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Facile synthesis of highly efficient one-dimensional plasmonic photocatalysts through Ag@Cu₂O core-shell heteronanowires

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Abstract

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Keywords

ag, photocatalysts, plasmonic, dimensional, one, efficient, highly, shell, synthesis, facile, heteronanowires, cu₂o, core

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Facile synthesis of highly efficient one-dimensional plasmonic photocatalysts through Ag@Cu₂O core-shell hetero-nanowires

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Abstract

A novel class of one-dimensional (1D) plasmonic Ag@Cu₂O core-shell hetero-nanowires have been synthesized at room temperature for photocatalysis application. The morphology, size, crystal structure and composition of the products were investigated by XRD, SEM, TEM, XPS, and UV-VIS instruments. It was found the reaction time and the amount of Ag nanowires play crucial roles in the formation of well-defined 1D Ag@Cu₂O core-shell hetero-nanowires. The resultant 1D Ag@Cu₂O NWs exhibit much higher photocatalytic activity towards degradation of organic contaminants than Ag@Cu₂O core-shell nanoparticles or pure Cu₂O nanospheres under solar light irradiation. The drastic enhancement in photocatalytic activity could be attributed to the surface plasmon resonance and the electron sink effect of the Ag NW cores, and the unique 1D core-shell nanostructure.

Keywords

Ag@Cu₂O, one-dimensional structure, core-shell nanowires, plasmonic photocatalysts.

1. Introduction

The synthesis of one-dimensional (1D) nanostructures and their potential applications in solar energy conversion have attracted much recent interest due to their unique 1D geometry with fast and long-distance electron transfer, superior electron conductivity and mobility, larger specific surface area, light-harvesting

efficiency, and length-to-diameter ratio, and high adsorption capacity.¹⁻¹⁶ An important application of 1D nanostructures is in photocatalytic degradation of organic pollutants, and recent decades have witnessed an exponential growth in the design and fabrication of highly efficient and active photocatalysts due to the growing awareness of environmental pollution issues and safety considerations. Various semiconducting nano-photocatalysts, especially metal oxide semiconductors such as TiO₂ and ZnO, are being extensively investigated.^{6, 7, 17-19} The wide band gap of some metal oxides limits their light absorption in UV region, however, leading to less use of sunlight.²⁰ In order to effectively utilize sunlight, noble plasmonic nanostructured metals, such as Au, Ag, and Pt, are deposited on the surface of semiconductors. The metals act as electron traps that introduce efficient interfacial charge separation in the composites, leading to a drastic improvement in photocatalytic activity over an extended wavelength range.²¹⁻²⁴ Metal nanoparticles are most commonly used, and they can also be attached to the surface of semiconductors to form core-satellite or core-shell semiconductor@metal nanostructures. The external metal nanoparticles are exposed to reactants and the surrounding medium, however, which could cause corrosion and detachment from the photocatalysts.²⁵⁻²⁷ An alternative option is to construct core-shell metal@semiconductor structures.

In addition to the use of plasmonic metal nanostructures, the selection of narrow-band-gap semiconductor photocatalysts can also effectively improve absorption of light harvesting. Cuprous oxide (Cu₂O) is one such attractive and

environmentally friendly *p*-type direct semiconductor, with a small band gap (2.17 eV) and unique optical and electrical properties, which make it an appealing candidate for photocatalytic applications.²⁸⁻³³ In order to overcome the aforementioned disadvantages of semiconductor-core@metal-shell plasmonic heterostructured photocatalysts, and to further enhance the photocatalytic performance of pure Cu₂O, metal-core@Cu₂O-shell hetero-nanostructures, such as Cu@Cu₂O core-shell microspheres,³⁴ Ag@Cu₂O core-shell nanoparticles,²⁶ and Au@Cu₂O core-shell cubes and octahedra,³⁵ have been widely chosen as photocatalysts in recent years. Compared with other noble metals, Ag is more attractive due to its high electrical and thermal conductivity, antibacterial characteristics, low cost, and nontoxicity. Ag nanostructures exhibit a wealth of optical and photoelectrochemical properties directly related to their geometry-dependent surface plasmon resonances, which makes 1D Ag nanostructures great potential candidates in the field of photocatalysis.^{25, 36-41} However, there is still no report on highly efficient plasmonic heterostructured photocatalysts based on 1D Ag-core@Cu₂O-shell architectures to our knowledge, which might be able to fully take advantage of the potential of 1D nanostructures.

Herein, a general procedure for rapid fabricating 1D Ag@Cu₂O core-shell hetero-nanowires for photodegradation of organic dyes is reported. The core-shell hetero-nanowires are made by overgrowth of Cu₂O nanocrystals on the surface of as-prepared Ag nanowires (NWs) via a simple solution process (Scheme 1). The resultant 1D core-shell Ag@Cu₂O nanowires show superior photocatalytic

degradation of methyl orange (MO) to core-shell Ag@Cu₂O nanoparticles and pure Cu₂O nanospheres.

2. Experimental section

Materials

Silver nitrate (AgNO₃), hydrazine solution (35wt % in H₂O), sodium chloride (NaCl), and polyvinylpyrrolidone (PVP40) were purchased from Sigma-Aldrich. Copper (II) nitrate 3-hydrate (Cu(NO₃)₂·3H₂O) and MO were purchased from BDH laboratory supplies. Ethylene glycol (EG) was purchased from Alfa Aesar. All of the chemicals were analytical grade and used directly without further purification.

Sample preparations

Ag nanowires (Ag NWs) were fabricated by a modified polyol process.⁴² In a typical synthesis, 10 mL EG containing PVP40 was loaded into a 25-mL vial, and heated with magnetic stirring in an oil bath at 120 °C for 1 h. 1 mL of NaCl in EG solution (1 mM) was then quickly added, and stirring for another 5 min. Finally, AgNO₃ (0.1 M solution in EG) was added to the mixture. The mixture solution was then heated at 120 °C with magnetic stirring for 1 h, yielding the grey Ag NWs.

Ag nanoparticles (Ag NPs) were prepared by the similar procedure without NaCl.

