

3D ZnO rod-like structures loaded with silver nanoparticles and their enhanced photocatalytic performance

Qiang Wang, Zhuanni Yu, Xiaowei Sun, Jing Lan ✉

College of Chemistry and Pharmaceutical Sciences, Qingdao Agricultural University, No. 700, Changcheng Road, Qingdao 266109, People's Republic of China

✉ E-mail: qdlanjing@mail.sdu.edu.cn

Published in Micro & Nano Letters; Received on 31st March 2017; Revised on 23rd June 2017; Accepted on 30th June 2017

Three-dimensional (3D) zinc oxide (ZnO) rod-like structures loaded with silver (Ag) nanoparticles (3D Ag/ZnO RLS) have been successfully synthesised by a facile hydrothermal and microwave method. The successful loading of Ag nanoparticles and the 3D hierarchical structure were characterised by scanning electron microscopy and X-ray diffraction. The pHs of zero point charge were 7.8 and 7.9 for 3D ZnO rod-like structures (3D ZnO RLS) and 3D Ag/ZnO RLS, respectively. The photocatalytic performances of the 3D RLS were evaluated by decomposing methylene blue under ultraviolet irradiation. Compared to 3D ZnO RLS, the enhanced photocatalytic performance of 3D Ag/ZnO RLS may be attributed to the 3D hierarchical structure of the Ag/ZnO, as the structure can lead to enhanced light absorption and lower recombination of photoinduced holes and electrons.

1. Introduction: Removal of dyes from aqueous solutions has been of concern during the past decades owing to their adverse effects on aquatic lives [1]. These dyes, especially azo dyes, have been proven to be resistant to biodegradation [2]. Photocatalytic degradation using semiconductors shows great promise, since they can convert these compounds into carbon dioxide without secondary damage to the environment [3].

Semiconductors, especially metal-oxide materials, have caused much attention owing to their unusual optical, electrical and catalytic properties [4]. Zinc oxide (ZnO), whose bandgap is 3.37 eV, is proposed as one of the most promising photocatalyst because of its high catalytic efficiency, broader ultraviolet (UV) light absorption, lower cost than titanium dioxide and environmental sustainability [5]. Recent studies have indicated that the microstructures of ZnO photocatalyst which significantly affects the photocatalytic activities can be easily manipulated to desirable morphologies [6–8]. Moreover, three-dimensional (3D) ZnO shows more superior photocatalytic properties than various low-dimensional ZnO nanostructures [9].

The rapid recombination of photoinduced hole-electron pairs has been considered as the major obstacle for increasing photocatalytic efficiency of photocatalysts [10]. To solve this problem, transition metals such as platinum, silver (Ag) and iron, have been introduced to improve the charge transfer and inhibit the recombination by trapping the photoinduced charge [11]. Among these metals, Ag has been proven to be one of the most promising candidates. Recently, a series of 3D Ag/ZnO heterostructural composites has been successfully prepared through UV-light irradiation [12], co-precipitation [13], solvothermal [14] etc. Moreover, these Ag/ZnO composites have presented enhanced photocatalytic performance. For example, spindle-like Ag/ZnO heterostructure composites prepared by using commercial microscale ZnO have presented good performance for the degradation of crystal violet [15]. Moreover, 3D flower-like Ag/ZnO heterostructures prepared by a facile two-step method have showed enhanced photocatalytic activity toward rhodamine B degradation [16]. It is confirmed that the manipulation of ZnO microstructures is still one of the most useful approaches for improving the photocatalytic activities. Among them, using series of hierarchical microstructures as the carrier of noble metal nanoparticles to improve the performance of photocatalyst is proposed as a promising strategy.

In this Letter, 3D Ag/ZnO RLS composed of 3D hierarchical ZnO microstructures (aggregates of rod-like structures) and Ag nanoparticles has been prepared by a facile hydrothermal and microwave process. The photocatalytic performance was evaluated by employing them as an efficient photocatalyst for the degradation of methylene blue (MB) under UV irradiation.

