Synthesis and Photocatalytic Property of SnO$_2$/ZnO Nanorod Composites

Jinxia Duan, Qiu Xiong, Dian Zhang, Wei Li, and Hao Wang*

Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Hubei Key Laboratory of Ferro & Piezoelectric Materials and Devices, Faculty of Physics and Electronic Science, Hubei University, Wuhan, China

Jinghua Hu

School of Science, Wuhan University of Technology, Wuhan 430070, PR China
(Received 16 November 2015; Accepted 11 March 2016; Published 30 April 2016)

SnO$_2$/ZnO nanorod composite photocatalysts have been successfully fabricated via combining the electrochemical deposition (ECD, for ZnO nanorod) with a simple solvothermal growth (for SnO$_2$ nanoparticle). As was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), SnO$_2$ nanoparticles in a tetragonal phase were attached on the side faces of ZnO nanorods to form the nanocomposites. SEM and TEM images indicated that the diameter and the length of the SnO$_2$/ZnO nanorod composites were 100–300 nm and 2–5 μm, respectively. The effect of ECD potential on the microstructure of ZnO nanorods was also investigated. The observation of the morphologies showed that the optimum spacing of ZnO nanorods grown on Cu substrates were obtained when ECD potential was −0.8 V at 80°C. The photocatalytic behavior of the SnO$_2$/ZnO nanorod composite photocatalysts has been examined by monitoring the photodegradation of rhodamine B (RhB) under UV-radiation exposure. SnO$_2$/ZnO nanorod composite showed higher photocatalytic activity toward photodegradation of RhB than bare ZnO nanorods, which was due to the efficient charge separation at the SnO$_2$/ZnO composite photocatalyst interface.

[DOI: 10.1380/ejssnt.2016.136]

Keywords: SnO$_2$/ZnO nanorod composites; Electrochemical deposition (ECD); Photocatalytic property

I. INTRODUCTION

During the past two decades, environmental pollution caused by detergents, dyes, and pesticides in water and air has provided the impetus for sustainable development and applied research interest in the area of environmental remediation [1, 2]. Among various photocatalytic semiconductor materials available, metal-oxide semiconductor photocatalysts, such as TiO$_2$ (3.2 eV), ZnO (3.2 eV), α-Fe$_2$O$_3$ (2.2 eV) and WO$_3$ (2.8 eV), have great potential for the complete elimination of toxic chemicals because of their high photocatalytic activities and economical synthetic routes [3–5]. TiO$_2$ and ZnO, two well-known wide-bandgap semiconductor photocatalysts, have been the subjects of considerable research interest due to their peculiar size-tunable physicochemical properties, high activities, and non-selective degradability toward various organic pollutants under UV irradiation [6–8]. Therefore, seeking nanostructured photocatalysts with efficient electron/hole transfer, high specific surface areas, excellent recycling characteristics and simple preparation is very important for practical applications.

Various types of ZnO micro/nanostructures have been prepared for photocatalyst applications because of their high photosensitivity and stability [8–10]. Owing to large specific surface area and length to diameter ratio, quasi-one-dimensional (1D) ZnO nanostructures, such as nanowires, nanorods and nanobelts, could potentially be a very good class of catalysis support structures [10–12]. However, the high recombination rate of photogenerated electron-hole pairs has limited its commercialization of this technology. The photonic efficiency of the photocatalyst can be increased by decreasing the rate of charge carrier recombination relative to that of interfacial charge transfer [13, 14]. The design and modification of semiconductor photocatalysts with high sensitivity and reactivity have attracted a great deal attention. Several reports have shown that coupling different semiconductor oxides with different band energies would improve the photocatalytic efficiency by increasing effectively electron-hole pair separation and extending the photo-responding range [5, 15, 16]. A large variety of coupled polycrystalline or colloidal semiconductor systems, in which the particles adhere to each other to form “sandwich structure” or present in “core-shell geometry”, have been prepared for photocatalytic reactions [3, 5, 16–19]. The nanocomposites represent a new opportunity for creating materials with novel and excellent properties resulted from the synergistic effect among the different components [16–19]. Typical examples of such couplings are SnO$_2$/TiO$_2$ [16, 17], ZnO/ZTO [18], ZnO/SnO$_2$ [6, 20], and SnO$_2$/V$_2$O$_5$ [19]. Hereby 1D ZnO nanostructure photocatalysts coupled with the other semiconductor may be a feasible strategy to improve the photocatalytic efficiency. As mentioned to 1D ZnO nanostructures, many methods such as hydrothermal process and vapor phase transport were employed for preparation. The electrochemical deposition (ECD) technique possibly is a good candidate to obtain 1D ZnO, and it has many advantages, such as simple, quick, cost-effective, and large scale up production. Herein, we have designed a nanorod composites configuration prepared via ZnO nanorods grown on the Cu substrate and followed by SnCl$_4$ solution treatment, aiming to understand the relevant chemical nature and photocatalytic property.

