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Optically Enhanced Ag@Cu₂O Core—Shell Nanoparticles for Visible Light Photocatalytic Hydrogen Evolution

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ABSTRACT: Enhancing the photocatalytic activity and robustness of cuprous oxide presents key challenges in the development of efficient cuprous oxide-based photocatalysts. This report outlines a facile synthesis method for integrating plasmonic silver with a cuprous oxide semiconductor in $Ag@Cu_2O$ core-shell nanostructures with controllable shell thicknesses. Additionally, the synthesis of monodisperse spherical bare silver and cuprous oxide nanoparticles through convenient procedures is presented. The photocatalytic performances of the $Ag@Cu_2O$ and Cu_2O nanoparticles for hydrogen evolution were evaluated using a custom-built photocatalytic reaction system. The results indicate that the core-shell $Ag@Cu_2O$ nanoparticles exhibit a tunable, strong absorption band within the visible spectrum and a significantly reduced electron-hole recombination rate



compared to the Cu_2O nanoparticles, thereby showing enhanced photocatalytic efficacy attributable to the presence of the plasmonic silver core. Notably, the Ag@Cu_2O core-shell nanoparticle photocatalysts demonstrate an increase in the hydrogen evolution rate by more than 6-fold and a 21% improvement in stability compared to their Cu_2O counterparts, positioning them among the top-tier cuprous oxide-based photocatalysts for hydrogen evolution.

KEYWORDS: silver, Cu₂O, core-shell, semiconductor, photocatalysis, electron-hole recombination, hydrogen evolution

INTRODUCTION

Amid growing energy demands and environmental concerns, coupled with the inherent intermittency of photovoltaics and wind turbines, the use of semiconductor materials in photocatalysis has emerged as a potential technology to address these challenges.¹ Photocatalysts have been shown to generate high-energy-density fuels and high-value-added products, as well as eliminate environmental pollutants using only solar radiation as the energy source.¹ Since Fujishima and Honda first reported photocatalysis using titanium dioxide $(TiO_2)_1^2$ significant research efforts have been devoted to developing various efficient photocatalysts for many practical applications.³ However, major challenges such as low photon absorbance in the solar spectrum, high recombination rates of photogenerated electron-hole pairs, and high costs have limited the applicability of many traditional photocatalysts.^{4,5} For example, the first reported photocatalyst, anatase TiO₂, with a large bandgap of ~ 3.2 eV, only absorbs photons in the ultraviolet region, which constitutes less than 5% of the total solar energy flux.^o With the advent of nanocrystal fabrication techniques in recent decades, nanoparticle-based photocatalysis has become a promising approach for enhancing the efficiency of various photocatalysts.⁷ The high surface-tovolume ratio of nanoparticles (NPs) not only significantly enhances the catalytic activity of nanosized photocatalysts but also substantially reduces the amount of material required for the application compared to bulk catalysts.⁸ Moreover,

nanoscale semiconductor photocatalysts can benefit from the quantum confinement effect, which improves the optical absorbance of the material.⁹

Due to their unique localized surface plasmon resonance (LSPR), various plasmonic nanostructures such as nanospheres, nanorods, and nanostars have been studied for numerous utilizations ranging from enhanced imaging to biomedical applications.^{10–13} In photocatalysis, plasmonic nanoparticles made of silver (Ag), gold (Au), and copper (Cu) have been shown to be effective solar radiation sensitizers, exhibiting absorption peaks in the visible region at around 407,¹⁴ 525,¹⁵ and 600 nm,¹⁶ respectively. In these plasmonic structures, the free electron cloud oscillates collectively under incident electromagnetic radiation, generating an enhanced electromagnetic field near the surface of the plasmonic material.¹⁷ When the characteristic frequency of the collective oscillation matches that of the external radiation, LSPR occurs, and the plasmonic structure displays an absorption peak at that LSPR frequency.¹⁸ The LSPR wavelength can be blue- or red-shifted by varying the size,

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morphology, and type of metal, or by changing the dielectric constant of the surrounding environment.^{19,20} Additionally, the locally amplified electric field can induce electron injection and energy transfer to the semiconductor materials in contact with the plasmonic nanostructures.^{21,22} Although plasmonic nanostructures can serve as photocatalysts on their own,^{23,24} their development has significantly inspired new approaches for the design and synthesis of more efficient photocatalysts by combining plasmonic metals with semiconductors in appropriate architectures.^{25,26} Owing to plasmon-induced resonance energy transfer (PIRET) and direct electron transfer (DET) from the metal to the coupled semiconductor, the photocatalytic activity of plasmonic metal-semiconductor nanocomposites can be significantly increased compared to semiconductor-only photocatalysts.^{27,28} Essentially, with their extended absorption range into the visible region of the metal components, plasmonic-semiconductor nanocomposites can absorb more solar energy across a broader spectrum of light wavelengths than their semiconductor counterparts.²

Among various plasmonic nanostructures, Ag NPs offer numerous advantages for photocatalytic applications, ranging from a high capacity to induce surface plasmon resonance³⁰ to exceptional thermal and electrical conductivity.³¹ Moreover, the LSPR wavelength at the violet end of the visible spectrum (~407 nm) of Ag NPs makes them excellent candidates for coupling with semiconductor materials.¹⁴ This coupling can shift the absorption band to the center of the solar spectrum, significantly enhancing the photocatalytic activity of the nanoparticles. As a p-type semiconductor, cuprous oxide (Cu_2O) is versatile in applications such as sensors,³ photovoltaics,³³ and electronics.³⁴ Cu₂O also boasts several key properties desirable in a promising photocatalyst, including a narrow bandgap,³⁵ high carrier mobility (~100 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$),³⁶ a long carrier diffusion length (~500 nm),³⁷ and a combination of low cost and material abundance. We envision that embedding a plasmonic Ag nanoparticle core within a Cu_2O shell (Ag@ Cu_2O) could further enhance the photocatalytic activity of Cu₂O due to the aforementioned enhancement mechanisms. Furthermore, coupling with plasmonic nanostructures can also suppress rapid electronhole recombination in the Cu₂O semiconductor, a major drawback associated with traditional metal oxide photo-catalysts.^{38,39} Several studies on Cu₂O-coated Ag NPs have been reported, employing various synthesis methods and focusing on different aspects of characterization.^{40–43} Despite these accomplishments, there remain numerous fabrication shortcomings and characterization inadequacies that need addressing, such as demanding synthesis conditions, 40,41 lack of control over structure and size distributions, 41,42 and insufficient study of photocatalysis-related properties. 41,43

In this report, we describe a convenient and efficient wet chemistry method for synthesizing spherical, monodisperse $Ag@Cu_2O$ core-shell and Cu_2O NPs under mild conditions (Scheme 1). This work also demonstrated the capability to

Scheme 1. Synthesis of Ag and Ag@Cu₂O Core–Shell Nanoparticles



fine-tune the thickness of the Cu₂O shell to adjust the absorption peak to the center of the solar spectrum. Moreover, the composite core-shell nanoparticles exhibited significant suppression of the photoluminescence (PL) signal in the Cu_2O semiconductor, suggesting that the plasmonic silver core can efficiently reduce the rate of photogenerated electron-hole recombination, which impedes the photocatalytic applicability of Cu₂O. With a conduction band minimum higher than the reduction potential for protons,⁴⁴ Cu₂O-based nanostructures are potential catalysts for the hydrogen evolution reaction (HER) to generate hydrogen as a clean and high-energycapacity alternative to gasoline, with solar radiation as the only required energy source. Consequently, the Ag@Cu₂O coreshell NPs synthesized in this work were tested for their photocatalytic hydrogen-generating performance under visible light irradiation conditions. Notably, the photocatalytic HER studies showed a significantly increased hydrogen evolution rate and higher photostability of Ag@Cu2O nanoparticle catalysts compared to their Cu₂O counterparts.