2. Experimental details: 3D ZnO RLS were prepared through a reported hydrothermal method [17]. In a typical process, 2.6 g sodium hydroxide (NaOH) and 1.6 g CTAB were successively added into 80 ml of 0.05 mol l⁻¹ zinc chloride under vigorously stirring for 30 min. Then, the mixture was transferred into a 100 ml Teflon-lined stainless steel autoclave, kept in a 180°C oven for 3 h and then cooled down naturally to room temperature. White precipitates were washed with deionised water and ethanol for three times. The dry 3D ZnO RLS were obtained by keeping the purified white precipitates in vacuum at 80°C for 8 h.

3D Ag/ZnO RLS were synthesised by the surface modification method which used commercial microscale ZnO as carrier and simple reduction of Ag nitrate (AgNO₃) by ethylene glycol (EG) [15, 18, 19]. Typically, 0.03 g 3D ZnO RLS was dispersed into 20 ml EG solution containing 0, 0.025, 0.050 and 0.075 mol l⁻¹ AgNO₃ under vigorously stirring for 30 min. They were labelled as Ag/ZnO-0, Ag/ZnO-1, Ag/ZnO-2 and Ag/ZnO-3, respectively. Another 20 ml EG solution containing 0.7 g polyvinylpyrrolidone was dropped into the above AgNO₃ solution under stirring. Then, the mixture was transferred to a microwave oven, heated with a power of 500 W for 10 min and then naturally cooled down. The obtained precipitates were centrifuged and washed with deionised water and ethanol several times. After being kept in vacuum at 60°C for 12 h, the dried 3D Ag/ZnO RLS could be obtained.

Scanning electron microscope (SEM) was used to investigate the morphology of 3D ZnO RLS and 3D Ag/ZnO RLS. X-ray diffractometer (XRD, $\lambda = 1.5418 \text{ \AA}$) was used to investigate their structural properties.

The photocatalytic performances of 3D ZnO RLS and 3D Ag/ZnO RLS were evaluated by decomposing MB in aqueous solution under UV light of a germicidal lamp. The lamp contains two 8 W tubes (OSRAM, Germany) with a maximum emission at about 254 nm. The distance between the solution and the light was kept at about 12 cm. Briefly, the 0.1 g catalyst was dispersed

in 100 ml MB aqueous solution (20 mg l^{-1}). Before irradiation, the reaction system was kept stirring in the dark for 30 min to reach an adsorption/desorption equilibrium. Then, the equivalent volume (2.5 ml) of the decomposed MB solution was collected at regular intervals. The collected solutions were filtered by $2.5 \mu\text{m}$ aqueous filters prior to analysis. UV-visible spectrometer was applied to examine the absorbance of MB. The decolourisation rate (R) was calculated according to the sample absorbance variation

$$R = (A_0 - A)/A_0 = (C_0 - C)/C_0$$

where C_0 and C represent the initial concentration and actual concentration at a given irradiation time, whereas A_0 and A represent their absorbance, respectively.

3. Results and discussion: Figs. 1a and b show the SEM images for 3D ZnO RLS and 3D Ag/ZnO RLS, respectively. It can be seen from Fig. 1a that the as-prepared ZnO is made up of well-defined 3D rod-like hierarchical microspheres with good monodispersity. These rod-like microstructures are built from a lot of microrods through self-assembly. The diameter of the ZnO microstructures is about $10 \mu\text{m}$, while the diameter of the ZnO rods ranges from 300 to 500 nm and their length is about $5.0 \mu\text{m}$. It is found from Fig. 1b that the Ag/ZnO still presents 3D hierarchical structure and its surface becomes coarse as a result of

the load of Ag nanoparticles. The coarse-surface hierarchical structure can improve the absorption of UV light and then enhance the photocatalytic performance [20].

The structural properties of the prepared RLS were studied by X-ray diffraction (XRD). The XRD patterns of 3D ZnO RLS and 3D Ag/ZnO RLS were shown in Fig. 2. All diffraction peaks of ZnO and Ag can be indexed to the pure wurtzite ZnO (JCPDS Card No. 36-1451) and the cubic phase of Ag (JCPDS Card No. 04-0783), respectively. No impurity-related signals are observed, indicating both of them have a good crystallinity. The corresponding lattice parameters of Ag/ZnO are very close to the ones of the standard Ag and ZnO, respectively, which confirms that the Ag nanoparticles are not incorporated into the ZnO lattice but loaded onto the surfaces of those 3D ZnO RLS. The calculated average crystalline size of Ag nanoparticles is $\sim 19 \text{ nm}$ by using Scherrer's formula.

