

# Ag/ZnO Heterostructure Nanocrystals: Synthesis, Characterization, and Photocatalysis

Yuanhui Zheng, Lirong Zheng, Yingying Zhan, Xingyi Lin, Qi Zheng,\* and Kemei Wei

National Engineering Research Center of Chemical Fertilizer Catalyst, Fuzhou University,  
Gongye Road 523, Fuzhou, Fujian 350002, China

Received April 11, 2007

A high yield of the dimer-type heterostructure of Ag/ZnO nanocrystals with different Ag contents is successfully prepared through a simple solvothermal method in the absence of surfactants. The samples are characterized by X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy, UV–vis spectroscopy, and IR spectroscopy. The results show that all samples are composed of metallic Ag and ZnO; Ag nanoparticles locate on the surface of ZnO nanorods; the binding energy of Ag 3d<sub>5/2</sub> for the Ag/ZnO sample with a Ag content of 5.0 atom % shifts remarkably to the lower binding energy compared with the corresponding value of pure metallic Ag because of the interaction between Ag and ZnO nanocrystals; the concentration of oxygen vacancy for the as-synthesized samples varies with the increasing Ag content, and the Ag/ZnO sample with a Ag content of 5.0 atom % has the largest density of oxygen vacancy. In addition, the relationship between their structure and photocatalytic property is investigated in detail. It is found that the photocatalytic property is closely related to its structure, such as heterostructure, oxygen defect, and crystallinity. The presence of metallic Ag nanoparticles and oxygen vacancy on the surface of ZnO nanorods promotes the separation of photogenerated electron–hole pairs and thus enhances the photocatalytic activity.

## 1. Introduction

Semiconductor-based heterostructures with the desired composition and/or morphology could modulate the properties of the materials and find a potential application in nanodevices.<sup>1</sup> For example, control over the composition and size of the semiconductors allows for the tuning of their band gaps, which determines the absorption and emission characteristics of the optoelectronic devices. Stimulated by the potential applications in biomedicine, photocatalysis, and nanodevices, significant advances have been made in recent years to design various kinds of semiconductor-based heterostructures, such as core/shell and anisotropic (e.g., dimer/trimer-type and hierarchical composite materials) heterostructures.<sup>2–6</sup>

Recently, environmental problems such as air and water pollution have provided the impetus for sustained fundamental and applied research in the area of environmental remediation. The wide-band-gap semiconductor metal oxides (SMOs), such as TiO<sub>2</sub> and ZnO, as photocatalysts have been proven attractive because these materials have a high catalytic efficiency and low cost and are environmentally sustainable.<sup>7–12</sup> Major efforts in the modern catalysis field are devoted to the design and fabrication of nanostructured SMOs with tunable physical–chemical properties for advanced catalytic applications. For example, the size dependence of the catalytic performance has been largely emphasized in the literature.<sup>13–17</sup> On the other hand, semiconductor-based

\* To whom correspondence should be addressed. E-mail: zhengqi@fzu.edu.cn. Phone: +86-591-8373-1234-8416. Fax: +86-591-8373-8808.

- (1) Park, W. I.; Yi, G. C.; Kim, M.; Pennycook, S. J. *Adv. Mater.* **2003**, *15*, 256.
- (2) Kamat, P. V.; Hirakawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 3928.
- (3) Liu, N.; Prall, B. S.; Klimov, V. I. *J. Am. Chem. Soc.* **2006**, *128*, 15362.
- (4) Choi, J.; Jun, Y.; Yeon, S.; Kim, H. C.; Shin, J.; Cheon, J. *J. Am. Chem. Soc.* **2006**, *128*, 15982.
- (5) Lao, J. Y.; Wen, J. G.; Ren, Z. F. *Nano Lett.* **2002**, *2*, 1287.
- (6) Jung, Y.; Ko, D. K.; Agarwal, R. *Nano Lett.* **2007**, *7*, 264.

- (7) Kamat, P. V. *Chem. Rev.* **1993**, *93*, 267.
- (8) Pelizzetti, E.; Serpone, N. *Homogeneous and Heterogeneous Photocatalysis*; Reidel: Dordrecht, The Netherlands, 1986.
- (9) Chiavello, M. *Photocatalysis and Environment, Trends and Applications*; Reidel: Dordrecht, The Netherlands, 1988.
- (10) Xu, F.; Du, G. H.; Halasa, M.; Su, B. L. *Chem. Phys. Lett.* **2006**, *426*, 129.
- (11) Pal, B.; Sharon, M. *Mater. Chem. Phys.* **2002**, *76*, 82.
- (12) Zheng, Y.; Chen, C.; Zhan, Y.; Lin, X.; Zheng, Q.; Wei, K.; Zhu, J.; Zhu, Y. *Inorg. Chem.* **2007**, accepted for publication.
- (13) Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693.
- (14) Roucoux, A.; Schlz, J.; Patin, H. *Chem. Rev.* **2002**, *102*, 3757.
- (15) Pradhan, N.; Pal, A.; Pal, T. *Langmuir* **2001**, *17*, 1800.

heterostructure (e.g., semiconductor/semiconductor and metal/semiconductor) nanocatalysts have also attracted much research attention in recent years because of their excellent catalytic activity.<sup>18–22</sup> However, to the best of our knowledge, there are only a few published studies of Ag/ZnO heterostructure photocatalysts.<sup>23,24</sup> On the basis of our previous study about nanostructured ZnO photocatalysts<sup>12</sup> and considering the promising applications of metal/oxide nanocrystals in photocatalysis, we expect to synthesize Ag/ZnO heterostructure nanocatalysts and understand the relationship between their structure and photocatalytic property.