MATERIALS AND METHODS

Materials. Silver nitrate (AgNO₃, Sigma-Aldrich), potassium iodide (KI, Aldrich), ascorbic acid (AA, Aldrich), trisodium citrate (NaCit, EM Science), polyvinylpyrrolidone (PVP, MW ~ 55,000, Aldrich), copper(II) sulfate pentahydrate (CuSO₄.SH₂O, Sigma-Aldrich), hydrazine monohydrate (64 wt % N₂H₄, Sigma-Aldrich), polyethylene glycol (EG, Sigma-Aldrich), sodium hydroxide (NaOH, Macron Chemicals), argon (Ar, Matheson) were used as received from the specified 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 h in a base bath, followed by treatment with piranha solution (3:1 H₂SO₄:H₂O₂) and aqua regia solution (3:1 HCl:HNO₃) for at least 6 h, and then dried in an oven at 150 °C followed by cooling prior to use. Extra caution should be exercised during the handling of the cleaning process.

Synthesis of Ag NPs. A modification of the method reported by Medhi et al.³⁸ was employed to prepare Ag NPs. Initially, 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 it reached boiling. Subsequently, 3 mL of 5 mM ascorbic acid solution was added. In the meantime, the Ag 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 μ L of 8 μ M KI solution. The Ag precursor mixture was well shaken and then sonicated for 5 min at 21 °C. It was then injected into the boiling ascorbic acid solution under vigorous magnetic stirring, ensuring the stirring rate was not too fast to avoid forming bubbles. The solution was stirred under reflux for an additional hour to complete the formation of Ag NPs. During this process, the solution quickly turned from colorless to brownish yellow, and subsequently to yellowish green, indicating the formation of Ag NPs. After cooling to room temperature within 30 min, the Ag NP solution was centrifuged at 7000 rpm for 15 min. The supernatant was removed, and the nanoparticles were redispersed in 25 mL of Milli-Q water. This washing process was repeated twice, and the resultant 25 mL Ag nanoparticle stock solution was stored at 4 °C if not immediately characterized or coated with Cu₂O. Note: The flask and stir bar should be thoroughly washed with deionized water and an aqua regia solution reserved exclusively for Ag nanoparticle synthesis to ensure consistent results.

Synthesis of Ag@Cu₂O Core–Shell NPs. The Cu₂O coating of Ag NPs was accomplished following a procedure reported by Chen et al.,⁴³ 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 ~ 55,000) in 8.5 mL of Milli-Q water with ultrasonication for 20 min. Different amounts of the Ag nanoparticle stock solution (200,

400, 800, 1600, 2400 μ L) were added to the surfactant solution. After an additional 10 min of ultrasonication for better dispersion and stabilization of the Ag NPs, 400 μ L of 0.1 M CuSO₄ solution was added to the mixture under vigorous magnetic stirring. The solution was stirred for another 2 min, then 125 μ L of 1 wt % N₂H₄ was injected over 5 min into the vigorously stirred mixture. After 1 h, the nanoparticles were collected by centrifugation at 7000 rpm for 15 min and redispersed in 5 mL of ethanol.

Synthesis of Cu₂O NPs. Spherical Cu₂O NPs were also synthesized using a method similar to the coating procedure, but without Ag NPs and with modifications to ensure particle uniformity. The process began with the dissolution of 800 mg of PVP (MW \sim 55,000) in 8.5 mL of Milli-Q water, followed by ultrasonication for 30 min. Next, 400 μ L of 0.1 M CuSO₄ aqueous solution was added to the surfactant solution under stirring at 400 rpm and a temperature of 30 °C. The solution was stirred for an additional minute before the stirring speed was increased to 600 rpm, and 125 μ L of 1 wt % N₂H₄ solution was injected into the mixture in 30 s. The solution quickly turned brick red after the N2H4 injection, signifying the formation of crystalline Cu₂O. The newly formed nanoparticles were then allowed to fully grow during another hour of stirring before being collected by centrifugation at 7000 rpm for 15 min, followed by a solvent exchange with ethanol. The Cu₂O NPs were finally dispersed in 5 mL of ethanol and stored at 4 °C. The increased amount of PVP, higher synthesis temperature, and faster injection of the reducing agent helped accelerate the nucleation process and reduce spontaneous seeding, which in turn, created a more monodisperse population of Cu₂O NPs.

Nanoparticle Characterization. All synthesized nanoparticles were imaged using a LEO-1525 scanning electron microscope (SEM) operating at 15 kV and a 5.5 mm working distance. SEM samples were deposited on precleaned silicon wafers and dried at 60 °C for 1 h prior to imaging. The crystalline nature of the nanoparticles was assessed using an X'Pert powder X-ray diffractometer (PXRD) operating at 45 kV and 30 mA. PXRD samples were prepared by drop-casting on glass slides and drying at 60 °C for 2 h. A JEOL JEM-2010 FX scanning transmission electron microscope (STEM) was utilized at 200 kV to confirm the morphology, core-shell structure, and shell thickness of the nanoparticles synthesized under these conditions. Samples for transmission electron microscopy (TEM) characterization were deposited on 300-mesh holey carbon-coated nickel grids and dried at 60 °C for 2 h prior to analysis. Elemental composition was evaluated using a Phi X-ray photoelectron spectroscopy (XPS) system equipped with a monochromatic Al K α X-ray source. XPS samples were deposited on silicon wafers and dried. Elemental distribution analyses were conducted using an energy dispersive X-ray spectroscopy (EDX) detector attached to the aforementioned STEM instrument. Optical properties of the synthesized nanoparticles were analyzed using a Cary 50 scan UVvisible (UV-vis) spectrometer, which operates over a spectral range from 200 to 1000 nm. Uncoated Ag and Cu₂O-coated Ag NPs were suspended in water and ethanol, respectively, for UV-vis measurements. PL response from Cu₂O and Ag@Cu₂O nanoparticle samples was evaluated using a PerkinElmer LS-55 fluorescence spectrometer in a quartz cuvette with an excitation wavelength of 500 nm and a 515 nm optical filter. Dynamic light scattering (DLS) measurements were performed using a Malvern Zetasizer model ZEN3600.

Photocatalytic Hydrogen Generation Test. The photocatalytic HER was conducted in a custom-made, airtight 25 mL glass flask connected to a digital pressure transducer and equipped with a septum-covered sampling window. The reaction flask was maintained at 25 °C using a jacketed flask coupled to a temperature-regulating water circulator. In a typical experiment, the nanoparticle photocatalyst was dispersed in 10 mL of a 10% ethylene glycol aqueous solution with vigorous magnetic stirring within the reaction flask, followed by purging with high-purity compressed argon gas for 15 min. Subsequently, the mixture was illuminated by an LED light source emitting at a wavelength of 460 nm with a power of 14.4 W for 6 h. The pressure transducer connected to the reaction flask monitored the volume of gas produced during the reaction. The gas

generated was collected through the sampling window and analyzed using a GOW-MAC Series 400-P thermal conductivity gas chromatograph with argon as the carrier gas. For stability studies of the nanoparticles, after each cycle, the photocatalyst was centrifuged at 7000 rpm for 15 min and underwent solvent exchange with deionized water three times before being subjected to the subsequent cycle.