The pH of zero point charge (ZPC) for 3D ZnO RLS and 3D Ag/ZnO RLS was measured according to salt addition method [21]. In the typical system, 0.04 g portion of the samples was dispersed in a 100 ml aqueous solution containing 0.1 mol l^{-1} potassium NO_3 . The initial pH of each suspension was adjusted by using HCl or NaOH solutions. Prior to analysis, the mixture was kept in an end-to-end water shaker bath for 18 h. The ZPC of the samples was recorded by plotting ΔpH ($\text{pH}_f - \text{pH}_i$) versus the initial pH values (Fig. 3). It is found that the pH of ZPC is around 7.8 and 7.9 for 3D ZnO RLS and 3D Ag/ZnO RLS, respectively. The similar pH_{ZPC} indicates that the loading of Ag nanoparticles does

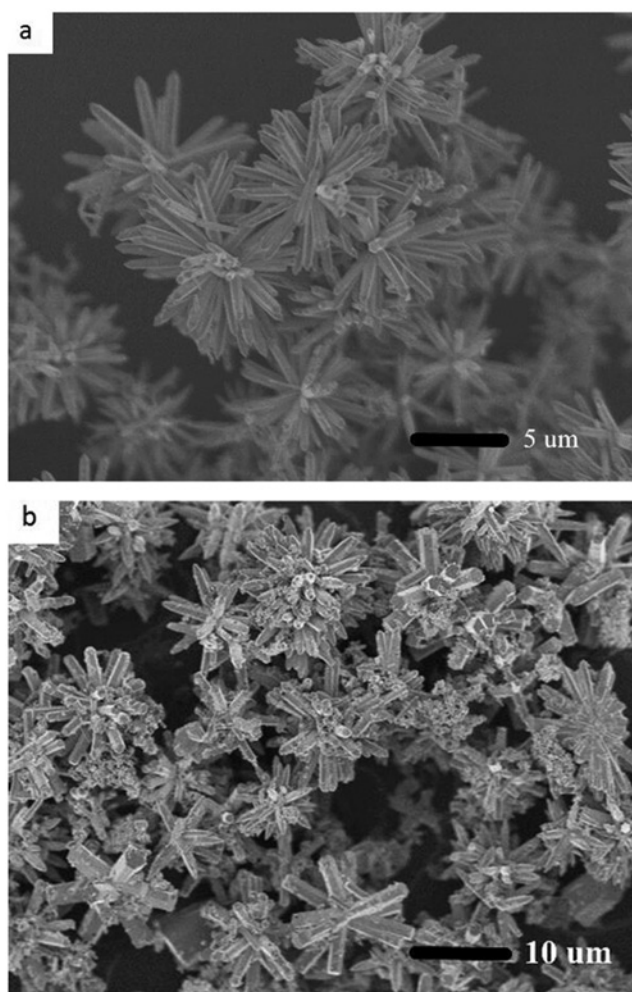


Fig. 1 SEM images for
a 3D ZnO RLS
b 3D Ag/ZnO RLS

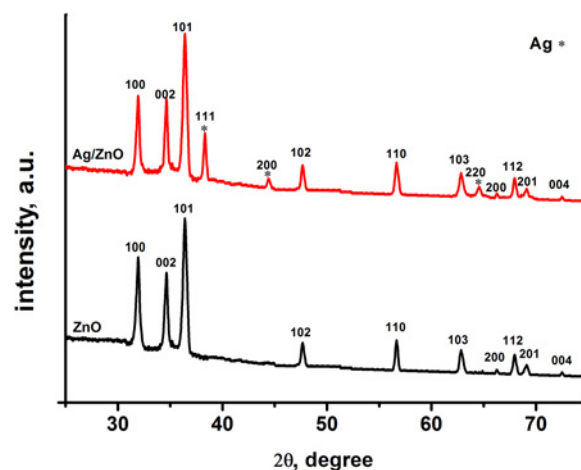


Fig. 2 XRD patterns of 3D ZnO RLS and 3D Ag/ZnO RLS

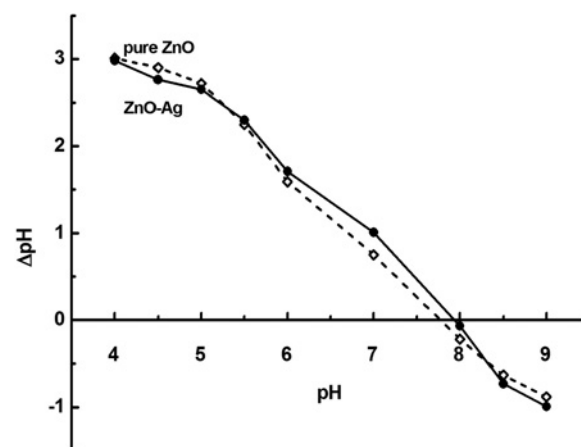


Fig. 3 pH_{ZPC} of 3D ZnO RLS and 3D Ag/ZnO RLS

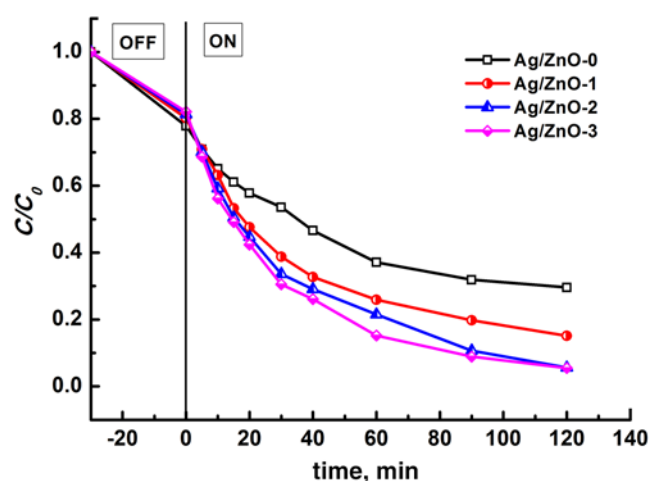


Fig. 4 Removal of MB by adsorption and photodegradation in the suspensions containing the prepared photocatalysts. Experimental conditions: the suspension volume is 100 ml, the concentrations of MB and the prepared photocatalysts are 20 mg L⁻¹ and 1.0 g L⁻¹, respectively

not have much impact on the diffusion and adsorption of MB on the surface of 3D Ag/ZnO RLS.

The photocatalytic performances of 3D ZnO RLS and 3D Ag/ZnO RLS have been studied by degrading MB in aqueous solution. Moreover, the adsorption and photodegradation results of MB using a series of as-prepared catalysts are shown in Fig. 4. It is found that the adsorption of MB onto the prepared photocatalysts cannot be neglected, with the concentration reduction of 22.1, 19.8, 18.6 and 17.9% for Ag/ZnO-0, Ag/ZnO-1, Ag/ZnO-2 and Ag/ZnO-3, respectively, before turning on the lamp. More MB molecules adsorbed onto Ag/ZnO-0 than others can be attributed to the covering of Ag nanoparticles on the surface of 3D ZnO RLS and then the occupying of active sites.