Combination of SnO$_2$ with ZnO has been examined to be potential for effective photocatalytic applications. SnO$_2$ is a wide band gap semiconductor with $E_g$ of 3.6 eV and can be easily synthesized via solution reaction of SnCl$_4$ and base. These make it a good candidate for the ZnO nanorod surface passivation due to the simplicity of solution treatment. SnO$_2$ is an important semiconductor...
material on account of its unique electronic and optical properties [20, 21]. SnO$_2$ can readily donate holes with high oxidation ability with no absorption of light more than 330 nm. There are some reports suggested that a combination of SnO$_2$ with TiO$_2$ [16, 17], ZnO [20, 22, 23] and Fe$_2$O$_3$ [5] could effectively boost the photocatalytic performance. When such binary metal oxides are exposed to UV-light, electrons in valence band (VB) are excited to the conduction band (CB) with generating the same amount of holes in the VB. Then, photogenerated electrons in the CB of the semiconductor with higher CB energy-edge are injected to the CB of the semiconductor with lower CB edge. Simultaneously, holes in VB are injected in the opposite direction, which increases the rate of charge separation and reduces the electron-hole pair recombination. Because of its lower CB edge, SnO$_2$ is a better electron acceptor than TiO$_2$ and ZnO that makes it a good candidate for the composites photocatalyst. Consequently, combining ZnO with SnO$_2$ has been the subject for efficient charge separation and excellent photocatalytic activity of binary oxides.

In this work, we examined the optimized conditions for the formation of SnO$_2$ and ZnO composite nanostructures along with its photocatalytic behavior evaluated using rhodamine B as a model organic compound. Furthermore, the UV-vis spectra of the samples were measured, and their bandgap energies were calculated according to the spectra.

II. EXPERIMENTAL

In the present work, we demonstrated that the nanorod composites were achieved via ECD and hydrothermal process. ZnO nanorods growth (first step) was followed by hydrothermal treatment with SnCl$_4$ solution (second step). Firstly, The ZnO nanorods were synthesized by an electrochemical deposition process. The synthesis method of ZnO nanorods basically was the same as that in previous work [24, 25]. In the first procedure, zinc nitrate hydrate (Zn(NO$_3$)$_2$ · 6 H$_2$O, 10 mmol), hexamethylenetetramine (C$_6$H$_{12}$N$_4$, 10 mmol) and 0.01 M potassium chloride (KCl) (A.R.) as electrolyte were dissolved in 200 mL of deionized water at room temperature and then heated to 80°C. ZnO would grow cathodically under a range of deposition conditions from −0.5 V to −1.2 V. A pure Zn (99.99% purity) sheet acted as the anode and a copper foil (99.99% purity) was the cathode in an electrochemical condition. The electrochemical deposition was performed under standard conditions in a two-electrode bath. Under these conditions, the electrochemical deposition typically was carried on for 30 min to achieve a layer of white film on the surface of Cu substrate. At the end of the growth period, the sample was removed from the solution and immediately rinsed in flowing deionized water to remove any residual salt from the surface. In the second step, 0.005 M of SnCl$_4$ · 2H$_2$O, 30 mL of ethanol, and 50 mL of distilled water were mixed and stirred before the pH value of above solution was adjusted to about 10 by adding 0.05 M NaOH (drop by drop). The above solution was then transferred into the 100 mL stainless steel Teflon-lined autoclave, and the product from the first-step-synthesis (a piece of Cu substrate with ZnO film) was added into the autoclave before sealing. The reactor was maintained at 120°C for 20 h before being cooled down to room temperature. After that, the copper foil was taken out from the solution and rinsed with distilled water and ethanol.

