion $(\bullet O_2)$, and the hole is responsible for the oxidation of water forming hydrogen gas and the hydroxyl radical (•OH). The superoxide anion and hydroxyl radical are oxidative agents, which can degrade a variety of different compounds. Photodegradation can follow complex pathways depending on the contaminant structure, contaminant concentration, water chemistry, experimental conditions, and nanomaterial loading. For example, sulfa drug (e.g. sulfachlopyridaxine, sulfapyridine, sulfisoxazole) degradation has been found to be dominated by hydroxyl radicals and holes created during photocatalysis.^[115] Holes are thought to initiate the reaction by breaking the sulfur-nitrogen bond of the drug followed by hydroxyl radical incorporation in the sulfa drug structure, which ultimately dominates the breakdown of the drug.^[115] In paracetamol photocatalytic degradation, the hydroxyl radical is also the predominant reactant causing the hydroxylation and breakdown of the aromatic rings.^[44,116] The compounds formed due to the hydroxylation of paracetamol (ex. hydroquinone) are further oxidized producing unstable structures, which break down in aqueous solutions.^[44] Furthermore, it has been found that when the concentration of the superoxide anion is greater than the hydroxyl radical, the superoxide anion is also capable of degrading paracetamol by acting as a Lewis acid.^[44]

Recent advancements in photocatalysts have effectively enabled the degradation of numerous EPCs as shown in Table 1.2. However, photocatalysts present several limitations that need to be overcome to increase their effectiveness.

Inherently, they require energy to overcome the band gap energy required for electron excitation. They may require additional energy due to insubstantial light penetration and absorption, which effectively increases cost requirements due to the increased power needed for UV lamps.^[117,118] Furthermore, recombination rate, charge carrier transfer rate, and charge carrier travel time can further limit the photocatalytic efficiency of the material.^[119] To improve efficiency, material alterations, such as structural changes or doping can be performed.^[117] These methods can make the bandgap smaller and may also decrease recombination rates. In addition to bandgap engineering, use of plasmonic material can further lower energy requirements.^[117,118]

Another limitation of photocatalytic material is their potential impact to the environment. The possible transformation products are of great concern especially if released in the environment. In some cases, as in the case of diclofenac degradation, the degradation can result in harmful constituents such as phenol derivatives.^[43] Pharmaceuticals commonly have aromatic rings which, if not degraded, can form phenolic compounds that are known for their toxicity.^[43] Additionally, they could form acids (as in the case of paracetamol degradation^[44]), which could alter environmental conditions causing harm to local organisms. Another concern with photocatalyst release in the environment arises due to their instability in water. The ions released during their dissolution in water can have harmful effects to the environment.^[120] Thus, the photocatalysts' degradation mechanisms as they pertain to EPCs and photocatalyst stability in water need to be understood prior to their use in water treatment facilities. Generating composites and using coatings such as polymers

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or stabilizing agents, whether natural or chemical in nature, can improve photocatalyst stability and efficiency.^[121] By improving their stability, their harmful effects in the environment can be reduced. To increase usability of photocatalysts, novel materials have been developed such as magnetic nanocomposites and polymer coated nanomaterials. Magnetic composites can make the removal of the photocatalysts from water easier and more effective reducing the chance that they may unintentionally end up in the environment. Furthermore, their degradative properties have been shown to increase with the introduction of magnetic materials in the composite.^[122,123] Recently, magnetic FeNi₃/SiO₂/CuS has been synthesized for tetracycline removal,^[124] while magnetic fluorinated mesoporous graphitic carbon nitride^[125] and a magnetic TiO₂-GO-Fe₃O₄^[122] have been synthesized for amoxicillin removal.

Polymer coatings, in particular conductive polymers, have also been utilized to improve the material by providing a stabilizing layer, reducing dissolution and photocorrosion.^[126–128] Due to their low cost, environmental stability, and desirable material properties (electrochemical, magnetic, and optical), they increase the photocatalytic activity of material, improving their utility in water treatment.^[128,129] Many studies have shown that coating metal oxide semiconductors with conductive polymers such as polyaniline, polypyrrole, polythiophene, and poly(3,4ethylenedioxythiophene) can improve photocatalytic degradation of a variety of contaminants due to the their ability to extend the light absorption range and enhance photogenerated charge carrier separation of the material they are coating.^[130] For instance, in a study examining polypyrrole as a coating of Ag₂MoO₄, removal of ciprofloxacin was achieved within 10 min with high recyclability, which was superior to the performance of either material alone.^[131] Polyaniline as a coating of ZrO₂ also resulted in improvements in the photocatalytic activity of the material, owed to the reduction of the material's bandgap energy and the production of π - π * transitions (electron excitation from a π bonding orbital to a π antibonding orbital).^[132]

Despite their limitations, photocatalysts offer great possibilities in commercial applications. For example, titanium dioxide, a UV activated photocatalyst, has been introduced in commercially available water purification products and could be potentially applied to the advanced oxidation processes to help degrade a variety of contaminants. With advancements in photocatalytic materials, photocatalysts are becoming increasingly more cost effective and their large-scale use more feasible. For example, several reported photocatalysts can utilize low power UV or visible light to degrade EPCs. Direct comparison of many of these novel photocatalysts is limited due to the complexity of the reactions, such as structural and chemical properties of the photocatalyst, type and amount of the EPC, light source parameters, stirring rate, among others, which can affect the results. For instance, when TiO₂-rGO loaded on optical fibers was used for degradation of different pharmaceuticals (ibuprofen, sulfamethoxazole, and carbamazepine) under the same concentrations (5 ppm) and same conditions (high pressure UV light of 140 W), the results were vastly different and with different reaction rates (8.98, 12.6, and 4.3×10⁻³/min, respectively).^[84] Furthermore, use of different light sources also yielded differing results in the degradation of ibuprofen (160 W high pressure UV yielded a reaction rate of 8.89×10⁻ 3 /min, 39 W low pressure UV yielded a reaction rate of 3.32×10^{-3} /min, and 40 W visible light yielded a reaction rate of 1.33×10^{-3} /min). With this in mind, we can safely say that the ability of a multiwall carbon nanotube with titanium dioxide photocatalyst to fully remove 10 ppm of tetracycline from water at a high reaction rate (64.2×10⁻³/min) utilizing a 12 W UV lamp is notable.^[107] Other materials tested on 10 ppm tetracycline either required more energy to fully degrade the EPC, or did not perform as well.

While photocatalysis effectiveness is increased when UV light is utilized, numerous materials have been shown to be capable of visible light photodegradation of pharmaceuticals.^[70,74–76,80,82,84,91,94,97–99,102,104,106,109–111,117,133,134] Although power utilization of many visible light lamps is equivalent to that of low-pressure UV lamps, the lifetime of UV lamps is significantly lower. Furthermore, with the increased availability of LED lighting options, the power consumption from using visible light photoreactors can be greatly reduced. Regardless of the type of lighting used, inclusion of photocatalysts in water decontamination can decrease energy requirements. Conventional techniques for removal of organic chemicals such as EPCs may require the use of AOPs, which not only are energy intensive processes but may be unable to fully remove EPCs. Use of photocatalysts, on the other hand, has been shown to remove non-biodegradable EPCs such as carbamazepine, iopromide, and norfloxacin.^[76–78,84,109,110]
5. M0O3 AND ITS APPLICATIONS IN WATER TREATMENT

Of the vast number of materials researched for water treatment, molybdenum oxides (MoO_{3-x}, where 2 < x < 3) have gained much attention throughout the years due to their tunable size, structure, and optical and electronic properties, making them highly versatile materials.^[135,136] In full stoichiometric MoO₃ (MoO_{3-x} where x = 3) the bandgap of this material is wide (> 2.7 eV).^[58,137] As oxygen defects are introduced, Mo⁺⁶ ions are reduced to Mo⁺⁵ and the bandgap of MoO₃ decreases. Further reduction of the molybdenum ions (Mo⁺⁵ reduction to Mo⁺⁴) results in MoO₃ taking the form of MoO₂, which is semimetalic.^[137] Oxygen defects in the structure of MoO₃ alter its optical and electrical properties, making it useful in a variety of applications such as catalysis, sensors, energy storage, lubricants, thermal materials, electrochromic systems, and in biosystems.^[137]

MoO₃ synthesis can be achieved via liquid- and vapor-based methods. Depending on the synthesis procedure and parameters (solvents, reagents, pH, temperature, pressure, reaction duration, etc.), the size and morphology can be easily tunned, creating nanorods, nanospheres, nanoplates, and nanowires, among others.^[138] Liquid-based methods such as sol-gel, hydrothermal, and solvothermal synthesis are the most utilized methods due to their low energy requirements, simple methodology, and ability to control the material's morphology.^[136,137] Depending on the synthesis parameters, several MoO₃ phases can be achieved, such as η -MoO₃, γ -MoO₃, β -MoO₃, ϵ -MoO₃, α -MoO₃, and h-MoO₃.^[137] Of the different phases, which differ in stability and in their structure, α -MoO₃ and h-MoO₃ are the most synthesized and studied. The orthorhombic structure of α -MoO₃ is the most thermodynamically stable phase and allows for the construction of two dimensional morphologies,^[137,139] while the h-MoO₃ phase is metastable and takes a hexagonal morphology.^[136] However, at temperatures above 436 °C h-MoO₃ changes to α -MoO₃.^[136] Structurally, both α -MoO₃ and h-MoO₃ are composed of MoO₆ octahedrons, however, they differ in the way the octahedrons are linked with each other. While in α -MoO₃ the octahedrons share edges and corners, forming zig-zag chains with a lamellar layered morphology, in h-MoO₃ the octahedrons are connected through the cis position of the chains, forming hexagonal structures that contain one-dimensional tunnels with diameters of ~3.0 Å.^[137,139]

Altering the phase and structure of MoO₃ not only changes the morphology of the material, but it also results in materials with different stabilities, and different optical and electronic properties.^[137,139] MoO₃ structure and its properties can be further altered by doping, generating of defects, or creating of composite materials.^[137,139] As different applications require material with specific properties, the versatility of MoO₃ makes it an excellent candidate for numerous applications including water treatment.

Since 2017, new MoO₃-based materials were developed to photocatalytically degrade pollutants (Table 1.3). Almost all materials were effective in degrading dyes such as methylene blue, methyl orange, rhodamine B, or crystal violet, but few were tested for their ability to degrade pharmaceutical contaminants, which are known to persist in the environment. In dye degradation, the most notable was the MoO_{3-x} material that was modified to have a large amount of defects.^[140] The material was

able to break down 95.9% of the rhodamine B molecules within 15 min in visiblelight.^[140] However, it was noted that the dye degradation was likely incomplete and intermediates were present in the solution as measurement of the total organic carbon in the solution revealed that only 43.3% of the dye was fully degraded to carbon dioxide and water.^[140] Another notable material in dye degradation was the Mo₂C/MoO₃ material, which was able to completely degrade methyl orange in 120 min in visible light.^[141] For pharmaceutical degradation, the most notable was the MoO₃/Zn-Al material, which demonstrated a 90.5% degradation of tetracycline within 60 min in visible light.^[142]

Regardless of the contaminant being degraded, recent research has been primarily focused on the development of heterojunction photocatalysts, which have shown to have improved photocatalytic efficiency. For instance, the aforementioned Mo₂C/MoO₃ and MoO₃/Zn-Al materials were able to degrade contaminants more effectively than if each component was tested on its own, due to the formation of heterojunctions between the material being combined.^[141,142] Heterostructures have shown to lead to enhanced photocatalytic activity due to the increase in charge transfer mechanism efficiency. In particular, charge carrier separation is increased when a heterojunction is formed, which lowers electron-hole recombination rate, allowing for the photoinduced electrons and holes to remain separated, thereby maintaining the redox capacity of the material.^[140,143,144]

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Material	Contaminant	Reaction Source	[Contaminant] (ppm)	Removal	Reaction time (min)	Ref
Bi ₂ O ₃ /MoO ₃	Methylene blue	Visible light (420- 800 nm, 500 W) 10		86.6%	120	[145]
Ag-MoO ₃ -TiO ₂	Methyl orange	Solar radiation 15 97%		300 min	[146]	
MnO ₂ /MoO ₃	Methylene blue	Visible light (>420 nm) 10 94%		40 min	[147]	
MoO ₃ /Zn-Al	Tetracycline	Visible light (300 W)	40	40 90.5%		[142]
C ₃ N ₄ /MoO ₃	Ofloxacin Levofloxacin	Visible light (> 400 nm, 150 W)	20	64% 80%	140 min	[148]
MnO ₂ /MoO ₃	Acid blue 92	Visible light (>400 nm, 300 W)	(>400 W) 15		50 min	[149]
MoO_3/Bi_2O_4	Rhodamine B	Visible light (420 nm, 100 W)	10	10 99.6%		[150]
Carbon quantum dots/MoO ₃ /g-C ₃ N ₄	Tetracycline	Visible light (>420 nm, 350 W)	20	88.4%	60 min	[151]
Bi5O7I-MoO3	Ibuprofen	Visible light	20	89.2%	120 min	[152]
Bi ₂ S ₃ /MoO ₃ /C ₃ N ₄	Methyl orange	Solar light (500 W)	10	75.2%	120 min	[143]
ZnIn ₂ /MoO ₃	Methyl orange	Visible light (> 420	10	99%	100 min	
	Rhodamine B	rm, 500 W	10	99%	80 min	[144]
	Paracetamol	,,	30	87%	100 min	
MoO ₃ /CoFe ₂ O ₄	Methylene blue		5	91%		
	Rhodamine B	UV-Visible (200 W)		54%	120 min	[153]
	Crystal violet			65%		
Mo ₂ C/MoO ₃	Methyl orange	Visible light (> 400 nm, 300 W)	10	100%	120 min	[141]
MoO _{3-x}	Rhodamine B	Visible light (> 400 nm)	40	95.9%	15 min	[140]

Table 1.3. Recently developed MoO₃-based photocatalytic materials

6. REASEARCH SCOPE AND OVERVIEW

Materials with photocatalytic properties are numerous. However, not all are suitable for use in water treatment. In this work, the efficacy of MoO₃ as a photocatalyst for water treatment was examined, and modifications to improve its properties were investigated. MoO₃-based nanomaterials were selected due to their environmentally friendly nature, ease of synthesis, low cost, and visible-light photocatalytic properties, which make it a promising material for use in water treatment.^[58,154] While the degradation effectiveness of photocatalytic nanomaterials is widely studied, as presented in Section 2, research on the properties of the materials that affect their usability in water treatment are often omitted, providing insufficient information to accurately ascertain the photocatalysts' efficacy for sustainable and safe water decontamination. For instance, studies of novel photocatalytic materials demonstrating superior photocatalytic properties, such in the study of multi-walled carbon nanotubes/TiO₂,^[107] granular activated carbon/TiO₂,^[100] FeNi₃/SiO₂/CuS,^[124] or polypyrrole coated Ag₂MoO₄,^[131] fail to address the dissolution or toxicity of the nanomaterials. Dissolved portions of the engineered nanomaterials can not only act as contaminants themselves but can also form complexes with degraded byproducts or organic and inorganic matter present in water, generating additional pollutants and posing added health and environmental concerns.^[1]

To close this research gap, different nanostructures of MoO₃ (nanorods, nanowires, and nanorods) were examined herein to determine their usability in water treatment. In Chapter 2, the morphology, surface chemistry, dissolution, and photocatalytic properties of three distinct MoO₃ nanostructures (nanorods, nanowires, and nanoplates) were examined. The investigation of the three nanostructures is continued in Chapter 3, where the aggregation behavior, dissolution, and photocatalytic activity of MoO₃ nanorods, nanowires, and nanoplates in the presence of inorganic and organic substances were elucidated. In Chapter 4, MoO₃ nanorods were modified via the introduction of a magnetic core (Fe₃O₄ nanoparticles) and were coated with conductive polymers (specifically, polyaniline and polypyrrole). The magnetic core was included to improve the ease of removal of the material from water,

and the polymer coatings were added to reduce the dissolution of the underlying material. The morphology, photocatalytic activity, dissolution, and surface chemistry of the polymer coated magnetic MoO₃ were investigated to examine the effect of polyaniline and polypyrrole on MoO₃ material properties, as well as to investigate the effect of MoO₃ surface chemistry on the polymerization of aniline and pyrrole. Finally, in Chapter 5, the efficacy of the polyaniline coated magnetic MoO₃ as a photocatalyst in the removal of tetracycline from water was investigated.

Overall, this work's aims were to synthesize and examine the photocatalytic properties of a promising photocatalyst, MoO₃, and investigate its dissolution and behavior in aqueous systems. Furthermore, as the dissolution of this material was determined to be high, making it a poor candidate for water treatment applications, polymer coatings were examined as a simple method in stabilizing nanoparticles while simultaneously improving the photocatalytic properties of the material. The importance of studying the multitude of properties materials need to possess to be usable for their intended application was demonstrated. However, while a more thorough examination of the usefulness of the material for water treatment was conducted in comparison to most other studies, additional research needs to be conducted in the future to fully determine the efficacy of the developed photocatalysts. New materials, such as the one discussed in this work, should undergo further examination to not only determine their basic properties but to also discover their toxicity towards humans, animals, and the environment, their ability to be used in preestablished industrial processes, and their fate in water systems.

CHAPTER 2 – MOLYBDENUM TRIOXIDE PHOTOCATALYSTS

Adapted from "Oxidation State of Mo Affects Dissolution and Visible-Light Photocatalytic Activity of MoO₃ Nanostructures" by J. Peña-Bahamonde, C. Wu, S. Fanourakis, S. Louie, J. Bao, and D. Rodrigues^[58]

1. INTRODUCTION

Recently, MoO₃ nanostructures have been described to present photocatalytic properties under visible light. Degradation of methylene blue^[155,156] and orange II dye,^[157] methanol oxidation,^[158] epoxidation,^[159] gas sensing properties,^[160] supercapacitor,^[161] optical properties,^[162] and lithium storage capabilities^[163] have been investigated with MoO₃ under visible light. The photocatalytic performance of MoO₃ has been associated to shape, size, and chemical properties. Different synthetic strategies have shown that MoO₃ exhibits *h*- and α - phases.^[164] The *h*-phase corresponds to nanorods morphologies while the α - phase corresponds to nanoplates and nanowires.^[165–167] Control of the morphology and nanoparticle size can be achieved by varying different parameters, e.g. the concentration of reactants, time, temperature, pressure, and solvents. Despite the fact that visible light photocatalysis makes MoO₃ an attractive material for contaminant degradation, prior studies have demonstrated that dissolution of MoO₃ can occur in aqueous systems,^[168–170] diminishing its utility for water treatment and other applications. However, a thorough study of the dissolution and photocatalytic activity of the various phases and morphologies of MoO₃ nanostructure has not yet been conducted, to our knowledge.

Many studies have shown that other types of nanoparticles, including silver,^[171,172] silica,^[173] ZnO,^[174,175] CeO₂^[175] nanoparticles (NPs) can dissolve. The

stability of the nanoparticles in terms of dissolution will depend on several factors such as presence of natural organic matter, ionic strength, and type of electrolyte, aggregation state, pH, and size.^[120] In the case of organic matter, the dissolution can be increased or decreased by steric shielding or ligand-promoted processes, respectively. When ionic strength, type of electrolyte, or pH are altered the behavior of the particles can also change and lead to increased nanoparticle aggregation influencing the exposed surface area to the media and dissolution. Size can also play a role, whereby smaller particles are more prone to dissolving than larger particles, as described by the well-known Ostwald-Freundlich equation. In the case of MoO₃, it has been shown, that pH changes can play an important role in the dissolution of this nanoparticle ^[176]. Dissolution of the NPs can be expected to change the heterogeneous catalytic reactions that occur at the NP surface and perhaps even affect the production of reactive oxygen species (ROS). The dissolution behavior of the nanoparticles is critical in determining both the toxicity and reactivity of the nanoparticles. This phenomenon will also be harmful in water treatment not only due to the toxicity effect of the dissolved ions but also because the catalytic processes that consume the catalyst are typically cost-prohibitive.

Previous investigations have shown that the production of reactive oxygen species (ROS) play an important in photocatalytic reactions. The quantification of individual ROS is a prerequisite to elucidate actual ROS functions in photocatalysis. The production of different ROS by TiO₂,^[177–180] graphene oxide,^[181] silver,^[182] ZnO,^[180,183] and iron oxide^[184] is well studied. However, the production of ROS by photocatalysts induced by visible light, specifically MoO₃, have not been reported thus far. In the present study, we take into consideration the role of pH in the dissolution of MoO₃ nanostructures as well as the effects of dissolution in ROS production and degradation of methylene blue (MB), as an example of a water contaminant, to understand the mechanisms of the photocatalytic degradation of MoO₃ nanostructures. We hypothesize that MoO₃ nanostructures with different material properties will show different propensities to dissolve, and that the dissolution behavior will then change the photocatalytic ability of the NPs.

2. EXPERIMENTAL

2.1 Materials

Ammonium molybdate tetrahydrate ((NH4)6Mo7O24·4H2O), nitric acid (HNO3), molybdenum powder (1-5 μ m, \geq 99.9%), hydrogen peroxide (H2O2), ethanol (EtOH), methanol (MeOH) HPLC grade, furfuryl alcohol, terephthalic acid, Isopropanol (> 99.7%), benzoquinone (AR grade), triethanolamine (> 99.0%) and methylene blue were purchased from Sigma-Aldrich and were used as received. Glutathione and 5,5'-Dithiobis (2-nitrobenzoic acid) (Ellman's reagent) were supplied by Fisher Scientific.

2.2 Synthesis

The MoO₃ nanomaterials were synthesized by the hydrothermal route using modified published procedures.^[138,157,185] Briefly, the modifications were: the nanorod

MoO₃ nanostructure were prepared by dissolving 2.46 g of (NH₄)₆Mo₇O₂₄·4H₂O in 20 mL of distilled water (DIW). To this solution, 5 mL of HNO₃ was added drop by drop. The solution was transferred to an 80 mL Teflon-lined stainless-steel autoclave and heated at 90°C. After 3 h of reaction a white precipitate was collected and washed several times with EtOH (70%) and then dried at room temperature.

Black MoO_{3-x} nanoplates and nanowires were prepared according to the procedures reported by Yin et al.^[185] with some modifications. For the nanoplates, 192 mg of molybdenum powder was added to a Teflon vessel (45 ml) containing 24 ml of ethanol under magnetic stirring. Then, 3 ml of H_2O_2 (30%, from Macron Fine Chemicals) was injected, and the mixture was stirred for 0.5 h to obtain a yellow solution. The Teflon vessel was then sealed in a stainless-steel autoclave, heated, and maintained at 160 °C for 14 h. The product was collected by centrifugation, washed with ethanol for several times, and finally dried under vacuum. The nanowires were prepared using the same procedure as the black nanoplates except using 384 mg of molybdenum powder, 30 ml of isopropanol, and 5 ml of H_2O_2 (30%, from Macron Fine Chemicals).

2.3 Nanomaterial Characterization

Crystallographic information of samples was determined by X-ray diffraction (XRD) (Philips X'pert Pro X-ray diffractometer). The Cu K α radiation was used ($\lambda = 1.54$ Å) at a scanning rate of 0.020° per second from 5° to 80° in 20. The voltage was set to 40 kV, and the current to 40 mA. Crystal sizes of the samples were

estimated from the full width at half maxima (FWHM's) of some intense XRD diffraction peaks using Scherrer's method.

Fourier-transform infrared spectroscopy (FTIR) was performed in a Thermo Scientific Nicolet IS50 FTIR Spectrometer in the wavenumber range from 4000 to 500 cm⁻¹. The ATR-FTIR was employed to evaluate the interaction between MB-MoO₃ and MB-ion. After each reaction, samples where centrifuged for collection of the pellet, which were subsequently freeze-dried. The spectra were obtained on a Digilab FTS 7000 equipped with a HgCdTe detector from 4000 to 600 (cm⁻¹) wavenumbers.

The morphology of crystal samples was examined by scanning electron microscopy (SEM). Samples were coated with gold for 30 seconds (Denton Desk V) and then, observed by SEM (Nova NanoSEM 230) at accelerating voltage equal to 5 kV at different magnifications. The size of the nanomaterials was estimated using ImageJ. MATLAB 2018a was used to generate histograms and determine the average particle sizes.

The Brunauer–Emmett–Teller (BET) surface area for all nanostructures were measured by N₂ physisorption using a Micromeritics-3FLEX and standard multipoint BET analysis methods. Prior to analysis, 0.2 g of powder were degas on Micromeritics-Smart VacPrep at a 120 °C for 24 hours.

X-ray photoelectron spectroscopy (XPS) was performed in a PHI Quantera SXM Scanning X-ray Microprobe with Al Kα (1486.6 eV) as the excitation source. The binding energy was calibrated by setting the adventitious carbon (corresponding to C-C bonds) to 284.8 eV. High-resolution spectra were acquired with a pass energy of 23.5 eV, an energy step size of 0.2 eV, and a time step of 50 ms. Energy band gap measurements were performed by UV-vis Diffuse Reflectance Spectroscopy (UV–vis DRS) and were recorded in a Hitachi UV-vis Spectrophotometer U-2001 using BaSO₄ as the reference. The bandgaps were determined based on the Kubelka-Munk function: $F(R) = (1 - R)^2/2R$. Zeta-potential measurements were performed in a Zetasizer Nano (Malvern) using the zeta potential transfer standard DTS 1235. The samples were measured with 100 mg/L of each nanomaterial at pH values varying from 2 to 10, adjusted with either HCl or NaOH.

