

Advancing the Capabilities of Plasmonic and Semiconductor Nanostructures for Light-Powered Applications

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DEDICATION

This dissertation is dedicated to my family and the timeless beauty of the universe for being the great sources of inspiration and motivation for my academic journey.

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ABSTRACT

Light-powered applications are attracting increasing attention in the rapidly developing field of nanomaterials, especially in photocatalysis and biomedical technologies. Such progress requires effective designs and fabrication methods for high-performance nanoparticles. The fabrication of nano-sized particles significantly increases the surface-to-volume ratio, which leads to cost reductions. Wet chemistry synthesis of nanoparticles offers precise control over the size and morphology of nanoparticles, as well as good scalability for bulk applications. Many light-active nanostructures suffer from shortcomings that arise from limited properties inherent to the nature of their structures as well as the inability to utilize the high-intensity region of the solar spectrum. Rational designs of new plasmonic nanostructures can lead to remarkably unique optical properties that offer emergent applications. Doping metal oxide semiconductors can tune the bandgap and recombination rate of the semiconducting nanoparticles, making them more effective photocatalysts. On the other hand, noble metal-semiconductor hybridizations can offer unique synergies that are beneficial for the intended applications.

Chapter 1 of this dissertation provides a detailed review of an important class of plasmonic nanoparticles known as "metal nanostars". Chapter 2 describes the synthesis and characterization of an entirely new metal nanostar; namely, semi-hollow gold-silver nanostars (hAuAgNSts). This unique bimetallic plasmonic nanostructure offers a new operational window in the ultraviolet and visible regions of the electromagnetic spectrum for metal nanostars that is complementary to the existing optical windows of conventional silver nanostars (AgNSts) and gold nanostars (AuNSts). The capability to tune the localized surface

plasmon resonance (LSPR) peak of hAuAgNSts in the visible region enables their usage in many solar-powered applications, such as photocatalysis or photovoltaics, and makes better use of the high-energy flux of this region of the solar spectrum. Importantly, the fabricated bimetallic nanostars exhibit greater stability than traditional AuNSts.

Chapter 3 of this dissertation reports a quick and easy method to fabricate cuprous oxide-coated silver core-shell nanoparticles Ag@Cu₂O. The method offers tunable shell thicknesses, leading to highly tunable extinction behavior of the core-shell nanoparticles in the center of the solar spectrum. This semiconductor-plasmonic combination significantly reduces the recombination rate of photogenerated electron-hole pairs in the composite core-shell nanostructures; moreover, the Ag@Cu₂O hybrid particles showed significantly enhanced hydrogen generation rates in photocatalytic tests.

Chapter 4 of this dissertation describes facile procedures for the syntheses of uniform, monodisperse titanium dioxide (TiO₂) and doped titanium dioxide nanoparticles. The bandgap and electron-hole recombination rates of the doped particles were successfully reduced by doping separately with niobium and tantalum. Dually-doped NTTO nanoparticles exhibited an even larger bandgap reduction compared to both singly doped NTO or TTO nanoparticle analogs. The photocatalytic hydrogen evolution rates of the doped TiO₂ nanoparticles were also enhanced when compared to pristine TiO₂ nanoparticles and reached the highest rate in the dually doped NTTO nanoparticles.

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Chapter 1: Plasmonic Nanostars: A Systematic Review of Their Synthesis and Applications

1.1. Introduction

The interaction of light and matter plays crucial roles in human life and activities, ranging from our cherished eyesight to the ubiquitous utilization of lasers in modern life to the sophisticated spectrometers utilized for space exploration. The accelerating development of nanotechnology in recent decades has brought attention to many exotic and useful properties of materials that are not observed in their bulk counterparts.¹ Among various classes of nanomaterials, plasmonic nanostructures, usually involving noble metals, have demonstrated better performances with superior chemical and physical properties compared to their bulk counterparts.² In addition to the characteristically high surface-to-volume ratio inherent to all nanosized materials, plasmonic nanostructures also exhibit many properties unique to only this class of nanostructures.³ Specifically, when plasmonic nanostructures have dimensions comparable to or smaller than the wavelength of incident light of the electromagnetic field they are interacting with, they exhibit a unique phenomenon called localized surface plasmon resonance (LSPR).³ LSPR occurs when conduction electrons in metallic nanostructures oscillate together with an irradiating incident electric field, as illustrated in Figure 1.1a. Consequently, when the frequency of the incident field matches the resonance frequency of the metal nanostructures, peak absorption appears at that resonant frequency (Figure 1.1b).

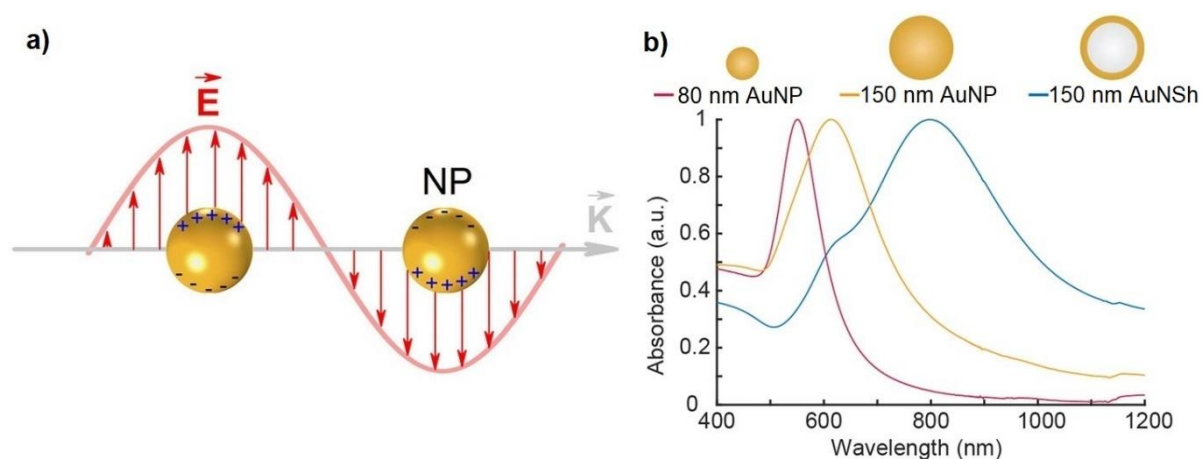


Figure 1.1. (a) Schematic illustration of the interaction between conduction electrons in a metallic nanostructure and the incident electromagnetic field E . (b) Sketch of the plasmonic nanoparticles and their absorption spectra in water. NP: nanoparticle, AuNP: gold nanoparticle, AuNSh: gold nanoshell. Adapted with permission from references 2 and 4. Copyright 2019 American Chemical Society and 2021 Wiley.

In addition to the material compositions and the dielectric environments surrounding them, the LSPR frequencies of plasmonic nanostructures vary with their size and shape (Figure 1.1b). Thus, many plasmonic nanostructures with different morphologies (Figure 1.2) and unique electrical, optical, and chemical properties have been synthesized and studied. Exploiting their LSPR characteristics, various applications spanning a wide range of technology fields have been explored, developed, and implemented based on plasmonic nanostructures, including photothermal treatment,² targeted drug delivery,⁵ precision sensing,⁶ enhanced imaging,⁷ catalysis,⁸ and photovoltaics.⁹

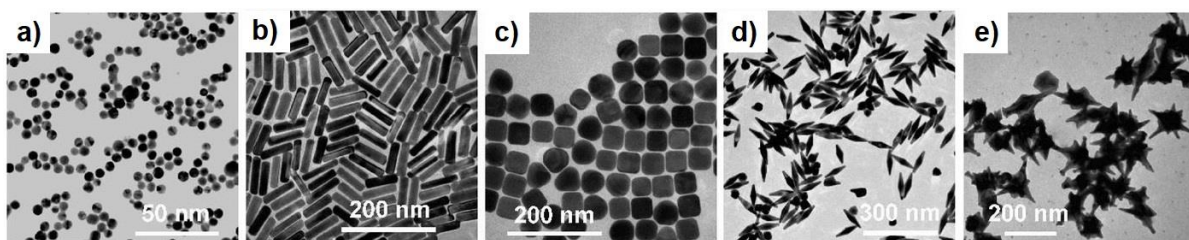


Figure 1.2. Representative transmission electron microscopy images of plasmonic AuNPs: (a) nanospheres, (b) nanorods, (c) nanocubes, (d) nanobipyramids, and (e) nanostars. Adapted with permission from reference 10. Copyright 2008 American Chemical Society.

Noble metal nanostars are one of the most recently developed types of plasmonic nanostructures and have drawn significant attention from many different research communities. The remarkable interest in plasmonic nanostars mostly originates from their superior specific surface areas and dominant numbers of plasmonic hot spots compared to those of other plasmonic nanostructures,¹¹ as illustrated in Figure 1.3. Combined with the opening of more crystal facets for surface modification as well as complex combinations, larger surface area-to-volume ratios make plasmonic nanostars much more promising for applications that would benefit from extended contact surfaces, such as sensing and catalysis.^{12,13} Moreover, a greatly intensified electric field¹⁴ with high numbers of plasmonic hot spots (Figure 1.3f) is another unique advantage inherent to noble metal nanostars. In addition to enhancing the physical,¹⁵ optical,¹⁶ electronic,¹⁷ or chemical¹⁸ properties of the plasmonic nanostructures, the greatly intensified electric fields of illuminated plasmonic nanostars also enable many exotic applications that are unconventional for plasmonic nanostructures, such as field electron generation¹⁹ or the optical control of electrical currents.²⁰

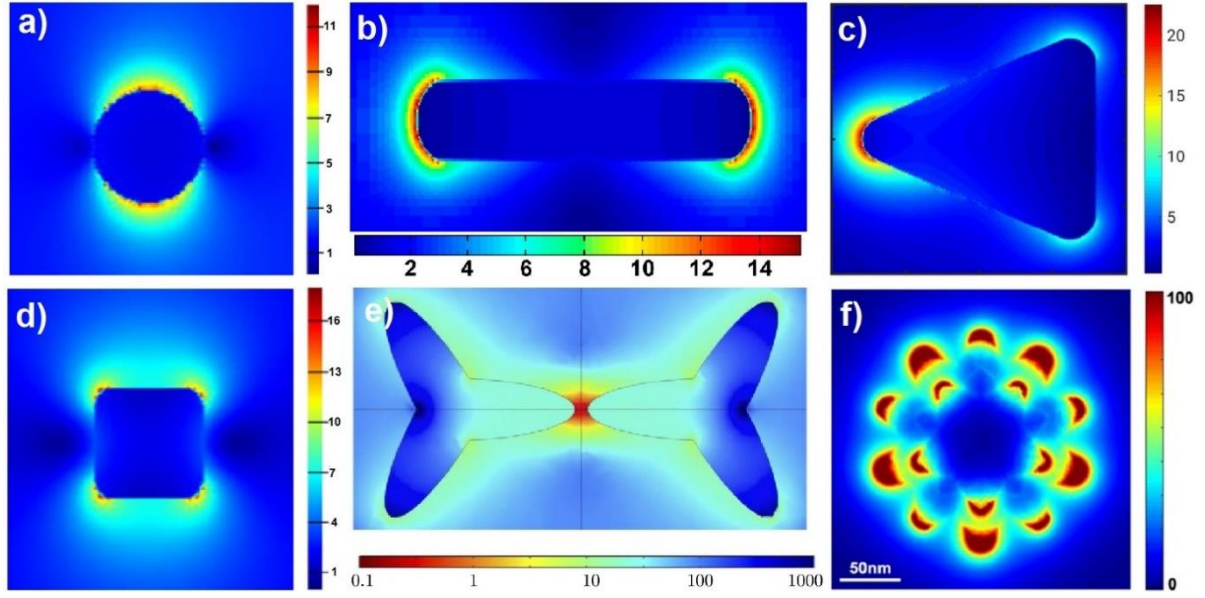


Figure 1.3. Simulated electric field distribution of plasmonic (a) nanospheres,²¹ (b) nanorods,²² (c) nanotriangles,²³ (d) nanocubes,²¹ (e) tripods,²⁴ and (f) nanostars.²⁵ Reproduced and adapted with permission from the indicated references.^{23,24,26–29}

With many unique advantages over other more conventional nanostructures, plasmonic nanostars have the potential to greatly advance many current applications and enable the development of next generations of important technologies, which can benefit human life or resolve urgent environmental problems. Despite the vast potential of plasmonic nanostars, a more rigorous understanding and better technological control are needed to realize the promise of this nascent class of nanostructures. Toward these efforts, this review aims to provide a comprehensive picture of the current status of research, development, and applications of plasmonic nanostars for advanced technologies and utilizations, ranging from targeted cancer eradications and diagnoses to SARS-CoV-2 vaccines or next-generation photovoltaic cells.

1.2. Synthesis of Plasmonic Nanostars

To synthesize plasmonic nanostars with various sizes, compositions, and optical properties, multiple methods have been developed over the last fifteen years using different approaches and reagents. Table 1.1 summarizes some representative methods for the syntheses of plasmonic nanostars with varying compositions and size ranges.

Table 1.1. Synthesis Methodologies for Plasmonic Nanostars

Entry	Nanostar Type	Method	Surfactant/ Directing Agent	Conditions	Size Range (nm)	Ref.
1	AuNSt	One-pot	-	RT	50–150	21
2	AuNSt	Seed-mediated	PVP	100 °C, RT	45–116	22
3	AuNSt	Seed-mediated, silver-assisted	Triton-X-100	RT	100–160	23
4	AuNSt	Seed-mediated, silver-assisted	CTAB	100 °C, RT	200–400	24
5	AuNSt	One-pot, silver-assisted	Triton-X-100	RT	100–300	25
6	AuNSt	One-pot, silver-assisted	SDS, AOT, BDAC	RT	74–196	26
7	AuNSt	One-pot, silver-assisted	-	RT	100–250	27
8	AgNSt	Seed-mediated	-	RT	60–500	28
9	Ag@AuNSt	Seed-mediated, gold coating	-	100 °C, RT	70–110	29
10	Au@AgNSt	Seed-mediated, silver coating	CTAB	100 °C	50–70	30
11	AuCuNSt	Seed-mediated	HDA	RT, 100 °C	~200	31
12	AuCuNSt	Seed-mediated	OLA, HDA	RT, 130 °C	130–220	32
13	hAuAgNSt	Seed-mediated, galvanic replacement	-	RT	150–300	11

Abbreviations: AuNSt: gold nanostar, AgNSt: silver nanostar, Ag@AuNSt: silver-gold core-shell nanostar, Au@AgNSt: gold-silver core-shell nanostar, AuCuNSt: gold-copper nanostar, hAuAgNSt: semihollow gold-silver nanostar, SDS: sodium dodecyl sulfate, AOT: dioctyl sodium sulfosuccinate, BDAC: benzylhexadecyldimethylammonium chloride, HDA: hexadecylamine, OLA: oleylamine, CTAB: cetyltrimethylammonium bromide, PVP: polyvinylpyrrolidone, RT: room temperature.

Mono-metal nanostars, the first members of star-shaped plasmonic nanostructures, have been synthesized by different methods under various conditions (Table 1.1, entries 1-8). In a recent report,²¹ Chandra et al. described the fabrication of gold nanostars (AuNSts) by a seedless synthesis method based on Good's buffers. By changing the synthetic parameters, the authors demonstrated the capability to tailor the dimensions, shape, and optical properties

of the synthesized AuNSts. Specifically, the study investigated the effects of different Good's buffers, such as 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES), 4-(2-hydroxyethyl)-1-piperazinepropanesulfonic acid (EPPS), and 3-(N-morpholino)-propanesulfonic acid (MOPS), on the size and shape of the resulting AuNSts. The results in Figure 1.4 show that the AuNSts synthesized with HEPES buffer had only one LSPR peak (Figure 1.4a), but the AuNSts synthesized with EPPS and MOPS buffers had two LSPR peaks, λ_1 and λ_2 (Figures 1.4b and c). The authors attributed the pronounced emergence of the secondary LSPR peaks of the EPPS- and MOPS-AuNSts to their longer star branches compared to the star branches of HEPES-AuNSts. For all three buffers, the authors also studied the effects of R_{buffer} ($[\text{buffer}]/[\text{HAuCl}_4]$ ratio) on the morphologies of the resulting AuNSts. Specifically, when increasing R_{buffer} , more buffer molecules bound to the particles and directed the particle growth, leading to more Au ions being reduced onto some specific facets of the nanoparticles. This directed growth led to AuNSts with longer branches, as observed by the TEM micrographs shown in Figure 1.4.

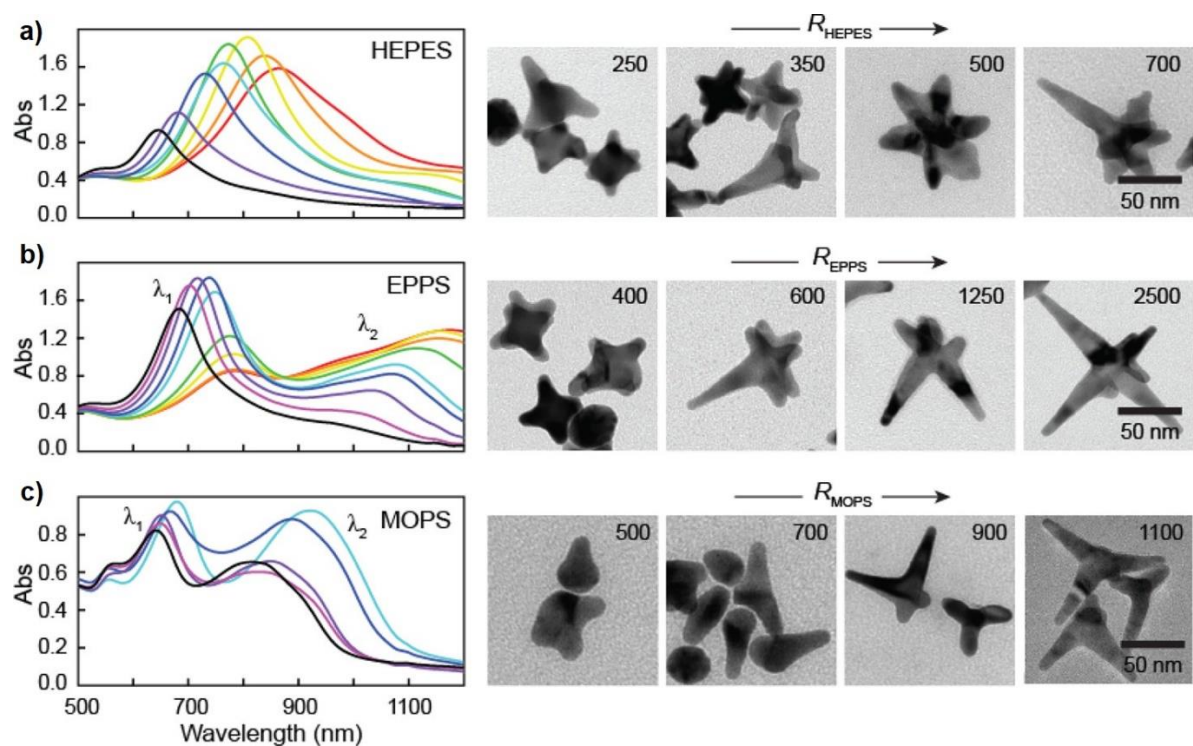


Figure 1.4. Absorbance spectra and TEM micrographs of AuNSts synthesized with (a) 250 to 750 R_{HEPES} , (b) 400 to 2500 R_{EPPS} , and (c) 500 to 1100 R_{MOPS} . From left to right is the lowest concentration (black) to the highest concentration (red or cyan). The number in the upper right-hand corner of each image is the corresponding R_{buffer} value. Adapted with permission from reference 21. Copyright 2016 American Chemical Society.

The authors also studied the influence of the pH of the synthesis solution on the stability of the resulting AuNSts. The pH values of the synthesis solutions were adjusted by adding NaOH to the buffers. For the HEPES synthesis solution ($\text{pK}_{\text{a}} = 7.5$), stable AuNSts were formed throughout the entire buffering range of 6.9–8.2 (Figure 1.5a) with slight redshifts in the LSPR peak wavelengths (Figure 1.5b). However, for both the EPPS ($\text{pK}_{\text{a}} = 8.0$) and MOPS ($\text{pK}_{\text{a}} = 7.2$) synthesis solutions, stable AuNSts could be obtained only from the synthesis solutions with pH values below or equal to the pK_{a} values of the buffers. At pH values above the buffer pK_{a} values, the aggregation of the EPPS- and MOPS-AuNSts occurred (Figure 1.5a), which limited the synthetic range of these buffers. This work provided further

insights into the influences of synthesis solution conditions on the seedless growth of AuNSts, which can be valuable when optimizing the synthesis conditions to obtain AuNSts with desired properties. Many other studies on the syntheses of mono-metal plasmonic nanostars were also reported using either seedless (one-pot) methods^{25–27} or seed-mediated processes with^{22–24} and without the use of surfactants.²⁸

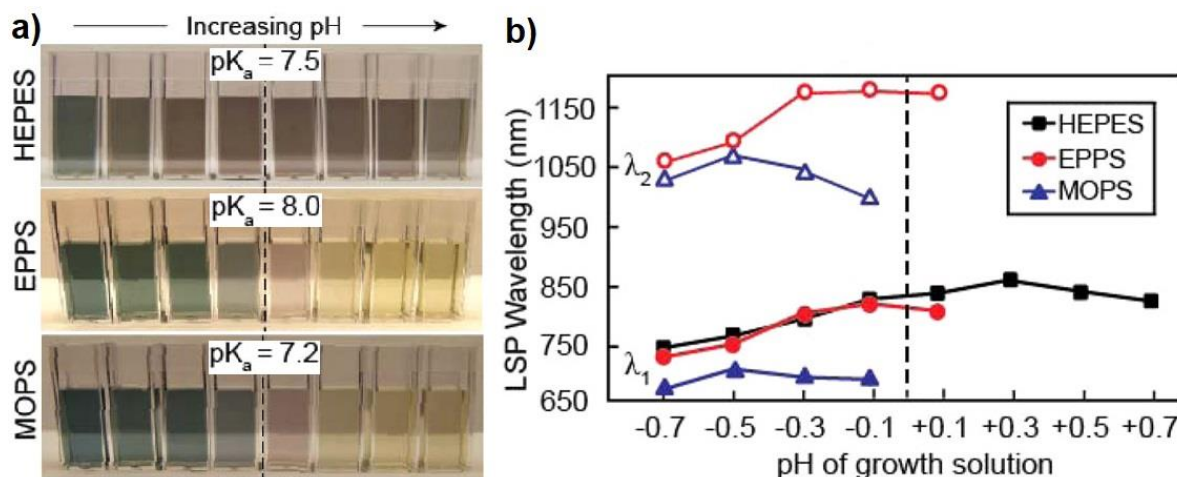


Figure 1.5. pH dependence of HEPES-, EPPS-, and MOPS-AuNSt formation throughout their respective buffering ranges. (a) Photographs of the solutions at different pH values; $pK_a \pm 0.7$. (b) Corresponding peak wavelengths of the absorbance spectra of AuNSts synthesized from solutions with different pH values. The solid symbols correspond to λ_1 , and the open symbols correspond to λ_2 . Adapted with permission from reference 21. Copyright 2016 American Chemical Society.

The applications of conventional mono-metal AuNSts are quite limited because they have with an optical window that only ranges from the red-end of the visible region to the near-infrared region. Recently, Ngo et al. were the first to report the fabrication of semihollow gold-silver nanostars (hAuAgNSts) with a new optical window in the ultraviolet and visible regions.¹¹ This work utilized a properly tuned galvanic replacement process of presynthesized silver nanostars (AgNSts) in open-air conditions at room temperature. The aqueous etching solution contained HAuCl_4 and potassium carbonate (K-Au). The procedure allowed the

formation of bimetallic hAuAgNSts (Figures 1.6a and b) with good size distributions (Figure 1.6a inset). The corresponding energy-dispersive X-ray spectroscopy (EDX) elemental maps showed uniform distributions of both gold (Figure 1.6d) and silver (Figure 1.6e) throughout the structures of the hAuAgNSt (Figure 1.6c), which confirms the presence of both metals in these unique bimetallic semihollow nanostars.

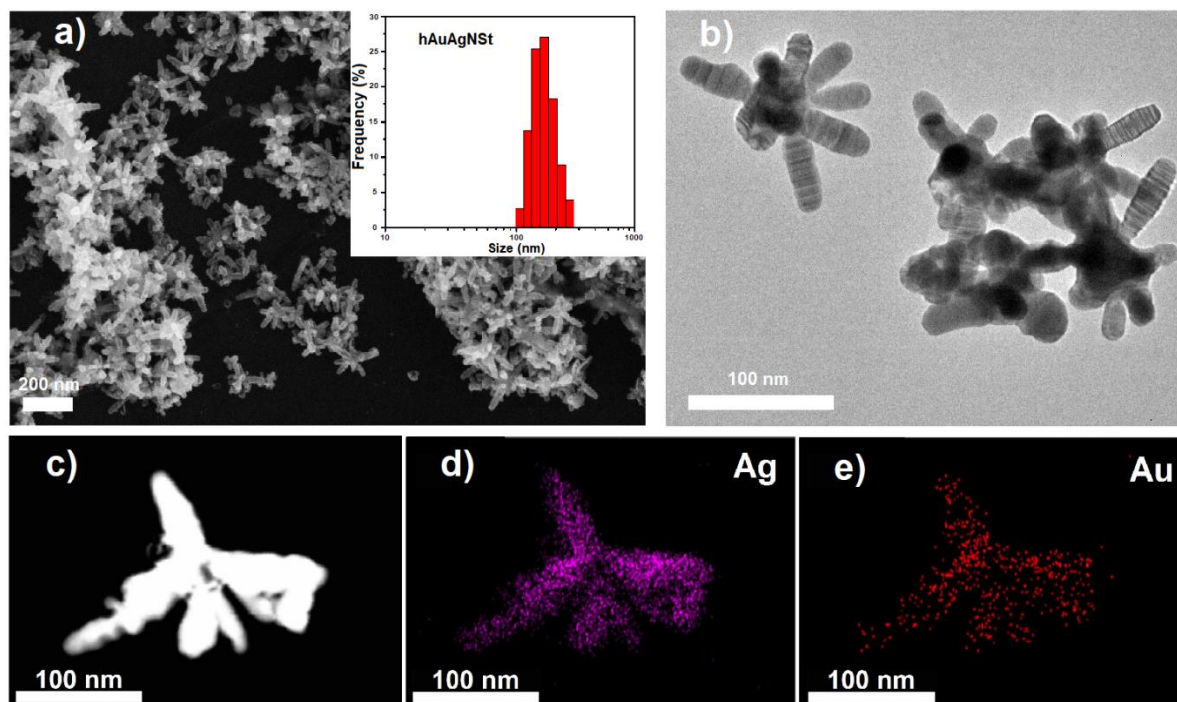


Figure 1.6. (a) SEM and (b) TEM images and the size distribution (inset) of semihollow gold-silver nanostars (hAuAgNSts). (c) STEM image and EDX elemental maps of (d) silver and (e) gold for a representative hAuAgNSt. Adapted with permission from reference 11.

The hAuAgNSts exhibited a linear correlation between the Au contents in the resulting nanostars and the K-Au/AgNSt ratios used in the fabrication process (Figure 1.7a).¹¹ This linear relationship allows hAuAgNSts to be synthesized with a desired Au content by adjusting the galvanic replacement conditions accordingly. These bimetallic nanostars showed a new LSPR active window for plasmonic nanostars in the ultraviolet and visible regions, which is spectrally complementary to the existing optical window of AuNSts, as

shown in Figure 1.7b. Notably, the LSPR peak position of the hAuAgNSts was also demonstrated to be tunable through the control of the Au contents in their structures. The linear predictability of the Au contents led to a much more versatile LSPR composition-based tunability of hAuAgNSts than the size-based tunability of AuNSts, as shown in Figure 1.4 of the previously discussed work. The new operational window offered by hAuAgNSts and the facile LSPR composition-based tuning method reported in this study have expanded the working range and further advanced the utilization prospect of plasmonic nanostars, especially for solar-powered applications, such as photocatalysis and photovoltaics. Several other studies also demonstrated different synthetic methods for bimetallic nanostars, such as Ag@Au,²⁹ Au@Ag,³⁰ or Au-Cu nanostars.^{31,32}

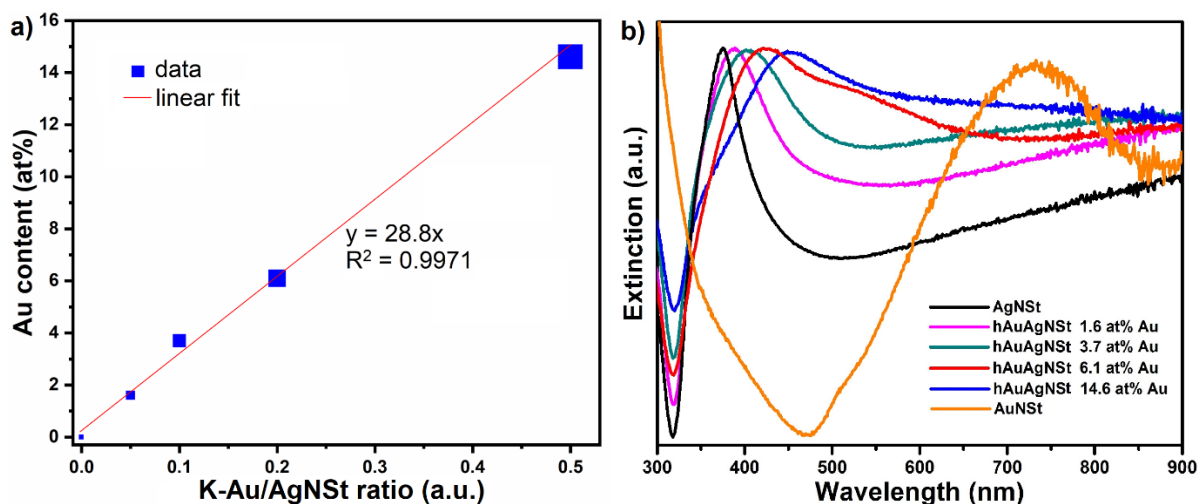


Figure 1.7. (a) Au content and (b) extinction spectra of hAuAgNSts synthesized using various ratios of K-Au and silver nanostar stock solutions compared to AuNSts and AgNSts. Adapted with permission from reference 11.

1.3. Applications of Plasmonic Nanostars

1.3.1. Biomedical Applications

Noble metal-based plasmonic nanostructures have attracted great research interest concerning biomedical diagnostics because of their high biocompatibilities and unique properties, including superior surface areas and large numbers of plasmonic hotspots.³³ Under the illumination of electromagnetic waves with suitable wavelengths, the plasmonic resonance generated by these nanostructures can enhance many physical phenomena, such as Raman scattering and fluorescence.³⁴ Such enhanced effects of NSt-based materials have been utilized in many biomedical applications, including diagnostics, drug delivery, photothermal and photodynamic therapies, and antibacterial applications.

1.3.1.1. Plasmonic Nanostar-Enhanced Diagnostics

The superior specific areas and numbers of hotspots³⁵ of nanostars compared to those of other plasmonic nanostructures (e.g., spheres, rods, triangles, or cubes) make them particularly interesting for diagnostic technology development. Specifically, the plasmonic resonance wavelengths in the first and second biological optical windows³⁶ together with the excellent biocompatibility³⁷ of gold nanostars endow them with great potential in high-performance diagnostics for many medical conditions and diseases. Table 1.2 summarizes the current use of plasmonic nanostars in the diagnosis of various diseases.

Table 1.2. Plasmonic Nanostars for Medical Diagnostics

Core NP	Combinatory Components	Target	Method	Level of Study	Key Results	Ref.
AuNSt-SiO ₂	Label DNAs	Cancer miRNAs	Bio-imaging	In vitro	21-fold fluorescence enhancement and 0.21 pM miRNA-21 LOD	35
Ag-AuNSt	Raman reporter molecule	CRS biomarker	SERS immuno-assay	In vitro, clinical	LOD up to 0.41 fg/mL	38
AuNSt	Raman reporter molecule	Breast cancer cell	SERS imaging	In vitro	Five types of breast cancer cells with reproducible signals and noncytotoxicity	39
AuNSt	Grapheme oxide	Breast cancer exosomes	SERS	In vitro	LOD of 380 exosomes/mL and FDTD simulation results showed 10 ⁴ -enhanced SERS signal	40
AuNSt	SERS tag	Prostate cancer PSMA	SERS	In vitro	Quantification of PSMA protein at pM-concentration both at the single-cell level and in tissue microassays	41
AuNSt	Aptamer probe	CTCs	Electro-chemical current	In vitro, clinical	Ultrasensitive label-free detection of CTCs at concentrations as low as 5 cells/mL	42
AuNSt	LK26 antibody	Ovarian cancer folate receptors	Ratio-metric imaging	In vitro, in vivo	Detection of ovarian tumors as small as 370 μ m	43
AuNSt	N/A	Breast cancer	SERS	In vitro	Label-free discernment of three cell phenotypes based solely on the acquired Raman spectra	44
AuNSt	EpCAM aptamer	CTCs	Electro-chemical aptasensing	In vitro, clinical	Single-cell detection of target cancer cell even in human serum	45
AuNSt	N/A	Cervical and liver cancer	SERS imaging	In vitro	SERS detection of cancer cells at a higher sensitivity with AuNSts than with Au nanospheres	46
AuNSt	Glycyrrhetic acid	Liver fibrosis	SERS	In vivo	Selectively detected liver fibrosis and demonstrated good biocompatibility	47
AuNSt@Ag@SiO ₂	Anti-AFP antibody	Liver cancer biomarker AFP	SERS immuno-assay	In vitro	Detected AFP at a low LOD of 0.72 pg/mL and a wide range of linear detection range from 3 pg/mL to 3 μ g/mL	48
AuNSt@SiO ₂	uPAR- and EGFR-targeting peptides	Breast cancer	SERS imaging	In vitro	Simultaneous quantitative detection and discrimination of both biomarkers without background interference	49

Abbreviations: PEF: plasmon-enhanced fluorescence, miRNA: microRNA, LOD: detection limit, CRS: cardiorenal syndrome, SERS: surface-enhanced Raman spectroscopy, GO: graphene oxide, FDTD: finite-difference time-domain, PSMA: prostate-specific membrane antigen, CTCs: circulating tumor cells, N/A: not applicable, EpCAM: epithelial cell adhesion molecule, AFP: α -fetoprotein, uPAR: urokinase plasminogen activation receptor, EGFR: epidermal growth factor receptor, MSOT: multispectral optoacoustic tomography.

In a recent report,³⁵ Gao et al. reported the in situ detection and imaging of intracellular microRNAs (miRNAs) using tumor cell miRNA-21. The work included the fabrication of plasmon-enhanced fluorescence (PEF) probes by conjugating silica-coated AuNSts with BHQ-3- and Cy5.5-labeled assistant DNAs, which were partially hybridized with each other. In the presence of miRNA-21, Cy5.5-labeled assistant DNAs were completely hybridized with miRNA-21, and BHQ-3 DNAs were removed. This led to an increase in the fluorescence signal because the signal-suppressing fluorescence resonance energy transfer between BHQ-3 and Cy5.5 DNAs was disrupted, as illustrated in Figure 1.8a. With the minimum fluorescence signal observed at 0.5 pM (Figure 1.8b), the authors calculated a limit of detection (LOD) of 0.21 pM ($3\sigma/s$) for miRNA-21. The study also demonstrates the capability to adjust the fluorescence enhancement of the PEF probes by regulating the silica shell thickness, with a maximum enhancement of 21-fold obtained at a shell thickness of ~ 22 nm.

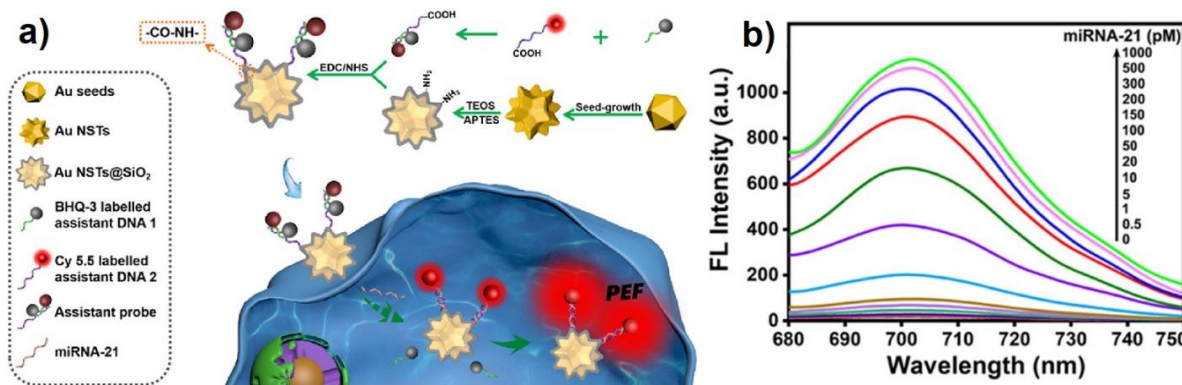


Figure 1.8. (a) Schematic illustration of the AuNSt@SiO₂-based plasmon-enhanced fluorescence probe for the in situ detection of intracellular miRNA-21 and (b) fluorescence spectra emitted by the probe in the presence of miRNA-21 at different concentrations. Adapted with permission from reference 35. Copyright 2021 American Chemical Society.

Through a comparison with other nanostructures, such as nanorods (4.2-fold fluorescence enhancement), nanobipyramids (8.9-fold fluorescence enhancement), and triangular nanoprisms (11.2-fold fluorescence enhancement), the superiority of nanostars was demonstrated with the 21-fold enhancement of the fluorescence signal (Figure 1.9).³⁵ The authors attributed this result to the large numbers of symmetric hotspots present in the AuNSTs-based probes, which produced stronger localized electric fields and led to a higher sensitivity and improved LOD. The experimental investigation of the influences of nanoparticle morphologies on the fluorescence enhancement in this work provides valuable guidance for the future design and utilization of plasmonic nanostars.

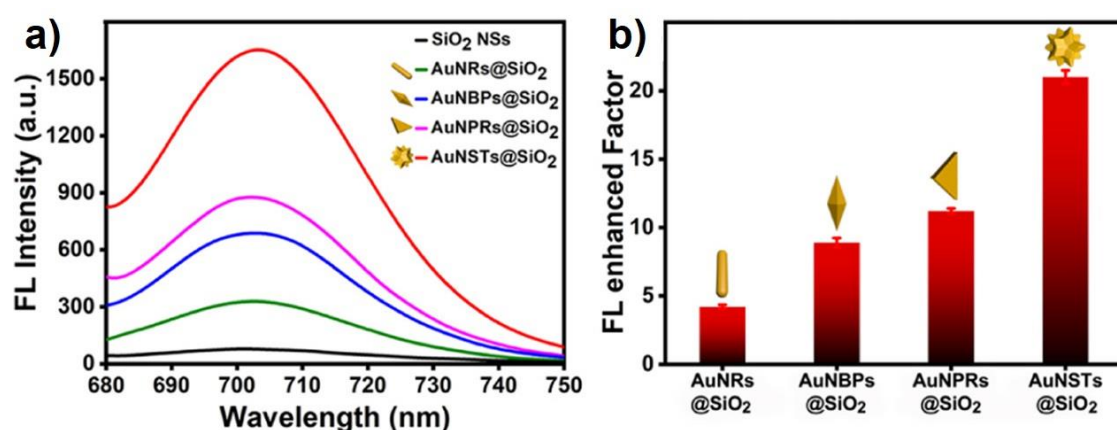


Figure 1.9. (a) Fluorescence spectra of silica-coated nanoparticles with different morphologies and (b) their corresponding fluorescence enhanced factors. Adapted with permission from reference 35. Copyright 2021 American Chemical Society.

Early diagnosis of cardiorenal syndrome (CRS) is important for treating the disease effectively and preventing the dysfunction of the heart and kidneys in affected patients. Recently, Su et al. reported a sandwich immunoassay based on surface-enhanced Raman scattering (SERS) for the simultaneous detection of cardiac troponin I (cTnI), the N-terminal prohormone of brain natriuretic peptide (NT-ProBNP), and neutrophil gelatinase-associated

lipocalin (NGAL) for early CRS diagnoses.³⁸ The authors used gold-silver core-shell nanostars (Ag@AuNSt) (Figure 1.10a) labeled with Raman reporter-molecule nanotags. The Raman reporters used in this study include 4-mercaptobenzoic (4-MBA), 5'-dithiobis(2-nitrobenzoic acid) (DTNB), and 2-naphthalenethiol (NT). The nanotags were then added to a macroporous Au-Ag-Au plasmonic array, which was used as a substrate in the immunoassay technique (Figure 1.10c). The array was fabricated by a series of deposition processes before anti-nTnI, anti-NT-ProBNP, and anti-NGAL antibodies were immobilized on its surface, as illustrated in Figure 1.10b.

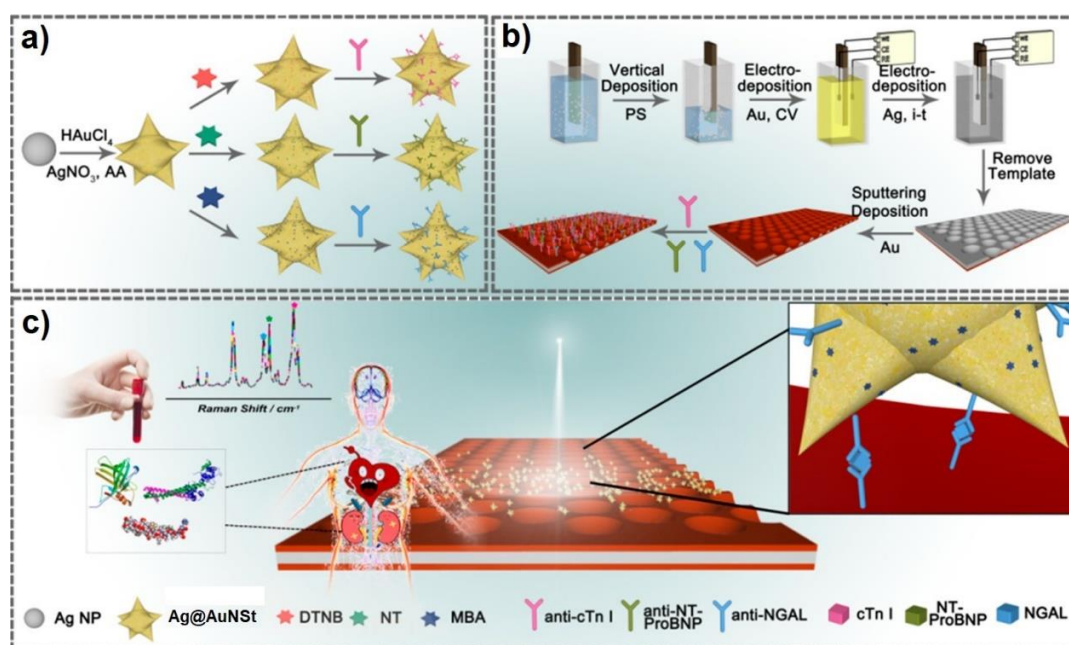


Figure 1.10. (a) Fabrication of the three Raman reporter molecules and three antibody-functionalized Ag@AuNSt hybrid nanotags. (b) Preparation of the Ab1-functionalized 3DOM Au-Ag-Au SERS substrate and (c) the SERS immunoassay platform for simultaneous detection of cTnI, NT-ProBNP, and NGAL. Adapted with permission from reference 38. Copyright 2019 American Chemical Society.

A greatly enhanced SERS signal (Figure 1.11a) of the immunosensors was obtained due to the plasmon near-field coupling that occurred when the plasmonic star nanotags and substrate came into contact through selective binding between the targeted antigens and their

antibodies, which were grafted onto the nanotags and plasmonic arrays, as shown in Figure 1.10c.³⁸ This work also observed linear relations between SERS signals and antigen concentrations in the range of 1 fg/mL to 1 μ g/mL (Figure 1.11b). Using linear regression calculations, the authors determined LODs of 0.76, 0.53, and 0.41 fg/mL for cTnI, NT-ProBNP, and NGAL, respectively. Such LODs are orders of magnitude smaller than those of other reported plasmonic nanoparticle-based platforms for the detection of cTnI,^{50,51} NT-ProBNP,⁵² and NGAL^{53,54}. These dramatic decreases in LODs enabled by the use of plasmonic nanostars highlight the superiority of this unique type of plasmonic nanostructure in developing advanced diagnostic technologies. The reported device was also able to perform multiplex detection of three biomarkers, DTNB, NT, and 4-MBA, in a single assay by using three distinguishable 1323, 1363, and 1584 cm^{-1} SERS peaks. This multiplexing capability not only reduced the device use but also allowed low-cost, fast diagnostics. This work demonstrated the unique strength of plasmonic alloy nanostars, especially their inherently high numbers of hot spots, in enhancing advanced spectroscopic diagnostic techniques.

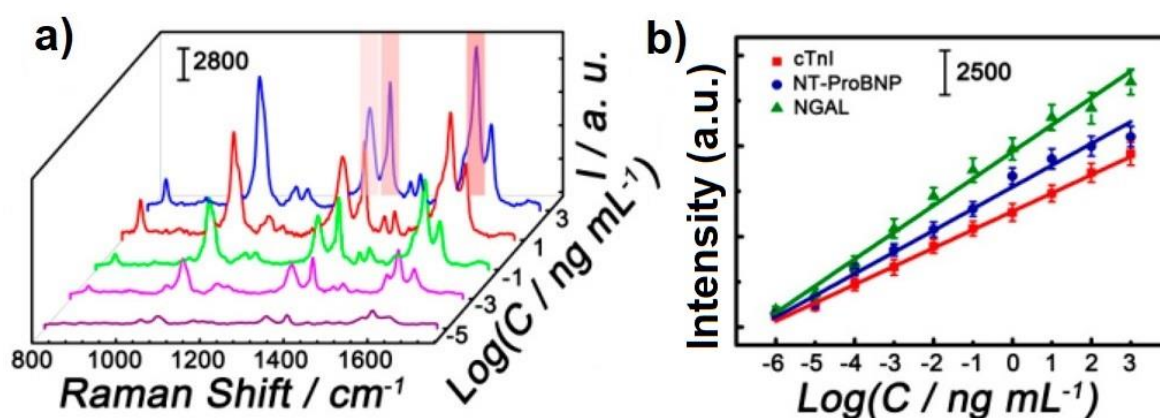


Figure 1.11. (a) Integrated SERS spectra of the immunosensor after cTnI, NT-ProBNP, and NGAL were incubated at different concentrations. (b) Calibration curves of nTnI, NT-ProBNP, and NGAL on a semilog scale. Adapted with permission from reference 38. Copyright 2019 American Chemical Society.

In addition to the highlighted works above, many remarkable studies on AuNSt-based diagnostics have also been reported recently, as listed in Table 1.2. Plasmonic nanostars have been used to develop diagnostic methods for various detrimental cancers, from breast,^{39,40,44,49} prostate,⁴¹ ovarian,⁴³ cervical,⁴⁶ to liver cancer.⁴⁸ Until now, most of the studies have remained focused on cancer-related techniques, possibly due to the severity of the diseases and the ease of adaptability when transitioning from the well-known gold nanoparticles, the most popular type of plasmonic nanoparticles, to gold nanostars. However, the use of plasmonic nanostars to diagnose other medical conditions can also facilitate promising research areas when AuNSts and/or other plasmonic nanostars are combined with suitable conjugates in proper structures.

1.3.1.2. Vaccine and Drug Delivery with Plasmonic Nanostars

The prevention and treatment of critical diseases, such as cancers or viral infections, are always attracting great attention. With the rapid progress of nanomaterial studies, a great amount of research effort has been spent on inventing nanobased methods for preventing and treating diseases while minimizing the unintended collateral damage that is inherent to traditional techniques (e.g., chemo- and radiotherapy, or general pharmaceutical intake).⁵⁵ High-specificity drug delivery enabled by nanostructures has been an attractive theme in developing applications of nanostructures.⁵⁶ The large surface area-to-volume ratios and high numbers of hotspots of plasmonic nanostars are great advantages for the development of efficiently targeted vaccine and drug delivery technologies based on this unique class of nanomaterials. Recent studies on vaccine and drug delivery utilizing plasmonic nanostars are summarized in Table 1.3.

Table 1.3. Plasmonic Nanostars for Vaccine and Drug Delivery

Core NP	Combinatory Components	Target	Triggering/ Transport Mechanism	Level of Study	Key Results	Ref.
AuNSt	Chitosan	Intranasal SARS-CoV-2 vaccine	N/A	In vitro, in vivo	Strong and consistent antibody surge, effective neutralization of viruses, enhanced antibody response within 1 week	57
AuNSt	Silica, liposome	DOX	Photothermal with NIR	In vitro	Enhanced cytotoxicity & growth inhibition to cancer cells; capable of codelivering hydrophilic-hydrophobic drugs	58
AuNSt	i-motif DNA	DOX	NIR, pH	In vitro	Effectively triggered drug release, good biocompatibility, combined photothermal effect enhanced therapeutic efficiency	59
Fe ₃ O ₄ @AuNSt	FAM-DEVD, PEI, SPDP	RGD-TRAIL and ATAP	External magnetic field	In vitro, in vivo	Successful site-specific delivery to tumor, outstanding inhibition of tumor growth, monitoring of cell apoptosis in real-time	60
AuNSt	Cucurbit[7]uril	Camptothecin	NIR	In vitro	Effective synergistic anticancer photothermal therapy and chemotherapy	61
AuNSt	HApt	HApt	N/A	In vitro	HApt-AuNSt inhibited cancer cell proliferation with induced cell death	62
AuNSt	Lipid bilayer nano-membrane	DOX	N/A	In vitro, in vivo	Significantly enhanced delivery of DOX to cancer cells compared to spherical NPs	63
AuNSt	EpCAM antibody	siRNA, mRNA	NIR laser	In vitro	Site-specific optoporation and selective delivery	64
AuNSt	ZIF-8	Bis-benzimide	NIR light	In vitro	High drug loading and thermoplasmonic capabilities together with aqueous and cellular stability	65
Fe ₃ O ₄ @SiO ₂ -AuNSt	Mesoporous silica	Paclitaxel	NIR laser	In vitro	Successful drug delivery and photothermal therapy with low toxicity	66
AuNSt @SiO ₂	Octadecyltrimethoxysilane, heneicosane	DOX	NIR laser	In vitro	Optically controlled release with no cytotoxicity even at low laser power density	67
AuNSt	HApt	DOX	NIR light	In vitro	High degree of on-demand DOX release with enhanced toxicity against cancer cells	68
AuNSt	Penetrating peptide	Ru(II) complex	NIR light	In vitro, in vivo	Luminescence-tracked drug delivery with high biocompatibility, hemocompatibility and low toxicity	69

Abbreviations: SARS-CoV-2: severe acute respiratory syndrome coronavirus 2, DOX: doxorubicin, NIR: near-infrared, AuNS: gold nanostar, DEVD-FAM: carboxyfluorescein-conjugated caspase 3-responsive aspartic-glycine-valine-aspartic acid, PEI: polyethylenimine, SPSP: N-succinimidyl 3-(2-pyridyldithio) propionate, RGD: arginine-glycine-aspartic acid, TRAIL: tumor-necrosis-factor-related apoptosis-inducing ligand, ATAP: amphiphilic tail-anchoring peptide, HApt: anti-HER2 aptamer, NPs: nanoparticles, EpCAM: epithelial cell adhesion molecule, ZIF-8: zeolitic-imidazolate-framework-8.