Both of the first-step and the final products were examined by the following characterization techniques. The general morphology and crystallinity of the products were examined by scanning electron microscopy (SEM, JSM6700) and X-ray diffraction (XRD). Transmission electron microscopy (TEM, FEI Tecnai G2, accelerating voltage: 200 kV) related techniques were employed to investigate the detailed microstructure of the products. UV-Vis spectra were recorded in air at room temperature in the wavelength range of 250–800 nm using a Shimadzu 3600 UV-visible-NIR spectrophotometer.

Rhodamine B (RhB) dye solutions in water were used as a test reaction to examine the photocatalytic behavior of ZnO and SnO$_2$ attached ZnO nanorods. The reaction solution was prepared by adding copper foil (6 cm$^2$) with ZnO and SnO$_2$/ZnO nanorods into 50 mL of RhB solution (0.01 mmol), respectively. Prior to irradiation, the solutions were stirred in the dark for 30 min to establish adsorption/degradation equilibrium.

After a period of UV irradiation (125 W, 360–365nm), the RhB concentration in the filtrates was analyzed by UV-vis- NIR spectroscopy with a Perkin-Elmer Lambda 35 UV-vis spectrophotometer spectrophotometer at its maximum absorption wavelength (ca. 554 nm). The degradation efficiency of RhB was calculated by the formula [26],

\[
\text{Degradation(\eta)} = \left(1 - \frac{C_t}{C_0}\right) \times 100\%
\]

\[
= \left(1 - \frac{A_t}{A_0}\right) \times 100
\]

where $C_0$ and $C_t$ are the initial concentration and the concentration after ‘t’ min UV irradiation, respectively. $A_0$ and $A_t$ are the initial absorbance and the absorbance after ‘t’ min UV irradiation, respectively. Reaction of the RhB solution was measured at the characteristic absorption wavelength of 554 nm.

III. RESULTS AND DISCUSSION

Macroscopically, cathodic copper substrates can be covered with a layer of white and homogeneous ZnO film or particle film in a square centimeter order. When the deposition potential was −0.5 or −1.2 V, ZnO nanorod arrays were obtained, as shown in Figs. 1a-c. But their microstructures showed a notable evolution with the increasing deposition currents. Figure 1a-c summarized the SEM micrographs of the prepared ZnO nanorods electrochemical deposited on the Cu cathodes as a function of electrodeposition potential from −0.5 to −1.2 V. When the ECD potential was controlled at −0.5 V, it was observed that no obvious separate ZnO nanorods were formed on the Cu substrate from Fig. 1a. Only flower-like ZnO structure composed of ZnO rods were sparsely distributed on the substrate. These nanorods were randomly oriented and about 100 nm in diameter. This indicated that few OH$^-$ ions were electrogenerated on the electrode surface.
and thus, the growth rate of ZnO rods was quite low at this potential. As the applied potential increased to −0.8 V, the nanorods exhibited an improved vertical orientation on the Cu substrate surface, as shown in Fig. 1b. The ZnO rods had hexagonal end plane irrespective of rod diameter. However, a continued increase in applied potential up to −1.2 V caused a significant increase in the nanorod diameter. The average diameter of the nanorods shown in Fig. 1c was 2 times larger than that shown in Fig. 1b. It should be noted that as-prepared ZnO nanorods at −1.2 V began to grow jointly with one another (Fig. 1c). The better photocatalytic performances in the case of the 0.8 V may be due to the optimum spacing of the nanorods. In the case where the potential was 0.5 V, the ZnO rod population was very low, and this reduced the available interface area for exciton dissociation by the nanostructures. In the case of 1.2 V, the rod population appeared too high, and the rods were densely packed. This could cause difficulties in the dye infiltration and therefore limited the dye-metal oxide contact area. After establishing the optimum conditions in terms of potential, we studied the effect of introducing second metal oxide. The ZnO nanorods were attached SnO$_2$ nanoparticles by solution hydrothermal method. Figure 1d showed SEM image of SnO$_2$ attached (the identity of the attached material, i.e., SnO$_2$, was discussed in the following XRD and TEM analyses) ZnO nanorods on a Cu substrate. This top-view image was taken at an edge of the cut sample, which showed that the nanorods were grown uniformly on a large area. In comparison, although the SnCl$_4$ solution treated sample maintains the shape of rod and tetragonal SnO$_2$ particles were clearly found on the ZnO nanorods (Fig. 1b). The shape was similar to the “matchstick”. The size of the SnO$_2$ particles was about 40–100 nm.