Core-shell Ag@Cu₂O hetero-nanowires were synthesized by a simple solution process used for the synthesis of Au@Cu₂O nanoparticles with some modifications.⁴³ Typically, 8 mL freshly prepared Ag NW solution was added into 50 mL of 0.05 M Cu(NO₃)₂·3H₂O aqueous solution under constant magnetic stirring for 30 min. Then, 100 μL of N₂H₄·H₂O solution was added into the reaction mixture. The reaction

mixture was stirred for 30 min, and then the resultant Ag@Cu₂O core-shell nanowires were separated by centrifugation, and washed with de-ionized water and absolute ethanol to remove impurities, and then dried at 60 °C.

Core-shell Ag@Cu₂O hetero-nanoparticles were prepared using the similar approach to Ag@Cu₂O core-shell hetero-nanowires, except 8 mL of Ag NPs solution was added rather than Ag NWs solution.

Pure Cu₂O nanospheres were prepared using the above similar procedure without Ag solution.

Characterization

The X-ray diffraction (XRD) measurements were performed on a GBC MMA X-ray diffractometer using Cu K α_1 radiation (40 kv). The XRD patterns were recorded from 20° to 80° with a scanning rate of 2°/min. SEM images were taken using a field-emission scanning electron microscope (JSM-7500FA, JEOL) operated at an accelerating voltage of 5 kV. TEM images were recorded on a field-emission transmission electron microscope (JEM-2011, JEOL), using an accelerating voltage of 200 kV. UV/vis absorption spectra were taken at room temperature on a UV-3600 (Shimadzu) spectrometer. X-ray photoelectron spectroscopy (XPS) was performed by a VG Scientific ESCALAB 2201XL photoelectron spectrometer with Al Ka X-ray as the excitation source to analyze samples' elemental composition. Analysis of the XPS data was carried out using the commercial CasaXPS 2.3.15 software package.

Photocatalytic test

Photocatalytic activity of the as-synthesized Ag@Cu₂O core-shell nanowires was evaluated by the degradation of MO under the irradiation of a LSC-100 Solar Simulator (Newport). In an experiment, 5 mg photocatalyst was added into 50 mL of MO solution at room temperature. Prior to irradiation, the suspension was stirred in the dark to ensure the establishment of an adsorption-desorption equilibrium between the photocatalysts and MO. Then the solution was exposed to solar light irradiation under magnetic stirring. At each irradiation time interval, 2 mL of the suspension was collected and then centrifuged to remove the photocatalysts. The concentration of MO was analyzed by a Shimadzu UV-3600 spectrophotometer, and the characteristic absorption of MO at 464 nm was used to evaluate its photocatalytic degradation. All of the measurements were carried out at room temperature.

3. Results and discussion

Figure 1(A-C) shows typical scanning electron microscope (SEM) images of the Ag nanowires prepared by a modified polyol reduction process,⁴² which serve as templates for the subsequent hetero-growth of Cu₂O nanoshells to form Ag@Cu₂O core-shell nanowires. These Ag nanowires are well crystallized [Figure S1 in the Supporting Information (SI)] and possess relatively smooth surfaces, and have an average diameter of about 100 nm and a length of about 10 μm. SEM images of the Ag@Cu₂O core-shell hetero-nanowires are displayed in Figure 1(D-F), which clearly show that the surface of the Ag@Cu₂O core-shell hetero-nanowires is not as smooth as that of the Ag NWs, due to the coating by a layer of dense Cu₂O nanoparticles. The

enlarged SEM image [Figure 1(F)] reveals that many tiny Cu₂O nanoparticles have densely grown on the entire surface of the Ag nanowires, including both ends, to form a rough surface.

Transmission electron microscopy (TEM) was used to further characterize Ag@Cu₂O core-shell hetero-nanowires [Figure 1 (G,H) and Figure S2]. Figure 1(G) clearly shows individual Ag@Cu₂O hetero-nanowire with a rough surface and a diameter of 170 nm, which consists of 90-nm Ag core and 40-nm Cu₂O shell. The interface between Ag nanowire and Cu₂O nanoparticles is also clearly observed. The HRTEM image in Figure 1(H) shows the lattice fringes of 0.25 and 0.24 nm, which correspond to Cu₂O (111) and Ag (111), respectively. The similar lattice fringes are attributed to the same cubic crystal structures of Ag and Cu₂O and their small lattice mismatch (i.e. $a_{Ag} = 4.08 \text{ \AA}$ and $a_{Cu_2O} = 4.27 \text{ \AA}$). The distribution of elements in the Ag@Cu₂O core-shell hetero-nanowires is shown in Figure 1(I). The upper-left image in Figure 1(I) is the area where the elemental mapping was performed. The green, blue, and red colors represent the distribution of the elements silver, copper, and oxygen, respectively. The presence of the three elements in the nanowires is in agreement with the proposed Ag@Cu₂O composition. The spatial distribution of the colors verifies the core-shell structure, with an Ag core inside and Cu₂O shell outside. The composition of the core-shell hetero-nanowires was further confirmed by the energy dispersive X-ray (EDX) spectrum (Figure S3). The EDX results also demonstrate that the as-prepared product is mainly composed of Ag, Cu, and O.

The crystalline structure and optical properties of the as-prepared Ag@Cu₂O core-shell hetero-nanowires are shown in Figure 2. The X-ray diffraction (XRD) pattern is compared with standard patterns of Ag (JCPDS 4-783) and Cu₂O (JCPDS 5-667) in Figure 2(A), where every peak can be indexed to Ag or Cu₂O, supporting the formation of Ag@Cu₂O core-shell hetero-nanowires. The absence of other impurity peaks indicates the high purity of the core-shell Ag@Cu₂O hetero-nanowires fabricated by this simple solution process. In addition, the peaks of Cu₂O are characteristic of a cubic structure with a lattice constant of $a = 4.27 \text{ \AA}$. Its relatively weak peaks indicate the low crystallinity of Cu₂O shell than that of Ag core. The X-ray photoelectron spectroscopy (XPS) results further confirm the successful synthesis of Ag@Cu₂O core-shell hetero-nanowires (Figure S4).