2.4 Dissolution Measurements of MoO₃ Nanostructures

Dissolution experiments were conducted at different pH values (2, 5, 7 and 10) and at room temperature (≈ 25 °C). A mass of 10 mg of MoO₃ nanostructure was dispersed in 30 mL of deionized water with adjusted pH using either HCl or NaOH prior to the addition of the nanostructures. The nanostructures' dissolution was evaluated for up to seven days (after 30 min, 1 h, 4 h, 6 h, 24 h, 48 h, 96 h, and 168 h in solution). For each time point, a 5 mL sample was taken and filtered with 0.2 µm Nylon filters, and then centrifuged using Amicon ultrafiltration devices (30,000 NMWL) to ensure that all solid particles were removed from the solution. After the filtration, the solutions were measured by flame atomic adsorption spectrometry (AAS) (AAnalyst 200, Perkin Elmer) using a Molybdenum lamp from Perkin Elmer. Five standard solutions with known Mo concentrations were prepared as calibration standards. Exact concentrations of Mo in the sample solutions were obtained using the working calibration curve generated from the standard solution data. The averages and standard deviations of triplicate measurements were reported for all dissolution measurements. The supernatant of each experiment was collected and characterized by XPS and UV-vis to determine the nature of the ion.

The isolated ions from the nanorods were also employed at a concentration of 500 mg/L for the evaluation of their interaction with MB using UV-Vis spectroscopy. The degradation of MB by the ions was investigated via HPLC. The ROS production by the ions followed the same procedures as the ROS production by the nanostructures as described below. The conditions and instrument settings used for the HPLC, ROS and UV-Vis were the same as described below for the nanostructures.

2.5 Photocatalytic Activity Experiments

Photocatalytic experiments were carried out at different pH values, varying from 2 to 10 to measure the amount of discoloration of methylene blue (MB) in aqueous suspensions of MoO₃, which were exposed to visible light (Nexlux LED light, which utilizes the 5050 RGB LED package with a wavelength range of 400 to 700 nm and maximum luminous intensities of 100, 400, and 100 mcd for the red, green, and blue regions, respectively). The initial concentration of MB was fixed at 50 mg/L with a catalyst loading of 500 mg/L and a final volume of 20 mL. Prior to photooxidation, the solution was stirred in the dark for 30 min to establish an adsorption–desorption equilibrium.^[156,186] During irradiation, 1 mL of the mixture solution was withdrawn every 30 min, and then centrifuged (Thermo Scientific Sorvall Legend XTR Centrifuge) at 10,000 rpm for 10 min to separate photocatalysts from the mixture. The extent of MB removal was determined by measuring the absorbance values on a UV–Vis spectrometer using a SynergyMX Microtiter plate reader (Biotek) at $\lambda = 664$ nm. The experiments were performed in triplicate. The results were analyzed and reported as discoloration of MB or MB photocatalytic degradation. The data for the MB discoloration in the light included both adsorption of MB to the nanoparticle, complexation of MB with the dissolved MoO₃ ion, and photocatalytic degradation. For the discoloration in the dark, any MB discoloration reported corresponded to adsorption of MB to the nanoparticle and complexation with the ion. In both conditions, dark and light, we needed to consider the complexation process between the dissolved MoO₃ ions and MB. In the case of photocatalytic degradation, the data corresponded to the true photocatalytic activity of the nanostructure. To obtain the true photocatalytic degradation, the discoloration of MB at the end of the light reaction (which included adsorption, complexation, and degradation) was subtracted from the MB discoloration at the end of the dark reaction (which included adsorption and complexation).

2.6 Reactive Oxygen Species Detection

Reactive oxygen species (ROS) detection was evaluated from pH 2 to 10 by quantifying the production of different species. The concentration of singlet oxygen (¹O₂) was determined by monitoring the concentration of furfuryl alcohol (FFA), as previously described.^[187] Hydroxyl radical (*****OH) was evaluated by the analysis of the degradation of terephthalic acid.^[187] The loss of thiol in glutathione (GSH) was used as an indirect method to measure hydrogen peroxide (H₂O₂) production by nanomaterials.^[188,189]

2.7 Loss Of Glutathione

MoO₃ nanostructures and ions, were investigated for hydrogen peroxide production in triplicate by measuring the loss of thiol in GSH. Briefly, 0.4 mM GSH was allowed to react for 2 h at room temperature with samples containing 500 mg/L of MoO₃ or $[MoO_4]^{2-}$. Negative controls with non-oxidative agent (H₂O₂), and positive controls containing hydrogen peroxide (30%) were also measured. All the samples where tested in dark and light conditions. After which, 100 mM of Ellman's reagent in Tris-HCl 100 mM was introduced into each tube and allowed to react for 10 min. Then, the nanostructures were removed by filtration using a 0.2 µm syringe filter (Corning, U.S.A.). The absorbance of the filtrate was read at 412 nm using a Synergy MX Microtiter plate reader to measure the loss of thiols. The results were expressed as the loss of GSH and represented by Equation 2.1,^[188]

$$ROS \ production \ (\%) = \frac{Negative \ control \ absorbance - Sample \ absorbance}{Negative \ control \ absorbance} \times 100.$$
(2.1)

2.8 Hydroxyl Radical

The production of hydroxyl radical was evaluated via the analysis of the hydroxylation of terephthalic acid (TA) to form fluorescent species. The fluorescent species of 2-hydroxylterephthalic acid was measured at 425 nm in the Synergy MX Microtiter plate reader. Negative controls (without MoO₃) and positive controls (TA) were also analyzed. A concentration of 500 mg/L of the nanostructures or [MoO₄]²⁻ were allowed to react with 2 mM of TA. After 2 hours, the nanostructures were removed by filtration with 0.2 μm nylon filters, and the 2-hydroxylterephthalic acid generated in the samples were quantified by fluorescence using a Synergy MX Microtiter plate reader. The fluorescence intensity was read at an emission wavelength of 425 nm in the fluorescence spectra for 312 nm excitation wavelength.^[190–192] The results were expressed using Equation 2.1.

2.9 Singlet Oxygen

Singlet oxygen species were evaluated from previously reported methods.^[193,194] Briefly, 500 mg/L of each nanoparticle or the isolated ion were mixed with 0.5 mL of furfuryl alcohol (10 μ M). Positive and negative controls without nanostructures were analyzed. When the reaction was completed, after 2 hours, the nanostructures were removed by filtration using 0.2 μ m nylon filters and analyzed by high performance liquid chromatography (HPLC). The chromatographic measurements were carried out on a HPLC Agilent technologies 1290 Infinity with a Zorbax Eclipse Plus C18 4.6 × 150 mm, 5 μ m column. The mobile phase was H₂O:MeOH (80:20) %. The flow rate was 1 mL/min, and the injection volume was 20 μ L. The concentration of ¹O₂ was calculated by the integration of the peak area for λ = 219 nm observed at a retention time of 2.6 min in the chromatographs.

2.10 Product Analysis and Identification

The MB and its degraded products were separated and identified based on the literature.^[195] The MB degradation products were analyzed and separated on the HPLC system described above, with the UV-vis diode array detector set to record the absorbance at 600 nm. The mobile phase was made from acetonitrile (solution A) and buffer solution (solution B). The buffer solution was 0.1M ammonium acetate and acetic acid (pH 5.3). The gradient elution was a linear gradient from 5% A to 95% A in 30 min, at a total flow rate of 0.8 mL/min, and the injection volume was 100 µL.

2.11 Scavenger Experiments

Isopropyl alcohol (IPA), triethanolamine (TEOA) and p-benzoquinone (p-BQ), were added to the reaction to evaluate the degradation mechanisms. The experiments were performed for the nanorods at pH 5.4 employing the same procedure as the one described in the photocatalytic activity experiments. Briefly, 50 mg/mL of MB with 500 mg/L of the nanomaterial in a final volume of 20 mL was prepared. To each reaction, 10 mM of TEOA, 75 mM of IPA and 1 mM of p-BQ were employed. After 30 min stirring in the dark to establish an adsorptiondesorption equilibrium, the samples were irradiated. An aliquot of 1 ml of sample was collected every 30 min and then centrifuged. The absorbance at $\lambda = 664$ nm was measured to analyze the discoloration of MB.

3. RESULTS AND DISCUSSION

3.1 Synthesis And Characterization of The Nanostructures

Three MoO₃ nanostructures with different morphologies were successfully synthesized, as shown in Figure 2.1. All the nanostructures showed smooth surfaces, as well as regular and monodisperse shapes and structures. The nanowires and nanorods presented diameters in the range of 59 nm and 180 nm, respectively. The nanoplates had a thickness around 74 nm and a width of approximately 180 nm. Both the nanorods and nanowires presented lengths greater than 5 μ m.



Figure 2.1. SEM images of a) nanorods b) nanowires and c) nanoplates. The scale bars correspond to 1 μ m size.

All the nanostructures showed smooth surfaces, as well as regular and monodisperse shapes and structures. The nanowires and nanorods presented diameters in the range of 59 nm and 180 nm, respectively. The nanoplates had a thickness around 74 nm and a width of approximately 180 nm. Both the nanorods and nanowires presented lengths greater than 5 µm. The chemical and crystalline structures of the nanostructures were determined by XRD, FT-IR spectroscopy, and XPS. XRD patterns for the MoO_3 nanostructures are shown in Figure 2.2. The strong diffraction peaks demonstrate that the samples are highly crystalline. For the nanoplates and nanowires most of the peaks for these samples were indexed as orthorhombic MoO₃ (JCPDS - 35-0569) and for the nanorods as hexagonal (JCPDS - 21-0569). Using the Scherrer equation^[196,197] and the FWHMs, the crystal sizes of the nanowires, nanoplates, and nanorods were calculated to be 32 nm, 29 nm, and 33 nm, respectively. The difference in sizes with those of the extrapolated sizes from the SEM images could be due to peak broadening caused by crystal lattice strain or lattice defects.^[198-200]

The specific surface areas of the prepared MoO₃ nanoparticles were presented in Table 2.1. The surface area measurements gave the surface areas of 28.5 m²/g, 26.1 m²/g, and 1.1 m²/g for the nanoplates, nanowires, and nanorods respectively. Comparatively, the different MoO₃ nanostructure obtained shows different surface area, which is inversely proportional to the nanostructure size.



Figure 2.2. XRD of the MoO₃ nanostructure.

The normalized FT-IR spectra of the MoO₃ nanostructures was done at wavenumbers 520, 537, and 564 cm⁻¹ for the nanorod, nanowire, and nanoplate spectra, respectively, and are shown in Figure 2.3. The peaks around 972, 969, and 984 cm⁻¹ were associated with the Mo=O stretching vibration. The bands around 896, 708, and 840 cm⁻¹ were associated with the Mo-O-Mo stretching, and the bands at 517, 555 and 538 cm⁻¹ were the result of the O-Mo3 single bonds.^[201–203] The weak peaks located around 1400 and 1600 cm-1 were related to the presence of the crystallization of water in the crystals of the MoO₃ nanostructures. The nanorods showed peaks in the 800-1000 cm⁻¹ and 500 to 600 cm⁻¹ ranges indicating presence of the Mo=O bond and Mo-O bonds, respectively. Similarly, the nanoplates presented both bond types as the nanorods. However, the nanowires seemed to have an increased presence of single bonds as observed with the 538 nm peak. The nanoplates did not have such a strong presence of the Mo-O single bonds. The Mo=O to Mo-O ratios shown in Table 2.1 confirmed this analysis since the nanowires double bond to single bond ratio was nearly half of that of the nanorods and nanoplates. Furthermore, the Mo-O-Mo peak in the nanoplates is shifted compared to nanowires and nanorods which is potentially caused by lattice distortion since the nanoplates has a significantly higher concentration of oxygen vacancies^[204] than the other two samples as shown in Figure 2.4.



Figure 2.3. ATR-FTIR spectra of the prepared nanostructures.

The surface chemistry of the nanostructures as well as the chemical states of the MoO₃ nanostructures were analyzed by XPS as shown in Figure 2.4. The Mo 3d spectra for all the nanostructures present different oxidative states. The spectrum for the nanorods showed presence of the binding energy (E_B) (Mo ${}^{3}d_{5/2}$) ${}^{1}\!/_{4}$ 233.15 eV and EB (Mo ${}^{3}d_{3/2}$) ${}^{1}\!/_{4}$ 236.3 eV corresponding to Mo⁶⁺; however, the spectra of nanowires and nanoplates exhibited the presence of the peaks (Mo ${}^{3}d_{5/2}$) ${}^{1}\!/_{4}$ 231.78 eV and EB (Mo ${}^{3}d_{3/2}$) ${}^{1}\!/_{4}$ 234.92 eV, which indicated the existence of Mo⁵⁺. Table A.1 shows all

the fitting parameters of the XPS spectra for all the nanostructures. In Table 2.1, the calculation of the ratio of peak/area is shown. As we can see, the different morphologies showed different fractional amounts of Mo⁶⁺ and Mo⁵⁺, indicating that the nanostructure with a higher amount of Mo⁵⁺ contained large quantities of oxygen (O) vacancies, which have been introduced during the synthesis of the nanomaterial. Typically, the presence of these vacancies causes a deficiency of O in the crystal structure, which causes a decrease in the energy band gap ^[205] as evident in Table 2.1. This decrease in the energy band gap is desirable as previous studies have shown that it can increase the photocatalytic properties of the material by allowing greater absorption of light ^[206]. The bandgaps of all three material were less than 3 eV (Figure A.1) making the material capable of generating photoexcited electrons via the absorption of visible or UV light, especially considering that the nanowires and nanoplates were able to absorb light due to their localized surface plasmon resonance. The heavily doped nonstoichiometric molybdenum oxide (MoO_{3-x}) is a typical and primary member of plasmonic semiconductors. It shows intense and tunable plasmonic resonance across the visible and NIR region.^[207–209] Due to the presence of oxygen vacancies (highly self-doped) and the free electrons, the dark MoO_{3-x} samples always show a plasmonic absorption in the vis-NIR region. This kind of absorption peak has been observed in our nanowires sample (Figure A.1.b, peak at above 800 nm). However, due to the limited sensitivity of our device, it hard to identify the plasmonic absorption of the nanoplates sample, which is the darkest one and it absorbs almost all the visible light. While from the XRD patterns the nanowires and

nanoplates appeared to have similar crystal structures, in the XPS the nanowires and nanorods appeared chemically more similar. This could be a result of the growth mechanism during synthesis resulting in different O vacancies in each nanostructure. Based on these results, the composition of the nanorods and nanowires nanostructures was similar regarding the oxidation states, however their structure was different due to the different growth mechanisms during synthesis. The differences in the chemical and physical structure of these nanomaterials could affect their stability, which is discussed later based on the dissolution stability of the different MoO₃ nanostructures. Furthermore, the differences in the morphology, surface area, and oxidative state, enhance the probability of the electron transition from Mo⁵⁺ valence band to Mo⁶⁺ conduction band.



Figure 2.4. XPS of all MoO₃ nanostructures.

Nanostructure	Mean Size (nm)		I _{M0-} 0/I _{M0=0}	M0 ⁶⁺	Mo ⁵⁺	Mo ⁶⁺ : Mo ⁵⁺	Surface area	Energy	
	From SEM	From XRD		WIO	1410	ratio	(m^{2}/g)	(eV)	
Nanorods	180	32	0.77	95.3	4.7	20.3	1.1	2.84	
Nanowires	59	29	0.48	86.5	13.5	6.41	26.1	2.95	
Nanoplates	74	33	0.99	34.7	65.3	0.531	28.5	2.64	

Table 2.1. Chemical properties of the three different MoO₃ NPs synthesized.

3.2 Stability of MoO₃ Nanostructures in Aqueous Solutions

Previous studies have described that the dissolution rate of nanoparticles can be affected by the size, crystallinity, shape, surface area, and exposed plane, among other factors.^[120] The dissolution of the MoO₃ nanostructures was analyzed from pH 2 to 10 for a period of 1 week, as shown in Figure 2.5. Interestingly, for all the nanostructures, the dissolution was only partial, *i.e.*, the nanostructures did not dissolve completely (*i.e.*, up to 100 mg/L of MoO₃ was dissolved) and eventually reached a plateau. The nanowires dissolved the most (approximately 80% dissolution corresponding to 260 mg/L of MoO₃) after 1 week at pH 10), compared to the nanoplates, which presented the lowest dissolution (< 20% at all pH conditions). These results seem to be directly correlated to the presence of the Mo-O single bonds and double bonds, as well as the different oxidative states. For instance, the nanowires presented the highest dissolution as well as the strongest presence of Mo-O single bonds as seen in the FTIR results compared to the nanoplates (Figure 2.3). In the case of the oxidative state, the nanoplates presented higher Mo⁵⁺ state as opposed to the nanowires and nanorods that had Mo⁶⁺ oxidative states and higher dissolutions (Table 2.1).

Further analysis of the Mo ionic species dissolved through XPS and UV-vis spectroscopy (Figure A.2) showed that for all the nanostructures, the primarily dissolved ion was Mo⁶⁺. These results are in accordance with the literature that the majority of the dissolution of the nanostructures are with Mo⁶⁺ oxidative state (e.g. nanowires and nanorods).^[210–213] Aqueous solutions of Mo⁶⁺ ions have been studied in detail showing a dependency on the ion concentration and pH. The Pourbaix diagram of the Mo-system has been extensively studied and is used to study the stability of compounds in aqueous solutions. Generally, it is used to simplify complex reactions. Based on the Pourbaix diagram of Mo,^[214,215] at 25 °C, molybdate anion [MoO₄]^{2–} is formed when pH is higher than 4.2 and at -0.9 V. However, at acidic pHs, MoO₃ can be formed at -0.35 V. Previous studies have shown that at low Mo concentrations, the predominant species in aqueous solutions is the monomeric tetrahedral [MoO₄]^{2–} ion^[216,217] and MoO₃ dissolution coincide that the overall reaction is of the MoO₃ in aqueous solutions

$$MoO_3 + H_2O \Leftrightarrow 2H^+ + MoO_4^{2-}.$$
 (2.1)

It is noteworthy mention that MoO₃ dissolution is pH and temperature dependent, and these structures are more stable at acidic pHs rather than neutral and basic.

In our study, dissolution increased when the pH increased for all the nanoparticles. Furthermore, material dissolution was higher coincidently with the more presence of Mo-O single bonds (i.e. nanowires>nanorods>nanoplates). These results suggest that the dissolution mechanisms can happen due to Mo-O single bonds since single bonds are more labile than double bonds.

In summary, the dissolution of the MoO₃ nanostructures depends on the pH of the media. The higher the pH is, the greater the dissolution. While it has been shown that nanoparticle dissolution is highly dependent on different factors, such as the crystal size and morphology, the extent by which the particles dissolve in solution, however, seems to be also dependent on the oxidation state and type of oxygen bonds found in the nanostructure.^[171]



Figure 2.5. Representation of %Mo dissolved vs. time at different pH values. From left to right, in order of increasing dissolution, nanoplates, nanorods, and nanowires.

3.3 MB Interactions with MoO₃ Nanostructures

Initial investigation of the interaction of MB with the nanostructures was determined via ATR-FTIR (Figure A.3). The results showed that the nanostructure surface adsorbs MB. The differences between the ATR-FTIR spectra of the MoO₃ with MB in the dark and light showed the combination of bands of MoO₃ and MB and a small shift to higher cm⁻¹ for some of the bands. For instance, the MB band at 880 shifted to 897 in the dark and to 884 in the light, and the MB band at 1596 cm⁻¹ shifted slightly to 1601 cm⁻¹ and 1602 cm⁻¹ for MB adsorbed to the nanostructure in the light and dark, respectively. To estimate the electric charge on the nanostructure surface and elucidate the ability of MB to adsorb onto the nanostructures, zeta potential measurements were performed. The magnitude of the zeta potential provides information about particle stability. Figure A.4 represents the zeta potential for all the nanostructure vs. pH. When the pH of the media increased, the zeta potential values for the nanorods and nanoplates decreased, while the zeta potential for the nanoplates increased slightly before decreasing slightly again. These patterns follow the degradation pattern due to light, as illustrated in Figure A.5, indicating that, due to the increasingly negative surface charge at higher pH values, the degradation decreases. This could be caused by the increased adsorbance of the MB (a positively charged molecule) to the nanostructure at higher pH values, which would decrease the ability of the nanostructure to absorb light. It could also be caused by the facilitated conversion of holes to hydroxyl radicals at high pH values.^[220] Since the holes are more active than hydroxyl radicals in this reaction, the conversion would result in a decline of the activity.

To verify whether degradation of MB or mere adsorption or complexation was taking place, XPS was utilized. The XPS results on the surface of the nanostructure (Figure A.6) showed a decrease in the pyridinic acid band when compared to the MB alone, indicating that photocatalytic degradation of MB is taking place. Furthermore, the decrease in the N quaternary was greater for the samples that were irradiated than for those kept in the dark.

The fact that all the nanostructures exhibited similar behavior with regards to their ability to decolorize MB, the evaluation of the degradation byproducts of MB was performed for the nanorod MoO₃. Figure A.6 shows the chromatographic separation of the methylene blue in dark and light conditions after 2 hours of reaction at pH 5.4. The data showed that MB was significantly degraded under light irradiation, while some adsorption was observed when the reaction was placed in the dark. The decrease in the methylene blue peak intensity and the appearance of new peaks at lower retention times have been reported previously.^[220] Consequently, photocatalysis of dye solutions not only caused its discoloration, but also an appreciable degree of transformation of the dye molecule.

In the case of the ions, the HPLC results of the reaction between the ions and methylene blue also showed some degradation byproducts. From the results, when the reaction was performed in the dark (Figure A.5 blue curve), the chromatograms did not show any peaks at lower retention times as opposed to light. The strong interaction between methylene blue and the isolated ions was confirmed with the ATR-FTIR spectra. In the spectra, it was possible to observe a decrease in the OH band for the ion-MB spectra, and the appearance of the MoO₃ band at 550 cm⁻¹ (Figure A.7). This result showed that a MB-Mo ion complexation was happening during the reaction. Figure A.8 showed a blue precipitate when the ion was in contact with MB. The small contribution of the ions in the degradation process and the complexation observed by

ATR-FTIR showed that both processes were happening simultaneously. That means that the peaks in the observed in the chromatogram are degradation byproducts and not complexes. These results confirm that the ions were also participating in the degradation process.

3.4 Photocatalytic Activity of The Nanostructures and Ions with MB

In this investigation, we tried to understand the role of the nanostructures' characteristics in relation to their ability to decolorize MB, i.e. simultaneous adsorption, ion-MB complexation, and photocatalytic activity, and true photocatalytic activity (Figure 2.6). In the discoloration assay (Figure 2.6), adsorption, complexation with the ion, and photocatalytic phenomena were reported for the light exposure, while in the dark only adsorption and ion complexation were observed. Figure A.9 shows the relative emission intensity of the lamp and the MB absorbance spectra. There is a small overlap in the emission wavelengths of the LED lights and the absorbance of MB. While MB is capable of absorbing some of the light emitted by the LED lights, it does not influence the absorption of the nanomaterial as the majority of the light emitted by the lights falls outside the region of light absorbance by MB (Figure A.9). In the case of the photocatalytic percentage discoloration (Figure 2.6), the photocatalytic activity, after subtraction of the discoloration reaction of MB in the dark and light conditions, was reported to show the amount each material was able to decolorize solely due to the influence of the light exposure, i.e. photocatalysis (Figure 2.6). All three materials were able to decolorize MB as shown in Figure 2.6, however, the nanorods displayed greater photocatalytic percentage discoloration, therefore was

considered to have the best photocatalytic activity. While the nanowires displayed the fastest discoloration activity due to the influence of their increased dissolution, they displayed the least photocatalytic activity.

In the case of the rate of discoloration of MB, herein defined as the time it took for each nanomaterial to decolorize MB, is shown in Figure 2.6 as the final timepoint of each discoloration experiment. The results show that the nanowires had the fastest reaction rate, which was capable of decolorizing MB after 90 minutes. The nanorods, on the other hand, decolorized MB after 210 minutes, and the nanoplates after 300 minutes. The rate at which each nanostructure decolorized MB could be explained in terms of the stability of the nanostructure. The nanowires, which were the particles that showed the highest dissolution, were the ones showing the highest reaction rate.

These results indicated that the photocatalytic activity of the material was not directly or completely related to the band gap energy of the material or the relative percentages of the different oxidation states of the Mo (Table 2.1). The nanorods presented the highest photocatalytic activity, while they had the second largest band gap and the largest ratio of Mo⁺⁶ to Mo⁺⁵ ions. The nanoplates presented the lowest photocatalytic activity, even though they had the smallest bandgap and smallest ratio of Mo⁺⁶ to Mo⁺⁵ ions. This indicates that while a smaller band gap can be beneficial in allowing greater absorption of light. Generally, the smaller bandgap can be beneficial in allowing greater absorption of light, however, the increase in defects and absorption of visible light by mid-gap states may not be efficient for exciton generation. Hence,

based on these results, the oxidation state seems to be also playing a significant role in the material's photocatalytic properties.



Figure 2.6. Discoloration activity of MoO₃ nanostructures at 500 mg/L with 50 mg/L MB at pH 5.4. Red and green correspond to control experiments with only MB present. Purple and pink correspond to control experiments with only molybdate present.

To confirm the role of dissolution on the photocatalytic activity, the photocatalytic degradation results of MB by the nanostructures were compared against the nanostructure dissolution at the end of each reaction at different pH values as shown in Figure 2.7 to understand the role of dissolution on degradation of MB. Increasing the pH from 2 to 10 resulted in enhanced dissolution of the nanorods and nanowires by 40% and 60%, respectively, which was accompanied by a decrease in decolorization of the MB. However, the difference in dissolution of the nanoplates did not show a detrimental impact on the degradation of MB, likely because of the lower extent of dissolution of the nanoplates (< 20% at all pH values over the experimental period). These results showed that the more dissolution exhibited by the nanostructure, the less degradation of MB is observed. This can be due to a competition mechanism between the ion and the nanomaterial. While the nanostructure is dissolving, a

competition between ion-MB to form a complex, and nanostructure-MB the degrade the MB is happening.



Figure 2.7. Nanomaterial dissolution and MB degradation after light reaction with dark reaction subtracted) at different pH values at the end of each experiment. Black dots indicate the % of Mo dissolved and red dots the % of MB degraded.

