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Mudit Mohan Singh

May 2018

**Sunlight Active (CoTiO₃) – Titania (TiO₂) catalyst with effective activity
for dye degradation and H⁺ evolution.**

A Thesis

Presented to

The Faculty of the Department of Engineering Technology at the

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Masters of Science

In

Engineering Technology

By

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Abstract

In the presented work we display experimental evidence of the effective photocatalytic activity of (CoTiO₃) – Titania (TiO₂) for dye degradation and H⁺ evolution. We present analysis of the photocatalytic activity of the CoTiO₃ that is 50-92 times effective than TiO₂ under visible light to Acid Orange 7 dye. At the same time the catalyst can produce 78 times more hydrogen than pure TiO₂. The results show that there is a co-catalytic effect among the substrate (TiO₂-rutile) and the CoTiO₃. The chemical composition, phases and frameworks are investigated due to their critical effects on the high degree of degradation observed on this catalyst. The particles have sizes above 100 nm to near micrometric ranges. This allows the potential to eliminate quantum confinement effects as the effective mechanism for rather unique catalytic activity. Instead, here we propose a new mechanism based on double harmonic effect on photocatalytic enhancement for dye degradation and strong field and Plasmonic effect for hydrogen generation. The results are based on the characterization of the catalysts by means of XRD, Raman, SEM and HRTEM. Band gap of all photocatalysts used is reported, that commensurate with the unprecedented photocatalytic activity of the materials. We present synthesis and experimental procedures, thorough characterization of the CoTiO₃ and detailed quantitative analysis of dye degradation and Hydrogen generation.

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Chapter I

Introduction

Introduction

Titania, commonly referred as Titanium dioxide (TiO_2) or Titanium (IV) oxide is an oxide of Titanium (Ti) formed by the natural interaction of Ti and Oxygen. Allotropic existence of Titanium dioxide (TiO_2) in nature is found as Rutile, Anatase and Brookite. These are the three principal stable phases of TiO_2 . Anatase and Rutile are comparatively easier to synthesize in laboratory conditions as compared to Brookite (1). Due to complexity of Brookite synthesis, Anatase and Rutile have been commonly employed in majority of the research related to TiO_2 . Titanium dioxide is an extremely versatile material that has gained exponential research and commercial attention in last three decades. Some of the major application of TiO_2 are pigments in paint coatings, cosmetic and skin care products, air purification, water treatment, anti-bacterial agents, solar cells and biosensors (2-6). The significance of these applications has propelled the understanding of the fundamentals of TiO_2 for advancing towards improved efficiency.

One of the most essential properties of TiO_2 is that it is an inexpensive, stable and environmentally friendly n-type semiconductor which exhibits ideal photocatalytic characteristics. In 1972, Fujishima and Honda reported the photocatalytic abilities of TiO_2 based electrodes for water splitting (7). Ever since the researchers have extensively put in efforts to understand the principles and enhance the photocatalytic effectiveness of TiO_2 . Unfortunately, it is only active in UV light ($>3\text{eV}$).

This principle of Photocatalysis is significant as it is the driving mechanism for all the photocatalytic applications. Photocatalysis is a green process that uses photonic or light energy greater than the band gap of the catalyst to initiate a chemical reaction. The reaction is initiated by energy being provided to TiO_2 and subsequent generation of electron - hole pair which can be utilized for a number of applications (8). The effective implementation of this phenomenon has increased the utility of TiO_2 . Titanium dioxide has been proven effective for photocatalytic applications (9). A Few of these major applications include degradation of organic compounds (10, 11), water purification by degradation of organic and azo ($-\text{N}=\text{N}-$) dyes (12-14) and H^+ evolution by water splitting (15, 16).

TiO_2 has a wide band gap, generally ~ 3.1 eV. Even though TiO_2 is an efficient photocatalyst, due to the wider band gap value, it can only be excited by Ultra-Violet (UV) light. This property of TiO_2 limits its use under UV radiation, which accounts for 5% of the sunlight spectra. The effectiveness in UV range has amplified the need of developing a TiO_2 photocatalyst active in visible or solar light in order to have diversified applications for the future generations. Various approaches have been incorporated in order to cope up with this drawback of TiO_2 . These approaches essentially focus on reducing the bandgap of TiO_2 and aim to achieve new states which could potentially be active under the visible light spectra. Some of these processes include: reduction with hydrogen,

modification of particle size, mechanical alloying, doping with noble metals or transition elements (17-20).

Doping of TiO₂:

Doping refers to the addition of impurities into a pure semiconductor. Doping forms an extrinsic semiconductor with enhanced properties compared to counterparts. Doping is one of the ways to achieve a narrow band gap. N-type doping allows addition of an extra valance electron that does not fit into the crystal lattice of the TiO₂ and is free to move. As the extra valance electron moves around, it leaves unoccupied quantum state that is easier for other valance electrons to fill as they move from low to high energy state. Fig. 1 explains the mechanism of an electron-hole pair schematic comparison of TiO₂ and Metal Doped TiO₂. The process initiates as a photonic energy " $h\nu$ ", greater than the band gap of TiO₂ ($V_2 - V_1$) is absorbed by the material, generally 3.1 eV.

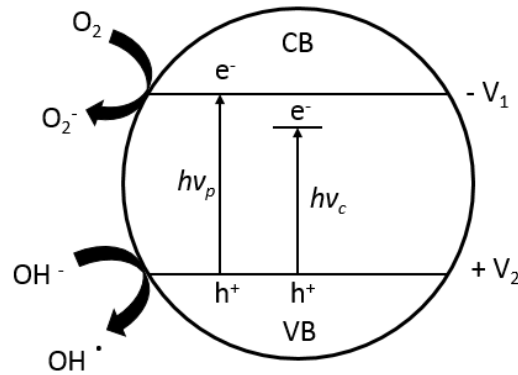


Fig. 1. Schematic comparison of pure TiO₂ band gap ($h\nu_p$) and Metal Doped TiO₂ ($h\nu_c$)

As the energy is absorbed, an electron is promoted from the conduction band (CB) to the valance band. Due to the promotion of electron, a positively charged hole is created in the valance band (VB). In presence of H₂O these holes can create powerful hydroxyl radicals with high oxidizing capabilities. The activity of doped TiO₂ is increased as a unique energy level is produced in the band gap ($h\nu_c$) due to the defect state created by the added metal particles.

Apart from the band gap reduction metal doping provides efficient locking of the electron that provides resistance to the recombination of electron and hole pair (21). Ideally, the band gap should be narrow to allow larger amount of naturally available visible light (sunlight) to benefit its photocatalytic effectiveness.

It has been proven that noble metals have a clear effect if doped in Titania particles (22-25). These noble metals like Platinum, Gold and Silver have shown a great effect in the photocatalytic activeness of TiO₂ nanoparticles. Although they have a significant effect on the activity in visible light, it makes the entire composite rather expensive and hard to be considered for large scale applications.

Cobalt on the other hand is cheaper as a dopant that increases the photocatalytic efficiency of TiO₂ (19, 20, 26-28). Decoration of CoO on TiO₂ particles has been proven to have good photocatalytic effects to improve the efficiency and is considered for various environmental application like degradation of organic pollutants. CoO nano particles

themselves have been proven effective to generate hydrogen from water splitting (29).

Cobalt doping in TiO_2 has been investigated, but up to minimal doping levels (27, 30-33). These levels have usually been in the range of 0.1 – 1 atomic% (at %). It should also be noted that in these ranges CoO has been active as a Co-Catalyst that enhances the photocatalytic potential along with altering the band gap. Doping of Cobalt at higher percentages 5-20 at %, has been less investigated.

In the current work we present a detailed analysis of Cobalt doping in higher concentrations (up to 20% by atomic weight). At higher concentration, and higher temperatures, the co-catalyst has even better supporting role due to a well-defined framework and interaction at the boundaries of TiO_2 . This is an alternative procedure to accomplish higher activities along with reduction of band gap. This catalyst has proven effective with various light sources like sunlight and visible light. Infrared pulsating lasers have also been used to activate the material unforeseen conditions.

In order for a material to be effective for a specific application it must be thermodynamically more active than the chemical potential of the reaction. Therefore, bandgap manipulation is of paramount interest in order to generate catalyst that are sunlight active. Although band gap is one of the major property, it is not the only crucial property to affect the photocatalytic capabilities of a material. Plasmonic effects (19, 27), band

edge position (8, 18, 19, 27) and co-catalysis (27) have had successful catalytic enhancement. On the contrary, our higher doped (Co-20 at %) catalyst is not usually reported, especially under pulsating light sources.

Motivation:

Environmental and energy issues are two of the major challenges that the modern 21st century is facing at a global level. There are many environmental problems related to remediation of contaminated water bodies especially those contaminated with textile organics. The presence of these substances in water bodies around the globe is causing a severe delay in utilizing these natural resources for human use. Over the past decade, the remediation challenges related to water bodies have come out as a significant priority at a global level. Up to 70% of the water, which is the likely source of human consumption is contaminated. These contaminants are toxic wastes that primarily include organics, textile effluents etc.(8). Acid Orange 7 is one of such pollutant. Like most other textile azo dyes, it is usually disposed inappropriately and poses severe threat to humans. It is highly toxic and can have severe effects on respiratory systems, eyes, mucous membranes and can cause bone diseases (8).

The depletion of hydrocarbon based fuel resources is leading to an obscure future of Energy production. To maintain the current standards of living it is essential to establish an environment friendly future. Hydrogen is a clean fuel source capable of energy production. One of the possible mechanisms to produce hydrogen is through water splitting using

photocatalysis. The generation of hydrogen from water using light could potentially form the basis of a clean and renewable source of energy. Water remediation and clean energy production are two major challenges being faced at the global level. We therefore, intend apply Photocatalysis by semiconductor composites to take a step towards the solution.

Chapter II

Experimental Methods

Experimental Methods

Stoichiometric Calculations:

The chemicals used in this work were essentially titanium isopropoxide ($\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$) (Fig 2.) and Cobalt (III) Fluoride (CoF_3). Detailed description of the chemicals used is shown in Table 1. For achieving precise doping levels, stoichiometric calculations were performed to calculate the atomic percentages Co that relates to the amount of CoF_3 needed to be added into the ($\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$) during synthesis.

Table 1. Chemicals used for synthesis with their respective purity and vendors.

Element	Formula	Purity (wt. %)	Vendor
Titanium isopropoxide	$(\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4)$	97.00	Sigma Aldrich
Cobalt (III) Fluoride	CoF_3	99.99	Sigma Aldrich

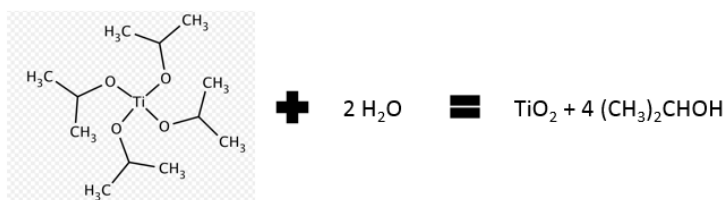


Fig 2. Chemical Structure of Titanium Isopropoxide to TiO_2 .

The abbreviations used to describe the stoichiometric calculations are presented below:

δ_x = Density of X material

$[X]$ = Concentration of X material

ISO = Titanium isopropoxide

Co = Cobalt

MW_X = Molecular Weight of X material

N_A = Avogadro constant = 6.022×10^{23} atoms/mol

V_{BOT}X = Volume used from the bottle (by vendor) of X material in mL

V_X = Actual Volume of X material in mL

n_X = Mole of X material

m_{BOT}X = Mass of X material from the bottle (by vendor) in grams

m_X = Actual mass of X material in grams

%at X = Atomic percentage of X atom

wt % X = Weight percentage of X atom

The known parameters for the stoichiometric calculations were the following:

$$MW_{Co} = 58.93 \text{ g/mol}$$

$$MW_F = 19 \text{ g/mol}$$

$$MW_{ISO} = 283.9 \text{ g/mol}$$

$$\delta_{ISO} = 0.96 \text{ g/mL}$$

The percentage of Co and F in CoF_3 can be calculated by the following equations:

$$\%at Co = \frac{1 \text{ atom of Co}}{4 \text{ Atoms}} * 100 = 25\%at Co$$

$$\%at F = \frac{3 \text{ atoms of F}}{4 \text{ Atoms}} * 100 = 75\%at F$$

Weight percentage of Co in CoF_3 can be calculated using the above values in the compositional weight percentage equation:

$$\begin{aligned} wt\% Co &= \frac{\left[\frac{\%at Co}{100} \right] \left[\frac{MW_{Co}}{N_A} \right]}{\left[\frac{\%at Co}{100} \right] \left[\frac{MW_{Co}}{N_A} \right] + \left[\frac{\%at F}{100} \right] \left[\frac{MW_F}{N_A} \right]} * 100 \\ &= \frac{0.25 * \frac{58.93 \text{ g/mol}}{6.022 * 10^{23} \text{ atoms/mol}} * 100}{\left[0.25 * \frac{58.93 \text{ g/mol}}{6.022 * 10^{23} \text{ atoms/mol}} \right] + \left[0.75 * \frac{19 \text{ g/mol}}{6.022 * 10^{23} \text{ atoms/mol}} \right]} \\ &= 50.83 \text{ wt\% Co} \end{aligned}$$

To calculate the amount of CoF_3 to be added to dope any “X” at % of Co with TiO_2 we need to perform the following calculations:

$$V_{ISO} = V_{BOTX} * [ISO] = (0.97)(V_{BOTX})$$

$$m_{ISO} = \delta_{ISO} * V_{ISO} = 0.96 \text{ g/mL} * [(0.97)(V_{BOTX})] = (0.9312)(V_{BOTX})$$

$$n_{ISO} = \frac{m_{ISO}}{MW_{ISO}} = \frac{(0.9312 \text{ g})(V_{BOTX})}{283.9 \text{ g/mol}} = (0.00328)(V_{BOTX})$$

$$n_{Co} = \frac{\%at Co * n_{ISO}}{100} = \frac{\%at Co * [(0.00328)(V_{BOTX})]}{100}$$

$$= (3.28 * 10^{-5})(\%at Co)(V_{BOTX})$$

$$m_{Co} = n_{Co} * MW_{Co} = [(3.28 * 10^{-5})(\%at Co)(V_{BOTX})] * 59 \text{ g/mol}$$

$$= (1.935 * 10^{-3})(\%at Co)(V_{BOTX})$$

$$m_{CoF_3} = \frac{m_{Co} * 100}{\%wt Co} = \frac{[(1.935 * 10^{-3})(\%at Co)(V_{BOTX})] * 100}{50.83}$$

$$m_{CoF_3} = (3.81 * 10^{-3})(\%at Co)(V_{BOTX})$$

From the above equation, the amount of Titanium Isopropoxide and CoF_3 can be calculated for any atomic composition of Cobalt. In the current work, four atomic compositions were prepared; pure Titania, 0.5% Co, 5% Co and 20%Co.

Table 2. Composition of TiO₂ with Co

% at Co	Titanium Isopropoxide (mL)	CoF₃ (g)
0	150	0
0.5	150	0.2855
5	150	2.8554
20	150	11.4216

The amount of CoF₃ added to achieve various atomic percentages of Co in TiO₂ is represented in Table 2.