The current COVID-19 global pandemic caused by the virus SARS-CoV-2 and its variants has been devastating the world medically, economically, and socially. Efficient and safe vaccines are arguably still the most feasible long-term approach to ending this medical crisis, and nanotechnology has contributed significantly to that effort.⁷⁰ In a recent study,⁵⁷ Kumar et al. studied the effects of intranasally administered AuNSt-based DNA vaccines against SARS-CoV-2 in mouse models. The work used chitosan-coated AuNSts to encapsulate the encoded sequence of SARS-CoV-2 S protein DNA (pcDNA) to form a vaccine delivery nanocarrier. Delivery of the AuNSt-based DNA vaccine yielded successful expression of the antigen in the respiratory mucosa and lungs of mouse models, which led to an enhanced antibody response, as shown in Figure 1.12. The antibody response developed as early as 1 week after the administration of 3 doses of DNA vaccine and was consistently elevated for several months without a significant decline in both the BALB/c and C57BL/6J mouse models.

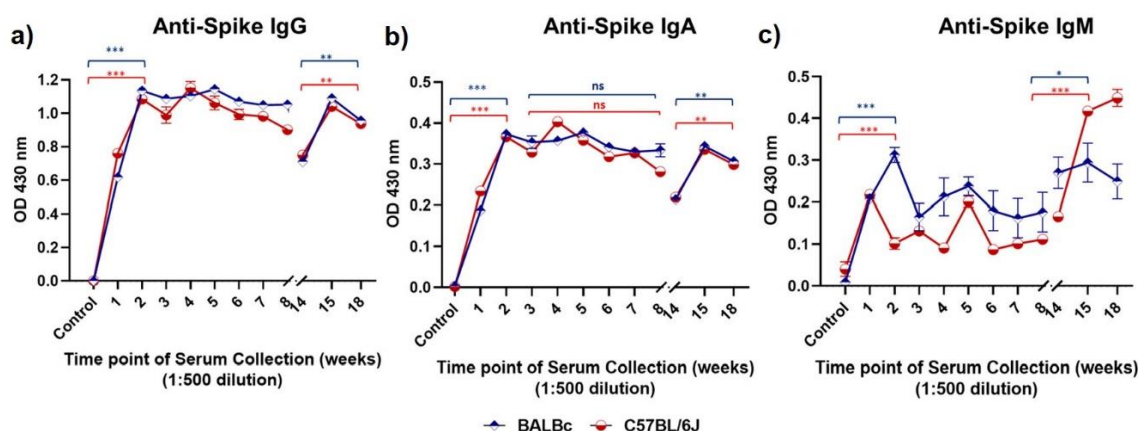


Figure 1.12. Antibody-mediated immune responses after intranasal immunization of SARS-CoV-2 S protein DNA vaccine using AuNSt-chitosan measured against (a) IgG, (b) IgA, and (c) IgM levels over 18 weeks. Adapted with permission from reference 57. Copyright 2021 American Chemical Society.

The AuNSt-facilitated DNA vaccine also effectively neutralized pseudoviruses expressing the S proteins of different SARS-CoV-2 variants (Wuhan, beta, and D614G), as shown in Figure 1.13.⁵⁷ The findings of this work highlight the merits of gold nanostars as carriers for delivering genetic vaccines and therapy both in vitro and in vivo. It also demonstrated a promising approach for developing a long-lasting and wide-spectrum antibody response to combat the increasing number of SARS-CoV-2 variants.

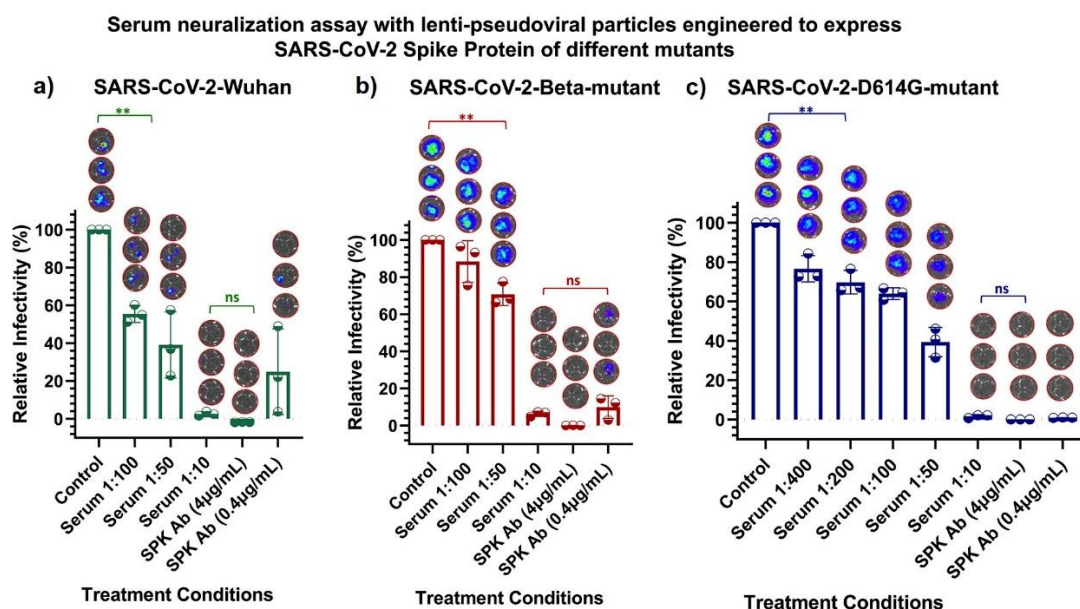


Figure 1.13. Inhibition of infectivity against lentiviral particles engineered with (a) S protein SARS-CoV-2-Wuhan, (b) SARS-CoV-2-beta mutant, (c) SARS-CoV-2-D614G mutant variants. Adapted with permission from reference 57. Copyright 2021 American Chemical Society. SPK Ab: simultaneous pancreas kidney antigen.

In addition to antiviral applications, cancer-related therapy has been a major focus of advanced nanoparticle-based drug delivery technologies.⁷¹ The development of plasmonic nanostars in recent years has facilitated the use of this promising new type of nanostructure for biomedical targeted delivery technologies.⁶⁷ Montoto et al. developed a laser-induced delivery method for anticancer drugs based on gold nanostars.⁶⁷ The silica-coated AuNSts

were used as doxorubicin (Dox) nanocarriers (Figures 1.14a and b), which could be triggered by an NIR laser to release the anticancer drug through the melting of the encapsulating paraffin, as illustrated in Figure 1.14a. Notably, the cumulative release of Dox over time can be adjusted by changing the laser power (Figure 1.14c). With proper dosages of Dox and incubation times after drug delivery, an eradication of ~95% of HeLa cancer cells was achieved after 10-15 min of laser irradiation and 48 h of incubation (Figure 1.14d). This level of cancer cell eradication is significantly higher than those of gold nanocages⁷² or nanorods⁷³ under similar conditions, indicating the advantage of plasmonic nanostars. The Dox-loaded AuNSt carriers also showed no leakage of the cargo in an aqueous solution before significant payload delivery was observed upon NIR irradiation, thus minimizing the cytotoxicity of the drug toward noncancer cells. The results demonstrated in this report show the potential of AuNSts and other plasmonic nanostars as components of efficient drug delivery methods with less collateral damage than traditional treatments such as chemo- or radiotherapy.

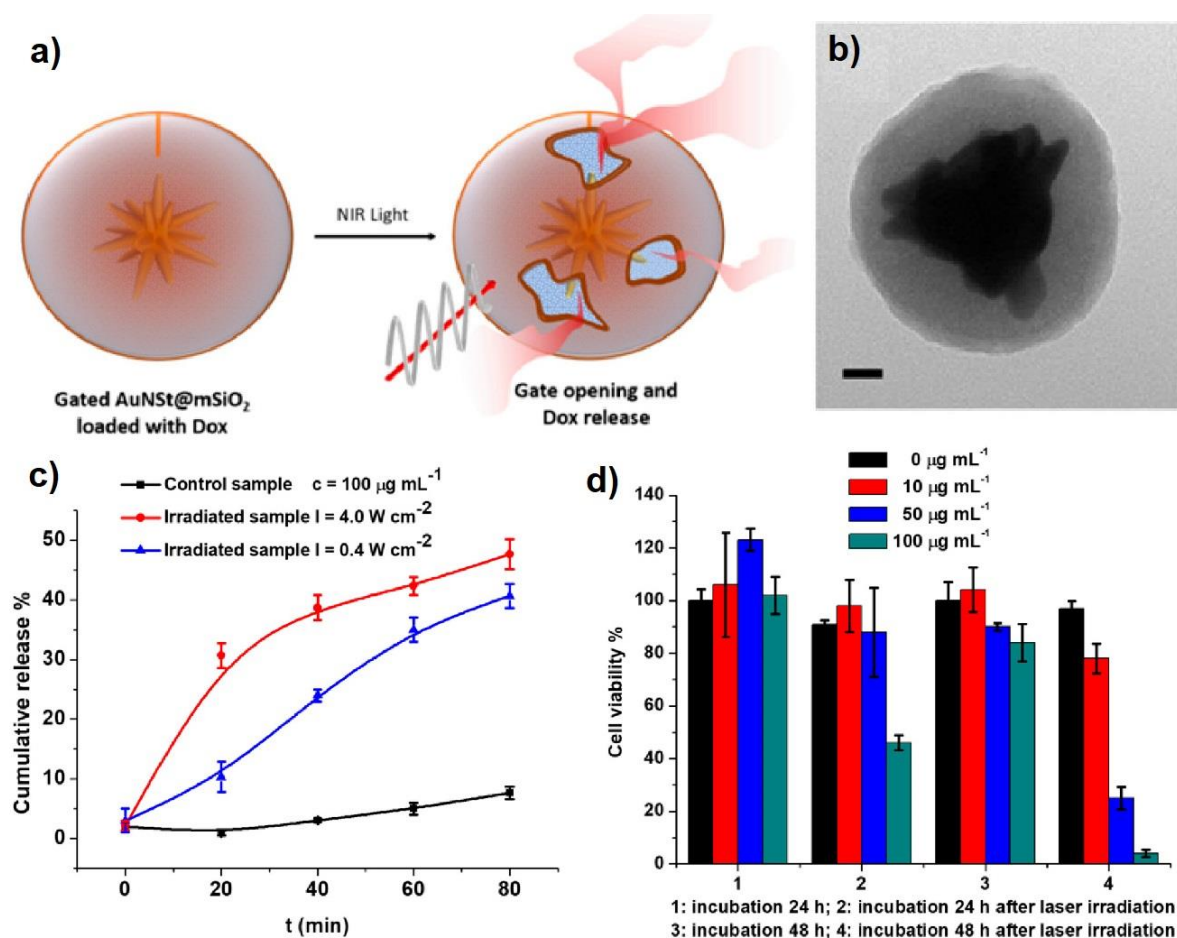


Figure 1.14. (a) Illustration and (b) transmission electron microscopy image of the drug release system based on AuNSts coated with mesoporous silica shells and paraffin as a thermosensitive release gate. (c) Cumulative release of Dox from AuNSt-based nanocarriers under different laser powers. (d) Viability of HeLa cancer cells in the presence of the Dox-loaded AuNSt drug carriers at different incubation times and concentrations upon 808 nm laser irradiation at 4 W/cm² for 15 min. Adapted with permission from reference 67. Copyright 2018 American Chemical Society.

Many other recent reports on nanostar-based drug delivery methods are summarized in Table 3, with delivery targets ranging from anticancer drugs^{58,59,63} to genetic agents.^{62,64} Many of these nanostar-based vaccine and drug delivery methods utilized the large numbers of hot spots present on plasmonic nanostars to enhance light-triggered heating effects, which enabled faster drug release compared to those of other plasmonic nanostructures. Furthermore, the more efficient heating facilitated by plasmonic nanostars can also enable even more

effective medical techniques through the incorporation of photothermal therapy into synergistic technologies, which will be discussed in more detail in Section 1.3.1.5 below.

1.3.1.3. Photothermal and Photodynamic Therapy with Plasmonic Nanostars

Localized surface plasmon resonance (LSPR), the collective resonant oscillation of free electrons in metal nanostructures under suitable electromagnetic irradiation, is a distinctive feature of plasmonic nanostructures.³ Through the occurrence of LSPR, nanostructures can convert electromagnetic radiation energy into heat, which in turn can eliminate tumors through photothermal therapy (PTT) or can be used for other purposes. Furthermore, in combination with suitable photosensitizers, plasmonic nanostructures can trigger the production of radical oxygen species (ROSs) or other photochemical processes.⁷⁴ These ROSs can be used for photodynamic therapy (PDT) in anticancer treatments with higher efficacy and fewer side effects compared to treatments involving the use of conventional plasmonic nanostructures. Recent works in PTT and PDT based on plasmonic nanostars are listed in detail in Table 1.4.

Table 1.4. Photothermal and Photodynamic Therapy Applications of Plasmonic Nanostars

Core NP	Combinatory Components	Therapy Target	Irradiation Source, Power Density	Level of Study	Key Results	Ref.
AuNSt	Anti-PD-L1 antibody	MB49 bladder cancer	808 nm laser, 0.6 W/cm ²	In vivo	Complete eradication of and long-lasting immunity against MB49 cancer cells in mice	75
AuNSt	ZIF-8	Photo-thermal cyclization	808 nm laser, 10 W/cm ²	In vitro	Photothermal-promoted chemical reactions in living cells for light-controlled therapies	76
AuNSt	siHSP72/HA/CD44	Breast cancer	808 nm laser, 1 W/cm ²	In vitro, in vivo	Successfully sensitized TNBC cells for PTT with superior conversion efficacy and hemo-/biocompatibility	77
AuNSt	Glycopolymer	Cancer	808 nm laser, 1 W/cm ²	In vitro, in vivo	Selectively targeted and photothermally reduced tumors with excellent biocompatibility	78
AuNSt	GO	Breast cancer	808 nm laser, 0.75 W/cm ²	In vitro	Cellular internalization and remarkable photothermal effect with extremely low cytotoxicity	79
AuNSt	NLS, HA, CD44	Cancer	808 nm laser, 1 W/cm ²	In vitro, in vivo	High-accuracy tumor targeting, internalizing and photothermal anticancer effect	80
AuNSt	N/A	Cervical cancer	980 nm laser, 1.34 W/cm ²	In vitro	Exhibited significantly higher photothermal transduction than AuNR and Au nanosphere as well as effective cancer cell ablation	81
AuNSt @ MnO ₂	PEI, Ce6, HA	Cancer cells	808 nm (3 W/cm ²) and 650 nm (30 mW/cm ²)	In vitro	PTT/PDT synergistic therapy killed cancer cells much more effectively than single therapy	82
AuNSt -dPG	HA, RA	CSCs eradication	808 nm laser, 1 W/cm ²	In vitro, in vivo	Effective elimination of the self-renewal of CSCs and tumor growth and prevention of relapse	83
AuNSt	Pt	MDR tumor	NIR laser, 0.9 W/cm ²	In vitro, in vivo	Efficient photothermal ablation and ferroptosis of MDR tumors by Pt-AuNSt with good biocompatibility	84

Abbreviations: PD-L1: programmed death-ligand 1, PDA: polydopamine, siHSP72: siRNA against heat shock protein 72, HA: hyaluronic acid, TNBC: triple-negative breast cancer, CD44: TNBC-overexpressed surface molecule, PTT: photothermal therapy, MIL-101-NH₂(Fe): amine-functionalized metal-organic framework, ZD2: TNBC-targeted peptide, NLS: nuclear localization sequence, N/A: not applicable, PEI: polyethylenimine, HA: hyaluronic acid, PDT: photodynamic therapy, dPG: dendritic polyglycerol, HA: hyaluronic acid, RA: retinoic acid, CSCs: cancer stem cells, MDR: multidrug-resistant.

In a recent report,⁸³ Haag and coworkers developed a photothermal therapy for efficiently eradicating breast cancer stem cells (CSCs) both in vitro and in vivo using a AuNSt-based nanoplatform. In this work, the authors functionalized AuNSts with dendritic polyglycerol (dPG) for better biocompatibility, hyaluronic acid (HA) for effective CSC targeting, and retinoic acid (RA) for the differentiation of breast CSC types (Figure 1.15).

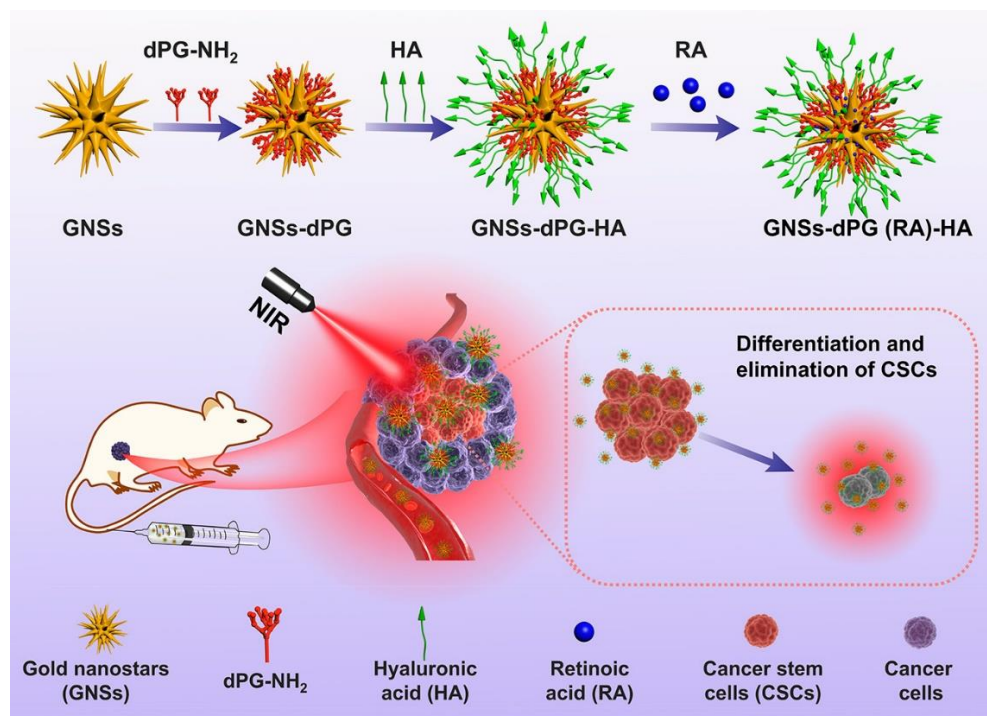


Figure 1.15. Schematic of RA-loaded AuNSt-dPG for targeted PTT in breast cancer stem cells. Reproduced with permission from reference 83. Copyright 2021 American Chemical Society.

After being illuminated by an NIR laser for 10 min in the presence of the AuNSt-dPG-RA-HA nanocomplex at a concentration of 40 $\mu\text{g/mL}$, MDA-MB-231 breast cancer cells were almost totally eradicated, as shown in Figure 1.16a.⁸³ This level of MDA-MB-231 cancer cell eradication was significantly greater than those achieved by gold clusters⁸⁵ or gold nanorods,^{86,87} demonstrating the comparatively greater photothermal performance of plasmonic nanostars over those of conventional plasmonic nanostructures. The self-renewal

of breast CSCs and tumor growth were also efficiently inhibited. This work also showed how the suppression of CSCs inhibited the formation and growth of the tumor by comparing the tumor sizes in mice treated with different AuNSt-based nanoparticles with/without laser irradiation. The results in Figure 1.16b revealed the significant inhibition of tumor growth and reduction in tumor size in mice treated with the AuNSt-dPG-RA-HA nanocomplex and illuminated with an NIR laser. In the mice treated with AuNSt-dPG-RA-HA but without NIR laser irradiation, the tumor size remained almost the same as that in the control group after 14 days (Figures 1.16b and c). The results highlighted the efficacy of the photothermal effect of the AuNSt-based nanoplatfroms on CSC elimination and tumor reduction. These findings demonstrate the great potential of AuNSt-based platforms for efficient targeted eradication and prevention of cancer relapse.

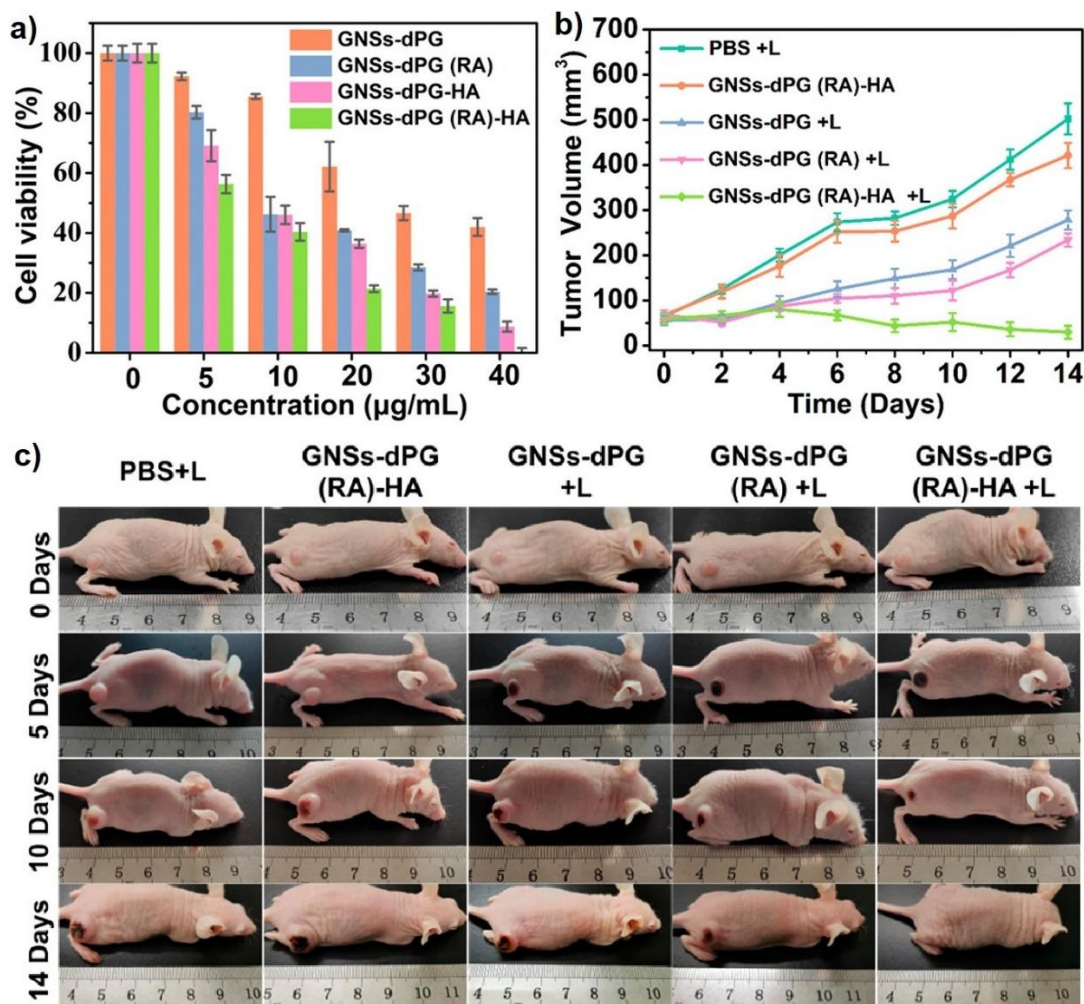


Figure 1.16. (a) Viabilities of MDA-MB-231 breast cancer cells treated with different AuNSt-based particles under laser irradiation for 10 min. (b) Tumor growth curves and (c) digital images of 4T1 tumor-bearing mice on different days injected with different AuNSt-based nanoparticles and treated with laser (+L). Adapted with permission from reference 83. Copyright 2021 American Chemical Society.

In addition to photothermal therapy, photodynamic therapy, such as those involving photopromoted chemical reactions, has been another promising approach for light-controlled therapies enabled by plasmonic nanostructures.⁸⁸ In one of the few relevant reported studies in the field,⁷⁶ Pino and coworkers described the use of AuNSt-based core-shell nanoreactors (NRs) to carry out NIR-driven photothermal cyclizations inside living cells, as illustrated in Figure 1.17.

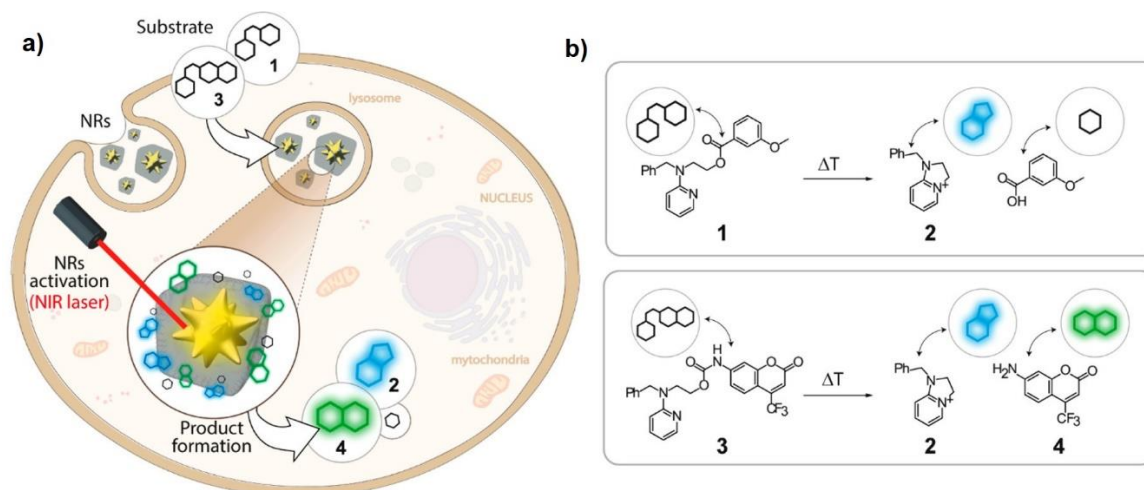


Figure 1.17. (a) Core-shell AuNSt-ZIF-8 nanoreactors for the photogated intracellular transformation of thermolabile substrates inside living cells (thermocyclization). (b) Reacting probes used (substrates 1 and 3) and fluorescent products (2 and 4) arising from the thermoplasmonic-promoted reaction. Adapted with permission from reference 76. Copyright 2021 American Chemical Society.

The nanoreactors included a AuNSt core embedded within a metal-organic framework (MOF) based on a polymer-stabilized zeolitic imidazole framework-8 (ZIF-8) (Figures 1.18a and b).⁷⁶ These nanoreactors were tested with HeLa cells, and the results showed that at low molar percentages of NR (%NR), a 98% yield of product 2 was obtained, as shown in Figure 1.18c (blue bar). The result demonstrated the feasibility of photothermal-promoted chemical reactions in the interior of living cells using AuNSt-MOF nanocomposites upon NIR irradiation. Thus, this report further elaborated on the potential scope of AuNSts for light-controlled therapies in addition to photothermal therapy.

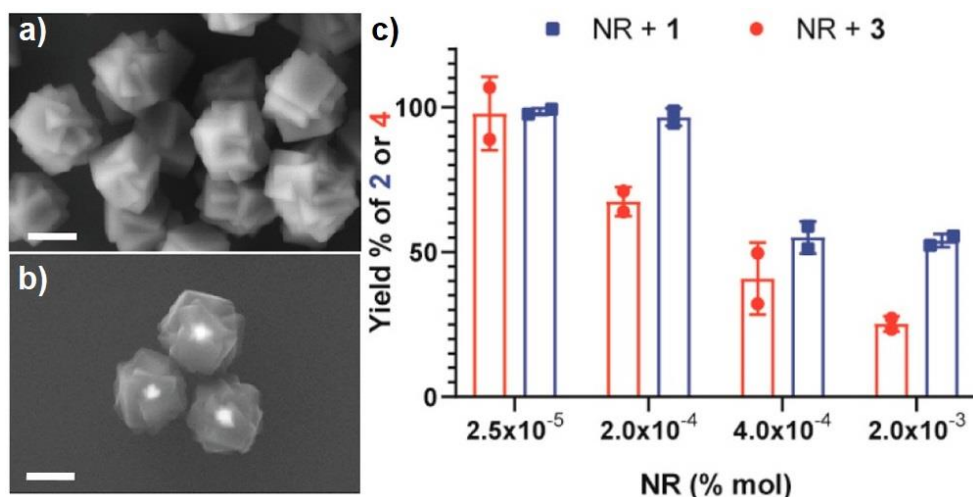


Figure 1.18. Scanning electron images of the AuNSt-ZIF-8 nanoreactors taken at (a) 3 kV and (b) 20 kV with a 200 nm scale bar. (c) Yields of product 2 (blue bars) and product 4 (red bars) after NIR treatment (8 W/cm^2 for 2 min) of substrate 1 or 3 with NRs dispersed in water (0.2 nM and 0.04 pmol) with different NR/substrate molar ratios. Adapted with permission from reference 76. Copyright 2021 American Chemical Society.

Other recent studies on the photothermal and photodynamic applications of plasmonic nanostars are summarized in Table 1.4. The majority of these studies focus on laser-activated therapy for cancer treatments ranging from breast^{77,79} and cervical⁸¹ to bladder cancer.⁷⁵ This myopic focus indicates the great potential for further explorations of plasmonic nanostars in regard to the light-enabled treatments of other noncancer diseases, such as viral infection.

1.3.1.4. Antibacterial Applications of Plasmonic Nanostars

Bacterial infections have a history as intractable public health problems, especially in developing countries. The development of nanomaterials has introduced new strategies for developing more efficient methods for the treatment of bacterium-induced diseases. By using a suitable stimulus, the heat and/or ROSs generated by nanostructures can circumvent the ever-increasing antibiotic resistance of bacteria, which is becoming a great threat to human society.⁸⁹ Due to their unique photothermal heating, ROS-generating properties, or even their

spiky morphologies, plasmonic nanostars have been studied and reported in many research efforts for antibacterial applications, as summarized in Table 1.5.

Table 1.5. Antibacterial Applications of Plasmonic Nanostars

Core NP	Combinatory Components	Target	Antibacterial Mechanism	Level of Study	Key Results	Ref.
AuNSt	rGO	MDR bacteria	Photothermal lysis	In vitro	Significantly enhanced inhibition and photothermal lysis of MRSA bacteria with high biocompatibility	90
AuNSt @PE	PSS, PDADMAC	Gram (+) and gram (-) bacteria	Chemo-photothermal effect	In vitro, in vivo	Synergistic chemo-photothermal elimination of bacterial infection and promoted wound healing	91
AuNSt	CV dye	Gram (+) and gram (-) bacteria	ROS generation	In vitro	Great antimicrobial activity with 5 and 2.5 orders of magnitude enhancement regarding Gram (+) and Gram (-) bacteria, respectively	92
AgNSt	N/A	P. aeruginosa, S. aureus	Silver antibacterial effect	In vitro	AgNSts showed greater potential for biocidal effects than when used in suspension	93
AuNSt	N/A	Propionibacterium acnes	Membrane destruction by AuNS	In vitro	Significant antibacterial effects against Propionibacterium acnes	94
AuNSt	Vancomycin	MRSA bacteria	Photothermal effect	In vitro, in vivo	Selective recognition and elimination of MRSA with satisfactory biocompatibility	95
AuNSt	Thiol monolayer	Planktonic bacteria	Photothermal effect	In vitro	99.99% elimination of bacterial strains even after three months on shelf	96
AuNSt ,AgNP	PVA film	E. coli, S. aureus	Photothermal effect	In vitro, clinical	On-demand, fast antibacterial action with 80-90% death of bacteria in contact with the AuNSt-containing film	97
AuNSt	PVA film	S. aureus	Photothermal effect	In vitro	Efficient bacterial eradication by photothermal effect under NIR irradiation	98
AuNSt	N/A	S. aureus	Photothermal effect	In vitro	AuNSt monolayer efficiently induced cell death in S. aureus	99
AuNSt	N/A	S. aureus	Morphological effect	In vitro	~4-fold increase in antibacterial effect with no indication of cytotoxicity	100

Abbreviations: rGO: reduced graphene oxide, MDR: multidrug-resistant, MRSA: methicillin-resistant Staphylococcus aureus, PE: polyelectrolyte, PSS: poly(sodium-*p*-styrenesulfonate), PDADMAC: polydiallyldimethylammonium chloride, CV: crystal violet, ROS: reactive oxygen species, AgNS: silver nanostar, N/A: not applicable, P. aeruginosa: Pseudomonas aeruginosa, S. aureus: Staphylococcus aureus, MRSA:

methicillin-resistant *Staphylococcus aureus*, PVA: polyvinyl alcohol, *E. coli*: *Escherichia coli*, NIR: near-infrared.

In a recent report,⁹⁵ Han and coworkers demonstrated the use of vancomycin (Van)-modified AuNSts (AuNSt@Van) for the selective targeting and effective eradication of methicillin-resistant *Staphylococcus aureus* (MRSA) bacteria. AuNSt@Van could target MRSA bacteria (as shown in Figure 1.19a), and when laser illumination was applied, the bacterial cell membranes were destroyed, resulting in an increase in the recorded red fluorescence signal arising from propidium iodide fluorescent dye staining (Figure 1.19b).

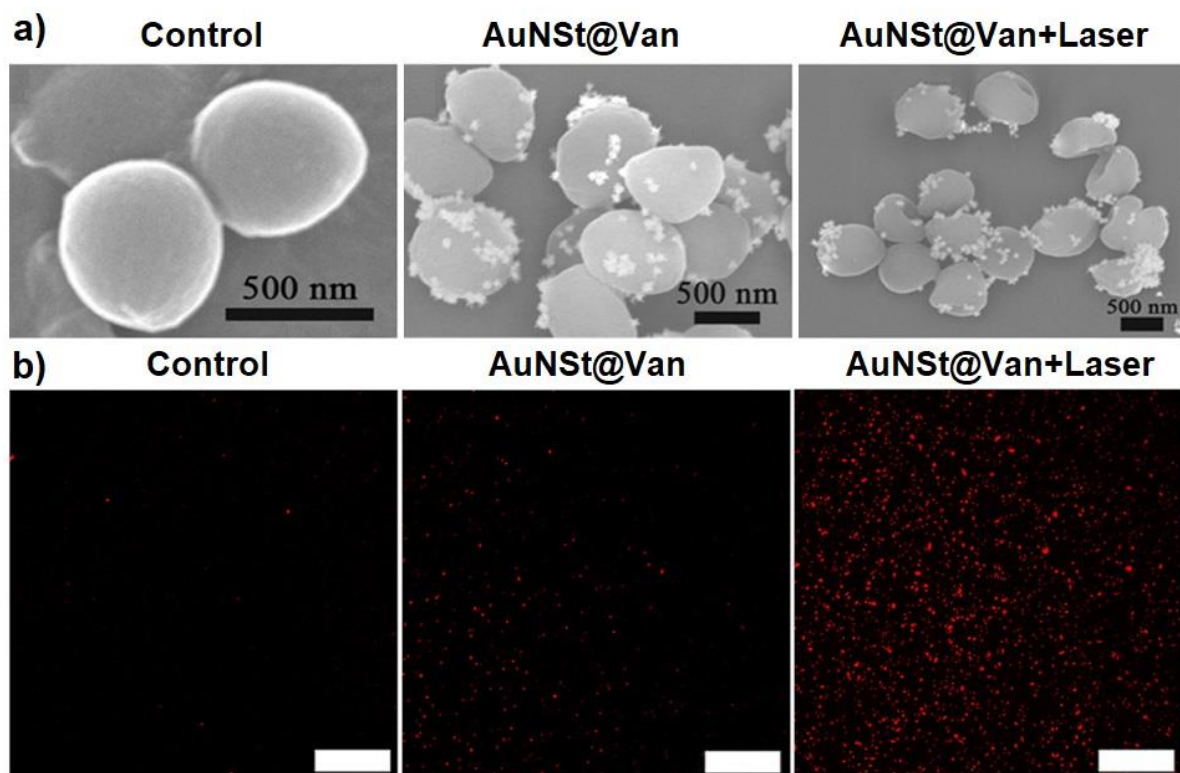


Figure 1.19. (a) Scanning electron microscopy images of MRSA untreated and treated with AuNSt@Van with and without NIR light irradiation. (b) Fluorescent images of MRSA stained by propidium iodide following various treatments. Adapted with permission from reference 95. Copyright 2019 American Chemical Society.

In vivo tests on mice infected with MRSA showed obvious reductions in the wound areas in the mice treated with AuNSt@Van and irradiated with an NIR laser (808 nm, 2.5

W/cm² in 10 min) (Figures 1.20a and b).⁹⁵ After 7 days, the AuNSt@Van-treated and irradiated mice had wound areas reduced to 11.98%, while the wound areas of mice in other groups (untreated, Van treatment, and dark treatment) remained over 45%. These results demonstrated the healing of bacterial infectious wounds promoted by the AuNSt-based treatment. Additionally, these reductions in cancer cell viability and wound area are greater than those of traditional nanoparticles,^{101,102} exhibiting the superior strength of the plasmonic nanostars in antibacterial treatments. Moreover, the antibacterial effect of the treatment was assessed by collecting the bacteria in the wounds of the mice, and the results (Figure 1.20c) showed a significant decrease in the numbers of bacterial colonies in the mice treated with AuNSt@Van, resulting in a bacterial survival rate of 5.26% (Figure 1.20d). Thus, the antibacterial agent designed and studied in this report highlights the potential of plasmonic nanostars in the development of high-selectivity and high-efficiency antibacterial therapy.

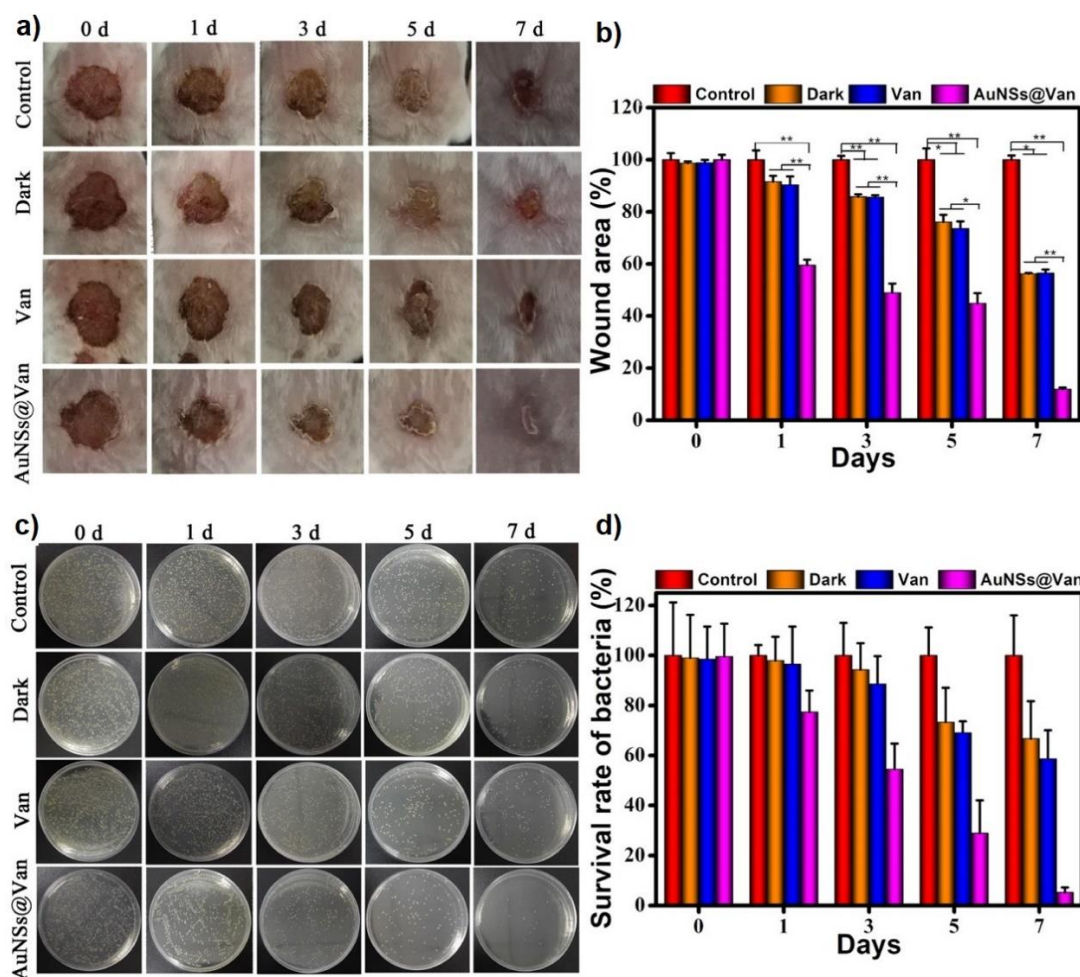


Figure 1.20. (a) Photographs and (b) corresponding wound areas from the four groups of infected mice under different treatments after 0, 1, 3, 5, and 7 days. (c) LB-agar plate images of surviving bacteria and (d) bacterial survival rates. Adapted with permission from reference 95. Copyright 2019 American Chemical Society.

In addition to gold, Bessa et al. reported an investigation of the antibacterial properties of silver nanostar (AgNSt)-coated surfaces.⁹³ Specifically, AgNSts were uniformly coated onto glass surfaces and dried before being used for antibacterial tests. The bactericidal effects of the AgNSt-coated surfaces were observable after 6 h of contact with the inoculated bacteria, *P. aeruginosa* and *S. aureus* (Figure 1.21). The bacteria deposited onto the AgNSt-coated surfaces were not able to replicate and were totally dead after 24 h. This work shows the

potential of the much less-studied silver plasmonic nanostars in the development of effective and affordable platforms for antibacterial applications.

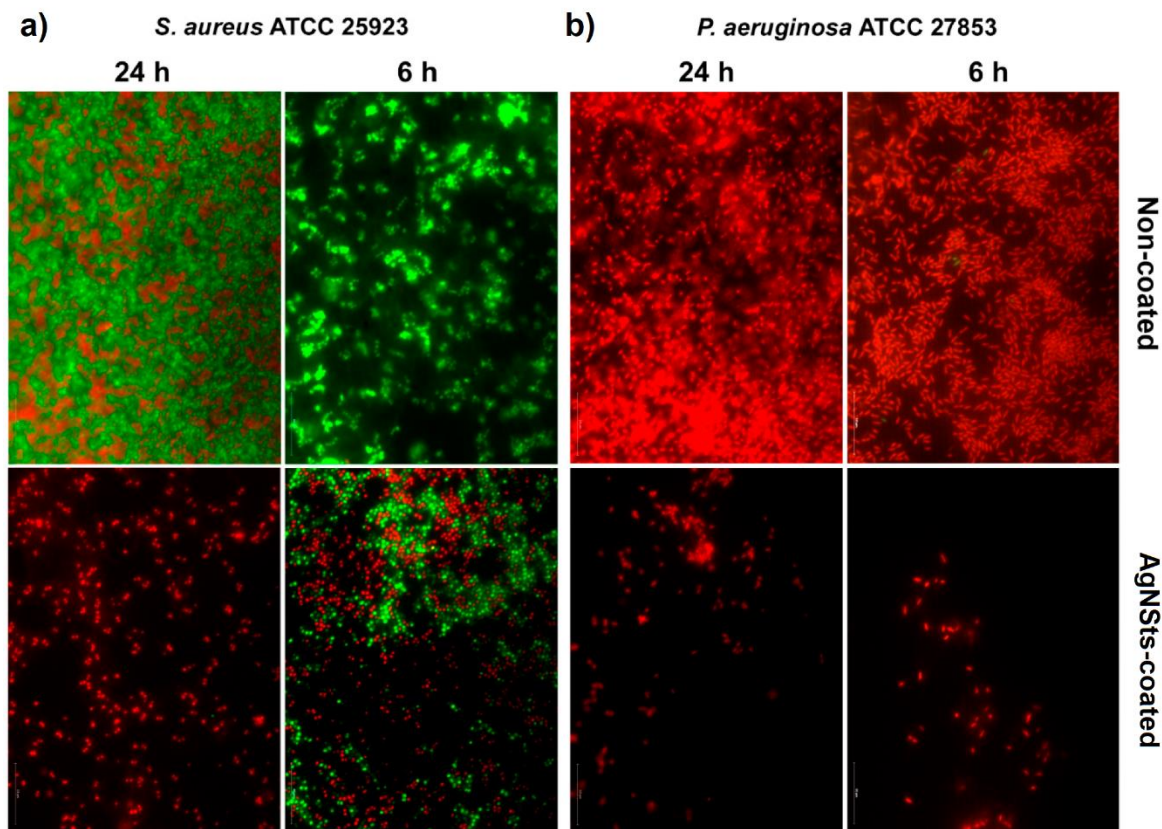


Figure 1.21. Staining images of (a) *S. aureus* ATCC 25923 and (b) *P. aeruginosa* ATCC 27853 bacteria deposited onto noncoated and AgNSt-coated surfaces for 6 and 24 h. Adapted with permission from reference 93. Copyright 2020 MDPI.

Various other reports on the antibacterial applications of plasmonic nanostars are summarized in Table 1.5. These studies used either bare nanostars^{94,99} or nanostars in combination with other conjugates.^{90–92} Most of the studies utilized the photothermal heating induced by the plasmonic nanostars under suitable electromagnetic irradiation as the antibacterial mechanism. These trends suggest the great potential of utilizing plasmonic nanostars, especially affordable AgNSts, for large-scale applications, such as the contact surfaces in hospitals or the glass panels of high-rise buildings.

1.3.1.5. Multifunctional and Theranostic Biomedical Applications of Plasmonic Nanostars

Conventional biomedical diagnostics and therapies mostly involve single modes, mechanisms, or applications, making medical procedures limited in efficacy and/or response time. The development of nanostructure-based technology has enabled the possibility of many different functions or multimode applications on one nanoplatform.^{55,103} Moreover, recent advances in these combinatory approaches, especially those based on plasmonic nanostructures, have allowed the collection of more in-depth medical information or guided therapies with better therapeutic performance and fewer side effects than traditional methods.^{103,104} In the last decade, the development of plasmonic nanostars has made multifunctional medical theranostics even more effective, as summarized in Table 1.6.

Table 1.6. Combined and Multifunctional Biomedical Applications of Plasmonic Nanostars

Core NP	Combinatory Components	Application	Functions/ Mechanisms	Level of Study	Key Results	Ref.
rGO-AuNSt	Lipid bilayer membrane	Pancreatic cancer guided therapy	Imaging-guided dual therapy	In vitro, in vivo	Dual-modal imaging-guided synergistic therapy for pancreatic cancer with negligible toxicity	105
AuNSt	ASON	Tumor margin demarcation	Fluorescent and photothermal	In vitro, in vivo	Precise tumor delineation with high fluorescence contrast and outstanding spatial resolution for guided tumor resection	106
AuNSt @ MOF	ZD2	Breast cancer theranostics	MRI and photothermal	In vitro, in vivo	Efficient MRI imaging and PTT for TNBC visualized theranostics with molecular classification and good biocompatibility	107
GO/AuNSt	Ce6	Cancer theranostics	PDT & PTT with fluorescence imaging	In vitro, in vivo	Efficiently photoablated EMT6 tumor through guided PDT and PTT effect with excellent biocompatibility	108

Table 1.6 Continued

SPION - AuNSt	TDF	Drug delivery	Magnetic and plasmonic	In vitro	Multimodal quantitative imaging and image-guided drug delivery with tunable drug release capacity	109
AuNSt	Fluorescent dye	Tumor-targeting PTT	Fluorescent and plasmonic	In vitro	Demonstrated excellent photothermally induced cell apoptosis with precise assessment of efficacy by fluorescence imaging	110
AuNSt @SiO ₂	DOX	Cancer theranostics	Photoacoustic imaging and chemo-PTT	In vitro, in vivo	Targeted imaging and chemo-photothermal synergistic therapy of tumor at low cytotoxicity	111
AuNSt	IR820/DTX	Prostate cancer theranostics	Dual-mode imaging and PTT/PDT/ChT	In vitro, in vivo	Dual-mode monitoring of tumor targeting and excellent antitumor effects by PTT/PDT/ChT synergistic strategy	112
AuNSt @SiO ₂	FA	FR-targeted theranostics	SERS imaging and PDT	In vitro	FR-specific SERS detection and PDT	113
AuNSt	DOX	Tumor-targeted theranostics	Chemo- and thermo therapy	In vitro	Fluorescence-based monitoring and PTT/ChT synergistic therapeutic efficiency together with targeted delivery of DOX	114
AuNSt	DOX	Cancer theranostics	Fluorescence guided drug delivery	In vitro, in vivo	Activatable visualization and controlled drug delivery for cancer therapy with good biocompatibility	115
SPION-AuNSt	Ce6	Breast cancer guided therapy	Fluorescence imaging and PTT/PDT therapy	In vitro, in vivo	Enhanced delivery efficiency and complete tumor growth suppression as well as tri-modal imaging of tumors	116
AuNSt/Rh-6G	DNA aptamer	SARS-CoV-2	Viral detection and inactivation	In vitro	Rapid diagnosis of SARS-CoV-2 at 8 viruses/mL concentration and infection blocking	117
AuNSt	Cy5-DEVD	Cancer treatment	Fluorescence-guided PTT	In vitro, in vivo	Cellular apoptosis by PTT with fluorescence guiding	118
AuNSt	pHLIPs	Tumor therapy	CT/PA-guided PTT	In vitro, in vivo	Desirable targeting efficiency and improved PTT efficacy with minimal effects on normal tissue	119
AuNSt-PDA	Ce6	Breast cancer photo-theranostics	PA imaging and PTT/PDT	In vitro, in vivo	Enhanced PA imaging and PTT performance that completely eliminated tumors as well as inhibited lung metastasis	120

Table 1.6 Continued

AuNSt	MRSA aptamer	Anti-bacterial treatment	Fluorescence imaging and PTT	In vitro, in vivo	Sensitive MRSA imaging and efficient PTT of diabetic and implanted bone infection	121
AuNSt	PDA	Anticancer theranostics	Multimodal imaging and PTT	In vitro, in vivo	Precise guidance of multimodal imaging and homogeneous photothermal ablation of bulky tumors	122
AuNSt-MOF	DOX	Cancer	Dual-mode imaging and synergistic therapy	In vitro, in vivo	Outstanding chemo-photothermal anticancer synergy while enabling NIR thermal and PA imaging	123
AuNSt	FA	Cancer theranostics	CT imaging and PTT/RT therapy	In vitro	Enhanced anticancer efficacy and good biocompatibility	124
AuNSt	CD147/IR820	Tumor theranostics	PA imaging and PTT/PDT therapy	In vitro, in vivo	Suppression of tumor growth by PTT/PDT synergistic effect under PA guidance	125
AuNSt-Fe ₃ O ₄	N/A	Cancer theranostics	Magnetic guidance and PTT	In vitro, in vivo	Synergistic inhibition of tumor growth under magnetic guidance	126
AuNSt	dsDNA-DOX	MDR breast cancer therapy	Chemo-therapeutic and PTT	In vitro, in vivo	Targeted delivery and controlled drug release with remarkable stability together with synergistic PTT to eliminate MDR tumor	127
AuNSt	Albumin	L929, NIH 3T3, KB cells treatment	CT diagnostics and PTT	In vitro, clinical	Good PTT effect, CT contrast and biocompatibility on three types of tested cells and human blood	128
AuNSt	Anti-H. pylori antibody	H. pylori theranostics	PA imaging and PTT	In vivo	Targeted killing of H. pylori in stomach with orally administered nanoprobes	129
Fe ₃ O ₄ @AuNSt	N/A	Tumor theranostics	CT, MRI, PA	In vitro, in vivo	PTT and PDT capacities without modification; multimodal in vivo imaging and good biocompatibility	130

Abbreviations: AuNSt: gold nanostar, SPION: superparamagnetic iron oxide nanoparticle, TDF: tenofovir disoproxil fumarate, PTT: photothermal therapy, rGO: reduced graphene oxide, ASON: antisense oligonucleotide, MOF: metal-organic framework, TNBC: triple-negative breast cancer, ZD2: TNBC-targeted peptide, MRI: magnetic resonance imaging, GO: graphene oxide, Ce6: Chlorin e6 photosensitizer, PDT: photodynamic therapy, EMT6: xenograft tumor, DOX: doxorubicin, ChT: chemotherapy, IR820: 820 nm near-infrared dye, DTX: docetaxel, FA: folic acid, FR: folate receptor, pHLIPs: pH (low) insertion peptides, CT: computed tomography, PDA: polydopamine, PA: photoacoustic, MRSA: methicillin-resistant *Staphylococcus aureus*, RT: radiotherapy, CD147: transmembrane glycoprotein, dsDNA: double-stranded DNA, MDR: multidrug-resistant, L929: mouse fibroblast, NIH 3T3: embryonic fibroblast, KB: oral epithelial carcinoma, H. pylori: *Helicobacter pylori*.

