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Growth and Photocatalytic Activity of Dendrite-like ZnO@Ag Heterostructure Nanocrystals

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ABSTRACT: Dendrite-like ZnO@Ag heterostructure nanocrystals are designed and fabricated by a facial two-step chemical method in a large scale. The heterostructure nanocrystals are composed of single crystal Ag nanowires as trunks and highly dense (0001) oriented ZnO nanorods as branches. ZnO nanorods with diameters of about 50–400 nm are vertically grown on the six lateral surfaces of the Ag nanowires. Ultrathin ZnO nanowires or nanotubes with a diameter of less than 30 nm are decorated on the ZnO nanorods. The photocatalysis test shows that the ZnO@Ag heterostructures exhibit a higher photocatalytic activity than the pure ZnO nanorods, thereby implying that the Ag/ZnO interfaces promote the separation of photogenerated electron–hole pairs and enhance the photocatalytic activity.

1. Introduction

Growth of heterogeneous nanocrystals with designed structures is one of the most important goals in the development of advanced nanomaterials.^{1–13} Recently, the fabrication of branched dendritic nanowire structures has attracted great research interest due to the increase of connection points in such structures, which provide a means for parallel connectivity and interconnection of functional elements. Thus, a high degree of complexity in such structures widens their application windows greatly.¹⁴ An enormous variety of such structures have been synthesized by a variety of techniques with ZnO nanowires on a variety of nanowires.^{8–11} For example, Lao et al. fabricated hierarchical ZnO nanostructures on In₂O₃ nanowires by a thermal vapor transport and condensation technique.⁹ High-density ZnO nanorods were grown on one-dimensional nanomaterials, such as carbon nanotubes, GaN nanowires, etc., by thermal chemical vapor deposition of Zn at temperature 500 °C.⁸ ZnO nanomaterials may play an important role in photocatalytic degradation of organic pollutants owing to their high photosensitivity, stability and wide direct band gap (3.37 eV), and high photocatalytic efficiency.^{15–17} In particular, transition metals, such as platinum, silver, iron, etc., could improve the charge transfer by trapping the photoinduced charge carriers and enhance the performance of the photochemical degradation process,^{18–24} which is caused by the recombination of electron and hole prior to the superoxide activation process.^{22,25} Silver nanoparticles can be in situ grown on the ZnO nanocrystals by chemical methods, and those synthesized Ag/ZnO heterostructures enhance the photocatalytic performance.^{21,22,24,26} With the assistance of microwave radiation, silver particles or clusters were inserted to 3-D mesoporous ZnO nanocrystals.²⁷ Although there are a large number of reports on the synthesis of Ag/ZnO heterostructures, there is no report on the growing ZnO on Ag nanowires so far in the literature. The present report is focused on the fabrication of a novel type of branched heterostructures, i.e. the dentrite-like ZnO@Ag nanowire heterostructure, by a simple chemical method. Moreover, the micro/nanostructures

and the photocatalytic activity properties of this novel heterostructure are also reported here.

2. Experimental Section

The ZnO@Ag heterostructure nanocrystals were fabricated by a facial two-step chemical method. The base Ag nanowires were synthesized by a classical polyol process.²⁸ First, 5 mL of ethylene glycol (EG) was injected into a 20 mL lidded glass bottle and preheated for 20 min at ~130 °C in an oil bath. Then, 5 mL of EG solution of AgNO₃ (0.1 M, ≥99.8%, Riedel-de Haen) and 5 mL of EG solution of poly(vinyl pyrrolidone) (PVP, $M_w \approx 55000$) (3 mM) containing Na₂S·9H₂O (1 mM) were injected into the bottle within 10 s and 2 min, respectively. Adding Na₂S into the reaction system forms Ag₂S colloids at the initial stage, which functions as both seeds and catalyst in the silver reduction.^{29,30} The reaction with magnetic stirring lasted for another 3 h. The product of Ag nanostructures was washed thoroughly with acetone and then with ethanol by centrifugation at 6000 rpm for 20 min. After that, the Ag nanostructures were deposited at the bottom of the centrifuge tube and the supernatants containing residual EG or/and PVP were removed with a syringe. Finally, the purified Ag nanostructures were preserved in ethanol to fabricate the ZnO@Ag heterostructure.

ZnO nanostructures can be facially fabricated by chemical solution routes.^{31–34} In this case, the synthesis of ZnO nanostructures was conducted by the thermal decomposition of Zn^{II} amino complex with reagent grade chemicals, as described in the literature.^{31,32} In the ZnO synthesis procedure, an equimolar (1 mM) aqueous solution of zinc nitrate, Zn(NO₃)₂·4H₂O, and hexamethylenetetramine (HMT), C₆H₁₂N₄, was placed in an oil bath at ~95 °C for 2 h with magnetic stirring. To fabricate ZnO@Ag heterostructures, a certain volume of Ag-nanowire–ethanol solution was added to the above reaction mixture and ultrasonic agitation was undertaken for about 20 min before the thermal process. When the chemical reaction was finished, the precipitates were washed thoroughly with ethanol by centrifugation at 6000 rpm for 20 min. Surfactant is generally used in the synthesis of Ag/ZnO systems^{35,36} to form heterointerfaces of the two crystals with a large lattice mismatch. In the present work, however, we did not employ any surfactant in the fabrication of Zn@Ag heterostructures. The intermolecular dehydrolysis is suggested to play a significant role in the formation of Ag/ZnO heterostructure in the absence of surfactant.²⁴

