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In Situ Partial Sulfidation for Preparing Cu/Cu_{2-x}S Core/Shell Nanorods with Enhanced Photocatalytic Degradation

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Abstract: Herein, we report an approach to prepare Cu/Cu_{2-x}S core/shell nanorods by in situ sulfidation of copper nanorods. Firstly, copper nanorods with tunable longitudinal surface plasmon resonances were synthesized by a seed-mediated method using Au nanoparticles as seeds. A convenient in situ sulfidation method was then applied to convert the outermost layer of Cu nanorods into Cu_{2-x}S, to increase their stability and surface activity in photocatalytic applications. The thickness of Cu_{2-x}S layer can be adjusted by controlling the amount of S source. The Cu/Cu_{2-x}S core/shell nanorods exhibits two characteristic surface plasmon resonances located in visible and near-infrared regions, respectively. The photocatalytic performances of Cu nanorods and their derivatives were evaluated by measuring the degradation rate of methyl orange dyes. Compared with Cu nanorods, the Cu/Cu_{2-x}S core/shell nanorods demonstrate more than a 13.6-fold enhancement in the degradation rate at 40 min. This work suggests a new direction for constructing derivative nanostructures of copper nanorods and exploring their applications.

Keywords: Cu nanorods; sulfidation; degradation

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1. Introduction

In the past few decades, one-dimensional, metal nanomaterials with surface plasmon resonances (SPRs) have attracted intense attention because of their unique properties [1–5]. In particular, the preparation process of nanorods (NRs) with gold or silver as the main component is very well-developed. On this basis, the growth of semiconductor components on plasmonic NRs forms metal–semiconductor heterogeneous nanostructures with a fascinating interaction between the plasmon and semiconductor [6–9]. These nanostructured materials show promising potentials in the applications of energy devices, photocatalytic hydrogen production, second-harmonic generation enhancement and ultrafast, optical, nonlinear properties [9,10].

Compared with gold and silver, copper is an abundant and low-cost metal resource. Nanostructured copper and its derivative compounds have many applications in catalytic degradation, hydrogen production and surface-enhanced Raman scattering (SERS) [11,12]. Nanoscale copper has a strong tendency to oxidize [1], and its preparation process is very difficult. In recent years, with the attempts of many scholars, the synthesis of one-dimensional copper NRs made great progress. Precious metal nanoparticles (Au, Pt, Pd) were used as seeds, and bimetallic copper NRs were prepared by reacting different amine reducing agents at a high temperature under an argon atmosphere [2]. Wang and colleagues reported that single-crystal Au nanoparticles were used as seeds to induce the local epitaxial growth of copper shells in the water phase, and the prepared NRs have thick centers and thin ends due to anisotropic growth [5]. Luo and colleagues used Pd decahedrons as seeds to synthesize Cu NRs with a uniform diameter and strong stability in the water phase,

and the Pd seeds are located at one end of the asymmetric Cu NRs [13]. Recently, Jeong et al. reported a seed-mediated method for synthesizing penta-twinned Cu NRs in the oil phase using Au nanocrystals as seeds [1]. The synthesized Cu NRs with a high purity have a uniform diameter and tunable aspect ratio in a wide range.

The shortcoming of oxidation also hinders the applications that use Cu nanocrystals. Especially in catalytic reactions, the stability of Cu nanocrystals is very poor. In order to address this issue, the preparation of Cu derivatives based on Cu nanocrystals made considerable progress [14–16]. Oxidation or sulfidation could produce a protective shell to improve the stability of Cu nanocrystals. The combination of Cu nanocrystals with newly formed derivatives, such as Cu_xO and Cu_xS , could achieve excellent catalytic performances. For instance, Xia and colleagues demonstrated a controlled surface oxidation of Cu nanowires, improving their catalytic selectivity and stability toward C_{2+} products in CO_2 reduction [17]. A copper-based catalyst Cu_2O -Cu, supported on carbon microspheres, exhibits Fenton-like, catalytic properties for organic dyes [18], providing a simple and cost-effective method for the catalytic degradation of organic dyes. Moreover, the catalytic performance of semiconductor nanomaterials can be further improved by doping copper nanocrystals and their derivatives. For example, doping copper or copper oxide into a zinc oxide nanostructure can delay the recombination of electrons and holes, broaden the absorption spectrum, promote certain specific reactions on the catalyst surface, and improve photocatalytic activity [19–22]. These copper compounds (copper oxide and copper sulfide) can absorb light energy under visible light illumination, causing holes (h^+) in the valence band (VB) and electrons (e^-) in the conduction band (CB) for catalytic reactions [23–25]. It is attractive that copper has two oxide states of Cu(II) and Cu(I), and they combine with H_2O_2 in a Fenton-like process to generate hydroxyl radicals ($\cdot\text{OH}$ s) and other reactive groups [26–30], which assist the reaction [31–33].