3.5 Role of Reactive Oxygen Species on The Degradation Mechanism of MB

The photocatalytic degradation mechanism by the MoO₃ nanostructures has been associated with the production of reactive oxygen species. In this study, the production of different ROS was evaluated for all three nanomaterials to better understand the degradation mechanisms of MoO₃ nanostructures under visible light. Figure 2.8-2.10 represents the production of OH⁻, ¹O₂ and H₂O₂ radicals at different pH values since pH clearly showed an important role in the photocatalytic activity of the MoO₃ nanostructures. Among the three different MoO₃ structures investigated, the nanorods produced the most ROS, which explains the increased photocatalytic activity of this nanomaterial as seen in Figure 2.6. In fact, the presence of light directly affected the ROS production of the nanorods, as seen in Figure A.10.

More importantly, all three nanomaterials showed production of ROS even in dark conditions indicating that the nanomaterial not only have photocatalytic properties, but also catalytic properties. Production of ROS in the dark is not novel in photocatalytic material as a number of studies report this phenomenon.^[221–223] Furthermore, the production of ROS increased with increasing pH values. It is well-known that different radicals are produced at different pH, and pH plays an important role in the generation of ROS.^[224] Figure A.10 shows the contribution of ROS production due to the introduction of visible light for the different nanostructures at the different pH values. As we can see, the increase in pH increases the concentration of hydroxyl ions in solution, which can promote the formation of H₂O₂, following oxidation reactions leading to the formation of singlet oxygen or undergoing reduction by forming hydroxyl radicals. The low amount formation of ¹O₂ can be explained because the singlet oxygen radical is not produced via electron transfer process.^[225]

Interestingly, if we compare the degradation results in Figure 2.6 with the production of the ROS in Figure 2.8-2.10, specifically the hydrogen peroxide production of the nanorods, nanowires, and nanoplates, we see similar patterns indicating that the most probable primary species responsible for the degradation of MB is hydrogen peroxide. For instance, with increasing pH, the hydrogen peroxide production contribution from the light of the nanorods and nanowires generally decreases as does the % degradation in Figure 2.6. However, the hydrogen peroxide production of the nanoplates increases slightly and then remains approximately the same as pH 2 exhibiting the same pattern as the % degradation in Figure 6.

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Figure 2.8. Hydrogen peroxide production.



Figure 2.9. Hydroxyl radical production.



Figure 2.10. Singlet oxygen production.

The ROS from the isolated ions produced by the nanostructures were also evaluated in the present study. In Figure A.11, it is evident that the ion resulting from the dissolution of the nanomaterial can have degradative effects due to ROS production. In the dark condition, hydroxyl radical and hydrogen peroxide production were not significant, while in the presence of light, there was a significant increase in these ROS. This finding signifies that the dissolved ions from the nanomaterial can also contribute to the degradation of MB. ROS production by molybdate ion can undergo a Fenton-like reaction in water and produce ROS.^[209,226–228]



Figure 2.11. MB degradation with each of the nanomaterial in the presence of scavengers in light and dark conditions. Reaction conditions were 500 mg/mL MoO₃ at pH 5.4 in the presence of 10 mM of TEOA, 75 mM of IPA and 1 mM of p-BQ.

To further understand the role of ROS in the photocatalytic mechanism of the MoO₃ nanostructures, we employed ROS scavengers and a hole scavenger. Isopropyl alcohol (IPA) was employed to trap \cdot OH, triethanolamine (TEOA) scavenges h+ and benzoquinone (BQ) scavenges \cdot O₂^{-.[229–232]} These scavengers were added to the reaction and the degradation results are shown in Figure 2.11. The greatest effect in the presence of ROS scavengers was seen with the addition of TEOA, which is a hole scavenger, as shown in Figure 2.11. Only with the presence of TEOA all three nanomaterials were unable to completely decolorize MB and no discoloration was observed, indicating that the production of holes plays an important role in MB

degradation. Furthermore, when the reaction took place in the dark in the presence of TEOA, no discoloration was observed. In this case, TEOA seemed to act as a competing adsorbent able to inhibit the MB adsorption on the surface of the nanostructures. Furthermore, this confirms that the likely pathway by which hydrogen peroxide is generated is via the oxidation of water molecules by the photogenerated holes. In addition, hydrogen peroxide is the most likely primary species responsible for the degradation of methylene blue since, when hydroxyl and singlet oxygen scavengers were added, complete degradation of MB was still possible. Interestingly, when isopropanol was present (a hydroxyl radical scavenger) the photocatalytic reaction became more efficient. A possible explanation could be that the generation of additional water molecules from the isopropanol and hydroxyl radical reaction may get oxidized by the photogenerated holes further increasing hydrogen peroxide concentrations.

4. CONCLUSIONS

In the present work, we have successfully synthesized MoO₃ nanostructures with different sizes, morphologies, and properties. We have demonstrated that the dissolution process also depends on the oxidative state, and nature of the Mo-O bond. For instance, the nanoplates, which contained more Mo⁵⁺ than Mo⁶⁺, dissolved less than the nanorods which had more Mo⁶⁺ rather than Mo⁵⁺ in their structure. The dissolution process reported here shows that MoO₃ nanostructures are not suitable for most water treatment applications due to high solubility at the pH employed in drinking water. These results suggest that more research should be done in order to
improve the stability of these nanostructures rather than present photocatalytic studies of different organic molecules. Given the limitations of this material it is no surprise that TiO₂ is more heavily utilized, as is an extremely insoluble material.

The photocatalytic experiments of methylene blue showed that the photocatalytic degradation of MB is influenced by the dissolution of the nanomaterials. Furthermore, there is a relationship between the degradation and complexation process. The dissolved ions can play an important role in the photocatalytic activity of the nanostructure. As shown in the HPLC experiments, the ion not only produces a complex between the MB, but it is also able to degrade MB.

While ROS production and subsequent degradation of MB were observed by the nanomaterial, some ROS production was observed by the dissolved product of the nanomaterial. We also quantified the production of different ROS and we saw that hydrogen peroxide is the most important ROS responsible for the degradation of MB. The analysis of the ROS and the employment of different scavengers showed that H_2O_2 and the photogenerated holes in the nanostructures play a role in the degradation process of methylene blue. The photogenerated holes increased the oxidation of water molecules while increasing the concentration of H_2O_2 , the ROS responsible for the degradation of MB.

CHAPTER 3 – MOLYBDENUM TRIOXIDE PARTICLE BEHAVIOR IN AQUATIC SYSTEMS

Adapted from "Inorganic Salts and Organic Matter Effects on Nanorod, Nanowire, and Nanoplate MoO₃ Aggregation, Dissolution, and Photocatalysis" by S. Fanourakis, J. Peña-Bahamonde, and D. Rodrigues^[154]

1. INTRODUCTION

Engineered nanomaterials have attracted great research interest due to their unique properties that differ from the properties of the bulk material. For instance, nanosized MoO₃ has been shown to have a variety of uses owing to its photocatalytic, capacitive, gas sensing, optical, and oxidative properties.^[58,233–238] MoO₃ has been of particular interest in water treatment due to its ability to be used in a great variety of applications and ability to control its shape and size.^[239,240] The chemical and electrical properties of the nanomaterial can be altered by controlling the size and shape of the material. For example, MoO₃ structure can be controlled by altering synthesis parameters such as amount and type of reagents present (i.e. amount and type of acid, absence or presence and type of surfactant), and different crystal structures can be synthesized, such as h- or α - MoO₃.^[58,164] The different MoO₃ morphologies have been shown to have different chemical and electrical properties, which can affect their dissolution and photocatalytic properties in different solution chemistries.^[58] Despite many studies showing MoO₃ can be promising in water treatment, it has recently been shown that its high solubility can lessen its utility.^[58] However, no systematic studies have been performed thus far examining the stability (aggregation behavior and dissolution) and photocatalytic activity of different morphologies of MoO₃ in complex

water chemistry solutions containing inorganic salts and/or natural organic matter (NOM).

Numerous studies have been conducted on other nanomaterials such as TiO₂, ZnO, SiO₂, CeO₂, and Ag examining how inorganic salts and NOM – specifically, humic acid (HA) – affect nanoparticle stability in solution.^[233,241–249] Highly stable material in solution present with low solubility and minimal to no aggregation. Aggregation in particular can be an important measure of nanoparticle colloidal stability, which is greatly influenced by the presence of inorganic and organic compounds.^[250] For example, the presence of inorganic salts can cause nanoparticle aggregation and presence of organic matter can stabilize nanoparticles significantly.^[1,250] However, depending on the stabilization mechanism (steric hindrance or surface modification), the properties of the material may be altered.^[58,248,251,252] For instance, peroxymonosulfate degradation of methylene blue can be either positively or negatively affected by the presence of HA depending on whether the concentration of HA is low or high, respectively.^[253] TiO₂ photocatalytic activity is hindered by the presence of HAs since these organic material can compete for active sites on the photocatalyst or act as light screens.^[252] Furthermore, increased aggregation can also hinder photocatalytic activity by reducing the available surface area effectively reducing light absorption.^[252] Thus, the presence of inorganic salts can greatly hinder photocatalyst degradative properties.

Solution chemistry is an important factor to consider when examining the photocatalytic properties of a material. However, nanomaterial photocatalytic activity is understudied in complex solutions. In this study, the photocatalytic degradation of methylene blue (MB) was examined in the presence of inorganic salts (NaCl or CaCl₂) and NOM such as HA or extracellular polymeric substances (EPS) produced by *E. coli*. These organic and inorganic compounds can be present in waters undergoing water treatment; thus, it is important to understand their effect on the nanomaterials' properties. Therefore, to understand the effect of organic and inorganic compounds on the degradative properties of structurally different MoO₃ nanomaterials, not only was their ability to degrade MB investigated in complex solutions, but the aggregation kinetics and dissolution properties of the nanomaterials were also examined.

2. EXPERIMENTAL

2.1 Materials

The chemicals used were purchased and utilized as received from Sigma Aldrich and include: Ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), sodium chloride (NaCl), calcium chloride (CaCl₂), Suwannee River Humic Acid (HA), sodium hydroxide (NaOH), hydrochloric acid (HCl), nitric acid (HNO₃), methylene blue (MB), potassium hydrogen phthalate, and ethanol. The hydrogen peroxide (H₂O₂ 30%) was purchased from Macron Fine Chemicals.

2.2 Nanoparticle Synthesis and Characterization

All three nanoparticles were synthesized as described in our previous work.^[58] Briefly, the nanorods were synthesized via the hydrothermal method in which 2.46 g of Ammonium molybdate tetrahydrate was dissolved in 20 mL MilliQ water, then 5 mL concentrated HNO₃ was added drop wise, and the solution was heated to 90 °C for 3 hours in a Teflon lined autoclave. The particles were cleaned by centrifugation using 70% ethanol and dried at room temperature. The batches of nanorods, nanowires, and nanoplates utilized were the same as our previous publication.^[58] Briefly, for the nanoplates, 192 mg of molybdenum powder was added to a Teflon vessel (45 ml) containing 24 ml of ethanol under magnetic stirring. Then, 3 ml of H₂O₂ was added, and the mixture was stirred for 0.5 h to obtain a yellow solution. The Teflon vessel was then sealed in a stainless-steel autoclave, heated, and maintained at 160 °C for 14 h. The product was collected by centrifugation (Thermo Scientific Sorvall Legend XTR Centrifuge), washed with ethanol, and dried under vacuum. The nanowires were prepared using the same procedure as the nanoplates with the difference of using 384 mg of molybdenum powder, 30 ml of isopropanol, and 5 ml of H_2O_2 .

The characterization was done by using scanning electron microscopy (SEM) (Nova NanoSEM 230) to examine the morphology of the crystal samples. Samples were first coated with gold for 30 seconds (Denton Desk V) and then examined with the SEM at accelerating voltage equal to 5 kV at different magnifications (×15,000 for the nanorods, ×30,000 for the nanowires, and ×40,000 for the nanoplates). Crystallographic information of samples was obtained via X-ray diffraction (XRD)

using Rigaku MiniFlex 600 diffractometer with a Cu anode (40 kV and 15 mA) at a scanning rate of 0.05° per second from 5° to 80° in 20. These materials were extensively characterized (XPS, FTIR, and bandgap measurements) in our previous publication.^[58]

2.3 Stock Solution Preparation

For each of the three nanomaterials, 1000 ppm stock solutions were prepared by mixing 3 mg of each nanoparticle in 3 mL MilliQ water and sonicating for 15 min in a bath sonicator (Branson 1800) to create more evenly dispersed particle solutions. Stock solutions were utilized within three hours to ensure dissolution was kept to a minimum (less than 20%).

A stock solution of 1 M NaCl was prepared by dissolving 1.23 g of NaCl in 100 mL MilliQ water. Similarly, to prepare a stock solution of 100 mM CaCl₂, 1.4 g CaCl₂ were dissolved in 100 mL MilliQ water. For the preparation of the stock HA solution, 50 mg of HA were dispersed into 50 mL MilliQ water. The total organic carbon (TOC) of this solution was measured and determined to be 13.16 ppm using the TOC Analyzer instrument (Shimadzu, TOC-L CPH) and using known concentrations of potassium hydrogen phthalate (1, 5, 10, 50, and 100 ppm) for the calibration curve.

To prepare a stock solution of EPS, *E. coli* K12 was grown in M63 media^[254] at 25°C for 48 hours until the culture was turbid at which point the cultures were centrifuged and filtered through a 0.2 μm vacuum filtration system to eliminate any cells present in solution. Then, they were combined and transferred to a dialysis bag (Spectrum labs 54 mm regenerated cellulose dialysis membrane with a 3.5 kDa pore size), which was kept in MilliQ water. The first day the MilliQ water was exchanged three times every three hours. Then the water was exchanged twice a day until the conductivity of the water matched that of the MilliQ water to ensure any salts from the media were removed and the salt content could be controlled for the experiments. Similar to the HA, the TOC of the EPS was determined using the TOC Analyzer instrument, which determined the EPS stock solution to have a TOC of 2.16 ppm. All stock solutions (nanomaterial, NaCl, CaCl₂, HA, and EPS) did not have their pH adjusted for the experiments performed at pH 5, but had their pH adjusted to 7 for the experiments performed at pH 7 using 0.1 M NaOH.

2.4 Particle ζ-Potential

Particle charge in solution was measured using the ZetaSizer (Malvern Nano ZS, Malvern) instrument and using the zeta potential transfer standard DTS 1235. Stock solutions of each nanoparticle were diluted from 1000 ppm to 250 ppm and approximately 1 mL of the diluted solution of each nanoparticle was transferred to a folded capillary cell for measurement. The concentration of 250 ppm of the nanoparticles was determined to be an appropriate concentration for acquiring stable measurements with minimal error. Measurements were collected at pH 5 and 7 and pH adjustments were performed using 1M NaOH or 1M HCl. Measurements were performed in triplicate.

2.5 Particle Aggregation Behavior

The aggregation behavior of each nanoparticle was studied in different concentrations of NaCl (ranging from 1 mM to 200 mM) and different concentrations of CaCl₂ (ranging from 1 mM to 20 mM) using Dynamic Light Scattering (DLS) (Malvern Nano ZS, Malvern). Additionally, experiments were performed at either pH 5 or 7 in which case the pH was adjusted using 1 M NaOH. To measure aggregation kinetics of each particle, 0.375 mL stock solution was transferred to a polystyrene cuvette suitable for DLS measurements to reach a final concentration of 250 ppm for each nanoparticle. To achieve each concentration of either NaCl or CaCl₂, appropriate amounts of each stock solution were calculated. Then MilliQ water was added to the sample, such that once the NaCl or CaCl₂ was added, the total volume reached 1 mL. Next, the salt solution was added, and the cuvette was vortexed for approximately 2 seconds and immediately placed in the ZetaSizer for measurement. The ZetaSizer was set to collect 3 measurements every 3 seconds for up to 20 minutes. Measurements were performed in triplicate. The aggregation rate, r, was calculated for each measurement period using Equation 3.1^[249,255,256] and subsequently Equation $3.2^{[249,255,256]}$ was utilized to calculate the attachment efficiency, α ,

$$r \propto \frac{1}{N_0} \left(\frac{d D_h(t)}{dt} \right)_{t \to 0}$$
 (3.1)

and
$$\alpha = \frac{r}{r_{diffusion limited}}$$
. (3.2)

In Equation 3.1, D_h denotes the hydrodynamic diameter measured by the DLS instrument and N_0 is the initial concentration of the nanoparticles. In Equation 3.2, r

denotes the aggregation rate at a particular concentration and r_{diffusion limited} is the aggregation rate at which the aggregation rate is no longer influenced by a change in ionic strength (IS).

The effect of humic acid on the aggregation behavior of each nanomaterial was studied to determine the minimum required concentration for colloidal stabilization of the nanoparticles. First, 0.5 ppm TOC of humic acid was studied at pH 5 and 7. Because there were minimal differences between aggregation rates between both pH values, the concentration of humic acid was increased to 1 ppm TOC and studied at pH 7. Finally, the effect of 1 ppm TOC of EPS was determined at pH 7. To achieve this condition, 0.75 mL of the stock EPS solution was added to the cuvette. These experiments were performed at the following conditions: 30 mM NaCl, 200 mM NaCl, 3 mM CaCl₂, and 15 mM CaCl₂. These conditions were selected such that for each type of salt the aggregation behavior would be either reaction or diffusion limited. Measurements were performed in triplicate.

2.6 Particle Dissolution – Effects of Salts And NOM

The solubility of each nanoparticle was examined in 6 mL MilliQ water at pH 7 with the concentration of each nanoparticle starting at 250 ppm. The dissolution of each material was quantified using Atomic Absorption Spectroscopy (AAS) (AAnalyst 200, Perkin Elmer) equipped with a Molybdenum lamp from Perkin Elmer and using duplicate samples and triplicate measurements per sample. The following solution conditions were examined: 200 mM NaCl, 15 mM CaCl₂, 1 ppm HA, and 1 ppm EPS. To achieve each condition, appropriate amounts from the stock solutions were added in MilliQ water and the nanoparticles were introduced, the solutions were mixed, and left standing for 3 hours at room temperature (~25 °C). A time length of three hours was chosen based on our previous work in which all three nanomaterial were able to significantly degrade MB by three hours.^[58] However, in that work the nanowire MoO₃ was much faster in removing MB, thus lower concentrations of nanomaterial and MB were analyzed in this work to allow for an improved comparison of the properties of each material in the presence of a variety of chemical conditions. Finally, the solutions were filtered using centrifugal Amicon ultrafiltration tubes (30,000 NMWL). The recovered solution was diluted 1:5 in order to ensure the measurements were within the linear range of the instrument.

2.7 Methylene Blue Decolorization

Photocatalytic experiments were performed at pH 7 to measure the change in coloration of methylene blue (MB) in aqueous suspensions of MoO₃ under different chemical conditions. The chemical conditions tested included the presence of the following solution conditions and combinations of solutions: a) 200 mM NaCl, b) 15 mM CaCl₂, c) 1 ppm HA, d) 1 ppm EPS, e) 200 mM NaCl and 1 ppm HA, f) 200 mM NaCl and 1 ppm EPS, g) 15 mM CaCl₂ and 1 ppm HA, and h) 15 mM CaCl₂ and 1 ppm EPS. Samples were exposed to visible light (Nexlux LED light, which utilizes the 5050 RGB LED package with a wavelength range of 400 to 700 nm and maximum luminous intensities of 100, 400, and 100 mcd for the red, green, and blue regions, respectively). The lights were mounted on the inside of a cylindrical hard surface to be

able to provide even lighting when on a magnetic hotplate stirrer (Heidolph). The samples were first arranged circularly on a shallow glass container with the diameter of the stirring plate such that each would receive an equal amount of light. Then, they were placed on the stirrer plate and the lights were mounted on the plate. A small amount of water was placed in the glass container such that the samples were in a water bath to maintain their temperature at room temperature. The temperature of the water bath was controlled to room temperature using a water pumping system. The initial concentration of MB was fixed at 25 mg/L with a catalyst loading of 250 mg/L and a final volume of 6 mL. Prior to photooxidation, the solution was stirred in the dark for 30 min to establish an adsorption–desorption equilibrium.^[58] After 3 hours of irradiation 0.5 mL of each sample solution was removed and centrifuged (Thermo Scientific Sorvall Legend XTR Centrifuge) at 12,000 rpm for 5 min to separate photocatalysts from the mixture. MB absorbance was measured using a UV–Vis spectrometer, SynergyMX Microtiter plate reader (Biotek) at $\lambda = 664$ nm. The experiments were performed in triplicate and the results were analyzed and reported as coloration of MB. The data for the MB coloration when nanoparticles were present were adjusted to remove the effects of any complexation occurring between MB and the ions and NOM present in the solutions.

2.8 Statistical Analysis of Results

The aggregation, dissolution, and MB degradation data (acquired by methods described in sections 2.4-2.7) were analyzed using the GraphPad Prism 8 software. A

two-way ANOVA test was utilized along with Tukey's multiple comparison test to determine statistical significance of the results.

3. RESULTS AND DISCUSSION

3.1 Characterization

SEM images (Figure 3.1) of the material and XRD (Figure 3.2) for the nanorods, nanowires, and nanoplates show the material utilized in this study, which is the same batch also used and thoroughly characterized in our previous publication.^[58] New SEM images and XRD data were acquired showing that the morphologies shown in Figure 3.1 and crystallographic information depicted in Figure 3.2 match our previously published data.^[58]



Figure 3.1. SEM images of a) nanorods (×15,000 magnification), b) nanowires (×30,000 magnification), and c) nanoplates (×40,000 magnification).

The nanowires and nanorods presented diameters in the range of 59 nm and 180 nm, respectively, with lengths greater than 5 μ m. The nanoplates had a thickness around 74 nm and a width of approximately 180 nm. The XRD patterns for the three nanomaterials showed strong diffraction peaks indicating a highly crystalline morphology. Furthermore, the nanoplate and nanowire XRD peaks were indexed as orthorhombic MoO₃ (JCPDS – 35-0569), while for the nanorods they were indexed as hexagonal (JCPDS – 21-0569).



Figure 3.2. XRD of each MoO₃ nanomaterial from 5° to 80° (2 θ)

3.2 Effects oh pH and NOM in Nanoparticle Charge and Aggregation Kinetics

The ζ -potential of each particle was measured at pH 5 and 7 (Figure 3.3) to provide information on the charge of the particles in solution. The nanorods and nanowires showed a decrease in potential (more negative) as pH increased from 5 to 7.



Figure 3.3. ζ -potentials of each nanomaterial at pH 5 and 7 in MilliQ water at 25°C. Stars indicate statistical significance between the pH 5 and 7 results for each material (one, two, and three stars indicate p<0.05, p<0.005, and p<0.0001, respectively).

These more negative results are expected since an increase in pH can cause the

deprotonation of surface OH groups. This decrease in potential could also be caused by the breakdown of the crystal structure due to increased dissolution at higher pH values (the increased presence of hydroxyl ions facilitates MoO₃ dissolution and, thus, molybdate ion formation).^[58,218,257] The nanoplates showed an increase in potential with the change in pH (the nanoplate surface in pH 7 became more positively charged). The different nanostructures exhibit differences in their Mo⁺⁶:Mo⁺⁵ ratio (20.3, 6.4, and 0.5 for nanorods, nanowires, and nanoplates, respectively), which relates to the dissolution of the nanostructures, where nanowires dissolve more than nanorods and nanoplates.^[58] Unlike the nanorods and nanowires, the nanoplates did not dissolve as much (only around 20% at basic pH after 6 days), and they contained an increased ratio of Mo⁺⁵ to Mo⁺⁶ in their structure, which was caused by oxygen vacancies in the MoO₃ structure.^[58] Such vacancies can be filled by hydroxyl groups.^[258] Thus, it is likely that the introduction of OH⁻ ions interacts with the Mo⁺⁵ structures, filling oxygen vacancies, decreasing the concentration of hydroxyl ions in solution, thus, preventing the deprotonation of surface -OH groups and making the particles' surface charge slightly less negative with this slight increase in pH.

The ζ - potential of each particle was further examined in the presence of either increasing concentrations of NaCl or CaCl₂ (Figure 3.4). As expected, with increasing IS, there was an increase in the ζ -potential of the material (the material becomes less negatively charged). At higher ionic strengths, the change in ζ -potential became less and less negatively charged since the electrical double layer becomes more and more compressed with the increase of IS.^[256] Additionally, the presence of CaCl₂ affected the surface charge more significantly than NaCl and much smaller changes in potential were observed. This is expected as the adsorption of calcium ions (a divalent ion) on the surface of the material increases the positive charges on the surface much more than sodium ions (a monovalent ion), thus, surface neutralization is greater with the presence of calcium ions rather than sodium ions.^[256,259,260] Furthermore, since the size of the two cations is similar, the differences that were observed indicate that charge is the most important factor, while cation size does not play a role in this case. Similar to these results, a greater effect from CaCl₂ than NaCl has also been observed when investigating ZnO aggregation.^[259] Interestingly, as the IS of NaCl is increased from 30 mM to 60 mM, the change in potential became larger for the nanorods and nanowires than the nanoplates This may indicate that the presence of more Mo⁶⁺ than Mo⁵⁺, which also contributes to the elongated structure of the nanorods and nanowires, influences the electrical double layer compression as IS changes. Furthermore, the ζpotentials each reach a plateau value indicating that they have reached a maximum

compression of the electrical double layer and the charge of the material is no longer affected by the increasing ionic strength.^[260]



Figure 3.4. ζ- potential of each nanomaterial (nanorods, nanowires, nanoplates) in (a) NaCl and (b) CaCl₂ salt solutions in MilliQ water adjusted to pH 7 using NaOH at room temperature. The dotted lines do not represent continuity of the data.

The attachment efficiency at each IS for each nanoparticle and for each salt (NaCl or CaCl₂) and pH value (5 and 7) was calculated by Equation 3.2 and is shown in Figure 3.5. From these curves it is evident that the aggregation of the nanoparticles follows the reaction and diffusion limited scheme. At low IS the aggregation rate is limited by the number of ions present in solution (referred to as the reaction limited region), and after a critical point (the critical coagulation concentration, or CCC) the aggregation rate goes from reaction limited to diffusion limited in which an increase in

IS no longer affects the aggregation rate. The CCC can be used to compare the stability of nanoparticles in aqueous environments since lower CCC values indicate lower stability due to those particles being more likely to aggregate.