The morphology of as-deposited Ag, ZnO and ZnO@Ag nanostructures were characterized by scanning electron microscopy (SEM, JEOL 6300F and JEOL 6390). Chemical compositions were analyzed with an X-ray energy dispersive spectroscope (EDS, BRUKER AXS) attached to the SEM. The crystal structure was identified by powder X-ray diffraction (XRD, Philips, PW-1830 X-ray diffractometer) with

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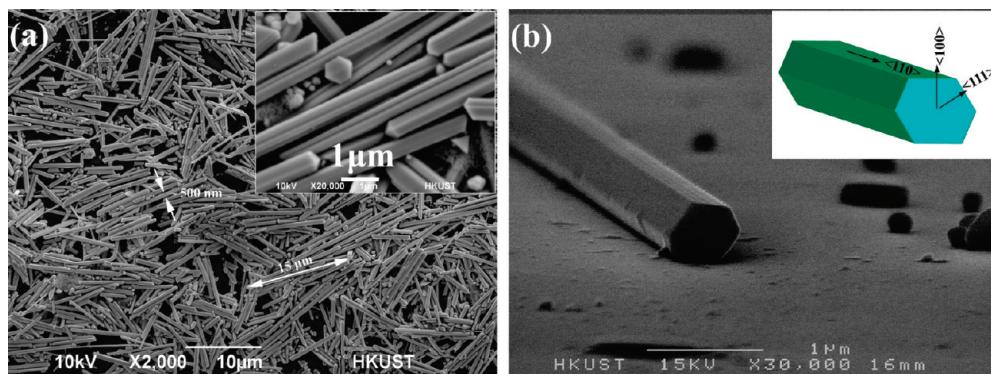


Figure 1. SEM images of as-synthesized Ag nanostructures. (a) Faceted Ag nanowires and particles and a high magnification image in the inset. (b) A hexagon-like cross-section of an Ag nanowire with a schematic depicted in the inset, where the Ag nanowire has a face centered cubic (fcc) structure and is axially oriented in the $\langle 110 \rangle$ direction and bounded by four $\{111\}$ and two $\{100\}$ surfaces.

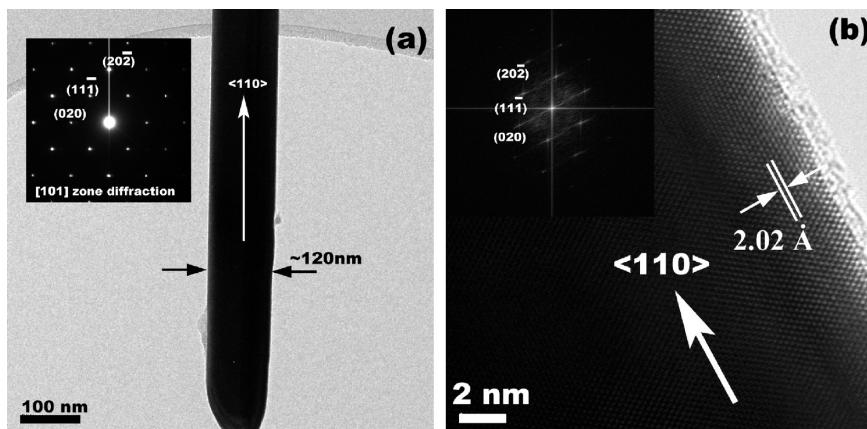


Figure 2. (a) TEM image of a single Ag nanowire with a diameter of about 120 nm and the corresponding SAED pattern as the inset. (b) HRTEM image of the fringe of the Ag nanowire shown in Figure 2 (a). The inset is the corresponding FFT pattern, showing the Ag nanowire axially oriented in the $\langle 110 \rangle$ direction.

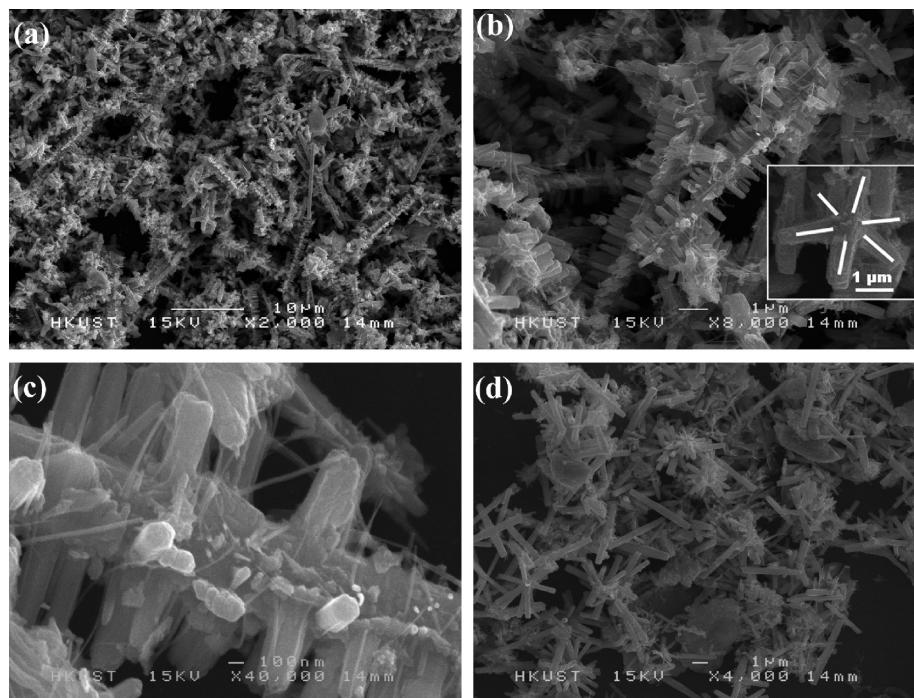


Figure 3. (a–c) SEM images of the dendrite-like ZnO@Ag heterostructure with different magnifications. The Ag content of the ZnO@Ag heterostructure crystals is about 8 atom %. (d) SEM image of pure ZnO nanorods fabricated by the thermal decomposition of Zn^{II} amino complex.