RESULTS AND DISCUSSION

Synthesis of Nanoparticles. Monodisperse Ag NPs with diameters approximately 45 to 50 nm were synthesized using a modified ascorbic acid-citrate reduction method assisted by KI.³⁸ The role of KI is to prevent the formation of Ag nanorods by selectively inhibiting growth along the (111) facet. Increased concentrations of sodium citrate and ascorbic acid accelerated the nucleation process, resulting in a homogeneous population of Ag NPs as shown in Figure 1a.



Figure 1. SEM images of (a) Ag NPs and Ag@Cu₂O core-shell NPs with shell thicknesses of (b) 10 ± 2 nm, (c) 13 ± 2 nm, (d) 17 ± 2 nm, (e) 27 ± 4 nm, and (f) 45 ± 4 nm. The inset figures display their corresponding TEM images.

Ag@Cu₂O core-shell NPs with varying shell thicknesses were synthesized through the controlled slow reduction of Cu²⁺ into Cu₂O nanocrystals around the Ag nanoparticle cores using hydrazine as the reducing agent (Figure 1b-f). The average Cu₂O shell thicknesses of 10 ± 2 , 13 ± 2 , 17 ± 2 , 27 ± 4 , and 45 ± 4 nm were achieved using 2400, 1600, 800, 400, and 200 μ L of the Ag nanoparticle stock solution, respectively. The representative low-magnification TEM images and histograms of the particles with shell thicknesses of 27 and 45 nm are shown in Figure S1. A uniform shell coating on the Ag core, without core-free particles or particle aggregation, was observed in the TEM images presented in Figures 1 and S1. The average shell thickness for each synthesis condition was obtained by measuring the shell thickness on 4 different directions from the silver core over 10 different core-shell nanoparticles. The Cu₂O shell thickness is inversely proportional to the volume of the Ag nanoparticle stock solution used. Uniform dispersion of Ag NPs in PVP solution, achieved by ultrasonication, and the slow injection of N2H4 under vigorous stirring are critical for obtaining core-shell nanoparticles with a single Ag core and a well-shaped shell. Synthesis under milder conditions, compared to those reported in previous studies,^{40,41} was key for fine control of the shell thickness. Interestingly, the overall spherical morphology of the core-shell nanoparticles is maintained, even when the shell thickness exceeds the diameter of the Ag core. The significantly enhanced control over the structure and size distribution of the

composite nanoparticles, compared to other studies,^{41,42} has enabled a more rigorous investigation of the optical properties and photocatalytic performance of the photocatalyst, as discussed below. Additionally, spherical Cu₂O NPs were synthesized with modifications to the coating step, resulting in monodisperse nanoparticles as evidenced by SEM imaging (Figure S2) and DLS measurements (Figure S3). This convenient synthesis route, characterized by very mild conditions, is an excellent candidate for large-scale production of highly monodisperse and consistent spherical Cu₂O NPs, addressing one of the significant challenges in the practical utilization of nanomaterials.

The XRD pattern of the synthesized $Ag@Cu_2O$ nanoparticles with 45 ± 4 nm shell thickness are provided in Figure 2, where combined diffraction peaks from both Ag and Cu₂O



Figure 2. XRD pattern of $Ag@Cu_2O$ core-shell NPs and reference patterns for Cu_2O and Ag.

phases are readily observed. The crystallographic planes of (111), (200), (220), and (311) from the Ag NPs (JCPDS: 04–0783) can be indexed for the diffraction peaks at 2θ = 37.7, 44.0, 64.5, and 77.5°, respectively. The remaining peaks at 2θ = 28.9, 36.7, 42.1, 61.7, and 73.5° correspond to the Cu₂O (110), (111), (200), (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 NPs (Figure S4) also confirms the formation of crystalline Cu₂O.

Compositional and Structural Analysis. The surface composition of the core-shell nanoparticles was examined

using XPS (see Figure 3). The sample of Ag@Cu₂O nanoparticles with 45 ± 4 nm average shell thickness was used. The strong Cu $2p_{3/2}$ peak at 933 eV (Figure 3b), along with a weak Cu²⁺ satellite peak at 945 eV, indicates the dominant presence of Cu⁺ in the Cu₂O shell. The presence of Cu₂O is also confirmed by the typical O 1s peak for metal oxides at 529 eV (Figure 3c). The C 1s peak observed in the survey spectrum may be attributed to organic contaminants introduced during the measurement process. Both XPS and XRD data strongly support the formation of crystalline Ag and Cu₂O phases within the core–shell nanoparticles.

STEM-EDX data were collected to determine the elemental composition and atomic distribution in the Ag@Cu₂O coreshell NPs. The data presented in Figure 4 are consistent with the XPS findings and further confirm the presence and uniform distribution of Ag, Cu, and O elements within the synthesized Ag@Cu₂O core-shell nanostructure. In addition to the STEM-EDX elemental mapping, an EDX line spectrum was also obtained to support the mapping data, as shown in Figure S5.

Optical Properties. Extinction spectra of bare Ag NPs and Ag@Cu₂O core-shell NPs with five different shell thicknesses were recorded using UV-vis spectroscopy (Figure 5). For reference, the extinction spectra of bare Cu₂O nanoparticles are presented in Figure S6. The Ag NPs displayed a strong LSPR peak at the violet end of the visible spectrum (~405 nm). Consequently, extending absorption into the visible and near-infrared (NIR) regions of the solar spectrum is essential for the broader applications of Ag NPs in photocatalysis and other photorelated applications. Notably, all the Ag@Cu2O core-shell NPs demonstrated a red-shift in the range from 405 to 500 nm. Specifically, as the Cu₂O shell thickness increases, the LSPR peak of the Ag core shifts further toward the red end of the spectrum from its initial position at 405 nm. This redshift can be attributed to changes in the dielectric environment surrounding the plasmonic Ag core as Cu₂O shells thicken.¹⁹ Importantly, by varying the amount of Ag nanoparticle stock solution used in the synthesis, the shell thickness and consequently, the extinction peak position of the Ag@Cu₂O core-shell NPs can be controlled. When the Cu₂O shell is thin (<20 nm), the LSPR peak exhibits more significant red-shifts 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.⁴⁵ In addition, the red-shift observed when coating a semiconducting shell on plasmonic core



Figure 3. (a) Full survey XPS spectrum of Ag@Cu₂O core-shell NPs and high-resolution spectra of (b) Cu 2p and (c) O 1s.



Figure 4. (a) STEM image and STEM-EDX elemental mapping for (b) Cu, (c) O, and (d) Ag in Ag@Cu₂O core-shell NPs.



Figure 5. Extinction spectra of bare Ag NPs and $Ag@Cu_2O$ core-shell NPs having various shell thicknesses.

nanoparticles has been consistently reported in numerous studies.^{38,46} This phenomenon is typically explained by the high refractive index (usually >2) of the semiconducting shell, compared to the refractive index of water, which is around 1.333. As demonstrated herein, this tunability of the extinction peak makes the Ag@Cu₂O core—shell NPs optically active within the visible region of the solar spectrum, where the majority of solar energy is concentrated. This capability is particularly significant for photocatalytic applications, where sunlight is the only energy source driving the reactions.