Figure 3.5. Attachment efficiency of each nanomaterial (nanorod, nanowire, and nanoplate) in pH 5 or 7 with increasing IS of either NaCl (10-200 mM) or CaCl2 (3-45 mM).

Using the attachment efficiency curves, the critical coagulation concentrations (CCC) of each nanoparticle for each salt and pH were calculated by finding the intersection of the line describing the reaction limited region and the line describing the diffusion limited region. Based on the calculated CCCs at each pH for each nanostructure (Figure 3.6), all investigated particles presented similar stability at the two pH values. With NaCl present, all nanoparticles had similar stability, however, differences between the stability of the nanoparticles in the presence of CaCl₂ were

larger than when in the presence of NaCl. In CaCl₂ the nanowires appear to be more stable at pH 5 than the nanorods and nanoplates. At pH 7, the nanowires and nanoplates have similar stability and the nanorods are more unstable than the nanowires and nanoplates. In addition, the nanorods have a statistically significant increase in CCC from pH 5 to 7 in the presence of CaCl₂ but not in the presence of NaCl. This lowering in stability at higher pH values is expected as the particles are more soluble as pH increases as presented in a previous work.^[58] Furthermore, the greater change in colloidal stability when CaCl₂ is present, rather than NaCl can be also attributed to Ca²⁺ ions contributing to a larger charge neutralization than Na⁺ ions along with potential complexation reactions and bridging effects. The nanowires followed the same pattern as the nanorods although the differences did not show statistical significance. Unlike the nanorods and nanowires, the nanoplates showed the opposite pattern; an increase in stability was seen when pH was increased from 5 to 7 (albeit the result was statistically significant only for CaCl₂). The difference in pattern between the materials' stabilities could be explained by the ζ -potential changes seen in Figure 3.3. While the nanorods and nanowires showed a higher negative potential at pH 7 than pH 5, the nanoplates show a more positive potential. Thus, an increase in pH can stabilize the nanoplates (reduce the CCC) rather than destabilize them further as with the nanorods and nanoplates (indicated by an increase in the CCC). These results complement the results from the ζ -potential measurements, further indicating that the ratio of Mo^{6+} to Mo^{5+} in the MoO₃ structure may play an important role in particle aggregation stability when salts are present and when pH is altered.



Figure 3.6. Critical Coagulation Concentrations (CCCs) of each nanomaterial at pH 5 and pH 7. Asterisks indicate statistically significant values (* = p<0.01, *** = p<0.000001) between pH 5 and pH 6 CCCs.

The effect of pH and natural organic matter (HA or EPS) on the aggregation rates in the reaction and diffusion limited regions of the nanoparticle kinetics was examined using NaCl or CaCl₂ (Figure 3.7). The change in pH does not significantly affect the aggregation rate of the nanorods and nanoplates but more so affects the aggregation rate of the nanowires when no NOMs are present and even more so when CaCl₂ is present instead of NaCl. This could be caused by the increased dissolution resulting from the higher pH, which would compete with the increased hydrodynamic radius caused by the aggregation of the nanoparticles due to the presence of salts (Figure 3.7). With the presence of 0.5 ppm TOC HA, the aggregation rates in some conditions for all three materials were reduced. These conditions include: 200 mM NaCl and 45 mM (IS) CaCl₂ for the nanorods, 45 mM (IS) CaCl₂ for the nanowires, and 200 mM NaCl, 9 mM and 45 mM (IS) CaCl₂ for the nanoplates. This indicates that HA at a concentration of 0.5 ppm TOC not only starts to alter the electrostatic interactions between particles, but it also starts to introduce some steric effects and

may potentially adsorb to the nanoparticles reducing the aggregation rates. Since the changes in aggregation rates were not significant in any of the conditions for each nanoparticle, the TOC of HA was increased to 1 ppm. Furthermore, since for all material there was not a significant difference between the aggregation rates when 0.5 ppm HA was present and the pH was changed from 5 to 7, the pH was adjusted to 7 for the remaining experiments to provide environmentally relevant data. With a 1 ppm TOC of HA at pH 7 there was a significant reduction in aggregation rates for all conditions for the three nanomaterials. This reduction was similar when EPS was introduced instead of HA. The steric effect of NOM and the resulting stabilization of nanomaterial has been observed in a number of different studies and confirmed via theoretical calculations and observations.^[248,251] These effects can have significant impact on the dissolution of the material and the ability of the photocatalyst to degrade contaminants as is discussed in the following sections.





3.3 Particle Dissolution in Different Salt and Organic Matter Solutions

Nanoparticle dissolution can be affected not only by nanoparticle size and

shape, but by the chemical conditions of the solution as well.^[120,261] As such, the effect

of salt (at a concentration at which the aggregation was diffusion limited for each salt according to the aggregation kinetics data), HA, and EPS on the dissolution of each MoO₃ structure were investigated (Figure 3.8). A length of time of three hours was selected for the dissolution of the nanoparticles based on the degradation behavior observed in our previous work. ^[58]



Figure 3.8. Dissolution of nanorods, nanowires, and nanoplate particles in different solution conditions. All solutions were adjusted to pH 7 and contained 250 ppm of the respective nanoparticle.

After 3 hours in pH 7 solution, the nanoplates are the least soluble, followed by the nanorods, and nanowires. All three material are least soluble when salts are present. The presence of salt promotes nanoparticle aggregation, which can effectively reduce the available surface area interacting with water molecules. Thus, particle dissolution can be reduced via the addition of salts.^[255] Interestingly, the monovalent salt stabilizes all three particles more than the divalent salt. The IS of the monovalent salt (200 mM) was much higher than that of the divalent salt (45 mM) indicating that IS plays a more significant role in the reduction of dissolution of the nanoparticles than the valency of the cations. It has been found that metal oxide dissolution occurs due to hydroxide ion interaction with the nanomaterial surface.^[262] While the presence

of calcium ions provides greater surface neutralization and formation of a more compact electrostatic double layer as discussed earlier, the higher ionic strength seems to play a greater role in dissolution reduction. The increased number of cations present can be more effective in preventing hydroxyl ion interaction with the material by attaching to the negatively charged surface of the nanomaterial. In addition, the higher number of chloride ions present due to the larger IS in the case of 200 mM NaCl can provide greater steric protection thus reducing the interaction of the nanoparticles with hydroxyl ions, effectively reducing the dissolution of the nanomaterial more than when 45 mM (IS) CaCl₂ is present.

Furthermore, EPS reduces dissolution more than HA indicating increased interaction between the nanomaterial and EPS compared to HA. Although EPS is overall negatively charged, it contains positive and negatively charged species unlike HA, which is mainly negatively charged. Thus, the greater decrease in dissolution by EPS rather than HA is expected. The greatest reduction in solubility is seen in the nanowires, which are significantly stabilized by both salts and NOMs. Unlike the nanowires, no significant reduction in solubility is observed for the nanorods or nanoplates in the presence of HA. Likely, the structure of the nanowires plays a role in the effectiveness of the steric protection by NOM. Although the nanowires have a similar chemical makeup as the nanorods, their smaller size could potentially lead to an increase in steric protection by NOM.

3.4 The Effects of Salts and NOM on The Nanomaterial Photocatalytic Activity

Methylene blue was utilized as a model contaminant to assess the photocatalytic activity of each nanomaterial with and without the presence of salts (either 200 mM NaCl or 45 mM IS CaCl₂) and/or 1 ppm NOM (HA or EPS). The different conditions were tested in the dark (includes effects from adsorption and complexation) and in the light (includes effects from photocatalysis, adsorption, and complexation), and the remaining coloration of MB in solution was assessed for each condition.

In Figure 3.9, it is evident from the control experiments, which contain no nanoparticles, that some complexation occurs between MB and each salt, NOM and, combinations of salts and NOM. Additionally, without the presence of nanomaterial, no photocatalytic activity occurred. The removal of MB by NaCl was larger likely due to the higher number of Cl⁻ ions present from the difference of IS between NaCl and CaCl₂. Furthermore, the removal was higher with HA present rather than EPS, which is expected, as the ζ -potential of the HA solution was more negative than that of the EPS solution, making HA more prone to complexation with the positively charged MB. When either salt was present with either HA or EPS, the removal of MB was more prominent in the presence of the salts rather than NOM.



Figure 3.9. Effects of 200 mM NaCl, 45 mM (IS) CaCl₂, 1 ppm HA, and 1 ppm EPS on the removal of MB by nanorods, nanowires, and nanosheets. Complexation of MB with each salt or NOM have been removed from the nanomaterial interaction with MB.

The effects from MB complexation with salts and/or NOM in Figure 3.9

(nanorods, nanowires, and nanoplates) were removed by adding the MB decolorization amount from the dark and light controls to the nanoparticle MB coloration data in the light and dark, respectively, to assess the effect of solution chemistry more accurately on nanostructure degradative properties. The type of MoO₃ present affected the removal of MB differently. For instance, the nanorods showed increased adsorption of MB when NaCl and HA, or CaCl₂ and HA or EPS were present. Furthermore, there was an increase in MB removal in light when each salt was present regardless of the presence of NOM. Except in the instance when NaCl and HA were present, where the increased removal in light could be accounted by the increased adsorption of MB by the material under the dark conditions. However, when CaCl₂ was present the photocatalytic removal of MB was greatly enhanced, and the presence of NOM did not alter the removal of MB in light. This phenomenon has been observed with other materials, however, the exact mechanism that causes increased photocatalytic activity of the nanomaterial in the presence of CaCl₂ has not been explored.^[262] It is speculated that, in the case of carbamazepine degradation by BiOCl the presence of Ca²⁺ increases adsorption via bridging effects, thus increasing photocatalytic degradation.^[262] Furthermore, it is interesting that the addition of NOM, while capable of reducing aggregation rates of the nanomaterial, does not affect MB removal. It is possible that the bridging or complexation effects due to the calcium ion have a higher affinity towards MB and the nanorods rather than the NOM present, thus any NOM in the solution will not compete in the photocatalytic reaction process.

Unlike the nanorods, the nanowires and nanoplates showed a general reduction in photocatalytic activity in the presence of salt or NOM. The nanowire removal of MB was most affected by the presence of salts and NOM. The adsorption of MB was significantly reduced by each salt and NOM. This was expected as the presence of salt causes increased aggregation, thus less surface area is available for MB to adsorb to and less surface area is available for light to interact with the material.^[252] In addition, with NOM present, especially with HA, the photocatalytic activity of the nanowires was greatly reduced. Likely, the increased interaction between NOM and the nanowires that results in decreased solubility also affects the ability of the material to degrade MB. This competitive interaction between MB, NOM, and the photocatalyst has also been observed in the degradation of MB by peroxymonosulfate^[253] and by cobalt-doped BiVO₄^[263].

Similar to the nanowires, the nanoplates also showed a decrease in MB adsorption but only in the presence of NaCl, CaCl₂, or HA. The adsorption of MB did not appear to be affected by the presence of EPS. In addition, MB adsorption was increased when both CaCl₂ and NOM were in the presence of nanorods. It is possible that when both CaCl₂ and NOM are present there is increased complexation between the nanomaterial, NOM, and MB allowing for greater adsorption of MB. For the nanoplates, however, when taking into account the increased adsorption in the presence of CaCl₂ and NOM, the photocatalytic activity of the material was reduced by the presence of salts or NOM.

While in our previous work we had determined that these materials would ultimately not be effective for use in water treatment due to their high solubility and low photocatalytic activity,^[58] taking into consideration these additional results, their usability for water treatment can be reconsidered. As per our previous work,^[58] for all the three different nanoparticles, we saw similar patterns where the holes are responsible for the oxidation of H₂O molecules forming hydroxyl radical and further increasing the H₂O₂ concentration. All three material showed a dramatic decrease in solubility in the presence of salts and either an enhancement or slight hindrance in photocatalytic activity. The nanorods for instance could be promising in water treatment when calcium chloride is present as it can greatly enhance the material's photocatalytic properties regardless of the NOMs present. The nanowires and nanoplates, however, do not show the same usability since their photocatalytic activity was reduced in the presence of salts and NOM. Ultimately, the importance of testing the behavior of new nanomaterial in a variety of solution chemistries is vital in understanding their usability outside the laboratory.

4. CONCLUSIONS

In this study the effects of inorganic salts (NaCl and CaCl₂) and natural organic matter (HA and EPS) on MoO₃ nanorods, nanowires, and nanoplates aggregation, dissolution, and ultimately on their photocatalytic properties of MB were examined. MoO_3 nanoparticles have shown high instability in solution due to their tendency to aggregate and dissolve. While nanorod, nanowire, and nanoplate MoO₃ had similar CCCs in NaCl, the nanorods showed higher instability in CaCl₂. However, all three nanomaterials showed exceptional reduction in dissolution in the presence of high ionic strength NaCl or CaCl₂ most likely due to the reduction in surface area caused by the high aggregation of the material. In addition, the presence of natural organic matter, whether HA or EPS, was effective in reducing aggregation rates of the material. Furthermore, only the dissolution of the nanowire structures showed significant reduction in the presence of HA or EPS likely due to the structure and significantly smaller size of the nanowires. Overall, the presence of inorganic salts causes high colloidal instability in the MoO₃ nanostructures in terms of aggregation behavior, but greatly aids in the reduction of dissolved MoO₃. NOM presence, however, can decrease aggregation rates, albeit dissolution is not similarly affected in all three structures.

When examining the potential usability of these nanostructures for photocatalysis, the effect of inorganic and organic components can be significant. For instance, while the nanowires were significantly more stable in the presence of salts and NOM, the photocatalytic activity of the material was reduced. The nanoplates also showed a reduction in photocatalytic activity. For these nanoparticles the steric effects from the NOM seemed to play a greater role in reducing the activity of the material. For the nanorods, while the presence of NOM alone did reduce degradative effectiveness, the presence of salts seemed to negate the effects from the NOM. Furthermore, the presence of CaCl₂ resulted in a highly enhanced photocatalytic activity regardless of the presence of NOM. Additional experiments will be required to ascertain the exact mechanisms of photocatalytic activity enhancement by the presence of calcium chloride.

Even though all three materials were composed of MoO₃, the structural and chemical differences of the nanostructures played a significant role in their aggregation, dissolution, and ability to photocatalytically degrade MB in solution while in the presence of inorganic and organic material. This denotes the importance of thoroughly investigating new materials for their intended application. While nanorod MoO₃ may not have high utility in water treatment due to its high solubility, in the presence of CaCl₂, it can be a promising material in degrading water contaminants. Without testing photocatalytic materials in more complex solutions, it cannot be known how effective they can be in degrading contaminants outside of the laboratory settings.

CHAPTER 4 – PHOTOCATALYSTS AND POLYMER COATINGS

Adapted from "In Situ Polymerization of Polypyrrole and Polyaniline on the Surface of Magnetic Molybdenum Trioxide Nanoparticles: Implications for Water Treatment" by S. Fanourakis, S. Barroga, J. Perez, L. He, and D. Rodrigues^[264]

1. INTRODUCTION

In recent years, molybdenum oxides including MoO₂, MoO₃ and other forms of MoO_{3-x} (2<x<3), have attracted enormous research efforts due to their broad applicability in catalysis, sensing, energy-storage, biomaterial, and field emission devices.^[137,265] Among these, MoO₃ has a wide bandgap (2.8-3.2 eV) with 20-30% ionic character for high visible light photocatalytic activity, thus favoring its use in photocatalysis for water treatment.^[1,58] Furthermore, introducing a magnetic core, i.e. Fe₃O₄ into MoO₃ can ease the removal of the nanoparticles via the use of magnetic separation instead of filtration techniques, which makes the nanocomposite particularly appealing for the use in water treatment.^[266] However, MoO₃ nanomaterials and modified MoO₃ nanocomposites are partially soluble in water, especially in neutral and basic conditions,^[58] which has hindered their use in the photocatalytic degradation of different organic pollutants such as dyes,^[267] phenols,^[268] volatile organic compounds (VOCs),^[269] antibiotics,^[270] and heavy metals.^[271] Dissolution rate of MoO₃ in aqueous systems is impacted by the size, crystallinity, shape, surface area, and exposed plane of the nanomaterial.^[1] To overcome this problem, MoO₃ nanostructures require modifications to improve their stability and decrease their dissolution in order to be utilized under neutral and basic conditions.

A suitable solution to solve the dissolution and reusability issues of nanoparticles is to coat them with polymers. For instance, polypyrrole (PPy) was used to coat cerium dioxide (CeO₂) nanoparticles for the reduction of Cr^{6+} . The polymer coated nanoparticle exhibited higher stability and reusability compared to pure CeO_2 due to the shell of PPy that prevents the dissolution of CeO₂ core.^[126] PPy on the surface of MoO₃ was also prepared as an anode material on aqueous supercapacitors and demonstrated that the dissolution of molybdenum during the cycling process was prevented due to the presence of a PPy coating layer.^[127] Furthermore, when PPy layers were fabricated on MoO₃ microrods, the underlying MoO₃ 1D structure was preserved in the material's conversion to PPy@MoS₂, when without the coating the microrod structure completely collapsed, indicating the necessity of the polymer layer in the stabilization of the material.^[128] In addition to dissolution and stability, polymer coatings can also add benefits to the properties of the nanoparticles. For instance, conductive polymers, such as PPy and PANI, have been used as coatings to nanomaterials due to their electrochemical, magnetic, and optical properties, low cost, and good environmental stability.^[128,129] These properties make them good candidates for coating MoO₃-based materials, such as the ones in this study. As PPy and PANI coatings have shown to improve the reusability and stability of metal oxide nanoparticles, we expect that the coatings will have a similar effect on our nanoparticles, which, uncoated, tend to dissolve in neutral pH conditions. Furthermore, the π -conjugated electron rich systems of conductive polymers help

inject electrons into the conduction band of semiconductor oxides making them good candidates for utilization in visible light photocatalysis.^[272]

In the present study, we selected PPy and PANI to coat magnetic MoO₃ nanoparticles because these polymers can improve material stability, have a high electron-hole carrying capacity, and have been shown to enhance light absorption capacity as well as enhance charge separation of photoexcited charge carriers, which we expect to enhance the performance of the MoO₃ nanoparticles.^[126,273] When they are mixed with transition metal oxide nanoparticles, the resulting material exhibits good photocatalytic performance.^[126,273] For instance, coating of PPy or PANI on semiconductor photocatalysts, such as MoO₃/PPy,^[274] PPy/TiO₂,^[275] PANI/ZnO, PANI/CoFe₂O₄, PANI/CeO,^[273] PPy-BiOI,^[276] resulted into a higher efficiency of organic dye degradation. Additionally, PPy encapsulated V₂O₅ nanohybrids showed enhanced degradation of ciprofloxacin and erythromycin antibiotics when exposed to visible light, which was attributed to the enhanced charge transfer properties due to the presence of PPy.^[272] PPy coatings also exhibited high photocatalytic activity in the reduction of hazardous Cr^{6+} to Cr^{3+} due to the increased electron transfer rate in the synthesized CeO₂@PPy.^[272] Furthermore, CeO₂@PPy exhibited higher reusability and stability compared to pure CeO₂.^[126] Overall, various studies on the applications of PPy and PANI on semiconductor photocatalysts have reported improved photocatalytic activity of the nanomaterials they were coating.

While previous studies have shown the improvement of the nanomaterial properties via coatings with conductive polymers, there is a lack of studies

investigating the parameters controlling the polymerization and their influences on the properties of the final polymer-nanoparticle composite. Many techniques have already been employed to indirectly investigate chain growth kinetics on different bulk materials by monitoring the change of monomer concentrations,^[277] changes in pH or temperature which might yield non-conducting oligomers,^[278] or utilizing neutron scattering, X-ray scattering, and light scattering techniques coupled with computational modeling to directly monitor the chain size with reaction time.^[279,280] Experimental data in conjunction with chemical calculations and computer simulations have allowed for the development of a number of theories regarding the polymerization kinetics of different polymers.^[232] However, to our knowledge, little research has been conducted on the growth kinetics of the polymer chains on the surface of nanoparticles during polymerization. Obtaining such information is challenging but allows us to elucidate how nanoparticle surface chemistry can affect the polymerization process and in turn better control the properties of coated nanocomposites.

In the present work, we first optimized the synthesis of two magnetic MoO₃ materials with distinct surface properties coated with PPy or PANI to be utilized in water treatment applications using response surface methodology (RSM) to minimize the dissolution of the materials while keeping photocatalytic activity at a maximum. Subsequently, we employed small angle neutron scattering (SANS) to monitor the growth process of PPy or PANI on these two variations of MoO₃ magnetic nanoparticles via monitoring the changes in the time resolved radius of gyration in the

polymer layer during in situ oxidative polymerization. The knowledge gained in this work advances the understanding on the effects of the base nanomaterial composition and chemistry in the polymer growth process, which sheds new insights on the optimization of polymer layers on the surface of the nanoparticles.

2. EXPERIMENTAL

2.1 Materials

The chemicals used in the synthesis, analysis, and photocatalytic degradation experiments were all analytical grade and were used as received. Ammonium molybdate tetrahydrate (AMT), Fe (II, III) oxide (CAS 1317-61-9), pyrrole monomer, aniline, deuterated water (D₂O), nitric acid, and ammonium persulfate were purchased from Sigma Aldrich. Aluminum chloride used in Atomic Absorption Spectrometry (AAS) analysis was purchased from Fisher Scientific. Methylene blue hydrate (MB), 96% was purchased from Acros Organics. A USP grade ethanol was purchased from Recon Lab, Inc. All stocks, standards and aqueous solutions were prepared using MilliQ water unless otherwise noted.

2.2 Methods

2.2.1. Material Optimization and Validation

To optimize the concentration of the MoO₃, Fe₃O₄, and PPy or PANI materials by obtaining a maximum percentage removal of methylene blue (MB) dye degradation and minimum dissolution of MoO₃, a numerical optimization technique, response surface methodology, was utilized. Details on the optimization process and results using response surface methodology are presented in the supplementary material, which include a statistical analysis of the resulting models (Table B.1), contour plots of the PPy@MoO₃@Fe₃O₄ model (Figure B.1), and contour plots of the PANI@MoO₃@Fe₃O₄ model (Figure B.2). Validation of the predicted models was performed by comparing the predicted values of the output response provided by the Design Expert software to the observed values from the experimental results of the optimized PPy@MoO₃@Fe₃O₄ and PANI@MoO₃@Fe₃O₄ material. Validation experiments of the optimized conditions were performed in triplicates and the materials were characterized as described below.

2.2.2. Photocatalytic Degradation Experiments for Nanoparticle Optimization and Validation

The photocatalytic degradation experiments were performed using an initial MB concentration of 40 ppm as previously described.^[58] Then, either PPy@MoO₃@Fe₃O₄ (PMF1) or PANI@MoO₃@Fe₃O₄ (PMF2) was added to achieve a final concentration of 500 ppm of the photocatalyst.^[58,281] The MB dye solution was stirred at room temperature with an agitation speed of 180 rpm and was allowed to undergo adsorption-desorption process in a dark environment to attain equilibrium for 30 min.^[58] The dark environment was achieved by covering the vials with aluminum foil to prevent passage of light into the MB dye solution. After equilibrating, the MB dye solution was irradiated using visible light (Philips F4T5 Soft white, 4W, intensity

199 lumens) with mechanical stirring to start photodegradation. Samples of MB dye solution (0.5 mL) were withdrawn at different time intervals. Prior to analysis, the catalyst in the solution was separated by magnetic separation followed by microcentrifugation using Eppendorf Centrifuge 5415C for 2 min at 13000 rpm. Each batch of the experiment was done in triplicate under identical conditions. A 0.1 ml of the withdrawn samples were transferred in a 96 well plate and analyzed with a UV-Vis spectrometer (Biotek SynergyMX Microtiter plate reader) using a target wavelength of 664 nm. A standard curve consisting of different concentrations of MB was used to determine the relationship of the MB dye's concentration and its absorbance. Then, the percentage of dye removal was computed using the following formula:

% MB dye Removal =
$$\left(\frac{A_o-A}{A_o}\right) \times 100 = \left(\frac{C_o-C}{C_o}\right) \times 100,$$
 (4.1)

where A_o and C_o , are the initial absorbance and initial concentration of the sample, and A and C are the absorbance and concentration of the sample at time t, respectively.

2.2.3. Dissolution Experiments for Nanoparticle Optimization and Validation

All dissolution experiments were conducted under neutral pH maintained at room temperature under static conditions. An aliquot of 500 ppm PMF1 or PMF2 photocatalyst was prepared by dispersing the photocatalyst (7.5 mg) in MilliQ water (15 mL) in a 15-mL centrifuge tube. The solution was stored for 48 h in the dark to allow the dissolution to take place. After 48 h of dissolution, the samples were filtered through a 0.2 µm syringe-drive PES Filter Media (VWR sterile syringe filter) into an Amicon centrifugation tube (Ultra-15, Millipore), which subsequently was centrifuged
at a speed of 4200 rpm for 15 min (Thermo Scientific Sorval Legend XTR Centrifuge). The samples were then analyzed using Perkin-Elmer AANalyst 200 Atomic Absorption Spectrometer using a molybdenum lamp.^[58]

MoO₃ stock solution (100 ppm) was prepared by dissolving ammonium molybdate tetrahydrate (AMT) with MilliQ water. Standard solutions were prepared by diluting the stock solution into 1, 10, 20, 30, and 40 ppm for the calculation of the calibration curve. Since the presence of Fe in the solution can depress the molybdenum signal, 0.5% aluminum chloride was added to the samples and standard solutions prior to analysis.^[282]

2.2.4. Synthesis of the optimized MoO₃@Fe₃O₄ nanoparticles

The magnetic MoO₃@Fe₃O₄ nanocatalyst (MF1) was prepared by precipitation method.^[283] In brief, MoO₃ precursor (AMT) (5.64 g) was dissolved in MilliQ water (50 mL). Then, Fe₃O₄, Fe(II, III) oxide (0.158 g), was added to the solution and homogenized by ultrasonication. The Fe₃O₄ utilized in this study was in the magnetite phase and was used without further modifications for the MoO₃@Fe₃O₄ synthesis. Concentrated nitric acid was introduced dropwise to the homogeneous solution under mechanical stirring until the pH of the solution reached 1.5. The mixture was heated in a water bath at 70°C for 8 h with mechanical stirring. After heating and stirring, the mixture was allowed to cool to room temperature. For the MoO₃@Fe₃O₄ (MF2), a modified procedure from our previous publication was utilized.^[58] In this case, AMT (2.46 g) was dissolved in MilliQ water (20 mL). Then, Fe₃O₄ (0.1 g) was dispersed in the solution, which was subsequently sonicated for 15 min to eliminate any aggregates. The mixture was introduced to an oil bath at 90°C and put under high stirring. Once the temperature of the mixture reached 90°C, nitric acid (5 mL) was added slowly. The material was kept at 90°C for 3 h under high stirring to allow the MoO₃ to nucleate and grow on the surface of the magnetite. Each precipitate, MF1 and MF2, was collected by magnetic separation using a strong magnet and washed with MilliQ water several times and then washed with 70% ethanol. The MF1 precipitate was dried in vacuum at 60°C (Isotemp Vacuum Oven Model 282A ThermoScientific), and the MF2 precipitate was oven dried at 60 °C.