a 1.5405 Å Cu K α rotating anode point source operated at 40 kV and 40 mA. Microstructure analysis was carried out by high resolution

transmission electron microscopy (HRTEM, JEOL 2010F). X-ray photoelectron spectroscopy (XPS) measurement was performed with

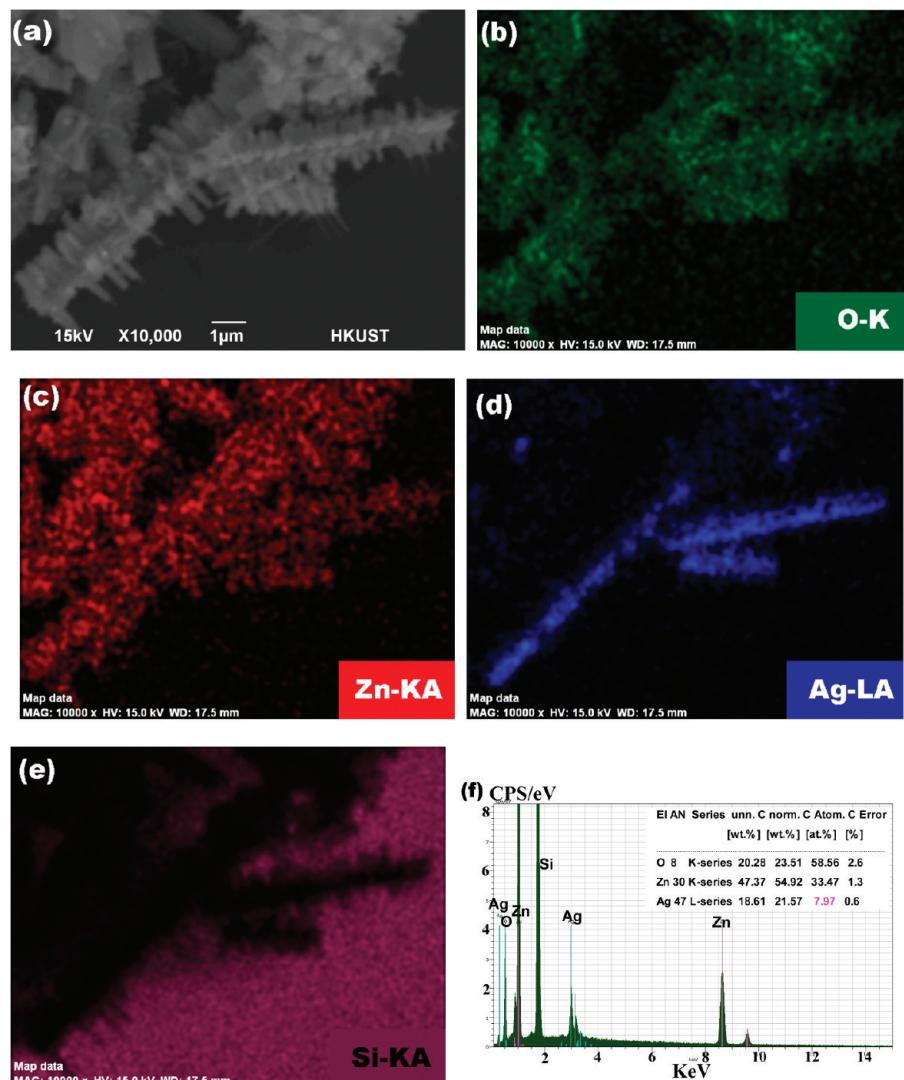


Figure 4. (a) Selected image of the dentrite-like ZnO@Ag heterostructure for the EDS mapping analysis. The corresponding elemental mapping images for O, Zn, Ag, and Si are presented in (b), (c), (d), and (e), respectively. (f) The elemental spectra and composition of the ZnO@Ag heterostructure crystals revealed by EDS analysis.

a PHI 5600 multitechnique system by using a monochromatic Al K α X-ray source. All core-level spectra were referenced to the C 1s neutral carbon peak at 284.8 eV. For photocatalytic measurement, 10 mg of each catalyst was suspended in 200 mL of methylene blue (MB) aqueous solution (20 ppm), and then the mixture was put into quartz tubes and agitated overnight in the absence of light to attain equilibrium adsorption on the catalyst surface. Ultraviolet (UV) irradiation was carried out by using a 500 W fluorescent Hg-lamp. After a given irradiation time, about 3.5 mL of the mixture was withdrawn and the catalysts were separated through centrifugation. The photocatalytic degradation process was monitored by UV-vis spectrophotometer (UV-2450) to measure the absorption of MB at the wavelength of 664 nm.