It is well-known that light corrosion and impurities (e.g., surfactants) on the surface of photocatalysts would hinder their practical applications. So, it is necessary to develop a simple and low-cost method to fabricate the objective photocatalysts with high crystallinity and clean surfaces. However, the challenge of this work is how to control the nucleation of one phase on the surface of the other phase. In the rational design of experiments, intermolecular dehydrolysis and the reduction of Ag(I) species are adopted to fabricate the Ag/ZnO heterostructure through an ethanol-mediated solvothermal method in the absence of surfactants. The key steps in this synthetic process are to control (1) the dehydrolysis between  $\text{Zn}(\text{OH})_4^{2-}$  and  $\text{Ag}(\text{OH})_2^-$  and (2) reduction of silver oxide on the surface of ZnO nanocrystals. In order to have an in-depth understanding of the relationship between their structure and photocatalytic property, the synthesized Ag/ZnO heterostructure nanocrystals are investigated in detail. The results show that there is a strong interaction between metallic Ag and ZnO nanocrystals because of the formation of  $\text{Zn}-\text{O}\cdots\text{Ag}$  bonds on the interface; the photocatalytic activity is dependent on the heterostructure and the concentration of oxygen vacancy; the Ag/ZnO heterostructure nanocrystals exhibit excellent catalytic stability because of their high crystallinity.

## 2. Experimental Section

### 2.1. Preparation of Ag/ZnO Heterostructure Nanocrystals.

**Materials.** Zinc acetate, silver acetate, sodium hydroxide, and alcohol are all analytical grades and used without further purification.

**Synthesis.** Large-scale Ag/ZnO heterostructure nanocrystals are synthesized through a simple solvothermal method, where the

intermolecular dehydrolysis and reduction reactions are utilized to form the heterostructure. In a typical procedure, a certain  $\text{Zn}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$  and  $\text{CH}_3\text{COOAg}$  was put into a Teflon tank of 50 mL capacity (the content of the Ag element is 2.5, 5.0, 10, and 20 atom %, respectively). Subsequently, 30 mL of a NaOH/ethanol solution (0.17 M) was added into the above tank drop by drop with agitation. The tank was put into a stainless steel autoclave, then moved into an oven, and heated at 160 °C for 24 h. When the reactions were completed, the autoclave was cooled to room temperature naturally. The brown-red precipitates were collected by filtration, washed with deionized water and ethanol several times, and finally dried in the air at 60 °C for 10 h.

**2.2. Characterizations.** The powder X-ray diffraction (XRD) patterns of the samples were recorded by a Rigaku DMAX2500 X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) at a scanning rate of 5°/min for  $2\theta$  ranging from 27° to 65°. The microstructures and morphologies were investigated by a JEM 2000EX transmission electron microscope (TEM) working at 200 kV. The IR and UV–vis diffuse-reflectance spectra were measured on a Perkin-Elmer Spectrum System 2000 FT-IR spectrometer and a UV–vis-near-IR spectrometer (Cary 500), respectively. Room-temperature fluorescent characterization was performed on an Edinburgh F900 with an excitation wavelength of 365 nm. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Phi Quantum 2000 spectrophotometer with Al K $\alpha$  radiation (1486.6 eV). For photocatalytic measurement, 30 mg of each catalyst was suspended in 90 mL of a standard methyl orange (MO) aqueous solution ( $5.0 \times 10^{-5}$  M), and then the mixture was put into quartz tube and agitated overnight in the absence of light to attain equilibrium adsorption on the catalyst surface. UV irradiation was carried out using a  $4 \times 4$  W fluorescent Hg lamp (Philips TUV 4 W; the strongest emission at 365 nm). After a given irradiation time, about 3.5 mL of the mixture was withdrawn and the catalysts were separated from the suspensions by filtration through 0.22  $\mu\text{m}$  cellulose membranes. The photocatalytic degradation process was monitored by a UV–vis spectrophotometer (UV-2450; measuring the absorption of MO at 463 nm).

## 3. Results and Discussion

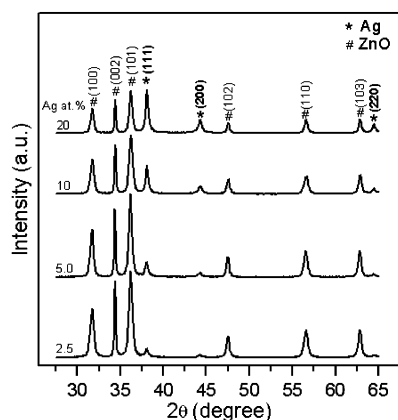
### 3.1. Synthesis of Ag/ZnO Heterostructure Nanocrystals.