Here, a seed-mediated method using Au nanoparticles as seeds was used to synthesize Cu NRs with tunable longitudinal SPRs (LSPRs) ranging from 740 nm to 1190 nm. Subsequently, Cu NRs were partially sulfurized by mixing with an ethanol solution of sodium hydrosulfide. The hetero-nanostructures were carefully characterized to reveal structural features. The photocatalytic performance of Cu/ Cu_{2-x}S NRs was evaluated via the degradation of methyl orange (MO). The results in this work provide new insight into exploring the preparation and application of Cu nanostructures and their derivatives.

2. Results and Discussion

The synthesis strategy of Cu/ Cu_{2-x}S NRs is schematically illustrated in Figure 1. Cu NRs were prepared by a seed-mediated growth method, using oleylamine as both a solvent and reducing agent. To protect Cu from oxidation, nitrogen gas blowing was maintained in the whole synthesis process. Heating a mixture solution of copper chloride and oleylamine to 180 °C reduced Cu^{2+} to Cu^+ , and the color of mixture solution was changed from blue to yellow in this process. Au seeds (Figure S1) were added to initiate the growth of Cu NRs, and Cu NRs with penta-twinned structure were obtained after 1 h reaction. After adding the gold seeds, the color of the solution changed from orange-red to red, then to black-red, and finally to brown-yellow within 10 min, indicating the morphology evolution of the Cu nanocrystals.

The length of Cu NRs can be controlled by the amount of Au seeds. Figure 2a illustrates the extinction spectra of Cu NRs with a varied amount of Au seeds. The prepared Cu NRs exhibit two extinction bands, corresponding to the transverse and longitudinal SPRs (TSPRs and LSPRs). When the amount of Au seeds is decreased, the LSPRs located in the near-infrared (NIR) region are red-shifted and can be tuned from 740 to 1190 nm. According to Jeong's experimental results [1], the aspect ratio of Cu NRs is estimated to range from 2.5 to 5.6. As the length increases, the TSPR is slightly blue-shifted from 576 nm to 571 nm, and the intensity ratio of LSPR/TSPR is increased from 1.04 to 5.25. Two transmission electron microscopy (TEM) images of Cu NRs with LSPRs of 740 and 821 nm are shown in Figure 2b,c. The average length of these two samples is about 44.5 and 57.5 nm,

respectively. We note that the Cu NRs exhibit a rough surface, which is caused by the deposition of Cu atoms and surface diffusion during the anisotropic growth of Cu NRs [1]. The rough surface of Cu NRs implies that they have abundant surface hotspots due to localized SPR field enhancements. Meanwhile, the rough structure also creates an active surface caused by the increased surface area and exposed high-index facets.

Figure 1. Scheme of seed-mediated growth of Cu NRs and subsequent sulfidation.

Figure 2. (a) Extinction spectra of Cu NRs with LSPRs located at 740 (purple), 821 (yellow), 888 (green), 960 (blue), 1054 (red) and 1190 nm (black). (b,c) TEM images of Cu NRs with LSPR of 740 nm (b) and 821 nm (c).

Compared with Au and Ag, Cu is an abundant and inexpensive metal. However, Cu nanocrystals are easily oxidized, especially in aqueous solutions, resulting in: (1) the controlled synthesis of Cu nanostructures remains a challenge, (2) the stability of Cu nanocrystals in catalytic applications is not good. Here, an in situ sulfidation method is applied to prepare a copper sulfide shell coating on Cu NRs. At room temperature, NaHS ethanol solution (1 mM), as a sulfur source, was added into Cu NRs dispersed in toluene. Figure 3 illustrates the extinction spectra of NRs with the addition of the sulfur source. The initial Cu NRs exhibit a LSPR band at 938 nm. When the sulfur source is increased from 50 to 120 μ L, the LSPR is red-shifted to 1100 nm, 1140 nm, 1190 nm, with broadened width and decreased intensity, respectively. The TSPR band is also red-shifted from 572 nm to 595 nm. Figure 4 shows the TEM images of sulfurized Cu NRs with varied amounts of sulfur sources. A coating layer is clearly observed on the surface of the Cu NRs. The rough surface is kept after partial sulfidation. In fact, in situ sulfidation could further increase the roughness. The average layer thickness is about 1.2 nm in Figure 4a and 2.9 nm in Figure 4b, respectively. The results indicate the thickness of the sulfide layer increases with the increase in the S source. In experiments, the sulfidation affects the dispersibility of the