3. Results and Discussion

3.1. Characterization of Ag Nanostructures. Figure 1 (a) gives the morphology of the as-synthesized Ag nanostructures on a silicon template, showing large-scale productive Ag nanowires and nanoparticles. The length of the Ag nanowires ranges from 5 to 20 μ m, and the diameter is about 100–800 nm. As shown in the inset of Figure 1 (a), the Ag nanowires or particles have regular facets. About 90% of Ag nanowires possess hexagon-like cross sections, which are also called the truncated-rhombic cross sections. Figure 1 (b) shows an Ag nanowire with the hexagon-like cross-section, which is similar to the top-down created Ag nanowire found in the molecular

dynamics simulations.³⁷ The truncated-rhombic Ag nanowire has a face centered cubic (fcc) structure and is axially oriented in the $\langle 110 \rangle$ direction and bounded by four $\{111\}$ and two $\{100\}$ surfaces, as shown in the inset of Figure 1 (b). The truncated-rhombic nanowires were predicted to be energetically more favorable than the rhombic structure³⁸ and have been specifically observed during in situ HRTEM observations of the top-down Ag nanowire fabrication.^{39,40} The present work demonstrates that the bottom-up wet-chemical method is able to fabricate the truncated-rhombic Ag nanowires. Usually, Ag nanowires fabricated by the similar PVP-assisted polyol reduction^{41–43} have a pentagonal cross-section with 5-fold symmetry. The multiply twin-induced pentagonal geometry of Ag nanowires is a stable structure produced by chemical growth methods.^{41–44} It should be noted that the diameter of pentagonal Ag nanowires is generally less than 70 nm,^{41–44} while in this study, the diameter of Ag nanowire is more than 100 nm. Therefore, the geometry of Ag nanowires might be diameter-dependent, which should be clarified by further work.

Figure 2 (a) is the TEM image of a single Ag nanowire with the diameter of about 120 nm and the corresponding selected-area electron diffraction (SAED) pattern as an inset. The SAED pattern shows the [110] zone diffraction of a face centered cubic (fcc) single crystal, thereby indicating that the Ag nanowire is

a single crystal and growth is along a preferential $\langle 110 \rangle$ direction. Figure 2 (b) gives the HRTEM image of the fringe of the Ag nanowire shown in Figure 1 (a). The inset is the corresponding fast Fourier transform (FFT) pattern, which also confirms that the truncated-rhombic Ag nanowire is axially oriented in the $\langle 110 \rangle$ direction. As shown in Figure 1 (b), the plane fringe with a 2.02 Å crystalline plane spacing is assigned to the {200} planes. According to ref 37 and the TEM results, the sides of truncated-rhombic Ag nanowire are bounded by four {111} and two {100} surfaces.

3.2. Characterization of ZnO and ZnO@Ag Heterostructures. The ZnO@Ag heterostructure and ZnO samples were dispersed in ethanol and spread onto a silicon template for SEM observations. Figure 3 (a)–(c) shows the SEM images of as-synthesized ZnO@Ag heterostructure with different magnifications. The Ag content of the ZnO@Ag heterostructure crystals shown in Figure 3 is about 8 atom % revealed by EDS. As shown in Figure 3 (a), large-scale ZnO@Ag heterostructure crystals are synthesized by the two-step chemical method. Figure 3 (b,c) gives the SEM images with higher magnifications of the ZnO@Ag heterostructures, showing clearly the dendrite morphology. A dendrite-like ZnO@Ag heterostructure consists of a main trunk of the Ag nanowire and highly dense branches of ZnO nanorods. Interestingly, all ZnO nanorods, one by one along the Ag nanowire length axis, vertically stand on the lateral surfaces of the Ag nanowire, as shown in Figure 3 (b). The diameter of the ZnO nanorods ranges from 50 to 400 nm, and the length is about 1 μm . As shown in Figure 1, most of the Ag nanowires possess hexagon-like cross sections. The ZnO nanorods grow along six directions, as highlighted in the inset of Figure 3 (b), meaning that the ZnO nanorods grow on the {111} and {100} facets. Figure 3 (c) illustrates that ZnO nanowires with the diameter less than 20 nm coexist with the ZnO@Ag heterostructure crystals. The cross-sections of the ZnO nanorods possess hexagonal geometry, which indicates that the ZnO is preferentially growing along the $\langle 0001 \rangle$ direction. No obvious interfaces can be found between the ZnO nanorods and the Ag nanowire in the Figure 3 (c). If we did not add any Ag nanowires into the reaction solution, we synthesized large-scale pure ZnO nanorods, with diameter about 100–400 nm and length of $\sim 4 \mu\text{m}$, as shown in Figure 3 (d).

Figure 4 (a) shows a selected area for the elemental mapping by EDS and Figure 4 (b–e) presents the O, Zn, Ag, and Si mappings, respectively. As expected, the Si intensity drops in the sample region (Figure 4 (e)). The Ag signal is very strong in the middle of the ZnO@Ag heterostructure crystals, while the Zn and O signals are detected around the Ag positions. The result confirms again that the dendrite-like ZnO@Ag heterostructure crystals can be successfully fabricated by the two-step chemical method. Figure 4 (f) gives the elemental spectra and composition of the ZnO@Ag heterostructure crystals revealed by EDS analysis, in which the Ag content is about 8 atom %.

Figure 5 illustrates the XRD patterns of the ZnO@Ag heterostructure crystals, where the XRD patterns of ZnO and Ag nanowire products are also shown for comparison. The wurtzite ZnO and fcc Ag phases coexist in the ZnO@Ag heterostructure crystals, and the XRD patterns match their JCPDS files nos. 36-1451 and 04-0783, respectively. Furthermore, no remarkable shifts of any diffraction peaks are detected, which indicates that no ZnO and Ag related solid solution is formed and the change in the lattice parameters of the ZnO nanocrystals is negligible.