In a recent report, Jia et al. fabricated AuNSt-based nanocarriers for the imaging-guided gene/photothermal synergistic therapy of pancreatic cancer.¹⁰⁵ The work combined both diagnosis and therapy on one platform, which can allow the recognition and specific binding of receptors on the surfaces of cancer cells. Specifically, the authors coated a positively charged lipid bilayer membrane on reduced graphene oxide@AuNSts (rGADAs) for selective tumor binding before activating dual-mode imaging with thermal (Figure 1.22b) or photoacoustics (Figure 1.22c). The temperatures at the tumor sites were increased to more than 55 °C for tumor ablations within 10 min using the photothermal heating property of AuNSts under laser irradiation (Figure 1.22a) at 24 h postinjection of rGADAs.

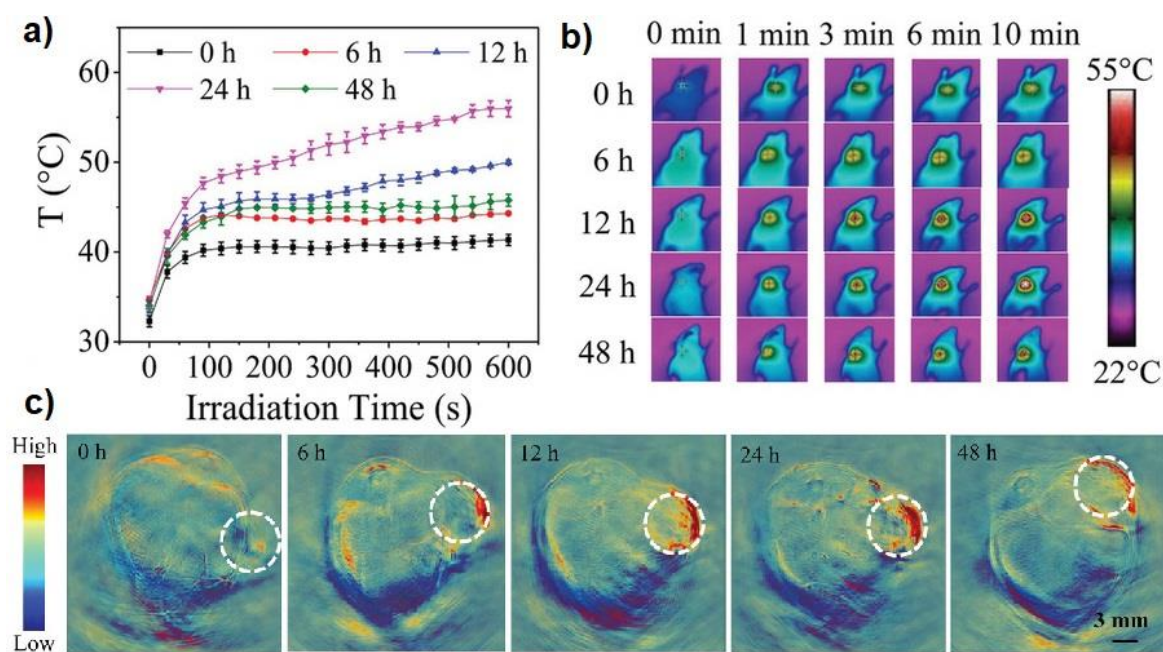


Figure 1.22. (a) Tumor temperature curves and (b) infrared thermal images acquired under 808 nm laser irradiation at a power density of 1.2 W/cm². (c) In vivo photoacoustic images of tumor regions taken at different time points. Adapted with permission from reference 105. Copyright 2020 Wiley.

The rGADAs were also used to deliver a K-Ras gene plasmid (KrasI) for pancreatic cancer gene and photothermal therapy.¹⁰⁵ The experimental results showed an excellent synergistic effect on the tumors that were virtually completely reduced after 14 days (Figure 1.23a), with the highest tumor growth inhibition rate of 98.5% in the gene/photothermal group (rGADA-KrasI+Laser) (Figure 1.23b). The lipid-coated platform was also found to be highly biocompatible. These results show not only the prospect of this platform in clinical applications of guided therapy for pancreatic cancer but also its potential adaptation to other cancers.

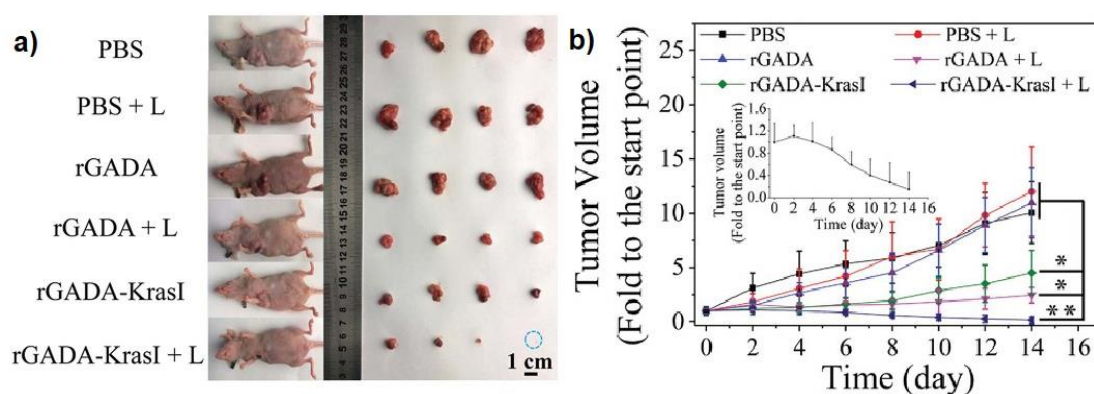


Figure 1.23. (a) Representative images of tumor-bearing nude mice and tumors after various treatments on Day 14. (b) Relative tumor volumes (inset: enlarged curve of the rGADA-KrasI + L (laser) group) after treatment with various combinations of rGADA and KrasI with/without laser irradiation compared to those of the control group treated with PBS solution. Adapted with permission from reference 105. Copyright 2020 Wiley.

In another recently reported endeavor, Xue and coworkers used magnetic-plasmonic nanoheterostructures (MGNs) for multimodal imaging-guided photothermal and photodynamic therapy of triple-negative breast cancer (TNBC).¹¹⁶ The star-shaped nanoheterostructures were coated with photosensitizer Ce6 to induce photothermal and photodynamic capabilities. The MGN@Ce6 nanostructures were then functionalized with cRGD (cyclo-Arg-Gly-Asp-D Phe-Lys) and TPP (4-carboxybutyl triphenylphosphonium)

cationic molecules to form MGN@Ce6@RT nanocomplexes for the specific targeting of cancer cell membranes. The fluorescence imaging results in Figures 1.24a and b, the photoacoustic images in Figure 1.24c, and the thermal images in Figure 1.24d show that the functionalization with cRGD and TPP significantly enhanced the delivery efficiency of MGN@Ce6@RT in TNBC tumors. The multimodal imaging results also showed the capability of the AuNSt-based nanocomplex to enable tumor imaging with various mechanisms, expanding the utility and versatility of this technology.

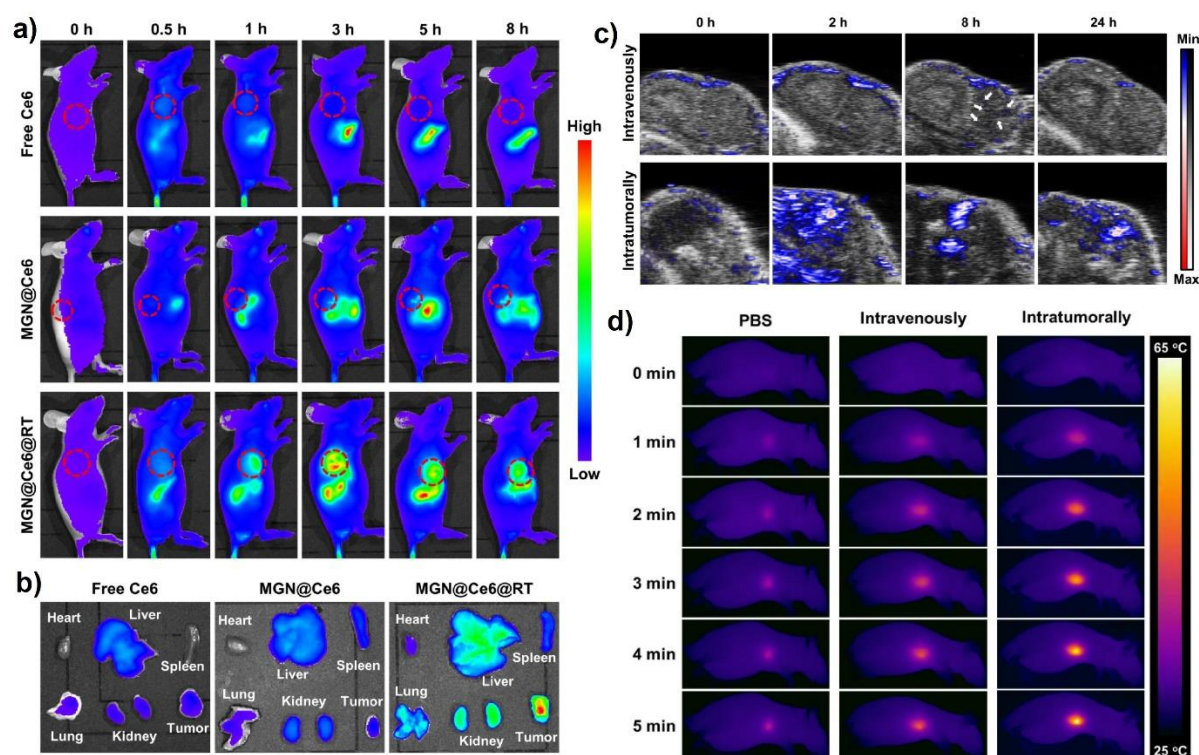


Figure 1.24. Fluorescent images of (a) mice at different times after intravenous injection of different formulations and (b) major organs and tumors collected from mice at 8 h postinjection. In vivo (c) photoacoustic images of tumor tissues and (d) thermal images of tumor-bearing mice at different times before and after intravenous and intratumoral injection of MGN@Ce6@RT. Adapted with permission from reference 116. Copyright 2021 Elsevier.

The antitumor effects of synergistic photothermal/photodynamic therapy were evaluated in tumor-bearing mouse models with nanoheterostructure treatment under 5 min of laser exposure.¹¹⁶ The results (Figures 1.25a and b) showed a remarkable inhibition of tumor growth, especially in mice treated with an intratumoral injection of MGN@Ce6@RT and 606 nm + 808 nm laser irradiation. There was a negligible variation in the average weights (Figure 1.25c) of the different groups of treated mice, implying the high biocompatibility of the AuNSt-based nanostructures.

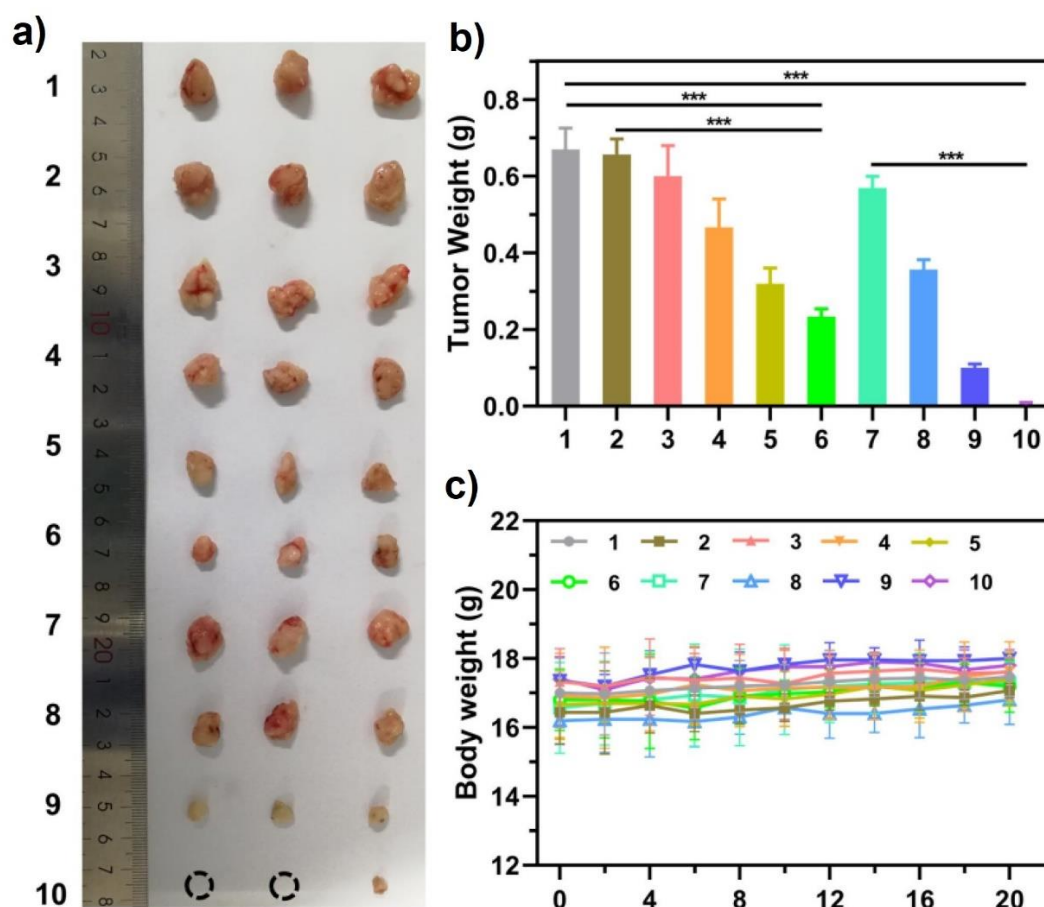


Figure 1.25. (a) Photographs of the sacrificed tumor tissues after various treatments (*** $P < 0.001$). (b) Average tumor weight after various treatments. (c) Average body weight variations during the treatment period. Note that 1–10 represent mouse groups with different treatments: (1) intravenous injection of PBS; (2) intravenous injection of PBS and 660 nm + 808 nm laser irradiation; (3) intravenous injection of MGN@Ce6@RT; (4) intravenous

injection of MGN@Ce6@RT and 660 nm laser irradiation; (5) intravenous injection of MGN@Ce6@RT and 808 nm laser irradiation; (6) intravenous injection of MGN@Ce6@RT and 660 nm + 808 nm laser irradiation; (7) intratumoral injection of MGN@Ce6@RT; (8) intratumoral injection of MGN@Ce6@RT and 660 nm laser irradiation; (9) intratumoral injection of MGN@Ce6@RT and 808 nm laser irradiation; and (10) intratumoral injection of MGN@Ce6@RT and 660 nm + 808 nm laser irradiation. Adapted with permission from reference 116. Copyright 2021 Elsevier.

The large numbers of recently reported studies on plasmonic nanostar-based multifunctional medical techniques, as summarized in Table 1.6, reflect the potential and attractiveness of this unique class of nanostructures in a one-stop approach for developing advanced guided therapy and/or theranostics for complex and detrimental diseases. Most of the reports understandably focused on the treatment of various types of cancer,^{105,107,108,111} but diseases related to SARS-CoV-2¹¹⁷ and bacteria¹²⁹ were also efficiently treated by these nanostar-based platforms, further highlighting the underexplored prospect of plasmonic nanostars in biomedical technology.

1.3.2. Sensing Applications of Plasmonic Nanostars

Plasmonic sensors have been well-known in the photonics and optics community for their extraordinary sensitivity resulting from the enhancement and localization of electromagnetic fields close to the interface of the metal nanostructures and a dielectric.¹³¹ Plasmonic nanostructures have enabled new sensing platforms with much lower limits of detection on a wide range of sensing targets. In addition to their high surface area-to-volume ratios, an enhanced electromagnetic field has been a crucial factor in the success of plasmonic nanostructure-based sensors.¹³² For plasmonic nanostars, both of these advantages are highly superior compared to other conventional plasmonic nanostructures (e.g., nanospheres,

nanorods, nanocubes, nanoprisms, or nanocubes), endowing them with unique potential for allowing plasmonic sensing technologies to achieve even higher performances.

1.3.2.1. Sensing of Biological Analytes with Plasmonic Nanostars

Various noble metal nanostructures have been utilized for biosensing applications by exploiting their unique electronic and optical properties.¹³³ Their LSPR characteristics have enabled fast, real-time, and label-free probing for biologically relevant analytes, where the main challenges are detecting small particles and molecules at ultralow concentrations and fabricating compact devices for point-of-care analyses.¹³⁴ Many of the desirable plasmonic properties for biosensing, such as highly-intensified local fields, large surface area-to-volume ratios, and superior numbers of hot spots, are highly characteristic of plasmonic nanostars, making them attractive for research efforts in biosensing, as summarized in Table 1.7 below.

Table 1.7. Biosensing Applications of Plasmonic Nanostars

Core NP	Combinatory Components	Target	Sensing Mechanism	Key Results	Ref.
AuNSt	AntiTC antibody	Tetra-cycline antibiotic	SPR	AuNSt improved the LOD by 3 orders of magnitude to 10 aM concentration with good selectivity in environmental samples	135
AuNSt	Biotinylated thiol	PSA	RI sensing	Biosensor demonstrated detecting capability at 10 ⁻¹⁷ M concentration of PSA in serum	136
AuNSt	EpCAM aptamer	Cancer biomarker	SERS	Nonlabel detection of EpCAM with single-cell detection for soluble protein	137
AuNSt	CRO	E. coli	SERS	Displayed significantly reduced detection time of biomarker produced by E. coli especially at 1358 cm ⁻¹ peak	138
AuNSt	SCARB2	EV71	SERS	EV71 detected in protein-rich sample within 15 min without the need for temperature-controlled sample incubation	139
AuNSt	N/A	Alkaline phosphatase	Photo-thermal immuno-assay	Large blueshift in the LSPR frequency by silver deposition on the AuNSt triggered by alkaline phosphatase and accompanied by a change in photothermal conversion efficiency	140

Table 1.7 Continued

AuNSt	BSA-Kem	PKA cancer biomarker	SERS	Identified two Raman peaks at 725 and 1395 cm ⁻¹ to distinguish MDA-MB-231 and MCF-7 breast cancer cells that overexpress PKA	141
AuNSt & others	N/A	DNA mutation	SERS	AuNS showed highest SERS activity with sensitive, direct, and rapid identification of DNA mutation in combination with PCR	142
AuNSt	α -ZIKV NS1, α -DENV NS1	Zika and dengue viruses	SERS-based Immuno-assay	15-fold and 7-fold lower LODs for Zika and dengue viruses, respectively	143
AuNSt	COFs	β -lactoglobulin	SERS immuno-assay	LOD of 0.01 ng/mL with a linear range from 25.65 to 6.2 x 10 ⁴ ng/mL by a low-cost, higher-recovery, and lower-cross-reactivity method	144
AuNSt @ SiO ₂	Raman reporter	CEA	SERS	Detected CEA in 30 μ L of whole blood at an LOD of 1 ng/mL with a portable, disposable, point-of-care test method	145
AuNSt	Raman label	Breast cancer miRNA	SERS	Successfully detected short miRNA from real biological cancer sample displaying multiplexed detection capability	146
AuNSt @ Ag	iMS	Nucleic acids	SERS	AuNSt-optical fiber combination enabled direct detection of miRNA in plant tissue extract without complex assays	147
AuNSt	Anti-human IgM, anti-human IgG	SARS-CoV-2	SERS-LFA	SARS-CoV-2 biomarkers detected in COVID-19 serum with at least 10-times higher sensitivity than conventional LFA	148
AuNSt @ SiO ₂	MIP	ENRO	SERS assay	Analytical performance yielded an LOD of 1.5 nM for 10 min of incubation with limited cross-reactivity	149
AuNSt	GO	Serum bilirubin	SERS	Label-free detection of bilirubin in blood serum with two linear ranges of 5-150 μ M and 150-500 μ M together with an LOD of 0.436 μ M	150
AuNSt -TiO ₂	Raman reporter	Leukemia	SERS	Enhanced Raman response indicating chemotherapeutic effects	151
AuNSt	Cortisol antibodies	Cortisol	SERS immuno-assay	AuNSt exhibited great SERS response in a faster and more reproducible immunoassay of biological fluid	152
AuNSt	GO	SARS-CoV-2	Electro-chemical response	Displayed an LOD of 1.68 x 10 ⁻²² μ g/mL and a sensitivity of 0.0048 μ A μ g/mLcm ² toward SARS-CoV-2 biological media	153
AuCu NSt	N/A	SARS-CoV-2	SERS	Consistent SERS signal for SARS-CoV-2 virion particles with well-defined spectra for viral detection	154
AuNSt	Activated GO	SARS-CoV-2	Electro-chemical sensing	Label-free detection of SARS-CoV-2 S1 protein in the blood samples of infected patients in 1 min with an LOD of 0.18 x 10 ⁻¹⁹ %V/V	155

Abbreviations: antiTC: anti-tetracycline, SPR: surface plasmon resonance, LOD: limit of detection, RI: refractive index, PSA: prostate-specific antigen, EpCAM: epithelial cell adhesion molecule, SERS: surface-enhanced Raman spectroscopy, CRO: β -lactam antibiotic ceftriaxone, E. coli: Escherichia coli, EV71: enterovirus 71, SCARB2: recombinant scavenger receptor class B, N/A: not applicable, BSA-Kem: bovine serum albumin-kemptide, PKA: protein kinase A, MDA-MB-231: human breast adenocarcinoma cell, MCF-7: human breast adenocarcinoma cell, PCR: polymerase chain reaction, ZIKV: Zika virus, DENV: dengue virus, NS1: nonstructural protein 1, COFs: covalent organic frameworks, CEA: carcinoembryonic antigen, miRNA: microRNA, iMS: inverse molecular sentinel, SARS-CoV-2: severe acute respiratory syndrome coronavirus 2, LFA: lateral flow assay, IgG: immunoglobulin G, IgG: immunoglobulin G, COVID-19: coronavirus disease 2019, MIP: molecularly imprinted polymer, ENRO: enrofloxacin, GO: graphene oxide, AuCuNS: gold copper nanostar, Rh-6G: rhodamine.

Rapid, sensitive, and on-site detection are critical in any effective response against regional epidemics or global pandemics, such as the COVID-19 pandemic, which has been disrupting the world over the last two years. In a recent report, Srivastav et al. demonstrated a rapid and sensitive lateral flow assay (LFA) based on surface-enhanced Raman scattering (SERS) for SARS-CoV-2 biosensing.¹⁴⁸ The biosensor was based on AuNSTs labeled with an NIR dye as Raman reporters and was able to detect SARS-CoV-2-specific IgG and IgM antibodies, as illustrated in Figure 1.26. The AuNSTs were functionalized with mouse anti-human IgM and anti-human IgG secondary antibodies for IgM and IgG antibody targeting, respectively.

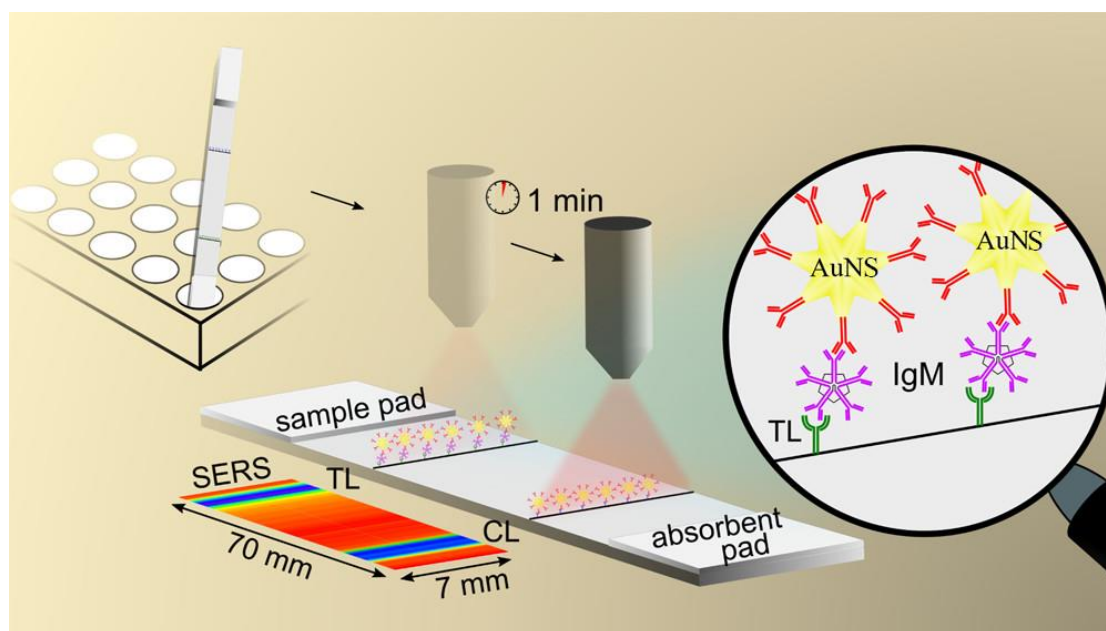


Figure 1.26. Schematics of the SERS-based LFA platform for SARS-CoV-2 IgM detection. TL: test line, CL: control line, and AuNS: gold nanostar. Reproduced with permission from reference 148. Copyright 2021 American Chemical Society.

The AuNS-based LFA test was able to facilitate the detection of both SARS-CoV-2-specific IgM and IgG antibodies in COVID-19-infected patient sera up to 4 months after the infection, as shown in Figure 1.27a.¹⁴⁸ The authors observed a clear decline in IgM signal in comparison to the signal of IgG, which is consistent with the reporting of previous studies that SARS-CoV-2-specific IgG antibodies remain much longer in the sera of infected patients compared to IgM antibodies. Utilizing the high IgM signal in the early period after the infection, the authors investigated the limit of detection (LOD) of this AuNS-based biosensor. The result demonstrated an LOD as low as 100 fg/mL (as displayed in Figure 1.27c), which is 7 orders of magnitude better than the ~ 1 $\mu\text{g/mL}$ of the naked eye detection (Figure 1.27b). The authors estimated that the sensitivity of this method is at least 10 times higher than that of conventional LFAs, highlighting the vast potential of AuNS-based biosensors with ultralow LODs.

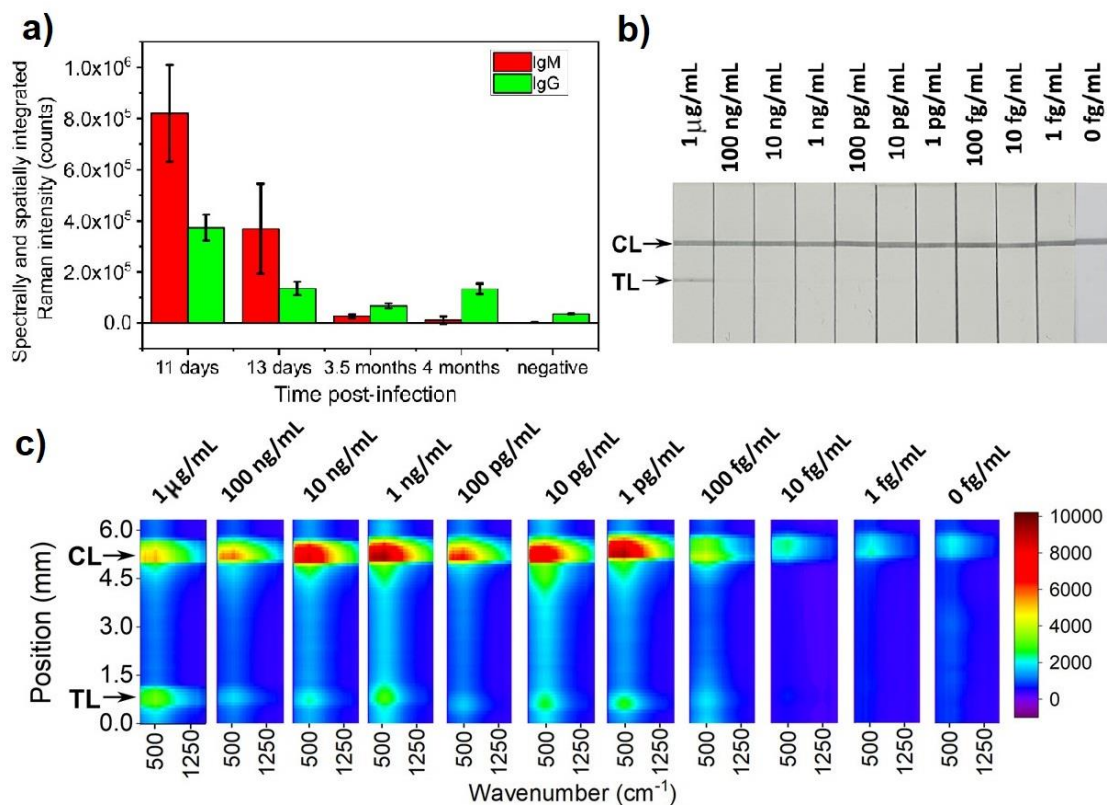


Figure 1.27. (a) Comparison of SARS-CoV-2-specific IgM and IgG antibody expression on AuNSt-based LFA strips. (b) Photograph of the test strips after the assay. (c) SERS-based false-color images of the areas between the sample pads and the absorbent pads on the LFA strips. Adapted with permission from reference 148. Copyright 2021 American Chemical Society.

The severe impacts of cancer on human life have always been of great motivation for the development of early and more efficient diagnostic methods. In a recent study,¹³⁷ Fabris and coworkers described a novel biosensor for the detection and quantification of the cancer biomarker epithelial cell adhesion molecule (EpCAM) at the single-cell level. The biosensor leveraged the field-enhancing characteristic of AuNSts together with improved recognition and capture for MCF-7 and PC-3 cancer cells, which were enabled by functionalization with EpCAM aptamer molecules, as illustrated in Figure 1.28.

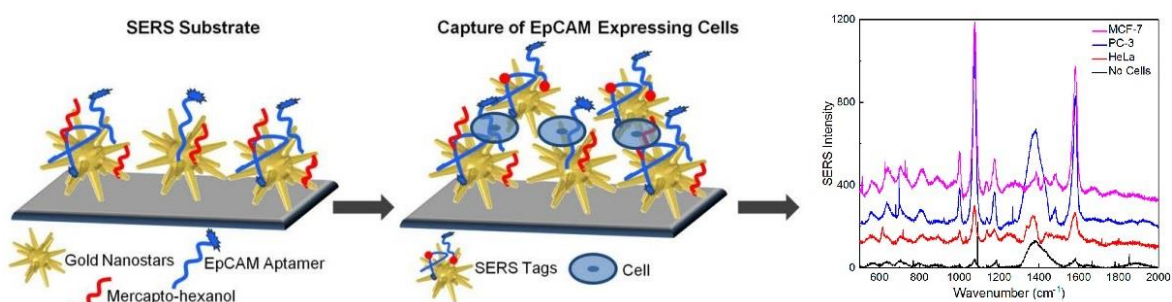


Figure 1.28. Schematics of AuNST-based biosensors used to recognize and capture cancer cells and generate SERS signals. Reproduced with permission from reference 137. Copyright 2018 American Chemical Society.

The plasmonic biosensor generated detectable SERS signals for soluble EpCAM at a detection limit of 10 pM (Figure 1.29a), which showed that the designed sensors could effectively detect soluble proteins.¹³⁷ With the same sensing substrate, by using the correlation between the number of EpCAM molecules per μm^2 and the SERS intensity at 1076 cm^{-1} (Figure 1.29b), it was feasible to identify and quantify biomarker expression at the single-cell level (Figures 1.29b and c). This single-cell level detection is a significant advancement from the thousand-cell level detection attained using gold nanoparticles¹⁵⁶ or nanorods¹⁵⁷ counterparts. This single-cell level quantification enabled discernment among cells carrying phenotype expression levels, allowing early cancer detection or monitoring of the onset of metastasis. These results demonstrate the strength of AuNSTs in plasmon-enabled signal enhancement based on the large numbers of hot spots present in their structures.

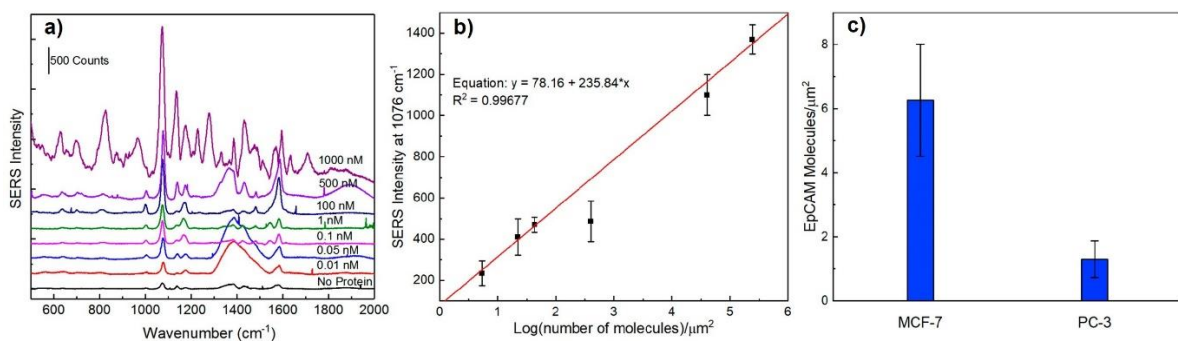


Figure 1.29. (a) SERS spectra generated by the AuNSt-based biosensor for protein capture carried out with increasing concentrations of 17-bp EpCAM aptamers. (b) Linear correlation between the log of the number of EpCAM molecules found per μm^2 area at different protein concentrations and their SERS response at 1076 cm^{-1} , and (c) the calculated number of EpCAM molecules present per μm^2 area on MCF-7 and PC-3 cancer cells. Adapted with permission from reference 137. Copyright 2018 American Chemical Society.

In addition to the detection of SARS-CoV-2^{153–155} and cancer biomarkers,^{141,151} many other studies also reported the development of various AuNSt-based biosensors for the detection of bacteria,¹³⁸ antibiotics,¹³⁵ cortisol,¹⁵² mRNA,¹⁴⁶ or nucleic acids,¹⁴⁷ as summarized in Table 1.7. The wide range of biological analytes detected by these AuNSt-enabled sensing platforms is indicative of the advantages and versatility of plasmonic nanostars.

1.3.2.2. Sensing of Other Analytes Based on Plasmonic Nanostars

In addition to the analytes of biomarker sensing for medical applications, many other analytes also require sensitive and efficient sensing methods for commercial and industrial uses. For this purpose, plasmonic nanostructures have also been demonstrated to be highly sensitive and efficient in the development of advanced sensors.¹⁵⁸ Since these sensors exploit the plasmonic characteristics of those metal nanostructures,¹⁵⁸ nanostars can be expected to greatly amplify the performance of plasmonic sensors with their superior field enhancements and surface areas. Recent works on plasmonic nanostar-based sensors for the detection of nonbiological analytes are summarized in Table 1.8.

Table 1.8. Nonbiological Sensing Applications of Plasmonic Nanostars

Core NP	Combinatory Components	Target	Sensing Mechanism	Key Results	Ref.
AuNSt	Polyaniline	Ammonia gas	Electrical conductivity	7-fold increase in sensitivity toward ammonia gas detection compared to pure polyaniline	159
AuNSt	pNIPAM	Pyrene gas	SERS	Demonstrated efficient trapping for gas phase pollutant pyrene	160
AuNSt	Cy3-cDNA	Hepa-totoxin	SERS, fluorescence	Achieved high sensitivity and selectivity toward hepatotoxin MC-LR in real water samples with high accuracy and reproducibility	161
AuNSt	4-mercapto-benzoic acid	pH	SERS	pH sensing a linear range of 6.5-9.5 for quantifying the pH _i and pH _e of breast cancer cells	162
AuN@SiO ₂	Antibody-SERS tag	MC-LR toxin	SERS immuno-sensing	SERS-based detection of MC-LR toxin at an LOD of 0.014 µg/L with a linear dynamic detection range of 0.01 to 100 µg/L	163
AuNSt	N/A	Gaseous meta-bolites	SERS	High sensitivity, reproducibility and stability toward the gaseous metabolites of foodborne bacteria such as <i>E. coli</i> , <i>E. aureus</i> , and <i>P. aeruginosa</i>	164
AuNSt	N/A	Cu(II) ions	Chemilumi-nescence	First use of AuNS in CTC; remarkably enhanced the CTC signal with an LOD of 0.9 nM and a linear calibration range of 2 nM to 9 µM for environmental and biological samples	165
AuNSt-GQD	Glutamic acid	Insecticide	Electro-chemical response	Ultrahigh sensitivity and selectivity for the detection of acetamiprid with an LOD of 0.37 fM and a linear range of 1 to 10 ⁵ fM	166
AuNSt ,AuNP	N/A	As(III), Hg(II), and Pb(II) ions	Electro-chemical response	AuNSt displayed higher sensing performance than AuNP with LODs of 0.8, 0.5 and 4.3 ppb for As(III), Hg(II) and Pb(II) ions, respectively.	167
AuNSt	4-amino-thiophenol	BPA	SERS-LFA	SERS LOD 20- and 205-times more sensitive than color and visual intensity, respectively	168
AgNSt	AuNP, 1LG	Rh-6G	SERS	137-fold enhancement in Raman response and an LOD of 0.1 pM as well as simultaneous detection of Rh-6G and MB	169
AuNSt	Aptamer	Multi-pesticides	Fluore-scence	LODs of 0.73, 6.7, and 0.74 ng/mL for chlorpyrifos, diazinon, and malathion, respectively, in a multiplexed manner with portable, smartphone-enabled platform	170
AuNSt	2-mercapto-ethanol	Pb ²⁺	Colorimetric method	Detected Pb ²⁺ ions with an LOD of 1.5 pM over the tested interfering Cu ²⁺ ions in water samples	171

Table 1.8 Continued

AuNSt	PEG	Hg ²⁺	SERS	Detected Hg ²⁺ with an LOD of 0.2 ppb in water and coastal seawater samples	172
AgNSt	N/A	Rh-6G	SERS	Detected Rh-6G with an LOD of 11.4 pg and analytical enhancement factor of $\sim 10^7$	173
AuNSt	AO-PAN	Uranyl cation	SERS	Reproducible sorption and detection of uranyl in real-world sample without the need for radioactive tracer and extensive sample pretreatment steps	174
AuNSt	N/A	MG	SERS	Effective control of AuNSt's morphology for enhanced detection of MG at nanomolar concentrations	175
AuNSt	L-Cysteine	Cu ²⁺ ion	SERS	Practical LOD of 10 μ M Cu ²⁺ with remarkable selectivity	176
AuAg NSt	N/A	Rh-6G	SERS	Extremely large enhancement factor of 4×10^{10} together with excellent control of hot-spot location, homogeneity and biocompatibility	177
AuNSt	PDMS substrate	Benzene-thiol	SERS	Enhancement factor of 1.9×10^8 even under 100 cycles of physical stimuli	178
AuNSt	AO-PAN film	Uranyl cation	LSPR, SERS	Detected uranyl with a linear range of ~ 0.3 to 3.4μ g uranyl/mg polymer and quantified the Gibbs free energy of the uranyl-carboxylate interaction as 8.4 ± 0.2 kcal/mol	179
AuNSt	DNA origami	TR dye	SERS	Achieved a SERS enhancement factor of up to 8×10^9 for single-analyte detection with tunable interparticle gap and controlled stoichiometry	180
Au@ AuNSt	Anti-CL antibody	Clenbuterol	Colorimetric /SERS-LFA	Dual-mode highly sensitive detection of clenbuterol with a visual LOD of 5 ng/mL and SERS LOD of 0.05 ng/mL	181

Abbreviations: pNIPAM: poly-*N*-isopropylacrylamide, SERS: surface-enhanced Raman spectroscopy, Cy3-cDNA: cyanine dye-modified complementary DNA, MC-LR: microcystin-LR, pH_i: intracellular pH, pH_e: extracellular pH, N/A: not applicable, E. coli: Escherichia coli, S. aureus: Staphylococcus aureus, and P. aeruginosa: Pseudomonas aeruginosa, CTC: computed tomography of chemiluminescence, LOD: limit of detection, GQD: graphene quantum dot, AuNP: gold nanoparticle, BPA: bisphenol A, LFA: lateral flow assay, AgNSA: silver nanostar array, 1LG: monolayer graphene, Rh-6G: rhodamine 6G, MB: methylene blue, PEG: polyethylene glycol, AuAgNS: gold-silver nanostar, MG: malachite green, LSPR: localized surface plasmon resonance, AO-PAN: amidoximated polyacrylonitrile, TR: Texas red, Anti-CL: anti-clenbuterol.

The presence of heavy metal ions in water has always been a critical, long-term threat to the wellbeing of humans and the environment worldwide due to its association with health problems, such as cancers, skin lesions, cardiovascular diseases, and neurological disorders.^{182,183} Thus, it is extremely important to develop sensitive, reliable, and cost-effective methods for identifying and quantifying these ions in water. In a recent report,¹⁶⁷ Dutta et al. developed electrochemical sensors based on AuNSts for the detection of As(III),

Hg(II), and Pb(II) ions in drinking water. The authors prepared and drop-casted AuNSts onto the carbon paste screen-printed electrodes (CPSPEs) of electrochemical sensors. The AuNSt-based sensors were tested for electrical responses to As(III), Hg(II), and Pb(II) ions in water under a wide range of concentrations, and the results are presented in Figure 1.30. The LODs were 0.8, 0.5, and 4.3 ppb for As(III), Hg(II), and Pb(II) ions, respectively. These LODs were significantly lower than those achieved by counterpart sensors with conventional plasmonic nanostructures for all targeted As(III),^{184,185} Hg(II),^{186,187} and Pb(II) ions.¹⁸⁸ The limits of quantification (LOQs) for the As(III), Hg(II), and Pb(II) ions were identified as 2.5, 1.5, and 13 ppb with linear ranges of 2.5-764.2, 1.5-538.9, and 13-323.6 ppb, respectively.

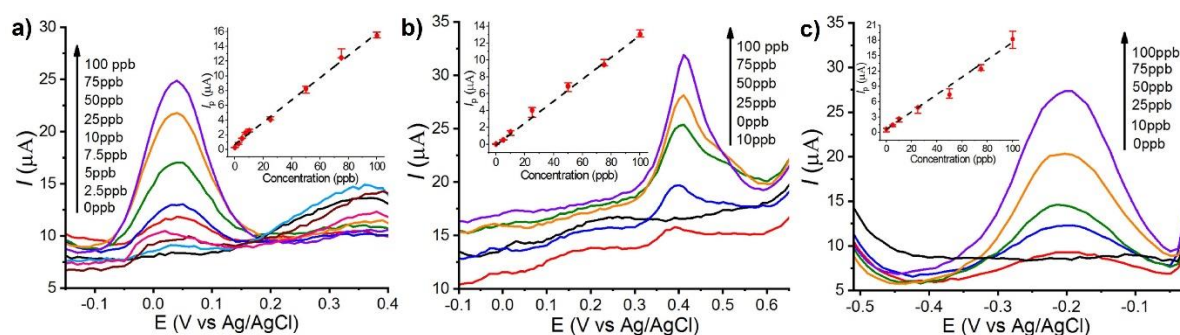


Figure 1.30. Calibration plots of (a) As(III), (b) Hg(II), and (c) Pb(II) ions in 0.1 M HCl on AuNSt-modified CPSPEs at different analyte concentrations. Insets: linear regression models applied to each data plot. Adapted with permission from reference 167. Copyright 2019 Elsevier.

This work also investigated the utility of AuNSt-based CPSPE sensors for the detection of all three analytes in the same solution.¹⁶⁷ The results revealed LODs of 3.57, 11.08, and 20.55 for As(III), Hg(II), and Pb(II) ions, respectively, as well as LOQs of 10.83, 33.59, and 62.26 with linear ranges of 10.8-419.4, 33.6-361.5, and 62.3-215.6 ppb (Figure 1.31). These results indicate the multianalyte detection capability of the AuNSt-based sensor.

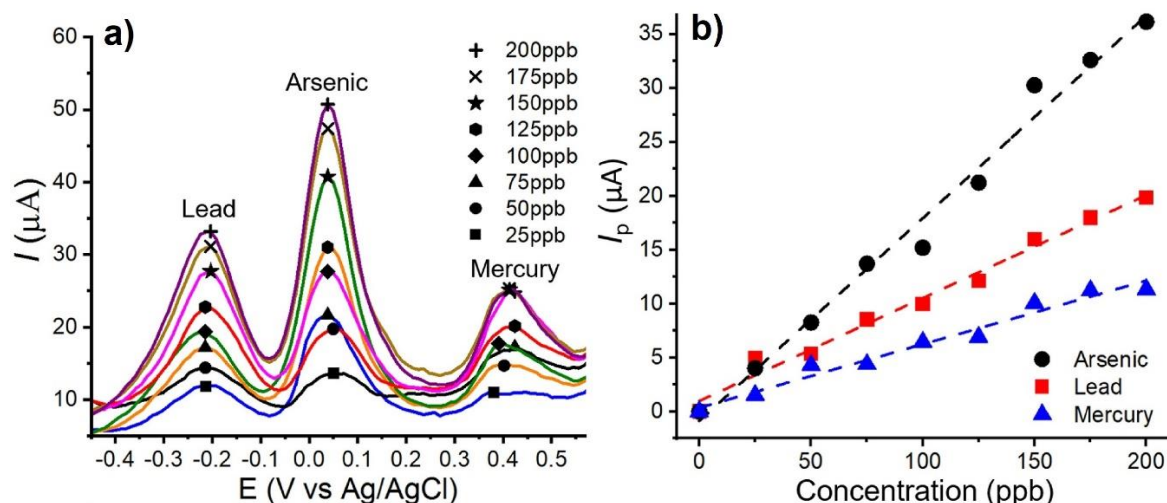


Figure 1.31. (a) Electrical response of the AuNSt-based CPSPE sensor for multianalyte detection of Pb(II), As(III), and Hg(II) ions over the concentration range of 0–200 ppb in 0.1 M HCl and (b) the corresponding linear calibration plots of peak heights vs. concentrations of three heavy metal ions. Adapted with permission from reference 167. Copyright 2019 Elsevier.

The widespread use of pesticides in agricultural activities is a serious concern for human health and the environment, thus necessitating efficient corresponding detection methods. Lin and coworkers reported a fluorescent aptamer-based lateral flow sensor integrated with fluorophore-quencher nanopairs and a smartphone spectrum reader for achieving triple-target detection of chlorpyrifos, diazinon, and malathion insecticides.¹⁷⁰ The authors used aptamers instead of antibodies as recognition elements for better specificity and stability. AuNSts and quantum dot (QD) nanobeads were used to form fluorophore-quencher nanopairs for emitting fluorescence signals in the presence of the targeted pesticides (Figure 1.32).