It is generally accepted that a surfactant or compatibility of the two phases is usually necessary to form the hetero-interface. For example, when the crystal structures are compatible and the lattice parameters of the two crystalline phases are well-matched, heterostructures usually arise;<sup>25–27</sup> in special cases, where there is a large overall lattice mismatch but there exist surfactants, some anisotropic structures (e.g., dimers where two nearly spherical particles are fused together with only one junction plane on each component) may be obtained.<sup>28,29</sup> However, in the incompatible Ag/ZnO system, intermolecular dehydrolysis should play a significant role in the formation of Ag/ZnO heterostructure in the absence of surfactant.

As discussed in the Experimental Section, the final brown-red products are prepared through a simple solvothermal

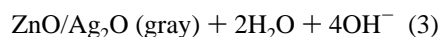
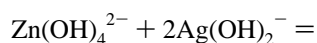
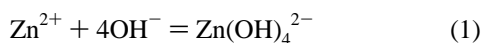
- (16) Narayanan, R.; El-Sayed, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 8340.  
 (17) Ye, C.; Bando, Y.; Shen, G.; Golberg, D. *J. Phys. Chem. B* **2006**, *110*, 15146.  
 (18) Kim, H. G.; Borse, P. H.; Choi, W.; Lee, J. S. *Angew. Chem., Int. Ed.* **2005**, *44*, 4585.  
 (19) Marci, G.; Augugliaro, V.; Lopez-Munoz, M. J.; Martin, C.; Palmisano, L.; Rives, V.; Schiavello, M.; Tilley, R. J. D.; Venezia, A. M. *J. Phys. Chem. B* **2001**, *105*, 1026; *J. Phys. Chem. B* **2001**, *105*, 1033.  
 (20) Zhang, F.; Jin, R.; Chen, J.; Shao, C.; Gao, W.; Li, L.; Guan, N. *J. Catal.* **2005**, *232*, 424. Wu, J. J.; Tseng, C. H. *Appl. Catal., B* **2006**, *66*, 51.  
 (21) Lee, M. S.; Hong, S. S.; Mohseni, M. *J. Mol. Catal. A: Chem.* **2005**, *242*, 135. Iliev, V.; Tomova, D.; Todorovska, R.; Oliver, D.; Petrov, L.; Todorovsky, D.; Uzunova-Bujnova, M. *Appl. Catal., A* **2006**, *313*, 115.  
 (22) Lam, S. W.; Chiang, K.; Lim, T. M.; Amal, R.; Low, G. K.-C. *Appl. Catal., B* **2007**, *72*, 363.  
 (23) Height, M. J.; Pratsinis, S. E.; Mekasuwandumrong, O.; Praserthdam, P. *Appl. Catal., B* **2006**, *63*, 305.  
 (24) Stroyuk, A. L.; Shvalagin, V. V.; Kuchmii, S. Ya. *J. Photochem. Photobiol., A* **2005**, *173*, 185.

- (25) Bae, S. Y.; Seo, H. W.; Choi, H. C.; Park, J.; Park, J. *J. Phys. Chem. B* **2004**, *108*, 12318.  
 (26) Shen, G.; Chen, D.; Lee, C. J. *J. Phys. Chem. B* **2006**, *110*, 15689.  
 (27) Kuang, Q.; Jiang, Z.; Xie, Z.; Lin, S.; Lin, Z.; Xie, S.; Huang, R.; Zheng, L. *J. Am. Chem. Soc.* **2005**, *127*, 11777.  
 (28) Gu, H.; Zheng, R.; Zhang, X.; Xu, B. *J. Am. Chem. Soc.* **2004**, *126*, 5664.  
 (29) Kwon, K. W.; Shim, M. *J. Am. Chem. Soc.* **2005**, *127*, 10269.

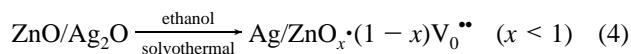


**Figure 1.** XRD patterns of the as-synthesized samples with different Ag contents.

method in the absence of surfactants. When a sodium hydroxide solution is added into a mixture of acetic zinc and silver acetate drop by drop with agitation, the gray precursor is formed gradually. The chemical reactions for the formation of the precursor can be formulated as



Intermolecular dehydrolysis (eq 3) is utilized to form the heterointerface between  $\text{Ag}_2\text{O}$  and ZnO. Also, subsequent crystal growth should happen on ZnO/ $\text{Ag}_2\text{O}$  nuclei. In addition, it is well-known that ethanol is a weak reducing agent under high temperature and pressure. When the precursor is treated solvothermally (ethanol as the solvent) at 160 °C for 24 h, the oxygen vacancy ( $\text{V}_\text{o}^{\bullet\bullet}$ ) should be generated on the surface of ZnO nanocrystals.<sup>12</sup> Also, the reduction of  $\text{Ag}_2\text{O}$  on the surface of ZnO nanocrystals should also occur during the process of solvothermal treatment because pure metallic Ag can be obtained in this synthetic system (see the Supporting Information, SI-1). The chemical reaction process for the generation of Ag/ZnO heterostructure nanocrystals is proposed as follows:



As mentioned above, ZnO and  $\text{Ag}_2\text{O}$  are connected through a Zn–O–Ag bond in the precursor. During the solvothermal process, the precursor is reduced by ethanol gradually and a Zn–O $\cdots$ Ag bond should be formed between metallic Ag and ZnO nanocrystals, resulting in the formation of Ag/ZnO heterostructure nanocrystals with a strong interaction.