Consistent with our observations, a study by Wang's group on Au@Cu2O nanoparticles with tunable shell thicknesses also reported a shift of the LSPR to the NIR region as the shell thickness increased, without saturating at a specific wavelength.⁴⁷ For a densely packed, single-crystal shell, the shape of the extinction spectra and the frequency of plasmonic absorption are primarily determined by the shell thickness. In contrast, for a polycrystalline shell, both the shell thickness and its porosity (packing density) influence the plasmonic absorption of the nanoparticles. A more porous shell leads to a decrease in the effective permittivity of the cuprous shell, giving a plasmonic resonance shift over a narrower spectral range. According to calculations presented in Wang's work, a shell with a low packing density (likely below 50%) would saturate the LSPR peak at a specific wavelength as the shell thickness increases. Based on the structural analysis of our sample, the cuprous shell is polycrystalline in nature, consisting of a collection of multiple tiny crystals. We anticipate that while all of the Cu₂O shells exhibit variations in thickness, they likely have similar packing densities due to comparable levels

of crystallinity. Importantly, we believe that the porosity of the cuprous shell is advantageous for photocatalysis, as it increases the surface area available for driving redox reactions.

When a semiconductor photocatalyst absorbs solar radiation of a suitable wavelength, it generates free electrons and corresponding holes that can participate in catalytic activities.⁴⁸ Therefore, electron-hole recombination in metal oxide nanoparticles is undesirable as it reduces photocatalytic efficiency.⁴⁹ The return of an electron from the excited state in the conduction band to recombine with the positive hole in the valence band gives rise to the emission of a photon. This photon emission, which produces a PL signal, indicates the recombination rate of electron-hole pairs in semiconductors.⁵⁰ For this reason, PL spectroscopy was employed to evaluate the influence of the plasmonic core on the electronhole recombination rate of Cu₂O NPs. The intensities were normalized based on the nanoparticle concentration and Cu₂O volume in the respective samples to minimize any analytical discrepancies due to differences in concentration and volume. As seen in Figure 6, the presence of the Ag core significantly



Figure 6. Photoluminescence spectra of spherical Cu₂O NPs and Ag@Cu₂O core-shell NPs having various shell thicknesses.

reduces the PL signal from the Cu₂O shell, with an average suppression of ~ 59% compared to bare Cu₂O NPs. This substantial reduction in PL intensity suggests that the plasmonic Ag core effectively decreases the electron-hole recombination rate by trapping charge carriers within the metallic core.⁵¹ PL measurements for Ag@Cu₂O NPs at various shell thicknesses also showed consistent signal reductions when normalized for their respective concentrations and Cu₂O volumes. Variations in the heights of the normalized



Figure 7. Photocatalytic evolution rates of Cu_2O and $Ag@Cu_2O$ NPs (a) before and (b) after normalization with the Cu_2O volume in the nanoparticles.

Table 1	. Selected	Examples	of Photocatal	ytic Hy	ydrogen	Evolution	Using	Doped	l or Com	posite l	Photocataly	ysts

entry	material	structure	reaction environment	light source power (W) (type, wavelength)	rate of H ₂ evolution $(\mu mol/g_{cat}/h)$	ref
1	TiO_2 - Ti_3C_2 /Ru-20	nanocomposite	MeOH 10 v%	300 (Xe lamp, 350–780 nm)	235	60
2	Pt/Zn _{0.75} Cd _{0.25} Se	particles	MeOH 10 v%	300 (Xe lamp, 420–800 nm)	95	61
3	Au-La2Ti2O2	nanosteps	MeOH 20 v%	300 (Xe lamp, AM 1.5G)	340	62
4	CdS@mZnS	nanorods	Na ₂ S 0.25 M, Na ₂ SO ₃ 0.35 M	300 (Xe lamp, 422–740 nm)	820	63
5	$Cu_2Sn_{0.38}Ge_{0.62}S_3$	powder	Na ₂ S, Na ₂ SO ₃ 10 mM	300 (Xe lamp, AM 1.5G)	~52	64
6	Sr _{1.8} La _{0.2} TiO _{4-y} N _y	powder	Na ₂ SO ₃ 0.05 M	300 (Xe lamp, 400–780 nm)	160	65
7	$Cu/TiO_2 @Ti_3 C_2 T_x$	2D sheets	MeOH ~7 v%	300 (Xe lamp, not provided)	860	66
8	$Pt-Pb_2Ti_2O_{5.4}F_{1.2}$	powder	MeCN:TEOA:H ₂ O (130:10:1)	300 (Xe lamp, ~ 440 nm)	~14	67
9	$SrTiO_{3-\delta}$	powder	MeOH 10 v%	300 (Xe lamp, > 300 nm)	~40	68
10	Ag@Cu ₂ O	core-shell nanoparticle	EG 10 v%	14.4 (LED, ~ 460 nm)	635	this work
11	C ₃ N ₄ -Pd-Cu ₂ O	stack nanostructure	TEOA 10 v%	300 (Xe lamp, 400–780 nm)	~33	56
12	Au NBP@Cu ₂ O	yolk-shell composite	H ₂ O	300 (Xe lamp, > 400 nm)	~5	57
13	$Zn/Cu_2O@C$	coated nanoparticle	HL 15 v%	300 (Xe lamp, AM 1.5G)	~26	58
14	Cu ₂ O/Cu ₂ Se	multilayer nanowires	MeOH 10 v%	300 (Xe lamp, > 420 nm)	~29	59

intensity peaks can be attributed to slight differences in nanoparticle size and experimental errors during measurements. The highly suppressed recombination rate, coupled with the tunability of the extinction peak, could significantly enhance the applicability of Ag@Cu₂O core–shell NPs in photocatalysis, such as hydrogen evolution (see below), toxic chemical degradation, and other applications in photovoltaics, biochemical sensing, and electronics.⁷

Photocatalytic Hydrogen Evolution Performance. Cu_2O , a p-type semiconductor, is a widely studied catalytic material for hydrogen evolution due to its favorable band-edge positions for water splitting and a suitable bandgap of approximately 2 eV, enabling the absorption of a significant portion of the solar spectrum.^{35,44} When a p-type semiconductor comes into contact with a protic liquid that contains a redox species, the alignment of the semiconductor Fermi level, which is close to the valence band, induces upward band bending.⁵² This band bending facilitates charge separation at the interface, promoting the injection of electrons (minority carriers) from the bulk of the semiconductor to the

semiconductor-liquid interface, thereby driving the reduction of protons (H^+) to hydrogen (H_2) . For Cu₂O, the reduction potential (Cu₂O/Cu) and the oxidation potential (CuO/ Cu₂O) lie within the bandgap.⁵³ Consequently, photogenerated electrons and holes can reduce or oxidize Cu₂O, leading to photocorrosion, which degrades the material and produces slow hydrogen evolution rates. In our system, the conductive Ag core can trap the unwanted electrons. Holes created after excitation can also combine with electrons in the conductive Ag core. The electrons at the interface can be efficiently separated to drive the hydrogen evolution reaction. Here, ethylene glycol is used as a sacrificial agent to complete the redox reaction. In some studies, ethylene glycol has been demonstrated to be an effective sacrificial agent that enhances photocatalytic activity.^{54,55} Combining with porous shell and enhanced plasmonic absorption, we anticipated that the Ag@ Cu₂O nanoparticles would outperform pristine Cu₂O nanoparticles in terms of both photocatalytic activity and stability.