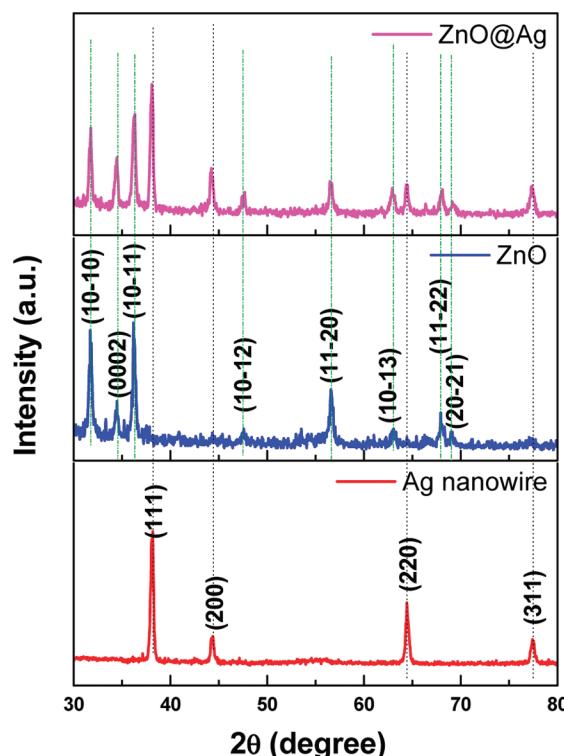


Figure 5. XRD patterns of the ZnO@Ag heterostructure crystals, where the XRD patterns of pure ZnO nanorods and pure Ag nanowires are also shown for comparison.

3.3. Growth Mechanism of the ZnO@Ag Heterostructures. TEM and HRTEM analysis provides more information of the microstructure and about the growth mechanism of the dendrite-like ZnO@Ag heterostructure. Figure 6 (a) shows a typical TEM image of the dendritic ZnO@Ag heterostructure crystals on the carbon-coated Cu grid. ZnO nanorods with diameter of about 350 nm are distributed densely along the Ag nanowire. The inset is the HRTEM image of the ZnO nanorod marked by the arrow, confirming that the preferential ZnO growth direction is along the $\langle 0001 \rangle$ direction. Furthermore, ultrathin ZnO nanowires with diameters less than 30 nm are found on the tops of ZnO nanorods or scattered on the TEM-carbon films, which are marked by circles in Figure 6 (a). Most of the ultrathin ZnO nanowires are tubular along their whole length, or at least at their tops, as shown in Figure 6 (b), where the diameter of the ZnO nanotube is only 15 nm and the preferential growth is also along the $\langle 0001 \rangle$ direction. The wall thickness of the tube is estimated to be about 5–10 nm, varying along the length direction. ZnO nanowires or nanotubes with diameters in the range of 10–30 nm are generally fabricated by the hydrothermal growth method.^{31,34,45} However, ultrathin ZnO nanotubes with diameter of less 20 nm are less reported.

If a Ag nanowire is densely decorated by the ZnO nanorods or nanowires, the cross-section of the ZnO@Ag heterostructure crystal would become too thick for TEM to examine. So, a ZnO@Ag heterostructure decorated with sparse ZnO nanorods, as shown in Figure 6 (c), is the best candidate for TEM examination. Three insets of Figure 6 (c) are the SAED patterns of the Ag trunk (A), the ZnO nanorod branch (B), and the interface (C), respectively, in which circle and box symbols are assigned to the Ag and ZnO crystals, respectively. The SAED patterns from the Ag trunk are a mixture of the Ag [110] zone diffraction, similar to that shown in Figure 2 (a), and the ZnO [1210] zone diffraction. The mixed diffraction is attributed to