2.2.5. Synthesis of the optimized polymer coated nanoparticles

The synthesis of PPy@MoO₃@Fe₃O₄ (PMF1) was done by a polymerization method.^[284] An amount of 2.0 g As-synthesized MoO₃@Fe₃O₄ (MF1) (2.0 g) was dispersed in MilliQ water (20 mL) and placed in an ice bath (0-5°C) with stirring. Once the solution reached a temperature between 0 and 5°C, pyrrole monomer (0.12 mL) was added to the solution with vigorous stirring for 30 min. Ammonium persulfate (APS) dissolved in MilliQ water (10 mL), an oxidative agent, was added dropwise to the pyrrole solution to initiate polymerization with continuous stirring. The ratio of pyrrole monomer (Py): oxidant (APS) (vol in ml:wt in g) used in the synthesis was 1:2. The polymerization process was continued overnight while maintaining the temperature at 0-5°C. The black precipitate was collected by magnetic separation using a strong magnet and washed with 70% ethanol followed by MilliQ water several times to remove the excess APS. The black precipitate was vacuum dried at 60°C.

For the synthesis of PANI@MoO₃@Fe₃O₄, a modified procedure similar to that of the synthesis of PMF1 and PANI-CeO₂ was followed.^[285] MoO₃@Fe₃O₄ (MF2) (1.012 g) was dispersed in 2 M HCl (10 mL) and then sonicated for 15 min using the bath sonicator. In the meantime, APS (234.1 mg) was dissolved in HCl (10 mL), and aniline (100 µL) was dispersed in 10 mL 2 M HCl. The three solutions were placed in an ice bath and their temperatures were allowed to equilibrate to that of the ice bath over a period of 30 min. The MoO₃@Fe₃O₄ mixture was placed under high stir in the ice bath prior to the addition to the aniline solution. Lastly, the APS solution was added dropwise. The mixture was kept in the ice bath under high stir for 2 h to allow for the polymerization of aniline on the MoO₃@Fe₃O₄ material. The resulting PANI@MoO₃@Fe₃O₄ (PMF2) was cleaned by centrifugation using MilliQ water and dried overnight at 50°C. The high-level synthesis procedure of the PMF1 and PMF2 particles is shown in Scheme 4.1.



Scheme 4.1. Schematic representation of the synthesis procedure of PPy@MoO_3@Fe_3O_4 and PANI@MoO_3@Fe_3O_4

2.2.6. Characterization of the nanoparticles

Morphological analysis of $MoO_3@Fe_3O_4$ and polymer coated $MoO_3@Fe_3O_4$ was conducted using SEM (Nova NanoSEM 230). Each sample was initially coated with gold for 30 seconds using a Denton Desk V gold coater and then observed with the SEM at an accelerating voltage of 5 kV at varying magnifications.

Crystallographic analysis of each material was performed by utilizing XRD (Rigaku MiniFlex 600 diffractometer with a Cu anode set to 40 kV and 15 mA and run with a scanning rate of 0.05° /second from 5° to 80° in 20. The XRD data was analyzed using Match 3.0 and x'Pert Highscore Plus software to obtain crystallographic parameters such as the crystal size, lattice strain, microstrain, and dislocation density.^[197,286] The surface chemical states were analyzed using XPS (PHI Quantera SXM Scanning X-ray Microprobe with Al K α (1486.6 eV) as the excitation source). The XPS measurements were calibrated using C1s 284.8 eV. The area ratio, spin-orbit splitting, and Full Width Half Maximum (FWHM) parameters were considered in the deconvolution of the spectra.^[287] The functional groups present in the samples were determined using an ATR-FTIR spectrometer (Nicolet iS10 Mid Infrared FTIR Spectrometer by Thermo Fisher Scientific, USA).

2.2.7. Polymer growth kinetics using SANS

To monitor the growth kinetics of aniline and pyrrole in situ, Small-Angle Neutron Scattering (SANS) was utilized. These experiments were conducted at the Oak Ridge National Laboratory using the General Purpose SANS instrument.^[288,289] Three configurations with different combinations of neutron wavelength (λ) and sample-detector-distance (SDD) were set to cover the scattering wavevector q range 0.001 - 0.4 Å⁻¹ for static scans. These configurations were $\lambda = 12$ Å, and SDD = 19 m, $\lambda = 4.75$ Å and SDD = 6.8 m, $\lambda = 4.75$ Å and SDD = 1.2 m respectively. The kinetics scans were performed with $\lambda = 4.75$ Å and SDD = 6.8 m to cover q range of 0.001 - 0.02 Å⁻¹. The time binning feature of SANS data reduction was used to obtained 5 min scans. To analyze the polymerization of aniline and pyrrole on MF1 and MF2 similar procedures to the synthesis of the PMF1 and PMF2 materials utilized in the RSM validation experiments and characterization were employed. However, amounts of materials were altered (scaled down to 1/16th) while keeping the molar ratios the same, and deuterated water was used instead of MilliQ water to accommodate the SANS instrumentation and to increase the contrast. Briefly, for PMF1, MF1 (0.125 g) was dispersed in deuterated water (1.25 mL) and placed in an ice bath. Then, pyrrole monomer (7.5 µL) was added to the solution. Subsequently, APS solution (0.625 mL) made by dissolving 240.0 mg APS (250.0 mg) in deuterated water (10 mL) was added to the mixture. Finally, part of the mixture (1 mL) was transferred to the reaction cell equipped on a tumbler for analysis. For PMF2, MF2 (63.25 mg) was dispersed in 2 M HCl (0.625 mL) in deuterated water, sonicated for 15 min, and placed in an ice bath. Subsequently, aniline monomer (6.25 µL) was added to 2 M HCl in deuterated water (0.625 mL) and this solution was mixed in to the MF2 suspension. Next, the APS solution (0.625 mL) made by dissolving APS (234.1 mg) in 2 M HCl with deuterated water (10 mL) was added to the mixture. Finally, part of the mixture (1 mL) was transferred to the reaction cell equipped on a tumbler for analysis. Two additional materials were analyzed with SANS, PMF3 and PMF3. PMF3 was synthesized using the same procedure as with PMF1, however, the base material of PMF1 (MF1) was replaced with MF2. Similarly, PMF4 was synthesized via the same procedure as PMF2, however, the base material of PMF2 (MF2) was replaced with MF1. The additional samples were analyzed to allow us to investigate how the base material affects the polymerization process of each polymer. Samples were loaded on quartz reaction cells equipped on a tumbler for analysis. The SANS instrument was set to take measurements of the sample every 5 min for a maximum of 2 h at a set temperature of 2°C. The resulting scattering data was analyzed and modeled using the Igor64 software with the unified fitting tools from the Irena tool suite.^[290–293] In the Irena unified model, each structural level of the unified equation contains two main terms, a Guinier exponential form and a structurally limited power law, where the sum of those terms allows us to approximate the intensity, I, at specific Q values (equation 2), as shown in the following equations:^[294,295]

$$I(Q) \cong \sum_{i=1}^{n} \left(G_{i} \exp\left(\frac{-Q^{2} R_{g,i}^{2}}{3}\right) + B_{i} \exp\left(\frac{-Q^{2} R_{g,i+1}^{2}}{3}\right) Q_{i}^{*P_{i}} \right) + Bkgd, \qquad (4.2)$$

where
$$Q^* = \frac{Q}{\left\{ \operatorname{erf}\left(\frac{kQR_{g,i}}{\sqrt{6}}\right) \right\}^3}$$
 (4.3)

is an error function to provide a smooth transition between the Guinier regime and the Porod regime. G_i and B_i are pre-factors for the Guinier exponential and power law terms, respectively, R_{g,i} is the radius of gyration of the structure feature, and P_i describes the fractal dimension of the material. Bkgd arises from the incoherent scattering background of the samples. By optimizing each parameter, a reasonably accurate approximation of the radius of gyration of the polymer layer is obtained.

3. RESULTS AND DISCUSSION

3.1 Validation of The Nanomaterial Synthesis

The Response Surface Methodology (RSM) software that uses a numerical optimization technique was employed to obtain the optimum concentration of the ammonium molybdate tetrahydrate (AMT), Fe₃O₄, and PPy or PANI when synthesizing PPy@MoO₃@Fe₃O₄ (PMF1) and PANI@MoO₃@Fe₃O₄ (PMF2), by maximizing the removal of methylene blue (MB) dye and minimizing material dissolution. To verify the validity of the models and to test the optimized material, a set of validation experiments (MB removal and dissolution analysis) were performed. For both PMF1 and PMF2 the validation experiment results (presented in Table B.2) indicated that the observed values for the MB dye degradation agree with the predicted values for both PMF1 and PMF2, respectively. PMF1 exhibited 95.39% removal of MB dye in light and 70.26% removal in dark, which agreed with the predicted values.

The dissolution of 4.12%, however, was better than the predicted value. In contrast, PMF2 showed 75.98% removal of MB dye in light, 60.18% removal in dark, and 5.6% dissolution, which showed no statistical significance when compared with the predicted values. Hence, based on these results, PMF1 exhibited better removal rates of MB and higher stability than PMF2.

To gain a better understanding of the polymer coatings' benefits on the nanoparticles, comparison of the uncoated and coated materials was also performed (Figure 4.1). Significant reduction in dissolution occurred when MF1 and MF2 were coated with PPy and PANI, respectively. The photocatalytic activity upon addition of PPy and PANI showed similar improvements, demonstrating improved MB removal when exposed to low power (4W) visible light when compared to other studies (Table B.3). In the case of PPy addition, photocatalytic activity increased, while MB dye adsorption showed no significant changes between the uncoated and coated material after the polymer coating (MF1 and PMF1, respectively). The increase of MB removal during photocatalysis indicates that PPy acts as a photosensitizer, which could have aided the transfer of electrons to the conduction band of MoO₃.^[272] Similarly, the PANI coating on MF2 demonstrated improved photocatalytic activity, indicating PANI is also beneficial in the photocatalytic process, albeit to a lesser extent than PPy. Likely, the synergistic interaction between MoO₃ and PPy was better than that of MoO₃ and PANI. It is also possible that the black color of PPy allowed improved light absorption compared to the green color of PANI, which ultimately affected the photocatalytic activity of the material.^[296] In this case, since more photons could reach the PMF1 material, more electron hole pairs could be created, consequently increasing the reactive oxygen species present in the solution, which allowed better degradation of MB. Overall, based on the results, both materials showed high MB removal in light and improved stability in water because of the introduction of the different polymer coatings, demonstrating the added benefits of the coatings to the nanoparticles.



Figure 4.1. Methylene blue removal in light and dark and dissolution after 3 h by uncoated and coated material (MF1, PMF1, MF2, AND PMF2)

3.2 Material Surface Morphology and Chemistry

Scanning electron microscopy (SEM) images were acquired at each step of the PMF1 and PMF2 synthesis process (Figure 4.2). The estimated particle size diameters of MoO₃@Fe₃O₄ -1 (MF1) ranged from 0.34 to 1.34 μ m and from 0.24 to 1.25 μ m for MoO₃@Fe₃O₄ - 2 (MF2). Qualitatively, the magnetite appeared to have low polydispersity, while both MoO₃@Fe₃O₄ materials (MF1 and MF2) presented larger polydispersity (Figure 4.2.a).



Figure 4.2. SEM images showing the morphology of material: a) Fe₃O₄ (×10,000 magnification),
b) MF1 (×6,500), c) MF2 (×5,000), d) PMF1 (large image: ×7,000, small image: ×6,000), e) PMF2 (large image:×5,000, small image×27,000).

MF1 (Figure 4.2.b) displayed an increased particle size homogeneity as opposed to MF2 (Figure 4.2.c), which can be attributed to the increased length of time in the synthesis of the material. The increased reaction time in solution allows the material to undergo a ripening process, such as Ostwald ripening or intraparticle growth.^[297] After coating the MF1 with PPy, the size distribution of the material decreased and the apparent smoothness of the material surface became more variable (Figure 2.d). Similarly to PMF1, the surface of MF2 became rougher after the polymerization process of aniline (Figure 4.2.e), indicating successful formation of PANI on MF2. Compared with PMF1, PMF2 showed a lower polydispersity than MF2, which was attributed to additional ripening occurring under the acidity of the solution in the PANI coating process and slower start of reaction indicated by the color of the solution.

3.3 Crystal Structures

The crystal structure and phase formation of the synthesized nanoparticles were measured by the X-ray diffraction (XRD) patterns. The XRD patterns of the Fe₃O₄, MF1, PMF1, MF2, and PMF2 shown in Figure 4.3 were correlated using Match 3.0 Software. The XRD pattern of Fe₃O₄ shows sharp diffraction peaks at $2\theta = 35.7^{\circ}$, 63.1° , 57.5° and 43.4° , which were assigned to the hkl values to planes (311), (404), (511) and (400), respectively. These diffraction peaks matched well with the 2 θ calculated by the Match software, which is based on the Crystallography Open Database (COD) entry number 96-900-6248 (COD 9006247) and indexed as cubic crystal Fe₃O₄ system.



Figure 4.3. XRD Pattern of Fe3O4, MF1, PMF1, MF2, and PMF2.

The hexagonal structure of MoO₃ was confirmed with the XRD spectra of MF1 and MF2, which were in good correlation with the spectra from the Crystallography Open Database (COD) entry number 96-431-6778 (COD 4316777).^[298] The detectable peaks were located at $2\theta = 9.9^{\circ}$, 25.9°, 29.6° and 19.8° for MF1 and at $2\theta = 9.6^{\circ}$, 25.7°, 29.3° and 19.4° for MF2, indicating hkl values of (100), (210), (111) and (200). Peaks of Fe₃O₄ were also observed in the spectra. The average crystal size of the MF1, PMF1, MF2 and PMF2 nanomaterials calculated using the Scherrer equation were found to be 26 nm, 32 nm, 37 nm and 44 nm, respectively.^[197,286] Additional crystallographic parameters are presented in Table B.4. The XRD patterns for both PMF1 and PMF2 showed that the peaks for MoO₃ in MF1

and MF2 were maintained, respectively, even after the addition of polypyrrole (PMF1) and polyaniline (PMF2). In addition, the peak position hardly changed, which indicates that polymerization of polypyrrole and polyaniline took place on the surface of MF1 and MF2.^[274] The sharp and detectable peaks indicate that the synthesized nanostructures are well-crystallized. Diffraction peaks of Fe₃O₄ have a lower intensity compared to the diffraction peaks of MoO₃ due to the small amount of Fe₃O₄ present in the MF and PMF nanostructures. In Figure B.3, there was a slight distortion and broadening of peaks in PMF1 between 20° to 30° indicating the presence of amorphous PPy.^[272,276] The PANI peaks in Figure 4.3 and Figure B.4 decreased in intensity due to the polymerization of PANI on the surface of MF1.^[299] Furthermore, a slight broad curvature of baseline at approximately 25° was observed, which was ascribed to the amorphous nature of PANI, however, this change is subtle due to the highly crystalline nature of the metal oxide.^[299] There was no further observation of diffraction peaks in the spectra, which indicated that the PPy and PANI do not hinder the crystalline behavior of MF. The presence of the polymers PPy and PANI in PPy@MoO₃@Fe₃O₄ and PANI@MoO₃@Fe₃O₄ was further confirmed through ATR-FTIR analysis.

3.4 Surface Components

X-ray photoelectron spectroscopy (XPS) was utilized to determine the chemical state of the key surface components, such as molybdenum and carbon. The survey spectra of the magnetite, the uncoated magnetic MoO₃ materials, and the polymer coated materials are shown in Figure 4.4. The Fe peaks were clearly present in the Fe₃O₄ spectra but were not as apparent in the coated materials.^[300] This was expected given that the magnetite is in the core of the material and XPS detailed analysis performance of embedded components (>10 nm) is limited as it is a surfacesensitive technique.^[301] In the MoO₃@Fe₃O₄ materials (MF1 and MF2) the Mo 3d_{3/2} and Mo 3d_{5/2} peaks were clearly present. Carbon and nitrogen peaks were also observed. Nitrogen was likely introduced during the synthesis process since nitric acid was utilized to allow the nucleation and growth of MoO₃. In the PMF2 spectra, a peak at Cl 2p was detected indicating introduction of Cl⁻ ions in the material. The carbon peak can be attributed to adventitious carbon as well as small amounts of carbon impurities in the material. In the polymer coated materials (PMF1 and PMF2), the carbon peaks became more prominent, as expected, due to the high carbon content of the polymers. In particular, the relative carbon content for MF1, MF2, PMF1, and PMF2 was calculated to approximately 13.6%, 19.1%, 31.3%, 51.2%, respectively (additional relative atomic concentrations are shown in Table B.5). This large increase of the relative carbon content in PMF1 and PMF2 as compared to MF1 and MF2 was indicative of the successful coating of PPy on MF1 and PANI on MF2.



Figure 4.4. XPS spectra of Fe3O4, MF1, PMF1, MF2, and PMF2 each offset by 60 x 10³ c/s

To further analyze the surface components of the uncoated MoO₃@Fe₃O₄ and the polymer coated MoO₃@Fe₃O₄, detailed spectra of the carbon and molybdenum spectra were acquired. Fe 2p spectra were also acquired and successfully verified the incorporation of Fe₃O₄ (Figure B.5). The Mo 3d spectra of the uncoated MoO₃@Fe₃O₄ are shown in Figure 5. MoO₃ is the primary photocatalytic component of the material and its oxidation state has been shown to directly affect the photocatalytic properties of the material.^[58] A high Mo⁺⁶ to Mo⁺⁵ ratio indicates increased photocatalytic activity.^[58] The beneficial effect of oxygen vacancies, resulting from the introduction of Mo⁺⁵ states, towards the photocatalytic activity of the material is owed to the narrowing of the bandgap due to delocalized states in the valence band overlapping with the valence band. The reduced bandgap increases light absorption in the visible spectral region, thus, enhancing the material's photocatalytic activity.^[58] While the increased amount of oxygen vacancies is beneficial in lowering the bandgap of the material, which can increase photocatalysis via increasing light absorption, it can also increase absorption of light by mid-gap states reducing the generation of excitons.^[58] The reduction of excitons lessens the number of reactive oxygen species generated by the material, thus, reducing its photocatalytic activity.

The fitted Mo 3d spectra of MF1 and MF2 and the percentage of each component present are shown in Figure 4.5 with additional information presented in Table B.6. For MF1 and MF2 the ratio of Mo⁺⁶ to Mo⁺⁵ was 12.0 and 20.8, respectively. Interestingly, the Mo⁺⁶ to Mo⁺⁵ ratio for MF2 was similar to that of the nanorods synthesized using a similar procedure^[58] indicating that the addition of the magnetic core had minimal influence on the chemical structure of MoO₃. Rather, the amounts of the starting material, temperature, and reaction duration were the main factors contributing to the chemical differences. Furthermore, the magnetite particles, which are positively charged under acidic pH, can act as nucleation centers for MoO₃ formation assisting in the reaction process and altering the growth of the particles. While MF1 had a lower ratio of Mo⁺⁶ to Mo⁺⁵ than MF2, the photocatalytic activity of PMF1 was greater than that of PMF2 as shown in Table B.2. This could be due to the fact that PPy, a black polymer, could favor light absorption more than PANI, a dark green polymer.^[296,302]



Figure 4.5. XPS Mo 3d spectrum and fittings of a) MF1, b) MF2, and XPS C 1s spectra of c) MF1, d) PMF1, e) MF2, and f) PMF2

The changes of the carbon bond types in the polymerization are shown in Figure 4.5 (the core-level oxygen spectra, which also show the incorporation of C, are depicted in Figure B.6). The peaks at ~284.8 eV in MF1 and MF2 correspond to carbon impurities or adventitious carbon.^[287,303] In PMF1 and PMF2, however, this peak is indicative of the presence of benzenoid rings from the polymers coated on the nanoparticles.^[304] Furthermore, the peaks at approximately 285.8 eV, 287 eV, and 288.5 eV were assigned to C-N/C=N/=C-NH+, C-O, and C=O bonds, respectively which were present in PMF1 and PMF2.^[305,306] The peaks at 290.7 eV and 290 eV for PMF1, and PMF2, respectively, were attributed to the π - π * transition component (shake-up signal) in the PPy or PANI aromatic rings.^[306,307]

3.5 Material Components

The ATR-FTIR analysis was conducted to further show the successful coating of polymers on the nanoparticles. The FTIR spectra of the Fe₃O₄, MF1, PMF1, MF2, and PMF2 in the range of 2000 - 450 cm⁻¹ are shown in Figure 4.6 and the spectra information for each of the materials is presented in Table B.7. The bands between 600 and 450 cm⁻¹ in the Fe₃O₄ and MoO₃ spectra in Figure 4.6 resulted from the metal-oxygen vibrations. In particular, the characteristic band for Fe_3O_4 at 559.9 cm⁻¹ corresponding to the torsion and vibration mode of the Fe-O bonds,^[308] and bands at 517.3 and 568.4 cm⁻¹ in the MoO₃ spectra corresponding to the Mo-O-Mo bending vibrations were observed.^[58,284] In addition, bands corresponding to the M=O stretching vibrations were present in the MoO₃ spectra at 878.9 and 895.3 cm⁻¹.^[154,309] The band at 1403.5 cm⁻¹ in the MoO₃ spectra indicates N-H bending of NH₄⁺ groups in the structure.^[309] In the PPy spectra, the band at 1042.8 cm⁻¹ was assigned to C-H stretching vibrations, and the bands at 1305.1, 1174.5 and 1461.8 cm⁻¹, and the PPy characteristic band at 1552.4 cm⁻¹ were assigned to C-N stretching vibrations and aromatic ring vibrations, respectively.^[310] In case of the PANI spectra, characteristic bands indicative of the emeraldine oxidation of PANI were observed. In particular, the C=N stretching band of the quinoid diamine unit at 1564.7 cm⁻¹ and C-C aromatic ring stretching band of the benzenoid diamine unit at 1488.3 cm⁻¹ were present.^[311] Furthermore, peaks at 1296 cm⁻¹ and 1245 cm⁻¹ were present due to the C-N stretching of secondary aromatic amine bonds^[312] and C-N⁺ stretching vibrations,^[313,314]

respectively. In addition, the 797.5 cm⁻¹ peak was designated to the out-of-plane C-H bond deformation on the 1,4-desubstituted rings in PANI.^[312]

When Fe₃O₄ was incorporated into MoO₃, the M-O-M (metal-oxygen-metal single bonds) and Mo=O bands were preserved. Additionally, there was a broadening and intensity increase in the N-H bending peak of MoO₃ at 1403.5 cm⁻¹ from the inclusion of ammonium ions (NH4⁺).^[309,315] When MF1 was coated with PPy, there was a dampening of the M=O and M-O-M peaks as well as peaks corresponding to C=C stretching vibrations and C-H in-plane vibrations, which are indicative of the coating of PPy on MF1.^[284] Likewise, in the case of MF2 being coated with PANI, there was also a decrease in the intensity of the Mo=O and M-O-M peaks. In addition, peaks corresponding to C-N stretching of the secondary aromatic amine and C-N⁺ stretching appeared in the PMF2 spectra and the peak due to the benzenoid diamine unit disappeared due to the coating of PANI on MoO₃. In the MF and PMF spectra several shifts and band changes were noticed as the MF material were coated with PPy or PANI. The N-H vibration peak in PMF1 and PMF2 vanished, while it was previously prominent in MF1 and MF2 indicating the change of NH4⁺ present in the structure of MoO₃ to NH₃.^[316] Furthermore, the Mo-O-Mo bending peaks in PMF1 and PMF2 underwent slight blue shifts, the C-N stretching vibration of PPy showed a clear blue shift in PMF1, and in PMF2 and the C-N stretching peak underwent a red shift, indicating strong intermolecular interactions by N-Mo in PMF1 and PMF2, likely as a result of hydrogen bonding or Van der Waals attraction forces.^[317–319]

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Figure 4.6. ATR-FTIR spectra of Fe₃O₄, MoO₃, MF1, PMF1, MF2, and PMF2. Metal-oxygen-metal shown as M-O-M (where M-O-M = Mo-O-Mo or Fe-O-Fe).

3.6 Polymerization Kinetics on The Surface of The Nanoparticles

The polymer chains coated on the nanoparticles not only significantly altered the stability of these materials in water, but also affected their absorptive and photocatalytic capabilities. Monitoring the kinetics of polymer growth on such materials can help us understand the effects of the base materials' composition and chemistry on the polymer growth process, which is critical for tuning parameters to optimize the properties of the materials in their broad applications.