HER studies utilizing $Ag@Cu_2O$ and Cu_2O NPs were monitored using gas chromatography equipped with a thermal conductivity detector as shown in Figure S7. Ag@Cu₂O nanoparticles with average shell thickness of 17 ± 2 nm were employed as catalysts to optimize light from the 460 nm LED light source that was used. The results demonstrated a significant enhancement in the hydrogen evolution rate per mass unit of photocatalyst, with the presence of the plasmonic nanoparticles (Figure 7a). The combination of the Ag core with Cu₂O shell increased the hydrogen evolution rate more than 6-fold to ~ 635 μ mol/g_{cat}/h, up from ~ 102 μ mol/g_{cat}/h observed with Cu₂O NPs. This faster rate can be attributed to plasmonically induced electron injection²⁰ and energy transfer²¹ occurring when the composite photocatalyst was illuminated by electromagnetic radiation at an optimized wavelength. Notably, the Ag@Cu₂O core-shell photocatalyst in this work showed a faster hydrogen evolution rate compared to most recently reported systems (see Table 1), highlighting the synergistic strength of plasmonic-semiconductor hybrid nanostructure in photocatalytic hydrogen generation. Among these examples, only CdS@mZnS nanorods (Table 1, entry 4) and $Cu/TiO_2@Ti_3C_2T_x$ nanosheets (entry 7) showed higher H₂ evolution rates than our Ag@Cu₂O core-shell NPs with 820 and 860 μ mol/g_{cat}/h, respectively. However, the relatively simple Ag@Cu₂O NPs in this work, with a rate of 635 μ mol/ g_{cat}/h , can be synthesized under milder conditions (lower temperature, shorter time, fewer chemicals and steps, noninert gas environment, and less hazardous chemicals) compared to both CdS@mZnS nanorods and Cu/TiO2@Ti3C2Tx nanosheets, making them more suitable for large-scale applications. Additionally, the light source used in this work consumes significantly less power (14.4 W) than those used in other systems (300 W) to achieve the reported evolution rates. Focusing more narrowly on Cu₂O-based photocatalysis, our Ag@Cu₂O catalysts also outperform some recent works (Table 1, entries 11 to 14). These include the C_3N_4 -Pd-Cu₂O stack nanostructures with ~ 33 μ mol/g_{cat}/h reported by Yin et al.,⁵⁶ the Au NBP@Cu₂O yolk-shell composites with ~ 5 μ mol/ g_{cat}/h reported by Ma et al.,⁵⁷ the Zn/Cu₂O@C coated NPs with ~ 26 μ mol/g_{cat}/h reported by Yuan et al.,⁵⁸ and the Cu_2O/Cu_2Se multilayer nanowires with ~ 29 μ mol/g_{cat}/h reported by Liu et al.⁵⁹ The good performance of the Ag@ Cu_2O catalysts can be attributed to (1) the advantages of coupling plasmonic and porous Cu_2O nanostructures, (2) the utilization of an appropriate light source, and (3) the use of suitable reaction environments. Although no direct comparisons can be made from Table 1 due to differences in testing conditions, the results hold promise for designing even more efficient Cu₂O-based photocatalysts for hydrogen evolution as a clean energy source.

To evaluate the influence of the plasmonic core on Cu₂O, the hydrogen evolution rates were normalized with the Cu₂O volume in the nanoparticles. The results indicated that per unit volume of Cu₂O, the hydrogen evolution rate increased significantly from $1.59 \times 10^{-6} \text{ mmol/g}_{cat}/\text{nm}^3$ to $14.58 \times 10^{-6} \text{ mmol/g}_{cat}/\text{nm}^3$ (more than 9-fold) by incorporating with Ag NPs (Figure 7b). This analysis was enabled by the high uniformity of the core–shell nanoparticles afforded by the synthesis method. To our current knowledge, this is the first study to evaluate this particular aspect of performance photocatalytic nanostructures. The substantial increases in evolution rate increases discussed above can also be attributed to the marked reduction in the electron–hole recombination rate, which is a major challenge for photocatalytic hydrogen generation with semiconductor materials.^{39,69} Furthermore, the recyclability of the photocatalysts was evaluated by washing them after each hydrogen evolution reaction (HER) and reusing them in subsequent tests under identical HER conditions. The results presented in Figure 8



Figure 8. Photocatalytic hydrogen evolution of Ag@Cu₂O and Cu₂O NPs over 3 consecutive cycles.

indicate that the hydrogen evolution rate for Cu₂O nanoparticles decreased by ~ 66% (from 102 to 35 μ mol/g_{cat}/h) after three cycles, while the rate for Ag@Cu₂O nanoparticles decreased by ~ 45% (from 635 to 348 μ mol/g_{cat}/h). The reduced degradation of Cu₂O in the presence of the Ag core can be attributed to the metallic core acting as a charge carrier scavenger,⁵⁶ which inhibits the movement of charge carriers and thus reduces the photocorrosion of Cu⁺ ions. Although the degradation of the photocatalyst remains significant, the observed 21% reduction in degradation is a promising result. Further research efforts to enhance the stability of Cu₂O-based photocatalyst are currently underway in our lab.

CONCLUSIONS

Ag@Cu₂O core-shell NPs with controllable Cu₂O shell thicknesses were successfully synthesized alongside bare Ag and Cu₂O NPs using convenient procedures under mild conditions. These nanoparticles were characterized using various techniques to verify their size, structural, morphological characteristics, as well as their elemental compositions and distributions. All synthesized core-shell nanoparticles exhibited strong LSPR peaks in the visible region. More importantly, optical studies demonstrated the ability to tune the red-shift of the LSPR position into the intense part of the solar spectrum by systematically adjusting the Cu₂O shell thickness. PL measurements indicated that the plasmonic Ag cores in the Ag@Cu2O core-shell NPs significantly suppressed the electron-hole recombination rate compared to bare Cu₂O NPs. Photocatalytic hydrogen evolution studies revealed more than a 6-fold increase in the evolution rate with the incorporation of the Ag core into the photocatalyst. Additionally, the degradation rate of Cu2O was reduced through the coupling with Ag cores, thus enhancing the stability of Cu₂O NPs. Despite many significant enhancements and several remaining challenges, it should be noted that the synthesis method in this work was quicker and less demanding,

facilitating easier scale-up applications for the hybrid photocatalyst. The use of abundant elements also enhances the applicability of the $Ag@Cu_2O$ core-shell NPs. Moreover, these results pave the way for combining a wide range of plasmonic and semiconductor materials beyond Ag and Cu_2O in nanostructures for improved photocatalytic activity and optoelectronic applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.5c00412.

Low-magnification TEM images and shell thickness histograms of the $Ag@Cu_2O$ core-shell nanoparticles (Figure S1), SEM of Cu_2O NPs (Figure S2), dynamic light scattering of Cu_2O NPs (Figure S3), XRD pattern (Figure S4) of Cu_2O NPs, STEM-EDX elemental line scan (Figure S5) of $Ag@Cu_2O$ core-shell nanoparticles, UV-vis diffuse reflectance spectrum of Cu_2O NPs (Figure S6), and gas chromatographs of photocatalytic hydrogen evolution tests (Figure S7) (PDF)

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

MeOH methanol MeCN acetonitrile TEOA triethanolamine

EG ethylene glycol

HL 2-hydroxypropanoic acid

REFERENCES

(1) Luo, J.; Zhang, S.; Sun, M.; Yang, L.; Luo, S.; Crittenden, J. C. A Critical Review on Energy Conversion and Environmental Remediation of Photocatalysts with Remodeling Crystal Lattice, Surface, and Interface. *ACS Nano* **2019**, *13*, 9811–9840.