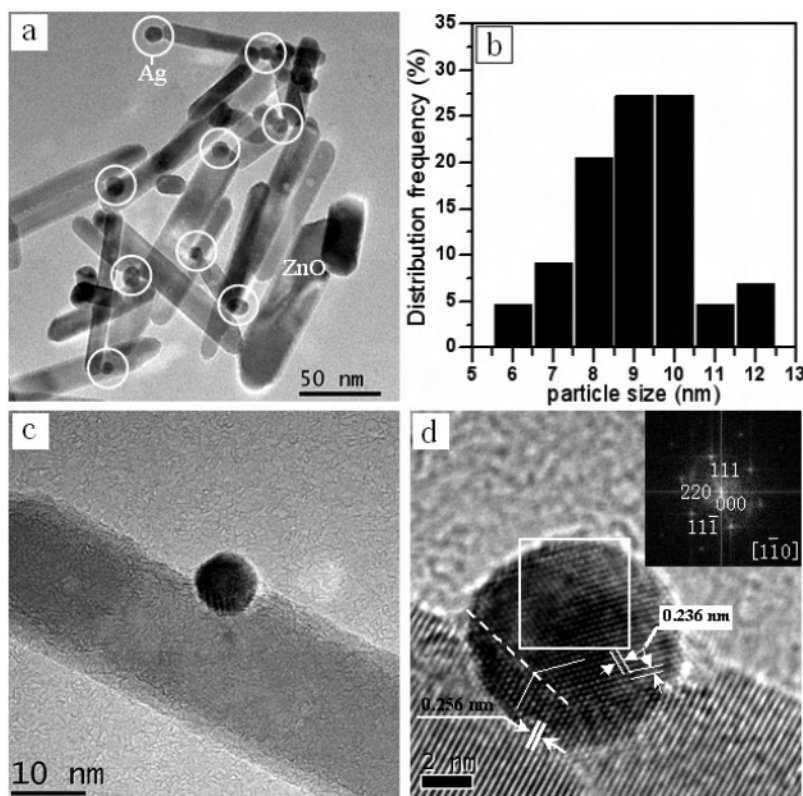
**3.2. Crystal Structure and Microstructure of Ag/ZnO Heterostructure Nanocrystals.** The XRD patterns of the as-synthesized samples with different Ag contents are shown in Figure 1. All curves in Figure 1 obviously show two sets of strong diffraction peaks, indicating that the as-synthesized products are composite materials with high crystallinity.

Those marked with “#” can be indexed to hexagonal wurtzite ZnO (JCPDS file no. 36-1451), while the others marked with “\*” can be indexed to face-centered-cubic (fcc) metallic Ag (JCPDS file no. 04-0783); no other crystalline impurities are observed. In addition, there is no remarkable shift of all diffraction peaks, implying that no  $\text{Zn}_{1-x}\text{Ag}_x\text{O}$  solid solution is formed and the change of the lattice parameters of ZnO nanocrystals should be negligible.

In order to obtain detailed information about the microstructure and morphology of the as-synthesized samples, TEM observations are carried out. Figure 2 shows the representative TEM images of the synthesized sample with a Ag content of 5.0 atom %. A low-magnified TEM image of this sample shows a high yield of Ag/ZnO heterostructure nanocrystals consisting of metallic Ag nanoparticles (highlighted by circles) and ZnO nanorods, as presented in Figure 2a. Also, one can see that each nanoparticle is attached to a nanorod. Although there are some ZnO nanorods without Ag nanoparticles on the surface, self-nucleated and isolated Ag nanoparticles are hardly observed. Moreover, Ag aggregates are also not found in our TEM observations, indicating that all metallic Ag nanoparticles are completely dispersed in ZnO nanorods. Most of the ZnO nanorods in Figure 2a are about 20 nm in width and 100 nm in length (aspect ratio of about 5:1), in good agreement with our previous study.<sup>12</sup> Figure 2b shows the metallic Ag nanoparticle size distribution of the sample. It is obvious that the diameters of Ag nanoparticles are in the range of 6–12 nm and the average diameter of Ag nanoparticles is about 9 nm. A typical magnified TEM image of an individual Ag/ZnO heterostructure (Figure 2c) reveals that the metallic Ag nanoparticle is embedded in the ZnO nanorod (i.e., the formation of a dimer-type heterostructure). The high-resolution TEM (HRTEM) image (Figure 2d) from Figure 2c shows a distinguished interface and the continuity of lattice fringes between the ZnO nanorod and metallic Ag nanoparticle, confirming the formation of chemical bonds between them. It also shows the uniform lattice structure and single-crystalline nature of the ZnO nanorod. The spacing between adjacent lattice fringes is 0.256 nm, which is close to the  $d$  spacing of the (002) plane, indicating the [001] direction ( $c$  axis) being the preferential growth direction of ZnO nanorods. On the other hand, as to the nanoparticle of the heterodimer (Figure 2d), lattice fringes with interplanar spacing of 0.236 nm corresponding to the {111} planes of fcc Ag are observed. The Fast Fourier transform (FFT) pattern (inset in Figure 2d) also confirms fcc metallic Ag along the  $[\bar{1}10]$  zone axis. In addition, there is an aberrant microtwin interface (highlighted by a dashed line) in the metallic Ag nanoparticle due to the oriented attachment between the ZnO nanorod and Ag nanoparticle.