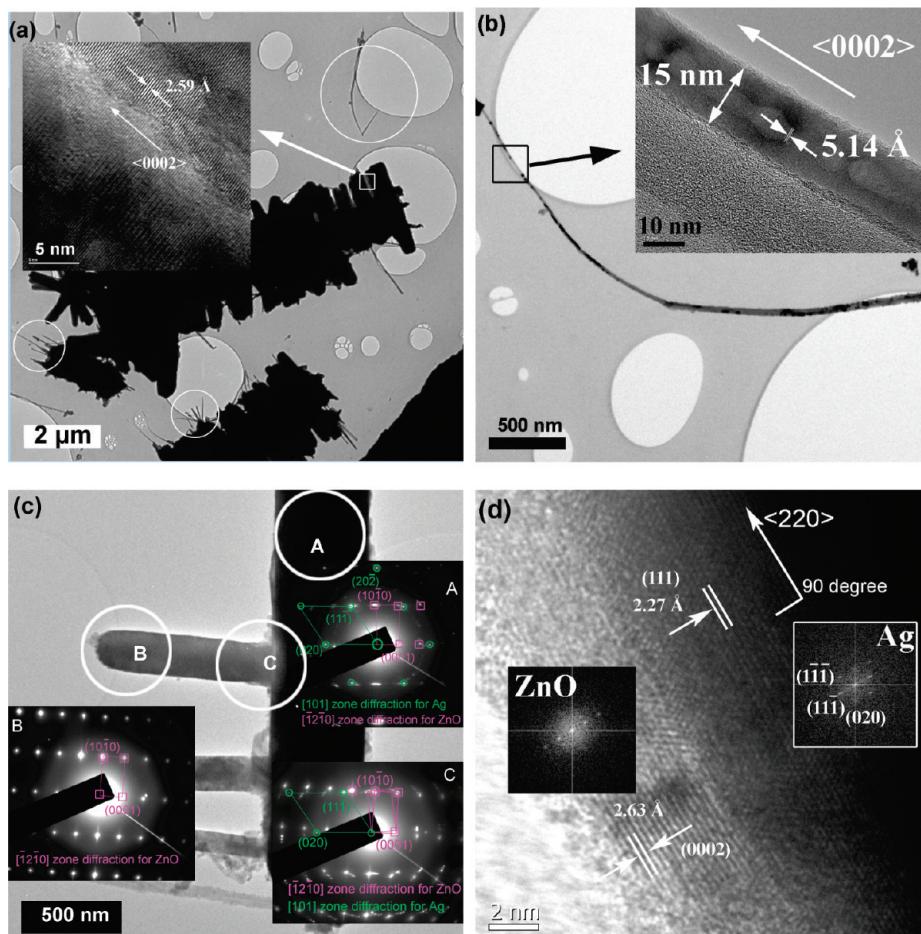


Figure 6. (a) A typical TEM image of the dendrite-like $\text{ZnO}@\text{Ag}$ heterostructure crystal on the carbon-coated Cu grid. The inset is the HRTEM image of the ZnO nanorod marked by the arrow. Ultrathin ZnO nanowires are marked by circles. (b) HRTEM image of an ultrathin ZnO nanowire. (c) A TEM image of few ZnO decorated Ag nanowire with the insets of SAED patterns corresponding to the Ag trunk (A), ZnO nanorod branch (B), and the interface (C). The circle and box symbols are assigned to the Ag and ZnO crystals, respectively. (d) HRTEM image of the interface between ZnO and Ag . The two insets are the FFT patterns corresponding to ZnO and Ag , respectively.

the ZnO crystal nucleus attached on both sides of the Ag nanowire. Inset B shows only the $\text{ZnO} [\bar{1}\bar{2}\bar{1}0]$ zone diffraction pattern, indicating that the ZnO nanorod is a single hexagonal wurtzite crystal and preferentially grows along the $\langle 0001 \rangle$ direction. Inset C shows the SAED patterns just like a combination of those shown in Insets A and B, which indicates that the ZnO nanorod grows on the $\text{Ag} (100)$ plane. Figure 6 (d) shows a HRTEM image of the interface between the ZnO nanorod and the Ag nanowire. Two insets are the FFT patterns from the ZnO and Ag HRTEM images, respectively. The plane fringe with a 2.27 \AA crystalline plane spacing is assigned to the $\text{Ag} \{111\}$ planes, and the growth direction of the Ag nanowire is along the $\langle 220 \rangle$ direction. The plane fringe with a 2.63 \AA crystalline plane spacing is assigned to the $\text{ZnO} \{0002\}$ planes. Figure 6 (d) is also the evidence of the ZnO growth on the $\text{Ag} \{111\}$ planes.

From the SEM and TEM images, we may propose a possible growth sequence of the dendrite-like $\text{ZnO}@\text{Ag}$ heterostructure. At first, a single crystal Ag nanowire with the truncated-rhombic cross-section is dispersed in the zinc nitrate and HMT solution. The Ag nanowire has four $\{111\}$ and two $\{100\}$ lateral surfaces, on which ZnO nanorods are grown up. Then, ZnO crystal nucleus are formed on the Ag lateral surfaces by the thermal decomposition of Zn^{II} amino complex and following by the preferential growth along the $\langle 0001 \rangle$ direction during the

continuous chemical reaction. The ZnO nanorods grow vertically to the Ag nanowire length direction to minimize the interaction or competition among themselves. Lastly, ultrathin ZnO nanowires or nanotubes could also grow from the ZnO nanorods.

3.4. Surface Structure of the $\text{ZnO}@\text{Ag}$ Heterostructure. The XPS analysis is carried out to investigate the surface structure of the $\text{ZnO}@\text{Ag}$ heterostructure sample shown in Figure 3, and the results are shown in Figure 7. The binding energies in the XPS spectra are calibrated by using that of $\text{C} 1s$ (284.8 eV). All peaks in the XPS full spectrum shown in Figure 7 (a) can be ascribed to Zn , Ag , O , and C elements. The presence of C comes mainly from pump oil in the vacuum system of the XPS equipment. It is indicated that the $\text{ZnO}@\text{Ag}$ heterostructure is only composed of three elements, Zn , Ag , and O , which is consistent with the above XRD and EDS results. The high-resolution spectra for O , Zn , and Ag species are shown in Figures 7 (b), (c), and (d), respectively. In Figures 7 (b) and (c), the peaks profiles are symmetric and center at 531.5 and 1022.2 eV , which are attributed to $\text{O} 1s$ and $\text{Zn} 2p_{3/2}$ of ZnO specimen, respectively.^{46,47} Interestingly, the binding energies of $\text{Ag} 3d_{5/2}$ and $\text{Ag} 3d_{3/2}$ for the $\text{ZnO}@\text{Ag}$ heterostructures shift remarkably to the lower binding energy compared with the corresponding values of the synthesized pure metallic Ag (the standard binding energies of $\text{Ag} 3d_{5/2}$ and $\text{Ag} 3d_{3/2}$ for bulk Ag