(2) Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, *238*, 37–38.

(3) Wang, L.; Zhao, J.; Liu, H.; Huang, J. Design, Modification and Application of Semiconductor Photocatalysts. *J. Taiwan Inst. Chem. Eng.* **2018**, 93, 590–602.

(4) Wang, Q.; Domen, K. Particulate Photocatalysts for Light-Driven Water Splitting: Mechanisms, Challenges, and Design Strategies. *Chem. Rev.* **2020**, *120*, 919–985.

(5) Yang, X.; Wang, D. Photocatalysis: From Fundamental Principles to Materials and Applications. ACS Appl. Energy Mater. 2018, 1, 6657-6693.

(6) Dette, C.; Pérez-Osorio, M. A.; Kley, C. S.; Punke, P.; Patrick, C. E.; Jacobson, P.; Giustino, F.; Jung, S. J.; Kern, K. TiO₂ Anatase with a Bandgap in the Visible Region. *Nano Lett.* **2014**, *14*, 6533–6538.

(7) Medhi, R.; Marquez, M. D.; Lee, T. R. Visible-Light-Active Doped Metal Oxide Nanoparticles: Review of Their Synthesis, Properties, and Applications. *ACS Appl. Nano Mater.* **2020**, *3*, 6156–6185.

(8) Cherevan, A. S.; Deilmann, L.; Weller, T.; Eder, D.; Marschall, R. Mesoporous Semiconductors: A New Model To Assess Accessible Surface Area and Increased Photocatalytic Activity? *ACS Appl. Energy Mater.* **2018**, *1*, 5787–5799.

(9) Ahmed, T.; Edvinsson, T. Optical Quantum Confinement in Ultrasmall ZnO and the Effect of Size on Their Photocatalytic Activity. J. Phys. Chem. C 2020, 124, 6395–6404.

(10) Willets, K. A.; Wilson, A. J.; Sundaresan, V.; Joshi, P. B. Super-Resolution Imaging and Plasmonics. *Chem. Rev.* 2017, *117*, 7538– 7582.

(11) Ha, M.; Kim, J.-H.; You, M.; Li, Q.; Fan, C.; Nam, J.-M. Multicomponent Plasmonic Nanoparticles: From Heterostructured Nanoparticles to Colloidal Composite Nanostructures. *Chem. Rev.* **2019**, *119*, 12208–12278.

(12) Zheng, J.; Cheng, X.; Zhang, H.; Bai, X.; Ai, R.; Shao, L.; Wang, J. Gold Nanorods: The Most Versatile Plasmonic Nanoparticles. *Chem. Rev.* **2021**, *121*, 13342–13453.

(13) Ngo, N. M.; Tran, H.-V.; Lee, T. R. Plasmonic Nanostars: Systematic Review of Their Synthesis and Applications. *ACS Appl. Nano Mater.* **2022**, *5*, 14051–14091.

(14) Lin, X.; Lin, S.; Liu, Y.; Gao, M.; Zhao, H.; Liu, B.; Hasi, W.; Wang, L. Facile Synthesis of Monodisperse Silver Nanospheres in Aqueous Solution via Seed-Mediated Growth Coupled with Oxidative Etching. *Langmuir* **2018**, *34*, 6077–6084.

(15) Ziegler, C.; Eychmüller, A. Seeded Growth Synthesis of Uniform Gold Nanoparticles with Diameters of 15–300 Nm. J. Phys. Chem. C 2011, 115, 4502–4506.

(16) Rohner, C.; Pekkari, A.; Härelind, H.; Moth-Poulsen, K. Synthesis of Cu Nanoparticles: Stability and Conversion into Cu_2S Nanoparticles by Decomposition of Alkanethiolate. *Langmuir* **2017**, 33, 13272–13276.

(17) Mantri, Y.; Jokerst, J. V. Engineering Plasmonic Nanoparticles for Enhanced Photoacoustic Imaging. *ACS Nano* **2020**, *14*, 9408–9422.

(18) Henry, A.-I.; Bingham, J. M.; Ringe, E.; Marks, L. D.; Schatz, G. C.; Van Duyne, R. P. Correlated Structure and Optical Property Studies of Plasmonic Nanoparticles. *J. Phys. Chem. C* 2011, *115*, 9291–9305.

(19) Mahmoud, M. A.; Chamanzar, M.; Adibi, A.; El-Sayed, M. A. Effect of the Dielectric Constant of the Surrounding Medium and the Substrate on the Surface Plasmon Resonance Spectrum and

Sensitivity Factors of Highly Symmetric Systems: Silver Nanocubes. J. Am. Chem. Soc. 2012, 134, 6434–6442.

(20) Chaffin, E. A.; Bhana, S.; O'Connor, R. T.; Huang, X.; Wang, Y. Impact of Core Dielectric Properties on the Localized Surface Plasmonic Spectra of Gold-Coated Magnetic Core–Shell Nano-particles. J. Phys. Chem. B 2014, 118, 14076–14084.

(21) Sistani, M.; Bartmann, M. G.; Güsken, N. A.; Oulton, R. F.; Keshmiri, H.; Luong, M. A.; Momtaz, Z. S.; Den Hertog, M. I.; Lugstein, A. Plasmon-Driven Hot Electron Transfer at Atomically Sharp Metal–Semiconductor Nanojunctions. *ACS Photonics* **2020**, *7*, 1642–1648.

(22) Ma, X.-C.; Dai, Y.; Yu, L.; Huang, B.-B. Energy Transfer in Plasmonic Photocatalytic Composites. *Light: Sci. Appl.* **2016**, *5*, No. e16017.

(23) Yuan, L.; Lou, M.; Clark, B. D.; Lou, M.; Zhou, L.; Tian, S.; Jacobson, C. R.; Nordlander, P.; Halas, N. J. Morphology-Dependent Reactivity of a Plasmonic Photocatalyst. *ACS Nano* **2020**, *14*, 12054–12063.

(24) Wang, S.; Gao, Y.; Miao, S.; Liu, T.; Mu, L.; Li, R.; Fan, F.; Li, C. Positioning the Water Oxidation Reaction Sites in Plasmonic Photocatalysts. *J. Am. Chem. Soc.* **2017**, *139*, 11771–11778.

(25) Ha, H. D.; Yan, C.; Katsoukis, G.; Kamat, G. A.; Moreno-Hernandez, I. A.; Frei, H.; Alivisatos, A. P. Precise Colloidal Plasmonic Photocatalysts Constructed by Multistep Photodepositions. *Nano Lett.* **2020**, *20*, 8661–8667.

(26) Hong, J. W.; Wi, D. H.; Lee, S.-U.; Han, S. W. Metal– Semiconductor Heteronanocrystals with Desired Configurations for Plasmonic Photocatalysis. *J. Am. Chem. Soc.* **2016**, *138*, 15766–15773. (27) Cushing, S. K.; Li, J.; Bright, J.; Yost, B. T.; Zheng, P.; Bristow,

A. D.; Wu, N. Controlling Plasmon-Induced Resonance Energy Transfer and Hot Electron Injection Processes in Metal@TiO₂ Core– Shell Nanoparticles. J. Phys. Chem. C 2015, 119, 16239–16244.