The crystallinity of ZnO nanorods and SnO$_2$/ZnO nanocomposites was investigated by XRD. A typical X-ray diffraction pattern in Fig. 2a revealed that the ECD ZnO nanorods were of wurtzite structure (space group: P6$_3$mc) with a (0002) preferential orientation. The XRD spectrum corresponding to the SnO$_2$/ZnO nanorod composites was presented in Fig. 2b. The diffraction peaks could be indexed with the wurtzite ZnO and the tetragonal structured SnO$_2$ (JCPDS No 41-1445). The peaks at about 26.4°, 33.3° and 51.3° are the typical (110), (101) and (211) diffraction peak of the SnO$_2$ structure, respectively.

The obtained SnO$_2$/ZnO nanorod composites were scratched off to investigate the crystal structure and phase transformation by transmission electron microscopy (TEM). Figure 3a showed the bright-field TEM image of a representative SnO$_2$ attached ZnO nanorod. As was shown in Fig. 3, the distribution of the ZnO and SnO$_2$ phase (a composition structure) could be clearly distinguished from the bright field image. The size of the tetragonal SnO$_2$ particles was about 40–100 nm. This was rea
reasonable because only tips of the nanorods were facing the solution. The SnO\(_2\) particles deposited in this way was not dense, as can be seen from the inhomogeneous contrast. This result was line with Sun’s work [27].

Before examining the photocatalytic activity, it is important to study the optical absorption of the as-prepared nanorods because the UV-vis absorption edge is relevant to the energy band of the semiconductor catalyst [28, 29]. The UV-vis spectra of SnO\(_2\)/ZnO nanorod composites in Fig. 4 showed a broad absorbance from 410 to 550 nm and a shift in the absorption edge to the UV region compared to the pure ZnO nanorods. For comparison, the absorption peaks of pure ZnO nanorods and SnO\(_2\) nanoparticles were also presented in Fig. 4. The wavelength of the absorption edge was determined by extrapolating the horizontal and sharply rising portions of the curve and defining the edge as the wavelength of the intersection [30]. The band gap absorption edge of ZnO was determined to be 388 nm, corresponding to the \(E_g\) of 3.19 eV. It is in reasonable agreement with the values of 3.2 eV reported in the literature [31]. The band gap absorption edge of SnO\(_2\)/ZnO nanorod composites was determined to be 395 nm, corresponding to the \(E_g\) of 3.14 eV. The band gap absorption edge of SnO\(_2\) is determined to be 402 nm, corresponding to the \(E_g\) of 3.08 eV. However, this value is much less than the reported value of 3.6 eV [32]. It was reported that SnO\(_2\) is a n type semiconductor oxide with not only the direct \(E_g\) of 3.5–3.9 eV, but also an indirect \(E_g\) of \(\sim\) 2.6 eV, so the band gap value of SnO\(_2\) nanoparticles indicates an indirect transition as reported in literature [33, 34]. In fact, it had been previously observed that the major free carriers in sol-gel derived nanocrystalline SnO\(_2\) are, in fact, monoionized oxygen vacancies. It was likely that for the SnO\(_2\) nanoparticles large amount of oxygen vacancies retained in the material explains the departure in the band gap values. The \(E_g\) of SnO\(_2\)/ZnO nanorod composites fall in between that of neat ZnO and SnO\(_2\). This was due to that the \(E_g\) was the contribution of the corresponding ZnO and SnO\(_2\) crystallite phases in the nanorod composites.