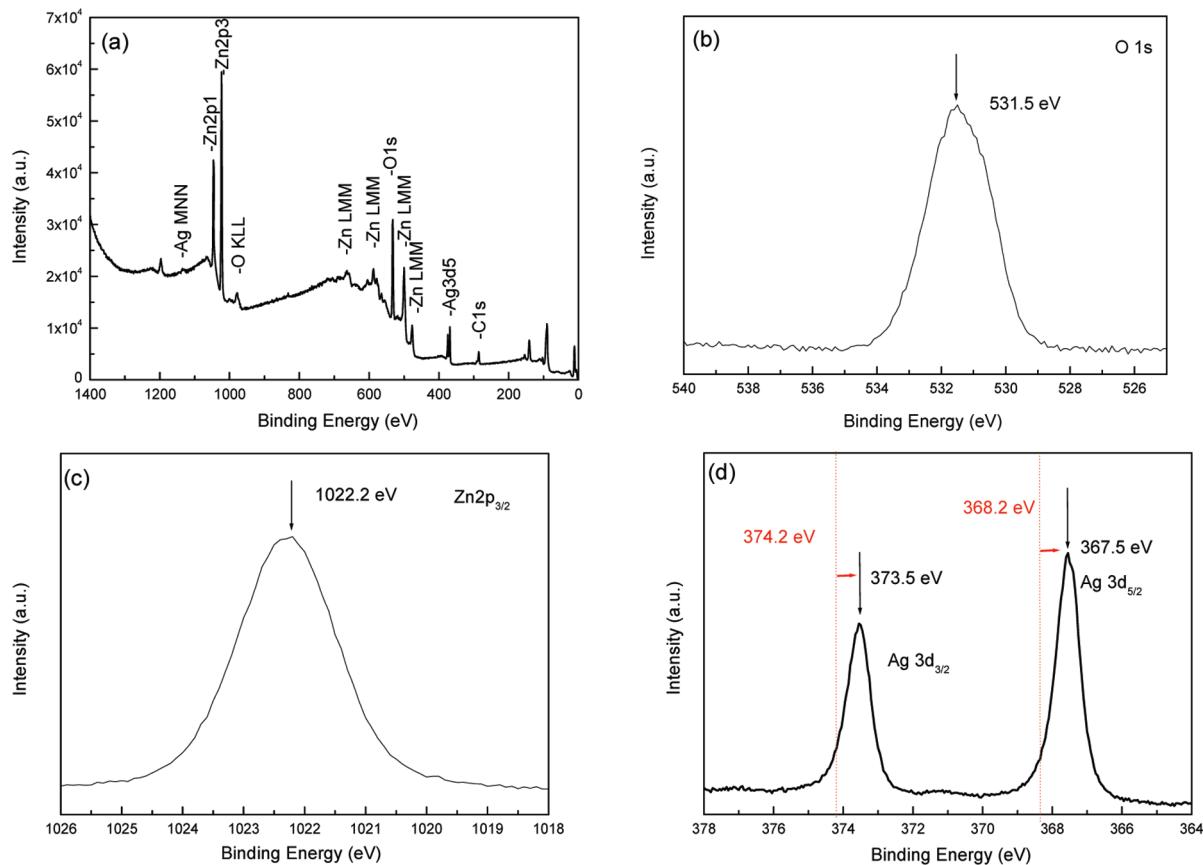


Figure 7. (a) The XPS full spectrum of the ZnO@Ag heterostructure sample shown in Figure 3. The high-resolution spectra for O, Zn, and Ag species are shown in (b), (c), and (d), respectively.

are about 368.2 and 374.2 eV,⁴⁶ respectively). Zheng et al. also found a similar negative shift of the Ag binding energy in the dimer-type Ag particle/ZnO heterostructure nanocrystals, which is attributed to the Ag/ZnO interaction.²⁴ The band structure of metal/semiconductor heterostructures, such as Au/ZnO and Ag/ZnO, was proposed by Wang et al.⁴⁸ and Zheng et al.²⁴ Since the work function of silver (4.26 eV) is smaller than that of ZnO (5.2–5.3 eV), electron transfer occurs from Ag to ZnO at the interfaces of the ZnO@Ag heterostructures,⁴⁸ resulting in a new Fermi energy level in ZnO@Ag heterostructures. The binding energy of monovalent Ag is lower than that of zerovalent Ag,⁴⁶ therefore, the binding energies of Ag 3d_{5/2} and Ag 3d_{3/2} shift to the lower ones in the ZnO@Ag heterostructures.

3.5. UV-Light Driven Photocatalysis of the ZnO@Ag Heterostructures. A representative organic pollutant MB was used to evaluate the photocatalytic performance of the dendrite-like ZnO@Ag heterostructure. Xu et al.⁴⁹ investigated the influence of particle size of TiO₂ on the photocatalytic degradation of MB and proposed that photodegradation of MB obeyed the pseudo-first-order kinetics law. The first-order rate constant for degradation, *k*, can be obtained from the first-order plot according to eq 1:^{49,50}

$$\ln\left(\frac{C}{C_0}\right) = -kt \quad (1)$$

where *C*₀ is the initial concentration and *C* is the concentration after the MB degradation for time *t*. Figure 8 shows the photodegradation curves of MB in the form of ln(*C/C*₀) as a function of time and the determined values of the reaction