(28) Li, G.; Cherqui, C.; Bigelow, N. W.; Duscher, G.; Straney, P. J.; Millstone, J. E.; Masiello, D. J.; Camden, J. P. Spatially Mapping Energy Transfer from Single Plasmonic Particles to Semiconductor Substrates via STEM/EELS. *Nano Lett.* **2015**, *15*, 3465–3471.

(29) Sun, M.; Fu, X.; Chen, K.; Wang, H. Dual-Plasmonic Gold@ Copper Sulfide Core-Shell Nanoparticles: Phase-Selective Synthesis and Multimodal Photothermal and Photocatalytic Behaviors. *ACS Appl. Mater. Interfaces* **2020**, *12*, 46146–46161.

(30) Kołątaj, K.; Krajczewski, J.; Kudelski, A. Plasmonic Nanoparticles for Environmental Analysis. *Environ. Chem. Lett.* **2020**, *18*, 529–542.

(31) Zhang, X.-F.; Liu, Z.-G.; Shen, W.; Gurunathan, S. Silver Nanoparticles: Synthesis, Characterization, Properties, Applications, and Therapeutic Approaches. *Int. J. Mol. Sci.* **2016**, *17*, 1534.

(32) Jiang, Y.; Xia, T.; Shen, L.; Ma, J.; Ma, H.; Sun, T.; Lv, F.; Zhu, N. Facet-Dependent Cu₂O Electrocatalysis for Wearable Enzyme-Free Smart Sensing. *ACS Catal.* **2021**, *11*, 2949–2955.

(33) Izaki, M.; Fukazawa, K.; Sato, K.; Khoo, P. L.; Kobayashi, M.; Takeuchi, A.; Uesugi, K. Defect Structure and Photovoltaic Characteristics of Internally Stacked CuO/Cu₂O Photoactive Layer Prepared by Electrodeposition and Heating. *ACS Appl. Energy Mater.* **2019**, *2*, 4833–4840.

(34) Napari, M.; Huq, T. N.; Meeth, D. J.; Heikkilä, M. J.; Niang, K. M.; Wang, H.; Iivonen, T.; Wang, H.; Leskelä, M.; Ritala, M.; Flewitt, A. J.; Hoye, R. L. Z.; MacManus-Driscoll, J. L. Role of ALD Al₂O₃ Surface Passivation on the Performance of p-Type Cu₂O Thin Film Transistors. *ACS Appl. Mater. Interfaces* **2021**, *13*, 4156–4164.

(35) Luo, J.; Steier, L.; Son, M.-K.; Schreier, M.; Mayer, M. T.; Grätzel, M. Cu₂O Nanowire Photocathodes for Efficient and Durable Solar Water Splitting. *Nano Lett.* **2016**, *16*, 1848–1857.

(36) Wong, T. K. S.; Zhuk, S.; Masudy-Panah, S.; Dalapati, G. K. Current Status and Future Prospects of Copper Oxide Heterojunction Solar Cells. *Materials* **2016**, *9*, 271.

(37) Dasineh Khiavi, N.; Katal, R.; Kholghi Eshkalak, S.; Masudy-Panah, S.; Ramakrishna, S.; Jiangyong, H. Visible Light Driven Heterojunction Photocatalyst of $CuO-Cu_2O$ Thin Films for

Photocatalytic Degradation of Organic Pollutants. *Nanomaterials* **2019**, *9*, 1011.

(38) Medhi, R.; Li, C.-H.; Lee, S. H.; Srinoi, P.; Marquez, M. D.; Robles-Hernandez, F.; Jacobson, A. J.; Lee, T.-C.; Lee, T. R. Antimony- and Zinc-Doped Tin Oxide Shells Coated on Gold Nanoparticles and Gold–Silver Nanoshells Having Tunable Extinctions for Sensing and Photonic Applications. *ACS Appl. Nano Mater.* **2020**, *3*, 8958–8971.

(39) Collado, L.; Reynal, A.; Fresno, F.; Barawi, M.; Escudero, C.; Perez-Dieste, V.; Coronado, J. M.; Serrano, D. P.; Durrant, J. R.; de la Peña O'Shea, V. A. Unravelling the Effect of Charge Dynamics at the Plasmonic Metal/Semiconductor Interface for CO₂ Photoreduction. *Nat. Commun.* **2018**, *9*, 4986.

(40) Lee, C.; Shin, K.; Lee, Y. J.; Jung, C.; Lee, H. M. Effects of Shell Thickness on Ag-Cu₂O Core-Shell Nanoparticles with Bumpy Structures for Enhancing Photocatalytic Activity and Stability. *Catal. Today* **2018**, 303, 313–319.

(41) Karle, A.; Deepa, E.; Kapur, I.; Therese, H. A. An Investigation on the Synergistic Effect of Cu_2O -Ag Nanoparticle on Its Bactericidal and Anticancerous Properties. *Mater. Res. Express* **2020**, *7*, 015410.

(42) Li, J.; Cushing, S. K.; Bright, J.; Meng, F.; Senty, T. R.; Zheng, P.; Bristow, A. D.; Wu, N. Ag@Cu₂O Core-Shell Nanoparticles as Visible-Light Plasmonic Photocatalysts. *ACS Catal.* **2013**, *3*, 47–51.

(43) Chen, L.; Sun, H.; Zhao, Y.; Zhang, Y.; Wang, Y.; Liu, Y.; Zhang, X.; Jiang, Y.; Hua, Z.; Yang, J. Plasmonic-Induced SERS Enhancement of Shell-Dependent Ag@Cu₂O Core–Shell Nano-particles. *RSC Adv.* 2017, 7, 16553–16560.

(44) Pan, L.; Kim, J. H.; Mayer, M. T.; Son, M.-K.; Ummadisingu, A.; Lee, J. S.; Hagfeldt, A.; Luo, J.; Grätzel, M. Boosting the Performance of Cu_2O Photocathodes for Unassisted Solar Water Splitting Devices. *Nat. Catal.* **2018**, *1*, 412–420.

(45) Haes, A. J.; Zou, S.; Schatz, G. C.; Van Duyne, R. P. Nanoscale Optical Biosensor: Short Range Distance Dependence of the Localized Surface Plasmon Resonance of Noble Metal Nanoparticles. *J. Phys. Chem. B* **2004**, *108*, 6961–6968.

(46) Oldfield, G.; Ung, T.; Mulvaney, P. Au@SnO₂ Core-Shell Nanocapacitors. *Adv. Mater.* **2000**, *12*, 1519–1522.

(47) Zhang, L.; Jing, H.; Boisvert, G.; He, J. Z.; Wang, H. Geometry Control and Optical Tunability of Metal–Cuprous Oxide Core–Shell Nanoparticles. *ACS Nano* **2012**, *6*, 3514–3527.

(48) Serpone, N.; Emeline, A. V. Semiconductor Photocatalysis — Past, Present, and Future Outlook. *J. Phys. Chem. Lett.* **2012**, *3*, 673–677.

(49) Paramanik, L.; Reddy, K. H.; Sultana, S.; Parida, K. Architecture of Biperovskite-Based $LaCrO_3/PbTiO_3 p-n$ Heterojunction with a Strong Interface for Enhanced Charge Anti-Recombination Process and Visible Light-Induced Photocatalytic Reactions. *Inorg. Chem.* **2018**, *57*, 15133–15148.