Catalyst Synthesis:

The catalyst was synthesized using sono-assisted chemical precipitation of Titanium Isopropoxide. Fig. 3 presents the initial setup required for synthesis. Fig. 4 presents an ordered flowchart for synthesis of Co-Ti-O catalyst. Precise amounts of chemicals were used based on the stoichiometric calculations discussed. 150 ml of Titanium Isopropoxide (Ti[OCH(CH₃)₂]₄) in a separation funnel was suspended over 500 ml of deionized water in a beaker during sonication. The stopcock of the separation funnel was adjusted to have a drop wise flow of Titanium

Isopropoxide for 30 minutes into water. The sonication was assisted by a Misonix S-2000 system. The Apparatus was operated with a micro-tip with an amplitude of 100%, 20 kHz for 30 minutes that delivered 25 j/s. The Respective amounts of CoF_3 (0.5%, 5%, and 20%) were gradually added by hand during the entire 30 minutes of trickling and sonication process. After 30 minutes, the sonication was stopped and a colloid was achieved. The colloid was then dried in a petri dish on the hotplate for 24 hours at a temperature of 60°C . At this point of time, the dried colloid was a mixture of amorphous Co-Ti-O and organic residue. To ensure the removal of organic residue the mixture was washed with 2500 ml of deionized water and drained using micro pore filter paper connected to a vacuum system via funnel-flask. The product was dried for 12-15 hours until the powder had a loose appearance.

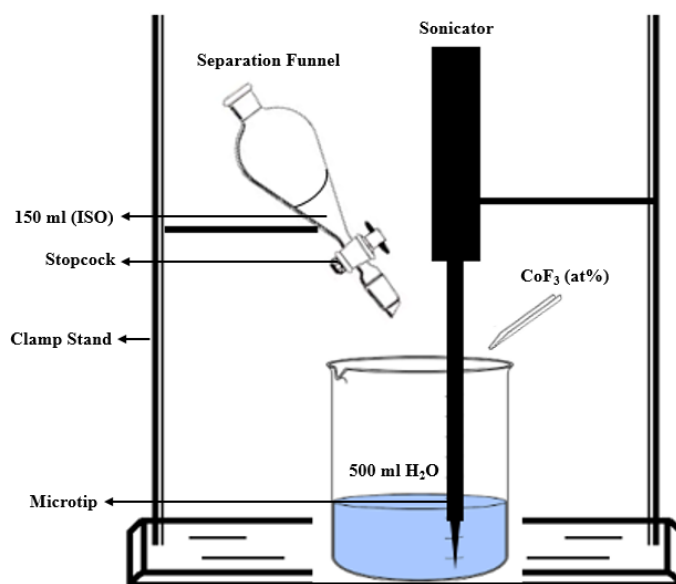


Fig. 3 Experimental Setup for Synthesis of Co-Ti-O Catalyst

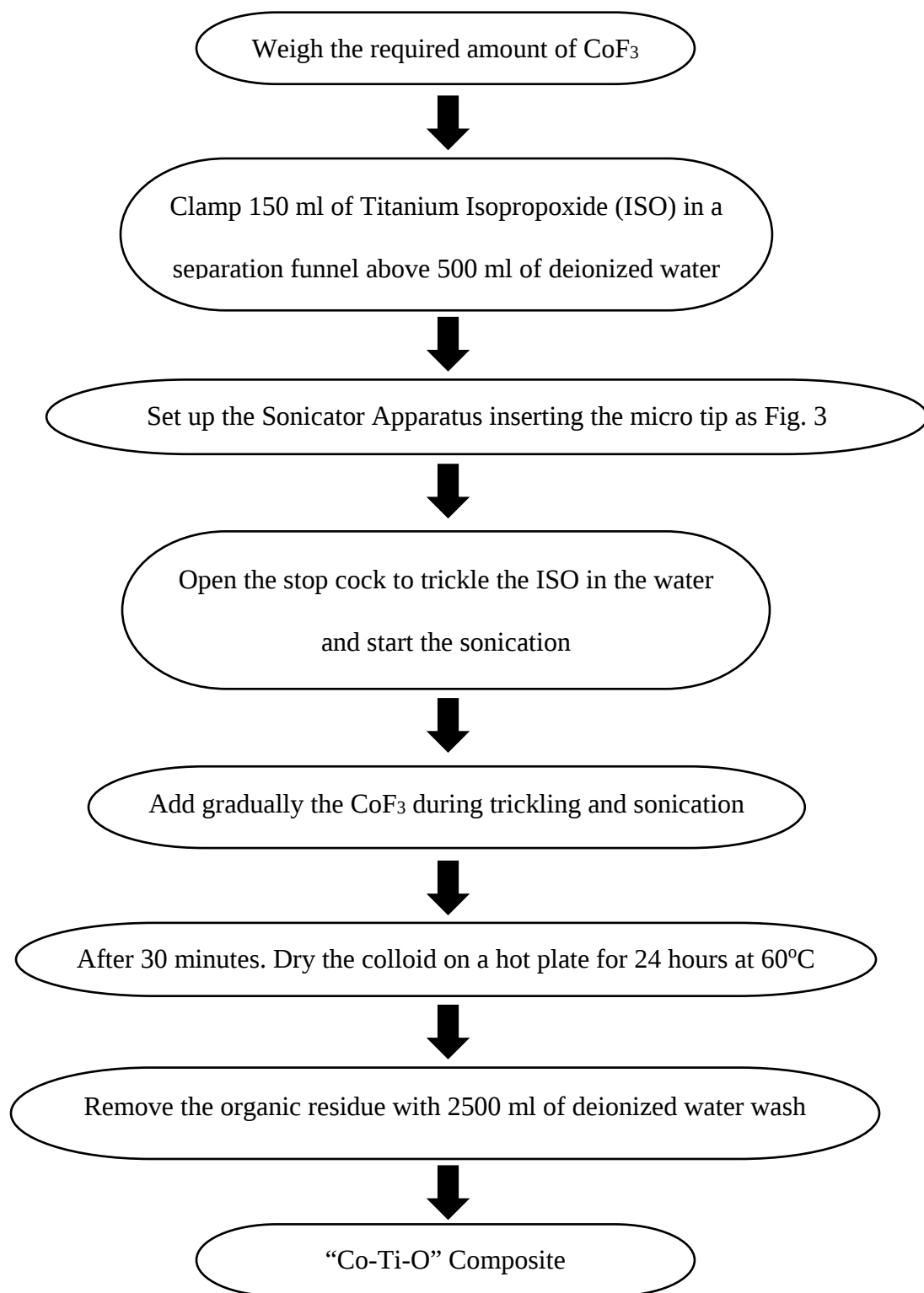


Fig. 4. Process Flow-Chart for Synthesis of Co-Ti-O Catalyst

Two similar compositions were heat treated for 300°C and 800°C in a conventional electric resistance furnace in open air atmosphere for 3 hours. All 4 compositions including the pure Titanium dioxide was prepared with the same process under the same conditions including heat treatments. Pure Titanium dioxide was produced as a reference sample.

Characterization:

X-Ray Diffraction: The X Ray Diffraction (XRD) was carried out on a SIEMENS Diffractometer D500 which was equipped with a Copper Tube. The XRD machine was operated at 40 kV and 30 A with a corresponding $K_{\alpha} = 0.15406$ nm. The powders were prepared to have a flat even surface to record accurate diffraction patterns. The measurement were conducted by scanning from 20° to 60°, 2 θ . The scanning speed used was 2° / minute and the readings were recorded every 0.02°.

Raman Spectroscopy: Raman Spectra and Spatial Raman Mapping were recorded for the catalysts on a Horiba Jobin Yvon Xplora™ confocal Raman microscope equipped with a motorized sample stage from Marzhauser Wetzlar (00-24-427-0000). Green laser of intensity 532 nano meters (nm) was used on medium intensities to record the spectra. The power was always kept below 2mW without noticeable powder heating. The shift was 1cm⁻¹ with a spot size of 1µm with a resolution of 0.5 cm⁻¹ and a 100X objective lens.

UV-vis: The Ultraviolet–visible (UV-vis) absorption tests were conducted for the analysis of bandgap of the catalysts. A modified version of Kubelka–Munk method (34) was used to calculate the band-gap of the catalysts.

Photo-Catalytic Degradation of Acid Orange 7:

The catalysts were tested for the degradation of Acid Orange 7 dye (AO7). In a typical experiment, a known quantity of Orange II was added in 60 ml of deionized water to maintain an AO7 concentration of 2×10^{-5} M. This concentration is closer to the upper range of concentrations often reported in textile effluents and waste waters. (10^{-4} to 10^{-6}). Two Control experiments were performed, where the AO7 solution was tested in identical light conditions without adding any catalyst and under no illumination after adding the photocatalyst. A pre-measured 40 mg of catalyst was added in the solution and the solution was sonicated for 5 minutes. The sonication parameters were maintained exactly as same for the synthesis. The suspension was stirred continuously at the room temperature with a magnetic stirrer at 160 rpm. The glass container was sealed to avoid any evaporation of organics.

Illumination source was a CONTINUUM SURELIGHT – III 10 Hz LASER that produces an output of 1064 nm. A second harmonic generator was installed to produce an output of 532 nm. Power measurements were

performed for both the wavelengths. 3000 mW and 400 mW were the average power values recorded for 1064 nm and 532 nm respectively. The spot size of the laser had a diameter of 0.8cm with area about 2 cm². 1500 mW/cm² and 200 mW/cm² were the power power densities for 1064 and 532 nm lasers respectively.

Time for the Photocatalysis was varied from 0-180 minutes and aliquots were withdrawn at designed intervals. The aliquots were centrifuged in a VWR Centrifuge for 15 minutes at 4000rpm to remove precipitates. Degradation analysis was performed by measuring the absorption spectrum of the sample by means of UV-Vis. The spectrum was recorded from 200 nm to 800 nm range. The absorption was measured essentially at 485 nm, 310 nm and 228 nm. 485 nm is the band in the visible spectrum that arises due to the intermolecular hydrogen bonding tautomeric corresponding azo-linkage. 310 nm and 228 nm are naphthalene and benzene absorption peaks. The adsorption was measured every 30 minutes. The equilibrium concentration at each interval was calculated by:

$$\%C_e = \frac{C}{C_o}$$

Where % C_e is the equilibrium concentration of azo bond, naphthalene and benzene, C_o is the initial concentration and C is the concentration at that time interval.

Catalytic Water Splitting:

The water splitting experiments were performed in 125 ml flask that were sealed air tight. 60 ml of de-ionized water was used for the experiments. 40 mg of the catalyst was added to the water. The suspension was thereafter illuminated for 3 hours under 1064 nm pulse laser and stirred with the help of a magnetic stirrer. The generated hydrogen and oxygen were then measured using sampling syringe into a Gas Chromatograph (GC) equipped with a thermal conduction detector. The spot size of the laser had a diameter of 0.8cm with area about 2 cm². 1500 mW/cm² was the power corresponding power density.

Control experiments were carried out in the similar fashion for hydrogen generation as for the dye degradation. De ionized water without catalyst was illuminated under 1064 nm. The sample was added and the solution was stirred in dark under no illumination for same time under exact same conditions.

Based on the peaks of the GC signals the area of the peaks were calculated that corresponded to a certain injection volume of hydrogen and generation injected. The injected volume was 0.3 ml. Based on the ratios of generation of Hydrogen and Oxygen, the total volume generated by the catalysis was calculated for the entire volume of the flask. Injection was performed multiple times to ensure constant results. All results were repeated several times to ensure the consistency of the process.

Chapter III

Results and Discussion

Results and Discussion

X-Ray Diffraction:

The XRD characterization was performed for all the synthesized and heat treated samples with different composition. The heat treatment conditions were selected to produce specific frameworks. At 300°C we usually have pure Anatase, while at 800°C the predominant phase is rutile. This is not necessarily the case for all investigated samples. Nevertheless, the intention is to have comparable conditions for all samples. Fig. 5 presents the XRD patterns of the catalysts (Pure, 0.5 at%, 5 at% and 20 at% doped). Fig. 5(a) shows the results of pure TiO₂ at different heat treatments conditions (As synthesized, 300°C and 800°C). Those samples are considered as references and are used to compare with the other doped catalysts. In this figure one can see that the pure Titania in the as synthesized condition is significantly amorphous with only partial transformation of Anatase. In this case the Scherer Method (35, 36) to determine the grain size is rather inaccurate. At 300°C the transformation to Anatase is clear and 4 broad peaks were observed as the following reflections: (110), (112), (200) and (105). The pure Titania sample heat treated at 800°C is semi crystalline with high intensity peaks for rutile and Anatase combined. Rutile has 7 reflections identified as: (110), (101), (200), (111), (210), (211) and (220).

Fig. 5(b) shows the XRD patterns for 0.5 at% cobalt doped catalyst. As observed by the results, the growth of the anatase phase is promoted right away