Cu NRs in toluene, which is caused by the damage of surface capping agents during the sulfidation process. When the amount of sulfur source is further increased to a very high level, the dispersibility of sample becomes poor.

Figure 3. Extinction spectra of Cu NRs when adding different amounts of sulfur source (1 mM NaHS).

Figure 4. TEM images of Cu NRs with the addition of (a) 10 μL and (b) 60 μL of NaHS solution. The insets show the amplifying TEM images around the tip region of sulfurized Cu NRs.

To reveal the composition of the coating layer on Cu NRs, we performed carefully structured characterizations of the sulfurized Cu NRs. Figure 5 shows the energy-dispersive X-ray spectroscopy (EDS) element mapping of sulfurized Cu NRs in scanning TEM (STEM). The feature of rough surface is clearly observed in the STEM image (Figure 5a). The merged image of element mapping shown in Figure 5B indicates the distribution of Cu, S, and Au along the NRs. The main component of these NRs is Cu, with an atomic percentage of 81.2%. A small amount of S distribution (16.9%) along the NRs is due to the partial sulfidation on the surface of Cu NRs. A trace of Au distribution (1.9%) along the NRs is caused by the atom diffusion during the synthesis of Cu NRs, which is consistent with previous reports [1].

Figure 5. STEM-EDS elemental analysis of the sulfurized Cu NRs: (a) STEM image, (b) merged element mapping, (c–e) element distributions of Cu, S, and Au. The atomic percentage is also shown.

The X-ray diffraction (XRD) patterns of initial and sulfurized Cu NRs are shown in Figure 6. The diffractive peaks of initial Cu NRs at 43.3° , 50.5° , and 74.1° are consistent with the diffractions from the (111), (200) and (220) planes of face-centered cubic (fcc) Cu. These three peaks of sulfurized Cu NRs shifted by about 0.2° to the left, to 43.1° , 50.2° , 73.9° , respectively. For the sulfurized Cu NRs, a raised wide band below 35° indicates that an amorphous structure may be formed after sulfidation. Three special peaks at 26.6° , 27.9° and 29.4° are matched with the (101), (0015), and (107) diffractions of the hexagonal close-packed (hcp) Cu_9S_5 ($\text{Cu}_{1.8}\text{S}$) phase. In addition, as can be seen in Figure S2, the three special peaks could correspond to the diffraction peaks at 26.5° (211), 26.6° (103), 27.9° (022) and 29.0° (113) of the orthorhombic Cu_7S_4 ($\text{Cu}_{1.75}\text{S}$) phase, or at 26.5° (002) and 29.2° (101) of the hcp Cu_2S phase. Therefore, the coating layer may be a variety of mixed phases of copper sulfide, and it is termed as Cu_{2-x}S in this work. The formed Cu_{2-x}S layer by partial sulfidation could protect the inside of the Cu from oxidation. Meanwhile, Cu_{2-x}S is a p-doped semiconductor associated with copper deficiency, supporting tunable SPRs in the NIR spectral region [34,35], and has an active surface for catalytic applications [36].

The structural characterizations demonstrate that the sulfurized Cu NRs consist of a Cu core and a Cu_{2-x}S shell. The formed Cu/ Cu_{2-x}S core/shell NRs integrate many advantages including: (1) the SPRs of Cu NRs have intense absorption and local field enhancements, (2) the rough surface is kept during the sulfidation, which provides large-area active surface of Cu_{2-x}S , (3) the copper ions of Cu_{2-x}S have both oxidizing and reducing properties, (4) Cu_{2-x}S is a functional semiconductor possessing optical absorption and hole-induced SPRs. All of these properties indicate that the prepared Cu/ Cu_{2-x}S is a promising material for photocatalytic application.