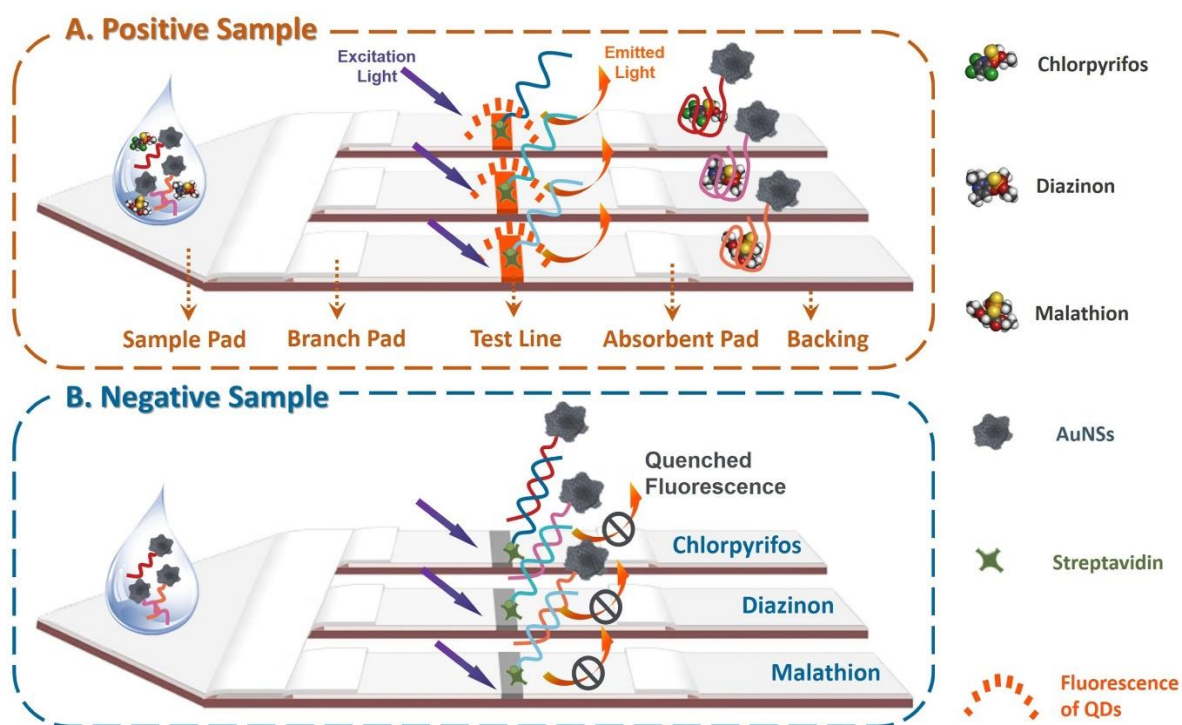


Figure 1.32. Schematics of a fluorescent aptamer-based lateral flow sensor in positive and negative samples. Adapted with permission from reference 170. Copyright 2018 Elsevier.

After optimization, the sensors were tested in the presence of different concentrations of the target pesticides from 100 pg/mL to 100 μ g/mL.¹⁷⁰ The data showed obvious and continuous increases in the intensities of the yellow and red zones when the target concentrations increased (Figure 1.33a). With increasing target concentration, clear maxima near a 610 nm wavelength emerged for all three types of pesticides (Figure 1.33b). By plotting the target peak area at $\sim$ 610 nm vs. the log of the concentration, the authors obtained the standard curves shown in Figure 1.33c and determined LODs of 0.73, 6.7, and 0.74 ng/mL for chlorpyrifos, diazinon, and malathion, respectively. These LODs are lower than the results reported for other sensing platforms based on conventional plasmonic nanostructures for all three pesticides, chlorpyrifos,^{189,190} diazinon¹⁹¹ and malathion.^{192,193} The portable sensing

platform described in this study, with its high sensitivity and reliability, might be suitable for on-site applications of multipesticide quantification.

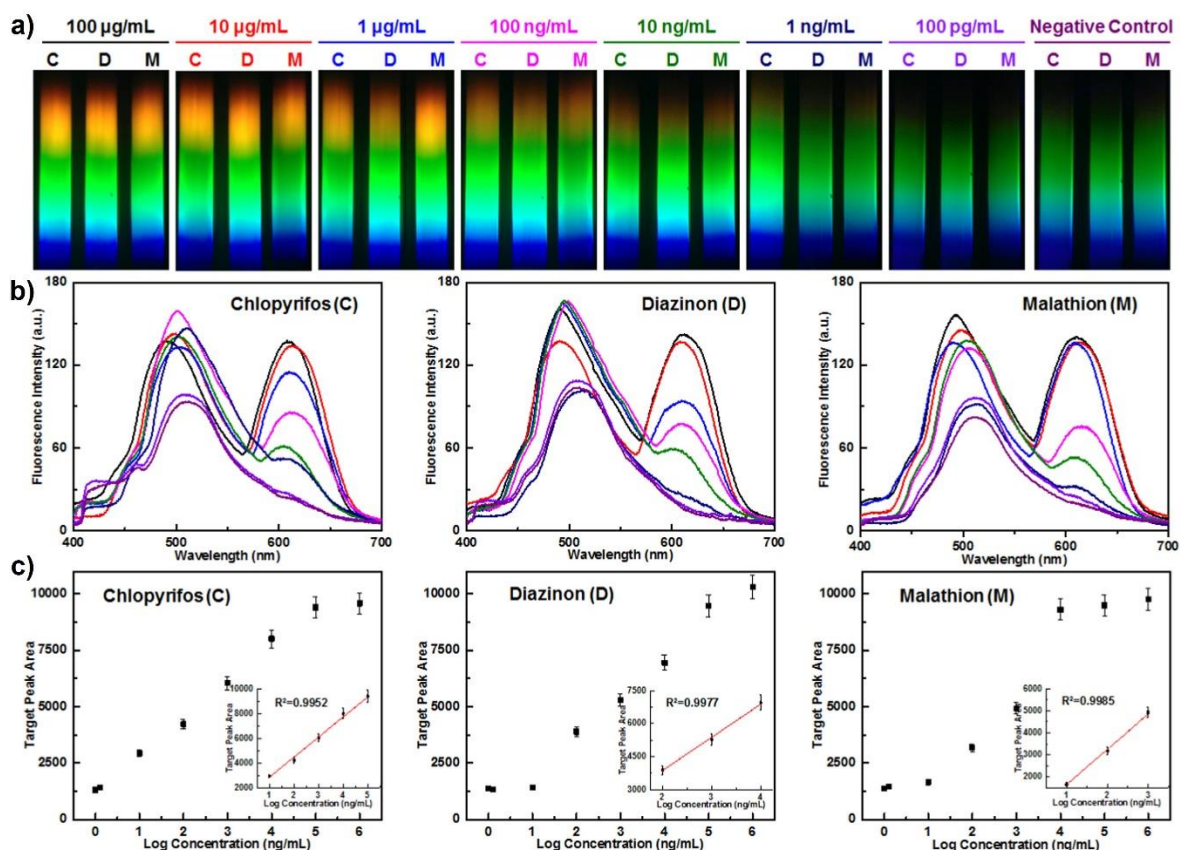


Figure 1.33. (a) Photographs with different target concentrations from 100 pg/mL to 100 $\mu\text{g/mL}$ and negative control. Targets: chlorpyrifos (C), diazinon (D), and malathion (M). (b) Fluorescence curves of chlorpyrifos, diazinon, and malathion obtained by plotting fluorescence spectra versus concentration. (c) Standard curve of chlorpyrifos, diazinon, and malathion obtained by plotting the target peak area versus the log of concentration (ng/mL). Adapted with permission from reference 170. Copyright 2018 Elsevier.

AuNSts were also used to develop sensors for detecting and quantifying various other harmful analytes, from bisphenol A (BPA)¹⁶⁸ and clenbuterol¹⁸¹ to the uranyl cation^{174,179} in radioactive waste, as summarized in Table 1.8. These studies further highlighted the high performance and versatility of AuNSt-based sensors for the detection, quantification, and

monitorization of many nonbioanalytes, which are harmful and toxic to human health and the environment.

1.3.3. Imaging Applications of Plasmonic Nanostars

Imaging is a powerful tool for different applications in modern life, especially in biomedical fields. The development of plasmonic nanotechnology has significantly advanced imaging methods with the use of plasmonic nanoparticles as optically stable bioimaging agents.¹⁹⁴ Thus, plasmonic nanostars are promising platforms for advanced imaging applications. Table 1.9 lists recently reported works based on plasmonic nanostars for imaging.

Table 1.9. Imaging Applications of Plasmonic Nanostars

Core NP	Combinatory Components	Target	Imaging Mechanism	Key Results	Ref.
AuNSt	N/A	MBA molecule	SERS	pH-sensitive label-free Raman mapping of MBA molecules with an enhancement factor of ~ 105 over an area of hundreds of μm^2	195
AuNSt - PS bead	4-mercapto-benzoic acid	Lung epithelial cancer cell	SERS, DF optical, fluorescence	Enhanced cell uptake for the in vitro multimodal imaging of living cells with intermediate yielding high-SERS response	196
AuNSt @Ag @SiO ₂	Raman reporter	Soft- and hard-wood	SERS	AuNSts penetrated both soft- and hardwood for fast SERS imaging even at low quantities without any matrix interactions	197
AuNSt	RGD peptide	Micro-vascu-lature	PAM, OCT	In vitro and in vivo multimodal PAM and OCT visualization with 17-fold and 167% increase in PAM and OCT contrast, respectively	198
AuNSt	pMBA	Tumor cells	SERS, immunoPET	In vivo real-time multimodal multiplexed tumor profiling with dynamic tracking of multiple immunomarkers	199
AuNSt	RGDFC peptide	Cancer cells	SERS	Super-resolution SERS imaging for probing membrane receptor interactions in cells with a localization precision of ~ 6 nm	200

Table 1.9 Continued

AuNSt	DNAzyme	Intra-cellular Ca^{2+}	SERS, fluorescence	Dual-mode monitoring of intracellular Ca^{2+} concentration with good selectivity and sensitivity	201
AuNSt @SiO ₂	Raman reporter	Micro-scopic tumors	SERS	Visualization of different cancer types with a low LOD of 1.5 fM and a ~400-fold improvement in Raman signal	202
AuNSt -Fe ₃ O ₄	4-mercapto-benzoic acid	Alveolar basal epithelial cells	MRI, CT, PA, optical, SERS	Multimodal cellular imaging with many advantages in Janus-like over core-shell structures	203
AuNSt	SERS-labeled antibodies	SMCs	SERS	Visualized the presence SMCs in aortic walls and within atherosclerotic plaque areas by multiplex immuno-SERS microscopy	204
AuNSt	NIR dye	HeLa cells	MEF	19-fold fluorescence enhancement in NIR fluorescence imaging of cells with tunable enhancement factors and high signal-to-noise ratio	205
AuNSt	4-mercapto-pyridine	Lyso-somal pH	SERS	Monitored pH changes in lysosomes during cellular autophagy and apoptosis with high reliability by high-speed SERS imaging	206
AuNSt	4-mercapto-benzoic acid	i-pH	SERS	Visualized local changes in i-pH via high-resolution 3D SERS imaging with good biocompatibility and stability	207
Ag-tip AuNSt	SERS nanotag	Cervical cancer exfoliated cells	SERS	Ultrasensitive dual detection of cervical cancer biomarkers in clinical samples with strong and reproducible signals	208
AuNSt @SiO ₂	N/A	Brain tumors	SERS and MSOT	Accurate three-dimensional depicting of glioblastoma with high specificity and resolution	209

Abbreviations: PS: polystyrene, DF: dark field, SERS: surface-enhanced Raman spectroscopy, N/A: not applicable, MBA: mercaptobenzoic acid, RGDFC: arginine-glycine-aspartic acid-phenylalanine-cysteine, i-pH: intracellular pH, LOD: limit of detection, SMCs: smooth muscle cells, RGD: arginine-glycine-aspartic acid, PAM: photoacoustic microscopy, OCT: optical coherence tomography, pMBA: para-mercaptobenzoic acid, immunoPET: immuno-positron emission tomography, MRI: magnetic resonance imaging, PA: photoacoustic, CT: computed tomography, MEF: metal-enhanced fluorescence. NIR: near-infrared.

In an effort to develop better imaging techniques for brain tumor diagnostics, Neuschmelting et al. used silica-coated AuNSts as a contrast agent for a noninvasive dual-modality depiction of glioblastoma (GBM), the deadliest and most common primary brain cancer.²⁰⁹ The AuNSt@SiO₂ probes were injected intravenously in a mouse model and

capable of sending enhanced multispectral optoacoustic tomography (MSOT) signals only 1 min postinjection (Figure 1.34a). The MSOT signals were significantly increased (Figure 1.34b) and lasted for at least several hours postinjection (Figure 1.34c).

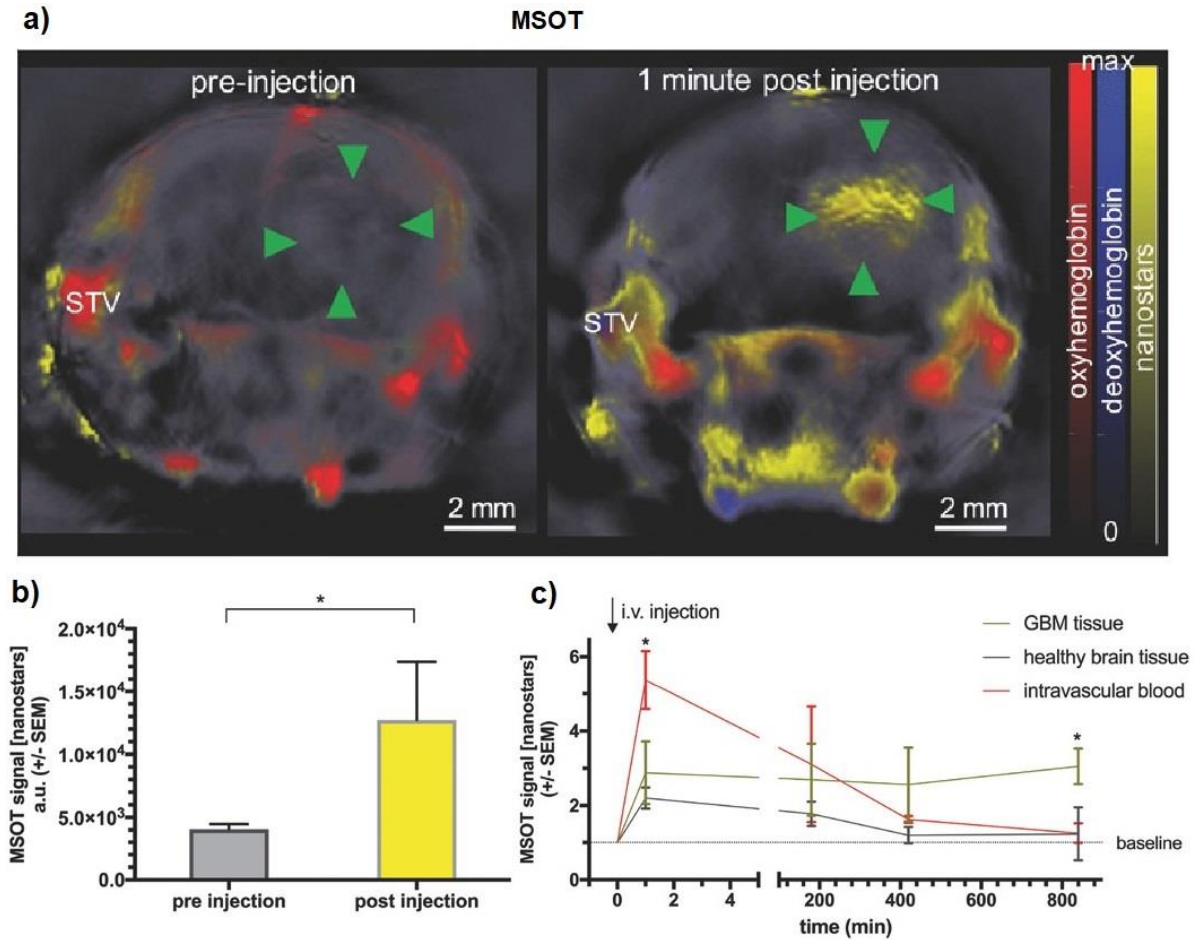


Figure 1.34. Pharmacokinetic profile of SERRS-MSOT-AuNSTs in GBM-bearing mice with (a) MSOT imaging of the tumorous area; (b) increased MSOT signal in the tumor; (c) MSOT signal from the tumor over time following injection of the AuNST-based contrast agent. Adapted with permission from reference 209. Copyright 2017 Springer.

Notably, the AuNST-based contrast agent was able to produce both MSOT (Figure 1.35a) and surface-enhanced resonance Raman scattering (SERRS) (Figure 1.35b) in vivo imaging of brain tumors in mouse models with high signal sensitivity and specificity.²⁰⁹ The MSOT imaging also accurately and three-dimensionally depicted GBMs with high specificity,

as shown in Figure 1.35c. A high penetration depth of several millimeters and real-time imaging also made MSOT an ideal complimentary method to the highly sensitive and specific but more time-consuming and depth-limited SERRS imaging. Additionally, no adverse effects were recorded over the period of 14 h postinjection in any of the mice. The results reported in this work paved the way for a dual-mode noninvasive in vivo imaging method for brain tumors with high sensitivity and high specificity in a much less time-consuming procedure.

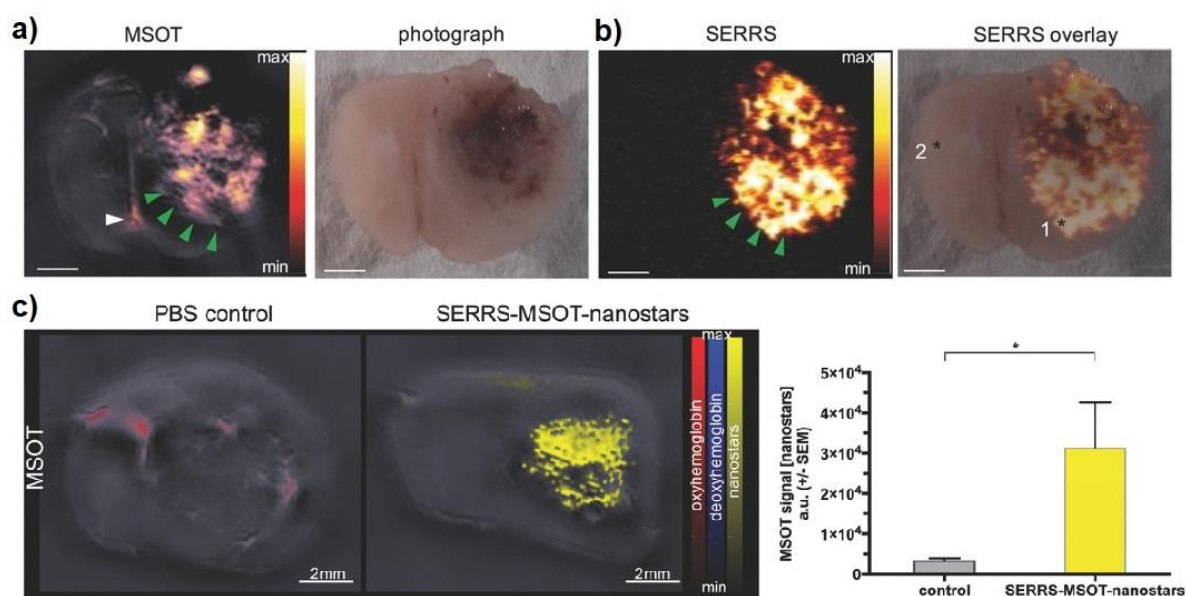


Figure 1.35. Performance comparisons between a (a) MSOT image and photograph and a (b) SERRS image and overlay photograph of SERRS-MSOT-AuNSt contrast agent. (c) Signal specificity of contrast-enhanced MSOT imaging in GBM tumors. Adapted with permission from reference 209. Copyright 2017 Springer.

In another work, Paulus and coworkers developed a AuNSt-based technique for the visualization of microvasculature using both photoacoustic microscopy (PAM) and optical coherence tomography (OCT).¹⁹⁸ AuNSts functionalized with arginine–glycine–aspartic acid (RGD) peptides were used as multimodal contrast agents for both PAM and OCT in vivo imaging, as illustrated in Figure 1.36. The good biocompatibility of the functionalized AuNSt

contrast agents was confirmed by flow cytometry analysis and an MTT assay using HeLa cells. The modified AuNSts were then tested in rabbit models for their performance as contrast agents for both PAM and OCT in vivo imaging.

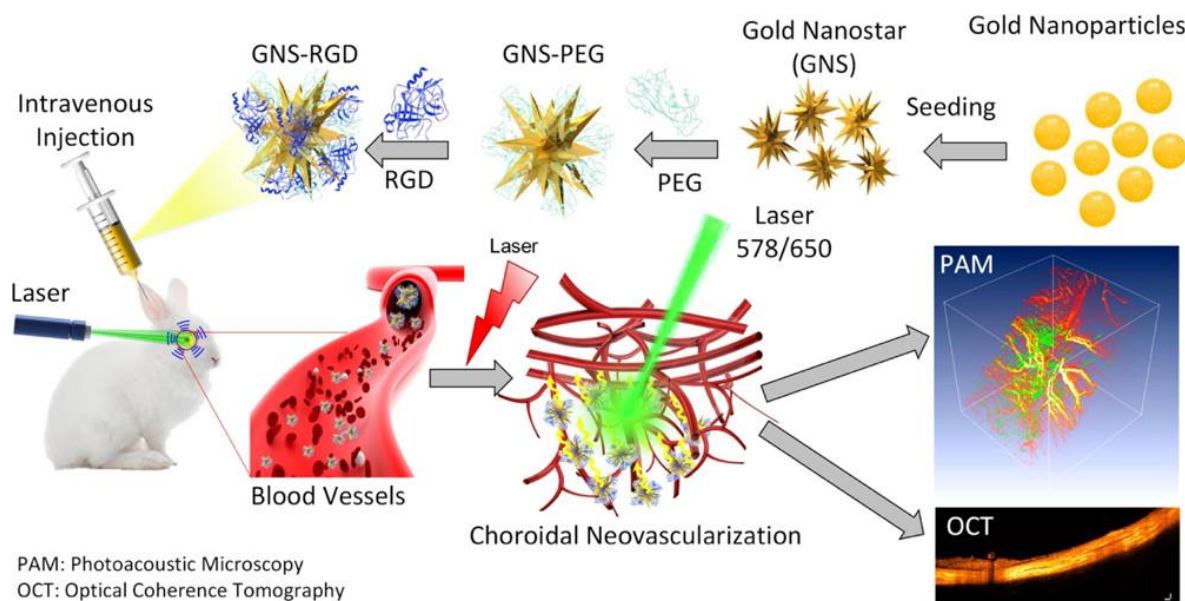


Figure 1.36. Illustration of AuNSt-based contrast agent for in vivo imaging of microvasculature with photoacoustic microscopy and optical coherence tomography. Adapted with permission from reference 198. Copyright 2020 American Chemical Society.

The PAM image showed choroidal neovascularization (CNV) in the rabbit models with great contrast, as shown in the 3D photoacoustic volumetric visualization (Figure 1.37a), and maximum intensity projection PAM images could be obtained for the selected region of interest (Figures 1.37b and c).¹⁹⁸ The retinal vascular network was clearly observed in PAM images obtained at 578 nm. Great discrimination between CNV and hemoglobin was achieved by imaging at a longer wavelength of 650 nm because of the low optical absorption of hemoglobin at 650 nm. In addition to PAM imaging, OCT-based visualization was also demonstrated with the same conjugated AuNSt contrast agent. After injection of the AuNSts contract agent, CNV was clearly observed with a greater OCT contrast (Figure 1.37e) due to

increased backscattering from the AuNSTs compared to the preinjection image (Figure 1.37d), thus demonstrating the signal enhancing capability of AuNSTs for OCT imaging.

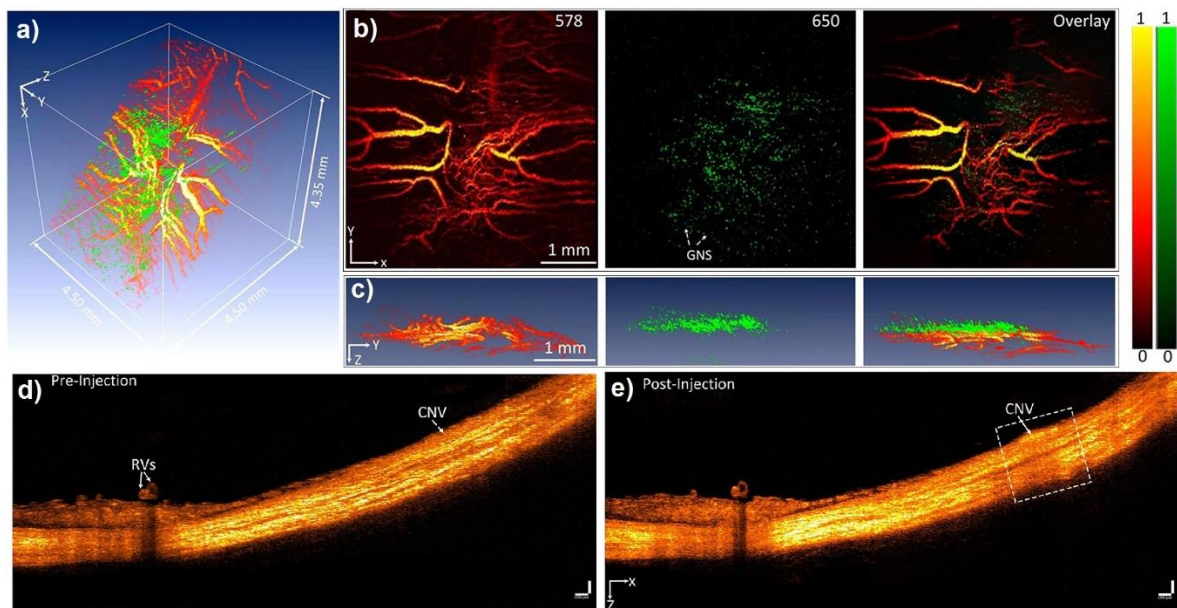


Figure 1.37. (a) 3D volumetric rendering of PAM images and the (b) horizontal (y-z) and (c) vertical PAM images of choroidal neovascularization in rabbit models. The pseudogreen color indicates the distribution of AuNSTs. AuNST-enhanced B-scan OCT images obtained (d) before and (e) after injection of AuNST-based contrast agent. Adapted with permission from reference 198. Copyright 2020 American Chemical Society.

In addition to these representative works, Table 1.9 also summarizes many other studies that used AuNSTs to enhance imaging techniques with various imaging targets and signal-transducing mechanisms. They span from the imaging of HeLa cells by enhanced fluorescence,²⁰⁵ alveolar basal epithelial cells by computed tomography,²⁰³ and tumor cells by immuno-positron emission tomography.¹⁹⁹ The wide range of signal-transducing mechanisms enhanced by plasmonic nanostars demonstrates the strength and versatility of this type of nanostructure for enhancing signals based on their great plasmonic properties.

1.3.4. Catalytic Applications of Plasmonic Nanostars

Catalysis plays an important role in industry as well as everyday life, and the development of catalysts with better activities, selectivities, and stabilities is an attractive research field. Plasmonic-based catalysis has been emerging as a promising approach for developing photocatalysts with greatly enhanced properties by exploiting the excitation of charge carriers in irradiated metal nanostructures.²¹⁰ The ability to control the plasmonic response in metal nanomaterials by varying their size, shape, composition, and functionalization has enabled exciting opportunities for exploring and developing better catalytic technologies.²¹¹ Plasmonic nanostars with greatly enhanced fields offer particularly advantageous approaches for accelerating the growth and applications of the nascent field of plasmonic catalysis. Table 1.10 summarizes recent developments in plasmonic nanostar-based catalysis.

Table 1.10. Catalytic Applications of Plasmonic Nanostars

Core NP	Combinatory Components	Structure/Form	Catalytic Application	Key Results	Ref.
SiO ₂ @AuNSt	TiO ₂	TiO ₂ decorated on AuNSt	Organic pollutant degradation	Degraded organic dye with remarkable stability and dispersibility; however, the efficiency strongly depended on the anisotropy of the plasmonic component	212
Au-NSt, NR, NP	TiO ₂	Core-shell NP	PC H ₂ generation	Dependence of photocatalytic H ₂ generation rate on dimensionality and anisotropy of the plasmonic core with highest rate at 76.6 $\mu\text{mol g}^{-1}\text{h}^{-1}$ for AuNSts	213
AuNSt	Ag	Core-shell NP	PC coupling of 4-amino-thiophenol	NS displayed rapid photocatalytic conversion of PATP to DMAB within a few seconds	214
AuNSt	Egg shell membrane	Immobilized particle	PNP reduction	Good catalytic performance with enhanced stability and reusability even after 10 reaction cycles and 100 days	215
AuNSt	N/A	Deposited on carbon electrode	Electrocatalytic oxidation of EG	High electrocatalytic activity for EG oxidation and better poisoning-resistant ability in alkaline media than irregular Au nanocrystals	216

Table 1.10 Continued

AuNSt	TiO ₂ NR	Deposited on TiO ₂ photoanode	PEC properties	350% and 20% increases in photocurrent density under visible light and simulated sunlight, respectively as well as an over 10-fold increase in IPCE efficiency	217
AuNSt	N/A	Colloidal NSt	Electro-catalytic oxidative reaction	Significantly enhanced electrochemical performance upon LSPR excitation with AA detected at an LOD of 10 μ M	218
AuNSt	N/A	Decorated on GCN and rGO surfaces	PC pollutant degradation	Degraded methylene blue under visible light with reusability and excellent photostability	219
AuNSt	AgPt alloy	AgPt-tipped, AgPt-edged, AgPt-covered AuNSt	PEC H ₂ evolution, MeOH oxidation	AgPt-tipped AuNSts showed remarkable electrocatalytic H ₂ generation and MeOH oxidation with NIR light	220
AuCu NSt	CdS	Core-shell NP	PC H ₂ generation	H ₂ evolution rate increased 2.94-times to 607 μ molg ⁻¹ h ⁻¹ with the combination of AuCuNSts and CdS under light with $\lambda > 400$ nm	221
AuNSt	N/A	Colloidal NSt	PATP PC reaction	AuNSts showed faster PATP catalytic and reduction reaction than AuNP with illustration by FDTD simulation	222
AuNSt	CALB enzyme	Colloidal NSt	Enzymatic catalysis	58% increase in enzyme activity by LSPR excitation under NIR illumination enabled by photothermal heating	223
AuNSt	N/A	Colloidal NSt	4-NTP, 4-NP, 4-NA reduction	High catalytic efficiency in reducing aromatic nitro compounds with selective dependence on the orientation of the compound molecule on the nanostar surface	224
AuNSt	TiO ₂	Core-shell NP	PC benzyl alcohol aerobic oxidation	Enhanced the aerobic oxidation of benzyl alcohol to benzaldehyde at ambient temperature under visible light irradiation	225
AuNSt	Mesoporous SiO ₂	Core-shell NP	4-NP reduction	High catalytic performance of 4-NP reduction; more star branches led to higher activity	226
AuPd NSt	N/A	Colloidal NSt	4-NP reduction, Suzuki coupling	Synthesized AuPdNSts with tunable LSPR; efficiently enhanced catalytic activity in 4-NP and nitrobenzene reduction and in Suzuki coupling reaction	227
AuNSt and others	Pt	Core-shell NP	PEC and PC reaction	AuNSts showed better PEC and PC activities than other morphologies	228

Abbreviations: PC: photocatalytic, NSt: nanostar, NP: nanoparticle, AuNR: gold nanorod, PATP: para-aminothiophenol, DMAB: 4,4'-dimercaptoazobenzene, PNP: p-aminophenol, EG: ethylene glycol, N/A: not applicable, IPCE: incident photon-to-current conversion efficiency, LSPR: localized surface plasmon resonance,

AA: ascorbic acid, LOD: limit of detection, GCN: graphitic carbon nitride, rGO: reduced graphene oxide, NIR: near-infrared, MeOH: methanol, PEC: photoelectrocatalytic, AuCuNSt: gold-copper alloy nanostar, FDTD: finite-difference time-domain, CALB: *Candida antarctica* fraction B, 4-NTP: 4-nitrothiophenol, 4-NP: 4-nitrophenol, 4-NA: 4-nitroaniline, AuPdNSt: gold-palladium nanostar.

In a recent report,²²⁸ Grzelczak and coworkers conducted a comparative study of the morphological effects of Pt-coated nanostars, nanocubes, and nanorods on the photogeneration of coenzyme molecules (nicotinamide adenine dinucleotide: NADH) using triethanolamine (TEAOH) as the sacrificial agent. The gold nanostructures were decorated with platinum via a reduction process that allowed platinum growth on the surfaces of gold structures in the presence of silver cations, as shown in Figures 1.38a-i. To better understand the optical responses of these multimetal nanostructures, the authors simulated the scattering of their cross-sections with the surface integral equation-method of moments (SIE-MoM). The results (Figure 1.38k) showed much less scattering by nanostars than by nanocubes and nanorods. This low level of scattering suggests that nanostars are better light harvesters than other-shaped nanostructures, which can be beneficial for photoelectrocatalytic reactions when using light with a similar spectral range (Figure 1.38j).

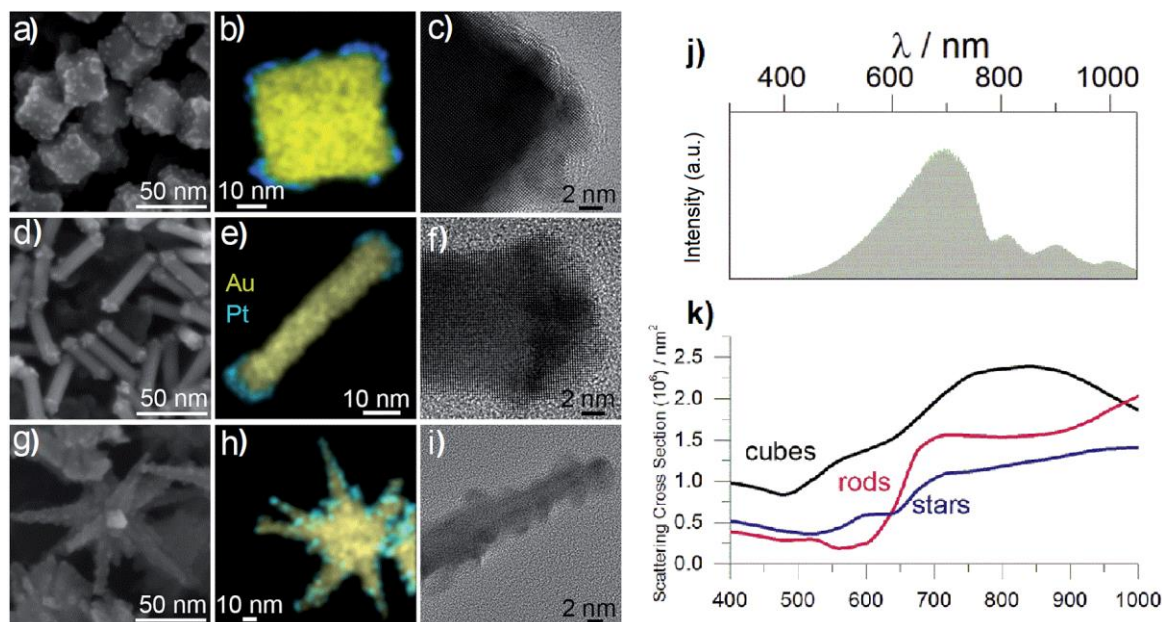


Figure 1.38. Electron microscopy analysis of Pt-coated gold nanostructures with different shapes: (a-c) cube, (d-f) rod, and (g-i) star. SEM images (a, d, and g) and EDX mapping (b, e, and h) confirming the presence of Pt on the gold surfaces. (c, f, i) HRTEM images of the nanostructures. All structures were covered with 10 mol% Pt. (j) Spectral profile of the lamp used in all experiments. (k) Simulated scattering cross-section spectra of the substrate comprising three different nanostructures. SEM: scanning electron microscopy, EDX: energy-dispersive X-ray spectroscopy, HRTEM: high-resolution transmission electron microscopy. Adapted with permission from reference 228. Copyright 2016 Royal Society of Chemistry.

When tested in the photochemical regeneration of cofactor molecules (NADH), all Pt-decorated nanostructures were found to increase the regeneration of NADH by ~6-fold in comparison to the bare nanostructures with the same morphology, as shown in Figure 1.39a.²²⁸ Importantly, the best catalytic activities were observed for the nanostars, demonstrating the geometrical advantage of nanostars over other morphologies in enhancing photocatalytic activity. The amperometric i-t curves for the electrodes covered with the alloy nanostructures of all three morphologies were obtained (Figure 1.39b). The presence of Pt boosted the photocurrent by approximately ten times compared to the photocurrent obtained from the bare gold nanostructures regardless of their shape, suggesting the significant contribution of Pt in

the photoelectrocatalytic process. Moreover, the magnitude of the photocurrent in the nanostars was 3.5- and 1.5-times higher than those in the nanocubes and nanorods, respectively. This enhancement showed that the shape–activity relationship of photoelectrocatalytic nanostars is better than those of photocatalysts with other morphologies.

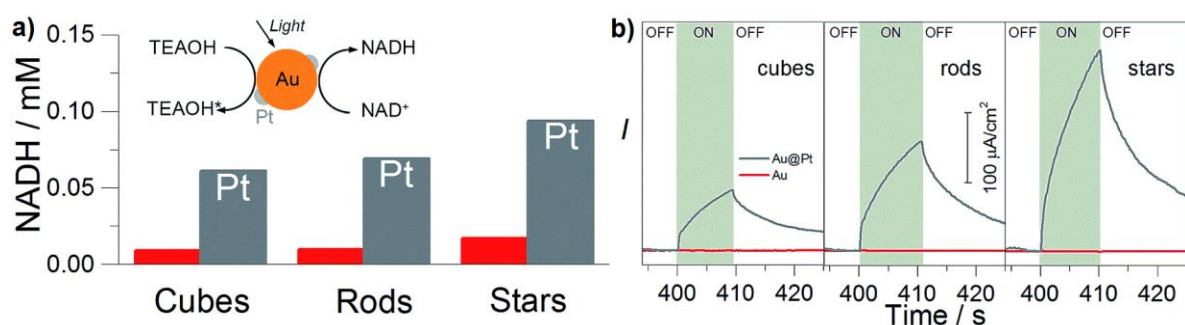


Figure 1.39. (a) Photochemical regeneration of cofactor molecules (NADH) under visible light irradiation on plasmonic substrate containing different particle shapes. Inset: Scheme showing the simultaneous oxidation of TEAOH and reduction of NAD^+ to NADH. (b) Fast current components for three samples containing Pt-coated nanostructures of different shapes, showing better performance of stars than rods and cubes. Adapted with permission from reference 228. Copyright 2016 Royal Society of Chemistry.

In another recent work,²²³ de Barros et al. investigated the biocatalytic effect of AuNSts functionalized with lipase from *Candida antarctica* fraction B (CALB) yeast under 808 nm near-infrared (NIR) laser light excitation. The authors coated CALB on AuNSts and gold nanospheres (AuNSphs) to form nanobioconjugates, which were then used for the biocatalytic hydrolysis of 4-nitrophenyl palmitate (pNPP) to 4-nitrophenolate (pNP) (Figure 1.40a). Under NIR laser irradiation, AuNSt@CALB displayed much higher enzymatic activity than AuNSph@CALB over a wide range of laser powers (Figure 1.40b). These significant enhancements of CALB activity on the surfaces of AuNSts compared to AuNSphs indicated the greatly enhancing characteristic of AuNSts enabled by the shape of the plasmonic nanostructure.

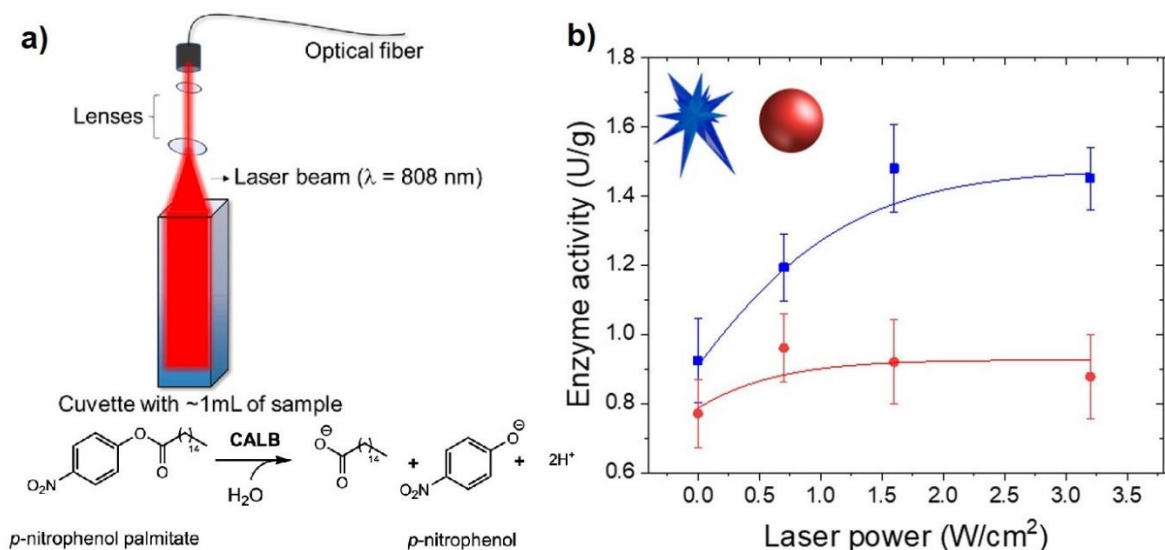


Figure 1.40. (a) Schematic illustration of the laser irradiation setup for the biocatalytic testing of plasmonic-based nanobioconjugates. (b) Effects of NIR laser power ($\lambda=808$ nm) on the enzymatic activity of AuNSt@CALB (blue) and AuNSph@CALB (red). Adapted with permission from reference 223. Copyright 2021 American Chemical Society.

In addition to the highlighted studies, various other efforts to develop AuNSt-based catalysts have also been reported in recent publications, as summarized in Table 1.10. Specifically, AuNSt-based catalysts have been used for hydrogen generation,^{213,220,221} methanol oxidation,²²⁰ Suzuki coupling,²²⁷ and pollutant degradation^{212,219} via different catalytic approaches, including photocatalytic, electrocatalytic, and photoelectrocatalytic approaches. The wide range of the catalytic applications of AuNSTs further indicates the versatility of this unique type of plasmonic nanostructure.

1.3.5. Photovoltaic Applications of Plasmonic Nanostars

Recently, the studies and applications of photovoltaic devices for converting sunlight directly to electricity have been a critical focus in the global response to the growing concern over fossil fuel-based energy usage. With more than half a century of research and development, photovoltaics is currently a mature field of science.²²⁹ Further advancements to

achieve higher-efficiency solar cells might benefit from new approaches in addition to gradual improvements in the structure and active layer materials.²³⁰ Recent developments in the exploitation of plasmonic nanoparticles as efficient light absorbers and current collectors in photovoltaic devices have demonstrated the potential of plasmonic nanomaterials in photovoltaics.²³¹ The development of plasmonic nanostars has also allowed the development of plasmonic photovoltaics, as summarized in Table 1.11.

Table 1.11. Photovoltaic Applications of Plasmonic Nanostars

Core NP	Combinatory Components	Role/ Position	Application	Key Results	Ref.
HEPES-AuNSt	SnO ₂	ETL	PSCs	ETLs exhibited higher conductivity and greater efficiency in the extraction, transfer, and collection of electrons; PCE reached 21.13% with negligible hysteresis. Enabled much stronger light trapping and increased J _{SC} and PCE up to 5.2% and 3.85%, respectively; systematic investigation of AuNSt's role in these enhancements	232
AuNSt	PEDOT-PSS	Light trapping	GaAs SCs		233
AuNSt	mPEG	Light absorption and scattering	PSCs, OSCs	PCE improved by 6% and 14% in OSCs and PSCs, respectively; better charge separation/transfer and reduced charge recombination rate	234
AuNSt	N/A	Between HTL and active layer	OSCs	Synergistic plasmon-optical and plasmon-electrical effects resulted in a PCE of up to 10.5% for OSCs with AuNSts and ZnO as ETL	235
AuNSt	TiO ₂	Photo-electrode	PSCs	Achieved a PCE of 17.72% due to enhanced light-harvesting efficiency	236
AuNSt and others	PEDOT-PSS	Buffer layer	OSCs	PCE increased the most with AuNSt at 29% compared to 14% of AuNR or 11% of AuNP	237
AuNSt	TiO ₂	Photo-anode	DSSCs	PCE increased up to 30%; IPCE was improved over the wavelength of 380-1000 nm	238
AuNSt	PbS/CdS QD	Light absorption	Heterojunction SCs	PCE of 4.16%; increased J _{SC} and photoresponse over broad spectral range	239

Abbreviations: HEPES: 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid, PSCs: perovskite solar cells, ETL: electron transporting layer, PCE: power conversion efficiency, PEDOT-PSS: poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate), J_{SC}: short-circuit current density, mPEG: methoxypolyethylene glycol, OSCs: organic solar cells, N/A: not applicable, HTL: hole transport layer, DSSCs: dye-sensitized solar cells, QD: quantum dot, SCs: solar cells.

In a recent paper,²³² Yang and coworkers introduced 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid-modified gold nanostars (HEPES-AuNSts) into the SnO₂ electron transporting layers (ETLs) of heterojunction perovskite solar cells (PSCs), as illustrated in Figures 1.41a and b. The presence of AuNSts was expected to modify the energy band alignment to facilitate better charge transport for enhanced photovoltaic efficiency (Figure 1.41c).

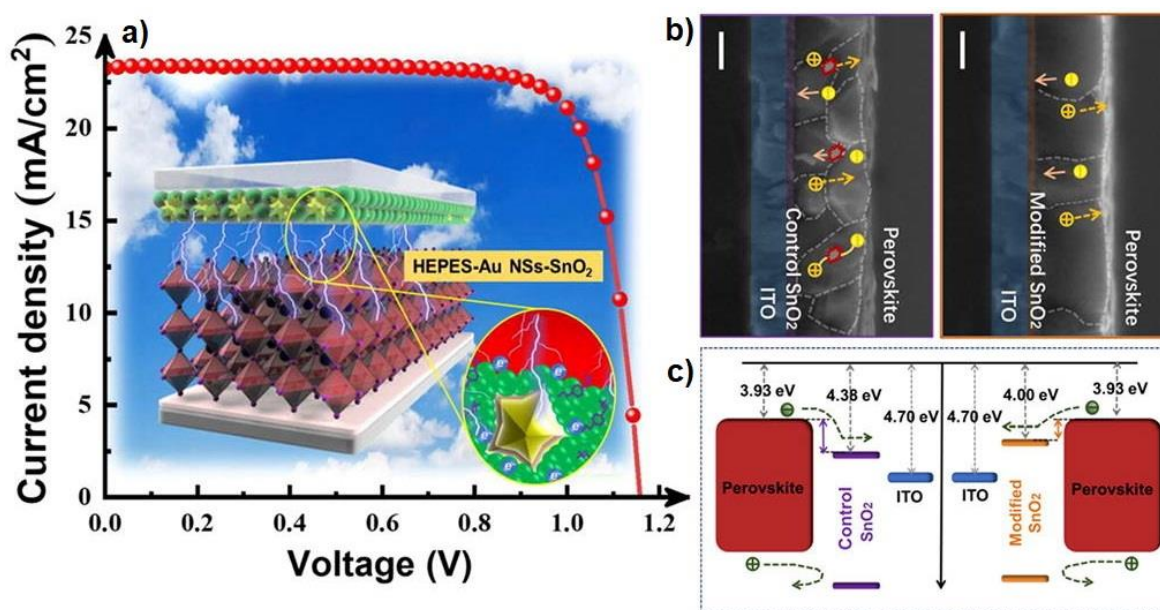


Figure 1.41. (a) Schematic and (b) cross-section illustration of the incorporation of HEPES-AuNSts into the electron transporting layers of PSCs. (c) Energy diagram of the PCS device with and without AuNSts. ITO: indium tin oxide electrode. Adapted with permission from reference 232. Copyright 2022 Elsevier.

The current density vs. voltage (J-V) responses of the AuNSt-modified PSCs were recorded in reverse scan (R-S) and forward scan (F-S) directions at a scan rate of 130 mV/s under 100 mW/cm² AM 1.5G illumination. The J-V curves of AuNSt-modified PSCs remained almost constant (Figure 1.42a) regardless of the scanning direction. The authors calculated the power conversion efficiencies (PCEs) of R-S and F-S to be 21.13% and 21.10%,

respectively, yielding a valid 21.12% efficiency for the AuNSt-modified PSCs. This behavior is significantly better than that of the unmodified PSCs, while also exhibiting negligible hysteresis behavior. In addition, the AuNSt-enhanced PSCs showed a spectral response superior to that of the unmodified PSCs in the wavelength range of 350-800 nm (Figure 1.42b). These results indicate the potential of plasmonic nanostars for enhancing the efficiency and performance of perovskite solar cells, which is worthy of further exploration.

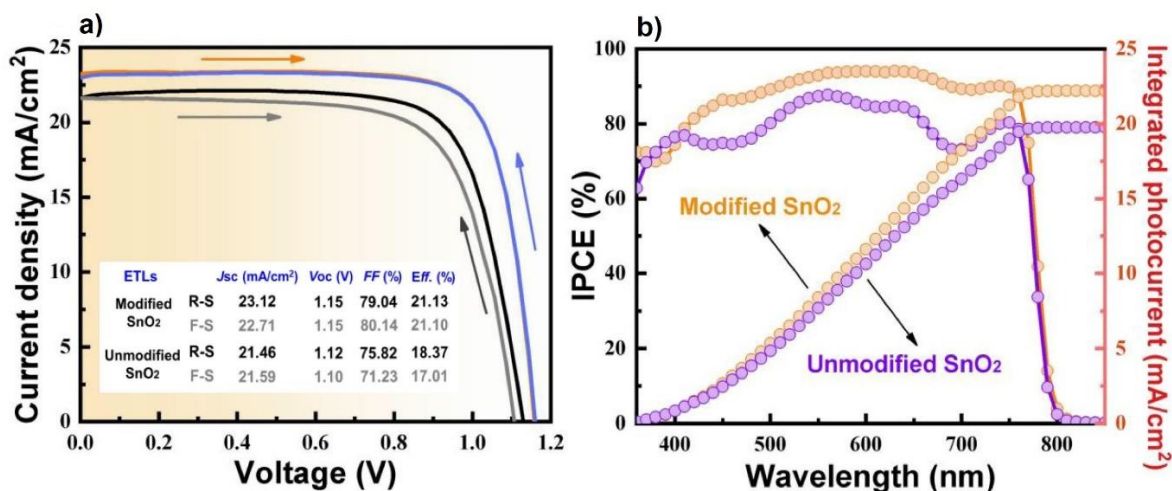


Figure 1.42. (a) J-V curves and (b) corresponding incident photon-to-current efficiency (IPCE) spectra under forward and reverse scans of the best-performing planar PSCs fabricated with ETLs modified and unmodified with HEPES-AuNSts. Adapted with permission from reference 232. Copyright 2022 Elsevier.