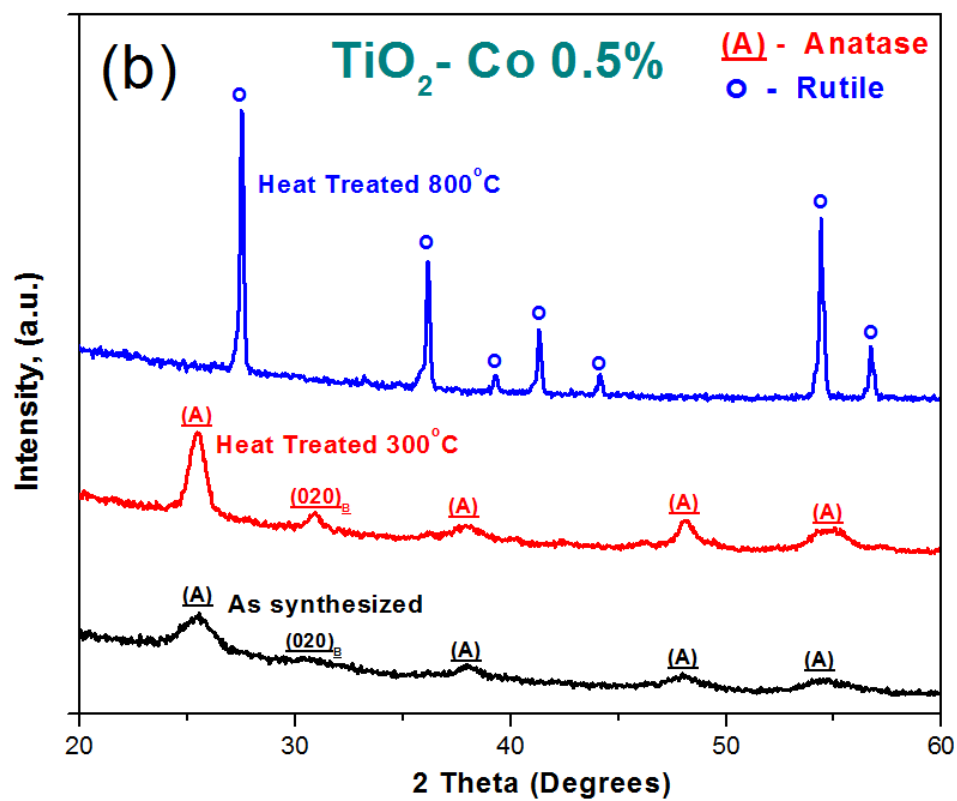
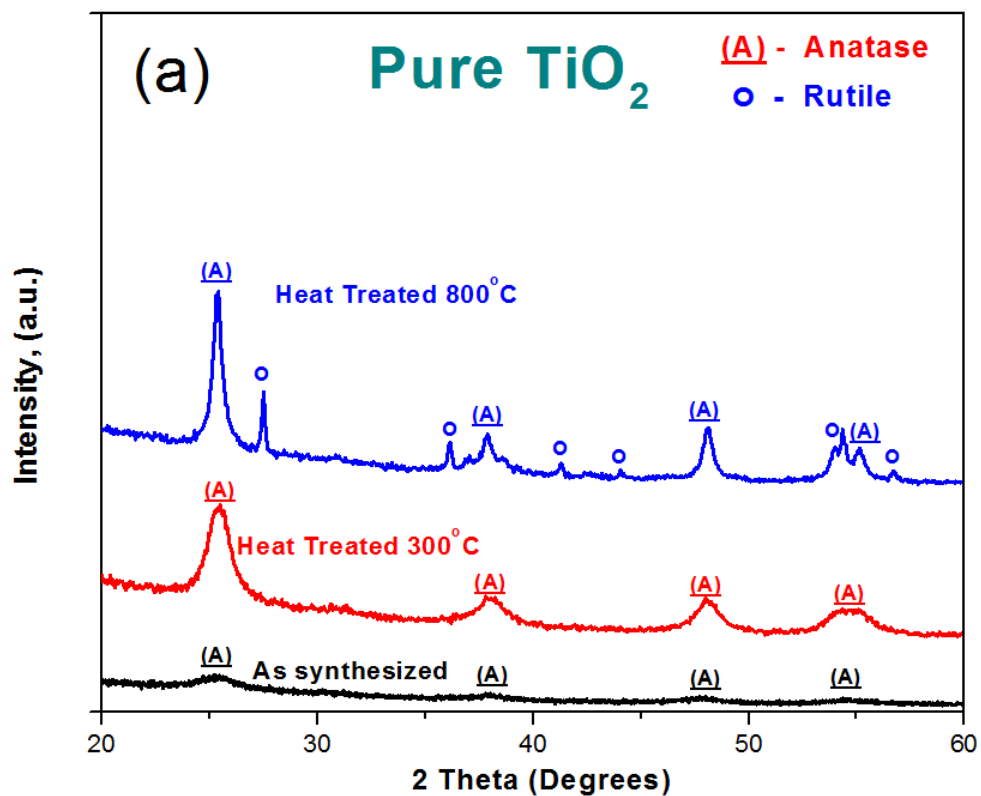
by adding Co into the synthesis process. The anatase reflections are intensified and commensurate with the reduction of amorphous appearance. A significant difference in the 0.5 at% Co-TiO₂ is the presence of Brookite phase identified with the reflection “(020)_B”. This reflection is present in the synthesized sample and the one heat treated at 300°C. This is the only composition in which Brookite phase is present and suggests a bi-crystal framework among Anatase and Brookite. Bi-crystal framework in temperatures between 200°C and 300°C has been reported in literature (19). Rutile at 0.5%at Co has significant changes in the reflections as the concentration of Co is added. This sample does not show any signs of Anatase existing in the sample as it has typical 7 reflections of rutile. Since the concentration of Co is, minimal the reflections of Co in the patterns is not dominant.

Fig.5 (c) presents the results of 5 at% cobalt doped Titania. It can be observed from the XRD pattern that the Anatase is strongly promoted by the additions of the dopant at higher concentrations. At 300°C it can be noticed that, the pattern represents a new peak which corresponds to reflection at (211). This sample at 800°C started showing significant other peaks than Rutile phase due to the high concentration of Co in the synthesis.

The spectra has same peaks of Rutile phase with developed CoTiO_3 that are later better identified in 20 at% Co doped sample. An observation at this point is that dopant and temperature promote change in color from light brown in the as synthesized sample to the light green after heat treatment of 5% at Co- TiO_2 at 800°C

Fig. 5 (d) presents the result of the 20% cobalt doped TiO_2 that shows same Anatase dominance at 300°C with the (211) reflection. The 20% doped sample has a grainsize of 10^3 nm as determined by the Scherer Method (35, 36). The 800°C heat treated sample is highly crystalline with bi-crystal framework composing Rutile and the fully developed phase of inorganic CoTiO_3 . The reflections were well defined and correspond to XRD JCPDS 88-1175 for Titania (Rutile) and the JCPDS 77-1373 for CoTiO_3 charts (37, 38). The sample appears dark green in color promising light absorption in the visible spectra. The grain size of this catalyst is around $1.4\text{ }\mu\text{m}$ that is approximately 3 times larger than the crystals as synthesized with the same composition. The size of these crystals is definitely above the quantum confinement of the rutile that has been reported to be less than 2.5 nm in the literature (39-41).

This is a significant claim that the effectiveness of this material being active of catalysis is not related to a nanostructured characteristics. Yet it is of outstanding interest to investigate the material in nanostructured conditions, this topic is proposed in future work.



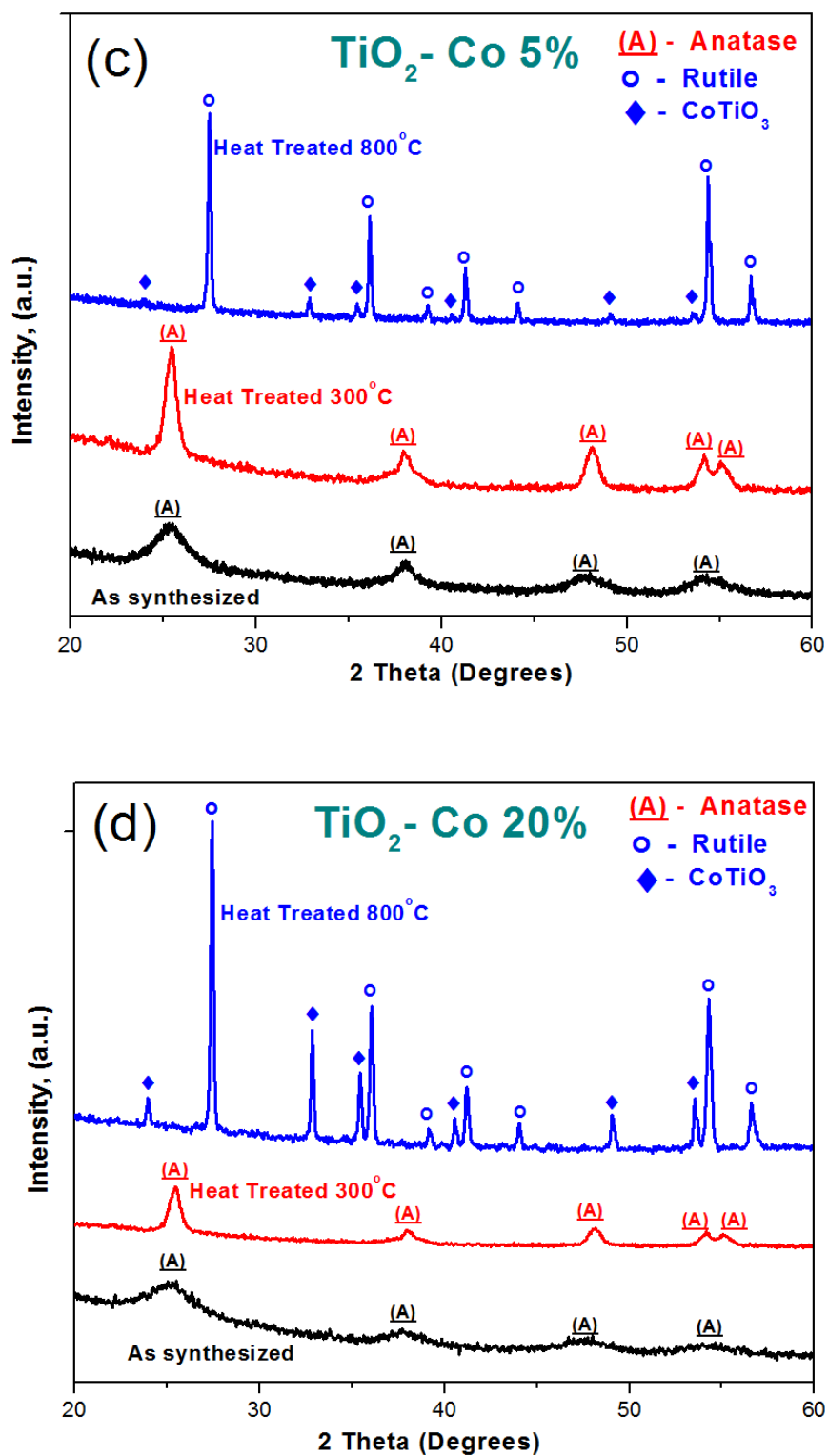


Fig. 5. XRD characterization of as synthesized, 300°C and 800°C heat samples at (a) pure (b) 0.5 at% (c) 5 at% and (d) 20 at% doped Co

Raman Spectroscopy:

The Raman Spectroscopy was performed for all the synthesized and heat treated samples with different composition. Fig. 6 presents the Raman spectra of all the catalysts (Pure, 5% and 20% doped). Fig. 6(a) shows the results of pure TiO₂ at different heat treatments conditions (As synthesized, 300°C and 800°C) were recorded to be used as references as for comparison purposes with the other doped catalysts. The upper labels “A” and “R” stand for anatase and rutile respectively. This nomenclature is to simplify identification. As synthesized pure TiO₂ has a well resolved E_(1g) band. This band is observed at 151 cm⁻¹. This gives an identification of the Anatase presence in the sample. The sample at 300°C showed growth in both the B_{1g} (1) and B_{1g} (2) + A_{1g} shoulder representing growth in Anatase. The E_g mode is represented by three bands (151, 193 and 630 cm⁻¹) and the B_{1g}, A_{1g} and B_{1g} (2) are represented by 400, 508 and 512 cm⁻¹. By comparing the spectra presented in Fig. 6(a) to the literature (42), one can claim that the synthesized material is amorphous with limited atomic order as predicted by the XRD. The sample treated at 800°C represents similar bands of Anatase with some additional partially developed Rutile bands. These bands are found at 244, 364 cm⁻¹ and ^RE_g at 455 cm⁻¹. This spectra is in agreement with the XRD results representing a mix phase of Anatase and Rutile at 800°C.

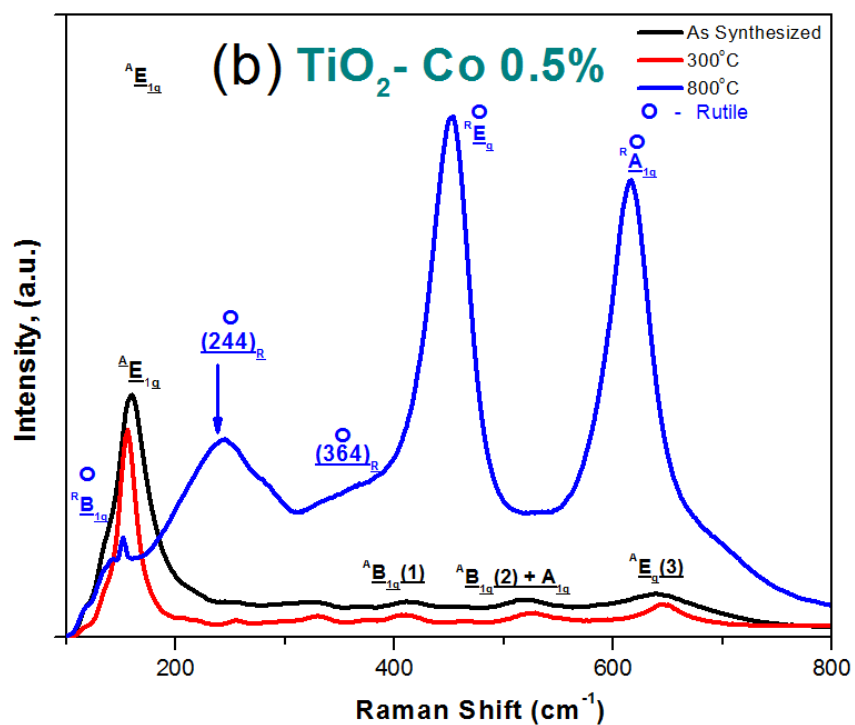
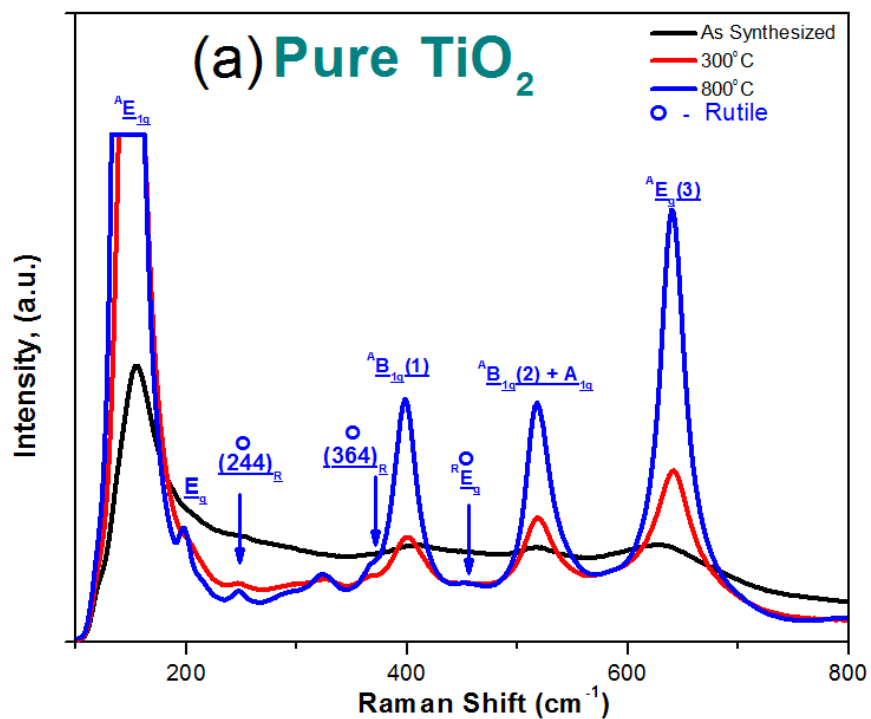
Fig. 6(b) presents the Raman spectra of Co doped sample using 0.5 at% Co. The as-synthesized and the 300°C sample show similar bands as

pure TiO₂. The peaks however have higher intensities implying that Co as dopant acts as an Anatase promoter. The 800°C heat treated sample showed bands of mainly Rutile at ^RB_{1g} at 142 cm⁻¹, 244, 364 cm⁻¹, ^RE_g and ^RA_g at 455 and 608 cm⁻¹ respectively. This completes the bands for pure rutile.