Ag NWs show intense surface plasmon resonance (SPR) absorption in the visible region, which is highly sensitive to their diameter, length-to-diameter ratio, as well as the optical and electronic properties of their surroundings.^{26, 38, 44-46} The ultraviolet-visible (UV-vis) absorption spectra of Ag@Cu₂O core-shell hetero-nanowires and pure Ag NWs in ethanol are presented in Figure 2(B). The pure Ag NWs exhibit two absorbance peaks at 350 and 385 nm. The peak at 350 nm could be attributed to the longitudinal mode of nanowires similar to that of bulk Ag^{38, 47, 48} or the out-of-plane quadrupole resonance of Ag NWs.⁴⁹⁻⁵¹ The peak at 385 nm is assigned to the transverse plasmon resonance of Ag NWs.^{38, 47, 48} Upon the formation of Cu₂O shell, the transverse plasmon resonance of the Ag core is significantly

red-shifted from 385 nm to 515 nm, due to the higher refractive index of Cu_2O (~ 2.7 at wavelengths above 600 nm)^{43, 52-53} than ethanol (~ 1.359)^{27, 38} and its high dielectric constant ($\epsilon=7.2$).^{43, 52, 54} Their broad absorbance from visible to UV window is crucial for full use of sunlight.

All the above results confirm our success in obtaining $\text{Ag@Cu}_2\text{O}$ core-shell hetero-nanowires through this simple solution approach. Figure S5 and Figure S6 present SEM images and UV-vis absorption of the core-shell hetero-nanowires collected at different reaction times. As shown in Figure 1(A-C), before the growth of Cu_2O , the Ag NWs possess very smooth surfaces. After the Ag NWs were dispersed in $\text{Cu}(\text{NO}_3)_2$ solution, the hetero-growth of Cu_2O on the surface of the Ag NWs occurred immediately upon the addition of the reducing agent N_2H_4 , accompanied by the rapid change of the reaction solution from grey to yellow. As shown in Figure S5(A), a well-defined core-shell heterostructure with a rough surface was formed within 2 min, indicating that the formation of Cu_2O is very fast. As the growth reaction progresses, the obtained core-shell hetero-nanowires show no significant changes, and the surfaces of the Ag NWs are totally covered by the Cu_2O nanoparticles [Figure S5(B-D)]. If the reaction was carried out for 12 h, however, some Cu_2O nanoparticles disappeared, and the smooth surface of the Ag NWs was observed [Figure S5(E)]. Further prolonging the reaction time to 24 h led to disappearance of most Cu_2O nanoparticles [Figure S5(F)]. These results indicate the reversibility of the Cu_2O reactions in our system. The reason for the gradual

disappearance of the Cu_2O nanoparticles could be due to the gradual oxidation/dissolving of the Cu_2O by NO_3^- ions in the acidic environment (Figure S7). The pH of reaction mixture is maintained between 3.72 and 3.03 within the initial 60 min, however, it is increased to 4.32 after reaction for 24 h. Therefore, the pH of the solution significantly influences the formation of the Cu_2O nanoparticles on the surface of the Ag NWs.

As shown in Figure S6, the Ag@ Cu_2O NWs obtained at 2 min, 20 min, 40 min, and 60 min exhibit similar absorption profiles, in which the SPR peak of Ag cores remained at 515 nm, and didn't shift with the increase of reaction time. This means that Ag NWs were completely covered by sufficient Cu_2O shell [Figure S5(A-D)], and their optical properties were not influenced by external surroundings.⁵² The SPR peak of Ag cores in the product obtained at 12 h, however, shifted to shorter wavelength at 395 nm, principally due to the change in the refractive index of surroundings caused by the decrease of Cu_2O thickness. As shown in Figure S5(E), Ag cores are not completely covered and some parts are exposed to solvent, which leads to the change in the effective refractive index of surroundings. The decrease in the refractive index causes the shift of SPR band to shorter wavelength.⁵² The SPR peak in the product collected at 24 h shifted to 386 nm due to the disappearance of most Cu_2O shells [Figure S5(F)], resulting in a similar spectrum to that of pure Ag NWs.

It should be noted that the amount of Ag NWs and $\text{Cu}(\text{NO}_3)_2$ solution also play important roles in the formation of $\text{Ag}@\text{Cu}_2\text{O}$ core-shell hetero-nanowires. As shown in Figure 3(A), when 1 mL of Ag NW solution (~ 0.038 mmol) is used, the Ag NWs are coated with many nanoparticles, while many free Cu_2O nanospheres with a diameter of about 200 nm are formed at the same time. The reason could be the fast formation of Cu_2O via the reduction of $\text{Cu}(\text{NO}_3)_2$ and insufficient amount of Ag NWs as anchoring sites, leading to the self-aggregation of the excessive produced Cu_2O nanocrystallites. Increasing the Ag NW solution to 4 mL (~ 0.15 mmol) leads to an increase in the formation of $\text{Ag}@\text{Cu}_2\text{O}$ core-shell NWs and a decrease in the fraction of free Cu_2O nanospheres [Figure 3(B)]. Further increasing the volume of the Ag NW solution to 8 mL (~ 0.3 mmol) resulted in perfect $\text{Ag}@\text{Cu}_2\text{O}$ core-shell hetero-nanowires. The Ag NWs are fully covered by Cu_2O nanoparticles, and there are almost no free standing Cu_2O nanospheres to be found [Figure 3(C)]. A thin layer of very small nanoparticles are partly coated on the surfaces of Ag NWs, however, when the amount of Ag NW solution is further increased to 16 mL (~ 0.6 mmol) [Figure 3(D)]. Changing the amount/concentration of $\text{Cu}(\text{NO}_3)_2$ couldn't result in well-coated $\text{Ag}@\text{Cu}_2\text{O}$ nanowires (Figure S8) either. The above results demonstrate that well-defined $\text{Ag}@\text{Cu}_2\text{O}$ core-shell hetero-nanowires can be only achieved under certain conditions.