**3.3. Surface Structure of Ag/ZnO Heterostructure Nanocrystals.** The surface structure of the as-prepared sample with a Ag content of 5.0 atom % is also investigated by using XPS analysis, and the corresponding experiment results are shown in Figure 3. The binding energies in the XPS spectra presented in Figure 3 are calibrated by using that of C 1s (284.8 eV). In Figure 3a, all of the peaks on the





**Figure 2.** TEM images of the as-synthesized sample with a Ag content of 5.0 atom %: (a) low-magnified TEM image of Ag/ZnO heterostructure nanocrystals; (b) size distribution of Ag nanoparticles in Ag/ZnO heterostructure nanocrystals; (c) high-magnified TEM image of a single Ag/ZnO heterostructure nanocrystal; (d) HRTEM image of the Ag/ZnO heterostructure nanocrystal in Figure 2c (the inset is the FFT pattern from the squared region of Figure 2d).

curve are ascribed to Zn, Ag, O, and C elements and no peaks of other elements are observed. The presence of C comes mainly from pump oil due to vacuum treatment before the XPS test. Therefore, it is concluded that the sample is composed of three elements, Zn, Ag, and O, which is in good agreement with the above XRD and TEM results. Parts b–d of Figure 3 display the high-resolution spectrum for O, Zn, and Ag species, respectively. In Figure 3b, the O 1s profile is asymmetric and can be fitted to two symmetrical peaks ( $\alpha$  and  $\beta$  locating at 530.0 and 531.6 eV, respectively), indicating two different kinds of O species in the sample. The peaks  $\alpha$  and  $\beta$  should be associated with the lattice oxygen ( $O_l$ ) of ZnO<sup>30,31</sup> and chemisorbed oxygen ( $O_a$ ) caused by the surface hydroxyl,<sup>32</sup> respectively. Moreover, the calculated ratio of the adsorption oxygen to the lattice oxygen ( $O_a/O_l$ ) is 0.45. The peaks appearing in parts c and d of Figure 3 are symmetric and center at 1021.4 and 367.2 eV, which are attributed to Zn 2p<sub>3/2</sub> and Ag 3d<sub>5/2</sub>, respectively. Interestingly, the binding energy of Ag 3d<sub>5/2</sub> for the Ag/ZnO sample with a Ag content of 5 atom % shifts remarkably to the lower binding energy compared with the corresponding value of the synthesized pure metallic Ag due to the interaction between Ag and ZnO nanocrystals (the standard binding energy of Ag 3d<sub>5/2</sub> for bulk Ag is about 368.2 eV<sup>31</sup>).

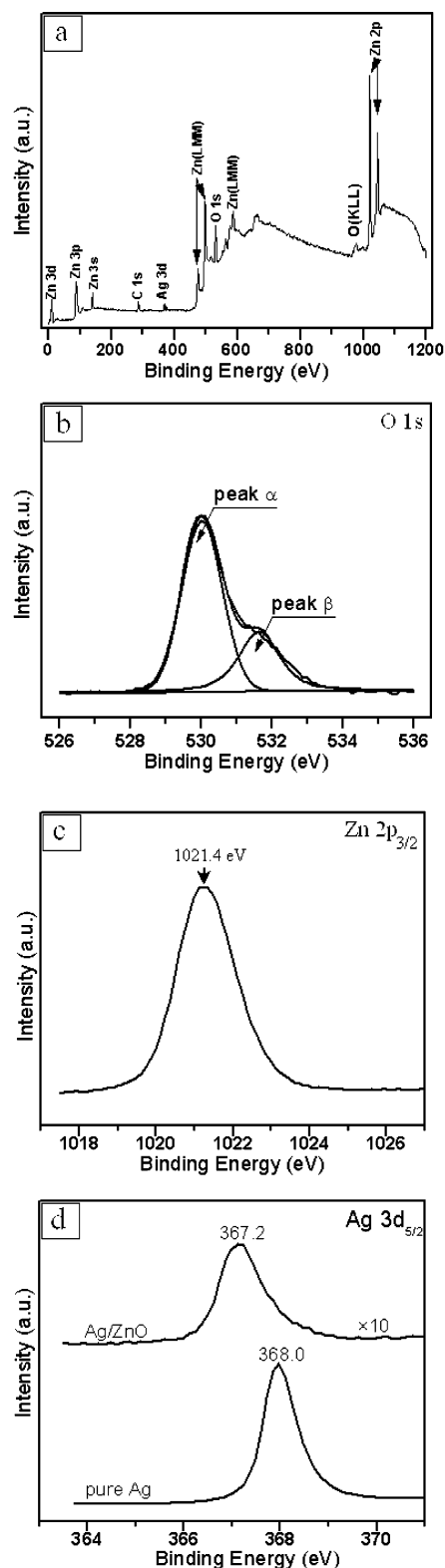
(30) Peng, W.; Qu, S.; Cong, G.; Wang, Z. *Cryst. Growth Des.* **2006**, *6*, 1518.