In another work, Ginting et al.²³⁴ demonstrated the use of AuNSts to enhance light absorption in organic solar cells (OSCs) and PSCs. The AuNSts were functionalized with methoxypolyethylene glycol (mPEG) to induce dispersion. The functionalized mPEG-AuNSts were then embedded into the blended layers of thieno[3,4-*b*]thiophene/benzodithiophene (PTB7):[6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM; hereinafter denoted as PCBM) in OSCs and the perovskite/2,2',7,7'-tetrakis-(N,N-di-*p*-methoxyphenyl-amine)-9,9'-spirobifluorene (spiro-OMeTAD) interfaces in PSCs, as shown

in Figure 1.43a. The modified AuNSts were incorporated into the aforementioned active layers, with the expectation that the characteristically enhanced field around the AuNSts under light irradiation might assist not only light absorption but also charge transport between these active layers.

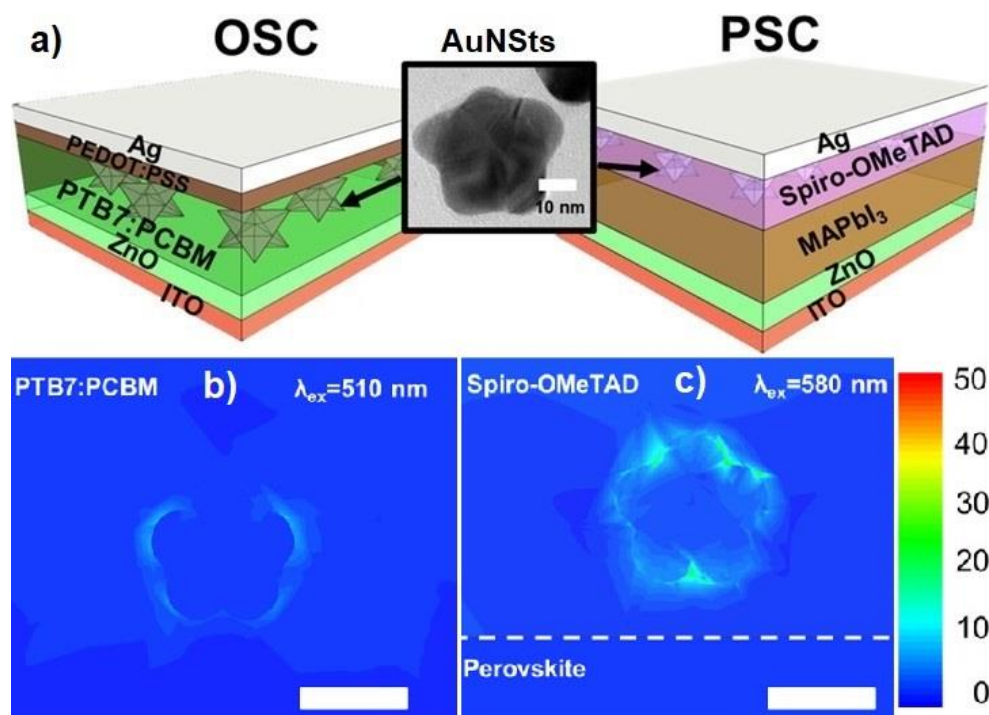


Figure 1.43. (a) Device configurations showing the positions of gold nanostars (AuNSts) in inverted OSCs and planar-based PSCs. Simulated local electric field distribution around a gold nanostar with respect to the incident light field in (b) PTB7:PCBM and (c) spiro-OMeTAD. ITO: indium tin oxide electrode. Adapted with permission from reference 234. Copyright 2017 American Chemical Society.

To verify the improvement in light absorption after incorporating AuNSts into the solar cells, the authors used the finite element method to simulate the electric field distribution around AuNSts positioned in the PTB7:PCBM and spiro-OMeTAD layers.²³⁴ The results in Figures 1.43b and c show enhanced electric fields around the surfaces of the AuNSts, suggesting the higher absorption properties of the AuNSt-embedded layers. The recorded J-V characteristics with the incorporation of AuNSts demonstrated that the PCEs were boosted

from 8.3 to 8.78% and 12.49 to 13.97% for OSCs (Figure 1.44a) and PSCs (Figure 1.44b), respectively. These PCEs of the AuNSt-incorporated solar cells are significantly higher than the PCEs in AuNP-incorporated OSCs^{240,241} or PSCs.²⁴² These results suggested that the embedding of AuNSts into the active layers of OSCs and PSCs enhanced their PCEs by 6 and 14%, respectively.

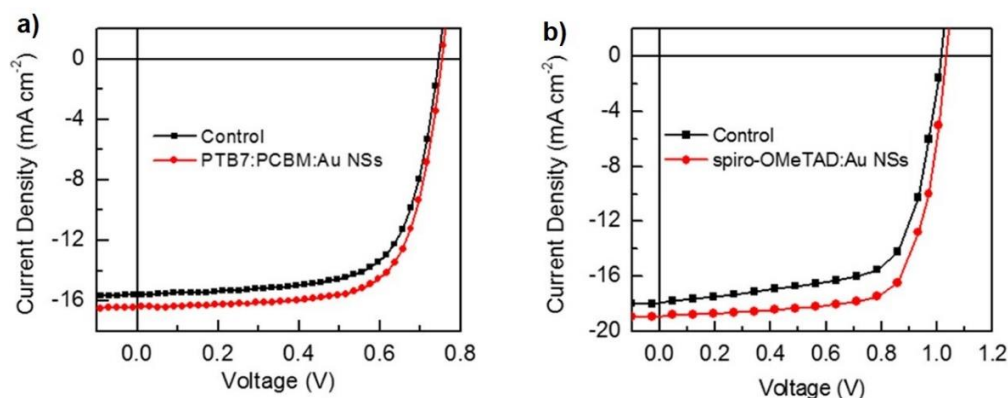


Figure 1.44. J-V characteristics of (a) OSCs and (b) PSCs under 100 mW/cm² AM 1.5G illumination, with and without (control) the incorporation of AuNSts. Adapted with permission from reference 234. Copyright 2017 American Chemical Society.

In addition to the studies detailed above, many other works on AuNSt-assisted photovoltaics have also been reported, as summarized in Table 1.11. The photovoltaic configurations incorporated with AuNSts included not only OSCs and PSCs but also GaAs solar cells²³³ and dye-sensitized solar cells (DSSCs).²³⁸ Moreover, the assistance that plasmonic nanostars can provide in photovoltaic devices included not only light absorption^{234,239} and electron transporting layers²³² but also photoanodes²³⁸ or hole transporting layers.²³⁵ These reports laid out an experimental and simulation basis for further studies and developments to fully understand and realize the potential of plasmonic nanostars to boost photovoltaic performance.

1.3.6. Other Applications of Plasmonic Nanostars

Plasmonic nanostars have enabled a wide range of enhanced technologies for advanced applications that benefit from the high specific areas, large numbers of hot spots, and intensified field characteristics of this unique nanostructure class. In addition to the five “large” fields of applications mentioned above, the versatility of plasmonic nanostars also makes them useful in various other “niche” applications, from fundamental research to technological development, as listed in Table 1.12.

Table 1.12. Other Applications of Plasmonic Nanostars

Core NP	Combinatory Components	Role/Position	Application	Key Results	Ref.
AuNSt	CB[7]	Photothermal activation	Cargo delivery	Precisely controlled absorption for tunable release of high-loading cargo for biomedicine	243
AuNSt	PLA	Photothermal heating	Maskless lithography	Successfully transferred designed patterns on rigid and flexible substrates with local temperature increased to more than 100 °C	244
AuAg NSt	SiO ₂	Luminescence enhancement	OLED	Increased current-densities as well as photo- and electroluminescence up to 50% in OLED	245
AuNSt	N/A	Local field intensity enhancement	Field electron source	Nonlinear photoemission from individual AuNSt with >10 ⁹ -fold enhancement of three-photon electron yield	19
AuNSt	N/A	Photocathode	Optically controlled directional currents	Displayed all-optical control over driving, switching, and steering of photocurrents in nanoelectronic devices	20
AuNSt @Ag	SiO ₂	Gain media enhancement	Coherent random laser	Substantially reduced pumping threshold in different gain media; coherent random lasing intensity and pumping threshold not influenced by SiO ₂ coating	246
AuNSt	N/A	Broadband scatterer	Random laser	Random lasing in an immense spectral coverage of over 410 nm throughout the visible up to the infrared range with efficient feedback mechanism	247
AuNSt	Amine-terminated PEG	Photothermal neuro-modulation	Neural activity control	Inhibited neural activity of neurons by NIR laser in both chip-attached and cell-attached mode; confirmed single-neuron signal suppression by DMD	248

Abbreviations: CB[7]: cucurbit[7]uril, PLA: polylactic acid, OLED: organic light-emitting diode, N/A: not applicable, NIR: near-infrared, DMD: digital micromirror device, PEG: polyethylene glycol.

In a recent report,²⁴⁴ Rettori et al. demonstrated maskless lithography techniques (MLTs) based on the photothermal properties of AuNSts and the thermoplastic characteristics of polylactic acid (PLA) biopolymers. The patterning process involved the deposition of poly(sodium 4-styrenesulfonate) (PSS)-stabilized AuNSts on a PLA film, which was incorporated with Er^{3+} -doped upconversion nanoparticles (UCNPs) for the visualization of the NIR laser spot and simultaneous probe of the local temperature. A computer numerical control (CNC) system was developed to drive the laser writing beam following a designed pattern on the AuNSt/PLA-UCNPs nanocomposite (Figure 1.45a). The irradiated area demonstrated PLA polymer photothermally heated to a temperature higher than its glass transition point and solidified. The irradiated film was then washed to remove the nonirradiated part, revealing the designed patterns without the need for a photomask as in traditional lithography. The author could also adjust the synthesis of AuNSts to achieve an absorption peak matching the wavelength of the NIR laser used at ~ 976 nm, as shown in Figure 1.45b. By analyzing the emission spectra in the regions covered and not covered by AuNSts, the study showed a linear relationship between the laser power density and the local temperature on the irradiated AuNSts/PLA-UCNPs film, as displayed in Figure 1.45c. The temperature range generated by the photothermal heating of AuNSts in this work was much higher than the glass temperature of the PLA polymer at ~ 60 °C, allowing enough thermal energy for the thermoplastic conversion of PLA for MLTs.

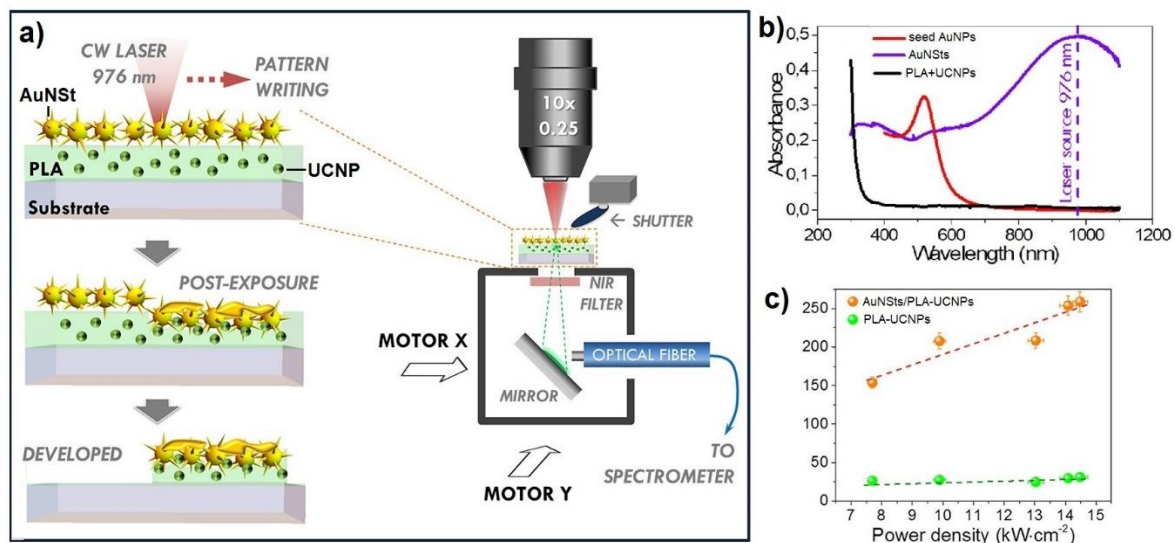


Figure 1.45. (a) Experimental setup and multilayer samples formed by a substrate, the PLA-UCNPs nanocomposite, and AuNSts. (b) UV–visible spectrophotometry of seed AuNPs and AuNSts in water colloid and nanocomposite PLA-UCNP film compared to the laser source at 976 nm. (c) Calculated local temperature under different laser power densities in the regions covered or uncovered by AuNSts. Adapted with permission from reference 244. Copyright 2019 American Chemical Society.

The thermoplastic maskless lithography (TML) technique developed in the report was demonstrated to successfully transfer predesigned patterns onto both rigid glass surface (Figure 1.46a) and flexible polyimide tape (Figure 1.46b) substrates.²⁴⁴ The incorporation of UCNPs into the PLA polymer film provided additional luminescence properties that enabled the formation of luminescent patterns (Figure 1.46c), which can be used in displays, optical sensors, and anticounterfeiting technologies. The authors also produced a quick response (QR) code (Figure 1.46d) by this TML technique, which further demonstrates the potential use of TML as an encryption tool.

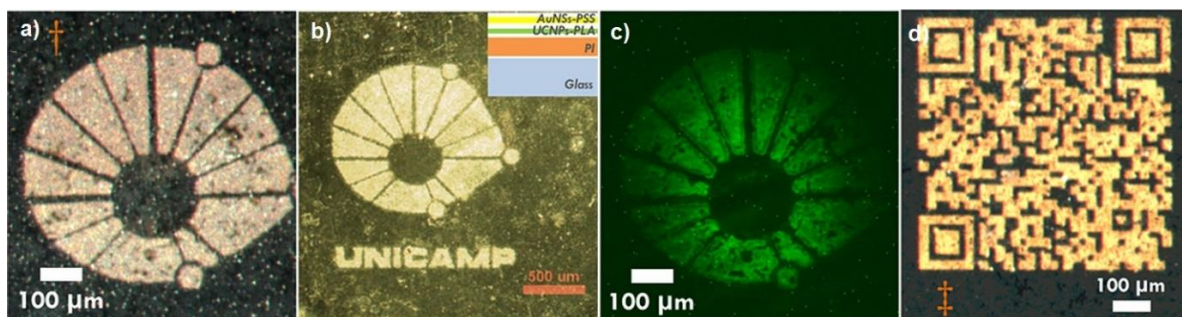


Figure 1.46. Dark field microscopy images of the predesigned patterns on (a) glass and (b) flexible polyimide tape deposited with AuNSts and developed by TML. (c) Photon upconverting luminescence image under NIR (976 nm) excitation of the TML pattern. (d) A sample of QR code on a glass substrate. Adapted with permission from reference 244. Copyright 2019 American Chemical Society.

Another interesting application of plasmonic nanostars for the modulation of neuronal signals via photothermal stimulation was reported by Nam and coworkers.²⁴⁸ The authors used AuNSt-modified multielectrode array (MEA) chips to manipulate neural signals in hippocampal neurons. The work involved the deposition of AuNSts and hippocampal neurons on MEA chips, which were then illuminated by near-infrared lasers (785 and 808 nm), as illustrated in Figure 1.47a. Moreover, cell viability tests for the neurons in the presence of the plasmonic nanostructures were performed, and the results (Figure 1.47b) showed no significant difference in viability between the control sample and the AuNSt samples even though there was a significant viability decrease in the gold nanorod samples, indicating the higher biocompatibility of AuNSts.

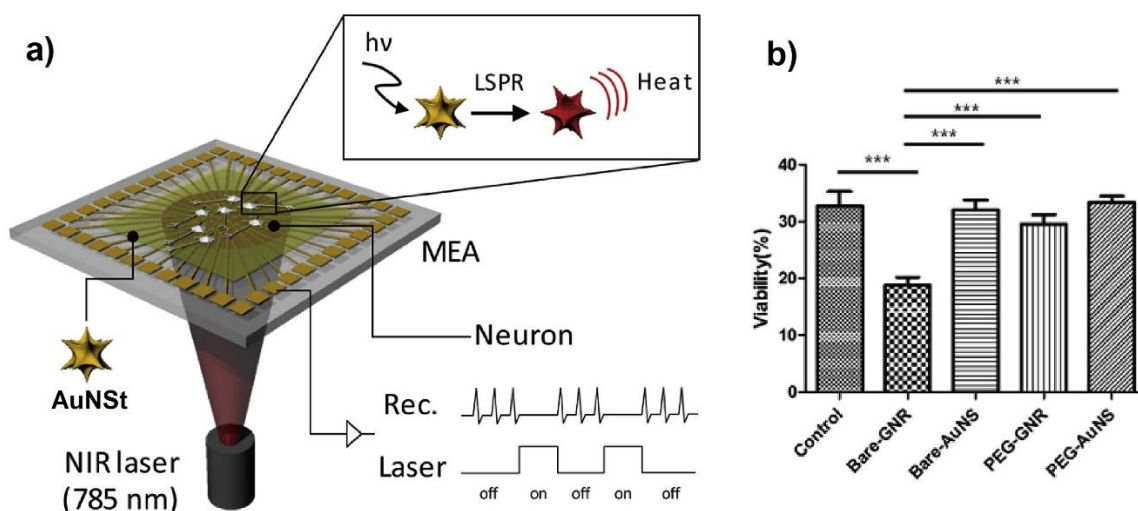


Figure 1.47. (a) Schematic of the gold nanostar (AuNS)-mediated NIR light-based neuronal cell stimulation system. (b) Viability tests of neuronal cells in the presence of plasmonic nanostructures under various conditions. *** ($p < 0.0001$). PEG: polyethylene glycol, GNR: gold nanorod. Adapted with permission from reference 248. Copyright 2018 Elsevier.

This work then demonstrated the capability of the NIR-sensitive AuNS-coated MEA chips to inhibit the neural activity of hippocampal neurons, as shown in Figure 1.48.²⁴⁸ The authors first tested the controlled neural inhibition on a neural network deposited onto the AuNS-coated MEA chips. With increasing power densities of laser irradiation, the neural signal started to be dampened at 3 mW/mm^2 and became virtually completely suppressed at 15 mW/mm^2 (Figure 1.48a). The study was further extended to neural inhibition on a single neuron located in the vicinity of the recording electrode. To achieve single-neuron signal reading, a digital micromirror device (DMD)-based illuminating system was used to generate a localized light pattern as small as the single-cell size (Figure 1.48b). Under irradiation with an NIR laser at a power intensity of 116.24 W/mm^2 , the neural signal spike rate was significantly decreased during light stimulation, as displayed in Figure 1.48c. Similar experiments were also carried out for 8 different single neurons located at other electrodes, and similar results were obtained in most of the cases. This work successfully showed that

plasmonic nanostars can be used to modulate neuronal activity based on the plasmon-initiated photothermal effect. This modulating capability can be beneficial in studies of neurological disorders (e.g., epilepsy) and for the development of optogenetic technologies.

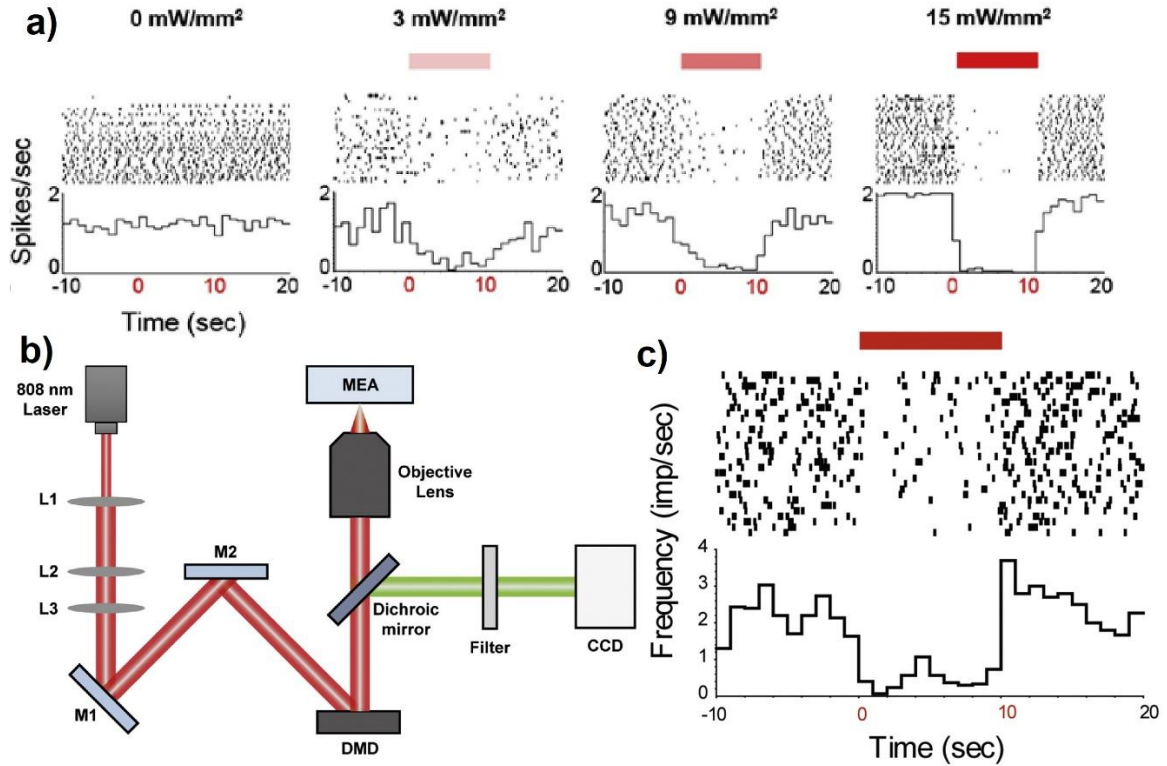


Figure 1.48. Photothermal inhibition of the spontaneous activity of cultured neuronal networks: (a) experimental setup for AuNSt-coated MEA chips and AuNSt-attached cultured neuron and (b) Peri-stimulus time histogram and raster plots for AuNSt-coated MEA chips with varying laser power. Photothermal inhibition of the spontaneous activity of a single neuron: (c) schematic setup of the DMA-based optical illuminating system with AuNSt-coated MEA for hippocampal neurons. Adapted with permission from reference 248. Copyright 2018 Elsevier.

In addition to the works highlighted in detail above, many other nonconventional studies have also been reported on the applications of plasmonic nanostars as field electron sources¹⁹ and gain media for coherent lasers²⁴⁶ or current control,²⁰ as summarized in Table 1.12. The wide range of application possibilities for plasmonic nanostars in many niche areas further indicates the great potential and versatility of this class of nanostructures. The limited

number of reported works, however, calls for more research and development focused on better understanding the complex behaviors of plasmonic nanostars in these systems and further realizing their application potential.

1.4. Summary and Outlook

Plasmonic nanostars, as one of the newest types of plasmonic nanostructures, have exhibited many superior advantages over their other more conventional counterparts. These strengths mainly originate from their inherently large specific surface areas and immensely intensified electric fields with the arguably largest numbers of plasmonic hot spots in all of the plasmonic nanostructures that have been fabricated up until now. Over the last decade, by exploiting their unique advantages, plasmonic nanostars have been increasingly used to advance the state-of-the-art in many technologies, which are crucial for human health, safety, and the resolution of environmental challenges. These contributions span a wide range of fields, such as ultrahigh-sensitivity biomedical diagnostics for early disease screening, targeted triggerable drug deliveries with minimal or no side effects for anticancer or antiviral therapies, activatable and nontoxic photothermal therapies for antibacterial treatments, highly selective bio and toxin sensors with ultralow detection limits, multimodal imaging for the real-time monitoring of medical procedures, greatly enhanced catalysts for fuel generation and chemical reactions, improved efficiency and stability for photovoltaics, and even neural activity modulations for neurological disease diagnostics and therapies. It is noteworthy that within one plasmonic nanostar template, different capabilities can be integrated for multimodal, multiplexed, multifunctional, and/or synergistic purposes, which opens new

avenues for establishing one-stop, real-time, modular platforms for universal applications, especially in medical technologies.

Despite the vast range of applications and impressive performances, plasmonic nanostars are still in their nascent stage and require deeper fundamental scientific understanding, as well as technical insights, to introduce plasmonic nanostar-enabled methodologies into mainstream technologies and utilizations. It is obvious through this review that gold nanostars have been dominant among the different types of plasmonic nanostars partly due to their status as arguably the first metal nanostar reported, in addition to their high biocompatibility and LSPR frequency in the first and second biological optical windows, making them very attractive for biomedical-related technologies. However, greater potential and opportunities for the discovery and development of other types of plasmonic nanostars still exist, such as silver, copper, alloy, and hollow nanostars, which can be optically active in UV–visible region of the electromagnetic spectrum complementary to the NIR-region of gold counterparts.¹¹

In conclusion, this review has summarized the most recent developments in plasmonic nanostar-enabled technologies and their state-of-the-art applications in various areas with great significance for health care, safety, energy supply, environmental remediation, and fundamental studies. This review also discussed the shortcomings of plasmonic nanostars that need further investigation and the vast potential of this relatively new class of nanomaterials for future exploration and development.

Chapter 2: Stable Semi-Hollow Gold-Silver Nanostars with Tunable Plasmonic Resonances Ranging from UV-Visible to Near-Infrared Wavelengths

2.1. Introduction

Metallic nanostructures have been studied for years because of their unique plasmonic properties and potential applications in various fields including solar cells, energy storage, sensing and biosensing, and biomedical therapies including treatments for COVID-19 infection.^{70,103,249–255} Under the illumination of an electromagnetic field, noble metal nanostructures exhibit localized surface plasmon resonance (LSPR) that arises from the collective oscillation of the electron cloud induced by an incident electromagnetic field.²⁵⁶ This localized resonance phenomenon leads to numerous exotic properties of plasmonic nanostructures such as optical absorption,²⁵⁷ spectroscopic enhancement,²⁵⁸ plasmonic heating,²⁵⁹ hot electron injection,²⁶⁰ and plasmon-induced resonance energy transfer.²⁶¹

Metallic nanostars such as gold nanostars (AuNSts) and silver nanostars (AgNSts) represent a relatively new class of plasmonic nanostructure with unique and attractive optical characteristics.^{20,199,262} The morphologies of these nanostars provide enhanced surface-to-volume ratios compared to more conventional plasmonic nanostructures (e.g., spherical nanoparticles and nanorods). With many interfacial spikes, plasmonic nanostars can produce intense electromagnetic fields with numerous electromagnetic hotspots compared to other structures as illustrated in Figure 2.1.

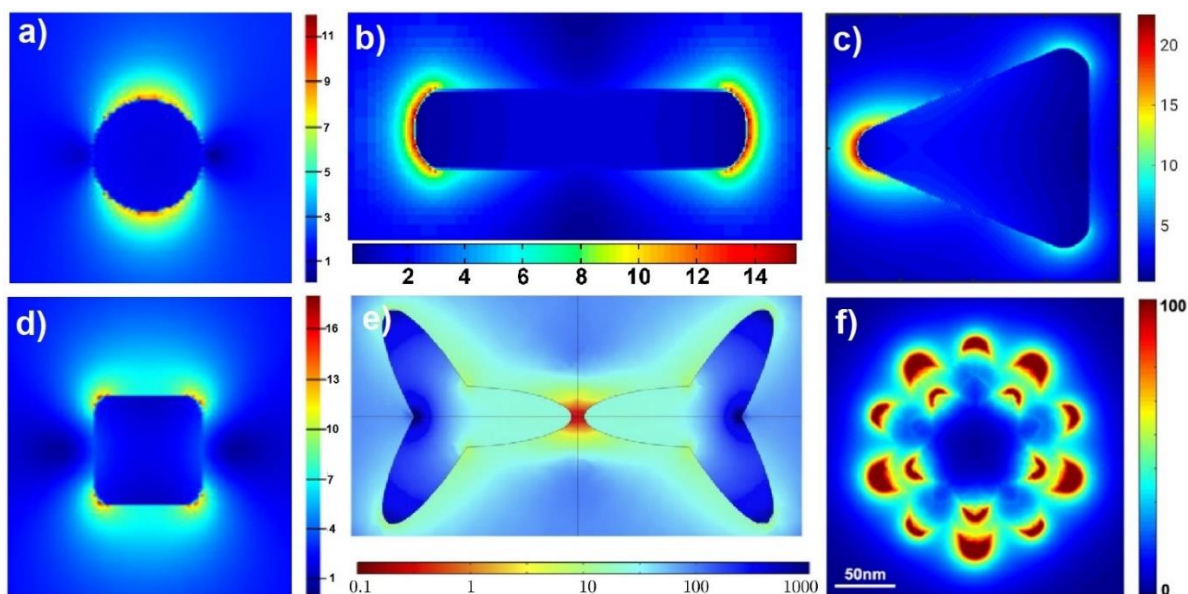


Figure 2.1. Simulated electric field distribution of plasmonic (a) nanospheres,²⁶³ (b) nanorods,²⁶⁴ (c) nanotriangles,²⁶⁵ (d) nanocubes,²⁶³ (e) tripods,²⁶⁶ and (f) nanostars.³⁵ Reproduced and adapted with permission from the indicated references 265–270.

Although AuNSts offer greatly enhanced properties compared to conventional plasmonic nanostructures due to their unique shape, control of the optical properties of AuNSts requires delicate handling of the synthetic steps to obtain reproducible sizes and morphologies.^{271,272} Further, due to their modest stability, gold nanostars usually require judicious surface modification, which can limit their use in certain applications. Importantly, their greatly intensified electromagnetic fields, superior surface-to-volume ratios, as well as their inherent biocompatibility have enabled unique opportunities for a wide range of applications including optoelectronics,²⁰ biosensing,^{273,274} catalysis,^{223,275} photovoltaics,^{234,236} spectroscopies,^{177,276} light-controlled therapies,¹²² and drug delivery.⁵⁸ Strategies to overcome the synthetic challenges^{271,277} include growing a secondary nanostructure²⁷⁶ or creating core-shell structures²⁷⁸ to tune the plasmonic properties of the nanostars. However, these approaches require even more careful handling and modification to obtain the desired optical

properties. Moreover, the optical range of these nanostructures is confined to ~700 nm to near-infrared (NIR) wavelengths,^{36,223} which further limits their breadth of applications.

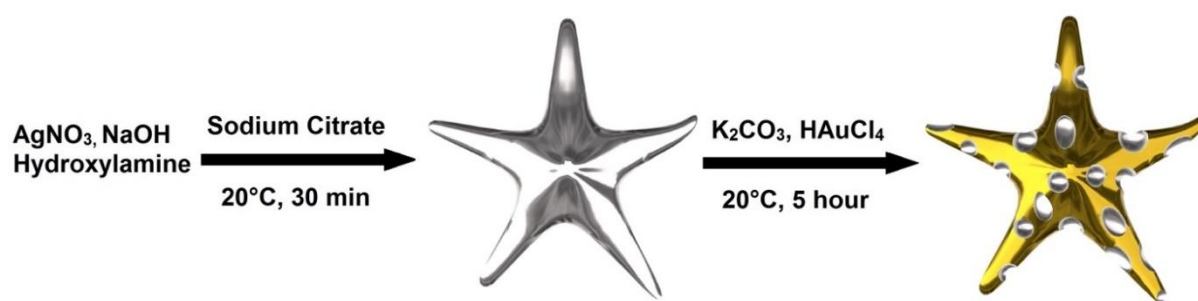
Another bottleneck in the development and applications of AuNSts is their propensity for aggregation, which occurs for many types of gold nanostructures.^{279–281} The common strategy employed to deal with this problem is to functionalize the Au nanostructures with stabilizing ligands.^{69,119,282–284} This additional modification step, however, further complicates the synthetic process; moreover, the introduction of a molecular coating layer can negatively impact applications that require intimate contact between the electromagnetic field of the metallic nanostars, such as catalysis or photovoltaics.^{233,285,286}

Silver nanostars (AgNSts) have also been used in several applications, such as surface-enhanced Raman spectroscopy (SERS)-based sensing^{173,287–289} and antimicrobial surfaces.⁹³ Notably, the plasmonic resonance wavelengths of silver nanostars (~375 nm)¹⁷³ are found in the ultraviolet region in contrast to the usual range for gold nanostars (~700 nm and longer).^{36,223} However, the LSPR peak position of silver nanostars exhibits limited tunability, remaining largely constant despite changes in size,²⁸ which limits the practical applications of AgNSts in solar-powered applications such as photocatalysis and photovoltaics because the ability to operate in the visible region (400–700 nm), which makes up ~43% of solar energy that reaches the surface of the earth,²⁹⁰ is critical for optimal performance.

In this work, we report the synthesis and characterization of a new nanostar architecture: semi-hollow gold-silver nanostars (hAuAgNSts), which we prepared via galvanic replacement on AgNSts as shown in Scheme 2.1. The new bimetallic gold-silver

nanostars were characterized by electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction, UV-Vis extinction spectroscopy, and thermal stability tests. The results demonstrate a highly stable semi-hollow gold-silver nanostar with LSPR maxima that can be tuned simply by adjusting the ratio of Ag:Au in the nanostar composition without the need to modify the nanostar dimensions.^{271,277} Notably, the optical extinctions of the gold-silver nanostars span both ultraviolet and visible regions with an extended tail in the NIR. Compared to gold nanostars the bimetallic gold-silver nanostars also exhibited superior thermal and colloidal stability at elevated temperatures without the need for surface modification. Coupled with their enhanced stability, the ability to tune the extinction maxima of the new hAuAgNSTs across UV-to-NIR wavelengths offers new opportunities in photocatalysis, biosensing, and other applications that utilize plasmonic nanoparticles.

Scheme 2.1. Synthesis of Silver Nanostars and Semi-Hollow Gold-Silver Nanostars



2.2. Results and Discussion

2.2.1. Synthesis of Silver Nanostar Starting Materials

Colloidal silver nanostars were obtained using the method described in the experimental section. The scanning electron microscopy (SEM) and transmission electron

microscopy (TEM) images in Figures 2.2a and 2.2b reveal that the synthesized silver nanostars have an average size of ~190 nm with the number of arms varying from 8 to 16. A small number of overgrown silver nanostars exhibit secondary arms when the nanostar size is bigger than 300 nm. The size distribution of the silver nanostars is provided in the inset of Figure 2.2a.

2.2.2. Synthesis and Morphology of Semi-Hollow Gold-Silver Nanostars

As outlined in Scheme 1.1, the fabrication of semi-hollow gold-silver nanostars (hAuAgNSts) was achieved by galvanic replacement of silver nanostars in a basic gold salt (K-Au) solution containing potassium carbonate and hydrogen tetrachloroaurate hydrate. In the K-Au solution, metallic silver is oxidized by Au^{3+} ions to form Ag^+ ions and metallic gold. During this process, silver atoms of AgNSts are replaced by gold atoms to form semi-hollow bimetallic gold-silver nanostars. The formation of the semi-hollow Au-Ag nanostars revealed characteristic pinhole features as shown in Figures 2.2c and particularly Figure 2.2d. The pinhole features correspond to the sites of highly active galvanic replacement, which creates hollow cavities like those observed in previous studies involving the synthesis of hollow gold-silver nanoshells and other galvanically replaced bimetallic hollow nanostructures.^{291–293} The size distribution of the Au-Ag nanostars is provided in the inset of Figure 2.2c. Interestingly, the etching process led to a shrinkage in size of the newly formed bimetallic hAuAgNSts; when compared to the starting Ag nanostars (~190 nm), the average size of the gold-silver nanostars was found to be ~170 nm.

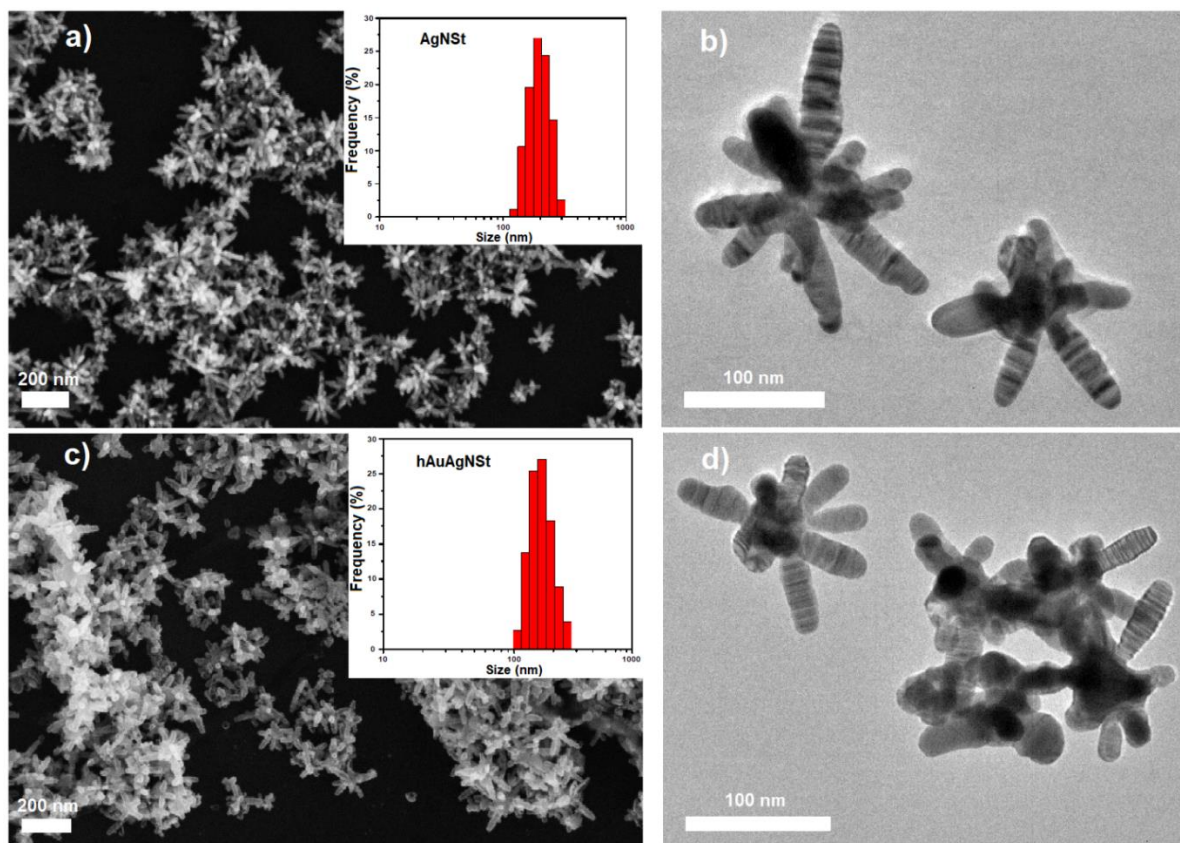
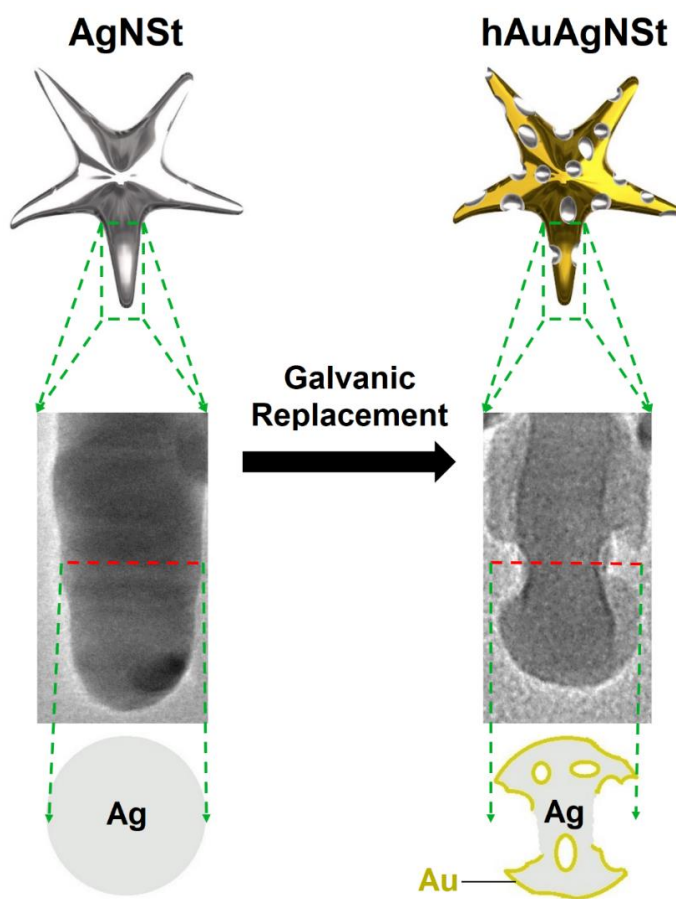


Figure 2.2. (a) SEM, (b) TEM images, and size distribution (inset) of the Ag nanostar starting materials and (c) SEM, (d) TEM images, and size distribution (inset) of the semi-hollow gold-silver nanostars.

The galvanic replacement process involved in the formation of the AgNSts is illustrated in Scheme 2.2. When K-Au and AgNSt colloidal solutions are mixed together, Ag atoms on the surface of the AgNSts are oxidized to form Ag^+ ions in solution, while the Au atoms formed via the galvanic reduction of Au^{3+} ions are deposited on the surface of the Ag nanostar substrates.^{291,292,294} The rapid oxidation taking place at the pinhole sites leads to rapid removal of silver atoms and the consequent generation of hollow cavities as illustrated in Scheme 2.2.

In addition to the pinhole features, a greater number of depression-areas can be observed on the surface of the gold-silver nanostars (see Figure 2.2d and Scheme 2.2.) compared to the smoother surface of silver nanostars (Figure 2.2b). The widespread presence of the depression-areas on the surface of the Au-Ag nanostars indicates that the galvanic corrosion and replacement of silver atoms by gold ions occurred at multiple sites across the nanostar structure. It should be noted that rapid and thorough mixing of the K-Au solution after adding to the AgNSt stock solution is critical to achieving a uniform population of hollow gold-silver nanostars.

Scheme 2.2. Formation of Semi-Hollow Gold-Silver Nanostars via Galvanic Replacement on Silver Nanostars by Treatment with K-Gold Solution



2.2.3. Elemental Characterization of Semi-Hollow Gold-Silver Nanostars

We used energy-dispersive X-ray spectroscopy (EDX) to study the elemental composition and distribution of the semi-hollow gold-silver nanostars. Figure 2.3 shows a representative transmission electron microscopy (TEM) image and the corresponding EDX elemental maps of the semi-hollow gold-silver nanostars prepared using our methodology. While Figure 2.3b confirms the presence of Ag atoms throughout the bimetallic nanostar, Figure 2.3c shows a uniform distribution of Au atoms throughout the bimetallic nanostar, which is consistent with the introduction of gold atoms via galvanic replacement. Additionally, the line-scan spectrum along one arm of a typical semi-hollow gold-silver nanostar (Figure 2.4) also demonstrates the presence and uniform distribution of Ag and Au within the bimetallic gold-silver nanostar structure.

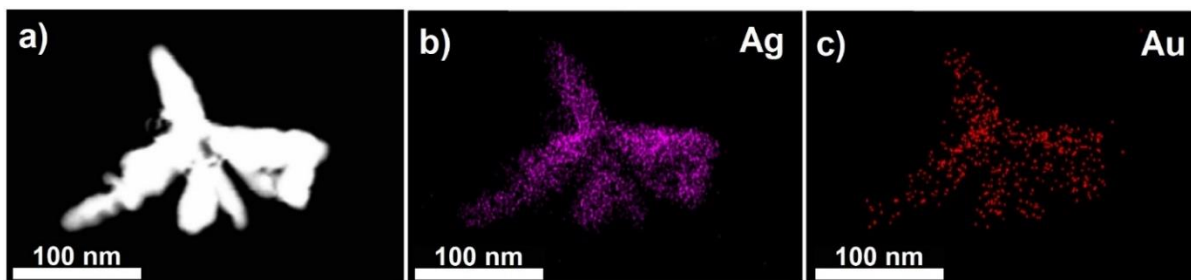


Figure 2.3. (a) TEM image and TEM-EDX elemental maps for (b) Ag and (c) Au in a typical semi-hollow gold-silver nanostar.

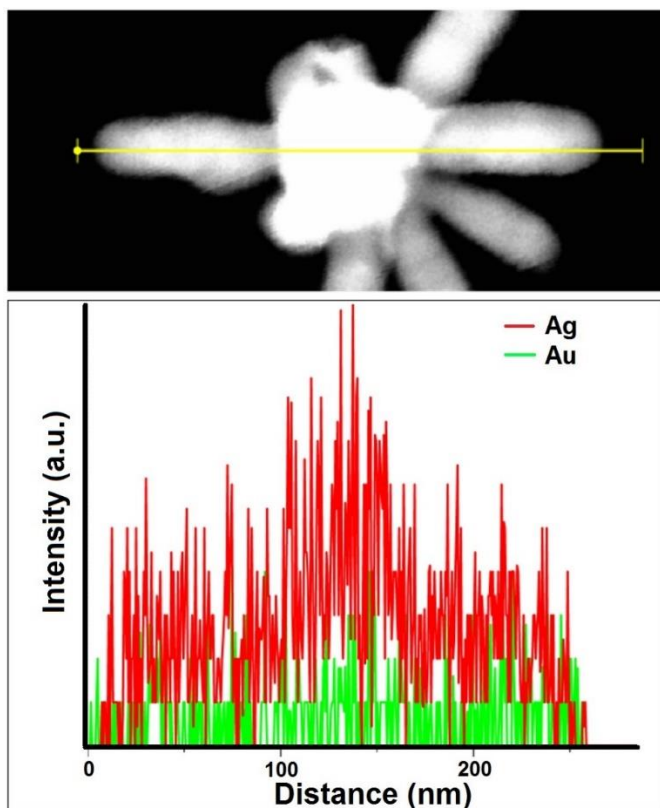


Figure 2.4. TEM-EDX elemental line scanning spectrum of semi-hollow gold-silver nanostars (hAuAgNSTs).

The EDX spectrum of the hollow gold-silver nanostars Figure 2.5 confirms the presence of the characteristic $L\alpha$ (2.98 keV) and $L\beta$ (3.21 keV) peaks of silver, as well as the characteristic $L\alpha$ (9.71 keV) and $M\alpha$ (2.13 keV) peaks of gold. A small $L\alpha$ peak at 0.93 keV was also observed for the supporting copper grid of the TEM sample holder used in the measurement. Moreover, the atomic concentrations of gold in the bimetallic gold-silver nanostars formed in various etching conditions were also determined.

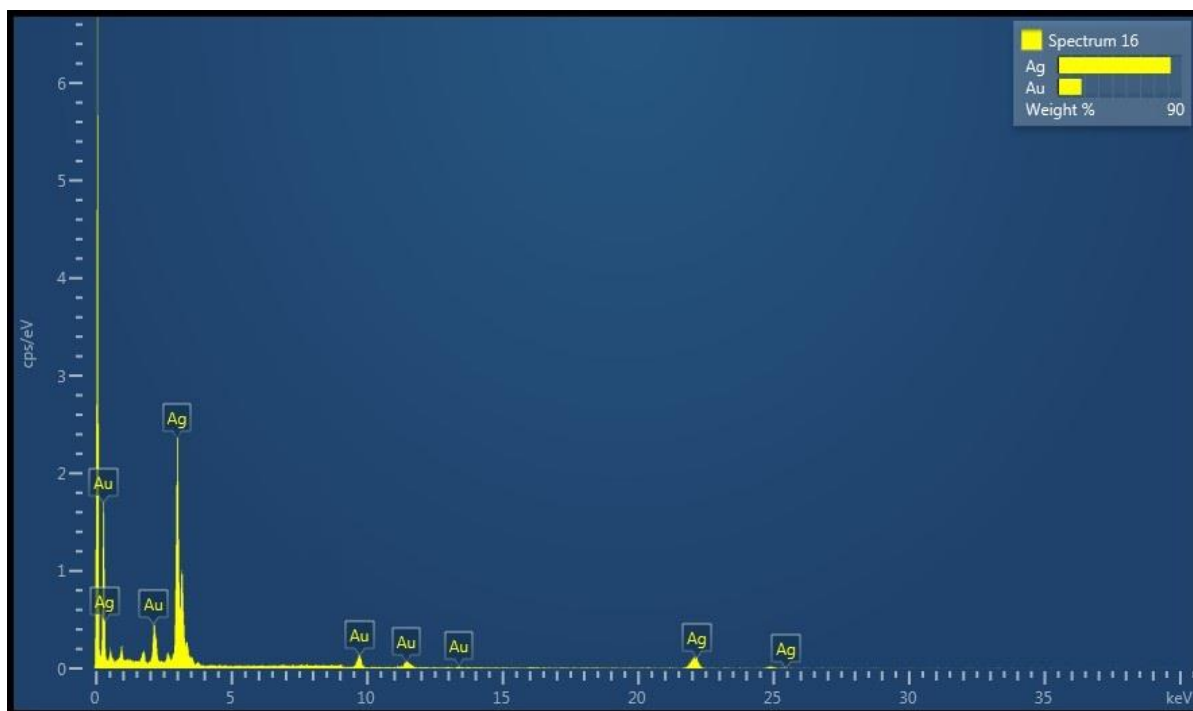


Figure 2.5. TEM-EDX spectrum of semi-hollow gold-silver nanostars (hAuAgNSts).

The graph in Figure 2.6 shows the average Au atomic percentages in hAuAgNSts prepared with K-Au/AgNSts solution volume ratios of 0, 0.05, 0.1, 0.2, and 0.5. The linear relationship between Au content in hAuAgNSts and K-Au/AgNSt ratio allows for precise tunability of the elemental composition of the targeted bimetallic semi-hollow gold-silver nanostars. This compositional flexibility is critical to fine-tune the extinction maximum of the plasmon resonance of the hAuAgNSts and will be discussed in more detail in the Optical Properties section below.