Fig. 6(c) presents the Raman spectra of Co doped sample using 5 at% Co. The as-synthesized and the 300°C sample show similar bands as pure TiO₂ and 0.5 at.%. The sample at 800°C showed bands of mainly Rutile. This sample also has two partial bands at 268 and 693 cm⁻¹ that represents the under developed CoTiO₃ in the sample.

Fig. 6(d) presents the Raman spectra of Co doped sample at 20 at% Co. The as synthesized sample and 300°C heat treated samples have similar bands as the 5 at% Co doped samples. The 800°C heat treated sample is distinct from the other samples. This heat treated sample was mainly composed by a bi-crystal framework between the base material TiO₂ and CoTiO₃. The main bands of CoTiO₃, commonly known as ilmentite, are reported in the literature (33, 43). The main Raman bands for this phase were identified at 208, 234, 268, 334, 384, 608 and 693 cm⁻¹. Typically the band at 693 cm⁻¹ is the band with the highest intensity of this phase, which is in agreement with the literature. The other bands in this spectra are due to the presence of rutile (e.g. ^RB_{1g} at 142 cm⁻¹, 244, 364 cm⁻¹, ^RE_g and ^RA_g at 455cm⁻¹). The bands that correlate to the presence of rutile were also in correlation with the those reported in literature (27, 28) for rutile. The

identification of both phases with Raman Spectroscopy are in agreement with the XRD results.



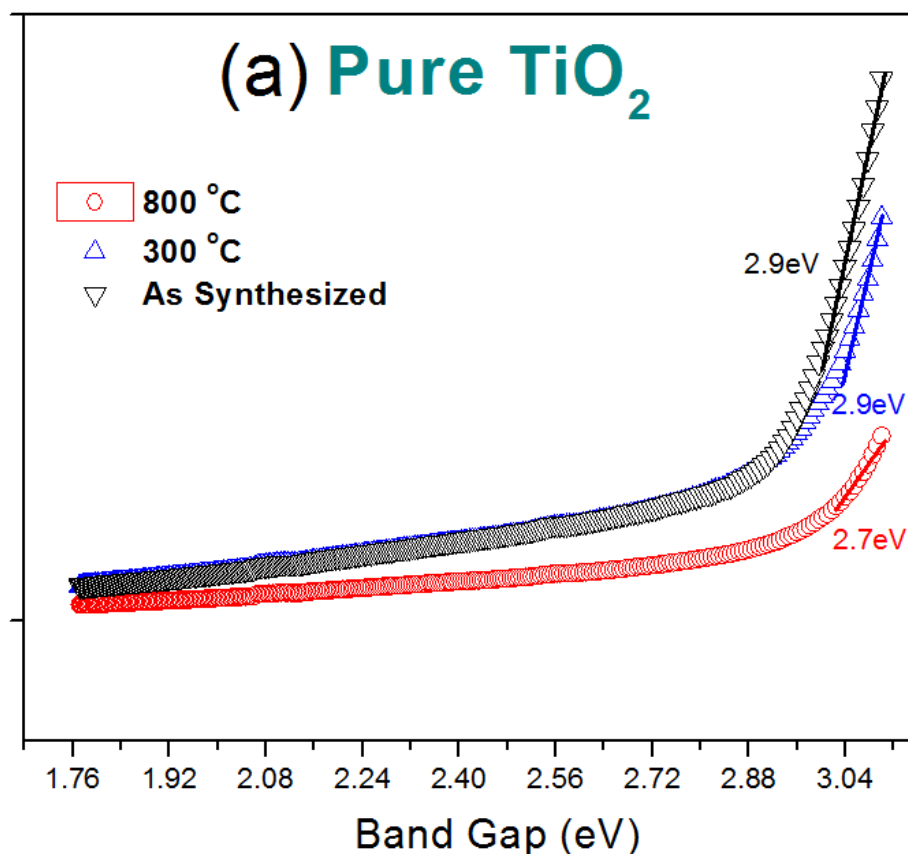
Band gap Analysis:

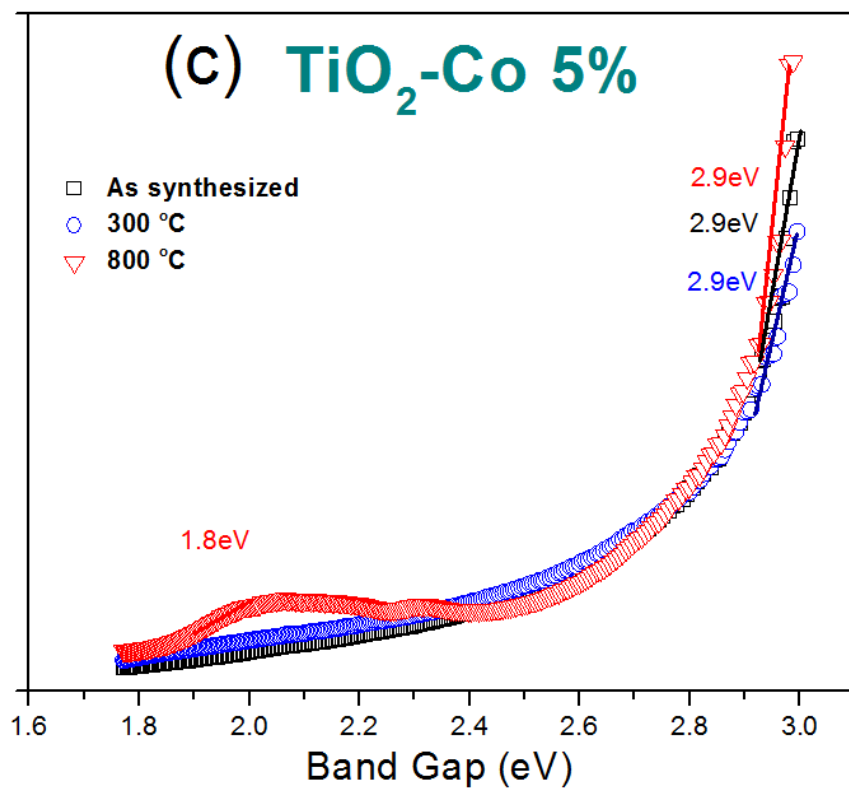
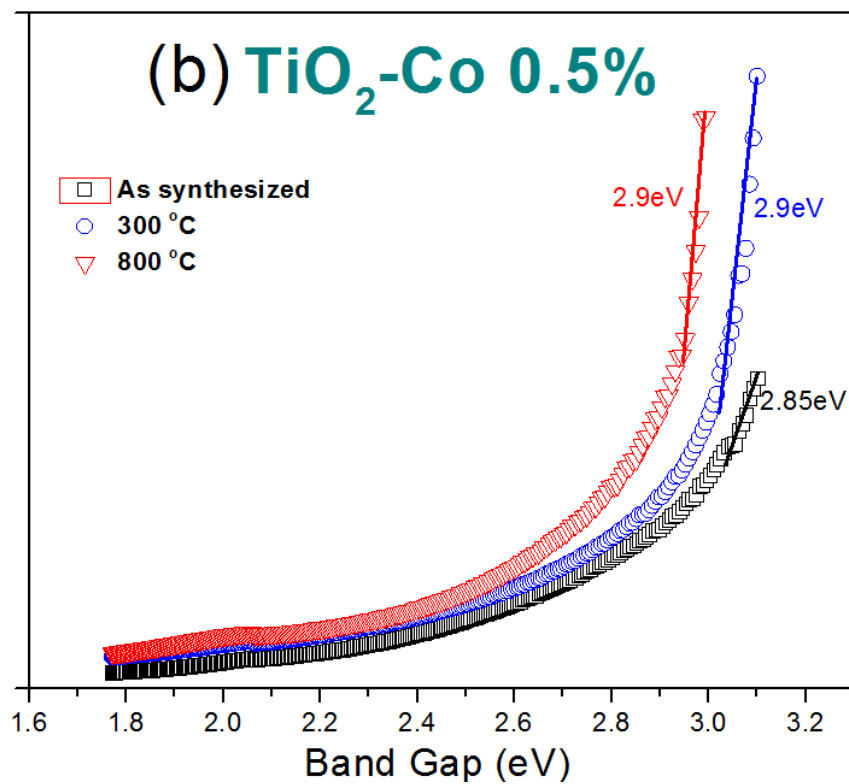
The Band gap analysis was performed for all the synthesized and heat treated samples with different composition. Fig. 7 presents the band gaps of all the catalysts (Pure, 0.5 at %, 5 at % and 20 at % doped). Fig. 7(a) shows the results band gap analysis of pure TiO₂ at different heat treatments conditions. TiO₂ band gaps were recorded as references to compare with the other doped catalysts. All the non-doped samples have only one band gap within the range of 2.7 to 2.9 eV that is correlated with the similar finding observed in (20, 27, 28). These band gap values are in the rutile range reported as 3.0eV in (44). 0.5 % Co-doped samples also exhibited the band gap in the similar range that are displayed in Fig. 7. (b).

Band gaps of Co doped samples at 5% are shown in Fig. 7(c). A notable difference is in the sample treated at 800°C. This sample displays a multiple band gap at 2.9 and 1.8 eV. The latter band gap can be activated by the photonic energy of visible light and the color of the sample is also in agreement with the band gap measurements.

Fig. 7(d) displays the bandgap values of 20% Co doped catalysts. The three 20 at % samples are nano-crystalline with anatase frameworks. They have high density of dangling bonds or imperfect stoichiometries. Similar observations have been reported in extreme cases with band gaps of up to 2.8 eV (20, 28). One can observe three distinct band gaps in the 800°C heat treated, Co-20% doped sample that has been characterized as TiO₂-CoTiO₃ by Raman and XRD. The first band gap is 2.8 eV that is

attributed to the TiO_2 -Rutile phase which is in agreement with the literature. This band gap value is also in agreement with the XRD and Raman characterizations that shows the presence of rutile in the heat treated catalyst. The second value of the band gap is 2.27 eV which is presumably related to CoTiO_3 and comparable to the value reported in literature (45). The last band gap is located at 1.88 eV similar to samples doped with 5 at% Co. It should be noted that this phase (1.88 eV) has not been identified in XRD or Raman characterization and therefore, if present, it should be in the range of traces. This band gap value however can arguably be associated to CoO (27).





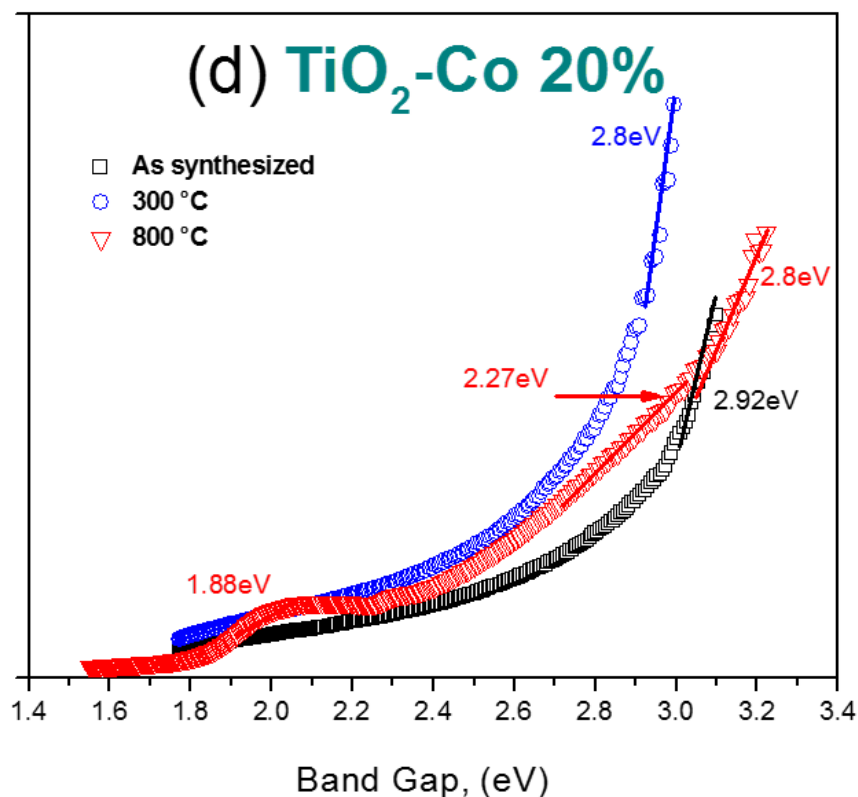


Fig. 7. Band gap analysis of as synthesized, 300°C and 800°C heat samples at (a) pure (b) 0.5 at% (c) 5 at% and (d) 20 at% doped Co

The physical appearance of all the catalyst are displayed in Table 3. One can notice the increasing brown color in the as synthesized materials due to the increasing presence of Cobalt. It is noticeable that the 5 at% and 20at% doped samples turned light and dark green respectively after 3 hours of heat treatment at 800°C. This is promising as the catalyst now displays improved visible light absorption. The color of the samples are in direct correlation with the band gap (1.88 eV and 2.27 eV) values allowing a rather empirical identification of the respective samples.

	As Synthesized	300°C	800°C
Pure			
0.5%Co			
5%Co			
20 %Co			

Table 3. Physical Appearance of all Titania-Cobalt based catalysts after synthesis and heat treatments (300 and 800°C).

The sample doped with 20% Co has ideal band gaps of 1.88 eV and 2.27eV that can be activated by most of the visible light spectra (e.g. 532nm). This catalyst is an example the potential of high concentration of doping on Ti-O systems which is why we chose to perform a series of photocatalytic experiments with this sample and using as reference the well-known TiO₂.

Photocatalytic Degradation of Orange 7 dye:

The UV-Vis absorbance spectra of Acid Orange 7 dye is represented in Fig.8. Orange 7 spectra consists of 4 major absorbance peaks. The azo dye orange 7 is typically observed at 430 nm. This form is commonly termed as azo form. The second peak corresponds to the hydrated molecule of the Orange 7 which is dominant at 485 nm. This form of Orange 7 is often termed at Hydrazone form. The 485 nm and 430 nm are the bands in the visible spectrum that arises due to the intermolecular hydrogen bonding tautomeric corresponding to azo-linkage and the orange color of the dye. Essentially 485 nm is the peak used to measure the equilibrium concentration C_e . The other two peaks are 310 nm and 230 nm which represent naphthalene ring and benzene absorption peaks. The benzoic and naphthalene rings are identified by their respective $\pi-\pi^*$ bonds.

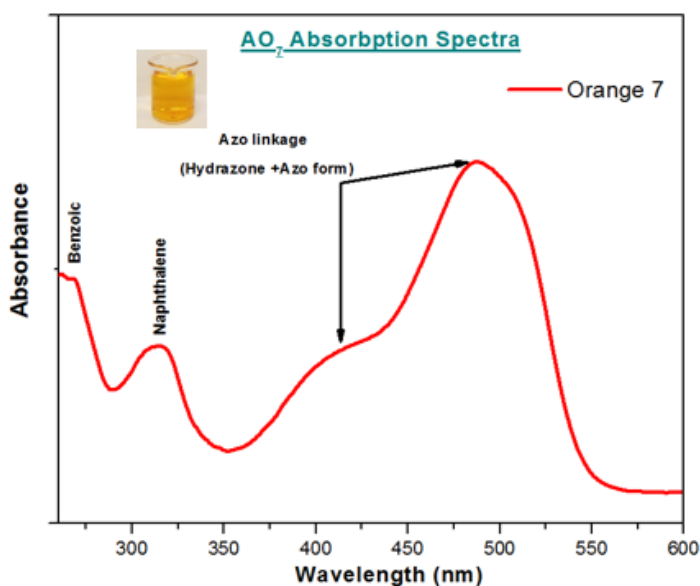


Fig. 8. UV-Vis absorbance spectra of Acid Orange 7 dye

Fig. 9 shows the degradation sequence of Orange 7 molecule. The figure shows the typical degradation of Orange 7 as the azo bond breaks, which decolorizes the dye and eventually separates the molecule in benzene and naphthalene rings respectively. This is in agreement with the initiation of degradation sequence as reported in literature (46).