In this study, we used in situ SANS to monitor the growth of polymers on the

surface of the nanoparticles. SANS data was collected when either pyrrole or aniline

polymerized on MF1 and MF2 to examine how the polymerization of PPy and PANI are affected by the base nanomaterial. The SANS profile and model fitting of each sample at the end of the polymerization are shown in Figure 4.7 and Table B.8, respectively. The materials exhibited multilevel structure, which is reflected by the multiple "knees" and linear regions on the log-log plots of the SANS curves. The curves were fitted using the unified exponential model.^[290,295,320]

Each scattering curve was modeled using three structural levels as shown in Figure 4.7. However, PMF2 (PANI on MF2) had a fourth structural level. The 4th structural level located in the low Q region in PMF2 (Figure 4.7.d) indicated the presence of larger structures in the PMF2 data compared to other samples (PMF1, PMP3 and PMF4). Such structures may arise from large nanoparticle aggregates; unfortunately, the size of these aggregates cannot be determined by SANS since it is outside the instrument's resolution.^[294] The structural features corresponding to levels 1 and 3 arose from the base material (MF1 or MF2) as P exponent values between 3 and 4 indicate a surface fractal type for these levels.^[320] The R_g of the level 3 fell between 274 and 300 nm. The level 2 structure was ascribed to the polymer chains on the material considering the P exponents fell between 1.5 and 3 corresponding to the mass fractals of polymer chains.^[320] This region changed the most during the polymerization process as evidenced by the R_g changes. In Table B.8, the final R_g values of Level 2 after the polymerization ended were 56.1 ± 0.56 nm, 136.9 ± 0.92 nm, 63.5 ± 0.22 nm, and 124.5 ± 3.6 nm for PMF1 (PPy on MF1), PMF2 (PANI on MF2), PMF3 (PPy on MF2), and PMF4 (PANI on MF1), respectively. The different

 R_g values indicate that polymer type and base material's surface properties influenced the polymer chain growth, agreeing with previous reports in which R_g was found to depend on the base material surface, polymer type, as well as the original concentration of the base material in the solution.^[321,322]



Figure 4.8. Radius of gyration as a function of time from the fitted curves of each polymer coated material.

The growth of the PPy and PANI chains on the surface of the base materials as a function of time are shown in Figure 4.8. PPy polymerization initiated faster yet had a slower rate than PANI, while PPy was more affected by the base material properties than PANI polymerization. These observations resulted from the differences in polymerization mechanisms between the two polymers. In the mechanism of PPy

growth, oxidation of pyrrole monomers led to the formation of positively charged dimers.^[323] The negative charge of MoO₃ offered a strong electrostatic attraction towards the pyrrole dimers promoting polymerization as the dimers could readily attach to the negatively charged surface of MoO₃, which initiated the polymer chain growth (Figure 4.9.a). Polymerization rate was hindered, however, by the competitive interaction between the dimers attaching to MoO₃ and attaching to each other to form longer chains. PANI's chain growth was much faster than that of PPy once polymerization started. Polymerization of aniline on both base materials started after 60 min, which was consistent with our visual observation of solution color change. PANI formation mechanism is affected by many factors (acidity, monomer concentration, temperature, etc.) and is still controversial.^[324] To initiate polymerization, aniline needs to be oxidized to cation radicals. These radicals have different resonating forms with varying reactivities, which may result in the formation of diverse chain architectures.^[324] Furthermore, the acidity of the media impacts the degree of protonation of oligomers, which may lead to a different reaction pathway, thereby altering polymerization kinetics.^[324] Our results were consistent with the theory behind aniline polymerization in acidic media in which oligomer nucleates form slowly.^[278,325] This induction period can be very slow depending on the starting temperature and acidity of the media; however, the subsequent polymerization rate is rapid.^[277,278,325] In highly acidic solutions, intermediate compounds are thought to be formed in the induction period (iminoquinonid compounds consisting of compounds similar to nigraniline and pernigraniline).^[326] The intermediates act as strong oxidants

due to their protonation in acidic media.^[326] However, rather than oxidizing aniline, which is a neutral compound, such protonated compounds can preferentially react with the MF surface in areas in which oxygen vacancies generate donor states, and as a consequence, prolong the induction period. The reactivity of the species that participate in the PPy polymerization process and the PANI polymerization process is vastly different, which led to the changes in polymerization initiation and rate depicted in Figure 4.8. Additionally, the polymerization process not only depends on the rate of the reactions, it also depends on adsorption equilibrium constants.^[277] Competitive interaction between oligomers and nucleates adsorbing on the surface of the MF material and assembling with other oligomers or nucleates can further slow polymer chain growth initiation and affect polymerization rate.

The ultimate size of polymer chains grafted on nanoparticles largely depended on the concentration of the nanoparticles. The size of PANI chains after the polymerization ended was almost double the PPy chain size. In the PPy polymerization process, the concentration of the base material was much larger than the base material concentration in PANI chain growth (0.66 g/mL and 0.34 g/mL, respectively). Due to the greater amount of available substrate surface present and the fixed monomer concentration in PPy polymerization, the average polymer chain length was expected to be shorter (Figure 4.9.b), which was consistent with the SANS results. The difference in monomer structure between pyrrole and aniline is another factor that can affect the final chain length of the grafted polymers. PPy exhibits a zigzag shape while PANI has a straight

conformation (Scheme B.1). If the polymerization number is the same, the final size of PANI is expected to be longer than that of PPy.



C. Effect of the presence of substrate oxygen vacancies (leading to negatively charged regions) on dimer and oligomer attachment on the substrate and the subsequent chain elongation (dashed lines indicate some potential reactions)



Figure 4.9. Base material effects on polymer formation. (a) Competition of attachment on existing polymer chains or oligomers and base material surface, (b) base material concentration effects, (c) effect of oxygen vacancies

An important similarity between the polymerization of PPy and PANI on MF1 and MF2 was the tendency of the material that had MF1 as the core to result in a smaller final R_g of polymers. Since the difference in size of MF1 and MF2 was subtle, the determining factor in the magnitude of R_g could be associated with the surface chemistry of the base material. Material defects in the MoO₃ structure, in particular oxygen vacancies, are capable of enhancing dimer attachment as well as promoting pyrrole and aniline monomer oxidation, due to their higher surface reactivity, which facilitates the generation of donor or acceptor states.^[137,327] As shown in the XPS analysis of the MoO₃ in MF1 and MF2, MF1 presented a larger number of oxygen vacancies than MF2 as indicated by the smaller Mo⁺⁶:Mo⁺⁵ ratio. Thus, the MF1 surface was more reactive than the MF2 surface, which could have promoted monomer oxidation or provided attachment centers for PPy dimers or PANI oligomers (Figure 4.9.c). Therefore, an increase in PPy and PANI R_g and rate of polymerization on MF2 rather than on MF1 was expected, which was consistent with the SANS results.

Furthermore, polymerization for both PPy and PANI could be enhanced or hindered depending on the reaction conditions (monomer, oxidant, substrate material concentrations, media acidity, etc.). Due to their polycationic nature, their oligomers preferentially adsorb on hydrophobic areas of surfaces.^[325] Hydrophobicity in a material is introduced by oxygen vacancies^[328] supporting our data that showed increased surface adsorption of either PANI or PPy on MF1 rather than MF2 due to the higher amount of oxygen vacancies present in the MF1 structure (Figure 4.9.c). Additionally, the Rg growth can be affected by the uniformity via which the oligomers attached on each surface. Chain attachment tends towards higher uniformity when the surface is more hydrophobic, which leads to the formation of polymer brush type structures rather than granular ones.^[325] While the charge differences between MF1 and MF2 was unlikely to change the architecture formed, a more ordered attachment

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allowed more oligomers to adsorb on the surface of the material. Thus, for MF1, the higher number of oligomers attaching to its surface resulted in the formation of shorter chains due to the fixed availability of monomers in solution and increased probability of polymer growth termination.^[329] Furthermore, the increase in density of polymer chains on the surface of MF1 hindered polymerization rate likely due to the increase of mass-transfer limited reactions at the surface rather than reaction limited polymerization.^[329] As such, polymer length and polymerization rate were reduced and the final R_g was smaller for MF1 rather than MF2.

4. CONCLUSION

In this study, we developed two visible-light photocatalytic magnetic MoO₃ nanomaterials, with varying oxygen vacancies, which were coated with conducting polymers (PPy or PANI) to decrease the solubility of the nanomaterials and increase their photocatalytic properties, improving their utility in water treatment. Furthermore, we monitored the polymerization kinetics of the nanomaterials to elucidate how the surface chemistry of base materials, in particular oxygen vacancies, would affect polymerization of pyrrole and aniline. Our results revealed that particle surface chemistry can have numerous effects, including the promotion of monomer oxidation, enhancement of dimer or oligomer adsorption on the surface of the particle, and oligomer attachment uniformity. Despite the complexity of polymer growth on nanostructured materials, neutron scattering allowed us to form a more concrete theory on the polymerization kinetics of two conjugated polymers.

CHAPTER 5 – TETRACYCLINE PHOTOCATALYSIS 1. INTRODUCTION

As pharmaceutical production and use continue to increase, contamination of waterways due to emerging pharmaceutical contaminants (EPCs) has been of rising concern. Many EPCs in the environment have shown to bioaccumulate and persist in soils, plant tissues, and aquatic environments leading to acute and long term harm.^[1,330] Conventional methods of removing EPCs such as filtration, adsorptionbased, and advanced oxidation processes can have significant drawbacks. For instance, filtration and adsorption-based processes present low removal of several EPCs (sulfamethoxazole, venlafaxine, piroxicam, among others) and produce sludge containing the removed EPCs, which is a major source of secondary pollution.^[1,330] Advanced oxidation processes (such as ozonation and UV radiation) are able to break down pollutants, however, they are energy intensive and costly, and most are unable to fully degrade pharmaceutical contaminants,^[1,330] As such, there has been considerable research interest in investigating visible light photocatalytic materials, in particular metal oxides, which are less energy intensive and have demonstrated their effectiveness in degrading a variety of EPCs (analgesics, antibiotics, and anticoagulants, among others).^[1,61,330–337] MoO₃, a promising visible light photocatalyst, is easily synthesized and modified in terms of size and morphology and has demonstrated its utility in energy storage, field-effect transistors, thermoelectric devices, gas sensing, among others.^[137] Furthermore, MoO₃ is vastly underutilized in the degradation of EPCs.^[1,330] Only recently, MoO₃-based materials have begun to be

studied for pharmaceutical contamination removal and have demonstrated effective removal of a variety of EPCs: ibuprofen,^[335] diclofenac,^[334] tetracycline,^[142,270,338,339] ofloxacin,^[340] trimethoprim,^[331] metronidazole,^[341,342] and ciprofloxacin.^[343] However, an important drawback of MoO₃-based materials used in water treatment is its high solubility, which can greatly reduce its long term effectiveness and introduce additional water contamination, thus, reducing its usability in water treatment.^[58,137,344] Despite this limitation, to our knowledge, no study has investigated a mechanism to reduce the solubility of MoO₃ in aquatic systems in conjunction with examining whether MoO₃ photocatalytic activity can be maintained in the degradation of EPCs.

To reduce the solubility of metal oxides, polymer coatings, and in particular, conductive coatings, can be utilized.^[126,127,264,345–347] The conductivity of such coatings has been shown to contribute towards enhanced material stability against structural collapse or dissolution^[126,127,264,345–347] and enhanced photocatalytic activity.^[264,273,275,276,346,348–350] Polyaniline (PANI) is one such conductive polymer, which has notable advantages over other conductive polymers, namely, environmental stability, high conductivity, good electrochemical activity, ease and low cost of synthesis, and biocompatibility.^[351–353] These properties have made it particularly appealing for use in water treatment. For instance, the incorporation of PANI on TiO₂-based materials has led to improved ability of the nanocomposite to photodegrade methylene blue^[349] and azo dye, while remaining stable even after solar irradiation.^[350] PANI was further demonstrated to improve photodegradative properties in the degradation of dyes when coated on MoO₃^[274] or ZnO^[354], and in the degradation of

tetraethylated rhodamine when coated on Bi₂WO₃.^[346] These improvements were attributed to the increase of photogenerated electron-hole pair separation and decrease of the recombination rate.^[346,350] Furthermore, PANI has shown to reduce metal oxide breakdown in solution increasing material stability, which has made it particularly useful for metal corrosion protection in basic and acidic media.^[345] Additionally, PANI incorporation in material used in energy storage has demonstrated improvement of electrochemical performance, which has been partly attributed to the reduction of metal oxide structural collapse during charge-discharge cycles by providing a protective layer.^[347,348]

In this study, we examined the effectiveness of PANI as a coating for MoO₃ nanoparticles for application in EPC removal as well as its reduction of the solubility of the underlying metal oxide material. Specifically, we studied the degradation of tetracycline (TC) by PANI coated magnetic MoO₃ and the dissolution of the coated and uncoated material at the conditions that show the highest photocatalytic activity. TC was selected as the model contaminant as it is an antibiotic of particular environmental concern, negatively impacting the environment and harming human health.^[336] TC is one of the most widely utilized antibiotics, especially in animal feed and, due to its poor absorption by people and animals, an alarming amount of this compound and its metabolites are released into the environment.^[336,355] It has also been demonstrated that it can contribute towards emergence of bacterial antibiotic resistance in water and wastewater,^[1,355,356] which make the presence of such antibiotic in water systems alarming. The magnetic MoO₃ (MoO₃@Fe₃O₄) utilized in this study,

has previously demonstrated photocatalytic properties in methylene blue degradation and is easily removable from water due to its magnetic properties.^[264,357] The synthesized PANI@MoO₃@Fe₃O₄ (PMF) was able to improve both photocatalytic activity (without yielding any detectable levels of TC degradation byproducts) and also reduce the solubility of the uncoated material, MoO₃@Fe₃O₄ (MF), indicating PANI can be a useful addition on unstable metal oxide photocatalysts.

2. EXPERIMENTAL

2.1 Materials

The following materials were purchased from Sigma Aldrich: ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄ · 4H₂O, AMT), iron (II, III) oxide (Fe₃O₄), nitric acid (12M HNO₃), ethanol, aniline, hydrogen chloride (12M HCl), ammonium persulfate (APS), tetracycline (TC), aluminum chloride, sodium hydroxide, isopropyl alcohol, furfuryl alcohol, terephthalic acid, 2-hydroxyterephthalic acid. Ethylenediaminetetraacetic acid (EDTA) and high-pressure liquid chromatography (HPLC) grade acetonitrile were purchased from (VWR chemicals, Radnor, PA. Potassium dichromate fine crystals and methanol (HPLC grade) were purchased from Fisher Scientific. Tetraacetic acid disodium salt (Ethylenedinitrilo) and Dihydrate (EDTA-2Na) were purchased from Macron Fine Chemicals. L(+) ascorbic acid GR and Tris-HCl ultrapure reagent were purchased from EM Science and J.T. Baker, respectively. Materials were used without further purification.

2.2 Synthesis of PANI-Coated Magnetic MoO₃

Firstly, magnetic MoO₃ was synthesized using a procedure similar to our previous publication.^[58] Briefly, 2.46 g ammonium molybdate tetrahydrate (AMT) was dissolved in 20 mL deionized (DI) water. Then, 0.1 g Fe₃O₄ was dispersed in the AMT solution and bath sonicated for 15 minutes to create a homogeneous dispersion using a Bransonic Ultrasonic sonicator. The mixture was heated at 90°C with high stirring (900 rpm) in an oil bath. Finally, 5 mL nitric acid was added slowly to the mixture when it had reached 90 °C and was left in the oil bath for three hours under continuous stirring to allow the growth of MoO₃. The resulting material was cleaned via magnetic separation first using 70% ethanol and then DI water. The water was removed by centrifugation (Thermo Scientific Sorvall Legend XTR Centrifuge) at 1200 rpm (69 x g) for 40 min and the material was subsequently oven dried at 60°C.

To synthesize the PANI coated material (PANI@MoO₃@Fe₃O₄), a synthesis procedure derived from the synthesis of PANI-CeO₂^[285] was utilized and the optimization of the components of the material were determined previously.^[264] An amount of 0.1 mL of aniline was dispersed in 10 mL 2M HCl, and, separately, 234.1 mg of ammonium persulfate (APS) was dissolved in a 10 mL 2M HCl solution. Additionally, 1.012 g of the MoO₃@Fe₃O₄ (MF) material was dispersed in 10 mL 2M HCl and sonicated for 15 minutes. The three solutions were placed in an ice bath to allow their temperatures to equilibrate. Subsequently, the mixture with MoO₃@Fe₃O₄ was allowed to stir using high stirring speed (500 rpm) and the aniline solution was introduced to the mixture. Finally, the ammonium persulfate solution was added dropwise. The resulting mixture was stirred for 2 hours in the ice bath to allow aniline to polymerize on MoO₃@Fe₃O₄. Once the polymerization was complete the PANI@MoO₃@Fe₃O₄ (PMF) material was cleaned with DI water and centrifugation at 1200 rpm (69 × g) for 30 min and was then oven dried at 50 °C overnight.^[264]

2.3 Characterization

A detailed characterization of the material was conducted in our previous publication,^[264] in which the PMF was analyzed via scanning electron microscopy (SEM), X-ray diffraction spectroscopy (XRD), X-ray photoelectron spectroscopy (XPS), and attenuated Fourier transform photoelectron spectroscopy (ATR-FTIR). Herein, we provide additional SEM images of the material, the ζ - potential of the material over a range of pH values, and additional ATR-FTIR data. To obtain the ζ potential of the material, first, a stock suspension of 1000 ppm was prepared in DI water. Then, 5 mL of the stock suspension was transferred to a separate container where the pH was adjusted using either 0.1 M HCl or 0.1 M NaOH. The final volume of the pH adjusted suspensions was 10 mL to obtain solutions with 500 ppm of the material. The ζ -potential and hydrodynamic radius were measured at room temperature using dynamic light scattering (DLS) with the Malvern ZetaSizer Nano instrument using the Smoluchowski model. Prior to testing the samples, the ζ -potential and hydrodynamic radius of a Zeta Transfer Standard (ZTS1250, Malvern Panalytical) were measured to ensure proper instrument functionality. All the measurements were performed in triplicate.

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2.4 Dissolution

Dissolution experiments were conducted at pH 3, 5, 7, and 10 to determine the relationship between pH and material dissolution for the uncoated and coated materials. DI water at the different pH values was prepared using either 0.1 M HCl or 0.1 M NaOH. Then, either MoO₃@Fe₃O₄ (MF) or PANI@MoO₃@Fe₃O₄ (PMF) were added to 15 mL of pH adjusted solutions to achieve starting concentrations of 500 ppm of each material. The starting concentration utilized was based on the optimal concentration of the photocatalyst in the photocatalysis process in the degradation of tetracycline by the PMF photocatalyst. Each mixture was kept under static conditions at room temperature. After 35 min (the length of reaction in the photocatalysis experiments) samples were filtered using a 0.2 µm syringe filter (VWR sterile syringe filter). Then, an Amicon centrifugation tube (Ultra-15, Millipore, molecular weight cutoff of 30,000 Da) was utilized to remove any remaining solid particles by centrifuging the solutions for 15 min in a Thermo Scientific Sorvall Legend XTR centrifuge at a speed of 4200 rpm. The resulting solutions were analyzed using a Perkin-Elmer AANalyst 200 Atomic Absorption Spectrometer equipped with a molybdenum lamp^[58]. For the instrument calibration, 100 ppm MoO₃ stock solution was prepared by dissolving ammonium molybdate tetrahydrate in DI water, and standard solutions were prepared by diluting the stock solution to 1, 10, 20, 30, and 40 ppm. Since the presence of Fe in the solution can suppress the molybdenum signal, 0.5% aluminum chloride was added to the samples and standard solutions prior to analysis.^[282] Samples were prepared in duplicate and tested in triplicate.

2.5 Tetracycline Removal

Removal experiments were carried out in a 96 well plate wherein the concentration of tetracycline, photocatalyst, and pH were varied. In a typical experiment, stock solutions of 20 ppm TC in DI water and 1000 ppm of the photocatalyst in DI water were prepared at the target pH by adjusting the pH using either 0.1 M HCl or 0.1 M NaOH. Appropriate amounts of each stock solution were added to two separate 96 well plates and each plate was set in dark conditions by covering with foil to allow initial adsorption of TC to the nanocomposite. The total volume in each well was 200 μ L. The PMF concentration was tested at 100 ppm, 200 ppm, 250 ppm, 300 ppm, 500 ppm, 600 ppm, 800 ppm, and 1000 ppm. The initial TC concentration was tested at 1 ppm, 2 ppm, 5 ppm, 8 ppm, and 10 ppm. The pH values utilized were 3, 5, 7, and 10. Due to the high affinity of TC towards the photocatalyst, the plates were set in dark conditions for five minutes. As seen in Figure C.1, the adsorption of TC shows no significant change between five minutes and thirty minutes. This higher adsorption capacity with a five minute equilibration time has also been observed with PANI/TiO₂.^[353] After the five-minute adsorption time in the dark, one plate was uncovered and irradiated using visible light (Philips F4T5 soft white, 4W) for 30 minutes. Fluorescence measurements were obtained for each plate prior to irradiation and after 30 minutes using a UV-Vis fluorimeter (Biotek SynergyMX Microtiter plate reader) with an excitation wavelength of 390 nm and an emission wavelength of 520 nm.^[358] Experiments were performed in triplicate, and controls containing the tetracycline solution without the PMF material were also included.
2.6 Tc Degradation Mechanism

To investigate the species responsible for TC photocatalytic degradation, the TC removal experiment at the optimal conditions (500 ppm photocatalyst, 5 ppm initial TC dose, pH 5) was repeated while adding known reactive species scavengers (EDTA as a hole (h^+) scavenger, K₂Cr₂O₇ as an electron (e^-) scavenger, isopropanol (IPA) as an OH radical (\cdot OH) scavenger, and ascorbic acid (ASC) as a superoxide anion (\cdot O₂⁻) scavenger).^[359] The concentrations of each scavenger were 10 mM, 50 mM, 75 mM, and 75 mM for EDTA, K₂Cr₂O₇, IPA, and ASC, respectively.^[360,361] High pressure liquid chromatography (HPLC) was utilized to quantify singlet oxygen (1 O₂) production of PMF by degradation of a probe compound (furfuryl alcohol) in the light and dark, as well as for analysis of possible byproducts.

2.7 HPLC Procedures

2.7.1. Singlet Oxygen Detection

A previously reported method was utilized in the evaluation of the singlet oxygen (¹O₂) species.^[58] PMF (500 ppm), as described in the photocatalysis section, was mixed with 10 μM furfuryl alcohol (FFA), and the same experimental procedure as the TC degradation experiments was performed. Blank (with PMF only) and negative controls (without PMF and only FFA) were also prepared. After the 30 min reaction, the PMF was removed by filtration using 0.05 μm nylon filters. High performance liquid chromatography (HPLC) was utilized for the analysis of the filtrate samples using an Agilent Technologies 1290 Infinity HPLC with a Zorbax Eclipse Plus C18 (4.6 \times 150 mm, 5 μ m). The mobile phase was 80% H₂O: 20% MeOH, 1

mL/min was used as the total flow rate, and the injection volume was set to 20 μ L. ¹O₂ was determined via quantification of the FFA using the UV peak area for $\lambda = 219$ nm (retention time of 2.6 min) and the %FFA degradation was calculated by the equation

$$FFA(\%) = \frac{Negative \ control \ concentration - Sample \ concentration}{Negative \ control \ concentration} \times 100.$$
(5.1)

An FFA calibration standard was prepared and analyzed using HPLC with the same conditions.

2.7.2. Tetracycline quantification

The HPLC analysis for the quantification of tetracycline and degradation byproducts was carried out on the same Agilent 1290 Infinity HPLC system used for the FFA analysis. All the samples were filtered using 0.1 µm PVDF syringe filter (Durapore, Merck Millipore, Carrigtwohill Co., Cork, Ireland) prior to injection. The sample injection volume was 20 µL and flow rate was 0.5 mL min⁻¹. The gradient method was optimized on mixtures of tetracycline and several of its degradation byproducts (4-epitetracycline, oxytetracycline, tetracycline, methacycline, doxycycline, chlortetracycline, minocycline, and anhydrotetracycline) to allow for the separation and quantification of a variety of compounds (Figure C.2).^[362–365] A gradient elution was used for a 30 min total run duration using mobile phase (A) 0.001 M ethylenediaminetetraacetic acid (EDTA) in deionized water and (B) HPLC grade acetonitrile (VWR chemicals, Radnor, PA). The mobile phase composition was ramped from 90% A (10%B) to 85% A (15% B) over the first 3 minutes, then ramped to 75% A (25% B) over the next 12 minutes, and finally ramped to 50% A (50% B) over 10 minutes. Then, the composition was ramped back to 90% A (10% B) over 2 minutes and held for 3 minutes to equilibrate for the next injection. Tetracycline was quantified using the UV peak area at 355 nm as the peak wavelength.

2.7.3. Statistical analysis and chemical structures

Statistical analysis was performed using the software Prism 9 utilizing twoway ANOVA analysis with multiple comparisons (correcting for multiple comparisons using the Bonferroni test). 2-D chemical structures were drawn using MarvinSketch Version 21.9 by ChemAxon, and 3-D molecules used in illustrations were created using Avogadro: an open-source molecular builder and visualization tool, Version 1.2.0. Illustrations were created using Affinity Designer Version 1.9.3.

3. RESULTS AND DISCUSSION

3.1 Material Characteristics

The SEM images (Figure 5.1) of the uncoated MoO₃@Fe₃O₄ (MF) displayed a hexagonal rod type structure (Figure 5.1.a) with rod diameters ranging from approximately 0.24 to 1.25 μ m.^[264] The MF material presented a smooth surface, which changed once coated with the emeraldine salt form of PANI. The surface appeared rough after the coating process indicating the presence of the polymer in the PANI@MoO₃@Fe₃O₄ (PMF) material (Figure 5.1.b). The polymer layer appeared to cover the majority of the MF surface and was determined to have a radius of gyration of 136.9 ± 0.92 nm using small-angle neutron scattering data analysis in our previous

publication, which examined the growth of the polymer layer on the nanoparticles.^[264] The measured hydrodynamic radius of the material changed from 794.90 \pm 15.13 nm to 889.20 \pm 12.02 nm when coated with PANI, and its polydispersity decreased from 0.477 to 0.449. The PANI coating was determined to have a significant effect on the dissolution of the MoO₃ in the material (Figure 5.2). MF exhibited significant dissolution of MoO₃ as pH was increased from 3 to 10 reaching a maximum dissolution of 22.9 \pm 1.0% at pH 10. The PANI coating was able to reduce this dissolution to a maximum of 5.6 \pm 0.2%. In the MF material, dissolution at pH 3 was determined to be 2.9 \pm 0.1% (a 20% difference when compared to the dissolution at pH 10 of the MF material), while in the PMF material, the dissolution at pH 3 was 1.6 \pm 0.2% and increased significantly less (4% increase) than that of the MF material as pH was increased to 10. Overall, pH increased dissolution in the coated and uncoated materials, however, the effect of pH in the dissolution of the PANI coating.