We performed the degradation of methyl orange (MO) to evaluate the photocatalytic performance of Cu/ Cu_{2-x}S core/shell NRs. Figure 7a compares the degradation of MO over Cu NRs and Cu/ Cu_{2-x}S NRs under natural light. The MO concentration is measured by the absorbance of MO at 464 nm (Figure S3). C_0 and C_t are the concentrations of MO dyes initially and at time t (min), respectively. The degradation rate is calculated by $(C_0 - C_t)/C_0$. For the Cu NRs under natural light, only 3.6% MO dyes are degraded after 40 min. For the Cu/ Cu_{2-x}S NRs under natural light, the degradation rate is 48.9% after 40 min, which is 13.6-fold higher than that of the Cu NRs. Figure 7b illustrates the degrada-

tion performance of Cu/Cu_{2-x}S NRs on MO dyes under the conditions of dark, natural light, and xenon lamp irradiation. Even under the dark condition, the sulfurized NRs exhibit a 35.7% degradation rate within 40 min. The dye degradation in the dark was reported previously for Cu_{2-x}S nanocrystals [37], and this may be due to a self-cyclic redox reaction of multivalent copper [18,26], or a low-temperature, thermocatalytic reaction in the dark system [38]. On the other hand, natural light can improve the degradation rate to 51.5% at 40 min, and xenon lamp irradiation can further improve the degradation rate to 62.6% at 40 min. Under natural light and xenon lamp irradiation, the degradation rates of the Cu/Cu_{2-x}S core/shell NRs at 40 min are 1.4 times and 1.8 times higher than those in darkness, respectively.

Figure 6. XRD patterns of Cu NRs before and after sulfidation. The bottom column diagram represents the standard diffraction pattern of Cu (#85-1326), Au (#04-0784), and Cu₉S₅ (#47-1748).

Figure 7. Logarithmic plots of C_t/C_0 as a function of time for MO degradation by (a) Cu and Cu/Cu_{2-x}S NRs under natural light, (b) Cu/Cu_{2-x}S NRs under three irradiation conditions (dark, natural light and xenon lamp).

The logarithmic plots, as a function of time, indicate that there is a two-stage process during the photocatalytic degradation reaction by the Cu/Cu_{2-x}S NRs. A pseudo-first-order equation $\ln(C_t/C_0) = kt$ is used to fit the experimental data (Figure S4), where k is the reaction rate constant (min^{-1}). There is only one k value of $9.4 \times 10^{-4} \text{ min}^{-1}$ for the Cu NRs under natural light, whereas for the sulfurized NRs, the k values of the two stages of the photocatalytic degradation process are $6.1 \times 10^{-3} \text{ min}^{-1}$ and $2.2 \times 10^{-2} \text{ min}^{-1}$,

respectively. In Figure S4b, the photocatalytic degradation reaction of Cu/Cu_{2-x}S NRs under each condition has two stages. Under the dark condition, the k values are $5.8 \times 10^{-3} \text{ min}^{-1}$ and $1.6 \times 10^{-2} \text{ min}^{-1}$, respectively. Under xenon lamp irradiation, the k values are $8.2 \times 10^{-3} \text{ min}^{-1}$ and $3.4 \times 10^{-2} \text{ min}^{-1}$, respectively. The two stages are supposedly related to the dye adsorption process [11] and photocatalytic degradation reaction [39]. The dye adsorption process by catalysts can be demonstrated in the dark condition [40–42]. In this work, the kinetic process in the dark is clearly divided into two stages, indicating the coexistence of the adsorption process and degradation reaction under the dark condition.

We performed another photocatalytic reaction for methyl blue (MB) by Cu/Cu_{2-x}S NRs. Figure S5 illustrates the degradation performance of Cu/Cu_{2-x}S NRs on MB dyes under xenon lamp irradiation. The degradation is faster for MB molecules because the stability of MB dyes is poorer than that of MO molecules [18,42]. The results show that 33% of MB molecules with no catalysts are spontaneously degraded under xenon lamp irradiation after 20 min (Figure S5). On the contrary, no MO degradation is observed under xenon lamp irradiation after 40 min when the catalyst is not added (see Figure S6).