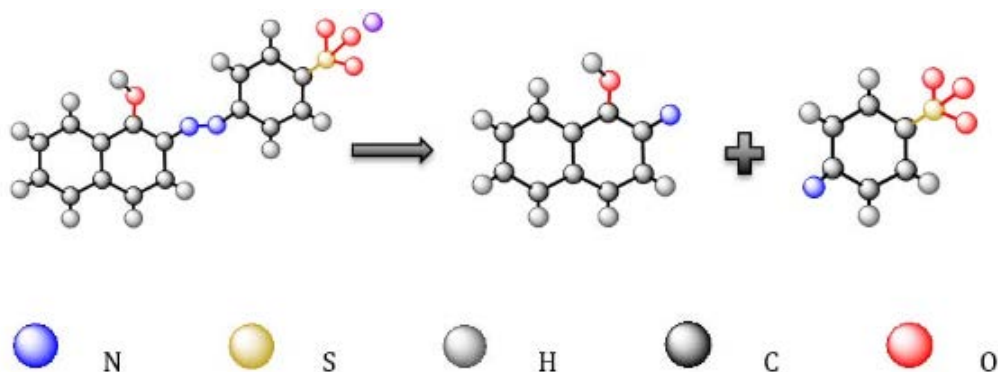


Fig. 9. Sketch of the chemical degradation of Orange 7

The degradation activity of Orange 7 $\text{TiO}_2\text{-CoTiO}_3$ under 532 nm pulse laser can be observed in Fig.10. This figure presents the absorbance spectra of the solution before and after the reaction along with the spectra of intermediate aliquots which were taken with time intervals of 30 minutes. The drop in the intensity of the peaks was clear as the solution was illuminated under 532 pulse laser. The 485 nm peak completely dissipates which can also be observed as the solution decolorized. The peaks of benzene and naphthalene rings are beyond the visible range, also tend to fall corresponding to the opening of benzene and naphthalene rings as reported in literature (46).

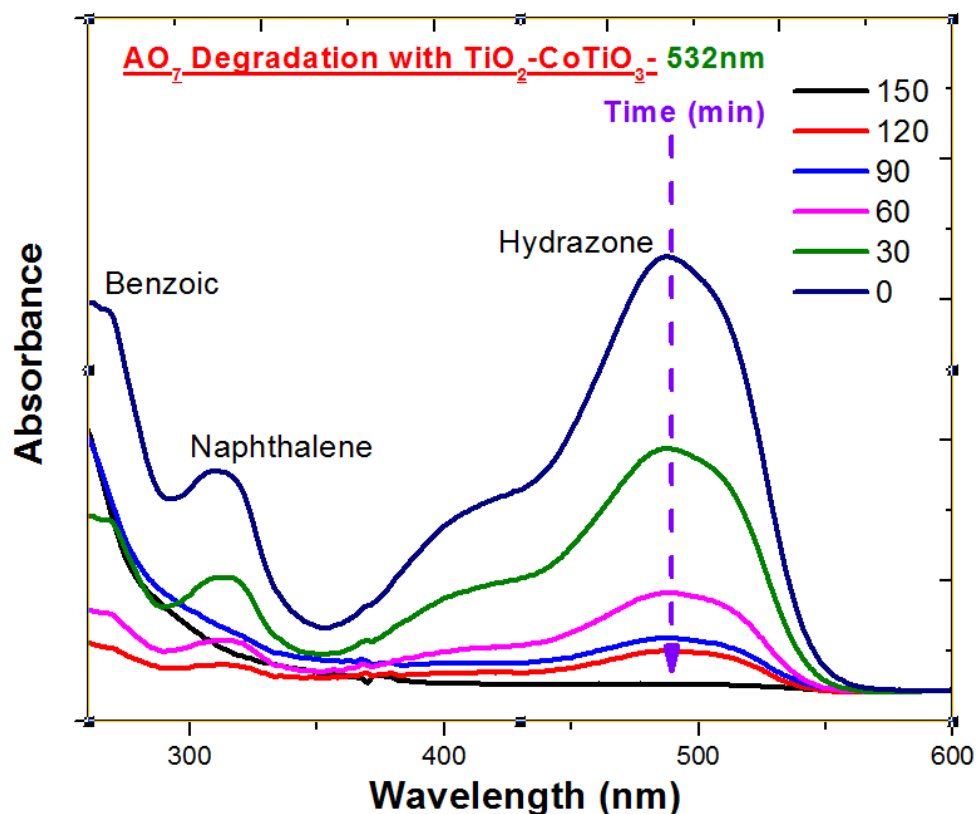


Fig. 10. Photocatalytic Degradation of Orange 7 as observed by UV-Vis analysis

A set of control experiments were performed that are displayed in Fig. 11. These experiments were designed to confirm that the degradation is due to the photonic energy of illumination and not due to any other source like chemical catalysis. From these set of results one can notice when, Orange 7 dye was placed in dark with the CoTiO_3 suspended in the dye solution, no degradation was observed. By this experiment that one can see that the material is not adsorbing the dye on the surface as can be seen in Fig 11.

The Second control experiment in Fig 11 was illumination of Acid orange 7 dye under 532 nm pulse laser. The UV-Vis absorbance has the same intensity after 3 hours of illumination. This confirmed that the photonic energy itself was not sufficient to cause any decomposition or degradation to the dye.

The pure TiO_2 was always used as a reference catalyst for all the experiments to compare the results. The absorbance spectra of dye after 2 hours and 3 hours of illumination can be observed in the Fig 11. The dominant peaks of Hydrazone, benzene and naphthalene show that pure TiO_2 is extremely less efficient towards degrading Orange 7.

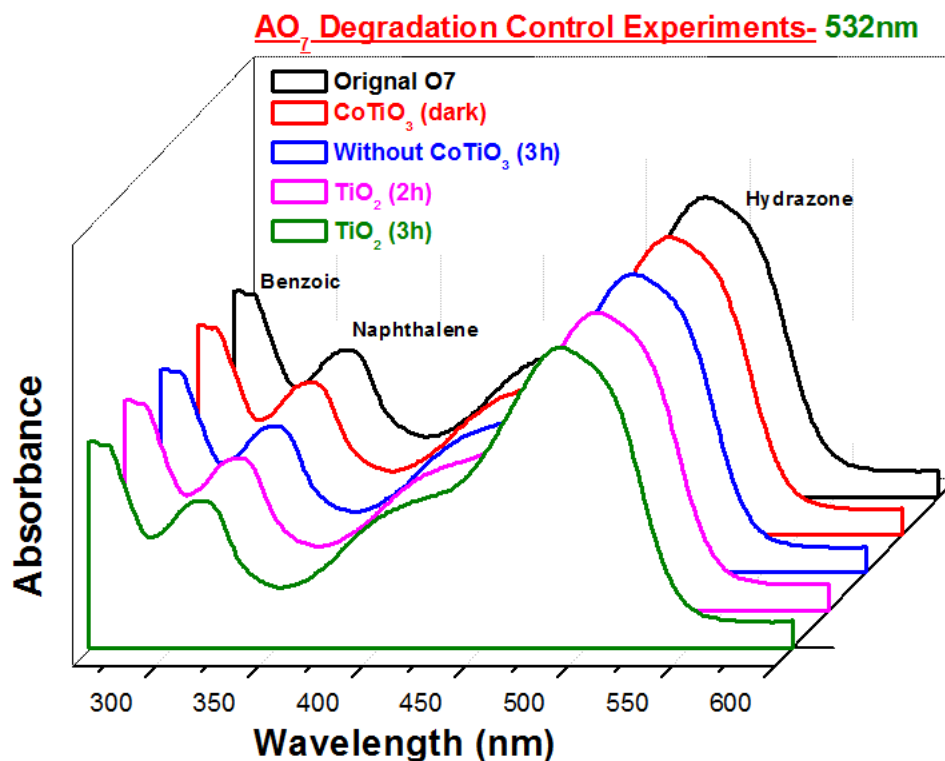


Fig. 11. Control Experiments and the UV-Vis absorbance spectra.

Quantitative analysis were performed based on the absorbance spectra of UV-Vis to compare $\text{TiO}_2\text{-CoTiO}_3$ to the reference TiO_2 sample. These results are displayed in Fig. 12. The degradation activity displayed was plotted using Equilibrium Concentration $\%C_e$. The plot compares degradation activity of $\text{TiO}_2\text{-CoTiO}_3$ and the reference TiO_2 sample under 532 nm and 1064 nm illumination. For, 532 nm, it can be seen that immediate degradation is observed with $\text{TiO}_2\text{-CoTiO}_3$ which is observed as 42% in first 30 minutes. This is equivalent to 58% C_e . The degradation rate followed a similar trend at further intervals until 150 minutes. At this point the amount degraded was 93% leaving behind only 7% of the Dye ($C_e = 7\%$). Figure 13 also is in support of the analytical data as it shows the colors of centrifuged samples taken out at regular intervals. It can be observed that the dye is completely decolorized after 150 mins, which also means that the azo bond ($-\text{N}=\text{N}-$) has been broken.

An effective degradation of 93% is observed after which the process achieves equilibrium and no more degradation is observed. Here, it is important to note that the degradation occurs purely using purely visible source of light in this case a 532 nm laser.

On the other hand 1064 pulse laser degrades up to 98% of the dye in 90 mins. A similar degradation rate is observed for the first 60 minutes. The degradation of 1064 nm laser is faster than the 532 nm due to the high order of power density of the 1064 nm laser (discussed later).

If the degradation rates of $\text{TiO}_2\text{-CoTiO}_3$ are compared to that of Pure TiO_2 , one can compare that we observe only 1% removal of AO7 for TiO_2 , which can also be considered as a systematic error rather than actual degradation, in the same time frame as of $\text{TiO}_2\text{-CoTiO}_3$. In other words, TiO_2 has rather no effects of the Orange 7 dye. This can translate to a degradation improvement for the $\text{TiO}_2\text{-CoTiO}_3$ photocatalyst by two orders of magnitude when compared to pure TiO_2 . More importantly, the degraded concentration is way below the range of concentrations reported in the textile effluents and wastewaters, which is considered safe for environmental disposal (46).

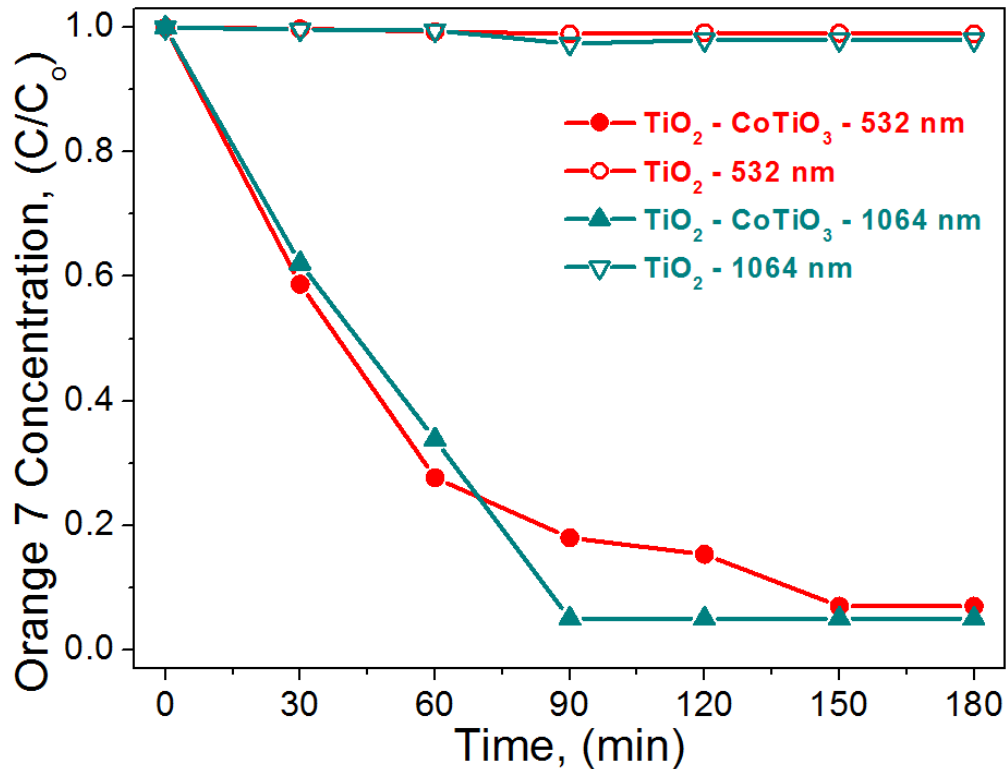


Fig. 12. Degradation rate of Acid Orange 7 with TiO_2 and $\text{TiO}_2\text{-CoTiO}_3$

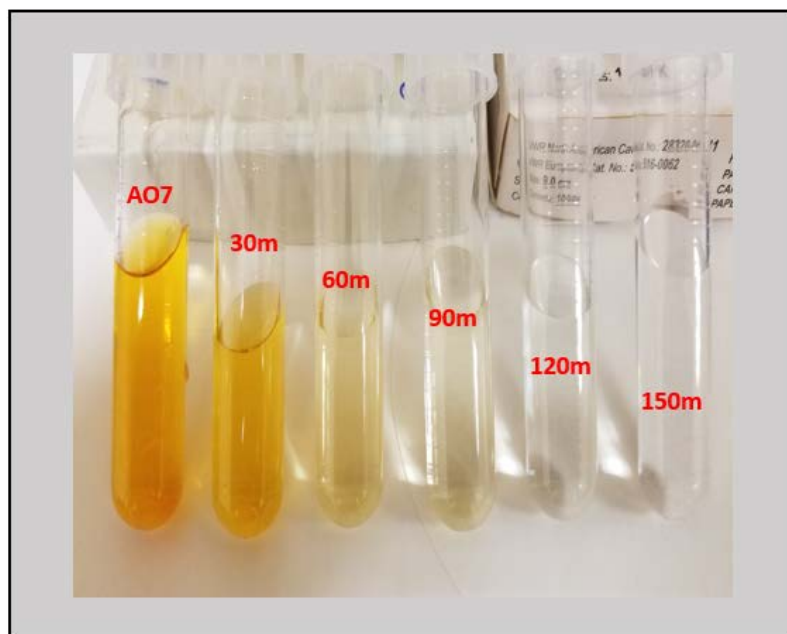


Fig. 13. Physical Appearance of Dye samples at regular intervals.