(31) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer: Eden Prairie, MN, 1992.

Then what is the nature of this phenomenon? It is suggested that the shift of the binding energy of Ag 3d<sub>5/2</sub> should be mainly ascribed to the interaction between the Ag nanoparticle and ZnO nanorod. When the Ag nanoparticle and ZnO nanorod attach together, they adjust the position of their corresponding Fermi energy levels to the same value (see the Supporting Information, SI-2). Thus, there are many free electrons above the new Fermi level of metallic Ag nanoparticles. Because the conduction band (CB) of ZnO nanocrystals is vacant, the free electrons could tunnel into the CB, resulting in the higher valence of Ag. The binding energy of monovalent Ag is much lower than that of zerovalent Ag;<sup>31</sup> therefore, in our XPS experiments, the binding energy of Ag 3d<sub>5/2</sub> shifts to lower binding energy. In addition, based on the above XPS analysis, the calculated proportion of Zn, lattice O, and Ag on the surface of the sample is 1:0.96:0.04, revealing the oxygen deficiency on the surface of ZnO nanocrystals. The Zn/O ratio calculated from XPS decreases after Ag is introduced, indicating the reduction of the oxygen defect's density (the calculated Zn/O ratio of bare ZnO nanorods is 1:0.93<sup>12</sup>).

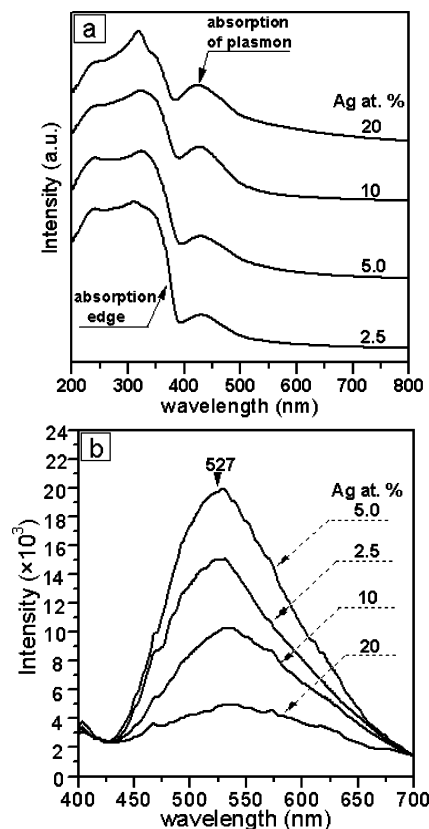
**3.4. Optical Properties of Ag/ZnO Heterostructure Nanocrystals.** The diffuse-reflectance and photoluminescence (PL) spectra of the as-synthesized Ag/ZnO heterostructure nanocrystals are shown in Figure 4. In Figure 4a, two prominent absorption bands are observed in the UV–

(32) Jing, L.; Xu, Z.; Shang, J.; Sun, X.; Cai, W.; Guo, H. *Mater. Sci. Eng. A* **2002**, *332*, 356.



**Figure 3.** XPS spectra of the as-synthesized sample with a Ag content of 5.0 atom %: (a) XPS full spectrum of the sample; (b) O 1s spectrum; (c) Zn 2p<sub>3/2</sub> spectrum; (d) Ag 3d<sub>5/2</sub> spectra (the corresponding figure of pure Ag was also given for comparison).

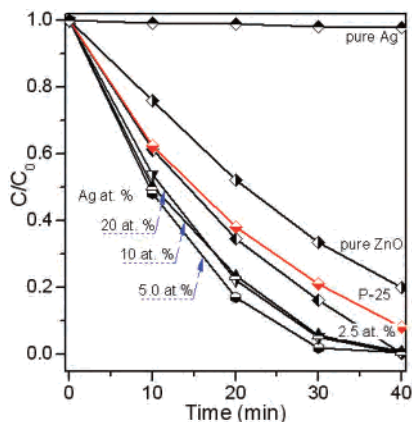
visible region. The former can be assigned to the absorption of the ZnO semiconductor, and its corresponding absorption edge is located at around 375 nm. The latter can be attributed to the characteristic absorption of surface plasmon resulting



**Figure 4.** (a) Diffuse-reflectance spectra and (b) PL spectra of the as-synthesized Ag/ZnO heterostructure nanocrystals.