rate constant, *k*, from linear fitting for different samples. The reaction rate constant, *k*, for the pure Ag nanowires is $3.0 \times 10^{-4} \text{ min}^{-1}$, so small similar to the blank one. Therefore, the degradation of MB over the pure Ag nanowires is negligible. Notably, the ZnO@Ag heterostructures exhibit higher photocatalytic activity compared to the pure ZnO nanorods and the ZnO@Ag heterostructure with the Ag content of about 8 atom % shows the highest photocatalytic activity. Increasing the Ag content in the ZnO@Ag heterostructure from 8 atom % to about 11 atom % reduces the photocatalytic activity, as shown in Figure 8. The ZnO@Ag heterostructure with Ag content higher than 11 atom % is not investigated in this study. Zheng et al. also found that the photocatalytic activity of the Ag particle/ZnO heterostructure decreased with increasing Ag content, when the Ag content exceeded 5.0 atom %, and attributed this phenomenon to oxygen-related defects.²⁴ In light of the photocatalytic mechanism of the Ag particle/ZnO heterostructures by depositing Ag particles on the surface of ZnO nanocrystals,²⁴ the photocatalytic reaction process of the novel ZnO@Ag heterostructures is proposed as follows and shown in Figure 8 (b):

- (1) Both the ZnO nanorods and the ultrathin ZnO nanowires and nanotubes act as electron and hole sources. When the ZnO catalysts absorb photons of energy greater than or equal to the band gap, photoelectrons may be promoted from the valence band (VB) to the conduction band (CB), leaving behind same amount of electron vacancies or holes in the VB.
- (2) Since the energy level of the bottom of the CB of ZnO is higher than the new Fermi energy level of the

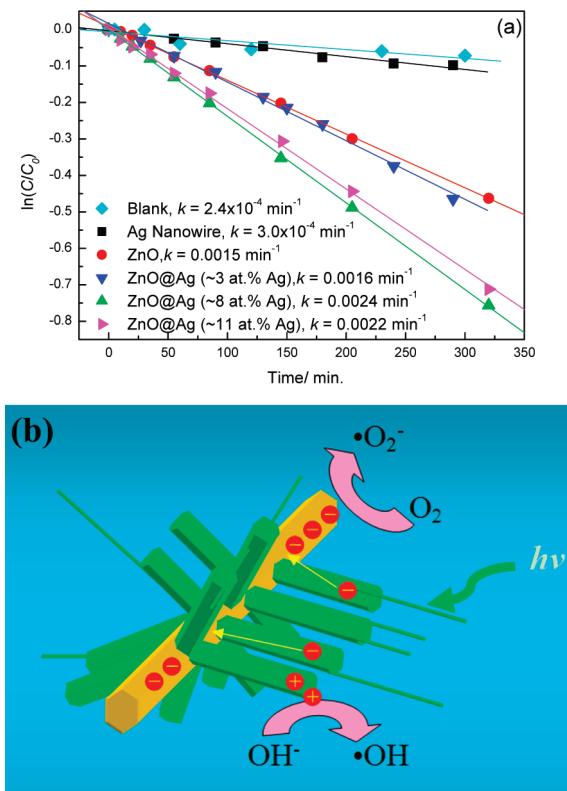


Figure 8. (a) MB degradation curves of $\ln(C/C_0)$ versus time for photodegradation without any catalyst (blank one) and with catalyst of Ag nanowires, ZnO nanorods, and ZnO@Ag heterostructures of different Ag concentrations; and the reaction rate constant, k , from linear fitting. (b) Proposed photocatalytic mechanism of the dendrite-like ZnO@Ag heterostructures.

ZnO@Ag heterostructures, the photoelectrons could transfer from ZnO to Ag driven by the energy difference.²⁴ The Ag nanowires act as electric cables for transferring the photoelectrons. Thus, the recombination of photoelectrons and holes prior to the superoxide activation process is avoided and the photoinduced generation of electron–hole pairs will continue.

- The photoinduced holes may react with surface-bound H_2O or OH^- to produce the hydroxyl radical species ($\cdot\text{OH}$), which is an extremely strong oxidant to most organic chemicals.^{17,51} Free electrons may be picked up by oxygen molecules dissolved in the solution to generate superoxide radical anions ($\cdot\text{O}_2^-$),⁵² which are the active species for the overall photocatalytic oxidation.^{21,53}

The photocatalysis test results may demonstrate that the presence of Ag/ZnO interfaces in the ZnO@Ag heterostructure enhances the separation of photogenerated electron–hole pairs and thus improves the photocatalytic activity.

4. Conclusion

Dendrite-like ZnO@Ag heterostructure nanocrystals were fabricated by a facial two-step chemical method. Single crystal truncated-rhombic Ag nanowires were first synthesized by the polyol process. Then, highly dense ZnO nanorods with diameters of about 50–400 nm were vertically grown on the lateral surfaces of the Ag nanowires, by a simple aqueous solution route, with a uniform growth along the $\langle 0001 \rangle$ direction. Ultrathin ZnO nanowires and nanotubes with a diameter of less than 30 nm were grown on the tops of the ZnO nanorods. HRTEM observations revealed the heteroepi-

taxial orientations of ZnO nanorods on the Ag {111} and {100} surfaces. The photocatalysis test results show that the ZnO@Ag heterostructures exhibit a higher photocatalytic activity in comparison with the pure ZnO nanorods and the ZnO@Ag heterostructure with about 8 atom % Ag reveals the highest photocatalytic activity.

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