A set of quantitative analysis was also performed for the degradation rates of benzene and naphthalene due to the reduction observed in the intensity of the peaks in the UV-Vis Spectra. Fig. 14 presents the degradation rate of benzene and naphthalene in the dye at regular intervals during photocatalysis with the 532 nm laser. The analysis of benzene and naphthalene show a respective 23% and 12% C_e (remaining) in the presence of laser. This indicates that the photocatalyst $\text{TiO}_2\text{-CoTiO}_3$ is capable to opening the benzene and naphthalene rings degrading them to comparably less harmful species under the illumination of visible (532 nm) light source. Pure TiO_2 on the other hand is incapable to degrade organics such as benzene and naphthalene as seen by the results.

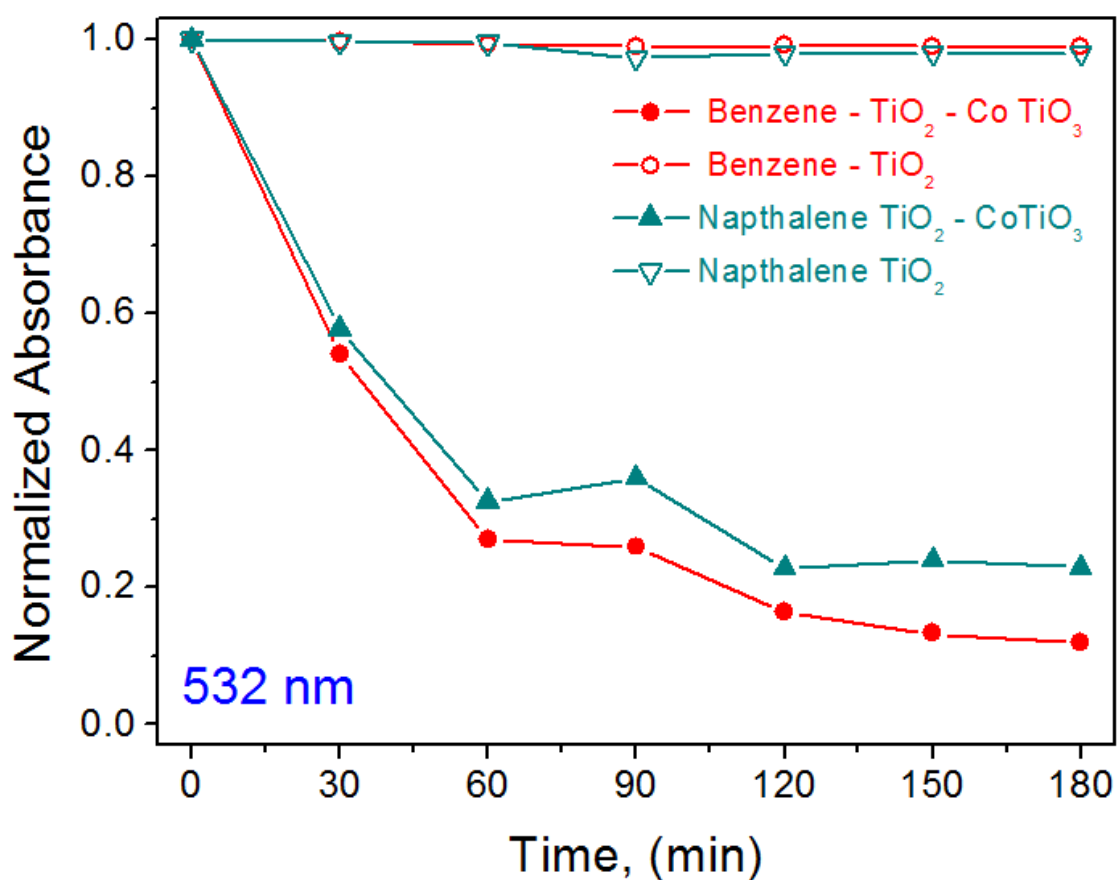


Fig. 14. Degradation rate of benzene and naphthalene

In order to clarify the difference between 1064 nm and 532 nm effects, we plotted the results in a normalized manner. This plot is represented in Fig. 15. This plot investigates the photocatalytic reductions of O7 by 532 and 1064 nm lasers in the presence of TiO_2 - CoTiO_3 . The data is a good fit to the pseudo first order model represented by $\ln (C_o/C_e) \times I^{-1} = k T$, where k is the apparent rate constant (k_{VIS} for 532 nm and k_{IR} for 1064 nm) and I is the power density of the lasers. It is important to consider the power density (W/cm^2) of the light source when comparing kinetic efficiency as it plays a major role in the photocatalysis. As mentioned before, the spot size of the

laser had a diameter of 0.8cm with area about 2 cm². Therefore the power densities are 1500 mW/cm² and 200 mW/cm² for the respective 1064 nm and 532nm. It can be seen that even though the degradation was achieved faster by 1064 nm, the kinetic efficiency of 532 nm laser is higher as it has greater slope in the kinetic curve. This essentially means that the 532 laser has higher degradation capacity per Watt of photonic energy received. Nevertheless, 1064 nm is faster in our case due to its high power density.

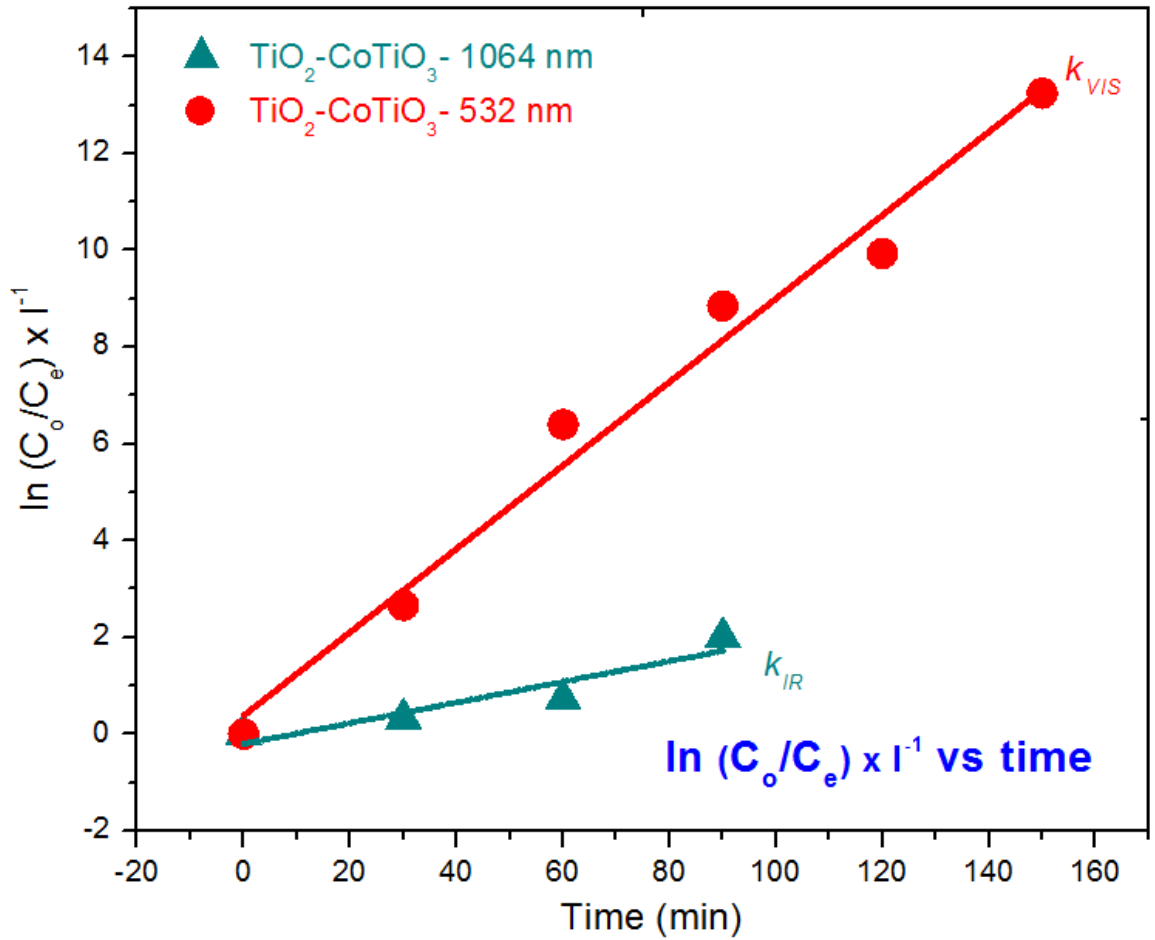


Fig. 15. Normalized Kinetic Curve Plot for 1064 and 532 nm.

The results represented in Fig 12 – 15 clearly show that the photocatalyst $\text{TiO}_2\text{-CoTiO}_3$ is effective to degrade organic dyes such as Acid Orange 7. To a great extent it is even capable of degrading organics such as benzene and naphthalene. It is 92 times more effective than pure TiO_2 in visible light spectrum.

The mechanism of 532 nm laser being effective is clear. 532 nm relates to 2.33 eV of photonic energy which is capable enough to activate the bandgap of CoTiO_3 (2.27 eV) and also of the presumed CoO (1.88 eV). This energy promotes electrons from valence band to conduction band creating an electron-hole pair that attacks the Orange 7 and degrades it down. On the other hand, one needs to understand that $\text{TiO}_2\text{-CoTiO}_3$ photocatalyst requires at least a power source of 660 nm or higher to activate the photocatalyst. The 660 nm relates to 1.88 eV. This contradicts the fact that with 1064 nm illumination, the sample can degrade the Orange 7. Even using a relatively high power density the 1064 nm should not be able to activate the catalyst.

Due to these interesting results, a set of further tests were performed as 1064 nm energy source does not seem to have a firm reason for activating the photocatalyst. A set of new experiments were performed with the same dye concentration and catalyst mass, but under various illumination sources to clearly unfold the acting mechanism. These new illumination sources included continuous lasers, pulse lasers along with sunlight simulator.

The light sources that were chosen are as follows:

1. 785 nm – Continuous Laser
2. 1064 nm – Pulse Laser
3. 532 nm – Continuous Laser
4. 532 nm – Pulse Laser
5. Fluorescence Lamp
6. Solar Simulator (Sunlight)

For the above mentioned illumination sources were used to carry photocatalysis and better understand the physics behind this paradigm. Thus, degradation was carried using standard conditions for all laser excitations to have an opportunity to compare them directly. Again the degraded concentration (C_d) was measured using UV-Vis. Here we propose the following model to quantify the actual degradation efficiency for each condition.

$$K = \frac{C_d}{T * P_d}$$

Where, K is the degradation efficiency, P_d is the power density of each source, C_d is the degraded concentration and T is time. Fig. 16 represents the K values for all the illumination sources. It can be noticed that the 785 nm continuous laser could not degrade the dye which is due to the insufficient photonic energy of the laser that is incapable to activate the

band gap. The 785 nm laser has an energy of 1.58 eV that is 0.41 eV above that of 1064 nm laser. Here is where this material becomes unique as it is excited by a pulse laser with lower energy. This implies that the pulse laser has a unique interaction with our catalyst.

Similar can be observed with 532 nm pulse lasers. Now comparing to 532 nm continuous laser we can see how the degradation efficiency is comparable to that in 1064 nm. The energy in 532 nm is double (2.33 eV) as compared to 1064 nm (1.16 eV). However, the 532 nm pulse has 3 times higher efficiency than the other two described cases. It means pulse laser somehow is enhancing the photocatalytic activity of $\text{TiO}_2\text{-CoTiO}_3$, but it has no effect over pure TiO_2 .

The results of the photocatalyst in sunlight show that sunlight is the most efficient source of illumination which is expected as it offers continuous illumination from around 220 nm to >2500 nm. Yet the important part is that below 400 nm, it excited TiO_2 . Furthermore, TiO_2 (pure) and $\text{TiO}_2\text{-CoTiO}_3$ have comparable efficiencies under sunlight. This implies that CoTiO_3 is not active in sunlight and can be activated only by pulse lasers.

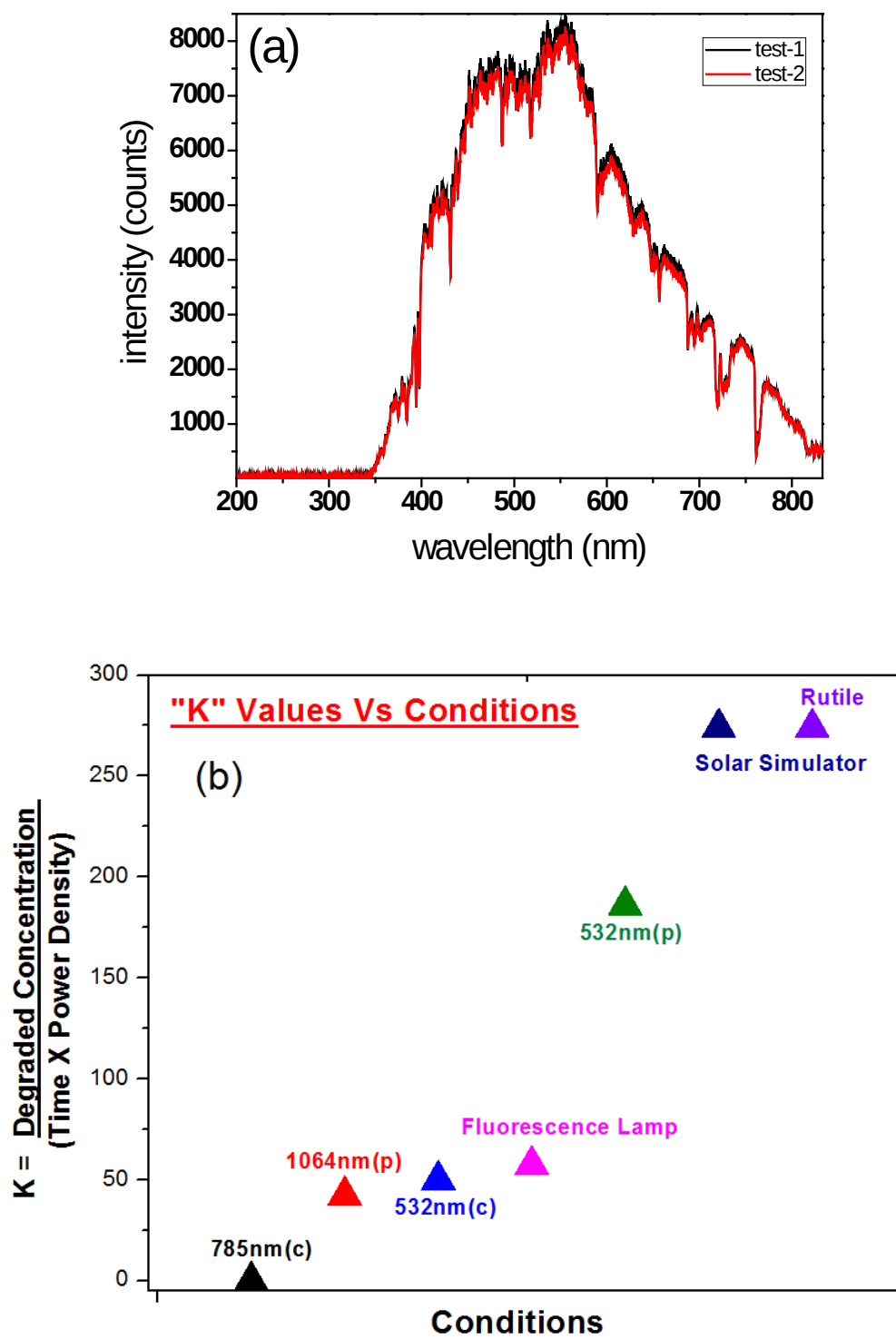


Fig. 16. (a) Spectra of Sunlight used for degradation (b) Comparison of light sources based on K values