from the metallic Ag in the Ag/ZnO heterostructures.<sup>33</sup> The appearance of two kinds of characteristic absorption bands also confirms that the as-synthesized samples are composed of zerovalent Ag and ZnO. In Figure 4b, a broad green emission peak centering at around 527 nm is observed for all samples in the visible region when the samples are excited at 365 nm. Despite the intensive studies on the green emission of ZnO nanocrystals, its nature remains controversial and a number of hypotheses have been proposed to explain this emission, such as a singly ionized oxygen vacancy  $V_o^{\bullet}$ ,<sup>34</sup> a  $V_o^{\bullet\bullet}$  center,<sup>35</sup> an oxygen antisite,<sup>36</sup> and a zinc vacancy  $V_{Zn}$ .<sup>37</sup> On the basis of our previous study,<sup>12</sup> we ascribe the green emission at about 527 nm to the  $V_o^{\bullet\bullet}$  defect on the surface of ZnO nanocrystals. It is obvious that the green emission intensity of the as-synthesized Ag/ZnO heterostructure nanocrystals increases at first and then decreases with an increase of the Ag content. This phenomenon reveals the variation of the  $V_o^{\bullet\bullet}$  defect density on the surface of ZnO nanorods and the Ag/ZnO sample with a Ag content of 5 atom % has the largest concentration of the oxygen defect. It has been reported that the IR vibration peak

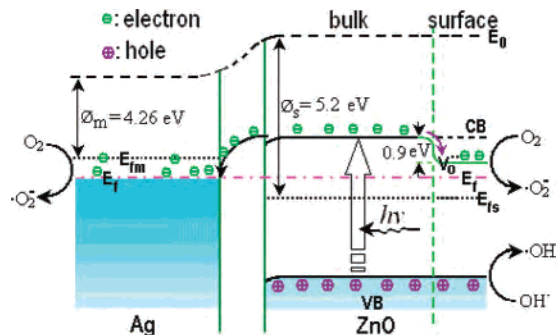
- (33) Zhang, L.; Dou, Y. H.; Gu, H. C. *J. Colloid Interface Sci.* **2006**, *297*, 660.  
 (34) Vanheusden, K.; Seager, C. H.; Warren, W. L.; Tallant, D. R.; Voigt, J. A. *Appl. Phys. Lett.* **1996**, *68*, 403.  
 (35) van Dijken, A.; Meulenkamp, E. A.; Vanmaekelbergh, D.; Meijerink, A. *J. Phys. Chem. B* **2000**, *104*, 1715.  
 (36) Lin, B.; Fu, Z.; Jia, Y. *Appl. Phys. Lett.* **2001**, *79*, 943.  
 (37) Zhao, Q. X.; Klason, P.; Willander, M.; Zhong, H. M.; Lu, W.; Yang, J. H. *Appl. Phys. Lett.* **2005**, *87*, 211912.  
 (38) Wang, X.; Kong, X.; Yu, Y.; Zhang, H. *J. Phys. Chem. C* **2007**, *111*, 3836.



**Figure 5.** Photodegradation of MO by the as-synthesized Ag/ZnO heterostructure nanocrystals.

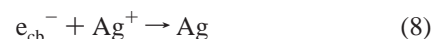
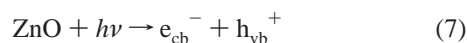
of the  $E_1(\text{LO})$  mode of ZnO nanocrystals should shift with a change of the oxygen vacancy defect's density.<sup>12</sup> The IR spectra of the as-synthesized samples (see the Supporting Information, SI-3) further confirm the highest oxygen vacancy defect's density for the Ag/ZnO sample with a Ag content of 5 atom %. It is suggested that the variation of the  $V_{\text{O}}^{\bullet\bullet}$  defect density on the surface of ZnO nanorods should be related to the surface-to-volume ratio of ZnO nanorods and the interface between Ag nanoparticles and ZnO nanorods.

**3.5. UV-Light-Driven Photocatalysis and Photocatalytic Mechanism.** MO is presently adopted as a representative organic pollutant to evaluate the photocatalytic performance of Ag/ZnO heterostructure nanocrystals. In the experiments, the commercial  $\text{TiO}_2$  (Degussa P-25) is used as a photocatalytic reference to qualitatively understanding the photocatalytic activity of Ag/ZnO catalysts. The photocatalytic activities of the as-prepared samples with different Ag contents and Degussa P-25 are shown in Figure 5.  $C_0$  and  $C$  in Figure 5 are the initial concentration after the equilibrium adsorption and the reaction concentration of MO, respectively. As seen in Figure 5, the degradation of MO over pure Ag nanocrystals is negligible, and the Ag/ZnO heterostructure nanocatalysts exhibit higher photocatalytic activity compared to pure ZnO; for example, the required time for an entire decolorization of MO over Ag/ZnO catalysts is less than or equal to 40 min, much shorter than the corresponding value over pure ZnO nanocrystals. Moreover, one can see that the Ag/ZnO heterostructure catalysts with a Ag content of 5.0 atom % show the highest photocatalytic activity. When a Ag content is relatively lower ( $<5.0$  atom %), the photocatalytic activity of the Ag/ZnO heterostructure increases gradually with an increase of the Ag content (5.0-Ag/ZnO  $>$  2.5-Ag/ZnO  $>$  ZnO). However, when the Ag content exceeds 5.0 atom %, the photocatalytic activity of the Ag/ZnO heterostructure decreased with an increase of the Ag content (5.0-Ag/ZnO  $>$  10-Ag/ZnO  $\sim$  20-Ag/ZnO  $>$  Ag). In addition, the catalytic stability of the Ag/ZnO heterostructure catalyst with a Ag content of 5.0 atom % is carried out (see the Supporting Information, SI-4). It shows that this catalyst has an excellent catalytic stability because of the high crystallinity of the synthesized sample.