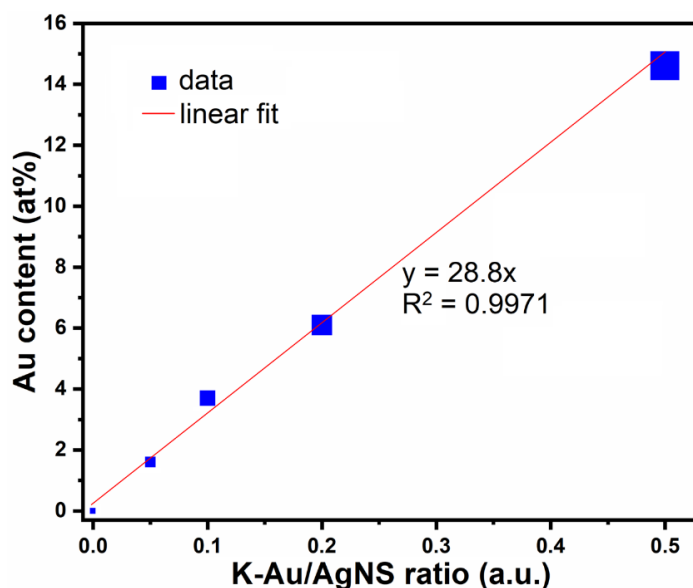


Figure 2.6. Au content of semi-hollow gold-silver nanostars synthesized using various ratios of K-Au and silver nanostar stock solutions. The size of the symbol reflects the error in the measured data point.

2.2.4. Crystallinity of the Semi-Hollow Gold-Silver Nanostars

The crystalline characteristics of the three types of nanostars were evaluated using X-ray diffraction (XRD). Figure 2.7 shows the XRD patterns of hAuAgNSTs, AuNSTs, and AgNSTs together with the reference peaks for pure Au (JCPDS card no. 04-0784) and pure Ag (JCPDS card no. 04-0783). For Ag nanostars (Figure 2.7a), strong diffraction peaks at $2\theta = 38.15^\circ$, 44.15° , 64.42° , and 77.34° corresponding to the respective (111), (200), (220), and (311) crystallographic planes of silver were observed. For Au nanostars (Figure 2.7b), strong peaks at $2\theta = 38.21^\circ$, 44.33° , 64.72° , and 77.74° corresponding to the respective (111), (200), (220), and (311) crystallographic planes of gold were observed. In the case of hollow gold-silver nanostars (Figure 2.7c), strong peaks at $2\theta = 38.19^\circ$, 44.23° , 64.61° , and 77.58° corresponding to the respective (111), (200), (220), and (311) crystallographic planes were observed. The similar reflections and close proximity of the diffraction peaks from the three

types of metallic nanostars can be attributed to the fact that both gold and silver have the same crystal structure (face-centered cubic) and possess similar atomic radii. Moreover, the average lattice constants of 408.29, 407.71, and 407.84 pm for AgNSts, AuNSts, and hAuAgNSts, respectively, were also calculated from the XRD patterns. Thus, the XRD results confirm the crystalline characteristics of metallic Au, Ag, and semi-hollow Au-Ag nanostars.

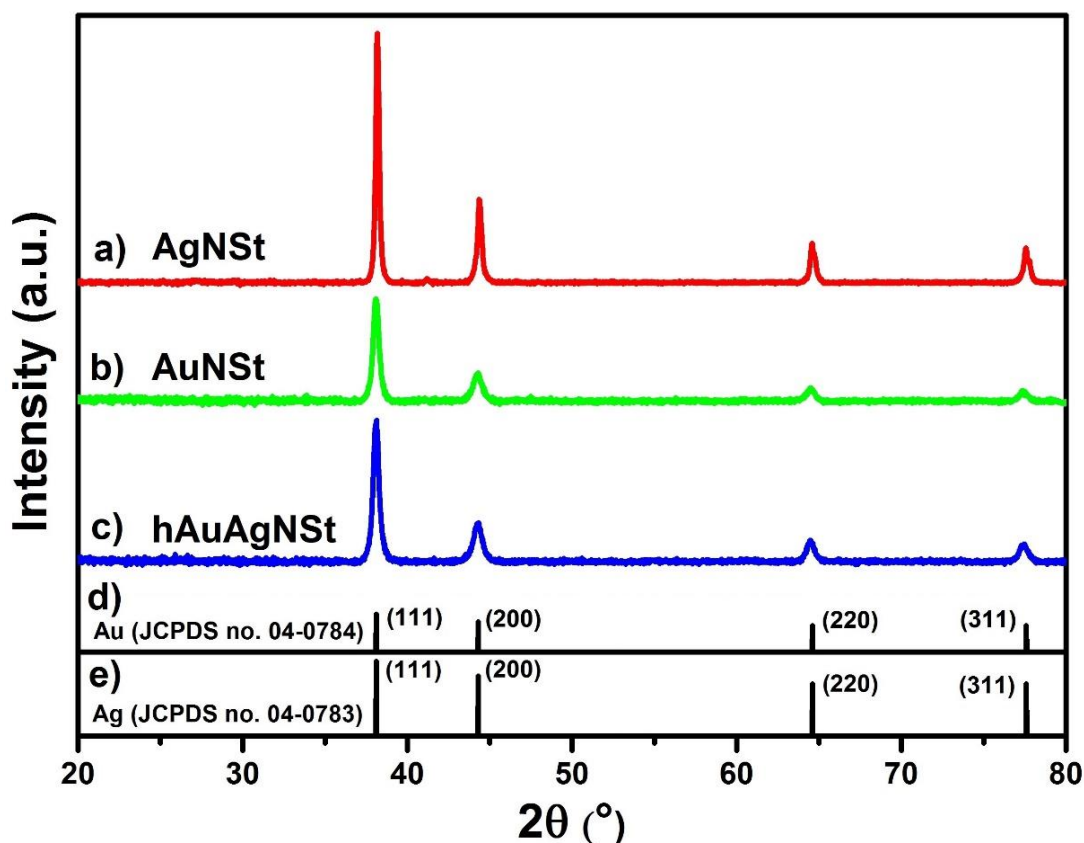


Figure 2.7. XRD spectra of (a) silver nanostars, (b) gold nanostars, (c) semi-hollow gold-silver nanostars in comparison with the reference patterns of (d) gold, and (e) silver.

2.2.5. Optical Properties

UV-Vis extinction spectra of the AgNSts, hAuAgNSts, and AuNSts were recorded and are presented in Figure 2.8; the corresponding localized surface plasmon resonance (LSPR) maxima as a function of Au content are provided in Table 2.1. The data show that

the extinction maxima redshift from ~ 375 nm for the AgNSts to ~ 450 nm for the hAuAgNSts with increasing atomic concentrations of gold to ~ 730 nm for the AuNSts. Notably, at the highest concentrations of gold, the hAuAgNSts exhibit strong extinction tails that span the entire visible spectrum and parts of the near infrared. This broadband extinction characteristic makes the semi-hollow gold-silver nanostars potentially useful for radiation blocking.^{295,296} Furthermore, the expansion from the UV region (5% of solar radiation)²⁹⁰ into the visible (43% of solar radiation)²⁹⁰ and NIR-regions of the solar spectrum offers unique opportunities for a myriad of solar-driven applications that include photocatalysis,^{223,275,286} photovoltaics,^{234,236} and photothermal power generation.²⁹⁷

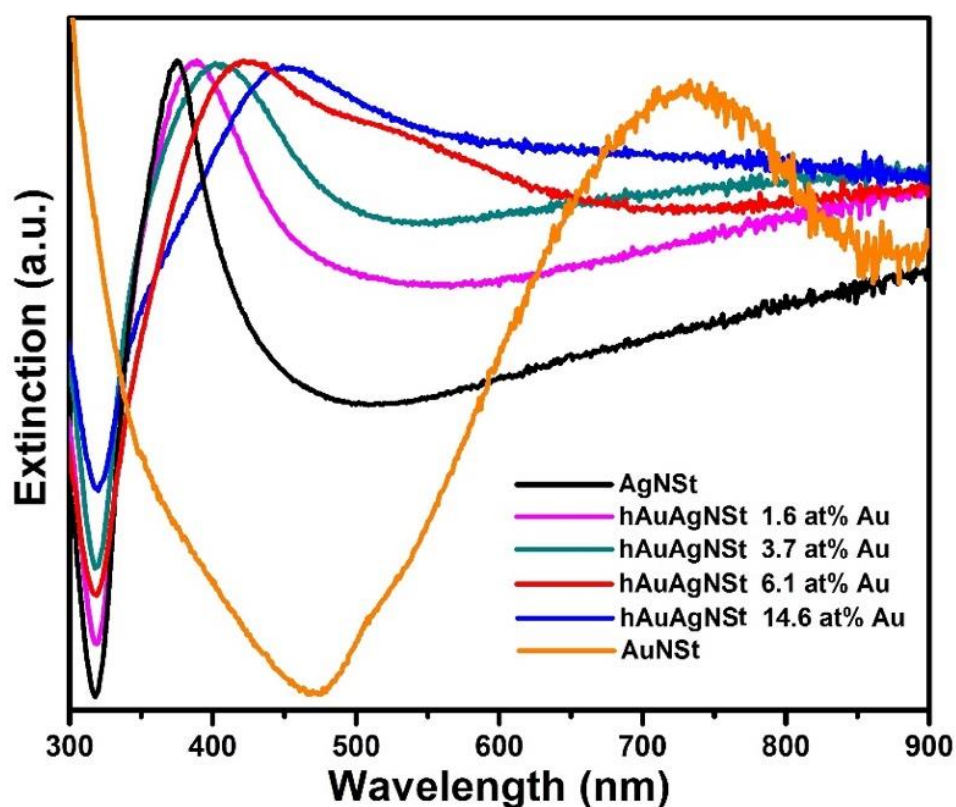


Figure 2.8. Extinction spectra of silver nanostars, semi-hollow gold-silver nanostars with varying Au content, and gold nanostars.

Table 2.1. Localized Surface Plasmon Resonance Maxima and Au Content of Semi-Hollow Gold-Silver Nanostars at Various Ratios of K-Au/AgNSt

Sample	AgNSt	hAuAgNSt	hAuAgNSt	hAuAgNSt	hAuAgNSt	AuNSt
K-Au/AgNSt	0	0.05	0.1	0.2	0.5	--
Au at%	0	1.6 ± 0.2	3.7 ± 0.3	6.1 ± 0.3	14.6 ± 0.5	100
LSPR (nm)	~375	~390	~405	~425	~450	~730

Similar to the phenomenon observed with plasmonic nanorods,²⁹⁸ the broadening of the extinction peaks of hAuAgNSts with increased Au content can be attributed, at least in part, to the size shrinkage of the hAuAgNSts compared to the starting AgNSts (vide supra). Furthermore, it is likely that the extinction tail arises in part from the various longitudinal oscillation modes^{299,300} along the many different arms of the gold-silver nanostars.³⁰¹ And perhaps more importantly, the broadening and redshifting of the extinction maxima can be attributed to the change in the Au-Ag nanostar composition^{302,303} as well as the increased formation of hollow cavities when increasing the K-Au/AgNSt ratio in solution.^{304,305} These relationships, when coupled with the previously discussed capacity to adjust the elemental composition of the hAuAgNSts, enables facile tuning of the optical responses of the semi-hollow gold-silver nanostars simply by adjusting the galvanic replacement conditions used in their preparation.

2.2.6. Stability Studies

Since the tendency of gold nanostars to aggregate leads to complications that often require surface functionalization^{69,119,282,283} that limit the range of potential applications, we evaluated the thermal and colloidal stabilities of our unfunctionalized bimetallic gold-silver nanostars at elevated temperatures. As a first step, we determined the surface charges of AgNSts, hAuAgNSts, and AuNSts²³ at room temperature using zeta potential measurements,

which found that both AgNSts and hAuAgNSts have greater surface charges (-31.3 and -28.9 mV, respectively) than AuNSts (-25.5 mV); these measurements thus predict a higher colloidal stability for the new hAuAgNSts when compared to the more common AuNSts.

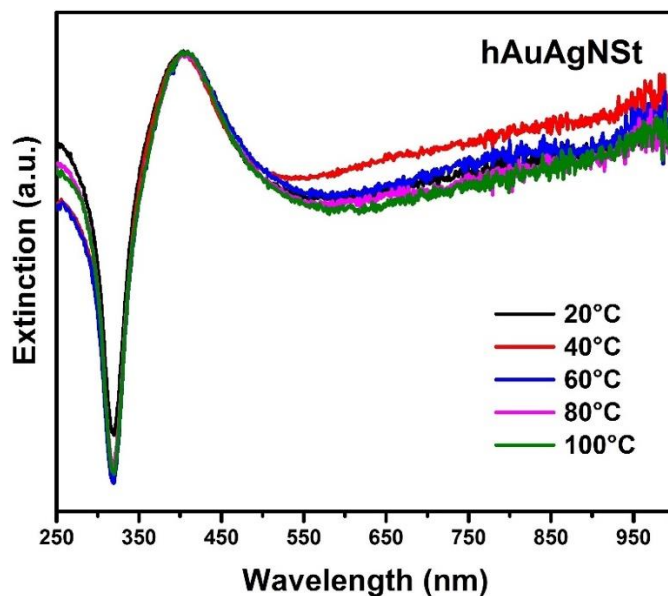


Figure 2.9. Extinction spectra of hollow gold-silver nanostars after heating at the indicated temperatures.

In further studies, Figure 2.9 shows the extinction spectra of the hollow gold-silver nanostars after heating for 1 h at 40, 60, 80, and 100 °C. Importantly, the spectra remained constant at all temperatures, indicating a high thermal and colloidal stability for the semi-hollow bimetallic Au-Ag nanostars. Notably, the size and morphology of the hAuAgNSts were largely unchanged after the heating (Figure 2.10), which can be taken as a further indication of the stability of the hAuAgNSts.

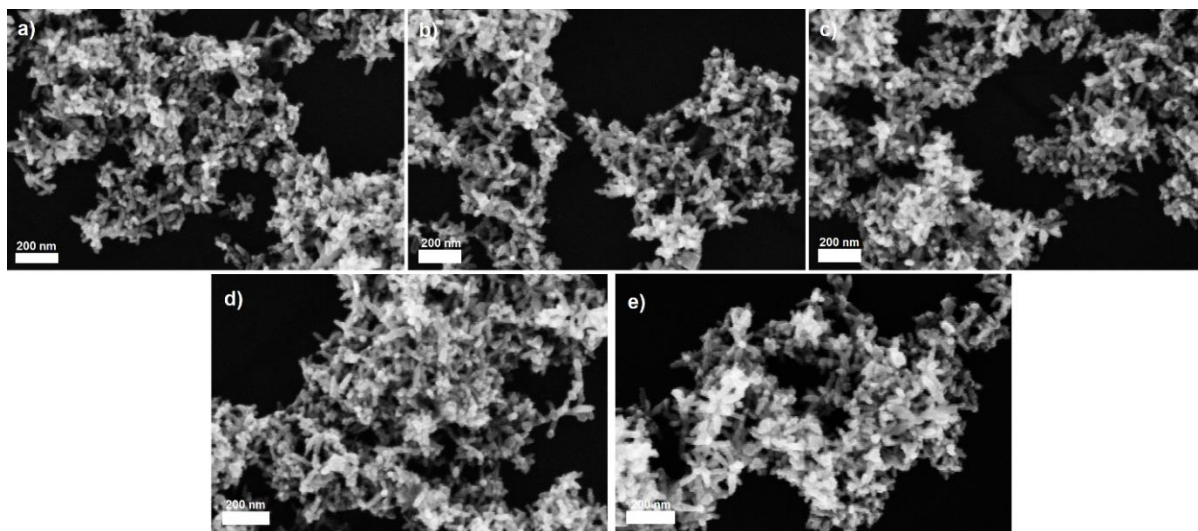


Figure 2.10. SEM images of semi-hollow gold-silver nanostars (hAuAgNSts) held in water for 1 h at (a) 20 °C, (b) 40 °C, (c) 60 °C, (d) 80 °C, and (e) 100 °C.

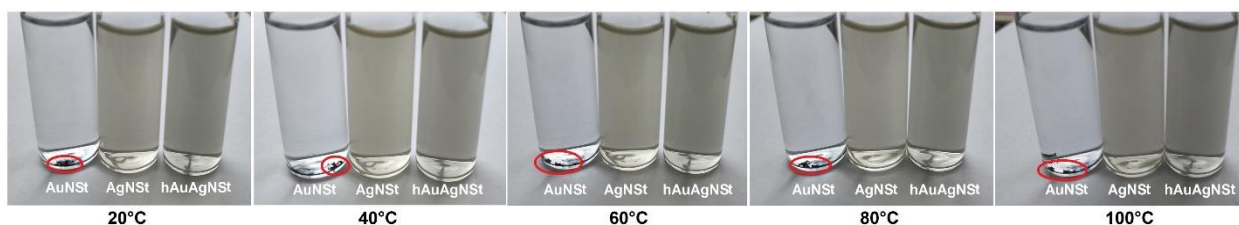


Figure 2.11. Images of gold, silver, and semi-hollow gold-silver nanostars (hAuAgNSts) in water after heating at the indicated temperatures.

Moreover, the hAuAgNSt solutions remained colloidal stable even after heating at 100 °C, as shown in Figure 2.11. In comparison, the AuNSt solution had visible aggregation even at room temperature (Figure 2.11). The optical response of AuNSts also varied significantly with temperature (Figure 2.12a and Table 2.2). The high stability even at elevated temperatures gives the newly developed bimetallic semi-hollow gold-silver nanostars significant potential for applications that require non-aggregated and/or non-functionalized nanostructures such as catalysis, photovoltaics, biosensing, and drug delivery.

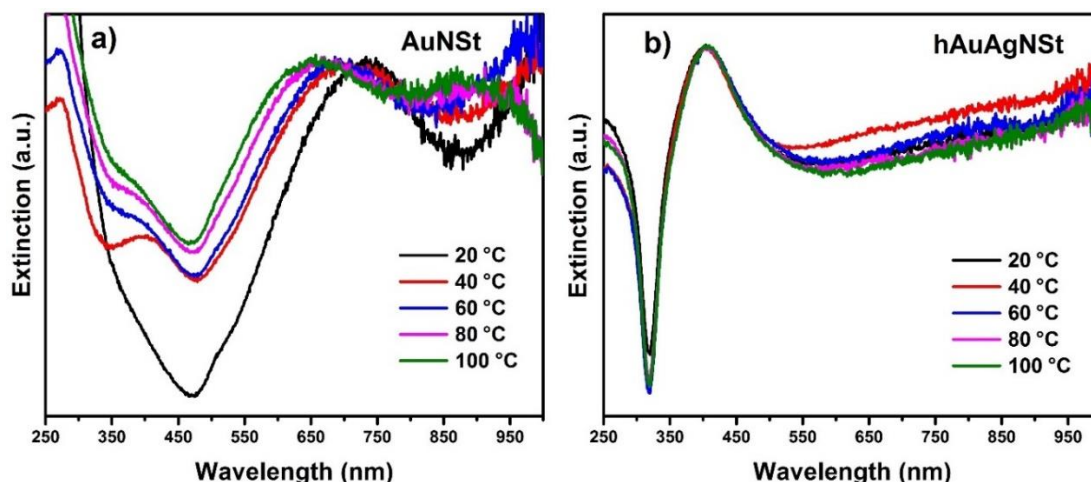


Figure 2.12. Extinction spectra of (a) gold and (b) semi-hollow gold-silver nanostars after heating at the indicated temperatures.

Table 2.2. LSPR Peak Positions of AuNSts and hAuAgNSts after Heating for 1 h at the Indicated Temperatures

Sample	LSPR Peak Position					Nanoparticle Aggregation				
	20 °C	40 °C	60 °C	80 °C	100 °C	20 °C	40 °C	60 °C	80 °C	100 °C
AuNSts	730	710	695	670	650	high	high	high	high	high
hAuAgNSts	405	405	405	405	405	-	-	low	low	moderate

2.3. Conclusions

This report demonstrates the fabrication of semi-hollow gold-silver nanostars (hAuAgNSts) via galvanic replacement of silver nanostars (AgNSts). The morphology, size distribution, surface charge, composition, crystallinity, and optical properties of the newly developed bimetallic Au-Ag nanostars were thoroughly characterized. Notably, the semi-hollow gold-silver nanostars exhibited enhanced thermal and colloidal stability when compared to conventional gold nanostars (AuNSts). Furthermore, simply by controlling the composition of the gold-silver nanostars, the optical extinctions of the hAuAgNSts were found to be tunable across ultraviolet and visible wavelengths with strong tailing into the near-infrared. The versatile optical tunability, the broad and strong extinctions, and the enhanced

thermal and colloidal stability render the hAuAgNSTs potentially useful for a multitude of solar-driven applications such as photocatalysis, photovoltaics, radiation blocking, and biosensing.

2.4. Materials and Methods

2.4.1. Materials

Silver nitrate (Sigma-Aldrich), trisodium citrate (EM Science), sodium hydroxide (Macron Chemicals), hydroxylamine (Thermo Fisher Scientific), hydrogen tetrachloroaurate(III) hydrate (Strem), potassium carbonate (J. T. Baker), nitric acid (EM Science), hydrochloric acid (EM Science), Triton X-100 (Sigma-Aldrich), sodium borohydride (Sigma-Aldrich), and ascorbic acid (Sigma-Aldrich) were purchased from the indicated suppliers and used without further purification. Deionized water was obtained from an Academic Milli-Q Water System (Millipore Corporation). All glassware used in the syntheses was cleaned with aqua regia solution ($\text{HCl}:\text{HNO}_3 = 3:1$), rinsed with Milli-Q water, and dried prior to use.

2.4.2. Synthesis of Silver Nanostars

Silver nanostars were prepared via modification of a previously reported method.²⁸⁹ In a typical experiment, a mixture of 0.5 mL of 0.06 M hydroxylamine and 0.5 mL of 0.05 M NaOH was added into 9 mL of 0.111 mM AgNO_3 under magnetic stirring at 20 °C for 5 min in a 20-mL glass vial. Afterward, 100 μL of 0.03 M sodium citrate solution was added into the vial followed by 15 min of stirring. Shortly after the addition of sodium citrate, the mixture turned from clear to grayish murky indicating the formation of silver nanostars. The

final solution was then centrifuged at 8000 rpm for 15 min and the volume reduced to 200 μ L and kept as the AgNSt stock solution for further use.

2.4.3. Synthesis of Semi-Hollow Gold-Silver Nanostars

A potassium-containing gold salt solution (K-Au solution) was prepared by mixing 5 mL of 2 mM K_2CO_3 aqueous solution with 100 μ L of 30 mM $HAuCl_4$ aqueous solution for 1 h. Semi-hollow gold-silver nanostars were fabricated via galvanic corrosion of the as-synthesized silver nanostars upon treatment with the K-Au solution. In typical experiments, 1 mL aliquots of AgNSt stock solution were placed in glass vials under vigorous stirring. Selected amounts of K-Au solution (0.05, 0.1, 0.2, 0.5 mL) were injected into the vials containing the AgNSts followed by 5 h of stirring for the formation of hAuAgNSts possessing various amounts of gold. The final solutions were centrifuged at 8000 rpm for 15 min and then washed with deionized water 3 times before storage.

2.4.4. Synthesis of Gold Nanostars

Gold nanostars were synthesized via modification of a previously reported method.²³ Gold nanoseeds were prepared by adding 10 mL of 0.2 mM aqueous $HAuCl_4$ solution to 10 mL of 150 mM Triton X-100 aqueous solution; 600 μ L of fresh cold 10 mM sodium borohydride was then added to the mixture to form the gold nanoseeds. Separately, the AuNSt growth solution was prepared by adding 280 μ L of 4 mM $AgNO_3$ solution and 0.4 mL of 25 mM $HAuCl_4$ solution to 20 mL of a 150 mM aqueous solution of Triton X-100. Then, 300 μ L of 0.78 M ascorbic acid solution was added to the growth solution at rt with stirring. When the mixture became colorless, 14 μ L of the gold nanoseed solution was added to the growth

solution. The solution turned blue and was stirred for another 8 h at rt to generate the gold nanostars.

2.4.5. Nanoparticle Characterization

All synthesized nanoparticles were imaged using a LEO-1525 scanning electron microscope (SEM) operating at 15 kV and 5.5 mm working distance. All SEM samples were deposited on pre-cleaned silicon wafers and dried at 60 °C in an oven for 1 h before imaging. An X'Pert powder X-ray diffractometer operating at 45 kV and 30 mA was used to assess the crystalline nature of the nanoparticles. All powder X-ray diffraction (PXRD) samples were prepared by drop-casting and drying on glass slides in an oven at 60 °C for 2 h. A JEOL JEM-2010 FX transmission electron microscope (TEM) with electron dispersive X-ray spectroscopy (EDX) function operating at 200 kV was used to assess the morphology and the elemental distribution of the nanostars. All samples for TEM characterization were deposited on 300-mesh holey carbon-coated nickel grids and dried at 60 °C for 2 h before analysis. A Cary 50 scan UV-visible (UV-Vis) spectrometer operating over a spectral range of 200–1000 nm was used to measure the optical properties of the synthesized nanostars. Zeta potential measurements were conducted on a Malvern Zetasizer model ZEN3600.

2.4.6. Stability Studies

The stability of the synthesized hAuAgNSts, and AuNSts were assessed by heating their aqueous solutions at 20, 40, 60, 80, and 100 °C for 1 h followed by cooling to room temperature. At each temperature, the cooled-down nanostar solutions were checked for visible aggregation before having their extinction spectra recorded.

Chapter 3: Optically Enhanced Ag@Cu₂O Core-Shell Nanoparticles for Visible Light Photocatalytic Hydrogen Evolution

3.1. Introduction

In the midst of the growing energy demand and environmental concerns, as well as the intermittency inherent to photovoltaics and wind turbines, photocatalysis with the use of semiconductor materials has emerged as a potential technology to overcome the challenges.³⁰⁶ Photocatalysts have been demonstrated to generate high energy density fuels and high value-added products as well as to eliminate environmental pollutants with solar radiation as the only required energy source.³⁰⁶ Since the first work on photocatalysis using titanium dioxide (TiO₂) reported by Fujishima and Honda,³⁰⁷ much research effort has been spent to develop various efficient photocatalysts for many practical applications.³⁰⁸ However, low photon absorbance in the solar radiation spectrum, high recombination rate of photogenerated electron-hole pairs, as well as high cost have been major challenges for the applicability of many traditional photocatalysts.^{309,310} For instance, the first reported photocatalyst anatase TiO₂ with a large band gap at ~3.2 eV only absorbs photons in the ultraviolet region which makes up less than 5 % of the total solar energy flux.³¹¹ With the emergence of nanocrystal fabrication techniques in recent decades, nanoparticle-based photocatalysis has become a promising approach to improve the efficiency of numerous photocatalysts.^{312–314} The high surface-to-volume ratio of nanoparticles (NPs) not only can significantly enhance catalytic activity of the nano-sized photocatalysts but also substantially reduce the number of materials required for the application compared to bulk catalysts.³¹⁵ Moreover, nanoscale

semiconductor photocatalysts can also benefit from the quantum confinement effect to improve the optical absorbance of the material.³¹⁶

Due to their unique localized surface plasmon resonance, various plasmonic nanostructures such as nanospheres,²¹¹ nanorods,³¹⁷ and nanostars¹¹ have been studied for various utilizations from enhanced imaging¹⁹⁴ to biomedical applications.^{70,103} In photocatalysis, plasmonic silver, gold, and copper-based nanoparticles have been demonstrated to be good solar radiation sensitizers with absorption peaks in the visible region at ~ 407 ,³¹⁸ 525 ,³¹⁹ and 600 nm,³²⁰ respectively. In plasmonic nanostructures, the free electron cloud oscillates collectively under an incident electromagnetic radiation generating an enhanced electromagnetic field close to the surface of the plasmonic nanomaterial.⁷ When the characteristic frequency of the collective oscillation matches that of the external radiation, localized surface plasmon resonance (LSPR) occurs and the plasmonic structure shows an absorption peak at that LSPR frequency.³²¹ The LSPR wavelength can be blue- or red-shifted by varying the size, morphology, and type of metal or by changing the dielectric constant of the local environment surrounding the structure.^{322,323} Furthermore, the locally amplified electric field can also induce electron injection and energy transfer on the semiconductor materials that are in contact with the plasmonic nanostructures.^{324,325} Although plasmonic nanostructures can be used as photocatalysts by themselves,^{326–328} their development has strongly inspired new approaches for design and synthesis of more efficient photocatalysts by combining plasmonic metal materials with semiconductors in proper architectures.^{329–331} Due to the plasmon-induced resonance energy transfer (PIRET) and direct electron transfer (DET) from the metal to the coupling semiconductor, the photocatalytic activity of plasmonic metal-

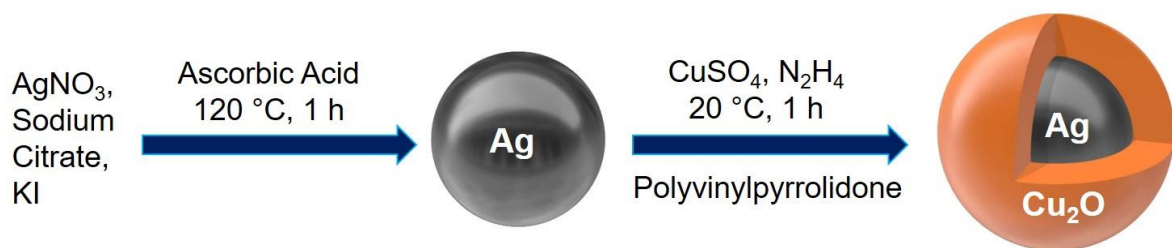
semiconductor nanocomposites can be significantly increased compared to semiconductor photocatalysts.^{332,333} Essentially, with the extended absorption range into the visible region of the metal parts, plasmonic-semiconductor nanocomposites can absorb more solar energy in a wider range of light wavelengths than their semiconductor counterpart.³³⁴

Among various plasmonic nanostructures, silver nanoparticles possess many advantages for photocatalytic applications from high capacity to induce surface plasmon resonance³³⁵ to high thermal and electrical conductivity.³³⁶ Moreover, the LSPR wavelength at the violet end of the visible region (~ 407 nm) of silver nanoparticles³¹⁸ makes them great candidates for couple with semiconductor materials to shift the absorption band to the center of the solar spectrum which can significantly enhance the photocatalytic activity of nanoparticles. As a p-type semiconductor, cuprous oxide (Cu_2O) exhibits a wide range of applications in sensors,³³⁷ photovoltaics,³³⁸ and electronics.³³⁹ Cu_2O also possesses many important properties for a promising photocatalyst such as a narrow band gap,³⁴⁰ a high carrier mobility ($\sim 100 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$),³⁴¹ a high carrier diffusion length of ~ 500 nm,³⁴² as well as low cost and high abundance of materials. We envision that a plasmonic Ag NP core embedded within a Cu_2O shell ($\text{Ag}@\text{Cu}_2\text{O}$) might further improve the photocatalytic activity of Cu_2O due to the aforementioned enhancement mechanisms. Furthermore, coupling with plasmonic nanostructures can also suppress the rapid electron-hole recombination in the Cu_2O semiconductor, a major drawback associated with traditional metal oxide photocatalysts.^{343,344}

Several studies on cuprous oxide-coated silver nanoparticles have been reported with different synthesis methods and characterization focuses.^{345–348} Besides the accomplishments, there are still various fabrication shortcomings and characterization inadequacies that should

be addressed such as the use of demanding synthesis conditions,^{345,346} lack of control on structure and size distributions,^{346,347} or insufficient photocatalysis-related properties study.^{346,348} In this report, we describe a convenient and efficient wet chemistry method to synthesize spherical, monodisperse Ag@Cu₂O core-shell and Cu₂O nanoparticles at mild conditions (Scheme 3.1).

Scheme 3.1. Synthesis of Silver and Ag@Cu₂O Core-Shell Nanoparticles



The work also demonstrated the capability to fine-tune the thickness of the Cu₂O shell to adjust the absorption peak into the center of the solar spectrum. Furthermore, the composite core-shell nanoparticles showed significant suppression of photoluminescence signal on Cu₂O semiconductor suggesting that the plasmonic silver core can efficiently reduce the photogenerated electron-hole recombination rate which impedes the photocatalytic applicability of Cu₂O. With a conduction band minimum higher than the reduction potential for proton,³⁴⁹ Cu₂O-based nanostructures are potential catalysts for hydrogen evolution reaction (HER) to generate hydrogen as a clean and high energy capacity alternative for gasoline with solar radiation as the only required source of energy. Hence, the Ag@Cu₂O core-shell nanoparticles synthesized in this work were tested for their photocatalytic hydrogen generating performance under a visible light irradiation condition. Notably, the photocatalytic hydrogen evolution reaction studies showed significantly increased hydrogen evolution rate

as well as higher photostability of Ag@Cu₂O nanoparticle catalysts compared to Cu₂O counterpart.

3.2. Materials and Methods

3.2.1 Materials

Silver nitrate (AgNO₃, Sigma-Aldrich), potassium iodide (KI, Aldrich), ascorbic acid (AA, Aldrich), trisodium citrate (NaCit, EM Science), polyvinylpyrrolidone (PVP, MW~55 k, Aldrich), copper(II) sulfate pentahydrate (CuSO₄·5H₂O, Sigma-Aldrich), hydrazine monohydrate (64 wt% N₂H₄, Sigma Aldrich), polyethylene glycol (EG, Sigma-Aldrich), sodium hydroxide (NaOH, Macron Chemicals), argon (Ar, Matheson) were used without any further treatment after purchased from the indicated suppliers. Deionized water with a resistivity of 18.2 MΩ-cm was obtained from the Academic Milli-Q Water system of Millipore Corporation. All glassware used in the experiments was cleaned for at least 12 hours in a base bath, followed by piranha solution (3:1 H₂SO₄:H₂O₂) and aqua regia solution (3:1 HCl:HNO₃) for at least 6 hours, and then dried in an oven at 150°C followed by cooling prior to use. Extra caution should be used in handling the cleaning process.

3.2.2. Synthesis of Silver Nanoparticles

A modification of the method reported by Medhi et al.³⁴³ was used to prepare silver nanoparticles. Firstly, 200 mL of Milli-Q water in a 250-mL round-bottom flask was heated in an oil bath at 120°C under active reflux until boiling before 3 mL of 5 mM ascorbic acid solution was added. In the meantime, the silver precursor mixture was prepared by dissolving 35 mg of AgNO₃ in 4 mL of water, followed by the addition of 4 mL of 1 wt% sodium citrate

solution and 150 μL of 8 μM KI solution. The silver precursor mixture was well shaken and placed in an ultrasonic bath for 5 min at 21°C before being injected into the boiling aqueous solution of ascorbic acid under vigorous magnetic stirring without making any air bubbles in the solution. The solution was stirred under reflux for another hour for the complete formation of Ag nanoparticles (Ag NPs). During the process, the solution quickly turned from colorless to brownish yellow and then yellowish green after a few minutes indicating the formation of Ag NPs. After cooling down to room temperature in 30 min, the Ag NP solution was centrifuged at 7000 rpm for 15 min followed by the supernatant removal before being redispersed in 25 mL Milli-Q water. This washing process was repeated two more times, then the resulted 25-mL Ag NP stock solution was stored at 4 °C if not immediately characterized or coated with Cu_2O . Note: The flask and stir bar need to be washed thoroughly with deionized water and an aqua regia solution reserved exclusively for the Ag NP synthesis to yield consistent results for Ag NPs.

3.2.3. Synthesis of Ag@Cu₂O Core-Shell Nanoparticles

The cuprous oxide coating of Ag NPs was accomplished following a procedure reported by Chen et al.³⁴⁸ with substantial modifications. Scheme 1 illustrates the synthesis and coating process of Ag@Cu₂O. In a typical experiment, a surfactant solution was prepared by dissolving 400 mg of PVP (MW~55000) in 8.5 mL Milli-Q water with ultrasonication for 20 minutes. Different amounts of the Ag NP stock solution (200, 400, 800, 1600, 2400 μL) were added into the surfactant solution. After ultrasonication for 10 minutes for better dispersion and stabilization of the Ag NPs, 400 μL of 0.1 M CuSO_4 solution was added to the mixture under vigorous magnetic stirring. The solution was further stirred for 2 minutes, then

125 μL of 1 wt% N_2H_4 was injected over 5 minutes into the vigorously stirred mixture. After 1 hour, the nanoparticles were collected by centrifugation at 7000 rpm in 15 min and redispersed in 5 mL of ethanol.

3.2.4. Synthesis of Cu_2O Nanoparticles

Spherical Cu_2O nanoparticles were also synthesized by a method similar to the coating procedure without Ag NPs and with some modifications to enhance particle uniformity. The process started with the dissolution of 800 mg PVP (MW ~55000) in 8.5 mL Milli-Q water with ultrasonication in 30 min. Next, 400 μL of 0.1 M CuSO_4 aqueous solution was added into the surfactant solution under the stirring speed of 400 rpm and the temperature of 30°C . The solution was stirred for 1 more minute before the stirring speed was increased to 600 rpm and 125 μL of 1 wt% N_2H_4 solution was injected into the mixture in 30 seconds. The resulted solution turned brick red soon after N_2H_4 injection signifying the formation of crystalline Cu_2O . The newly formed nanoparticles were then allowed to fully grow in another 1 hour of stirring before being collected by centrifugation at 7000 rpm in 15 min following by solvent exchange with ethanol. The Cu_2O nanoparticles were finally dispersed in 5 mL of ethanol and stored at 4°C . The increased amount of PVP, higher synthetic temperature, and faster reducing agent injection helped accelerate the nucleation process and reduce spontaneous seeding which, in turn, created a more monodisperse population of Cu_2O NPs.

3.2.5. Nanoparticle Characterization

All synthesized nanoparticles were imaged by a LEO-1525 scanning electron microscope (SEM) operating at 15 kV and 5.5 mm working distance. All SEM samples were

deposited on pre-cleaned silicon wafers and dried at 60°C in an oven for 1 hour before imaging. An X'Pert powder X-ray diffractometer operating at 45 kV and 30 mA was used to assess the crystalline nature of the nanoparticles. All powder X-ray diffraction (PXRD) samples were prepared by drop-casting and drying on glass slides in an oven at 60°C for 2 hours. A JEOL JEM-2010 FX scanning transmission electron microscope (STEM) was used at 200 kV to verify the morphology, the core-shell structure, and the shell thickness of the nanoparticles obtained under the synthesis conditions. All samples for characterization by TEM were deposited on 300-mesh holey carbon-coated nickel grids and dried at 60°C for 2 hours before analysis. A Phi X-ray photoelectron spectroscopy (XPS) system having a monochromatic Al K α X-ray source was used as a tool to evaluate the elemental composition of the nanoparticles. All XPS samples were deposited and dried on silicon wafers. Additionally, elemental distribution analyses were carried out using an energy dispersive X-ray spectroscopy (EDX) detector attached to the STEM instrument mentioned above. A Cary 50 scan UV-visible (UV-Vis) spectrometer operating over a spectral range of 200–1000 nm was used to evaluate optical properties of the synthesized nanoparticles. The uncoated Ag and cuprous oxide-coated Ag nanoparticles were suspended in water and ethanol, respectively, for the UV-Vis measurements. Photoluminescence measurements were performed on a PerkinElmer LS-55 fluorescence spectrometer to evaluate photoluminescence response from Cu₂O and Ag@Cu₂O nanoparticle samples in a quartz cuvette with an excitation wavelength of 500 nm and a 515 nm optical filter. Dynamic light scattering (DLS) measurements were conducted on a Malvern zetasizer model ZEN3600.

3.2.6. Photocatalytic Hydrogen Generation Test

The photocatalytic hydrogen evolution reaction (HER) was carried out in a custom-made air-tight 25 mL glass flask which is connected to a digital pressure transducer and has a septum-covered sampling window. The reaction flask was kept at 25 °C by a jacketed flask which was connected to a temperature regulating water circulator. In a typical test, the nanoparticle photocatalyst was dispersed with vigorous magnetic stirring in 10 mL of 10 % ethylene glycol aqueous solution in the reaction flask before being purged with high-purity compressed argon gas in 15 min. The mixture was then illuminated by an LED light source at the wavelength of 460 nm and power of 14.4 W in 6 hours. The pressure transducer connected to the reaction flask will monitor the amount of gas product generated during the reaction. The generated gas was taken through the sampling window and analyzed by a GOW-MAC series 400-P thermal conductivity gas chromatograph with Ar as the carrier gas. For the stability studies of the nanoparticles, after each cycle, the photocatalyst was centrifuged at 7000 rpm in 15 min and solvent-exchanged with deionized water 3 times before being tested in the next cycle.

3.3. Results and Discussion

3.3.1 Synthesis of the Nanoparticles

Monodisperse silver nanoparticles with diameter ~ 45-50 nm were synthesized using a modified version of the previously reported ascorbic acid-citrate reduction procedure with the assistance of KI.³⁴³ The presence of KI inhibits the growth of the (111) facet, therefore, limiting the formation of silver nanorods. The increased amounts of sodium citrate and

ascorbic acid speed up the nucleation process resulting in a homogeneous population of Ag NPs as shown in Figure 1a. Ag@Cu₂O core-shell NPs with five different shell thicknesses were synthesized via the controlled slow reduction of Cu²⁺ into Cu₂O nanocrystals around the Ag NP cores using hydrazine as the reducing agent (Figures 3.1b-f). The Cu₂O average shell thicknesses of 10, 13, 17, 27, and 45 nm were obtained by using 2400, 1600, 800, 400, 200 μ L of the Ag NP stock solution respectively. The Cu₂O shell thickness is inversely proportional to the volume of the Ag NP stock solution used. The good dispersion of Ag NPs in PVP solution by ultrasonication and the slow injection of N₂H₄ under vigorous stirring are important to obtain core-shell nanoparticles with a single Ag core and well-shaped shell. The mild conditions of the synthesis process compared to previously reported studies^{345,346} was a major reason for the capability to control the shell thickness to a small value. Interestingly, the overall spherical morphology of the core-shell nanoparticles is maintained even when the shell becomes thicker than the silver core diameter. The significantly enhanced control on the structure and size distribution of the composite nanoparticles compared to other works^{346,347} had enabled a more rigorous investigation of the optical properties and photocatalytic performance of the photocatalyst as discussed below. Additionally, spherical Cu₂O NPs were also synthesized with some modifications of the coating step procedure generating monodisperse NPs as shown in SEM image (Figure 3.2) and dynamic light scattering measurement (Figure 3.3). This convenient synthesis route with very mild conditions is a great candidate for large-scale production of highly monodisperse spherical Cu₂O NPs with high consistency, one of the key challenges in practical nanomaterials utilizing.

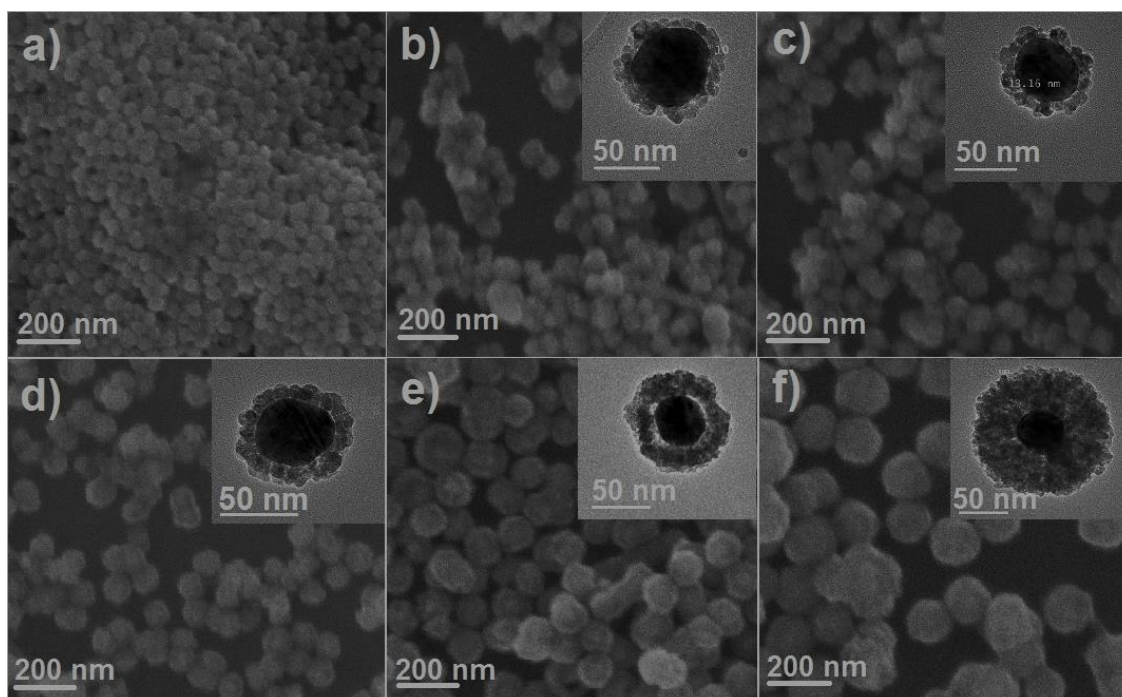


Figure 3.1. Electron micrographs of (a) Ag NPs and Ag@Cu₂O core-shell NPs with shell thicknesses of (b) 10 nm, (c) 13 nm, (d) 17 nm, (e) 27 nm, and (f) 45 nm.

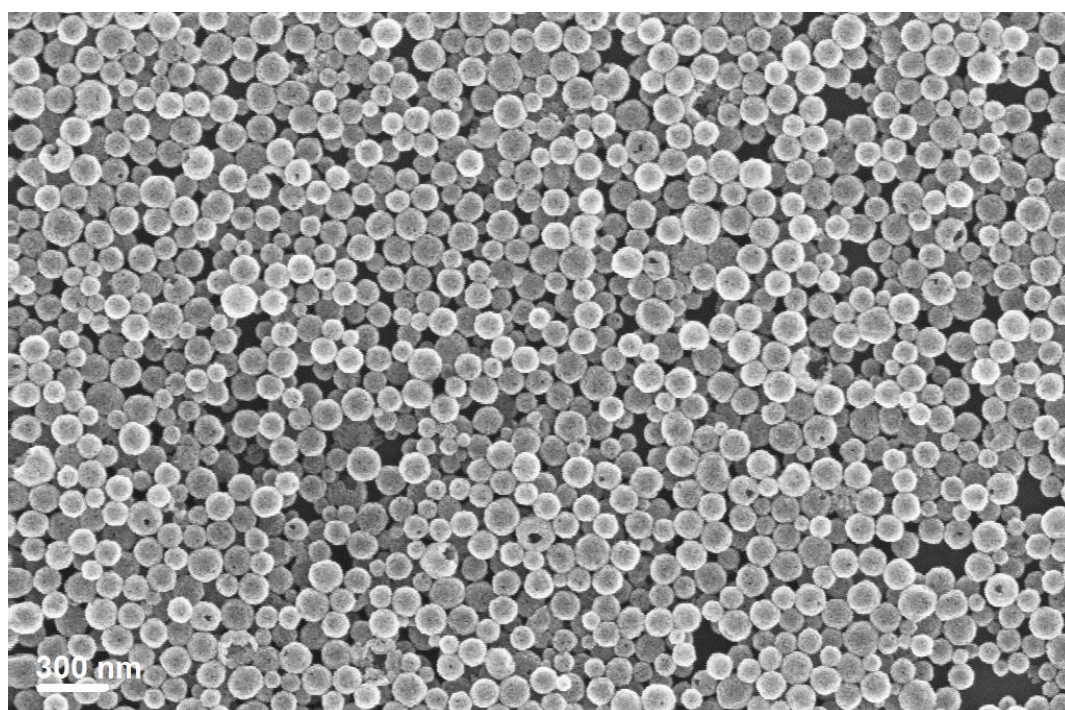


Figure 3.2. SEM image of Cu₂O nanoparticles synthesized with the modified procedure.

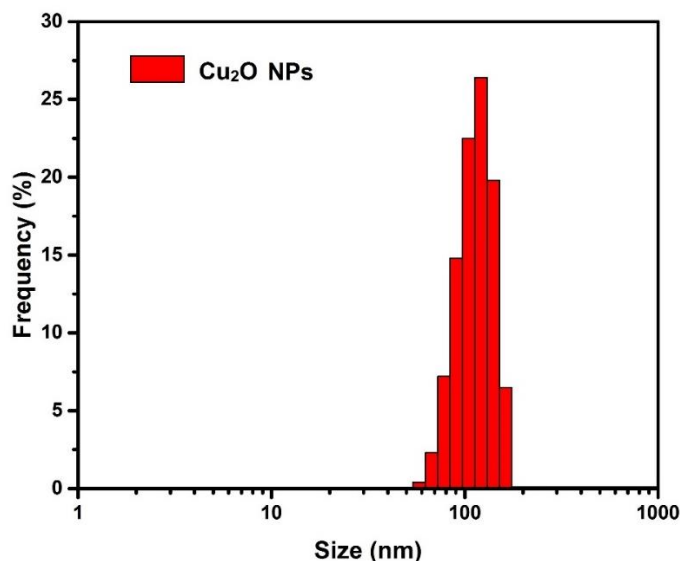


Figure 3.3. Dynamic light scattering measurement of the synthesized Cu₂O nanoparticles.

The XRD pattern of the synthesized Ag@Cu₂O NPs in Figure 3.4 shows the combined diffraction peaks from both Ag and Cu₂O phases. Crystallographic planes of (111), (220), (220), and (311) from Ag nanoparticles (JCPDS: 04-0783) can be indexed for the diffraction peaks at $2\theta = 37.7, 44.0, 64.5,$ and 77.5° , respectively. The remaining peaks at $2\theta = 28.9, 36.7, 42.1, 61.7,$ and 73.5° correspond to the Cu₂O (110), (111), (220), (220), and (311) crystalline planes, respectively. The results indicate that the sample structure is composed of crystalline Ag and Cu₂O phases. Additionally, the XRD data of Cu₂O (Figure 3.5) also confirm the formation of crystalline Cu₂O NPs.