RhB had often been used as a model dye molecule for photocatalytic degradation by a transition metal oxide [6]. The photocatalytic activity of SnO\(_2\)/ZnO nanorod composites was evaluated by the photocatalytic decomposition of RhB dye under the irradiation of UV light. Figure 5 showed the absorbance spectra of RhB aqueous solutions in the presence of ZnO nanorods and SnO\(_2\)/ZnO nanorod composites after UV visible light irradiation. It could be seen that the maximum absorbance at 554 nm disappeared completely after irradiation for 60 min. The photocatalytic degradation rates of RhB with the SnO\(_2\)/ZnO nanorod composites were shown in Fig. 5. For comparison, we also plotted the RhB concentration changes under the conditions of applying UV-radiation without catalyst and with ZnO nanorods catalyst. RhB was hardly degraded under UV-radiation without catalyst. Obviously, RhB was photodegraded rapidly with the addition of catalyst under UV light. From the almost linear relationship between \(C_t/C_0\) and \(t\), a first order degradation rate was suggested for all the samples in the degradation period tested in this research. The SnO\(_2\)/ZnO nanorod composites showed higher photocatalytic activity than pure ZnO nanorods.

This increase in the photocatalytic activity of the SnO\(_2\)/ZnO nanorod composites was might attributed to an increase in the specific surface area. This also increased the number of surface active sites, which improved the oxidation degradation rate of RhB. When ZnO nanorods
were attached by SnO$_2$, some ZnO active sites would be surrounded by SnO$_2$. This would hinder the contact between ZnO and oxygen containing species, resulting in the reduction of the photocatalytic activity. Figure 6 shows the mechanism of the charge separation and photocatalytic reaction for the SnO$_2$ attached ZnO photocatalysts. As was illustrated in the scheme, when the SnO$_2$ attached ZnO photocatalysts were irradiated by UV light with a photon energy higher or equal to the band gaps of ZnO and SnO$_2$, electrons ($e^{-}$) in the valence band (VB) were excited to the conduction band (CB) with simultaneous generation of the same amount of holes ($h^{+}$) in the VB. Because the CB of SnO$_2$ was lower than that of ZnO, upon light-activation the electrons transfer from the CB of ZnO to that of SnO$_2$, and SnO$_2$ acted as a sink for the photogenerated electrons. Conversely, the holes were transferred from the VB of SnO$_2$ to that of ZnO [6, 19]. The photogenerated electrons and holes in the SnO$_2$ attached ZnO photocatalysts could inject into a reaction medium and participate in chemical reactions. Therefore, efficient spatial separation of the charge carrier increased the lifetime of the charge carriers and reduced the probability of recombination relative at interfacial charge transport, thus increased the quantum efficiency. This resulted in the stronger photocatalytic efficiency for SnO$_2$/ZnO nanorod composites. In this design, Cu substrate is soft, which makes the photocatalyst could be applied in various fields. Moreover, Cu substrate is conductor, which could be the electrode in photoelectrocatalysis to improve the dye decomposition rate of photocatalyst.

### IV. CONCLUSION

We developed two-step solution-based synthetic route for the fabrication of SnO$_2$/ZnO nanorod composites. The SnO$_2$/ZnO nanocomposites exhibited significantly higher photocatalytic activity for the degradation of RhB under UV light than pure ZnO nanorods. The higher effective charge separation of SnO$_2$ and ZnO might be helpful to enhance photocatalytic efficiency. Also, we believe that our design could be applied in wide fields in soft substrate and photoelectrocatalysis.

### ACKNOWLEDGMENTS

This work was supported by the National Science Foundation of China (No. 11204070).