In order to demonstrate the applicability of our simple method, core-shell $\text{Ag}@\text{Cu}_2\text{O}$ nanoparticles (NPs) were prepared under similar conditions by using Ag

NPs as seeds. Pure Cu_2O NPs were also prepared in the absence of Ag for comparison. The resultant Ag@ Cu_2O NPs and Cu_2O NPs were examined by XRD and SEM, respectively. The XRD results [Figure 4(A) and Figures S9-S11(A)] clearly reveal that all the diffraction peaks can be indexed to Ag (JCPDS 4-783) and Cu_2O (JCPDS 5-667), and no other impurity diffraction peaks were observed. The SEM images [Figure 4(B) and Figure S9(B-D)] show that large quantities of Ag@ Cu_2O NPs in the range of 100 nm to 230 nm have been successfully fabricated. The pure Cu_2O nanospheres have an average diameter of 440 nm [Figure 4(D) and Figure S10(B-D)]. These results demonstrate that the final morphology of the Ag@ Cu_2O nanostructures greatly depends on the morphology of the Ag seeds.

The resultant Ag@ Cu_2O core-shell nanowires and nanoparticles are expected to show higher photocatalytic activity than pure Cu_2O NPs, due to the plasmonic enhancement of the Ag cores. The performance of the Ag@ Cu_2O NWs, Ag@ Cu_2O NPs, and pure Cu_2O nanospheres was evaluated by the photodegradation of MO under solar light irradiation. For comparison, the Ag NWs were also tested under identical experimental conditions. Figure 5(A-C) shows the absorption spectra of MO solutions after photocatalytic degradation for various durations over Ag@ Cu_2O NWs, Ag@ Cu_2O NPs, and pure Cu_2O nanospheres, respectively. Under solar light irradiation, the absorption peak at 464 nm diminishes gradually as the irradiation time increases. As shown in Figure 5(D), it can be clearly observed that in the absence of catalyst and in the presence of only Ag NWs under solar light irradiation, there is no

evident photodegradation of MO. In contrast, the as-prepared Ag@Cu₂O NWs, Ag@Cu₂O NPs, and pure Cu₂O nanospheres all exhibit excellent photocatalytic performance. Moreover, both the core-shell Ag@Cu₂O NWs and the Ag@Cu₂O NPs show higher photocatalytic activity than that of the pure Cu₂O nanospheres, while the Ag@Cu₂O core-shell NWs exhibit the highest performance, which can decolor 92% of MO within 140 min, while 83% and 71% of MO can be degraded over the Ag@Cu₂O NPs and pure Cu₂O nanospheres, respectively. In compared with previously reported Ag@Cu₂O nanoparticles and Cu₂O-Au composites, our nanostructures exhibit higher photoactivity in degradation of MO, e.g. 90% MO can be degraded by core-shell Ag@Cu₂O NWs within 2 h, but only ~75% MO was degraded by the Ag@Cu₂O nanoparticles within the same time²⁶ and ~60% MO was degraded within 4 h by Cu₂O-Au composites.⁵⁵ The results clearly demonstrate that the hetero-growth of Cu₂O nanoshells on Ag NWs to build 1D core-shell heterostructures has been proven to be a useful and successful strategy for improving the photocatalytic properties of Cu₂O crystals.

In order to better understand the good performance of our core-shell Ag@Cu₂O NWs, their XRD, XPS, SEM and TEM characterizations have been conducted after photocatalytic test. The XRD pattern shows that the dominant peaks of Cu₂O (111) and (200) become much weaker after photocatalysis test [Figure S12(A)]. In addition, there is no other peaks detected except that of Ag nanowires. The binding energies measured by XPS show two peaks at 934.4 and 954.2 eV, which are respectively

assigned to Cu 2p_{3/2} and Cu 2p_{1/2} of copper ions. Devolution of Cu 2p peaks into Cu²⁺ and Cu⁺ revealed two small peaks of Cu⁺ from Cu₂O at 932.6 and 952.3 eV, respectively [Figure S12(B)]. The peaks of Cu²⁺ stronger than that of Cu⁺ after photocatalytic test suggest a dense protection layer of CuO or Cu(OH)₂ on the surface of Cu₂O.

It should be noted that the morphology of photocatalysts changed after photocatalytic test. There are many sheet-like structures and uncovered Ag NWs formed due to the loss of Cu₂O nanoparticles [Figure S12(C)]. The TEM image in Figure S12(D) further confirms the loss of Cu₂O nanoparticles and the decrease of their density on the surface of Ag NWs. This result is similar to the previous reports,^{29, 56} and the morphology transformation could be explained as follows. Cu₂O nanoparticles are irradiated by solar light to produce electrons and holes. On the one hand, the photogenerated electrons quickly transferred and accumulated in Ag NWs, which further transferred to O₂ molecules adsorbed on the surface, and facilitated their multiple-electron reduction reactions. The formed reactive species ($\cdot\text{O}_2^-$) can effectively bleach the dye. On the other hand, Cu₂O are oxidized into CuO by the accumulated holes in them, and the intermediate CuO can also generate electron-hole pairs under irradiation of solar light. As the photogenerated holes are captured by MO and the accumulated electrons can reduce CuO into Cu₂O, accompanied by the formation of sheet structure.

It was reported that in the photodegradation of organic pollutants, reactive species such as $\cdot\text{O}_2^-$, h^+ and $\cdot\text{OH}$ played as bridge role of photocatalysts under the light irradiation,⁵⁷⁻⁶⁰ and they could vary with the different photocatalysts.^{61, 62} To investigate the photocatalytic mechanism and to understand the better performance of 1D Ag@Cu₂O core-shell photocatalysts, the effect of scavengers on the degradation of MO was examined to clarify the contribution of different reactive species during photocatalysis study. We used p-benzoquinone (PBQ) as $\cdot\text{O}_2^-$ scavengers,^{57-60, 63-65} triethanolamine (TEOA) as h^+ scavengers,^{61, 62, 65} and isopropanol (IPA) as $\cdot\text{OH}$ scavengers.^{63, 66} These scavengers were added into the MO solution together with the 1D Ag@Cu₂O core-shell hetero-nanowires before irradiation. As depicted in Figure 6, the complete inhibition of degradation of MO in the presence of TEOA suggests that photogenerated holes are the major reactive species for the photocatalytic degradation of MO. The dramatic decrease in degradation of MO arising from removal of oxygen with N₂ bubbling demonstrates that molecular oxygen also played an important role in the photodegradation of MO over 1D Ag@Cu₂O core-shell hetero-nanowires. This is attributed to the electron trapping role of molecular oxygen, which could produce $\cdot\text{O}_2^-$ to inhibit the recombination of electron-hole pairs, and leave over holes to oxidize MO. The elimination of molecular oxygen would diminish the amount of holes and prevent the oxidation of MO due to the fast combination of electron-hole pairs. In order to confirm the roles of $\cdot\text{O}_2^-$ in the degradation of MO, we employed PBQ as the $\cdot\text{O}_2^-$ scavenger. The results show that the presence of PBQ significantly decreased