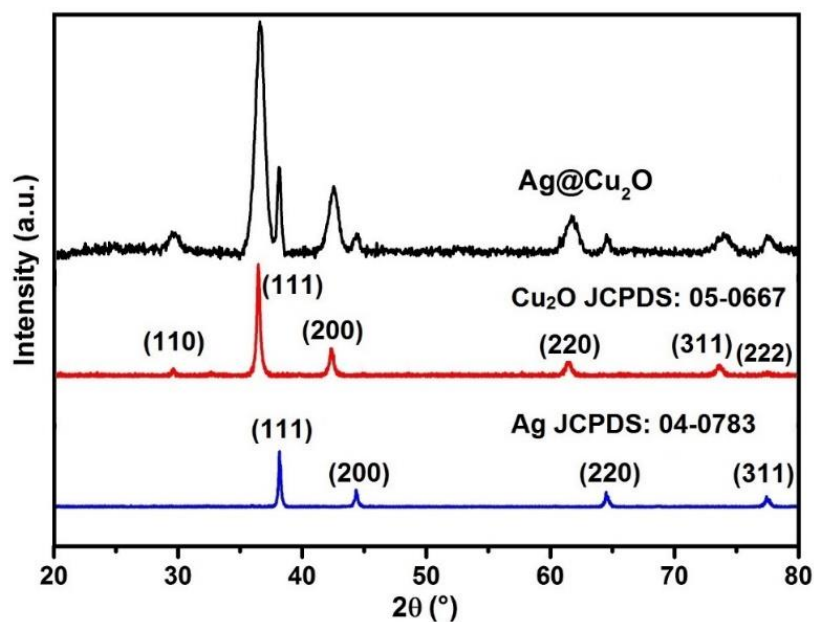


Figure 3.4. XRD pattern of Ag@Cu₂O core-shell nanoparticles and reference patterns for Cu₂O and Ag.

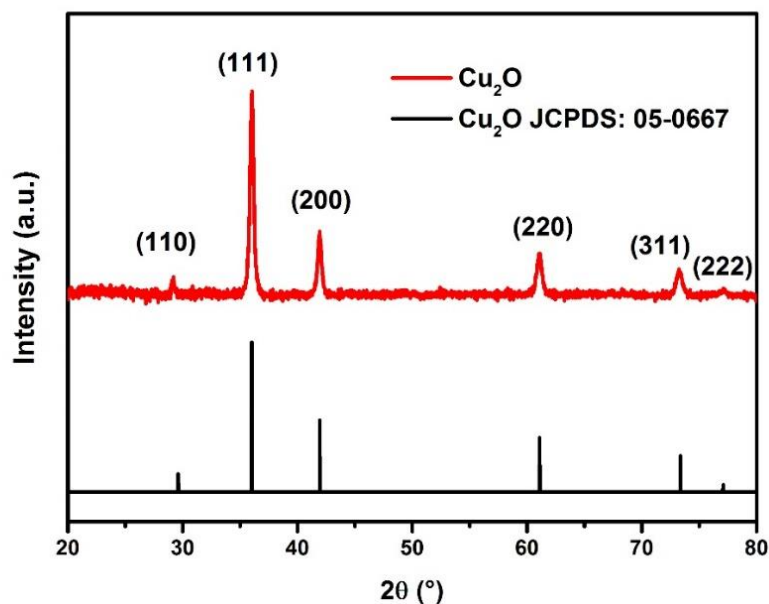


Figure 3.5. XRD pattern of Cu₂O nanoparticles synthesized compared with reference pattern for Cu₂O.

3.3.2. Compositional and Structural Analysis

The surface composition of the core-shell nanoparticles was examined using XPS (Figure 3.6). The strong Cu 2p_{3/2} peak at 933 eV together with a weak Cu²⁺ satellite peak at 945 eV indicate the dominant presence of Cu⁺ in the Cu₂O shell. The presence of cuprous oxide is also evident with the typical O 1s peak for metal oxides at 529 eV. The C 1s peak shown in the survey spectrum can be caused by organic contaminants during the measuring process. The combination of the XPS and XRD data strongly indicates the formation of crystalline Ag and Cu₂O phases in the core-shell nanoparticles.

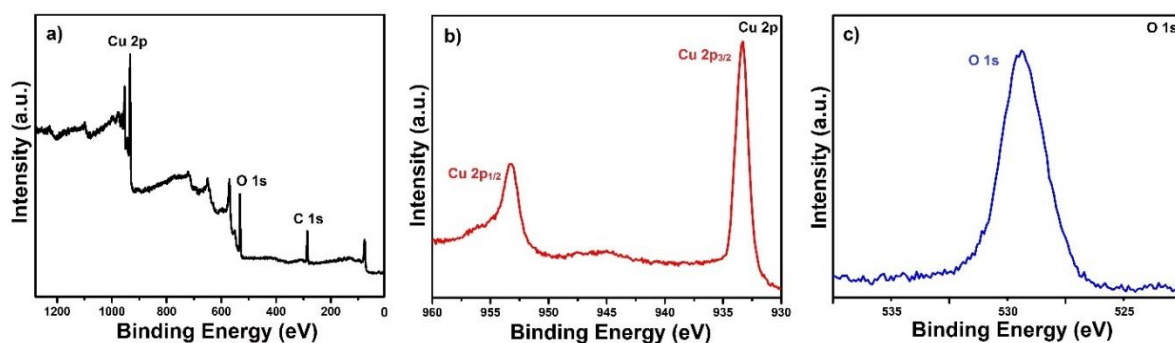


Figure 3.6. (a) Full survey XPS spectrum of Ag@Cu₂O core-shell nanoparticles and high resolution measurements for (b) Cu 2p peaks and (c) O 1s peak.

STEM-EDX data were collected to determine the elemental composition and atomic distribution in the Ag@Cu₂O core-shell nanoparticles. The EDX data in Figure 3.7 are consistent with the XPS data and further consolidate the presence and well-distribution of silver, copper, and oxygen within the synthesized Ag@Cu₂O core-shell nanostructure. Besides the STEM-EDX elemental mapping, the EDX line spectrum was also taken to support the mapping data as shown in Figure 3.8.

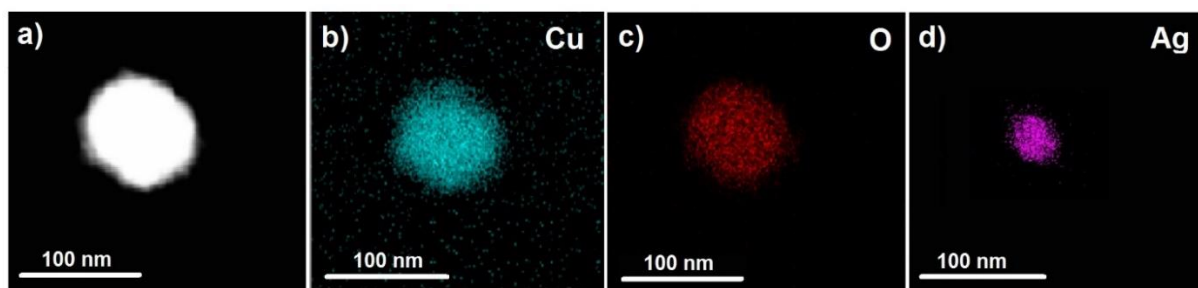


Figure 3.7. (a) STEM image and STEM-EDX elemental mapping for (b) Cu, (c) O, and (d) Ag in Ag@Cu₂O core-shell nanoparticle.

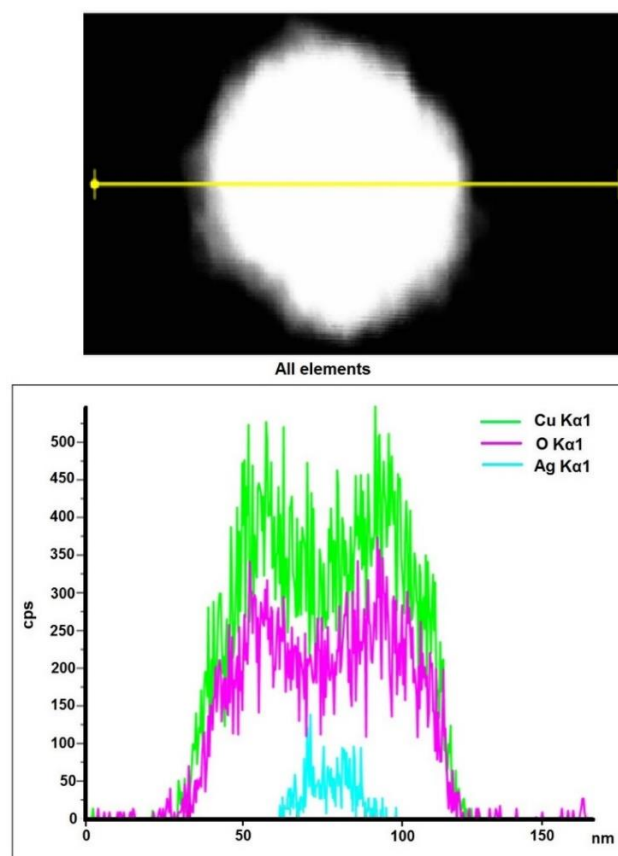


Figure 3.8. STEM-EDX elemental line scan of Ag@Cu₂O nanoparticle.

3.3.3. Optical Properties

Extinction spectra of the bare Ag NPs and Ag@Cu₂O core-shell NPs having five different shell thicknesses were recorded using UV-vis spectroscopy (Figure 3.9). The Ag NPs showed a strong LSPR peak at the violet end of the visible region (~405 nm).

Consequently, extending absorption into the visible and near-IR (NIR) regions of the solar spectrum is needed for the broader use of Ag NPs in photocatalysis and other photo-related applications. Appealingly, all the Ag@Cu₂O core-shell NPs exhibited red-shift in the range of 405–500nm. Specifically, when the Cu₂O shell gets thicker the LSPR peak of the silver core shifts further to the red end of the spectrum from its original position at 405 nm. This red-shift phenomenon could be attributed to the change in the dielectric environment around the plasmonic Ag core when Cu₂O shells grow onto it.³²² Notably, by changing the amount of Ag NP stock solution used in the synthesis procedure, the shell thickness can be adjusted and in turn, can control the extinction peak position of the Ag@Cu₂O core-shell NPs. When the Cu₂O shell is still thin (< 20 nm) the LSPR peak red-shifts much more than when the shell is relatively thicker. This phenomenon is due to the limited range of the amplified electric field around the plasmonic core which weakens rapidly with increasing distance from the core.³⁵⁰ As we demonstrate herein, this tunability of the extinction peak makes the Ag@Cu₂O core-shell nanoparticles optically active at more center of the solar spectrum's visible region where most of the energy from solar radiation resides. This extension of the working range is particularly significant for photocatalytic applications where the only source of energy to drive the catalytic operation comes from the Sun.

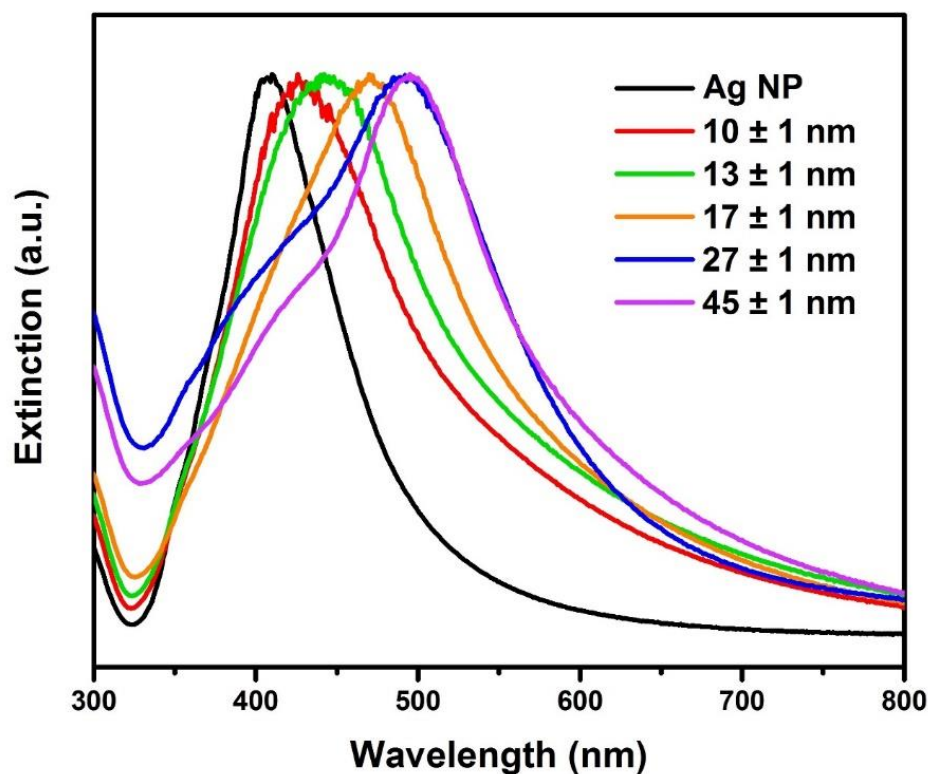


Figure 3.9. Extinction spectra of bare Ag NPs, and Ag@Cu₂O core-shell NPs with different shell thicknesses.

When semiconductor photocatalyst absorbs solar radiation of a suitable wavelength, free electrons and corresponding holes are generated which can then participate in catalytic activity.³⁵¹ The electron-hole recombination in metal oxide nanoparticles is, therefore, undesirable for photocatalytic applications.³⁵² When the electron returns from its excited state in the conduction band to recombine with the positive hole in the valence band, a photon is emitted to release the excess energy from the excited electron. This photon creates a photoluminescence (PL) signal and is an indication of the recombination rate of electron-hole pairs in semiconductors.³⁵³ For that reason, photoluminescence spectroscopy was used to evaluate the effect of the plasmonic core on the electron-hole recombination rate of Cu₂O nanoparticles. The intensities were normalized with the nanoparticle concentration and Cu₂O

volume in the respective nanoparticles to minimize any analytical discrepancy due to the difference in concentration and Cu₂O volume of the two samples. As seen in Figure 3.10, the presence of Ag core significantly reduces the PL signal from the Cu₂O shell with an average suppression of ~59 % compared to the bare Cu₂O NPs. This high reduction in PL intensity indicates that the plasmonic Ag core greatly decreases the electron-hole recombination rate by trapping charge carriers in the metallic core.³⁵⁴ The PL measurements for Ag@Cu₂O nanoparticles at different shell thicknesses were also performed and when the PL intensities were normalized with their respective concentrations and Cu₂O volumes, they yielded similar signal reductions. The fluctuations in the heights of the normalized intensity peaks can be attributed to small variations in the size of the nanoparticles as well as an experimental error during the measurements. The highly suppressed recombination rate together with the extinction peak tunability shown by the Ag@Cu₂O core-shell nanoparticles might significantly enhance its applicability in photocatalysis such as hydrogen evolution (see below), toxic chemical degradations, and other applications in photovoltaics, biochemical sensing, and electronics.

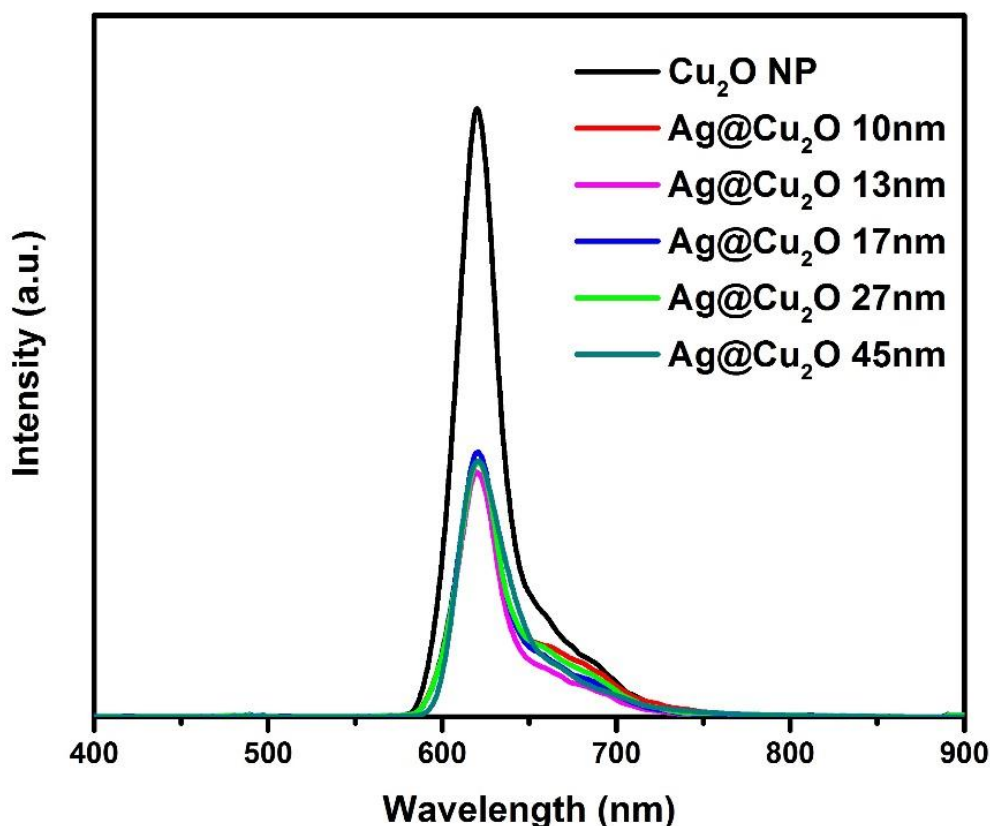


Figure 3.10. Photoluminescence spectra of the spherical Cu₂O nanoparticles and Ag@Cu₂O core-shell nanoparticles at different shell thicknesses.

3.3.4. Photocatalytic Hydrogen Evolution Performance

The HER studies on Ag@Cu₂O and Cu₂O nanoparticles demonstrated significant enhancement in hydrogen evolution rate per mass unit of photocatalyst used with the presence of the plasmonic nanoparticle (Figure 3.11a). The presence of generated hydrogen was confirmed by gas chromatography with a thermal conductivity detector as shown in Figure 3.12. The combination of the silver core with cuprous oxide had increased the hydrogen evolution rate more than 6-fold to $\sim 635 \mu\text{mol/g}_{\text{cat}}/\text{h}$ from $\sim 102 \mu\text{mol/g}_{\text{cat}}/\text{h}$ rate of Cu₂O nanoparticles. The improved rate might have been achieved by plasmonically induced electron injection²⁴ and energy transfer²⁵ that occurred when the composite photocatalyst was

illuminated by electromagnetic radiation at a suitable wavelength. Nevertheless, the photocatalytic hydrogen evolution rate of Ag@Cu₂O core-shell nanoparticles in this work are comparable to recently reported studies (see Table 3.1). Specifically, the core-shell photocatalyst in this work showed a superior evolution rate compared to most of the recently reported systems indicating the synergistic strength of plasmonic-semiconductor hybrid nanostructure in photocatalytic hydrogen generation. Among these examples, only CdS@mZnS nanorods (Table 3.1, entry 4) and Cu/TiO₂@Ti₃C₂T_x sheets (entry 7) show higher H₂ evolution rates than our Ag@Cu₂O core-shell NP with 820 and 860 $\mu\text{mol/g}_{\text{cat}}/\text{h}$, respectively. However, the relative simple Ag@Cu₂O nanoparticles in this work with a rate of 635 $\mu\text{mol/g}_{\text{cat}}/\text{h}$ can be synthesized in much friendlier conditions (lower temperature, shorter time, fewer chemicals and steps, non-inert gas environment, and less hazardous chemicals) than both CdS@mZnS nanorods and Cu/TiO₂@Ti₃C₂T_x sheets, making it more suitable for large-scale applications. Additionally, the light source used in this work also consumes much less power than that used in other systems (14.4 vs. 300 W) to achieve the reported evolution rate. In a narrower focus on Cu₂O-based photocatalysis, our Ag@Cu₂O nanoparticle catalysts are also superior compared to some recent works (Table 3.1, entries 10-14) such as C₃N₄-Pd-Cu₂O stack nanostructure with $\sim 33 \mu\text{mol/g}_{\text{cat}}/\text{h}$ reported by Yin et al.,³⁵⁵ Au NBP@Cu₂O yolk-shell composite with $\sim 5 \mu\text{mol/g}_{\text{cat}}/\text{h}$ reported by Ma et al.,³⁵⁶ Zn/Cu₂O@C coated nanoparticle with $\sim 26 \mu\text{mol/g}_{\text{cat}}/\text{h}$ reported by Yuan et al.,³⁵⁷ or Cu₂O/Cu₂Se multilayer nanowires with $\sim 29 \mu\text{mol/g}_{\text{cat}}/\text{h}$ reported by Liu et al.³⁵⁸

Table 3.1. Selected Examples of Photocatalytic Hydrogen Evolution Using Doped or Composite Photocatalysts

Entry	Material	Structure	Reaction Environment	Light Source Power (W)	Evolution Rates ($\mu\text{mol/g}_{\text{cat}}/\text{h}$)	Ref.
1	TiO ₂ -Ti ₃ C ₂ /Ru-20	nano-composite	MeOH 10 v%	300	235	359
2	Pt/Zn _{0.75} Cd _{0.25} Se	particles	MeOH 10 v%	300	95	360
3	Au-La ₂ Ti ₂ O ₇	nanosteps	MeOH 20 v%	300	340	361
4	CdS@mZnS	nanorods	Na ₂ S 0.25 M Na ₂ SO ₃ 0.35 M	300	820	362
5	Cu ₂ Sn _{0.38} Ge _{0.62} S ₃	powder	Na ₂ S, Na ₂ SO ₃ 10 mM	300	~52	363
6	Sr _{1.8} La _{0.2} TiO _{4-y} N _y	powder	Na ₂ SO ₃ 0.05M	300	160	364
7	Cu/TiO ₂ @Ti ₃ C ₂ T _x	2D sheets	MeOH ~7 v%	300	860	365
8	Pt-Pb ₂ Ti ₂ O _{5.4} F _{1.2}	powder	MeCN:TEOA:H ₂ O (130:10:1)	300	~14	366
9	SrTiO _{3-δ}	powder	MeOH 10 v%	300	~40	367
10	Ag@Cu₂O	core-shell nanoparticle	EG 10 v%	14.4	635	this work
11	C ₃ N ₄ -Pd-Cu ₂ O	stack nanostructure	TEOA 10 v%	300	~33	355
12	Au NBP@Cu ₂ O	yolk-shell composite	H ₂ O	300	~5	356
13	Zn/Cu ₂ O@C	coated nanoparticle	HL 15 v%	300	~26	357
14	Cu ₂ O/Cu ₂ Se	multilayer nanowires	MeOH 10 v%	300	~29	358

Abbreviations: MeOH: methanol; MeCN: acetonitrile; TEOA: triethanolamine; EG: ethylene glycol; HL: 2-hydroxypropanoic acid.

In order to more rigorously evaluate the influence of the plasmonic core on cuprous oxide, the evolution rates were normalized with the Cu₂O volume in the nanoparticles. The results showed that for a volume unit of Cu₂O, the hydrogen evolution rate increased even more significantly from $1.59 \times 10^{-6} \text{ mmol/g}_{\text{cat}}/\text{nm}^3$ to $14.58 \times 10^{-6} \text{ mmol/g}_{\text{cat}}/\text{nm}^3$ (more than 9-fold) by incorporating with silver nanoparticle (Figure 3.11b). This analysis was possible due to the high uniformity of the core-shell nanoparticles afforded by the described method, and

according to our current knowledge, this is the first study to evaluate this performance aspect of the photocatalytic nanostructure. These significant evolution rate increases discussed above can also be attributed to the strong reduction in the electron-hole recombination rate observed above which is a major challenge for photocatalytic hydrogen generation with semiconductor materials.^{344,368}

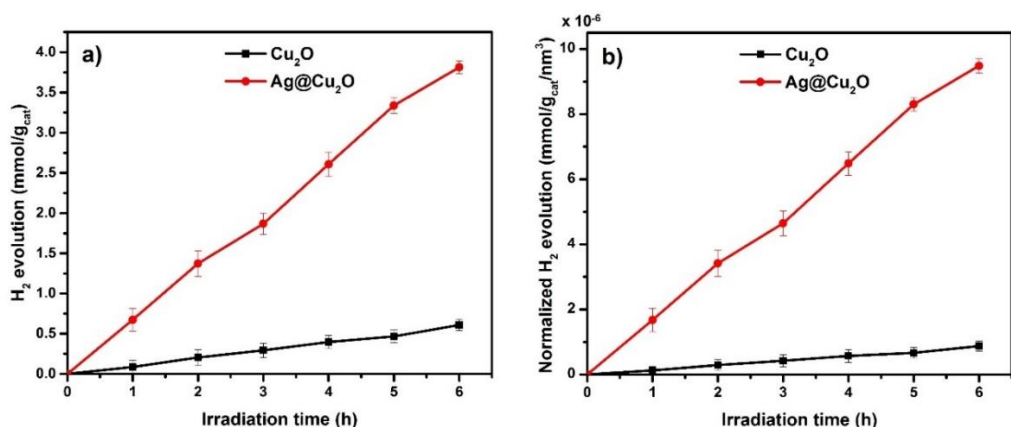


Figure 3.11. Photocatalytic evolution rates of Cu_2O and $\text{Ag@Cu}_2\text{O}$ nanoparticles (a) before and (b) after normalization with the Cu_2O volume in the nanoparticle.

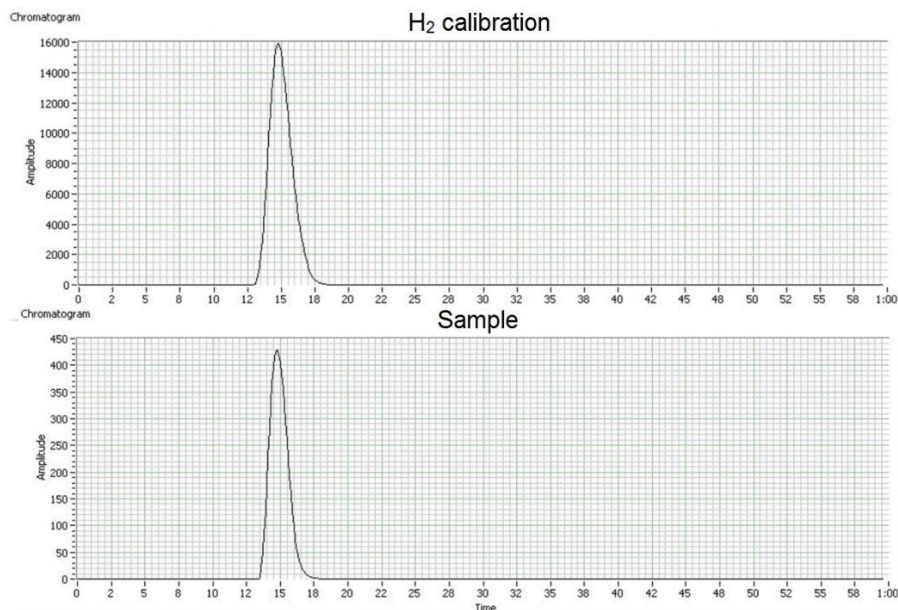


Figure 3.12. Gas chromatographs of photocatalytic HER study with hydrogen calibration and sample run.

Furthermore, the photocatalysts were also studied for their recyclability by washing after each hydrogen evolution reaction and reusing in next tests several times with the same HER procedure and conditions. The results in Figure 3.13 shows that Ag@Cu₂O nanoparticle photocatalyst still suffered the photocorrosion of Cu₂O. However, for Ag@Cu₂O photocatalyst, the evolution rate decreased ~45% (from 635 to 348 $\mu\text{mol/g}_{\text{cat}}/\text{h}$) while the evolution rate of Cu₂O nanoparticle reduced ~66% (from 102 to 35 $\mu\text{mol/g}_{\text{cat}}/\text{h}$) after 3 cycles yielding a 21% reduction in the photocatalyst's degradation. The reduction in the degradation of Cu₂O in the presence of the silver core can be attributed to the metallic core as a charge carrier scavenger⁵⁶ which inhibits the movement of the charge carrier thus reduce the photocorrosion of Cu⁺ ion. Even though the degradation of the photocatalyst is still quite significant, the 21% reduction in the degradation observed is an encouraging result and more research efforts to further improve the stability of the Cu₂O-based photocatalyst are being investigated in our lab.

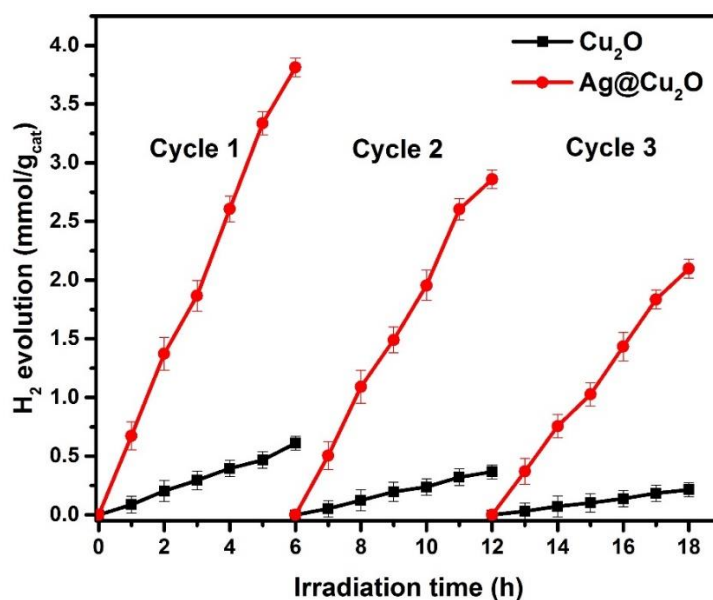


Figure 3.13. Photocatalytic hydrogen evolution of Ag@Cu₂O and Cu₂O nanoparticles in 3 consecutive cycles.

3.4. Conclusions

Ag@Cu₂O core-shell NPs with controllable Cu₂O shell thicknesses were successfully synthesized together with bare Ag and Cu₂O NPs by convenient procedures at mild conditions. The nanoparticles were characterized with various techniques to verify their size, structural, morphological characteristics, as well as elemental compositions and distributions. All of the synthesized core-shell NPs exhibited strong LSPR peaks in the visible region. More importantly, the optical studies showed an ability to tune the red-shift of the LSPR position into the intense part of the solar radiation by systematically adjusting the thickness of the Cu₂O shell. The photoluminescence measurements demonstrated that the plasmonic Ag core of Ag@Cu₂O core-shell nanoparticles has greatly suppressed electron-hole recombination rate compared to bare Cu₂O nanoparticles. Photocatalytic hydrogen evolution studies showed a significant increase in evolution rate of more than 6 times with the incorporation of the silver core into the photocatalyst. The degradation rate of Cu₂O was also reduced by the coupling with Ag NP cores, thus enhancing the stability of Cu₂O. Despite many significant enhancements and several remaining challenges, it should, however, be noted that the synthesis method in this work was quicker and required much less demanding conditions which make it easier for scale-up application of the hybrid photocatalyst. The use of abundant elements in this work also further enables the applicability of the Ag@Cu₂O core-shell nanoparticle. Moreover, these results further set the way for combining a wide range of plasmonic and semiconductor materials beyond Ag and Cu₂O in nanostructures for improved photocatalytic and optoelectronic performance.

Chapter 4: Enhanced Optical Properties and Photocatalytic Hydrogen Generation in Monodisperse Titanium Dioxide Nanoparticles Singly and Dually Doped with Niobium and Tantalum

4.1. Introduction

The rapidly growing demand for sustainable energy supply and increasing environmental concern about fossil fuels has inspired much effort to develop efficient and abundant photocatalyst for solar-powered hydrogen generation.³⁰⁹ Since the first report by Fujishima and Honda in 1972,³⁰⁷ semiconductor titanium dioxide (TiO₂) has been studied extensively to convert solar radiation to high energy density fuels such as hydrogen that would generate less polluting byproducts (e.g., water).^{359,369–373} Despite many advantages from high stability,³⁷⁴ nontoxicity³⁷⁵ to material abundance, the large band gap energy in the UV region³⁷² and high electron-hole recombination rate³⁷² remains major challenges for large-scale applications of TiO₂-based nanomaterials. With the development of nanoscience and nanotechnology in recent decades, nanoscale structures have shown great potential for catalytic applications due to their high surface-to-volume ratio and the quantum confinement.³⁷⁶

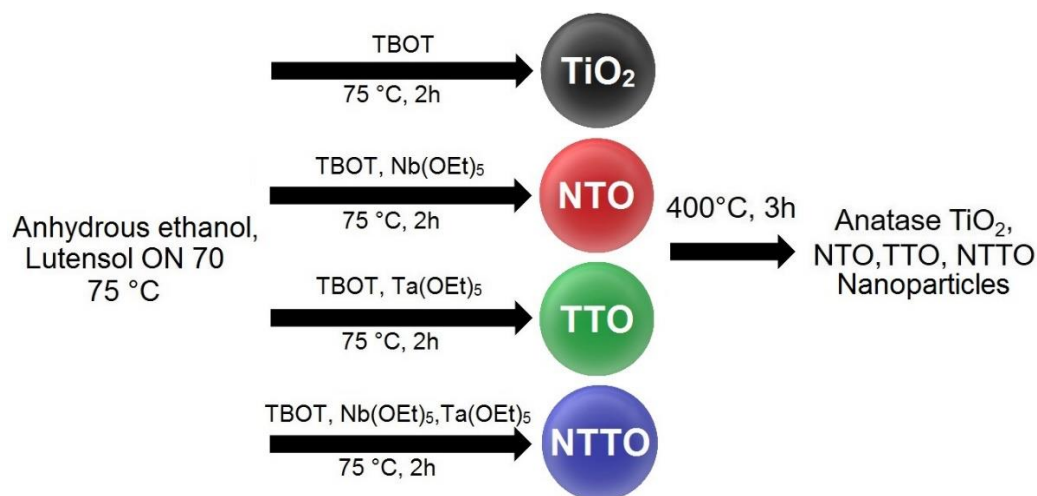
Doping has also been demonstrated as a feasible approach to reduce the band gap and improve the absorption coefficients of semiconductors.³⁷⁷ Multiple studies have also been reported^{378–382} to fabricate and introduce various dopants into TiO₂ nanomaterials to achieve desired optical and electronic properties for potential applications in catalysis,^{383–386} photovoltaic,^{387,388} or optoelectronics.^{389,390} Although many synthetic processes such as solvothermal,^{391–393} sol-gel,^{394–396} hydrothermal,^{397–399} molten salt flux,^{381,400}

electrochemical,^{401,402} or electrospinning^{386,403,404} methods have been developed for the preparation of doped TiO₂ nanoparticles; most of them required demanding and/or sophisticated conditions. Niobium- and tantalum-doped TiO₂ films showed high conductivity^{405,406} and visible transparency,^{405,407} indicating them as good candidates for indium tin oxide (ITO) alternative as transparent conducting oxide (TCO).^{408–410} These results also make niobium-doped and tantalum-doped TiO₂ potentially useful for photocatalysis or gas sensor; which benefit from the enhanced conductivity,^{411,412} especially when coupled with the high surface area of nanoscale structures.⁴¹² Several studies on niobium-^{413–415} and tantalum-doped^{415,416} titania particles have been reported with demanding synthetic procedures or a lack of control over the resulting nanoparticles. Consequently, developing facile methods for synthesis of niobium-, tantalum-, and other element-doped semiconductor titanium dioxide nanoparticles that are suitable for scale-up applications are needed to fulfill the potential of TiO₂-based nanomaterials. Furthermore, co-doping with multiple elements^{417–419} has also been demonstrated to significantly reduce the band gap^{417,418} or enhance optical properties⁴¹⁹ of the host semiconductor, which are beneficial for many solar-powered applications.

In this report, we describe the preparation of undoped, singly- (NTO, TTO), and dually-doped (NTTO) anatase TiO₂ nanoparticles with Nb and Ta dopants (see Scheme 4.1). The nanoparticles were synthesized by facile and quick wet chemistry methods at mild conditions using a properly controlled hydrolytic process. The morphological, structural, and compositional analyses demonstrated the formation of highly monodisperse spherical nanoparticles, as well as the uniform distribution of dopants in the crystalline doped

nanoparticles. Importantly, we are able to control the electron-hole recombination rates in doped TiO_2 nanoparticles via adjusting the dopant concentrations with the highest level of suppression recorded on the co-doped NTTO nanoparticles. Moreover, Nb and Ta doping also decreased the optical band gap of TiO_2 nanoparticles and reached the largest reduction in the dually-doped NTTO particles. Photocatalytic hydrogen generation studies showed significant increases in hydrogen evolution rates of the doped- compared to the pristine TiO_2 nanoparticles. Beneficially, the doped TiO_2 nanocatalysts also exhibited a high degree of photostability in the cyclability tests. Overall, the enhanced hydrogen evolution rates combined with the good scalability and mild conditions of the synthetic methods endow the NTO, TTO, and NTTO nanoparticles with great potential for photocatalytic fuel generation. Moreover, the tunable photoluminescence (PL) responses and optical band gaps of these doped TiO_2 nanoparticles also make them suitable for optoelectronic,⁴²⁰ photovoltaic,⁴²¹ gas sensing,⁴²² or biomedical^{70,423} applications.

Scheme 4.1. Synthesis of TiO_2 , NTO, TTO, and NTTO Nanoparticles^a



^a**Abbreviations:** TBOT: titanium (IV) butoxide, NTO: niobium-doped TiO_2 , TTO: tantalum-doped TiO_2 , NTTO: niobium/tantalum-codoped TiO_2 .

4.2. Experimental Section

4.2.1. Materials

Titanium (IV) butoxide (97% purity) (TBOT), niobium (V) ethoxide (99.95% purity), tantalum (V) ethoxide (99.98% purity), and anhydrous ethylene glycol (99.8% purity) were purchased from Sigma-Aldrich. Lutensol ON 70 was obtained from BASF SE Inc. Ethanol 200 proof anhydrous was purchased from Decon Labs Inc. Deionized water with a resistivity of 18 M Ω -cm was obtained from the Academic Milli-Q Water system of Millipore Corporation. Sodium hydroxide was purchased from Macron Fine Chemicals. Ultra high purity compressed argon gas was purchased from Matheson Tri-Gas Inc. All glasswares were cleaned with piranha solution (3:1 concentrated sulfuric acid: 30% hydrogen peroxide) and aqua regia solution (3:1 concentrated hydrochloric acid: nitric acid) for at least 1 hour and dried in an oven at 150 °C followed by cooling prior to use.

4.2.2. Synthesis of the Nanoparticles

Scheme 4.1 illustrates the synthetic strategy and heat treatment of the titanium dioxide, niobium-doped, tantalum-doped, and Nb/Ta dual-doped titanium dioxide nanoparticles. Stock solutions of TBOT, Nb(OEt)₅, and Ta(OEt)₅ were prepared by mixing 100 μ L TBOT, 10 μ L Nb(OEt)₅, and 10 μ L Ta(OEt)₅, respectively, with 10 mL of fresh anhydrous ethanol. The representative synthetic conditions for the preparations of undoped and doped TiO₂ nanoparticles are summarized in Table 4.1.

Table 4.1. Reaction Conditions Used for the Synthesis of TiO₂, NTO, TTO, and NTTO Nanoparticles^a

Nanoparticle*	Ethanol	0.1 M Lutensol ON 70	Pre-Heat Time & Temperature	TBOT	Nb(OEt) ₅	Ta(OEt) ₅
TiO₂	15 mL	352 µL	15 minutes, 75 °C	10 µL	-	-
NTO	15 mL	319 µL	15 minutes, 75 °C	17 µL	1 µL	-
TTO	15 mL	350 µL	15 minutes, 75 °C	15 µL	-	1 µL
NTTO	30 mL	640 µL	25 minutes, 75 °C	30 µL	1.765 µL	2 µL

^aNTO, TTO, and NTTO nanoparticles with average dopant concentrations of 2 at% Nb, 4 at% Ta, and 2 at% Nb/4 at% Ta, respectively. All the syntheses used 0.4 mL of deionized H₂O to activate the hydrolytic process and had a total synthetic time of 2 hours at 75 °C.

4.2.2.1 Synthesis and Heat Treatment of TiO₂ Nanoparticles

The formation of TiO₂ nanoparticles was achieved by hydrolyzing TBOT in an ethanolic environment with the presence of Lutensol ON 70 surfactant and strict control of the water content in the reaction process. In general, a mixture of 352 µL of 0.1M Lutensol ON 70 and 14 mL of anhydrous ethanol was heated at 75 °C for 15 minutes (mixture A). Then, 1 mL of TBOT stock solution was added to mixture A before 400 µL of deionized water was added in. The final solution was kept at 75 °C for 2 hours under vigorous magnetic stirring. Within 10 minutes of adding deionized water to mixture A, the combined solution gradually turned from transparent to translucent indicating the formation of TiO₂ nanoparticle seeds. After 2 hours of stirring at 75 °C, and 1 hour of cooling at room temperature the fully grown nanoparticles were collected by centrifugation at 7000 rpm in 15 minutes and washed with deionized water to remove the remnant reagents from the particle formation process. This washing process was repeated four times before the nanoparticles were redispersed and stored in ethanol.

4.2.2.2. Synthesis of Niobium-Doped TiO₂ (NTO) Nanoparticles

Niobium can be doped into TiO₂ by concurrent hydrolysis of TBOT and Nb(OEt)₅ in an ethanolic solution. In a typical synthesis of NTO NPs with 2 at% Nb, a mixture of 319 µL

of 0.1 M Lutensol ON 70 ethanolic solution and 13 mL of anhydrous ethanol was heated at 75 °C in 15 minutes (mixture B). A mixture of 1 mL of TBOT and 0.588 mL of Nb(OEt)₅ stock solution was injected into mixture B followed by the addition of 400 µL of deionized water after 1 minute. In the next 15 minutes, the solution started turning translucent, indicating the formation of NTO NPs; which fully grew after the hydrolytic reaction was completed in 2 hours of heating at 75 °C. The NP solution was then cooled at room temperature for 1 hour under vigorous stirring before the NPs were collected by centrifugation at 7000 rpm in 15 minutes. The Nb dopant concentration can be tuned by adjusting the reagent ratio of TBOT/Nb(OEt)₅ used.

4.2.2.3. Synthesis of Tantalum-Doped TiO₂ (TTO) Nanoparticles

Simultaneous hydrolysis of TBOT and Ta(OEt)₅ was carried out in a proper procedure to produce Ta-doped TiO₂ NPs. For the synthesis of TTO NPs with 4 at% Ta, a mixture of 350 µL of 0.1 M Lutensol ON 70 ethanolic solution and 12.5 mL of anhydrous ethanol was heated at 75 °C in 15 minutes (mixture C). A mixture of 1.5 mL of TBOT and 1 mL of Ta(OEt)₅ stock solution was injected into mixture C followed by the addition of 400 µL of deionized water after 2 minutes. Within 15 minutes after the addition of water, the mixture turned translucent, indicating the formation of TTO NPs; which grew fully after the reaction was completed in 2 hours of heating at 75 °C. The NP solution was cooled at room temperature for 1 hour under continued stirring before the NPs were collected by centrifugation at 7000 rpm in 15 minutes. The Ta dopant concentration can be tuned by adjusting the reagent ratio of TBOT/Ta(OEt)₅ used.

4.2.2.4. Synthesis of Niobium/Tantalum-Codoped TiO₂ (NTTO) Nanoparticles

TiO₂ nanoparticles dually doped with niobium and tantalum (NTTO) were synthesized by concurrent hydrolysis of TBOT, Nb(OEt)₅, and Ta(OEt)₅. In a typical synthesis of NTTO NPs containing 4 at% Nb and 2 at% Ta, a mixture of 25 mL of fresh anhydrous ethanol and 640 μ L of 0.1 M Lutensol ON 70 ethanolic solution was heated at 75 °C in 25 minutes (mixture D). A mixture of 3 mL of TBOT, 1.765 mL Nb(OEt)₅, and 2 mL of Ta(OEt)₅ stock solutions was well mixed and injected into mixture D, followed by the addition of 0.8 mL of deionized water after 2 minutes. After the solution turned translucent within 15 minutes due to the formation of NTTO seeds, the reaction was allowed to complete in 2 hours at 75 °C. The nanoparticle solution was then cooled at room temperature for 1 hour and centrifuged at 7000 rpm in 15 minutes to collect the NPs.

4.2.2.5. Heat Treatment of Nanoparticles

The amorphous undoped and doped TiO₂ nanoparticles obtained from the synthetic processes can be turned to the crystalline anatase phase by proper heat treatment. Typically, the nanoparticles were washed five times with centrifugation (7000 rpm in 15 minutes) and dispersed in ethanol in a clean 20 mL glass vial before being dried at 70 °C in an oven overnight. The glass vial with dried amorphous nanoparticles was then transferred to a pre-heated furnace at 400 °C for heat treatment in 3 hours. After cooling down, the crystallized anatase TiO₂ nanoparticles in the glass vial were redispersed in deionized water by sonication in 60 minutes.

4.2.3. Characterization Methods

All synthesized nanoparticles (NPs) had their images taken by a LEO-1525 scanning electron microscope (SEM) operating at 15 kV and 5.5 mm working distance. SEM samples were prepared on silicon surfaces which were cleansed and dried at 60 °C in an oven for 2 hours before measurement. Dynamic light scattering (DLS) measurements were conducted on a Malvern zetasizer model ZEN3600 with a 10 mW 632.8 nm laser beam to evaluate the size distributions of the synthesized nanoparticles. Zeta potentials of the nanoparticles were also measured by the Malvern zetasizer model ZEN3600 with a DTS1070 folded capillary zeta cell. All nanoparticle samples for DLS and zeta potential measurements were dispersed in deionized water from the Academic Milli-Q Water system. An X'Pert powder X-ray diffractometer (XRD) with a Cu K α X-ray source operating at 45 kV and 30 mA over the 2 θ range of 20°-80° was used to assess the crystalline characteristics of the nanoparticles. The obtained XRD data were analyzed by the PANalytical HighScore Plus software on which the background signal was subtracted. The crystallite size calculations were conducted using Scherrer equation with the peak positions and full width half maximum (FWHM) obtained by the software. All XRD samples were prepared by drop-casting highly concentrated nanoparticle solutions on amorphous glass slides followed by drying at 60 °C in 2 hours. Elemental analyses were carried out using an energy-dispersive X-ray spectroscopy (EDX) detector attached to a JEOL JEM-2010 FX scanning transmission electron microscope (STEM) operating at 200 kV. EDX samples were deposited on 300-mesh holey carbon-coated copper grids and dried at 60 °C for 4 hours before analysis. Surface elemental measurement was carried out by a PHI X-ray photoelectron spectroscopy (XPS) system having a

monochromatic Al K α X-ray source with 10 mA emission current and 15 kV emission bias. The XPS samples were prepared by depositing highly concentrated nanoparticle solutions on cleansed silicon wafers and drying at 60 °C in 6 hours. Diffuse reflectance spectra (DRS) were obtained for all crystalline nanoparticle samples by a Cary 5000 UV-Vis NIR spectrometer from Agilent Technologies. Photoluminescence measurements were performed on a PerkinElmer LS-55 fluorescence spectrometer with an excitation wavelength of 350 nm and a 430 nm high pass optical filter was used to minimize spectral noise.

4.2.4. Photocatalytic Hydrogen Generation Test

Photocatalytic hydrogen evolution reaction (HER) tests of the nanoparticle samples were carried out on a custom-made system, described in a previously reported work⁴²⁴ with a customized pico solar simulator from G2V Optics as the illumination source. The generated hydrogen product was verified by a GOW-MAC series 400-P thermal conductivity gas chromatograph with an 8 ft x 1/8 in stainless steel column packed with 3Å molecular sieves. The column, detector, and injector temperatures are set at 80, 120, and 120 °C respectively. Ultra high purity argon purchased from Matheson Tri-Gas Inc. in a pressurized gas tank was used as the carrier gas for the gas chromatograph system. In a typical test, 20 mg of nanoparticles were dispersed in a customized glass reaction flask with 10 mL of 10% ethylene glycol aqueous solution whose pH was adjusted to 11. The solution was then purged with ultra-high purity compressed argon gas in 15 minutes before being illuminated by the solar simulator. The amount of generated gas product was monitored by a digital pressure transducer connected to the reaction flask. The gas product was taken through a sampling port and analyzed by the GOW-MAC gas chromatograph with a 0.5 mL Hamilton glass

syringe. For the cyclability tests, the nanoparticle photocatalyst was collected by centrifugation at 7000 rpm in 15 minutes and washed with deionized water three times before being used in the following cycle.

4.3. Results and Discussion

4.3.1. Synthesis and Morphological Analysis of the Nanoparticles

We designed a convenient one-step wet chemistry method to synthesize undoped and doped TiO₂ nanoparticles (Scheme 4.1). The obtained nanoparticles are sphere-like with average sizes of ~118, ~106, ~98, and ~104 nm for TiO₂, NTO, TTO, and NTTTO, respectively (Figures 4.1). The nanoparticle's size can be adjusted by changing the concentrations of the stock solutions. The synthesized nanoparticles are also highly monodisperse as can be seen with the DLS size distribution profiles, as shown in insets of Figures 4.1. The DLS data also corresponds well with morphological characteristics observed on the SEM images. It should be noted that the preheating of the ethanol and Lutensol ON 70 mixture at 75 °C in 10-15 minutes is critical to achieving highly monodisperse nanoparticles. The heated solutions sped up the hydrolytic reaction and increased the concentration of the newly formed TiO₂ in a short amount of time. This accelerated supersaturation of TiO₂ minimized the nucleation period and separated more effectively the nucleation from the growth process, leading to a narrower size distribution for the resulting nanoparticles.⁴²⁵ Even though higher temperatures might be better to achieve the supersaturation needed for monodisperse nanoparticles, 75 °C was used to avoid the need for condenser use during the procedure. The use of reflux may have impacts on the solution concentrations over time, as well as potentially contaminate the synthetic

solutions. In doped TiO_2 nanoparticles, lower amounts of surfactant and higher amounts of precursors were needed to obtain the doped nanoparticles with a similar size to the undoped nanoparticles. We believe that the incorporation of dopant atoms into the host material introduces lattice strain, which makes it harder for the doped TiO_2 seeds to form than the undoped TiO_2 seeds.⁴²⁶ This nucleation challenge is consistent with the longer time it took the solutions to turn translucent and could be overcome by adjusting the concentrations in the synthetic procedure as mentioned above. Importantly, the synthesis procedure can be scaled up to 10-fold with little effect on the morphological characteristics of the synthesized nanoparticles.