[1] Y. Liu, J. Han, W. Qiu, and W. Gao, Appl. Surf. Sci. 263, 389 (2012).
[2] D. Ravelli, D. Dondi, M. Fagnoni, and A. Albini, Photo-catalysis. Chem. Soc. Rev. 38, 1999 (2009).
[3] D. Lin, H. Wu, R. Zhang, and W. Pan, Chem. Mater. 21, 3479 (2009).
[4] A. Fujishima, T. N. Rao, and D. A. Tryk, J. Photochem. Photobiol. C: Photochem. Rev. 1, 1 (2000).
[5] M. Niu, F. Huang, L. Cui, P. Huang, L. Yu, and Y. Wang, ACS Nano 4, 681 (2010).
[6] R. Liu, Y. Huang, A. Xiao, and H. Liu, J. Alloys Compd. 503,103 (2010).
[7] D. Li and H. Haneda, Chemosphere 51, 129 (2003).
[8] F. Lu, W. Cai, and Y. Zhang, Adv. Funct. Mater. 18, 1047 (2008).
[9] T. T. Ali, K. Narasimharao, I. P. Parkin, C. J. Carmalt, S. Sathasivam, S. N. Basahel, S. M. Bawaked, and S. A. Al-Thabaiti, New J. Chem. 39, 321 (2015).
[10] H. B. Lu, H. Li, L. Liao, Y. Tian, M. Shuai, J. C. Li, M. Fhu, Q. Fu, and B. P. Zhu, Nanotechnology 19, 045605 (2008).
[11] T. J. Kuo, C. N. Lin, C. L. Kuo, and M. H. Huang, Chem. Mater. 19, 5143 (2007).
[12] Z. Han, L. Liao, Y. Wu, H. Pan, S. Shen, and J. Chen, J. Hazard. Mater. 217-218, 100 (2012).
[13] D. D. Lin, H. Wu, R. Zhang, W. Zhang, and W. Pan, J. Am. Ceram. Soc. 93, 3384 (2010).
[14] H. Tsutsumi, and V. K. Prashant, J. Am. Chem. Soc. 127, 3928 (2005).
[15] D. L. Jian, P. X. Gao, W. J. Cai, B. S. Allimi, S. P. Alpay, Y. Ding, Z. L. Wang, and C. Brooks, J. Mater. Chem. 19, 970 (2009).
[16] J. Yang, D. Li, X. Wang, X. Yang, and L. Lu, J. Solid State Chem. 165, 193 (2002).
[17] L. Shi, C. Li, H. Gu, and D. Fang, Mater. Chem. Phys. 62, 62 (2000).
[18] S. Danwittayakul, M. Jaisai, and J. Dutta, Appl. Catal. B: Environ. 163, 1 (2015).
[19] M. Shahid, I. Shakir, S.-J. Yang, and D. J. Kang, Mater. Chem. Phys. 124, 619 (2010).
[20] J. Kong, Z. Rui, H. Ji, and Y. Tong, Catal. Today 258, 75 (2015).
[21] J. A. Aguilar-Martinez, M. B. Hernandez, A. B. Glot, and M. I. Pech-Canal, J. Phys. D: Appl. Phys. 40, 7097 (2007).
[22] Z. Yang, L. Lv, Y. Dai, Z. Xv, and D. Qian, Appl. Surf. Sci. 256, 2898 (2010).
[23] E. M. Seftel, E. Popovici, M. Mertsens, E. A. Stefaniak, R. Van Grieken, P. Cool, and E. F. Vansant, Appl. Catal. B: Environ. 84, 699 (2008).
[24] J. Cui, J. Phys. Chem. C 112, 10385 (2008).
[25] G. She, X. Zhang, W. Shi, X. Fan, and J. C. Chang, Electrochem. Commun. 9, 2784 (2007).
[26] G. Poongodi, P. Anandan, R. Mohan Kumar, R. Jayavel, Spectrochimica Acta A: Molecular and Biomolecular Spectroscopy 148, 237 (2015).
[27] Y. Yang, X. W. Sun, B. K. Tay, J. X. Wang, Z. L. Dong, and H. M. Fan, Adv. Mater. 19, 1839 (2007).
[28] L. Ren, L. Jin, J.-B. Wang, F. Yang, M.-Q. Qiu, and Y. Yu, Nanotechnology 20, 115603 (2009).
[29] F. Gao, X. Y. Chen, K. Yin, S. Dong, Z. F. Ren, F. Yuan, T. Yu, Z. G. Zou, and J.-M. Liu, Adv. Mater. 19, 2889 (2007).
[30] P. L. Provenzano, G. R. Jindal, J. R. Sweet, and W. B. White, J. Lumin. 92, 297 (2001).
[31] C. Wang, B.-Q. Xu, X. Wang, and J. Zhao, J. Solid State Chem. 178, 3500 (2005).
[32] A. Hagfeldt, and M. Graetzel, Chem. Rev. 95, 49 (1995).
[33] W. Cun, Z. Jincai, W. Xinning, M. Bixian, S. Guoying, P. Ping’an, F. Jiamo, Appl. Catal. B: Environ. 39, 269 (2002).
[34] C. Drake and S. Seal, Appl. Phys. Lett. 90, 233117 (2007).