The CB and VB edge potentials of Cu₂S are located at -4.1 and -5.5 eV, respectively, with a band gap of 1.4 eV (~ 886 nm) [37]. For the CuS, the CB and VB edge potentials are -2.2 and -4.45 eV, respectively, and the band gap is 2.25 eV (~ 551 nm) [37]. The optical responses of Cu_{2-x}S are not observed in the extinction spectra because the SPRs of Cu NRs are still strong after sulfidation and the amount of Cu_{2-x}S is small. Under light irradiation, the interaction between Cu NRs and the Cu_{2-x}S layer leads to an increased amount of photoexcited charge carriers and the effective separation of electrons and holes [35,36]. The photoexcited electrons (e^-) and holes (h^+) migrate to the surface of Cu/Cu_{2-x}S NRs, generating active species (such as the hydroxyl radicals of $\cdot\text{OH}$ and superoxide radicals of $\cdot\text{O}_2^-$) for a photocatalytic degradation reaction. To investigate the main active species generated during the decomposition process of MO, we used methanol and disodium ethylenediaminetetraacetate (EDTA) as scavengers to examine $\cdot\text{OH}$ s and h^+ , respectively [40]. Figures S6 and S7 show the effect of two scavengers on the degradation rate of MO degradation by Cu/Cu_{2-x}S NRs under xenon lamp irradiation. Compared with the scavenger-free sample, with a degradation rate of 89% at 40 min, the photocatalytic degradation rate decreases to 10% and 4% after the addition of methanol and EDTA, respectively. The result indicates that both $\cdot\text{OH}$ and h^+ are the major reactive species [40,41]. The MO molecules could be degraded into CO_2 , H_2O , NO_3^- , SO_4^{2-} , and other incomplete products after the reaction with active radicals [18]. Bubbles can be observed during the degradation process under natural light (Figure S8), which is due to the product of CO_2 from MO degradation.

3. Materials and Methods

3.1. Materials

Tetrachloroauric(III) acid tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), copper(II) chloride dehydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 99.999%), toluene (99.5%), acetone (99.5%), isopropanol (99.7%), ethanol absolute (99.7%), methanol, methyl orange (MO), methyl blue (MB), and ethylenediaminetetraacetate (EDTA, 99.5%) were purchased from Sinopharm Chemical Reagent limited corporation (Shanghai, China). Sodium hydrosulfide hydrate (68–72%), borane-tert-butylamine complex (TBAB, 97%), and oleylamine (80–90%) were purchased from Aladdin (Shanghai, China). Oleylamine (50%) was purchased from TCI Shanghai (Shanghai, China).

3.2. Synthesis of Au Seeds

Au seeds were synthesized by referring to the method of Jeong [1]. Oleylamine (10 mL, 50%) was loaded into a 100 mL three-necked flask with nitrogen flushing for 10 min at room temperature (25 °C). Then, 10 mL anhydrous toluene was added into the flask, followed by nitrogen purging for 10 min. Afterward, 100 mg of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ was added into the flask with N_2 purging for another 10 min. A solution mixture of 0.20 mmol (17 mg) of TBAB, 1 mL of oleylamine (50%) and 1 mL of anhydrous toluene was

quickly injected into the mixture, followed by stirring for 1 h at 25 °C. After the reaction, the product was precipitated with 50 mL of acetone and centrifuged at 6000 rpm for 5 min. Finally, the precipitate was dispersed in 40 mL of toluene for storage. The average size of Au seeds with a deep-red color was 7.8 nm.

3.3. Synthesis of Cu NRs with Tunable Length

For preparing Cu NRs, 0.5 mmol (85 mg) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 10 mL of oleylamine (80–90%) were firstly mixed in a 50 mL three-necked flask at room temperature. Nitrogen blowing was applied and maintained until the end of reaction. The mixture was heated to 180 °C, and stirred within 20 min. The reaction solution was maintained at 180 °C for another 30 min. At room temperature, the copper dichloride was partially dissolved, and the solution turned blue. At about 160 °C, the solution turned from blue to green and quickly turned yellow, indicating the reduction of Cu(II) to Cu(I). After heating for 30 min, a certain amount of Au seeds was injected into the mixture at 180 °C. When the Au seeds with a deep-red color were added, the color of the solution changed rapidly from yellow to orange–red. The reaction was allowed to continue at 180 °C for one hour. After the reaction was completed, the three-necked flask was placed in cold water to cool down to room temperature. Then, 10 mL of isopropanol was added to precipitate the products. The sample was centrifuged at 3000 rpm for 3 min and the precipitates were washed with 5 mL of toluene. Finally, the precipitates were re-dispersed in toluene.