Figure 5.1. SEM images of a) MF (× 20,000 magnification), and b) PMF (× 27,000 magnification).



Figure 5.2. Dissolution of uncoated magnetic MoO₃ (MF) and PANI coated magnetic MoO₃ (PMF).

The ζ -potential of the PMF material was measured at a wide pH range, with pH values in the range of 1 to 11 (Figure C.3) and the isoelectric point (IEP) was estimated to have a value of 7.44 ± 0.21. At more acidic pH values, the material was positively charged in solution, and as pH increased the effective surface charge of the material decreased. Likely, at more basic pH values the emeraldine salt started to change to emeraldine base, which reduced the number of protonated nitrogen groups in the PANI backbone (Scheme 5.1).^[278,366] Due to this change, the overall surface charge and conductivity were expected to decrease as pH increased.



Scheme 5.1. PANI doped (emeraldine salt) form and deprotonated form (emeraldine base).[367]

3.2 Photocatalytic Activity

To determine the conditions that led to high photocatalytic activity, the effects of changes in photocatalyst dosage, initial TC concentration, and pH level were examined (Figure 5.3 presents the photocatalysis results, which is also supported by the HPLC data in Figure C.1). Photocatalytic activity is defined herein as TC removal solely due to degradation induced by light exposure. Removal in the light is a result of adsorption, photocatalysis, and any catalytic processes, while removal of TC in the dark is a result of only adsorption and any Fenton reactions or catalytic processes that could be potentially occuring.^[58] Photocatalytic activity largely depends on the ability of the material to promote reactive oxygen species (ROS) generation since they are ultimately responsible for the degradation of TC. The primary species leading to TC degradation by a variety of materials are OH radicals (·OH) and superoxide radicals

(\cdot O₂⁻), with holes (h^+) also playing a role in the mechanism.^[368] To help with the investigation of the mechanism of TC degradation by PMF, optimal reaction conditions were first determined.

As the TC concentration was kept constant and the photocatalyst dosage increased from 100 to 1000 ppm, TC removal showed an upward trend (Figure 5.3.a). In addition, while removal values initially increased, eventually they reached a plateau, where the incremental increases in dosage did not show statistically significant changes in the removal values of TC in light and dark (Table C.1). The initial increase in photocatalytic activity can be attributed to the increase of PMF concentration. It has been found that an increase of the photocatalyst in solution increases photocatalytic and adsorption active sites and as a result increases the photogenerated reactive oxygen species responsible for TC degradation.^[60] However, as photocatalyst concentration increased so did the turbidity of the solution. An increase in turbidity limited the light from reaching the material, effectively reducing the photocatalytic activity.^[60,337] The minimum effective concentration of PMF in which TC removal in dark and light did not show statistically significant changes with the incremental increases in photocatalyst concentrations, but showed a statistically significant difference between light and dark TC removal (p value = 0.013), was 500 ppm. At this concentration TC removal reached $63.6 \pm 0.04\%$ in the light and $54.4 \pm$ 1.2% in the dark.



Figure 5.3. TC removal in light and dark using fluorescence. (a) [PMF] effects ([TC] concentration = 10 ppm at pH 5), (b) [TC] effects ([PMF] = 500 ppm at pH 5), (c) pH effects ([PMF] = 500 ppm, [TC] = 5 ppm, and shows (d) material comparison.

When TC concentration was increased from 1 to 10 ppm with the optimum photocatalyst concentration of 500 ppm (Figure 5.3.b), the TC concentration, which showed the highest photocatalytic degradation (removal of TC in the light not including adsorption), was 5 ppm ($82.1 \pm 2.6\%$ removal in light and $64.6 \pm 3.2\%$ removal in the dark, corresponding to 8.2 mg TC/g photocatalyst and 6.4 mg TC/gphotocatalyst, respectively) with a *p* value less than 0.0001 when comparing TC removal in the light and in the dark. Removal of TC was greatly reduced and the differences between TC removal in light and dark were largely insignificant when TC initial concentrations were larger than 5 ppm. Likely, as TC increased, the surface of PMF reached its adsorption capacity and the additional TC hindered light absorption by PMF by its excess presence in solution, which could have caused complexation with other TC molecules on the surface of the material. It is also likely that the excess TC led to an increase in degradation intermediates, which could have competed for ROS thus hindering the breakdown of TC.^[266]

The change in photocatalytic activity as pH became more alkaline (Figure 5.3.c) can be attributed to the effect of pH changes on TC and PANI. TC exhibits electron donor and acceptor moieties, and at a pH of approximately 6, it aquires a zwitterionic form (Scheme 2).^[369] For photocatalysis to occur, TC needs to be adsorbed to the surface of the photocatalyst. Adsorption of TC is highest when the adsorbent is a good electron donor.^[370] As evidenced in Figure 5.3.c, adsorption did not change significantly as pH increased, although photocatalytic activity diminished when pH was 7 and higher, likely, due to the chemical changes occuring in both TC and PANI as pH increased (Figure C.1, Scheme 5.1, and Scheme 5.2). As pH increased, deprotonation of emeraldine PANI occurred, thus, changing PANI to its emeraldine base form (Scheme 5.1) and reducing its surface charge as discussed in section 4.1.^[366] The protonation of PANI is what improves conductivity due to the polarons and bipolarons that are formed and act as charge carriers.^[366] The emeraldine base form of PANI is non-conductive, which can hinder electron mobility. It has been shown that PANI in its conductive form improves photocatalytic activity by reducing $e^{-}h^{+}$ recombination at valance and conduction bands of the metal oxide.^[350] In a study on the effect of PANI coatings on TiO₂ for the degradation of azo dye, it was determined that pH changes alter the degradation rate, while the removal amount is not changed.^[350] In another study examining the triethylamine (TEA) adsorptive properties of PANI coated α -MoO₃, it was determined that reduction in conductivity of PANI hinders hole transport around the interface due to the disruption of the junction's e⁻-*h*⁺ equilibrium.^[370] The result is an increase in the depletion region width, which can prevent hole transport in the juncton.^[370] Thus, the recombination of e⁻-*h*⁺ pairs of the metal oxide photocatalyst increases, effectively reducing photocatalytic activity.



Scheme 5.2. TC dependence on pH.

When comparing removal of TC with the coated and uncoated material (Figure 5.3.d) it is evident that PANI is critical in improving the photocatalytic activity of the material in the degradation of TC. Conductive polymers in general have demonstrated their role as stable photo-sensitizers due to their charge carrier separation efficiency.^[352] For PANI, its synergistic effect on semiconducting material has been observed to arise from its ability to form heterojuction interfaces via the generation of trapping levels.^[352] In a study of the effect of PANI on CdS, for instance, photoexcited electrons from PANI were shown to move to conduction band of the photocatalyst, and, in turn, the photogenerated holes from the photocatalyst were able to move to the surface of the composite thereby reducing the probability of recombination of electrons and holes.^[352] In PANI-TiO₂, it was speculated that in addition to the decrease in $e^{-}h^{+}$ recombination, PANI also protected the TiO₂ surface from being blocked by intermediates owing to the mobility of PANI active sites.^[350] It has been previously shown that the presence of MoO₃ in PANI enhances the conductivity of PANI via the emergence of trapping levels.^[370,371] This heterojunction formation has been shown to improve the adsorptive capabilities of α -MoO₃/PANI composite towards triethylamine (TEA).^[370] The α -MoO₃ component acts an n-type while PANI acts as a p-type in the p-n heterojuction, which was favorable in the physisorption of vapors that are good electron donors, such as the TEA studied.^[370] In the case of the PMF material tested herein, while it is possible PANI prevented byproducts from taking up active sites, the reduction of e^{-h^+} recombination and the movement of holes

to the surface of the material where likely the primary contributing factors in the observed increase in photocatalytic activity.



Figure 5.4. ATR-FTIR spectra of TC and TC adsorbed on PMF after 30 minutes in the dark and 30 minutes in the light.

The ATR-FTIR spectra of TC and PMF in the light and dark with and without TC were acquired to confirm the adsorption and degradation of TC by PMF and examine whether the chemistry of PMF was affected by light. The wide-range spectra (4000 cm⁻¹ to 675 cm⁻¹) are shown in Figure C.4.a, however, the spectra were primarily analyzed in the range below 1750 cm⁻¹ (shown in Figure 5.4 with more detailed spectra shown in Figure C.4) since the characteristic peaks of TC are in the range of 1700 to 1200 cm⁻¹.^[372,373] The spectra between 3100 cm⁻¹ and 2870 cm⁻¹ are also included due to the presence of a peak at 2981 cm⁻¹ in the PMF Light and Dark without TC spectra, which was attributed to the C-H stretching vibrations of PANI.^[317] The TC spectra presented two peaks in the 3100 cm⁻¹ and 2870 cm⁻¹ range at 3036 cm⁻¹ ¹ and 2950 cm⁻¹ attributed to the C-H and -CH₃ stretching, respectively.^[374,375] In the TC spectra, the peaks at 1693 and 1612 cm⁻¹ corresponded to the C=O stretching vibrations in the carbonyl in the amide group of ring A and carbonyl group of ring A of TC, respectively.^[373,376,377] The spectra of PMF with TC are very similar to that of PMF in the light and dark aside from the appearance of three additional distinct bands, indicating that the adsorption of TC primarily occured at the surface of PMF.^[378] The emergence of the peak at 1644 cm⁻¹ corresponding to C=O stretching vibrations after TC adsorption on PMF was likely a peak shift from the 1693 cm⁻¹ peak of TC, indicating the presence of hydrogen bonding between the amide group of TC and the surface of PMF.^[372,379,380] The peak of TC at 1318 cm⁻¹ and of PMF at 1300 cm⁻¹ from the C-N stretching in the amide group and C-N/C-N⁺ stretching vibrations, respectively, appearred to shift to the strong peak at 1278 cm⁻¹, which was present in

the PMF + TC in the dark spectra.^[264,373,378] The peak at 1278 cm⁻¹ was likely due to hydrogen bonding interactions between the C-N of the TC amine group and C-N/C-N⁺ of PANI. Furthermore, there were changes in the C-H vibrations of the TC and PMF spectra after TC adsorption. The C-H bending vibrations of TC at 829 cm⁻¹ shifted to 837 cm⁻¹ in the PMF + TC dark spectra. Given these changes, TC likely formed strong hydrogen bonds with the PANI coating at the TC amino, carbonyl, or C-H groups as shown in Figure 5.5. Upon light irradiation of the PMF + TC the peak at 837 disappeared, the and the C=O stretching vibrations and C-N vibrations decreased in intensity. Given that the difference between PMF in the dark and PMF in the light was insignificant, the ATR-FTIR spectra changes signified a decrease in the presence of TC on the surface of PMF indicative of TC degradation.



Figure 5.5. PMF and TC interaction based on ATR-FTIR analysis. TC primarily forms hydrogen bonds at the TC amide functional group and C-H and C=O along the structure.

3.3 ROS Involvement in TC Degradation

To elucidate the probable mechanism of photodegradation of TC by PMF, photocatalysis experiments were conducted in the presence of reactive species scavengers. In particular, EDTA was utilized as a hole (h^+) scavenger, K₂Cr₂O₇ as an electron (e^{-}) scavenger, isopropanol (IPA) as a hydroxyl radical (\cdot OH) scavenger, and ascorbic acid (ASC) as a superoxide anion $(\cdot O_2)$ scavenger.^[359] In addition, singlet oxygen production and presence of TC and several TC products were evaluated using HPLC. The TC degradation results from HPLC agreed with the results from the fluorescence spectroscopic analysis. HPLC chromatograms (see Figure C.2 and Figure C.5) were utilized to calculate the TC concentration progression in light and dark during its photocatalysis by PMF (Figure C.1) and assess TC products. The HPLC analysis on the byproducts did not reveal any other TC conformations or degradation byproducts. Figure C.2 shows the tetracycline products (4-epitetracycline, oxytetracycline, tetracycline, methacycline, doxycycline, chlortetracycline, minocycline, and anhydrotetracycline) tested to compare with the TC degradation samples in the 30 min run.^[362–365] While not every possible byproduct was able to be tested for identification, peaks in the HPLC data, other than TC, were too small to accurately ascertain their presence (see Figure C.2 and Figure C.5). Thus, either minute amounts of byproducts were generated in the solution, or any byproducts were adsorbed by the PMF, which would be beneficial in water treatment as any toxic byproducts would be prevented from being released.

Via the scavenger experiments, we can propose likely mechanisms of TC degradation by observing effects of ROS quenching by the scavengers on the photocatalysis of TC.^[266,338,339,381] As all scavengers, aside from K₂Cr₂O₇, eliminated any TC removal due to light absorption (Figure 5.6.a). From this data, we can conclude that the critical reactive species responsible for the photodegradation of TC were photogenerated h^+ , OH, and O_2^- . Specifically, since no change in adsorption and no photocatalysis were observed when the h^+ scavenger (EDTA), the \cdot OH scavenger (IPA), and the $\cdot O_2^-$ scavenger (ASC) were in the solution, all respective quenched reactive oxygen species participated in the degradation mechanism of TC by PMF. While some catalytic activity is possible in the dark as evidenced by the presence of less than 5% FFA removal by ¹O₂ generation, the increase in singlet oxygen production in the light indicates a greater amount of ${}^{1}O_{2}$ production in the light (Figure 5.6.b). Generation of ${}^{1}O_{2}$ can result from oxidation of ${}^{\cdot}O_{2}$, which forms via a stepwise procedure initiating when water molecules are oxidized to form OH or H₂O₂.^[56] The hydroxyl radicals can then dimerize to form H₂O₂, which can then be oxidized into $\cdot O_2^{-}$.^[56] In essence, ROS formation can follow either of these following reactions,

$$H_2O + h^+ \xrightarrow{\text{oxidation}} {}^{\bullet}OH \xrightarrow{\text{dimerization}} H_2O_2 \xrightarrow{\text{oxidation}} {}^{\bullet}O_2^- \xrightarrow{\text{oxidation}} {}^{1}O_2$$
 (5.2)

or

$$H_2 O + h^+ \xrightarrow{\text{oxidation}} H_2 O_2 \xrightarrow{\text{oxidation}} {}^{\bullet} O_2^- \xrightarrow{\text{oxidation}} {}^{1} O_2.$$
(5.3)



Figure 5.6. a) Effect of the addition of ROS scavengers on PMF TC removal where TC alone was used as a control and b) Singlet oxygen determination from FFA production by PMF in the light and dark.

Given that TC photocatalytic degradation was hindered by all three scavengers, it is likely TC degradation by PMF was primarily achieved via nucleophilic attacks by \cdot O₂⁻ and \cdot OH formed via the oxidation of water molecules. The significant role of \cdot O₂⁻ and \cdot OH in TC degradation has also been observed in the degradation of TC by CuS₄ and by the use of electro-catalysis.^[266,368] However, in the TC degradation by PMF, *h*⁺ also plays a critical role as evidenced in Figure 5.6, either via its participation in the formation of \cdot O₂⁻ and \cdot OH or in the TC degradation pathway. One potential degradation pathway, in which \cdot O₂⁻ and \cdot OH were the primary reactive species, was observed when CuS₄ was utilized.^[368] In this reaction, TC reacted with \cdot O₂⁻ and \cdot OH, resulting in the cleavage of -NH and inclusion of \cdot OH, respectively.^[368] Subsequent attacks by \cdot O₂⁻ and \cdot OH resulted in cleavage of the -CO group or addition of \cdot OH in the new products, respectively, leading to ring opening and eventual breakdown of the intermediate products by reactive species (Figure 5.7).^[368] In the electro-catalytic degradation of TC by a carbon nanotube/agarose/indium tin oxide electrode, $\cdot O_2^-$ and $\cdot OH$ also played major roles in the degradation of the TC molecules.^[266] It was speculated that $\cdot OH$ first reacted with TC areas high in electron density, and then was oxidized, primarily by $\cdot O_2^-$, forming three main intermediates, which were further degraded by the elimination of ketone groups, carboxylic groups, and ring opening reactions.^[266] In the visible-light photodegradation of TC by BiOCl@CeO₂ microspheres, $\cdot OH$ were thought to directly oxidize TC after being generated via the oxidation of OH⁻ or H₂O by h^+ in the BiOCl valence band.^[381] In addition, $\cdot O_2^-$, formed by e^- capture of O₂ in the conduction band of CeO₂, was thought to also play a role in degradation mechanism by oxidizing TC.^[381] Quenching of any step in the different degradation mechanisms would lead to the preservation of the TC molecule or byproduct structures.



Figure 5.7. Potential mechanism of photocatalytic degradation of TC by PMF

In the case of PMF degradation of TC, the generation of $\cdot O_2^-$ and $\cdot OH$ was most likely initiated by the oxidation of water by h^+ in the valence band of PANI, as in the case of the BiOCl@CeO₂ microspheres. Then, nucleophilic and radical attacks by $\cdot O_2^-$ and $\cdot OH$ could have been responsible for the degradation of TC. We should note that $\cdot O_2^-$ could also have formed via the reduction of O_2 by photoexcited e^- , where in this pathway $\cdot O_2^-$ could become reduced to H₂O₂, and then $\cdot OH$, leading to the breakdown the structure of TC. However, since the addition of EDTA to the reaction had little effect on the photocatalytic activity of PMF, photogenerated e^- do not appear to play a significant role in this reaction. This was expected as ROS generation takes place at the surface of the material and PANI exhibits p-type semiconducting properties when paired with MoO₃, making holes the more probable reactive species in the initiation of the photodegradative process.

4. CONCLUSION

In the investigation of PANI coated magnetic MoO₃ for photocatalysis of TC, the effect of the PANI coating on photocatalytic activity and dissolution were determined. The conductive and stabilization capabilities of PANI allowed for the reduction of dissolution and improvement in photocatalytic activity of the magnetic MoO₃. While PANI increased photocatalytic activity in pH 3 through pH 10 solutions, in pH 7 and above, a reduction of TC degradation was observed, likely due to the loss of conductivity as PANI transitions from its emeraldine salt to emeraldine base forms. At the optimal solution conditions (pH 5, 500 ppm PMF concentration, and an initial TC concentration of 5 ppm), the PMF material improved photocatalytic activity by more than 20% when exposed to visible light for 30 minutes. The primary reactive species responsible for TC degradation were likely the superoxide anion and hydroxyl radical. Their generation hinged on the production of photogenerated holes by the material and subsequent ability to oxidize water molecules and continue the oxidation process until the formation of superoxide anions and hydroxyl radicals. Given the type of ROS produced, a likely mechanism of TC photodegradation involves cleavage of the -NH and -CO group, ring opening, and breakdown of the smaller molecules generated. The lack of direct involvement of photoexcited electrons in ROS generation was attributed to heterojunction formation and the role of PANI as the p-type material of the p-n semiconductor. Furthermore, the MoO₃ material was stabilized via the considerable reduction in its dissolution across the pH range tested (pH 3 to 10) once coated with PANI. While substantial TC removal and photodegradation within 30 minutes was demonstrated, the solution had optimal conditions. To truly assess the usability of PMF in water treatment, additional studies must be conducted examining the photodegradative ability of the material when in complex solutions (multiple contaminants, ions, organic matter, among other substances). However, this study effectively provides an initial assessment of the material and elucidates its potential photodegradation mechanism

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CHAPTER 6 – SUMMARY & FUTURE PERSPECTIVES

In part adapted from "Nano-based Absorbent and Photocatalyst Use for Pharmaceutical Contaminant Removal During Indirect Potable Water Reuse" by S. Fanourakis, J. Peña-Bahamonde, P. Bandara, and D. Rodrigues^[1]

Molybdenum trioxide, as a nanomaterial for visible light photocatalytic activity, has shown much promise. Several different MoO₃ morphologies can be synthesized with ease including nanorods, nanowires, and nanoplates by varying the temperature, reaction time, and reagents used in the synthesis process. However, their final properties (surface chemistry, photocatalysis, dissolution, aggregation behavior) will vary depending on the synthesis properties. Nanoplates were shown to have the lowest dissolution (< 20%), but their photocatalytic activity in the decolorization of methylene blue (MB) was low (decolorized MB after 300 minutes). Nanowires and nanorods had higher dissolutions at 80% and 60%, respectively, and were able to remove MB in 90 min and 210 min, respectively. While the nanowires decolorized MB the fastest, their photocatalytic activity was the lowest as the majority of the decolorization was due to adsorption. The nanorods had the highest photocatalytic activity, which was owed to the higher amount of oxygen vacancies in the structure of the material as determined by the higher Mo⁺⁶ to Mo⁺⁵ ratio. All three materials demonstrated increasing dissolution values with increasing pH. The dissolution of the nanomaterials showed significant reduction when inorganic salts and organic matter were present in the solution, which was attributed to steric hindrance effects and increased aggregation of the nanomaterials once additional substances were introduced. However, the favorable reduction of dissolution proved to be a hindrance

when the photocatalytic properties of the materials were tested, except for the nanoplates in the presence of CaCl₂, which demonstrated a significant increase in photocatalytic activity.

To reduce the dissolution of the material, conductive polymer coatings, in particular polypyrrole and polyaniline, were investigated. In addition, a magnetic core was included in the MoO₃ to facilitate the removal of the nanomaterials from aqueous solutions. The molar ratios of the material components were first optimized to achieve high photocatalytic activity and low dissolution. The optimum material molar ratios for the polypyrrole (PPy) and polyaniline (PANI) coated materials required the use of base materials, $MoO_3@Fe_3O_4$ (MF), that were slightly different in composition. The base material for PPy@MoO₃@Fe₃O₄ (PMF1), named MF1, contained a higher number of oxygen vacancies than the base material for $PPy@MoO_3@Fe_3O_4$ (PMF2), named MF2, and the resulting photocatalytic activity was higher for PMF1 when compared with the photocatalytic activity of PMF2. The addition of the coatings resulted in a significant reduction in material dissolution (from 7.9% to 4.1% when MF1 was coated with PPy, and from 18.1% to 5.6% when MF2 was coated with PANI). Furthermore, the addition of the coatings improved the photocatalytic activity of both nanomaterials in the degradation of MB. In addition to the dissolution and photocatalysis analysis of the polymer coated nanomaterials, the polymerization process was also studied to understand the role of the base material composition in the polymers' growth. In this investigation, it was determined that oxygen vacancies significantly influenced the polymerization process. A larger amount of oxygen

vacancies resulted in smaller polymer chains and slower polymerization rate due to the higher number of available attachment sites for polymer monomers adsorption and the promotion of monomer oxidation.

The PANI coated nanomaterials underwent additional analysis to determine its effectiveness in removing antibiotics from water. In particular, the removal of tetracycline (TC) was studied. Not only did the PANI coating increased TC photocatalysis, but it also reduced MoO₃ dissolution across a wide pH range (MoO₃ dissolutions for the uncoated material were 2.9% at pH 3 and 22.9% at pH 10 and dissolution for the coated material was 1.6% at pH 3 and 5.6% at pH 10). PANI@MoO₃@Fe₃O₄ was able to remove 82.1% TC in visible light (8.2 mg TC/g photocatalyst) and 64.6% in the dark (6.5 mg TC/g photocatalyst) within a total of 35 min (5 min in dark and 30 min in light). During this time, the uncoated material had a lower TC removal, and no photocatalytic activity was present. The increase in photocatalytic activity was owed to the formation of a p-n heterojunction between PANI and MoO₃, which allowed photogenerated holes to oxidize water and generate reactive oxygen species, such as hydroxyl radicals and superoxide anion radicals. The generated reactive oxygen species were ultimately responsible for the degradation of TC.

Currently, AOPs such as ozonation and UV radiation are still the best strategies to remove EPCs from water. However, associated costs are a major concern in communities with limited financial support. Scaling novel techniques to match industrial levels are needed. The use of magnetic photocatalysts and stabilizing coatings resulted in significant EPC removal, which can help meet safe drinking water demands, while reducing EPCs entering the environment. However, when used in indirect potable water cycles, these techniques need to break down a great variety of EPCs. Thus, there is a need for further studies that can fill this knowledge gap between fundamental research and practical applications. Specifically, there needs to be a focus on the potential practical applications of novel EPC removal techniques in indirect potable reuse water systems.

In addition, while EPC removal efficiencies are important, it is important to investigate at what concentration these EPCs pose a threat to humans, animals, and the ecosystem regardless of demonstrating high EPC removal. Little is known about the fate of nanoparticles in water systems, and the effects of ingestion of the particles or their solutes is largely unknown. Furthermore, the production of toxic by-products from EPC degradation should be of concern. Intermediate degradation products can exhibit increased solubility as compared to that of the original contaminant, and higher toxicity values. Thus, it is important to thoroughly evaluate nanoparticle toxicity (toxic amount and maximum exposure time) and the risks associated with the employment of nanoparticles in water treatment.

To guarantee water safety, the water reuse process requires understanding environmental and health standards. As such, the employment of recent technologies needs thorough risk assessments and health and safety evaluations performed to mitigate potential risks of the technology itself. While no legislation pertaining to EPC maximum allowable concentrations in water has been established, legislations regulating drinking water processes tend to be very strict to ensure human health and environmental safety. For instance, in an ongoing effort to maintain the safety of drinking water and lessen the effect of EPCs, the European Union has added additional requirements for pharmaceuticals; whereby more extensive environmental risk assessments need to be conducted for each pharmaceutical's use to be allowed.^[382] Furthermore, pharmaceutical contaminants in the environment are to be potentially monitored more extensively in order to be able to better evaluate their risk and environmental effects. Still, maximum EPC removal may be necessary, and the employment of nanotechnology in water treatment can be critical when it comes to human health and EPC persistence in environmental systems.