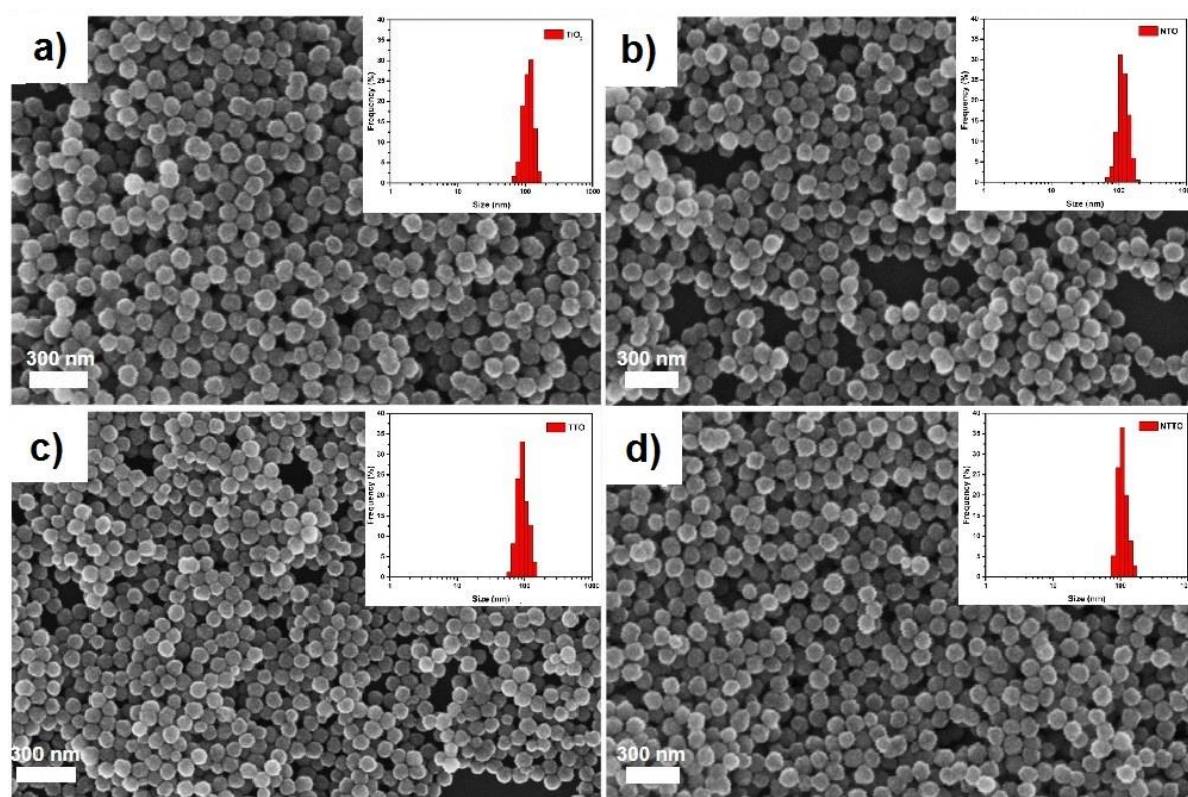


Figure 4.1. (a-d) SEM images with size distributions (insets) of TiO_2 , NTO, TTO, and NTTO nanoparticles, respectively.

4.3.2. Effect of Nb and Ta Doping on TiO₂ Nanoparticle Surface Charge

Even though the doping of TiO₂ with niobium did not significantly change the surface charge magnitude of NTO (-16.3 mV) compared to undoped TiO₂ NPs (+16.8 mV), the Ta-doping significantly increased the zeta potential magnitude of the TTO and NTTTO to 22.8 and 32.6 mV, respectively (see Table 4.2); making these nanoparticles are more colloiddally stable. Additionally, niobium and tantalum doping have changed the zeta potentials of the doped TiO₂ nanoparticles to negative from the positive value in undoped TiO₂, as shown in Table 4.2. This sign changes from positive to negative have made protons (H⁺) more electrostatically attracted to the reaction sites on the surfaces of the doped TiO₂ NPs. Consequently, the doped TiO₂ nanoparticles exhibited higher photocatalytic activities than the undoped NPs as observed in the hydrogen evolution (see below) and are consistent with the previously reported studies.^{427,428} Overall, our synthetic processes generated highly monodisperse spherical undoped, Nb-doped, Ta-doped, and Nb-Ta co-doped TiO₂ nanoparticles with the size ranges of ~98 to ~118 nm. Importantly, our doped NPs possessed more negative surface charges with larger surface charge magnitudes compared to the undoped TiO₂, which are potentially beneficial for photocatalytic and many other applications.^{427,428}

Table 4.2. Average DLS Size and Zeta Potential of TiO₂, NTO, TTO, and NTTTO Nanoparticles

	TiO ₂	NTO	TTO	NTTO
Size (nm)	118 ± 22	106 ± 19	98 ± 15	104 ± 17
Zeta potential (mV)	16.8 ± 4.8	-16.3 ± 3.7	-22.8 ± 4.1	-32.6 ± 4.5

4.3.3. Crystallographic Analysis

Powder X-ray diffraction (XRD) measurements on crystallized nanoparticle samples were performed to determine the crystalline characteristics in the fabricated nanoparticles (see Figure 4.2). The XRD pattern of anatase TiO_2 nanoparticles showed distinct peaks at 2θ angles of 25.25° , 36.90° , 37.76° , 38.52° , 47.91° , 53.89° , 54.95° , 62.60° , 68.77° , 70.07° , and 74.95° ; which can be attributed to the (101), (103), (004), (112), (200), (105), (211), (204), (116), (220), and (215) crystallographic planes, respectively. These data indicated the presence of the anatase TiO_2 (JCPDS no. 21-1272). In the case of TTO (4 at% Ta), NTO (2 at% Nb), and NTTO (4 at% Ta and 2 at% Nb) nanoparticles, XRD measurements displayed similar patterns (Figure 4.2 and Table 4.3) to that of undoped TiO_2 NPs. This similarity can be explained by the small difference in atom radii of niobium and tantalum compared with titanium, which minimizes lattice distortion leading to a negligible shift of diffraction peaks. Additionally, the low dopant concentrations introduced to the TiO_2 host material make any possible shift fall within instrumental error. The crystallite size calculations for all nanoparticles were performed using the Scherrer equation based on the XRD data (see Table 4.4). The crystallite size of the TiO_2 nanoparticles was determined to be ~ 40 nm while TTO, NTO, and NTTO particles showed significantly smaller crystallite sizes of ~ 33 , ~ 25 , and ~ 15 nm, respectively. These data points corresponded well with the lower intensities, broader XRD peaks, and less distinct peaks compared to pristine TiO_2 NPs. These results are also consistent with the observed difficulty of the nucleation process due to the inclusion of dopant atoms into the TiO_2 lattice as discussed in the synthesis process above.

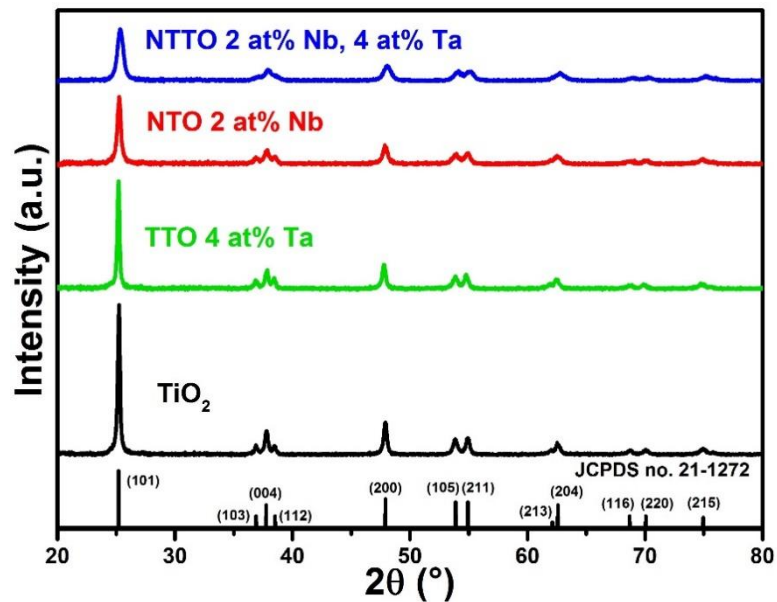


Figure 4.2. Powder XRD patterns for TiO₂, TTO, NTO, and NTTO nanoparticles with reference line pattern for anatase TiO₂.

Table 4.3. XRD Peak Positions and Reference Indexes of Correspondent Crystallographic Planes

	(101)	(103)	(004)	(112)	(200)	(105)	(211)	(213)	(204)	(116)	(220)	(215)
TiO₂	25.25	36.90	37.76	38.52	47.91	53.89	54.95	62.01	62.60	68.77	70.77	74.95
TTO	25.15	36.89	37.71	38.47	47.84	53.82	54.81	61.95	62.51	68.70	69.96	74.81
NTO	25.28	36.92	37.78	38.54	47.96	53.93	54.99	62.04	62.65	68.82	70.13	75.02
NTTO	25.26	36.90	37.77	38.52	47.95	53.91	54.96	-	62.63	68.79	70.10	74.97

Table 4.4. Crystallite Sizes of TiO₂, TTO, NTO, NTTO Nanoparticles

Sample	Peak Position (°)	FWHM (°)	Crystallite Size (nm)
TiO ₂	25.25	0.21	40 ± 2
TTO	25.15	0.23	33 ± 3
NTO	25.28	0.34	25 ± 4
NTTO	25.26	0.56	15 ± 4

4.3.4. Compositional Analysis of Doped TiO₂ Nanoparticles

Compositional characteristics and elemental distributions of the doped nanoparticles were determined by energy-dispersive X-ray spectroscopy on a scanning tunneling electron microscope (STEM-EDX). The STEM-EDX spectra of all doped nanoparticles contained

characteristic peaks $K\alpha$ and $L\alpha$ at 4.508 and 0.452 KeV for titanium, as well as $K\alpha$ peak at 0.525 KeV characteristic of oxygen, as shown in Figure 4.3-5. In the spectrum of NTO nanoparticles, the characteristic peaks for niobium $K\alpha$ and $L\alpha$ at 16.581 and 2.166 KeV were also recorded (Figure 4.3). Similarly, the STEM-EDX spectrum of TTO nanoparticles presented in Figure 4.4 showed $K\alpha$ and M characteristic peaks at 8.145 and 1.709 KeV for tantalum. In the case of the dually doped particles NTT0, the characteristic peaks of Nb $K\alpha$, Nb $L\alpha$, Ta $K\alpha$, and Ta M were all present at their respective energies as shown in Figure 4.5. The characteristic peaks Cu $K\alpha$ and Cu $L\alpha$ at 8.041 and 0.931 KeV, as well as the intense peak of C $K\alpha$ at 0.278 KeV, were also present and can be attributed to signals from the copper grid on the carbon films used to deposit the STEM-EDX samples.

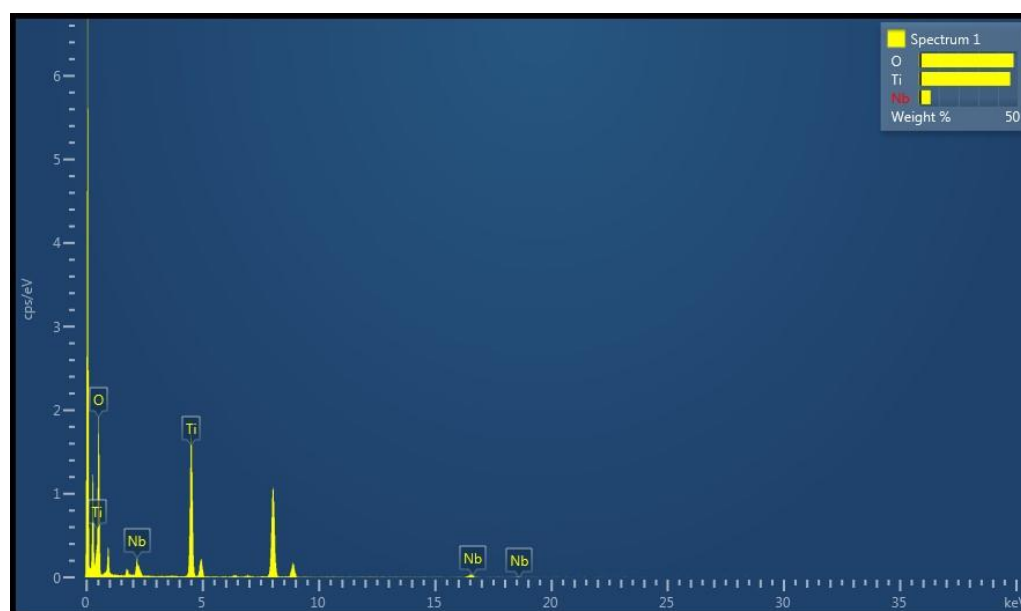


Figure 4.3. STEM-EDX spectrum of NTO nanoparticles.



Figure 4.4. STEM-EDX spectrum of TTO nanoparticles.

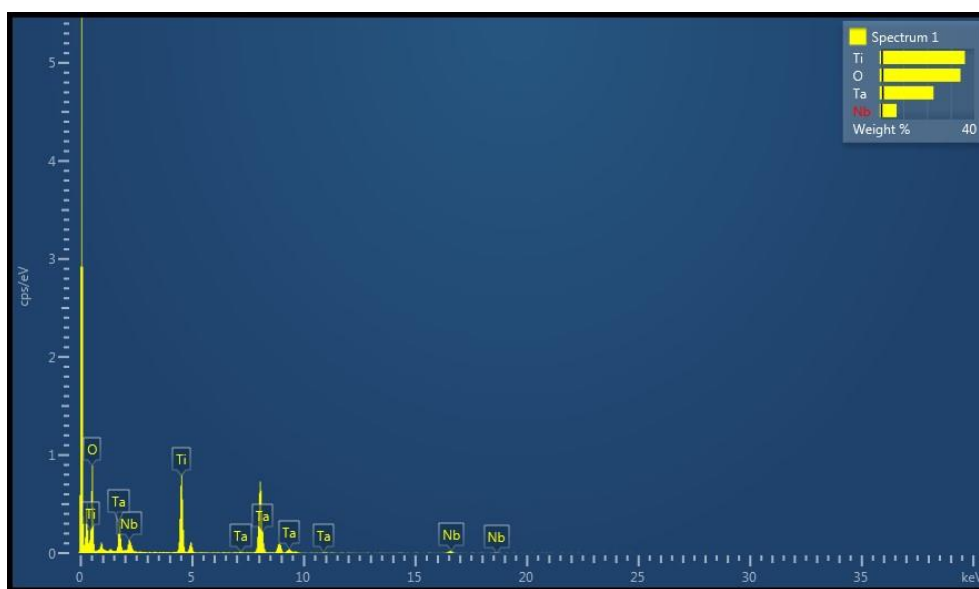


Figure 4.5. STEM-EDX spectrum of NTTO nanoparticles.

The STEM-EDX elemental maps for NTTO (Figure 4.6), NTO (Figure 4.7), and TTO (Figure 4.8) were also recorded to evaluate the compositional distributions of dopants in the doped TiO_2 nanoparticles. The elemental maps of doped nanoparticles demonstrated the successful incorporation and uniform distributions of the niobium and tantalum dopants in the

TiO₂ nanoparticles. Interestingly, the atomic concentrations of each dopant in the NTTO nanoparticles were closely consistent with the singly doped NTO and TTO nanoparticles (see Table 4.5 below). This behavior allows easy control of the dopant compositions even in the dually doped NTTO nanoparticles by our convenient synthetic processes. It should be noted that it is important for the good mixing of TBOT and the ethoxides of the doping elements in the same solution before injecting to the pre-heated ethanol/Lutensol ON 70 mixture to obtain consistent doping results.

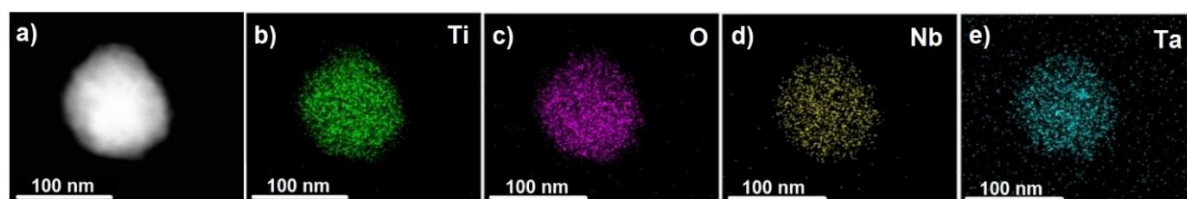


Figure 4.6. STEM image of NTTO nanoparticle and its STEM-EDX elemental maps for titanium, oxygen, niobium, and tantalum.

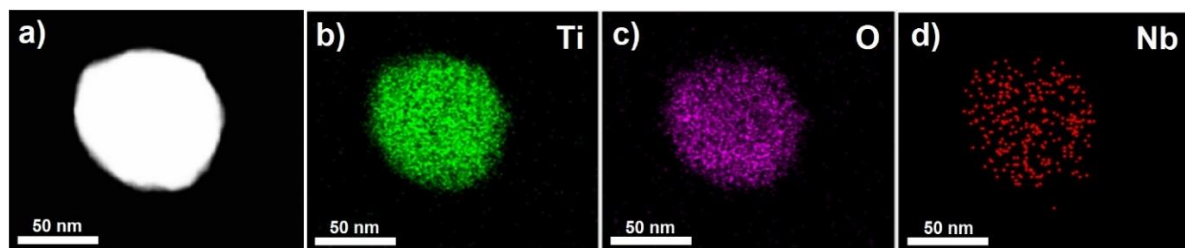


Figure 4.7. STEM-EDX elemental map of NTO nanoparticles.

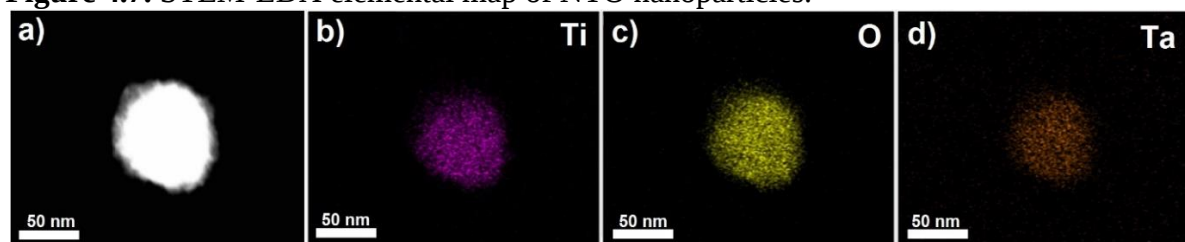


Figure 4.8. STEM-EDX elemental map of TTO nanoparticles.

4.3.5. X-ray photoelectron spectroscopy analysis of doped TiO₂ nanoparticles

In a complementary study of the dopant characteristics, X-ray photoelectron spectroscopy (XPS) was used to verify the incorporation of niobium and tantalum in TiO₂ lattice. The XPS results for NTTO (Figure 4.9), NTO (Figure 4.10), and TTO (Figure 4.11) show O 1s peaks at ~530 eV for the presence of oxygen as well as Ti 2p_{3/2} and Ti 2p_{1/2} peaks at ~458.5 and ~464.3 eV for titanium, respectively. The Nb 3d_{5/2} and Nb 3d_{3/2} peaks at 207.4 and 210.1 eV, respectively, confirm the inclusion of Nb into the TiO₂ lattice. Similarly, tantalum doping into TiO₂ was also verified by the characteristic Ta 4f_{7/2} and Ta 4f_{5/2} peaks with their respective binding energies of 26.7 and 28.5 eV.

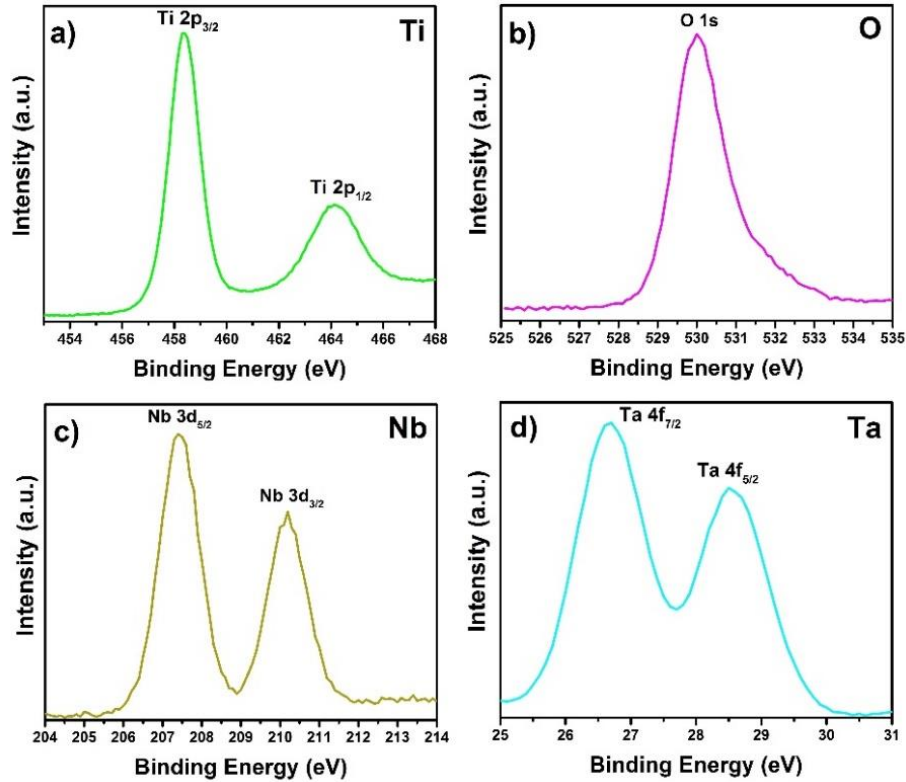


Figure 4.9. X-Ray photoelectron spectra for (a) titanium, (b) oxygen, (c) niobium, and (d) tantalum in NTTO nanoparticles.

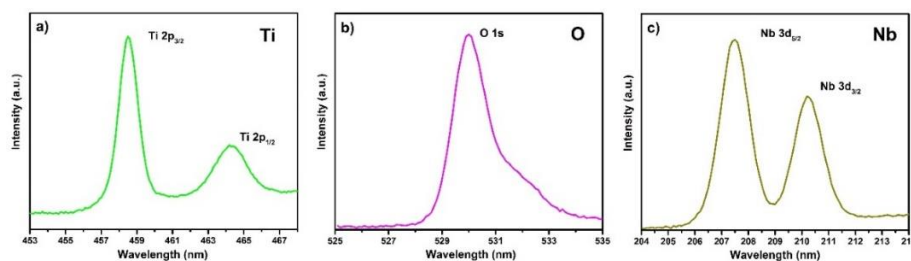


Figure 4.10. X-Ray photoelectron spectra for (a) titanium, (b) oxygen, (c) niobium in NTO nanoparticles.

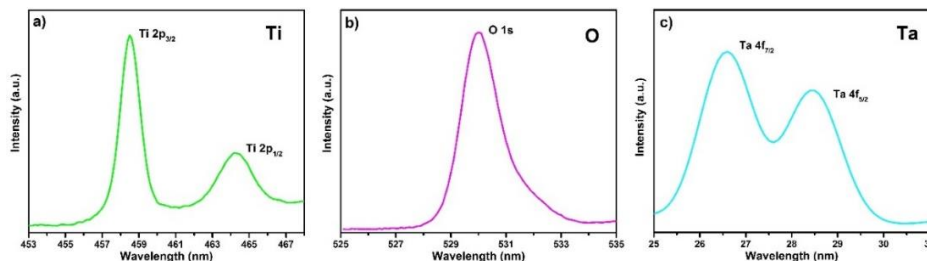


Figure 4.11. X-Ray photoelectron spectra for (a) titanium, (b) oxygen, (c) tantalum in TTO nanoparticles.

The atomic concentrations for dopant elements were also calculated for all doped TiO_2 nanoparticle samples. The results showed high consistency with that obtained from EDX data for not only NTO, TTO but also NTTO nanoparticles, as shown in Table 4.5. This consistency indicates that the dopant atoms were incorporated uniformly throughout the entire volume of the nanoparticles. Significantly, this verification allows a high level of predictability between the ratios of elements in starting materials used in the synthesis and the elemental compositions of the as-synthesized NPs, which are critical to obtaining desired properties as will be discussed below.

Table 4.5. Dopant Concentrations in Doped TiO_2 Nanoparticles Measured by XPS and EDX

	Nb (nominal) (%)	Nb (XPS) (%)	Nb (EDX) (%)	Ta (nominal) (%)	Ta (XPS) (%)	Ta (EDX) (%)
NTO	2.6	1.9 ± 0.1	2.0 ± 0.1	-	-	-
TTO	-	-	-	3.1	4.2 ± 0.1	4.1 ± 0.1
NTTO	2.6	2.0 ± 0.1	2.1 ± 0.1	3.1	4.0 ± 0.1	3.9 ± 0.1

4.3.6. Photoluminescence Spectra of Doped TiO₂ Nanoparticles

In semiconductor nanomaterials, the recombination of electron-hole pairs can significantly affect their photocatalytic activity.³⁷² The emitted energy resulting from this process can be recorded by photoluminescence (PL) spectroscopy, whose signal intensity indicates the electron-hole recombination rate in the semiconductor nanostructure.^{372,424} For better evaluation of the doping effects on electron-hole recombination rate, the nanoparticles studied in this report had their PL spectra collected and normalized for particle concentration and volume. The results showed PL peaks at ~ 525 nm similar to previously reported studies for TiO₂ photoluminescence.^{429–432} In general, a decreasing trend of PL signal intensities when increasing doping concentrations until a threshold was observed in the doped TiO₂ nanoparticles (Figure 4.12a-b). The minimum values of PL signal intensities were obtained at these thresholds (2 at% for Nb- and 4 at% for Ta doping, respectively). Further increase of doping concentrations over these thresholds (e.g., 3 at% Nb) resulted in higher PL signal intensities. These results indicate a correlation between the decreased electron-hole recombination rates and the dopant concentrations in TiO₂. This phenomenon can be attributed to the decrease of oxygen vacancies and defects in the host materials upon doping.⁴³³

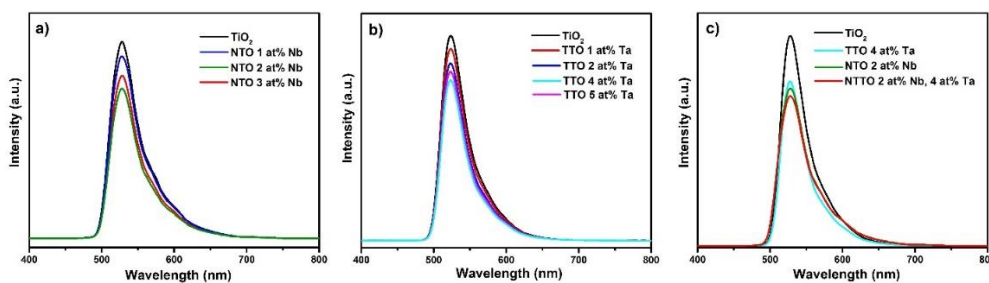


Figure 4.12. Photoluminescence spectra of (a) NTO, (b) TTO nanoparticles at various dopant concentrations, and (c) NTTTO nanoparticles at 2 at% Nb/4 at% Ta.

In NTO nanoparticles, the PL signal decreased proportionally with niobium concentration and reached 25.1% signal reduction at the threshold 2 at% Nb as shown in Figure 4.12a and Table 4.6. However, the PL signal reduction decreased to 14.2% when Nb concentration was further increased to 3 at% Nb. This reverse trend can be attributed to the formation of a different phase⁴³⁴ with a higher electron-hole recombination rate induced by the excess dopant level or newly created recombination centers.⁴³⁵ Similar observation was also recorded for TTO nanoparticles with a maximum PL signal reduction of 22.1% at 4 at% Ta doping (see Figure 4.12b and Table 4.6). These decreases in the electron-hole recombination rate of TiO₂ nanoparticles by doping with Nb and Ta make NTO and TTO more attractive for various photocatalytic and optoelectronic applications.

Table 4.6. Photoluminescence Signal Reduction at Different Dopant Concentrations

	Dopant Concentration	PL Signal Reduction*
NTO	1 at% Nb	7.8%
	2 at% Nb	25.1%
	3 at% Nb	14.2%
TTO	1 at% Ta	6.9%
	2 at% Ta	13.6%
	4 at% Ta	22.1%
	5 at% Ta	18%
NTTO	2 at% Nb/4 at% Ta	30.1%

*PL signals were normalized with the particle concentration and volume.

Based on the 2 at% Nb and 4 at% Ta thresholds, we optimized conditions for synthesizing the dually doped NTTO nanoparticles with atomic concentrations of 2 at% Nb and 4 at% Ta to evaluate the effects of simultaneous doping with Nb and Ta on TiO₂ nanoparticles. Compared to the single doped NPs, the codoped NTTO nanoparticles with 2 at% Nb and 4 at% Ta showed higher electron-hole recombination rate reduction with the 30.1% PL signal reduction compared to 25.1% and 22.1% of NTO with 2 at% Nb and TTO

with 4 at% Ta, respectively (Figure 4.12c and Table 4.6). This synergistic effect of multiple dopants on the doped semiconductor had also been observed for other material systems.^{436,437} These data showed that doping of multiple elements, whose radii are different, could have introduced more lattice stress to the host TiO₂ material. This stress might create more defects which were reflected by the significantly smaller crystallite size of NTTTO observed in XRD data, thus prolonging the path and time needed for the electron and hole to recombine. Importantly, the ability to tune the photoluminescence signal via dopant concentrations by a facile synthetic method described in this study also expands the utility of the NTO, TTO, and NTTTO nanoparticles. Due to their optimal electron-hole recombination rates, NTO with 2 at% Nb, TTO with 4 at% Ta, and NTTTO with 2 at% Nb and 4 at% Ta would be used for further evaluation of optical properties and photocatalytic hydrogen evolution reactions in the following parts of this report.

4.3.7. Band Gap Analyses for Doped TiO₂ Nanoparticles

The optical band gaps (E_g) of undoped, singly doped, and dually doped TiO₂ nanoparticles were determined using diffuse reflectance spectroscopy (DRS) absorbance measurements and the Tauc equation (eq (1)). With an indirect band gap,⁴³⁸ $r = 2$ was used for the Tauc plot calculations, where α , $h\nu$, E_g , and A are the absorption coefficient, incident photon energy, optical band gap, and proportional constant, respectively.

$$\alpha h\nu = A(h\nu - E_g)^r \quad (1)$$

The solid-state DRS measurements were carried out with dried nanoparticles. Figure 4.13 shows the absorption spectra of TiO₂, NTO, TTO, and NTTTO in UV-vis-NIR range. The

data showed slightly shifted positions of absorption peaks in all doped TiO_2 particles with the largest shift recorded in NTTO compared to undoped TiO_2 nanoparticles. The Tauc plots of $(\alpha h\nu)^{1/2}$ against the photon energy ($h\nu$) were generated and present in Figure 6b. The shifts toward lower energies were also observed in the Tauc plots, corresponding well with the shifts toward longer wavelengths in the absorption spectra shown in Figure 4.13a.

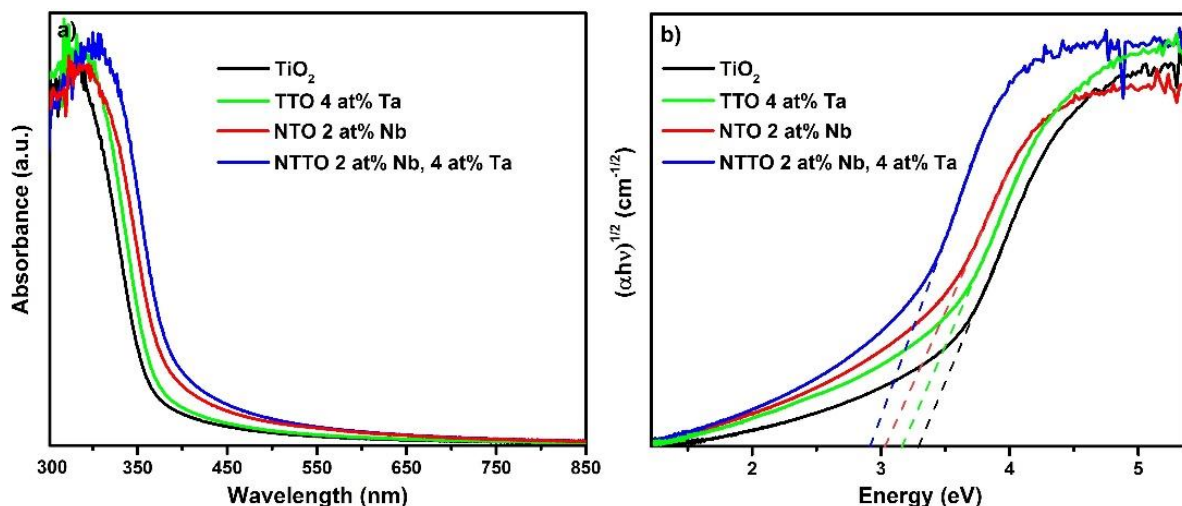


Figure 4.13. (a) Solid-state diffuse reflectance spectra and (b) Tauc plot of TiO_2 , TTO with 4 at% Ta, NTO with 2 at% Nb, and NTTO with 2 at% Nb/4 at% Ta nanoparticles.

The optical band gap of anatase TiO_2 nanoparticles was determined to be 3.27 eV, which is slightly larger than bulk anatase TiO_2 ⁴³⁹ as expected from the quantum confinement effect that might happen on nanoscale semiconductors. The doping of Nb and Ta into TiO_2 NPs had reduced the optical band gaps to 3.15, 3.02, and 2.90 eV for TTO, NTO, and NTTO, respectively (Figure 4.13b). The inclusion of dopants into metal oxide semiconductors might have introduced either donor or acceptor levels in the band gap region, which reduces the optical band gap.⁴⁴⁰ Interestingly, the dual doping of Nb and Ta into the same TiO_2 lattice

had further decreased the band gap energy of the nanoparticles, making NTTO NPs more efficient in the center of the solar spectrum. As shown in Figure 4.13b, the presence of the dopant elements also bent the Tauc plot toward lower energies. Which, consequently, extend the absorption tails of the nanoparticles (Figure 4.13a).

4.3.8. Photocatalytic Hydrogen Evolution

The photocatalytic performances of the undoped, singly doped, and dually doped TiO₂ nanoparticles in a basic environment under a simulated solar illumination were evaluated for hydrogen evolution reaction (HER) at 25 °C. The hydrogen gas product was verified by gas chromatography data as shown in Figure 4.14. The amounts of hydrogen generated in the HER tests with TiO₂, NTO, TTO, and NTTO nanoparticles as a function of time were recorded and shown in Figure 4.15a. Importantly, the hydrogen evolution rates of these nanoparticle samples remained steady for at least 5 hours. Without doping, anatase TiO₂ exhibited an evolution rate of ~281 $\mu\text{mol/g}_{\text{cat}}/\text{h}$, which was boosted to ~687, ~815, and ~1168 $\mu\text{mol/g}_{\text{cat}}/\text{h}$ in TTO, NTO, and NTTO nanoparticle catalysts, respectively (Figure 4.15b). Hence, compared to the undoped TiO₂, the photocatalytic hydrogen rate had increased ~2.4, ~2.9 times in the singly doped TTO, NTO NPs, respectively. Notably, the dually doped NTTO had significantly boosted the evolution rate to ~4.2 times of that compared to the undoped TiO₂. Thus, the dually doped NTTO nanoparticles showed significantly higher hydrogen evolution rate enhancement compared to the singly doped particles with 70% and 43% higher than TTO and NTO, respectively. These results could have come from a synergistic combination of the decrease of band gap energies, resulting in larger numbers of photons for

absorption at wavelengths closer to the center of the solar spectrum; and the reduced electron-hole recombination rates of the doped NPs.

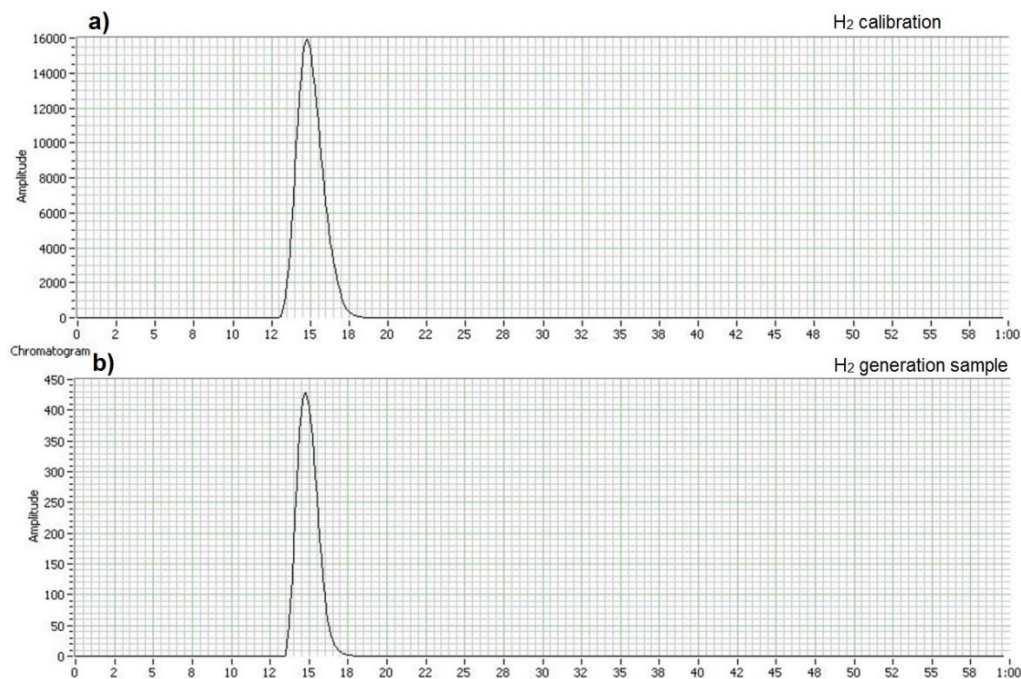


Figure 4.14. Gas chromatography measurements of (a) photocatalytic hydrogen evolution gas product as compared with (b) pure hydrogen calibration.

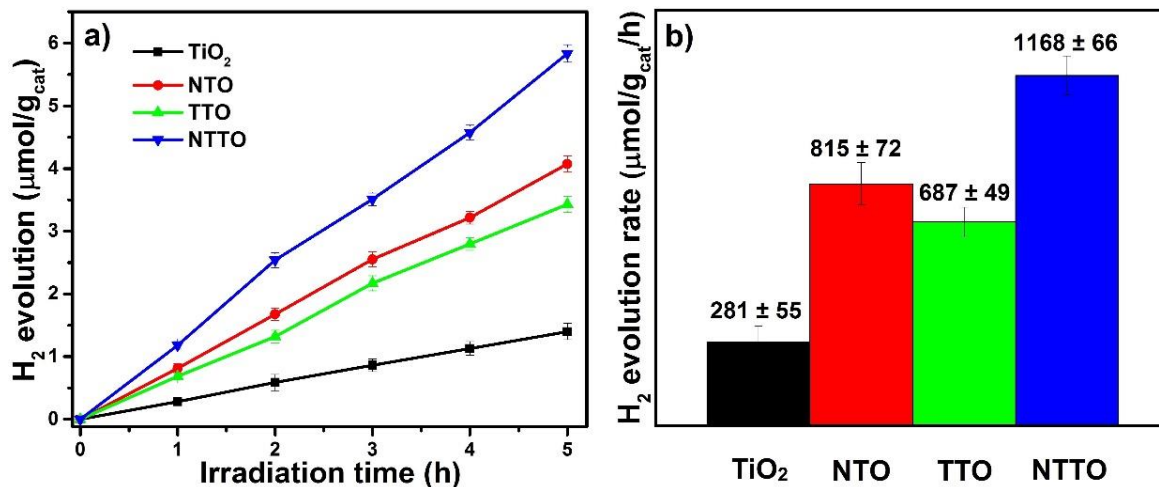


Figure 4.15. (a) Photocatalytic hydrogen evolution and (b) hydrogen evolution rates of TiO₂, NTO, TTO, and NTTO nanoparticles under simulated solar irradiation.

The apparent quantum yields (AQYs) for each nanoparticle sample tested in the photocatalytic hydrogen evolution were also calculated at 365 nm for all four testing nanoparticles. Apparent quantum yield (AQY) calculation is done at 365 nm with equation 2 below:

$$\text{AQY} = n_{\text{reacted electrons}}/n_{\text{hv}} = 2n_{\text{hydrogen}}/n_{\text{hv}} \quad (2)$$

$n_{\text{reacted electrons}}$: number of electrons reacted in the hydrogen generation process

n_{hydrogen} : number of hydrogen molecules generated in 1 second

n_{hv} : number of photons hitting the photocatalyst in 1 second

With enhanced hydrogen evolution rates by the presence of the dopants, the AQYs of TTO, NTO, and NTTO were significantly increased to ~3.69%, ~4.28%, and ~6.74%, respectively (Table 4.7), from ~2.18% of pristine anatase TiO₂. Thus, these results pinpointed that the doped nanoparticles were able to utilize the incident photons more effectively for hydrogen generation than the undoped TiO₂ NPs.

Table 4.7. Optical Band Gaps, Hydrogen Evolution Rates, and Apparent Quantum Yields of TiO₂, NTO, TTO, and NTTO Nanoparticles

	TiO₂	NTO	TTO	NTTO
Band Gap (eV)	3.27 ± 0.02	3.02 ± 0.03	3.15 ± 0.02	2.90 ± 0.02
H₂ Evolution Rate (μmol/g_{cat}/h)	281 ± 55	815 ± 72	687 ± 49	1168 ± 66
AQY* (%)	2.18 ± 0.23	4.28 ± 0.26	3.69 ± 0.28	6.74 ± 0.31

*AQY calculated at 365 nm.

Cyclability tests were also carried out on the same nanoparticle samples to evaluate their photocatalytic stabilities. Specifically, the nanoparticles were collected, washed, and reused after each photocatalytic hydrogen evolution test. Notably, all the nanoparticles remained

highly stable after five test cycles, as shown in Figure 4.16. The variations of the evolved hydrogens fell within experimental and instrumental errors. This could have happened when the testing process involved several transferring steps, which might have slightly reduced the actual amount of nanoparticle catalysts presented in some following test flasks. Thus, both the optical property analyses and hydrogen evolution studies have demonstrated significant enhancements in the niobium-, tantalum-, and especially the niobium/tantalum-codoped TiO₂ nanoparticles; enabling them for scale-up applications in photocatalytic hydrogen generation. Moreover, the applicability prospect of the doped TiO₂ can even be further boosted by hybridizing with suitable plasmonic nanostructures.^{11,424,441}

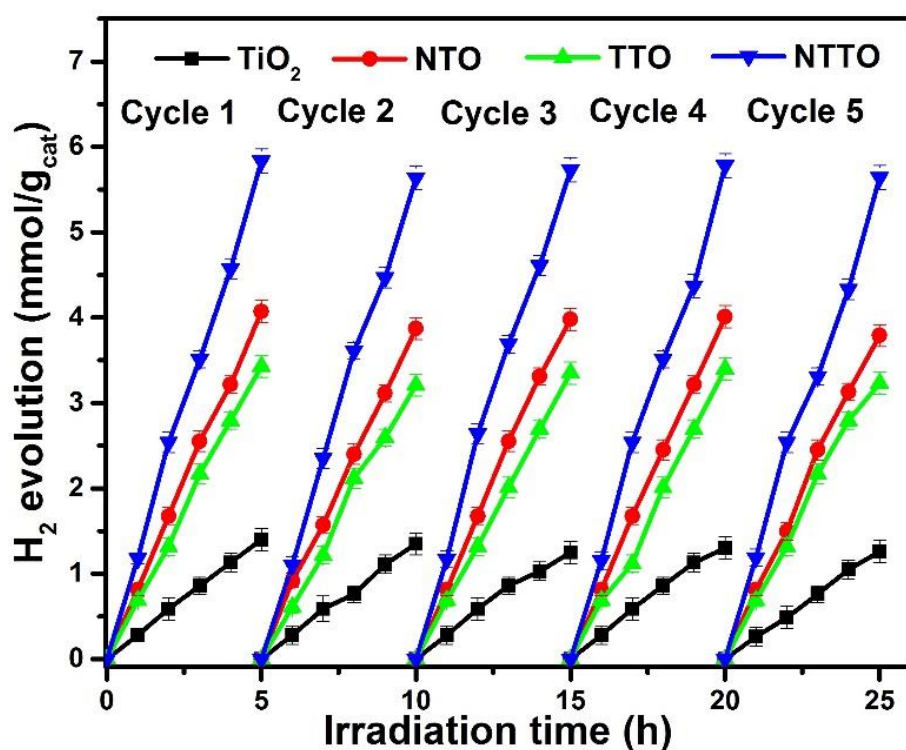


Figure 4.16. Cyclability tests of TiO₂, NTO, TTO, and NTTO nanoparticles for photocatalytic hydrogen evolution.

4.4. Conclusions

This work demonstrates reliable and convenient wet chemistry-based methods to synthesize highly monodisperse singly and dually doped with Nb and Ta, as well as undoped anatase TiO₂ nanoparticles. The electron-hole recombination rates were suppressed by the presence of the niobium and tantalum dopants. In the singly doped NPs, the electron-hole recombination rates were optimal at the thresholds of 2 at% for niobium and 4 at% for tantalum with 25.1% and 22.1% photoluminescence signal reductions, respectively. Notably, the reduction was further reduced to 30.1% in the dually doped nanoparticles when 2 at% niobium and 4 at% tantalum were co-doped. While the undoped TiO₂ nanoparticles had an optical band gap of 3.27 eV, it was significantly decreased to 3.15 and 3.02 for TTO, NTO, respectively by introducing dopants into the TiO₂ lattice. The most dramatic band gap reduction was recorded in the dually doped NTTTO nanoparticles (2.9 eV). Importantly, photocatalytic hydrogen evolution tests showed substantially enhanced hydrogen evolution rates of 2.4, 2.9, and 4.2 times on TTO, NTO, and NTTTO photocatalysts, respectively, compared to the undoped TiO₂ nanoparticles. Moreover, all the nanoparticles exhibited high stabilities after multiple photocatalytic hydrogen evolution test cycles. On the whole, the significant enhancement in the hydrogen evolution rates, especially in the dually doped particles, and the scalable synthetic methods at mild conditions make the doped TiO₂ nanoparticles reported here promising for fuel generation, as well as other photocatalytic applications. Additionally, optoelectronics and gas sensing applications can also benefit from the tunable PL responses and optical band gaps of these TiO₂-based nanoparticles.

Chapter 5: Conclusions

Noble metal nanostars with their superior surface-to-volume ratios and the arguably largest numbers of electric hotspots in all plasmonic nanostructures have great potential for applications in many advanced technologies. Conventional plasmonic nanostars typically operate in the near-infrared region, thus limiting their potential in solar-powered applications. On the other hand, the inability of metal oxide semiconductor nanoparticles to operate in the high-intensity parts of the solar spectrum and the high recombination rates of the photo-generated electrons and holes within their structures limit practical uses of metal oxide semiconductor nanoparticles. The limitations in both plasmonic nanostars and metal oxide nanoparticles can be overcome by proper designs, doping, and plasmonic-coupling. The work in this dissertation focused on: 1) fabrication and evaluation of a new type of plasmonic nanostars with a new active spectral range; 2) design, synthesis, and assessment of plasmonic-semiconductor core-shell composite nanoparticles for enhanced light absorptions and photocatalytic hydrogen evolutions; and 3) synthesis and characterization of monodisperse undoped as well as singly and dually doped metal oxide nanoparticles for enhancing their optical and electronic properties and boosting their photocatalytic performance.

In Chapter 2, the fabrication of highly stable semi-hollow gold-silver nanostars (hAuAgNSts) is described. Galvanic replacement between silver nanostars (AgNSts) and chloroauric acid afforded optically tunable hAuAgNSts with plasmonic resonances ranging from UV to visible to near-infrared wavelengths. Moreover, the compositionally unique bimetallic hAuAgNSts exhibited strong extinction maxima in the UV-Vis range, which contrasts AgNSts (centered in the UV) and the more common gold nanostars (AuNSts;

centered largely in the near-infrared). Notably, the hAuAgNSts exhibited enhanced thermal and colloidal stability without the need for surface modification when compared to AgNSts and AuNSts. This latter feature offers new opportunities in the fields of catalysis, photovoltaics, and sensing as well as new strategies for post-synthetic modification that enable applications in biosensing and theranostics.

Chapter 3 describes a facile synthesis method to combine both plasmonic silver and cuprous oxide semiconductor in Ag@Cu₂O core-shell nanostructures with controllable shell thicknesses. The syntheses of monodisperse spherical bare silver and cuprous oxide nanoparticles via convenient procedures were also reported. The photocatalytic performances of Ag@Cu₂O and Cu₂O nanoparticles were evaluated in hydrogen evolution reactions using a customized reaction system. The results showed that the hybrid nanoparticles possess a tunable strong absorption band in the visible regions and a highly reduced electron-hole recombination rate for enhanced photocatalytic applicability due to the presence of the plasmonic silver core. Importantly, the Ag@Cu₂O core-shell nanoparticle photocatalyst showed an increased hydrogen evolution rate of more than 6-fold and a 21% enhancement of stability compared to its Cu₂O counterpart, making it one of the best reported cuprous oxide-based photocatalysts for hydrogen evolution.

In Chapter 4, highly monodisperse spherical nanoparticles of undoped, singly doped (NTO and TTO), and dually doped (NTTO) anatase TiO₂ with niobium and tantalum dopants were prepared by scalable methods at mild conditions. The doped TiO₂ nanoparticles showed reduced bandgap energies and adjustable suppressions of electron-hole recombination rates with the largest reductions observed on the dually doped NTTO nanoparticles. The

photocatalytic hydrogen evolution rates and the quantum yields were also significantly increased by the introductions of Na-, and Ta dopants into the TiO₂ lattice. The codoped NTTO nanoparticles also exhibited the highest hydrogen evolution rate and quantum yield. Importantly, all the nanoparticles displayed high stabilities after multiple photocatalytic hydrogen evolution test cycles. From the results, the doped TiO₂ shows great potential for photocatalytic fuel generation and optoelectronic applications.

In summary, a new optical window for plasmonic nanostars has been opened via proper alloying of gold and silver for fabrications of new semi-hollow gold-silver nanostars (hAuAgNSts). Additionally, the operational scope of metal oxide nanostructures has been expanded via plasmonic coupling and doping strategies. The scalability and facility of the fabrication methods reported in this dissertation can significantly expand the applicability and range of applications of the plasmonic, doped, and plasmonic-coupled semiconductor nanostructures. Many potential directions for further development are available, ranging from combining doped semiconductors with suitable plasmonic nanostructures to achieving the synergistic enhancement from both doping and plasmonic coupling. Moreover, proper combinations of semiconductors and hAuAgNSts can also lead to greater performances in light-powered applications such as photocatalytic hydrogen evolutions, CO₂ reductions, and pollutant degradations. Certainly, we will continue to explore and expand the advance in this promising research area.

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