Fig. 17. HRTEM analysis of the investigated powders. (a) EDS map of a bi-crystal $\text{TiO}_2\text{--CoTiO}_3$, HAADF and compositional maps of the same particle, EDS results for areas 1 (TiO_2) and 2 (CoTiO_3), (b) lower magnification bright field showing the overall particle and the respective aberration corrected HRTEM image revealing the atomic resolution of the bi-crystal frameworks with the FFT for the regions “i” and “ii” and the respective atomic resolution

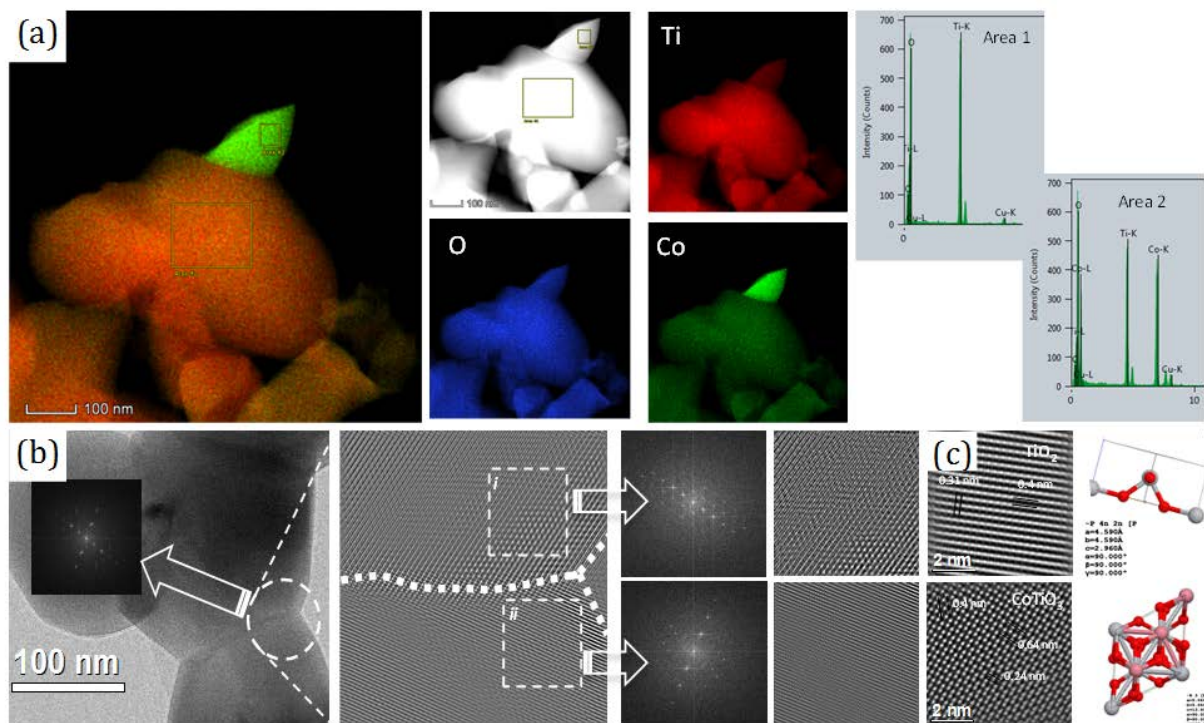


Fig. 17 shows the chemical composition analysis, particle morphology, size and the crystalline frameworks for one of the investigated particles. In the Fig 17 (a) one can observe that the EDS maps demonstrating the bi-crystal framework of $\text{TiO}_2\text{-CoTiO}_3$ catalyst. The particle size for either phase is above 500 nm, which is in agreement with the XRD results. It is also important to observe the stoichiometric domains for each phase. In the Fig 17 (b), can be seen a sequence of images from a lower magnification bright field of the particles to their respective FFT and an atomic resolution image of the interphase of each particle revealing their nature, the d-spacing. The investigated particles clearly matches that of TiO_2 and CoTiO_3 . Other images from different locations corresponding to each of the phases are presented in Fig. 17 (c). These images have significantly better resolution and they allow to match them with the respective simulated crystals for each phase confirming crystalline structure of phases. The planes and d-spacings shown in this image are characteristic only of the identified phase.

The activity of this material is very promising and the capabilities (90 minutes) to degrade organic dyes better than other $\text{TiO}_2\text{-Co}$ based catalyst is predicted due to the active boundaries of the bi-crystal framework. This is a new catalytic mechanism not related to quantum confinement which is not just direct photon excitation. The active region for this material, which is the interphase within frameworks, play a vital role in having a good photocatalytic efficiency.

One of the final tasks in the present work was to find out a mechanism for the interesting activation of photocatalyst under 1064 nm illumination. Although the bandgap of CoTiO_3 is 2.27 eV and that of TiO_2 (Rutile) is 2.94 eV, the absorption spectrum of $\text{TiO}_2\text{-CoTiO}_3$ shown in Fig. 5 (d) reveals a lower energy CoO band at 1.88 eV (660 nm). As expected, the excitation with a continuum laser of 785 nm (1.58 eV) did not produce photo activation of the $\text{TiO}_2\text{-CoTiO}_3$ catalyst.

Here we propose a possible mechanism for activation of $\text{TiO}_2\text{-CoTiO}_3$ catalyst by 1064 nm pulsed laser. This mechanism is based on an up-conversion of 1064 nm laser energy to reach the absorption range in the catalyst through second-harmonic generation (SHG). Fig. 18 represents the SHG effect of $\text{TiO}_2\text{-CoTiO}_3$ catalyst. The SHG is a non-linear optical effect that is possible only in non-centrosymmetric crystals. Although both TiO_2 and CoTiO_3 bulk crystals are centrosymmetric, therefore SHG intensity is zero. Yet, it is well known that strains and crystal boundaries such as crystal faces can break the centro-symmetry and become SHG active. The SHG generation has been reported at the (110) face of TiO_2 (Rutile) (47) and at the (101) face of Anatase (48). As seen under HR-TEM, TiO_2 in the $\text{TiO}_2\text{-CoTiO}_3$ catalyst is nanoscale grained with no well-formed crystal faces.

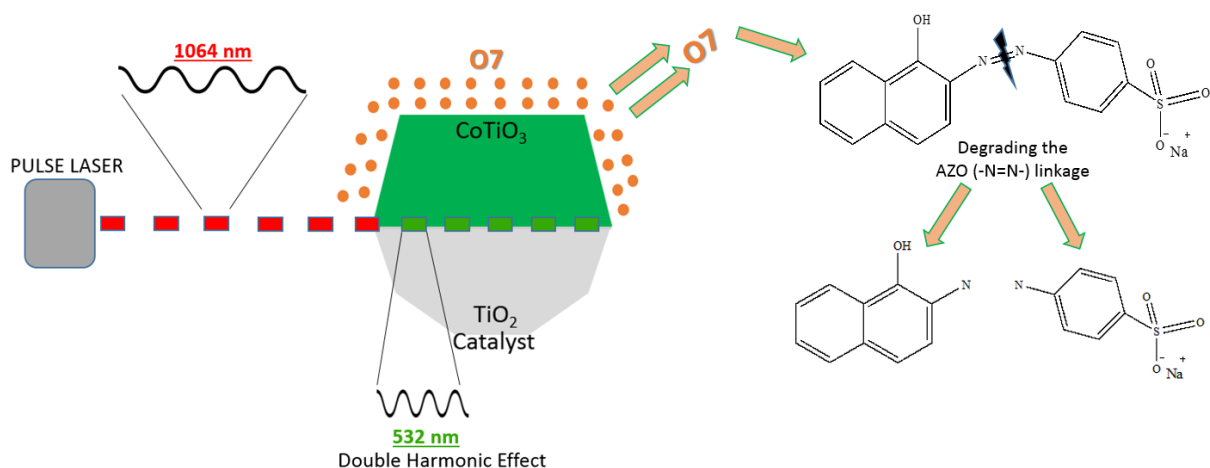


Fig. 18. Second Harmonic effect in TiO_2 - CoTiO_3 catalyst

On the other hand, CoTiO_3 forms well shaped nanocrystals and it should be the best candidate for SHG in this catalyst. Unfortunately, no reports on SHG at the crystal faces of CoTiO_3 were found so far. We believe that SHG at the crystal boundaries of CoTiO_3 is a viable scenario for explaining the photo activation of the catalyst at 1064 nm. Also, the high peak power in pulse lasers seems to be of crucial importance. More studies are needed to prove or reject the SHG effect in CoTiO_3 .

Catalytic Water Splitting:

To observe the potential of the photocatalyst based on the effects observed with degradation of Orange 7, we were inspired to check the activity of the $\text{TiO}_2\text{-CoTiO}_3$ catalyst (with 1064 nm) when applied for water splitting. Fig. 19 displays a typical GC trace of the control experiments. Both, without the catalyst (with 1064 nm) and with the catalyst (in dark) display the exact same GC trace. This GC trace confirms that with control experiment we had no presence of hydrogen. The oxygen calibration of control experiments was also performed and matched well with the ambient oxygen percentage. This confirmed that without the catalyst or in dark the system is unable to produce any amount of hydrogen or oxygen.

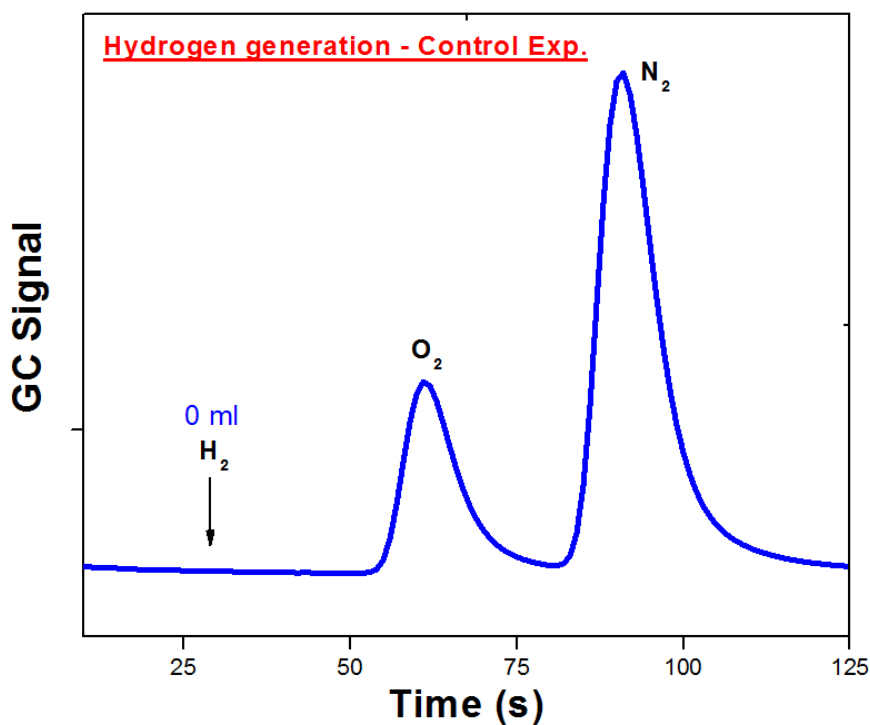


Fig. 19. GC Trend of control experiments.

It must be mentioned that in a typical GC trend for ambient air, there are usually 2 major peak bands. The first one is over usually over 50-75 seconds peaking at about 65 in our plot, represents the Oxygen (O_2). The second one, the more dominant one is Nitrogen (N_2) 80 -110 seconds in our plot (peaking at 95). The presence of Hydrogen is analyzed if a peak is present before Oxygen usually in the range of 30-60 peaking at 43 seconds. Fig 20, displays the GC trace of catalysis with $TiO_2-CoTiO_3$ under 1064 nm pulse illumination for 3 hours. The first sign of overall water splitting can be observed with the GC peak at 43 seconds.

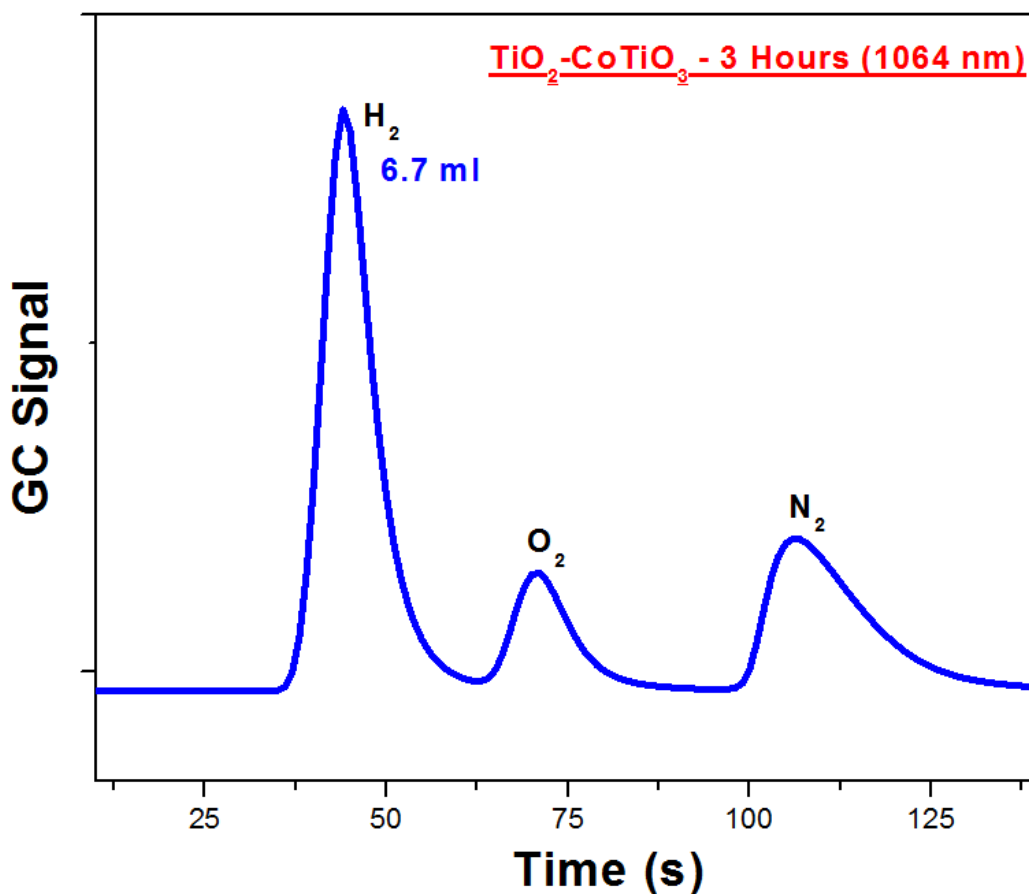


Fig. 20. GC Trend of Catalysis with $TiO_2-CoTiO_3$.