As with any new technology additional research needs to be conducted examining their safety to humans and the environment before large-scale utilization. While photocatalytic nanomaterials are continuously being improved (use of more environmentally friendly materials such as MoO₃ and use of conductive polymer coatings such as PANI), demonstrating high suitability for use in water treatment, without a full examination of their properties and environmental impact, measures should be taken to ensure they are not released in the environment.

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APPENDIX A



Figure A.1. Energy bandgap results of the nanostructures



Figure A.2. UV-vis spectra and XPS of the [MoO₄]²⁻ ion

Sample	MoO ₃ Nanorods					
	Mo ⁶⁺ 3d _{3/2}	Mo ⁶⁺ 3d _{5/2}	Mo ⁵⁺ 3d _{3/2}	Mo ⁵⁺ 3d _{5/2}		
Area (3d _{3/2} : 3d _{5/2} = 2:3)	18469.0	27703.5	902.6	1353.9		
FWHM (3d _{3/2} : 3d _{5/2} = 1:1)	1.40007	1.40007	1.28424	1.28424		
Position (3d _{3/2} - 3d _{5/2} = 3.13 eV)	236.3614	233.2314	235.1712	232.0412		
Concentration (%)	38.12	57.22	1.86	2.80		
Sample	MoO _{3-x} Nanowires					
	Mo ⁶⁺ 3d _{3/2}	Mo ⁶⁺ 3d _{5/2}	Mo ⁵⁺ 3d _{3/2}	Mo ⁵⁺ 3d _{5/2}		
Area (3d _{3/2} : 3d _{5/2} = 2:3)	32178.6	48267.8	902.6	1353.9		
FWHM (3d _{3/2} : 3d _{5/2} = 1:1)	1.1387	1.1387	1.07321	1.07321		
Position (3d _{3/2} - 3d _{5/2} = 3.13 eV)	236.5055	233.3755	235.1419	232.0119		
Concentration (%)	34.56	51.89	5.42	8.13		
Sample	MoO _{3-x} Nanoplates					
	Mo ⁶⁺ 3d _{3/2}	Mo ⁶⁺ 3d _{5/2}	Mo ⁵⁺ 3d _{3/2}	Mo ⁵⁺ 3d _{5/2}		
Area (3d _{3/2} : 3d _{5/2} = 2:3)	9301.2	13951.8	17523.8	26285.7		
FWHM (3d _{3/2} : 3d _{5/2} = 1:1)	2.44316	2.44316	2.78347	2.78347		
Position (3d _{3/2} - 3d _{5/2} = 3.13 eV)	236.1565	233.0265	234.9243	231.7943		
Concentration (%)	13.86	20.81	26.12	39.21		

Table A.1. Fitting parameters of the XPS spectra for all the nanomaterials



Figure A.3. ATR-FTIR results of nanorod MoO₃ after the reaction took place.



Figure A.4. ζ-potential measurements at different pHs for nanorods, nanowires and nanosheets



Figure A.5. HPLC analysis of the reaction between the nanorods and methylene blue after 2 hours in light and dark conditions. MB-ion and MB-MoO₃ (light) right axes and MB-MoO₃ (dark) left axes



Figure A.6. XPS analysis of the collected particles after the reaction took place.



Figure A.7. ATR-FTIR results of ion-MB after the reaction took place.



Figure A.8. Complexation process between MB-ion.



Figure A.9. Relative emission intensity of the lamp and MB absorbance spectra.



Figure A.10. ROS production difference between light and dark for each nanomaterial at each pH value after 2 hours of reaction. Production of H_2O_2 was quantified with 0.4 mM GSH, [$^{1}O_2$] with 10 μ M furfuryl alcohol, and [OH]- with 2mM terephthalic acid.



Figure A.11. ROS production by the dissolved ion in light and dark conditions at pH 7

APPENDIX B

1. EXPERIMENTAL DESIGN AND STATISTICAL ANALYSIS USING RSM

The Design Expert (DE) software was used to generate the total number of experiments, analyze the experimental data, and acquire the relationship between the different input parameters and output responses. The DE software estimates statistical parameters to assess the validity of the resulting models using Analysis of Variance (ANOVA).

For the synthesis of PPy@MoO₃@Fe₃O₄ (PMF1) and PPy@MoO₃@Fe₃O₄ (PMF2) sets of experiments were generated using this software. The experiments were carried out and the output responses for each respective experiment was added to the software. Models were generated by the software using reduced quadratic type modeling. Statistical significance was ensured for each term in each model using an α of 0.05 and by ensuring the lack of fit was insignificant. Furthermore, we ensured that the resulting F-values were greater than 25 for each model indicating that the signal to noise ratio was high enough to allow us to use the resulting models to predict our optimum material. Equation B-1 through B-6 describe the resulting models for each of the material and output responses as second-order equations for methylene blue (MB) dye removal and dissolution in terms of coded factors. Equation B-1 through B-6 are: PMF1 % MB Dye Removal (Dark) = 60.46 - 0.0642A + 5.10B - 10.09C +

$$9.67AB - 10.40A^2 - 21.92B^2$$
, (B-1)

(D 1)

PMF1 % MB Dye Removal (Light) = 81.25 + 3.75A + 2.80B - 11.81C +

$$16.63AB + 5.68BC - 16.92A^2 - 14.33B^2 + 7.37C^2$$
, (B-2)

 $PMF1 \% Dissolution = 11.48 - 1.23A - 1.10B - 1.26C - 8.52AC - 5.45B^{2},$ (B-3)

PMF2 % MB Dye Removal
$$(Dark) = 75.72 + 2.59A - 48.4D + 4.11AD +$$

$$16.52A^2 - 71.68D^2 + 52.87A^2D,$$
 (B-4)

(D 4)

 $(\mathbf{R}_{-}\mathbf{5})$

$$64.48A^2 - 122.14D^2 + 107.57A^2D,$$

$$PMF2 \% Dissolution = 9.86 + 4.62A + 4.38D + 4.44AD - 5.36A^{2},$$
(B-6)

where A is the amount of ammonium molybdate tetrahydrate (AMT), B is the amount of Fe₃O₄, C is the volume of pyrrole monomer, D is the amount of MoO₃@Fe₃O₄ (MF), AB is the interaction between the amount of AMT and amount of Fe₃O₄, AC is the interaction between the amount of AMT and volume of pyrrole monomer, BC is the interaction between the amount of Fe₃O₄ and volume of pyrrole monomer, AD, is the interaction between the amount of AMT in MF and the amount of MF in PMF2, and A², B², and C² are the quadratic terms for each of the main factors, respectively. The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. The negative sign indicates the antagonistic effects whereas the positive sign indicates the synergistic effects.^[383] The obtained R₂ values shown in Table B.1 for R₁, R₂ and R₃ were high (than 0.8) meaning that the models generated for each system have good predictability. Adequate precision of all responses was greater than 10.27 indicating adequate signals. The low standard deviations of the models for MB dye removal and dissolution also confirm the goodness of fit.

	R ₁ : % MB Dye Removal (Dark)		R ₂ : % MB Dye Removal (Light)		R ₃ : % Dissolution	
	PMF1	PMF2	PMF1	PMF2	PMF1	PMF2
Std. Dev.	6.73	0.5796	3.04	0.4458	3.21	1.28
Mean	45.25	40.39	70.01	45.96	8.92	5.61
C.V. %	14.88	1.44	4.34	0.97	35.94	22.8
R ²	0.8981	0.9997	0.9850	0.9998	0.7994	0.9714
Adjusted R ²	0.8370	0.9994	0.9997	0.9997	0.7082	0.9599
Predicted R ²	0.6474	0.9989	0.8705	0.9993	0.5309	0.955
Adequate Precision	10.9146	153.5627	25.5967	210.6617	10.2713	24.5496

Table B.1. Statistics of the Responses on the Reduced Quadratic Model.

The MB dye removal efficiency and dissolution of catalyst in the solution as predicted by Equation B-1 to Equation B-6. The results show a good correlation between the actual values and the predicted responses. Response surface contour plots for all responses are shown in Figure B.1 and Figure B.2 for PMF1 and PMF2, respectively. These plots allow us to understand the relationships of the independent variables to their responses. To understand the responses for PMF1, one of the independent variables (i.e., pyrrole) was held constant at its center level to show the interaction of the remaining factors (i.e., Fe₃O₄ and MoO₃ precursor) towards the response. Figure B.1.b.i and Figure B.1.c.i illustrate the surface of MoO₃ and Fe₃O₄ with a maximum response on MB dye removal. An increase in the amount on both factors showed an increase of MB dye removal first followed by a decrease. This trend agrees with Equation B-1 and Equation B-2, where the quadratic term A² and B² had a negative value indicating a downward curvature. The effects of pyrrole and MoO₃ concentrations (Figure B.1.a.ii and Figure B.1.b.ii) and the effects of pyrrole and Fe₃O₄ concentration (Figure B.1.a.iii and Figure B.1.b.iii) show a slight decrease of MB dye removal when pyrrole concentration increased. The slight upward curvature on the pyrrole was a result of the positive quadratic term (C²) in Equation B-2.

The interaction of the factors in Figure B.1.c.i and Figure B.1.c.iii illustrate that there is no significant effect on the dissolution of the nanomaterials. However, the interaction of the MoO₃ and pyrrole on the dissolution of the nanomaterial as shown in Figure B.1.c.ii was significant with a positive effect. The response surface contour plot illustrates a minimax response. The graph illustrates that increasing either factor while decreasing the other leads to an increase in the dissolution of the nanomaterial. Also, increasing or decreasing both factors at the same time leads to a decrease in the dissolution response.

Figure B.2 shows the contour plots describing Equations B-4 to B-6. The MB removal in light and dark (Figure B.2.a and Figure B.2.b, respectively), show similar trends. The amount of MF in PMF seems to be the predominant factor as to the extent of MB removal. While the amount of AMT results in an overall positive effect on the removal of MB (see Equations B-4 and B-5), the amount of MF produced a negative effect, which was counteracted by the interaction of the amount of AMT and amount of MF in PMF. From the contour plots we can see that there was an optimum region defined for the removal of MB in the light and dark. The amount of AMT, however, was the factor that most influenced the dissolution of the material as shown in Figure

B.2.c This as we expected since the larger the amount of AMT was, the more molybdenum was available in the material, which could readily dissolve. However, the PANI coating could help counteract the dissolution of MoO₃ when it could coat a sufficient amount of the material.



Figure B.1. Contour plots of methylene blue dye removal by PMF1 in a) dark and b) light, and c) dissolution of PMF1 material where (i) amount of Fe₃O₄ vs amount of AMT (ii) volume of pyrrole vs the amount of AMT, and (iii) volume of pyrrole vs the amount of Fe₃O₄.



Figure B.2. Contour plots of methylene blue dye removal by PMF2 in a) light, b) dark, and c) dissolution of PMF2 material.

2. ADDITIONAL TABLES AND FIGURES

Synthesis nom namerical openinzation.						
Response	Nanomaterial	Predicted Mean (%)	Standard Deviation (%)	95% PI low ^(a) (%)	Data Mean (Observed) (%)	95% PI high ^(a) (%)
MB Dye	PMF1	66.12	6.73	55.21	70.26	77.02
Removal (Dark)	PMF2	59.92	0.58	57.60	60.18	62.23
MB Dye	PMF1	90.75	3.04	85.65	95.39	95.85
Removal (Light)	PMF2	75.94	0.45	74.17	75.98	77.72
Dissolution	PMF1	13.17	3.21	7.38	4.12	18.97
	PMF2	3.78	3.21	1.50	5.6	6.07

Table B.2. Model Validation of the PPy@MoO₃@Fe₃O₄ (PMF1) and PANI@MoO₃@Fe₃O₄ (PMF2) synthesis from numerical optimization.

^{a)}Confidence = 95%

Table B.3. Comparison of our developed material with other photocatalysts in the removal of methylene blue (MB).

5					
Material	Material and Contaminant Concentrations	Light Source	Percent Removal	Time to Achieve Removal	Ref
Bi ₂ O ₃ /MoO ₃	500 ppm photocatalyst in 10 ppm MB solution	Visible, 500W	86.6%	120 min	[145]
h-MoO₃	25 ppm catalyst in 10 ppm MB solution	Visible, 350W	19 %	105 min	[147]
AgNPs decorated microstructure ZnO	600 ppm catalyst in 10 ppm MB solution	UV, 6W	87.74%	60 min	[384]
TiO ₂ /GO	1000 ppm catalyst in 0.01mM MB solution	Visible, 450W	51.3%	60 min	[385]
MoO ₃ /P25	100 ppm catalyst in 15 ppm MB solution	Visible, 110W	38%	150 min	[386]
PPy@MoO ₃ @ Fe ₃ O ₄ (PMF1)	500 ppm catalyst in 40 ppm MB solution	Visible, 4W	95.39%	120 min	(this work)
PANI@MoO ₃ @Fe ₃ O ₄ (PMF2)	500 ppm catalyst in 40 ppm MB solution	Visible, 4W	75.98%	120 min	(this work)
Material	Crystallite size ¹ (nm)	¹ Lattice strain (%)	Microstrain, ² ϵ (x10 ⁻³)	Dislocation density, ² δ (x10 ¹⁴ m ⁻²)	
----------	---------------------------------------	---------------------------------	---	--	
MF1	26	0.67	1.56	21.3	
PMF1	32	0.55	1.26	13.8	
MF2	37	0.46	1.06	9.7	
PMF2	44	0.36	0.89	6.6	

Table B.4. Material structural parameters calculated from the XRD data.

¹ Calculated using Scherrer calculator form X'Pert HighScore Plus software

² Calculated based from the formulas presented in literature^[197,387]



Figure B.3. XRD Pattern of a) MF1 and b) PMF1.





Material	C (%)	O (%)	Mo (%)	Fe (%)	Other (%)				
MF1	13.6	60.8	25.3	0.3					
PMF1	31.3	47.8	16.7	0.4	N: 2.8, S: 1.0				
MF2	19.1	57.8	21.8	1.3					
PMF2	51.2	33.9	12.8	0.1	N: 1.3, Cl: 0.7				

Table B.5. Relative atomic concentrations from XPS.



Figure B.5. XPS Fe 2p spectra of a) Fe_3O_4 and the fitted spectra of b) MF1 and c) MF2.



Figure B.6	XPS 01s	fitted s	pectra.
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	Tuble Die Hory Sucham Ar S fitting parameters.									
Material	Peak type	Peak Center (eV)	FWHM (eV)	Area	Concentration %					
MF1	Mo 3d _{5/2} (Mo ⁺⁶)	232.57	1.31	49196.01	56.0					
-	Mo 3d _{3/2} (Mo ⁺⁶)	235.72	1.31	31942.06	36.3					
-	Mo 3d _{5/2} (Mo ⁺⁵)	231.45	1.21	4053.00	4.6					
-	Mo 3d _{3/2} (Mo ⁺⁵)	234.60	1.21	2701.69	3.1					
MF2	Mo 3d _{5/2} (Mo ⁺⁶)	232.59	1.37	37399.71	57.3					
-	Mo 3d _{3/2} (Mo ⁺⁶)	235.77	1.37	24889.87	38.1					
-	Mo 3d _{5/2} (Mo ⁺⁵)	231.51	1.27	1774.23	2.7					
-	Mo 3d _{3/2} (Mo ⁺⁵)	234.66	1.27	1227.52	1.9					

|--|

E: O	Ma	DD	DANI	ME1	DME1	MES	DMES	E
F e ₃ O ₄	M0U3	РРУ	PANI	NIF 1	PMFI	NIF 2	PMF2	Functional group/assignment
-	-		1564.7 cm ⁻¹	-	-	-	1606.9 cm ⁻¹	C=C-C stretching vibrations (PANI- quinoid diamine, N=Q=N) ^[126,317,319,388]
-	-	1552.4 cm ⁻¹	-	-	1552.0 cm ⁻¹	-	-	Pyrrole ring vibrations(C=C stretching) ^[126,284,313,388]
-	-	-	1488.3 cm ⁻¹	-	-	-	-	C=C-C aromatic ring stretching of the benzenoid diamine (N- B-N) ^[313,317,319]
-	-	1461.8 cm ⁻¹	-	1433.4 cm ⁻¹	1443.5 cm ⁻¹	1442.5 cm ⁻¹	1442.0 cm ⁻¹	C-N stretching ^[126,284,310,319]
-	1403.5 cm ⁻¹	-	-	1405.2 cm ⁻¹	-	1405.7 cm ⁻¹	-	N-H bending ^[156,309]
-	-	1305.1 cm ⁻¹	-	-	1317.6 cm ⁻¹	-	-	C-H in-plane vibrations ^[310,317]
-	-	-	1296.0 cm ⁻¹	-	-	-	1305.6 cm ⁻¹	C-N stretching ^[319,371]
-	-	-	1245.0 cm ⁻¹	-	-	-	1246.8 cm ⁻¹	C-N ⁺ stretching ^[312,314]
-	-	1174.5 cm ⁻¹	-	-	-	-	-	C-N stretching ^[126,388]
-	-	1042.8 cm ⁻¹	~1145- ~1038 cm ⁻¹	-	-	-	-	C-H in plane vibrations ^[284,310,312,314,317]
-	956.1 cm ⁻¹	-	-	969.6 cm ⁻¹	965.2 cm ⁻¹	972.4 cm ⁻¹	971.5 cm ⁻¹	M=O stretching ^[58,309]
-	895.3 cm ⁻¹	-	-	895.8 cm ⁻¹	896.8 cm ⁻¹	895.8 cm ⁻¹	895.3 cm ⁻¹	M=O stretching ^[58,309]
-	878.9 cm ⁻¹	-	-	-	-	-	-	M=O stretching ^[58,309]
-	-	-	797.5 cm ⁻¹	-	-	-	-	C-H out of plane bending in aromatic ring ^[312,314,317]
-	568.4 cm ⁻¹	-	-	579.5 cm ⁻¹	579.0 cm ⁻¹	571.8 cm ⁻¹	565.1 cm ⁻¹	Mo-O-Mo bending ^[58,156,309,319]
559.9 cm ⁻¹	-	-	-	-	-	-	-	Fe-O-Fe bending ^[308]
-	517.3 cm ⁻¹	-	-	517.4 cm ⁻¹	518.3 cm ⁻¹	517.8 cm ⁻¹	517.3 cm ⁻¹	Mo-O-Mo bending ^[58]

Table B.7. ATR-FTIR peaks and corresponding bond vibrations of Fe₃O₄, MoO₃, MF1, PMF1, MF2,and PMF2.

Material	Level ^b	G	Rg (Å)	В	Р	Background	Reduced
						(cm ⁻¹)	χ²
PPy on MF1	1	$\begin{array}{c} 23.9 \pm \\ 0.64 \end{array}$	$\begin{array}{c} 286.7 \pm \\ 0.95 \end{array}$	4.72e-8 ± 1.62e-11	3.78 ± 1.52e-4	$0.066 \pm 7.26e-6$	1.05
	2	$\begin{array}{c} 312.4 \pm \\ 18.66 \end{array}$	$561.4 \pm \\5.56$	8.23e-6 ± 3.40e-8	$\begin{array}{c} 2.86 \pm \\ 0.007 \end{array}$		
	3	3.35e5 ± 1.69e3	$\begin{array}{c} 2744 \pm \\ 4.05 \end{array}$	4.49e-7 ± 9.77e-11	3.61 ± 5.30e-4		
PPy on MF2	1	$\begin{array}{c} 12.01 \pm \\ 0.57 \end{array}$	$\begin{array}{c} 259.9.00\\ \pm \ 0.57\end{array}$	1.17e-7 ± 6.35e-11	$3.53 \pm 1.52e-4$	0.064 ± 3.41e-6	1.14
	2	$502.6 \pm \\ 4.93$	$\begin{array}{c} 635.4 \pm \\ 2.23 \end{array}$	1.96e-5 ± 4.07e-8	$\begin{array}{c} 2.73 \pm \\ 0.060 \end{array}$		
	3	5.16e5 ± 1.10e4	$\begin{array}{c} 3300 \pm \\ 5.97 \end{array}$	4.36e-8± 1.39e-11	$\begin{array}{c} 3.90 \pm \\ 1.54 \text{e-}4 \end{array}$		
PANI on MF1	1	$\begin{array}{c} 1.37 \pm \\ 0.069 \end{array}$	$\begin{array}{r} 378.5 \pm \\ 110.46 \end{array}$	3.19e-8 ± 1.66e-10	3.19 ± 9.63e-3	$0.264 \pm 1.41e-5$	0.61
	2	50.71 ± 5.44	$\begin{array}{r} 1245 \pm \\ 35.94 \end{array}$	3.00e-5 ± 3.74e-7	$2.03 \pm 3.68e-3$		
	3	1781 ± 2.75e3	$2965.3 \pm \\236.72$	1.06e-7 ± 2.31e-9	$3.04 \pm 7.88e-3$		
PANI on MF2	1	$\begin{array}{c} 1.87 \pm \\ 0.05 \end{array}$	$\begin{array}{r} 304.5 \pm \\ 4.43 \end{array}$	8.07e-8± 3.26e-10	$\begin{array}{c} 3.11 \pm \\ 0.005 \end{array}$	0.20 ± 1.34e- 5	1.06
	2	$\begin{array}{c} 370.44 \pm \\ 8.18 \end{array}$	1369 ± 9.15	1.70e-6 ± 1.11e-8	$\begin{array}{c} 2.74 \pm \\ 0.001 \end{array}$		
	3	$\begin{array}{c} 3433.0 \pm \\ 1.63e3 \end{array}$	$\begin{array}{c} 2890 \pm \\ 21.03 \end{array}$	1.47e-7 ± 5.11e-9	$\begin{array}{c} 3.1 \pm \\ 0.007 \end{array}$		
	4	0	1e10	1.71e-5 ± 1.23e-7	$\begin{array}{c} 3.15 \pm \\ 0.083 \end{array}$		

Table B.8. Fitting curve values corresponding to equation 2 once polymerization was completed^a.

^a G is a pre-factor for the Guinier exponential term, B is a pre-factor for the power law term, R_g is the radius of gyration of the structure feature, P describes the fractal dimension of the material, and the background arises from the incoherent scattering background of the samples. The reduced χ^2 value describes the goodness of fit where the closer the value is to 1 the better the fit; ^b On each material, the Level 2 structure arose from the polymer.



Scheme B.1. Pyrrole and aniline monomers, cation radicals, and polymers

APPENDIX C



Figure C.1. HPLC analysis of the degradation of TC at pH 5 with an initial TC dose of 5 ppm and a photocatalyst concentration of 500 ppm



Figure C.2. HPLC chromatogram of tetracycline and potential products with UV detection at 355 nm with an initial TC dose of 5 ppm and a photocatalyst concentration of 500 ppm



Figure C.3. ζ -potential of PMF at pH values ranging from 1.5 to 11

DME concentrations		Light			Dark	
comparison (ppm)	Below threshold?	Summary	Adjusted P Value	Below threshold?	Summary	Adjusted P Value
0 vs. 100	Yes	****	< 0.0001	Yes	****	< 0.0001
0 vs. 200	Yes	****	< 0.0001	Yes	****	< 0.0001
0 vs. 250	Yes	****	< 0.0001	Yes	****	< 0.0001
0 vs. 300	Yes	****	< 0.0001	Yes	****	< 0.0001
0 vs. 500	Yes	****	< 0.0001	Yes	****	< 0.0001
0 vs. 600	Yes	****	< 0.0001	Yes	****	< 0.0001
0 vs. 800	Yes	****	< 0.0001	Yes	****	< 0.0001
0 vs. 1000	Yes	****	< 0.0001	Yes	****	< 0.0001
100 vs. 200	No	ns	0.7578	No	ns	0.8850
100 vs. 250	Yes	**	0.0025	Yes	*	0.0487
100 vs. 300	Yes	***	0.0001	Yes	*	0.0169
100 vs. 500	Yes	****	< 0.0001	Yes	***	0.0002
100 vs. 600	Yes	****	< 0.0001	Yes	****	< 0.0001
100 vs. 800	Yes	****	< 0.0001	Yes	****	< 0.0001
100 vs. 1000	Yes	****	< 0.0001	Yes	****	< 0.0001
200 vs. 250	No	ns	0.1657	No	ns	0.6220
200 vs. 300	Yes	*	0.0151	No	ns	0.3603
200 vs. 500	Yes	****	< 0.0001	Yes	*	0.0118
200 vs. 600	Yes	****	< 0.0001	Yes	**	0.0017
200 vs. 800	Yes	****	< 0.0001	Yes	***	0.0001
200 vs. 1000	Yes	****	< 0.0001	Yes	****	< 0.0001
250 vs. 300	No	ns	0.9815	No	ns	>0.9999
250 vs. 500	No	ns	0.0518	No	ns	0.5716
250 vs. 600	Yes	***	0.0005	No	ns	0.1940
250 vs. 800	Yes	*	0.0106	Yes	*	0.0288
250 vs. 1000	Yes	****	< 0.0001	Yes	**	0.0019
300 vs. 500	No	ns	0.3894	No	ns	0.8238
300 vs. 600	Yes	**	0.0094	No	ns	0.3969
300 vs. 800	No	ns	0.1260	No	ns	0.0790
300 vs. 1000	Yes	****	< 0.0001	Yes	**	0.0063
500 vs. 600	No	ns	0.7516	No	ns	0.9985
500 vs. 800	No	ns	0.9993	No	ns	0.8243
500 vs. 1000	Yes	*	0.0445	No	ns	0.2466
600 vs. 800	No	ns	0.9762	No	ns	0.9942
600 vs. 1000	No	ns	0.7648	No	ns	0.6552
800 vs. 1000	No	ns	0.1758	No	ns	0.9843

Table C.1. Tukey's multiple comparisons test of the different PMF concentrations in the removalof TC in the light and dark



Figure C.4. a) Full ATR-FTIR spectra, b) full spectra of TC, and spectra from 3100 cm⁻¹ to 2875 cm⁻¹ and 1800 cm⁻¹ to 675 cm⁻¹ of: (c) PMF under dark, d) PMF under light, e) PMF + TC present under dark, and (f) PMF + TC present under light



Figure C.5. HPLC chromatograms of Tetracycline (TC) in light and dark and TC with PMF in light and dark at different exposure times