the MO photodegradation efficiency from 92% to 45% within 140 min for 1D Ag@Cu₂O core-shell hetero-nanowires. In contrast, the addition of IPA had little effect on the MO degradation. The above results illustrate that both h⁺ and ·O₂⁻ are the main reactive species for 1D Ag@Cu₂O core-shell hetero-nanowires in the photocatalytic decolorization of MO under solar light irradiation, and the reactive ·OH preferred to react with MO dye, due to the presence of N=N double bond and benzene ring in the azo-dye MO molecules, which are more reactive than hydroxyl group in IPA.

The drastic enhancement in photocatalytic activity of the 1D core-shell Ag@Cu₂O NWs may be ascribed to the synergistic effects of Ag NWs and surface Cu₂O. As evidenced by SEM and TEM images, there are clear interfaces between Ag NWs and Cu₂O nanoparticles, which can effectively suppress the recombination rate of electron-hole pairs.⁶⁷ More specifically, first, the direct coupling of Ag NWs and Cu₂O causes the Fermi level to equilibrate, which can lead to trapping of charges and increase carrier life.²⁶ The Ag NWs in the core-shell structures produce a Schottky barrier at the interface between the core and shell, which facilitates the capture and quick transfer of photoexcited electrons from the Cu₂O nanoshells to the Ag NWs under solar light irradiation [Figure 5(E)].^{25, 67, 68} The electrons accumulated in the Ag NWs are transferred to O₂ molecules to produce superoxide radical anions (·O₂⁻) through the multiple-electron reduction reactions to decompose organic pollutant.³⁹ Accumulation of the photoinduced holes in the valence band of the Cu₂O nanoshells

leads to the production of the hydroxyl radical ($\bullet\text{OH}$) at the surface, which is responsible for the oxidation decomposition of the MO molecules.²⁵ Photo-excited electrons are effectively accumulated in the Ag NWs without recombining with holes, which could promote the effective separation of photogenerated electron-hole pairs. This leads to the significant enhancement of the photocatalytic activity of the Ag@Cu₂O core-shell structures. Second, the unique 1D Ag@Cu₂O core-shell nanostructures are expected to have excellent electron conductivity and mobility. The presence of metal nanowires can facilitate fast and long-distance electron transport, and the fast transfer of photo-induced electrons and holes over the Ag NWs and Cu₂O nanoshells suppresses the recombination of electron-hole pairs, which is favorable for highly efficient photocatalytic performance. Third, the core-shell Ag@Cu₂O nanowires have a large specific surface area for adsorbing dyes (45%, 32%, and 20% MO adsorption in the dark equilibration for Ag@Cu₂O NWs (10.3 m²/g), Ag@Cu₂O NPs (8.8 m²/g), and pure Cu₂O nanospheres, respectively, in our experiment), which can provide more active sites for the photodegradation of MO and thus promote diffusion of reactants and products during the reaction, accelerating the chemical reactions. Fourth, the high length-to-diameter ratio of the 1D metal-core@semiconductor-shell hetero-nanostructures may remarkably enhance the light absorption, trapping, and scattering through a local field enhancement effect of plasmonic Ag NWs,⁶⁹ and thus increase the quantity of photogenerated electrons and holes available to participate in the photocatalytic reactions, leading to an

enhanced photocatalytic property of the Cu_2O .⁶⁸ It should be noted, however, that the photocatalytic mechanism over such 1D $\text{Ag@Cu}_2\text{O}$ core-shell hetero-nanowires is still not completely understood, and a more detailed study is still underway.

4. Conclusion

In summary, 1D core-shell $\text{Ag@Cu}_2\text{O}$ hetero-nanowires have been fabricated by a facile solution process at room temperature. The resulting unique heterostructures exhibit greater plasmonic enhancement of photocatalytic activity in MO oxidizing than $\text{Ag@Cu}_2\text{O}$ nanoparticles and pure Cu_2O under solar light irradiation. Such rational design and fabrication of 1D metal-core@semiconductor-shell architectures may hold great potential in solar energy conversion, especially as an effective technique to improve photocatalytic activity.

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Supporting Information

Additional characterization data including XRD pattern of Ag NWs, HRTEM images, EDS pattern and XPS spectra of 1D Ag@Cu₂O core-shell hetero-nanowires, SEM images and UV-vis absorption spectra of the products obtained at different reaction times, SEM images of the products prepared from different concentration of Cu(NO₃)₂, the photographs of reaction systems composited of Ag NWs, Cu (NO₃)₂ solution and N₂H₄ before and after reaction at different stages, and XRD patterns and SEM images of Ag@Cu₂O NPs, Ag NPs, and pure Cu₂O, XRD pattern, XPS spectrum of Cu 2p, SEM image and TEM image of 1D Ag@Cu₂O core-shell hetero-nanowires after photocatalytic test. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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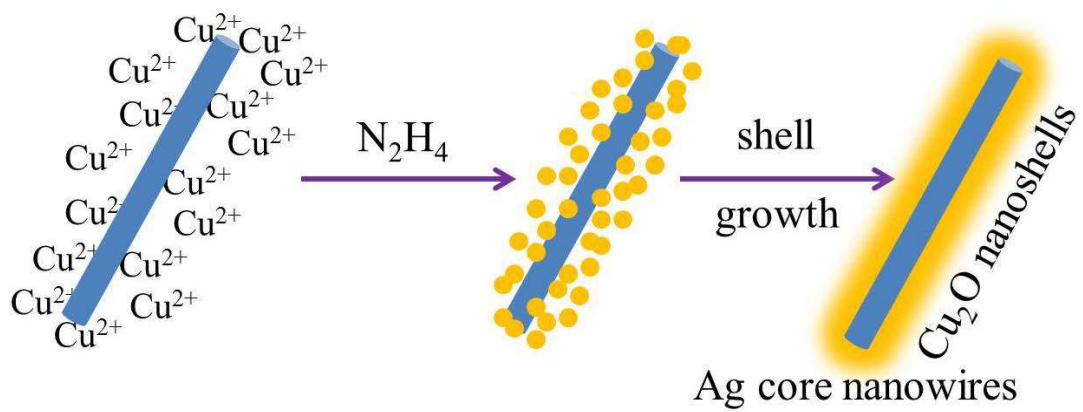
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Scheme 1. Schematic illustration of the plausible formation process of the 1D Ag@Cu₂O core-shell hetero-nanowires.