The amount of hydrogen generated in the flask was calculated to be 6.7 ml. This is an interesting observation as the catalysis was carried out from 1064 nm illumination. As described before this light has a lesser photonic energy than the minimum needed to activate the band gap.

It should be noted that the sample was also tested in solar light for hydrogen generation. The results showed that this sample was unable to produce any hydrogen or oxygen under solar light (exactly as Fig. 19) which has enough photonic energy to activate the band gap. The GC trend was very similar to the control experiments indicating no presence of hydrogen generated. This enables us to confirm that the principle of photocatalysis is not driving the generation of hydrogen unlike dye degradation.

We proceeded to investigate the reason behind the activity of the $\text{TiO}_2\text{-CoTiO}_3$ under pulse laser (1064 nm). It was important to investigate the individual phases of $\text{TiO}_2\text{-CoTiO}_3$ catalyst and observe the activity. As the XRD, Raman and the Band gap analysis suggest that the catalyst has the presence of 3 phases TiO_2 , CoTiO_3 and CoO . We synthesized the individual pure phases to carry out the catalysis under exact same conditions. Fig. 21 displays the GC trend for the pure and individual phases CoO , CoTiO_3 and TiO_2 when illuminated under 1064 nm pulse laser. In all cases the testing conditions are the exact same. It can be observed that the TiO_2 alone, produces 0.086 ml of hydrogen. The CoO , which has proved effective under sunlight conditions in other studies (26), was able to produce 0.36 ml of hydrogen. Pure CoTiO_3 is able to produce 0.41 ml of hydrogen. It can be

seen that the individual phases have signs of hydrogen generation. Even though individual phases can produce hydrogen the composite $\text{TiO}_2\text{-CoTiO}_3$ has the maximum potential to produce hydrogen. This also co-relates with the HRTEM microscopy images that identify distinctive boundary. These boundary interface and the bi-crystal framework play a major role in activation of the $\text{TiO}_2\text{-CoTiO}_3$ catalyst.

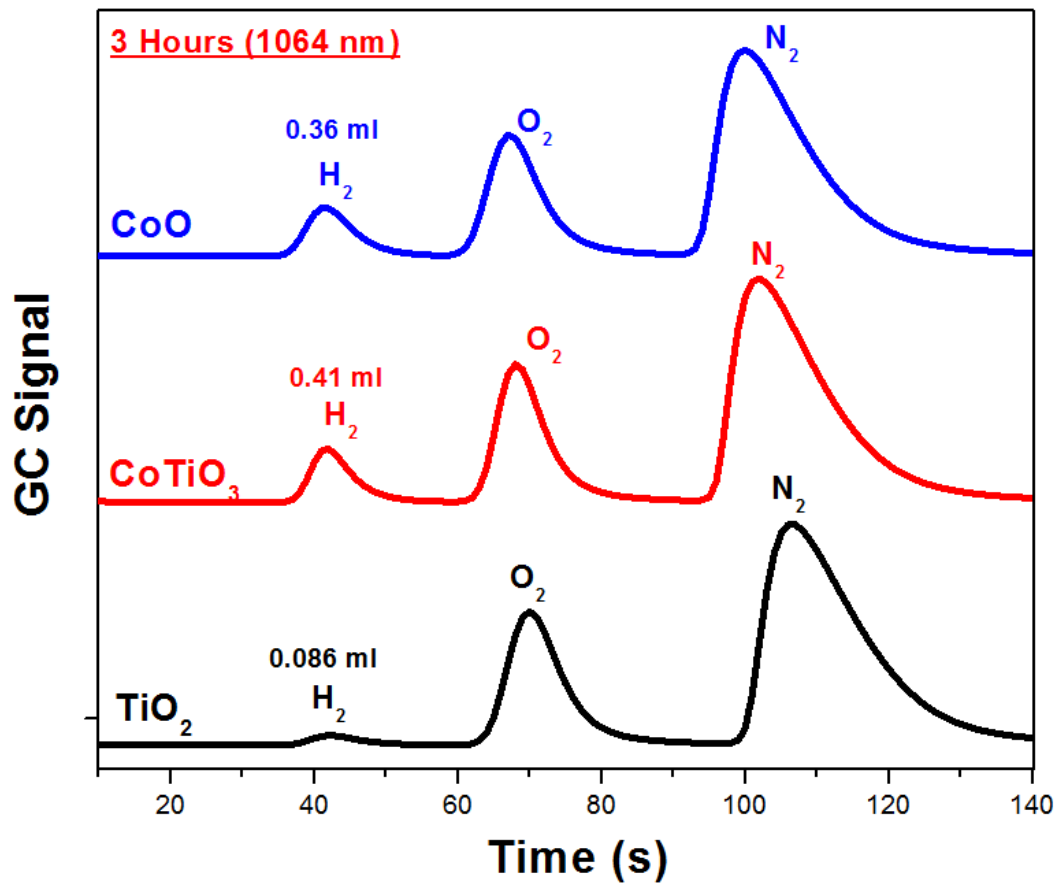


Fig. 21. GC Trend of Catalysis CoO, CoTiO₃ and TiO₂

For water splitting to occur, it is important to analyze the oxygen generation during the process. Fig. 22 indicates the calculated hydrogen and oxygen generation of $\text{TiO}_2\text{-CoTiO}_3$ catalysis. The ambient oxygen level was calculated with the GC peak. The GC trace for $\text{TiO}_2\text{-CoTiO}_3$ catalysis was then analyzed for the increase in oxygen amount to yield the O_2 generated during catalysis.

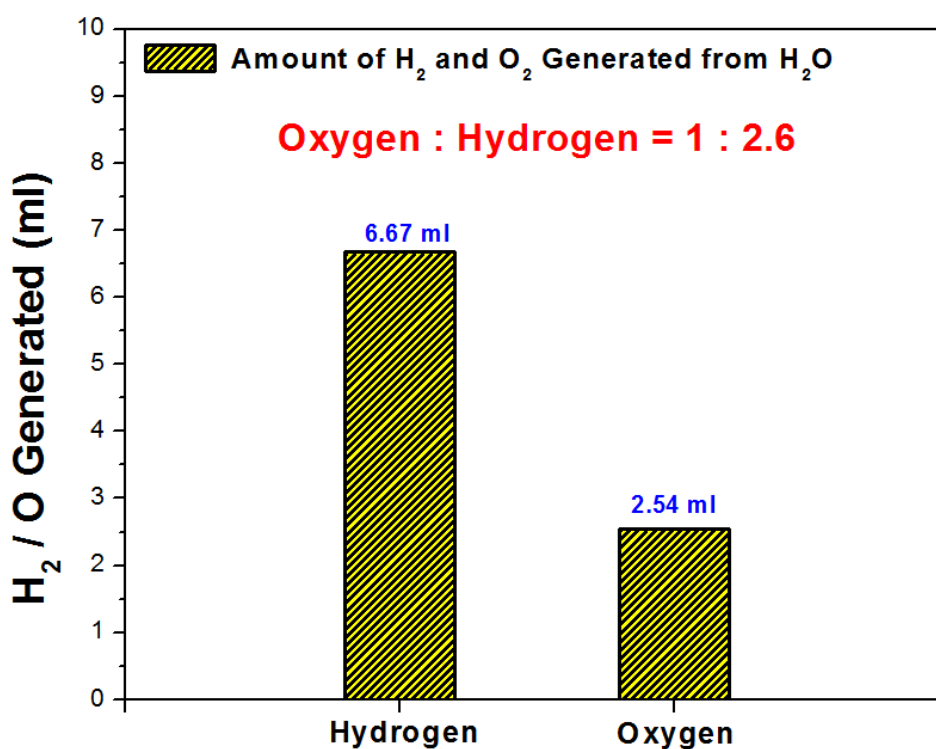


Fig. 22. Generation of H_2 and O_2 with $\text{TiO}_2\text{-CoTiO}_3$ Catalysis

It can be observed from the Fig. 22 that the hydrogen and oxygen ratio is 2.6:1, which is close to 2:1, confirming that the O_2 comes from water instead of $\text{TiO}_2\text{-CoTiO}_3$. The exact value of 2.6:1 indicated that the

holes and the OH^- may have reacted with the catalyst phases and oxidized them. A common example, could be oxidation of CoO to Co_3O_4 . This oxidation uses some of the oxygen generated that depreciated the 2:1 ideal ratio. Of course, further characterization and analysis of the catalyst after reaction is required to confirm the stated oxidations. A comparison curve for all tested materials, pure substances and composite is presented in the Fig. 23. In this figure, one can observe the amount of hydrogen generated with various conditions and catalysts under 1064 nm pulsed illumination. $\text{TiO}_2\text{-CoTiO}_3$ has the maximum amount of hydrogen generation. It must be noted that the composite catalyst $\text{TiO}_2\text{-CoTiO}_3$ is 80 times more effective than pure TiO_2 , 19 times more effective than CoO and 17 times more effective than CoTiO_3 .

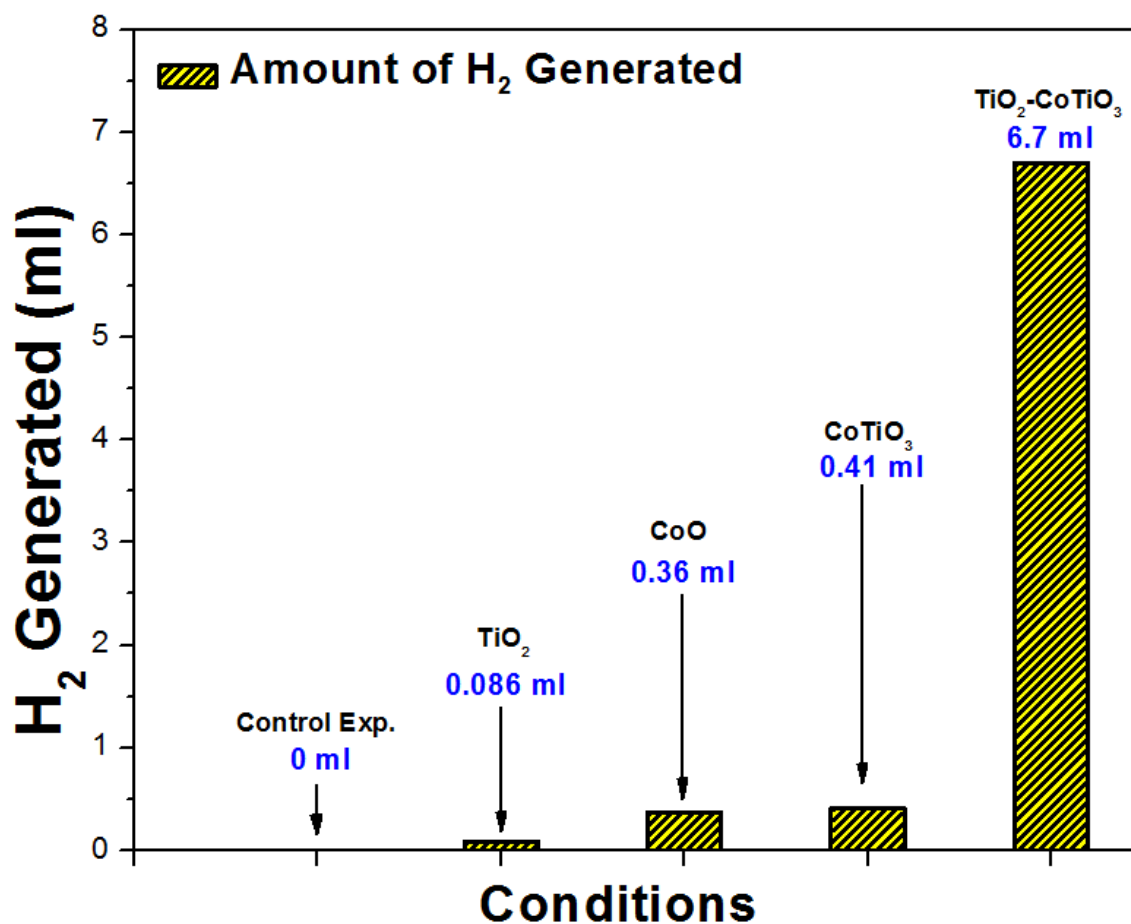


Fig. 23. Summarized amounts of hydrogen with different conditions.

The generation of hydrogen and oxygen in this case follows a complex mechanism that cannot be simply explained by the laws of Photocatalysis and linear optics. We believe it is a link between intense field harmonic generation and Plasmon heating effect. The laser 1064 nm, when hits any surface, creates a hot spot on the surface. One of the possible mechanism is Plasmonic enhancement of Photocatalytic water splitting.

Plasmonic enhancement of TiO_2 has been reported in (49). It is a fact that 1064 nm laser is a high energy laser production about 450 mJ of energy and $1500\text{mW}/\text{cm}^2$ of power density. Therefore, the local field generation is strong.

The 1064 nm generates a hot spot due to localized heating and generation of local field near the catalyst surfaces. The micro-heat transfer in this localized region restricts the temperature measurement due to fast heat dissipation in the region and the reliability to collect data with current technology. Nevertheless, we believe this phenomenon increases the electron-hole generation rate along with the charge contributing to the catalysis. To summarize, the Plasmonic effect with IR lasers has yet not been studied enough to affirm the mechanism. But, one can see, based on the work that it is done with high-harmonic generation (50, 51) and the Plasmonic effect with hot electron transfer (49, 52-55) that the mechanism very well aligns with the working of this pulse laser and the highly active $\text{TiO}_2\text{-CoTiO}_3$ catalyst. More studies are needed to prove or reject this effect for hydrogen generation with IR pulse lasers.

Chapter IV

Conclusions

Conclusions:

Here is presented a clear evidence of visible light active photocatalyst capable of degrading acid orange 7 dye. The 532 nm wavelength is capable of activating the bandgaps of CoO and CoTiO₃ as it explains the photocatalytic activity and high degradation potential of the investigated dye. At the same time the 1064 nm laser (1.16 eV) is incapable of activating any of the mentioned band gaps that are 2.94 eV for TiO₂, 1.88eV for CoO and 2.27eV for CoTiO₃. Therefore, here we present a new mechanism of catalysis for 1064 nm dye degradation that is not based on quantum confinement or direct photon excitation. Instead the material degrades dye due to the double harmonic effect of the composite along with highly active frameworks of TiO₂ and CoTiO₃. Potentially, the degradation comes for the interface between TiO₂ and CoTiO₃, which is nonmetric for most part.

The material TiO₂-CoTiO₃ has shown immense potential with water splitting under 1064 nm IR pulsed laser. It has proved to be more effective than any of the individual phases, proving that the crystal framework is a crucial reason behind the activity of the catalyst. We present the evidence of amount of hydrogen generated based on the phenomenon of high-harmonic generation and Plasmonic effect. This area is especially exciting as it has the potential to a route of direct solar fuel production using a wider spectra available from natural light.

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