**Figure 6.** Proposed band structure and photocatalytic mechanism of the as-synthesized Ag/ZnO heterostructure nanocrystals.<sup>12,38</sup>

Figure 6 shows the proposed band structure of the synthesized Ag/ZnO heterostructure. When the Ag/ZnO heterostructure nanocatalysts are dispersed in the solution with an organic pollutant, the surface electrons on Ag nanoparticles should eventually transfer to the dye in the dark. However, when these catalysts are radiated by UV light with photon energy higher or equal to the band gap of ZnO nanocrystals, electrons ( $e^-$ ) in the valence band (VB) can be excited to the CB with simultaneous generation of the same amount of holes ( $h^+$ ) in the VB. As presented in Figure 6, the energy level of the bottom of the CB is higher than the new Fermi energy level of the Ag/ZnO heterostructure, so the photoexcited electrons could transfer from ZnO nanorods to Ag nanoparticles driven by the above potential energy. The electronic acceptors like adsorbed  $\text{O}_2$  can easily trap the photoelectrons to produce a superoxide anion radical ( $\bullet\text{O}_2^-$ ).<sup>39</sup> Goto et al.<sup>40</sup> have concentrated on analyzing molecular oxygen reduction to  $\bullet\text{O}_2^-$ , which determined the overall photocatalytic reaction. The photoinduced holes can be easily trapped by  $\text{OH}^-$  to further produce a hydroxyl radical species ( $\bullet\text{OH}$ ), which is an extremely strong oxidant for the partial or complete mineralization of organic chemicals.<sup>41</sup> Therefore, the photocatalytic reaction process can be proposed as follows:



On the basis of the above discussion, it is concluded the following: (1) Ag nanoparticles on the surface of ZnO nanorods act as a sink for the electrons (eqs 5 and 8), promote interfacial charge-transfer kinetics between the metal and semiconductor, improve the separation of photogenerated

(39) Ryu, J.; Choi, W. *Environ. Sci. Technol.* **2004**, *38*, 2928.

(40) Goto, H.; Hanada, Y.; Ohno, T.; Matsumura, M. *J. Catal.* **2004**, *225*, 223.

(41) Yatmaz, H. C.; Akyol, A.; Bayramoglu, M. *Ind. Eng. Chem. Res.* **2004**, *43*, 6035.

electron–hole pairs, and thus enhance the photocatalytic activity of Ag/ZnO photocatalysts; (2) ZnO nanorods serve as electron and hole sources (eq 7) for degradation of an organic dye. It is worthwhile to mention that the content of ZnO nanorods decreases with an increase of the Ag loading. The correlation between the concentration of ZnO nanorods and the photocatalytic activity is studied (see the Supporting Information, SI-5). The result shows that the effect of the concentration of ZnO nanorods after Ag loading on the photocatalytic activity should be neglected. However, as presented in Figure 5, the photocatalytic efficiency of Ag/ZnO heterostructure nanocrystals decreases at a high Ag content. This should be related to the concentration of the  $V_o^{\bullet\bullet}$  defect in different samples. As presented in Figure 6, partial photogenerated electrons could transfer to the  $V_o^{\bullet\bullet}$  defect and then finally to the dye in solution. The more the  $V_o^{\bullet\bullet}$  defect is, the higher the photocatalytic activity should be. Therefore, it is reasonable that the Ag/ZnO heterostructure nanocatalysts with a Ag content of 5.0 atom % exhibit the highest catalytic activity in our system. Finally, a more detailed investigation about the effect of other structures such as semiconductor/semiconductor heterostructure and the impurity defect on the PL and photocatalytic properties of ZnO nanocrystals is being carried out.

#### 4. Conclusion

Ag/ZnO heterostructure nanocatalysts with excellent photocatalytic performance are successfully prepared through a simple solvothermal method. It is found that the addition of  $Ag^+$  results in the formation of zerovalent metallic Ag deposits on the surface of ZnO nanorods and the photocatalytic activity of Ag/ZnO nanocatalysts is dependent on their structure, especially the heterostructure and oxygen vacancy. The presence of Ag nanoparticles and oxygen vacancy on the surface of ZnO nanorods promotes the separation of photogenerated electron–hole pairs and thus enhances the photocatalytic activity.

**Acknowledgment.** The authors acknowledge financial support from the Department of Science of the People's Republic of China (Grant 20271012) and the Department of Science & Technology of Fujian Province (Grant 2005H201-2).

**Supporting Information Available:** Synthesis, XRD pattern, proposed band structure, IR spectra, photocatalytic stability, and degradation rates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC700688F