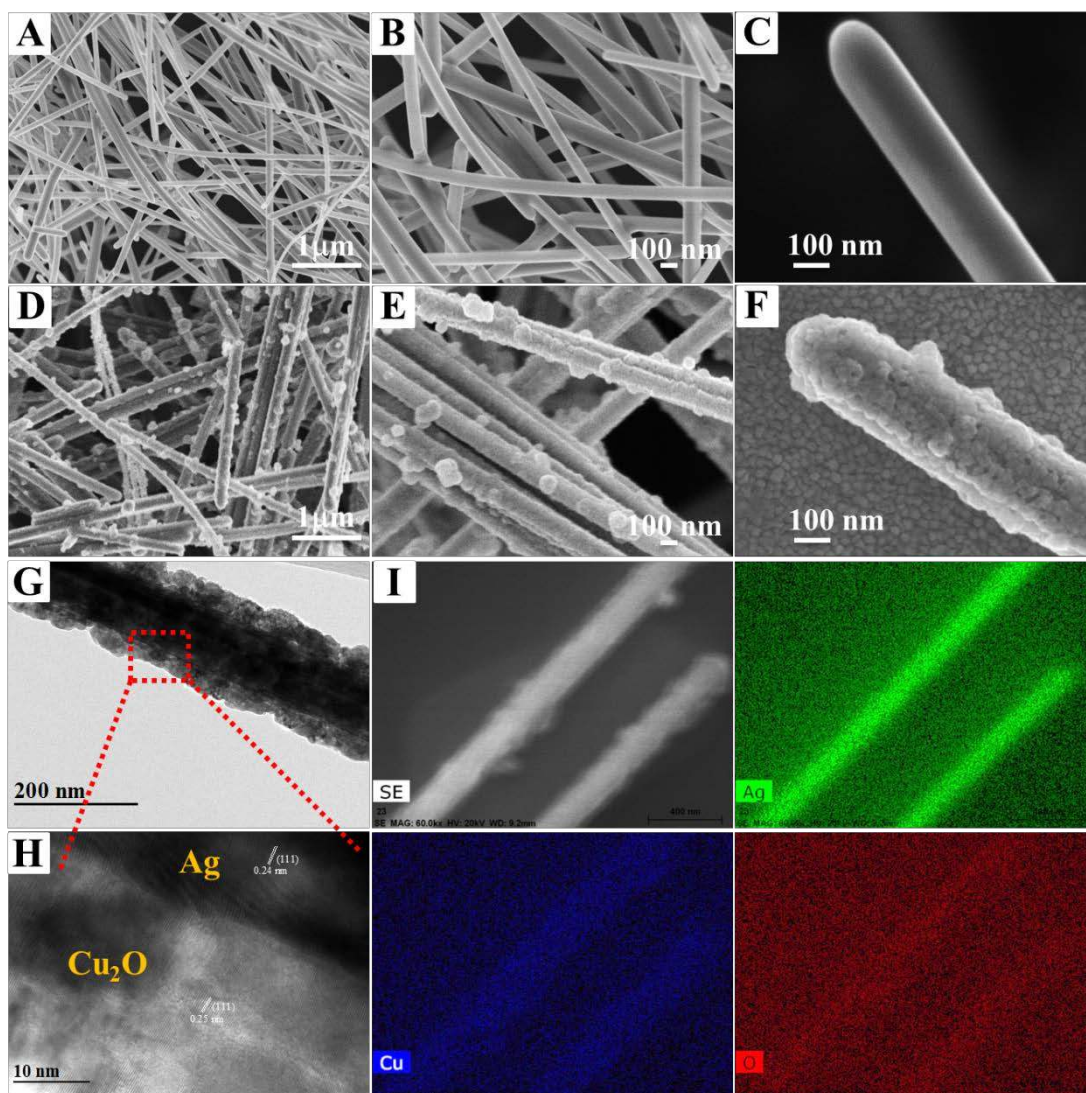


Figure 1. (A-C) SEM images of the Ag NWs, (D-F) SEM images of the as-prepared Ag@Cu₂O core-shell hetero-nanowires. (G) TEM image and (H) HRTEM of an individual Ag@Cu₂O core-shell hetero-nanowire. (I) EDX elemental mapping analysis of the Ag@Cu₂O core-shell hetero-nanowires.

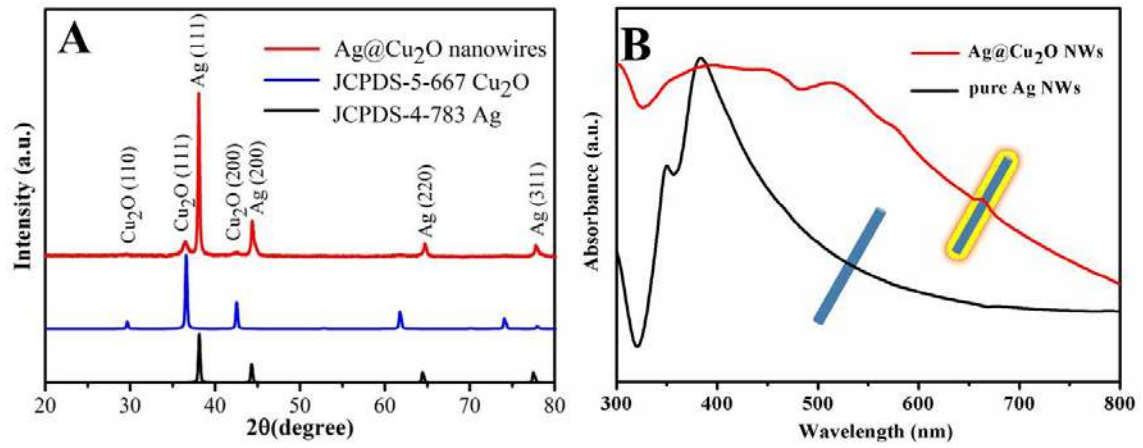


Figure 2. (A) XRD patterns and (B) UV-vis absorption spectra of as-prepared 1D Ag@Cu₂O core-shell hetero-nanowires and pure Ag NWs in ethanol.