3.4. In Situ Sulfidation of Cu NRs

Sodium hydrosulfide ethanol solution (1 mM) was used as the sulfur source, and 2 mL of Cu NR toluene solution was uniformly mixed with different amounts of sulfur source (50, 80, 120 μL) for 5 min. After that, the mixed solution was centrifuged at 3000 rpm for 3 min to obtain a black precipitate. The precipitate was re-dispersed in 2 mL of toluene.

3.5. Characterization

Extinction spectra were measured by a Varian Cary 5000 UV-Vis-NIR (Agilent, Santa Clara, CA, USA) spectrophotometer. XRD patterns were recorded by Bruker D8 advanced XRD (Karlsruhe, Germany) under $\text{Cu-}\alpha$ irradiation ($\lambda = 0.15418 \text{ nm}$). TEM analysis was performed by a JEOL JEM 2100 microscope (Tokyo, Japan). STEM imaging and EDS mapping were acquired on a JEOL JEM-ARM200F microscope (Tokyo, Japan) operated at 200 kV with a Schottky cold-field emission gun in Wuhan University.

3.6. Photocatalytic Degradation of Dye

A concentrated toluene solution of sulfurized Cu NRs was transferred to a 20 mL small beaker, which was then placed in a fume hood to air dry. After air drying, the solid was ultrasonically dispersed in 3 mL of water for subsequent degradation experiments. For photocatalytic degradation, 1.5 mL of 20 mg/L MO aqueous solution was mixed with 1.5 mL catalyst aqueous solution in a silica cuvette with optical path length of 1 cm. The sample was left undisturbed under different conditions (dark, natural light, xenon lamp irradiation). The xenon lamp irradiation was performed by placing the sample 10 cm away from a xenon lamp source (PLS-SXE300+) (Beijing, China). The irradiation power of xenon lamp was measured as 1.5 W. The concentration of MO dyes was measured every 5 min. The MO concentration is measured through directly measuring the absorbance of the sample at 464 nm by an UV-Vis-NIR spectrophotometer (Varian Cary 5000, Agilent, Santa Clara, CA, USA). The degradation test of MB dyes was carried out under xenon lamp irradiation. The concentration of 1.5 mL of MB was 40 mg/L. For the dye stability experiment, 1.5 mL of 20 mg/L MO solution and 1.5 mL of 40 mg/L MB solution were mixed with 1.5 mL of water, respectively. The samples were placed under xenon lamp irradiation and the absorption intensity was monitored.

EDTA and methanol were added in the photocatalytic degradation of MO to investigate the main active species, such as h^+ , $\cdot\text{OHs}$ [40,41]. The experiments were carried out

under the illumination of xenon lamp. Catalyst aqueous solution (1 mL) was added into 1 mL of 20 mg/L MO solution. Subsequently, 0.2 mL of water, methanol, or 0.05 M EDTA was added into the solution. Then, the absorption intensity of dyes was measured every 5 min.

4. Conclusions

In this work, Cu NRs with tunable LSPRs were successfully synthesized by the seed-mediated method, and the outermost layer of Cu NRs was transformed into the Cu_{2-x}S phase by a convenient in situ sulfidation method. The thickness of the Cu_{2-x}S layer could be adjusted by controlling the amount of S source. Compared with the pure Cu NRs, the Cu/Cu_{2-x}S core/shell NRs integrate plasmonic enhancement, functional Cu_{2-x}S material and a rough active surface, demonstrating an excellent photocatalytic dye degradation performance. Moreover, the coating of Cu_{2-x}S improves the stability of Cu NRs in the photocatalytic reaction. The experimental results show that the degradation rate of Cu/Cu_{2-x}S core/shell NRs at 40 min is 13.6 times higher than that of the pure Cu NRs, under natural light. The results in this work demonstrate a promising way to construct Cu nanostructures in optical and catalytic applications.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12020147/s1>, Figure S1: absorption spectrum and TEM image of Au seeds, Figure S2: XRD pattern analysis of Cu/Cu_{2-x}S NRs, Figure S3: absorption spectra of MO photocatalytic degradation, Figure S4: curve fitting for the plot of ln(C_t/C₀) vs. time, Figure S5: influence of radical scavengers on the MO degradation, Figure S6: sample photograph after MO degradation, Figure S7: absorption spectra of MO photocatalytic degradation with scavengers, Figure S8: photocatalytic degradation of MB dyes.

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Data Availability Statement: The supplemental data are provided in Supplementary Materials. Data presented in this study are available on request from the corresponding author.

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