(50) Ma, S.; Zhang, Z.; Harrison, I. Photoreduction of Hydrogen Cations on TiO_2 and Its Impact on Surface Band Bending and the Charge Carrier Recombination Rate: A Photoluminescence Study under High Vacuum Conditions. *J. Phys. Chem. C* **2018**, *122*, 8288–8294.

(51) Park, J. H.; Choi, Y.-R.; Chin, B. D. Charge Carrier Trapping and Enhanced Electroluminescent Efficiency of Blue Light Emitting Polymer with Gold Nanoparticles. *J. Nanosci. Nanotechnol.* **2009**, *9*, 7451–7455.

(52) Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q.; Santori, E. A.; Lewis, N. S. Solar Water Splitting Cells. *Chem. Rev.* **2010**, *110*, 6446–6473.

(53) Le, H. V.; Le, T. L.; Thuy, U. T. D.; Tran, P. D. Current Perspectives in Engineering of Viable Hybrid Photocathodes for Solar Hydrogen Generation. *Adv. Nat. Sci.: Nanosci. Nanotechnol.* **2018**, *9*, 023001.

(54) Wang, M.; Shen, S.; Li, L.; Tang, Z.; Yang, J. Effects of Sacrificial Reagents on Photocatalytic Hydrogen Evolution over Different Photocatalysts. J. Mater. Sci. 2017, 52, 5155–5164.

(55) Li, F.; Gu, Q.; Niu, Y.; Wang, R.; Tong, Y.; Zhu, S.; Zhang, H.; Zhang, Z.; Wang, X. Hydrogen Evolution from Aqueous-Phase

Photocatalytic Reforming of Ethylene Glycol over Pt/TiO₂ Catalysts: Role of Pt and Product Distribution. *Appl. Surf. Sci.* **2017**, *391*, 251–258.

(56) Yin, W.; Bai, L.; Zhu, Y.; Zhong, S.; Zhao, L.; Li, Z.; Bai, S. Embedding Metal in the Interface of a P-n Heterojunction with a Stack Design for Superior Z-Scheme Photocatalytic Hydrogen Evolution. *ACS Appl. Mater. Interfaces* **2016**, *8*, 23133–23142.

(57) Ma, Y.; Liu, X.; Wei, X.; Le, J.; Fu, Y.; Han, Q.; Ji, H.; Yang, Z.; Wu, H. Yolk-Shelled Gold@Cuprous Oxide Nanostructures with Hot Carriers Boosting Photocatalytic Performance. *Langmuir* **2021**, *37*, 4578–4586.

(58) Yuan, Y.; Sun, L.; Gao, H.; Mo, S.; Xu, T.; Yang, L.; Zhan, W.-W. Engineering a Highly Improved Porous Photocatalyst Based on Cu_2O by a Synergistic Effect of Cation Doping of Zn and Carbon Layer Coating. *Inorg. Chem.* **2020**, *59*, 16010–16015.

(59) Liu, B.; Ning, L.; Zhang, C.; Zheng, H.; Liu, S. F.; Yang, H. Enhanced Visible-Light Photocatalytic H_2 Evolution in Cu_2O/Cu_2Se Multilayer Heterostructure Nanowires Having {111} Facets and Physical Mechanism. *Inorg. Chem.* **2018**, *57*, 8019–8027.

(60) Liu, Y.; Li, Y.-H.; Li, X.; Zhang, Q.; Yu, H.; Peng, X.; Peng, F. Regulating Electron–Hole Separation to Promote Photocatalytic H_2 Evolution Activity of Nanoconfined Ru/MXene/TiO₂ Catalysts. ACS Nano **2020**, 14, 14181–14189.

(61) Kageshima, Y.; Gomyo, Y.; Matsuoka, H.; Inuzuka, H.; Suzuki, H.; Abe, R.; Teshima, K.; Domen, K.; Nishikiori, H. Z-Scheme Overall Water Splitting Using $Zn_xCd_{1-x}Se$ Particles Coated with Metal Cyanoferrates as Hydrogen Evolution Photocatalysts. *ACS Catal.* **2021**, *11*, 8004–8014.

(62) Cai, X.; Zhu, M.; Elbanna, O. A.; Fujitsuka, M.; Kim, S.; Mao, L.; Zhang, J.; Majima, T. Au Nanorod Photosensitized $La_2Ti_2O_7$ Nanosteps: Successive Surface Heterojunctions Boosting Visible to Near-Infrared Photocatalytic H₂ Evolution. *ACS Catal.* **2018**, *8*, 122–131.

(63) Lian, Z.; Sakamoto, M.; Kobayashi, Y.; Tamai, N.; Ma, J.; Sakurai, T.; Seki, S.; Nakagawa, T.; Lai, M.-W.; Haruta, M.; Kurata, H.; Teranishi, T. Anomalous Photoinduced Hole Transport in Type I Core/Mesoporous-Shell Nanocrystals for Efficient Photocatalytic H₂ Evolution. *ACS Nano* **2019**, *13*, 8356–8363.

(64) Kageshima, Y.; Shiga, S.; Ode, T.; Takagi, F.; Shiiba, H.; Htay, M. T.; Hashimoto, Y.; Teshima, K.; Domen, K.; Nishikiori, H. Photocatalytic and Photoelectrochemical Hydrogen Evolution from Water over $Cu_2Sn_xGe_{1-x}S_3$ Particles. *J. Am. Chem. Soc.* **2021**, *143*, 5698–5708.

(65) Sun, X.; Mi, Y.; Jiao, F.; Xu, X. Activating Layered Perovskite Compound Sr_2TiO_4 via La/N Codoping for Visible Light Photocatalytic Water Splitting. *ACS Catal.* **2018**, *8*, 3209–3221.

(66) Peng, C.; Wei, P.; Li, X.; Liu, Y.; Cao, Y.; Wang, H.; Yu, H.; Peng, F.; Zhang, L.; Zhang, B.; Lv, K. High Efficiency Photocatalytic Hydrogen Production over Ternary Cu/TiO₂@Ti₃C₂T_x Enabled by Low-Work-Function 2D Titanium Carbide. *Nano Energy* **2018**, *53*, 97–107.

(67) Kuriki, R.; Ichibha, T.; Hongo, K.; Lu, D.; Maezono, R.; Kageyama, H.; Ishitani, O.; Oka, K.; Maeda, K. A Stable, Narrow-Gap Oxyfluoride Photocatalyst for Visible-Light Hydrogen Evolution and Carbon Dioxide Reduction. J. Am. Chem. Soc. **2018**, 140, 6648–6655. (68) Nishioka, S.; Hyodo, J.; Vequizo, J. J. M.; Yamashita, S.; Kumagai, H.; Kimoto, K.; Yamakata, A.; Yamazaki, Y.; Maeda, K. Homogeneous Electron Doping into Nonstoichiometric Strontium Titanate Improves Its Photocatalytic Activity for Hydrogen and Oxygen Evolution. ACS Catal. **2018**, *8*, 7190–7200.

(69) Zhao, J.; Zhang, P.; Wang, Z.; Zhang, S.; Gao, H.; Hu, J.; Shao, G. Direct Evidence of Multichannel-Improved Charge-Carrier Mechanism for Enhanced Photocatalytic H₂ Evolution. *Sci. Rep.* **2017**, *7*, 16116.