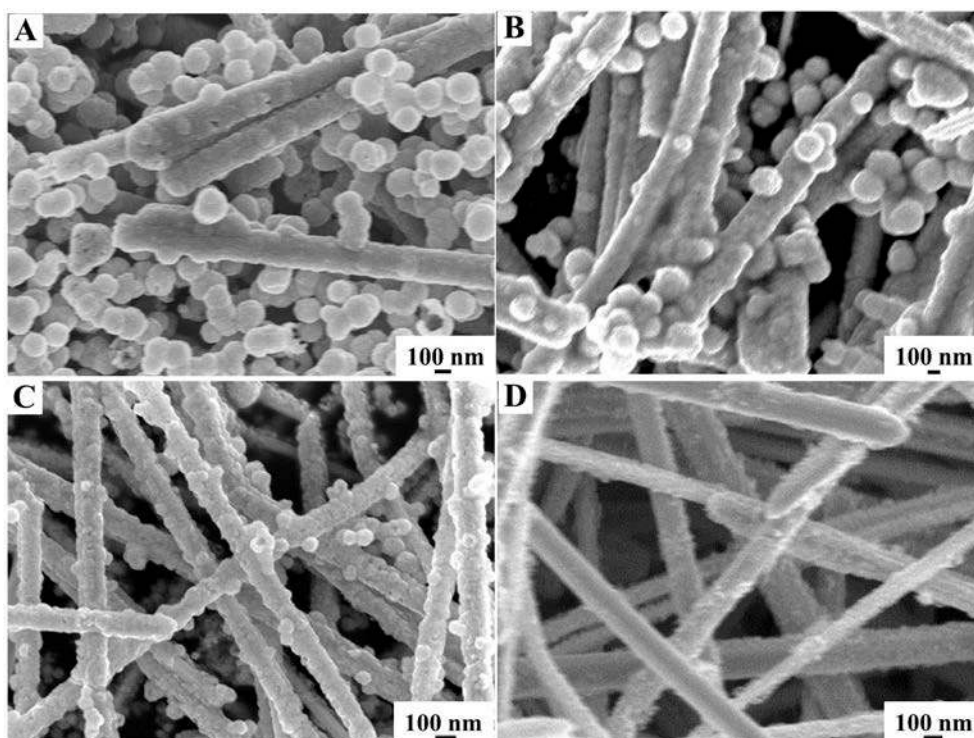


Figure 3. SEM images of the products prepared in the presence of different amounts of Ag solution: (A) 1 mL, (B) 4 mL, (C) 8 mL, and (D) 16 mL.

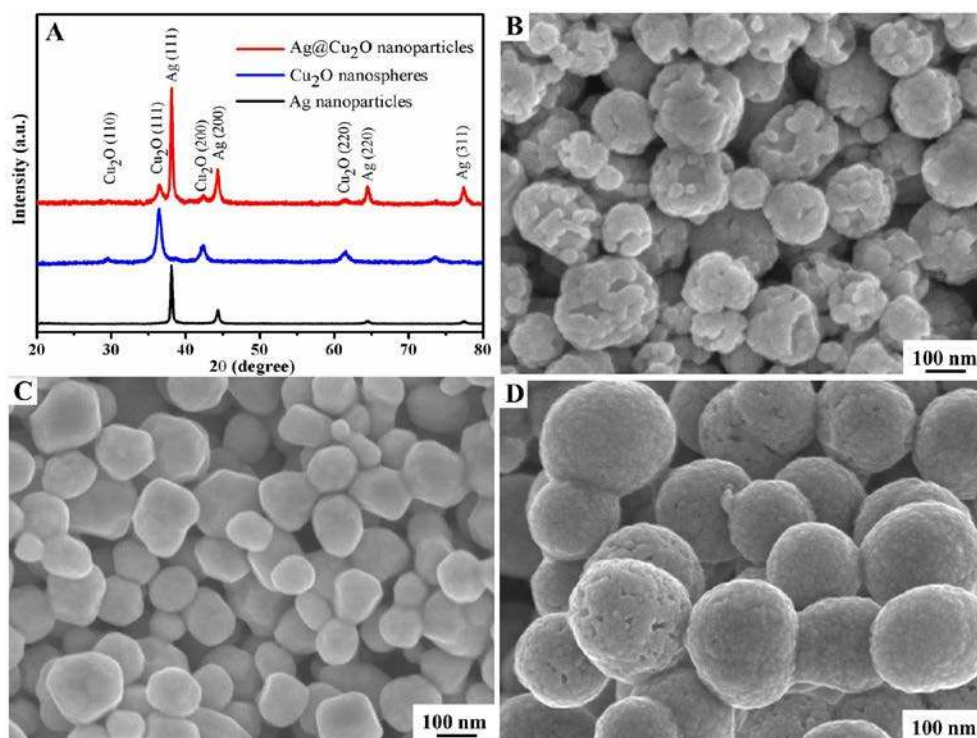


Figure 4. (A) XRD patterns, and SEM images of as-prepared Ag@Cu₂O nanoparticles (B), Ag nanoparticles (C), and pure Cu₂O (D).

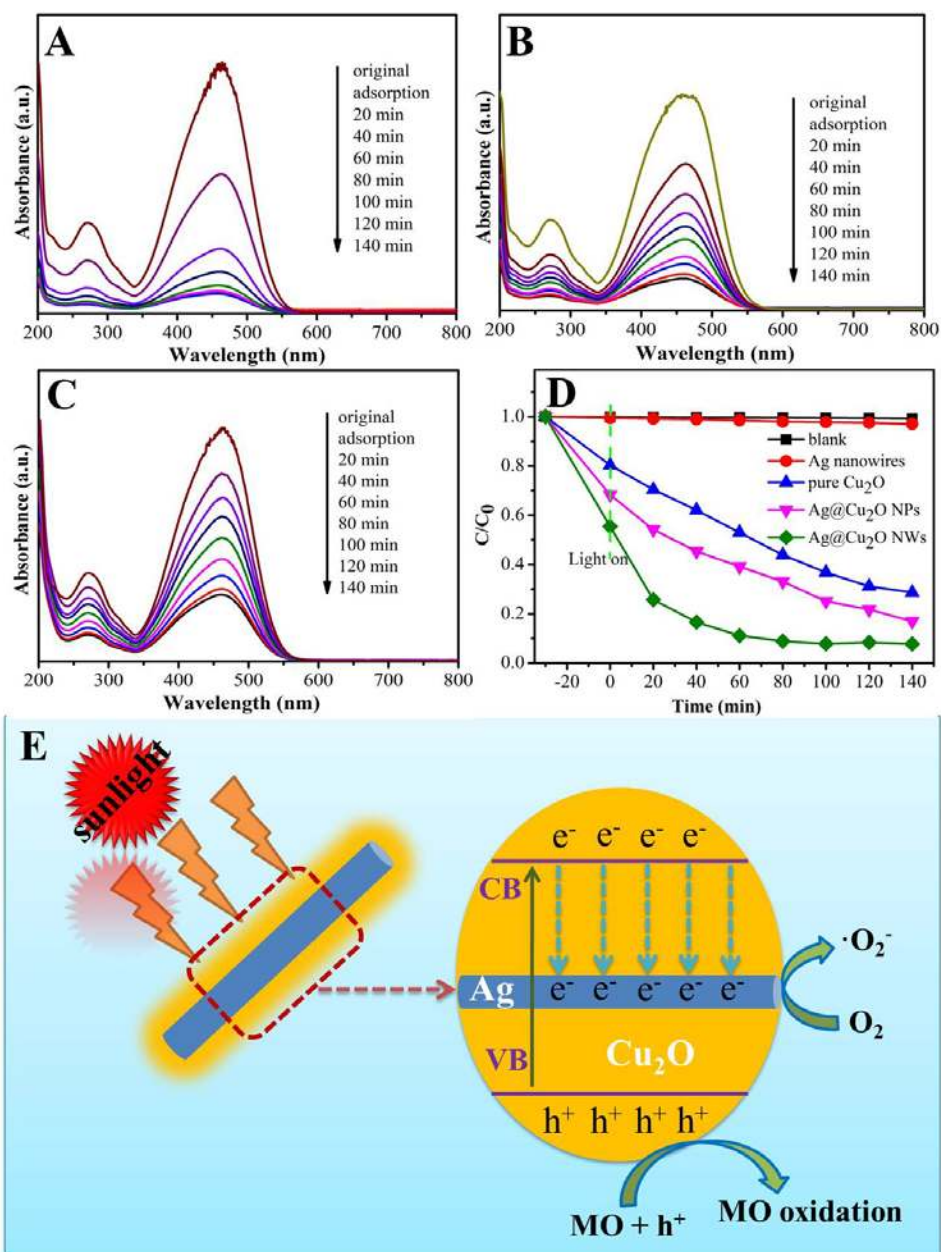


Figure 5. (A-C) Variation in the light absorption of the MO solution in the presence of the as-prepared photocatalysts under solar light irradiation for different irradiation times: (A) Ag@Cu₂O NWs, (B) Ag@Cu₂O NPs, and (C) pure Cu₂O nanospheres; (D) photocatalytic activity of MO oxidation under solar light irradiation; (E) schematic illustration of the transfer of photogenerated electron-hole pairs in the Ag@Cu₂O core-shell NWs under solar light irradiation.

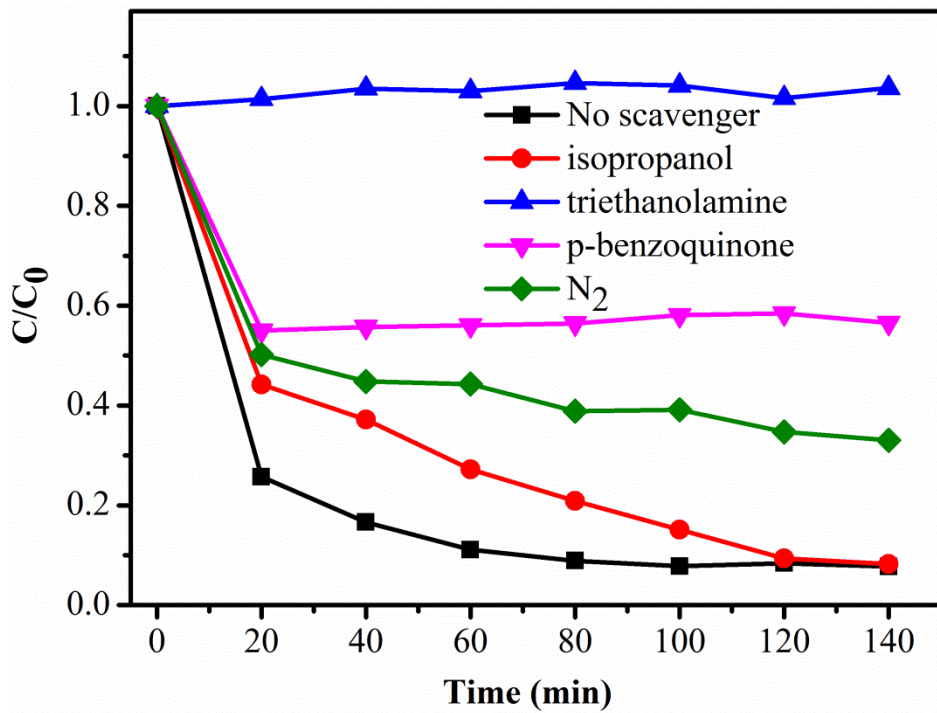


Figure 6. Photocatalytic degradation of MO over the 1D Ag@Cu₂O core-shell hetero-nanowires in the presence of scavengers.

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