Comparing to pure 3D ZnO RLS, it can be seen from Fig. 4 that the loading of Ag nanoparticles can significantly enhance the decolourisation of MB when the lamp is on. According to the decolourisation rate, the photocatalytic performance of these prepared photocatalysts arranges in the following order: 94.5% (Ag/ZnO-3), 94.4% (Ag/ZnO-2), 84.9% (Ag/ZnO-1) and 50.4% (Ag/ZnO-0). The enhanced photocatalytic performance of 3D Ag/ZnO RLS can be explained as follows: under the irradiation of UV light, hot electrons created by direct absorption of the UV photons were transferred from Ag nanoparticles to the conduction band of ZnO [22]. Meanwhile, the photoexcited electrons of ZnO from the valence band to the conduction band could be transferred from ZnO to Ag nanoparticles, which may be accelerated because of the presence of positive Ag ion, due to the higher bottom energy level of conduction band of ZnO than the equilibrium Fermi energy level of Ag/ZnO. Therein, the charge transfer, whether from Ag nanoparticles to ZnO or from ZnO to Ag nanoparticles, reduced the recombination of some photoinduced electrons and holes, and then the surface adsorbed O₂ could pick up these photoelectrons and generate superoxide radical anions (O₂⁻). The superoxide radical anions and photoinduced holes on the valence band would convert surface-bound H₂O or OH⁻ to hydroxyl radical species (·OH). These secondary radicals would react with organic chemicals such as MB and then degrade them [23].

4. Conclusion: 3D Ag/ZnO RLS have been successfully synthesised via a simple hydrothermal and microwave method and their photocatalytic performances have been evaluated by studying the degradation of MB under UV irradiation. The enhanced photocatalytic performance of the prepared 3D Ag/ZnO RLS can be attributed to their hierarchical crystal structures

which can enhance light absorbance and hinder the recombination of photoinduced holes and electrons. To meet the increasingly stringent demands on the discharge of dyes, the preparation of 3D hierarchical structures will be continued.

5. Acknowledgments: This work was supported by 'the National Natural Science Foundation' (grant no. 21407086) and the 'Doctor Fund of Qingdao Agricultural University' (grant nos. 63311330, 63311203).

6 References

- [1] Zhang F., Shi Y.J., Zhao Z.S., *ET AL.*: 'The photo-catalytic activities of MP ($M = \text{Ba, Ca, Cu, Sr, Ag}$; $P = \text{PO}_4^{3-}, \text{HPO}_4^{2-}$) microparticle', *Appl. Surf. Sci.*, 2014, **292**, (4), pp. 570–575
- [2] Kasanen J., Salstela J., Suvanto M., *ET AL.*: 'Photocatalytic degradation of methylene blue in water solution by multilayer TiO₂ coating on HDPE', *Appl. Surf. Sci.*, 2011, **258**, (5), pp. 1738–1743
- [3] Li G., Liu F., Zhang Z.: 'Enhanced photocatalytic activity of silica-embedded TiO₂ hollow microspheres prepared by one-pot approach', *J. Alloys Compd.*, 2010, **493**, (1), pp. L1–L7
- [4] Zhou H.L., Qu Y.Q., Zeid T., *ET AL.*: 'Towards highly efficient photocatalysts using semiconductor nanoarchitectures', *Energy Environ. Sci.*, 2012, **5**, (5), pp. 6732–6743
- [5] Jeong B., Kim D.H., Park E.J., *ET AL.*: 'ZnO shell on mesoporous silica by atomic layer deposition: removal of organic dye in water by an adsorbent and its photocatalytic regeneration', *Appl. Surf. Sci.*, 2014, **307**, pp. 468–474
- [6] Wang X.J., Zhang Q.L., Wan Q., *ET AL.*: 'Controllable ZnO architectures by ethanolamine-assisted hydrothermal reaction for enhanced photocatalytic activity', *J. Phys. Chem. C*, 2011, **115**, (6), pp. 2769–2775
- [7] Yu J., Yu X.: 'Hydrothermal synthesis and photocatalytic activity of zinc oxide hollow spheres', *Environ. Sci. Technol.*, 2008, **42**, (13), pp. 4902–4907
- [8] Lei A.H., Qu B.H., Zhou W.C., *ET AL.*: 'Facile synthesis and enhanced photocatalytic activity of hierarchical porous ZnO microspheres', *Mater. Lett.*, 2012, **66**, (1), pp. 72–75
- [9] Liang Y.M., Guo N., Li L.L., *ET AL.*: 'Fabrication of porous 3D flower-like Ag/ZnO heterostructure composites with enhanced photocatalytic performance', *Appl. Surf. Sci.*, 2015, **332**, pp. 32–39
- [10] Linsebigler A.L., Lu G.Q., Yates J.T.: 'Photocatalysis on TiO₂ surfaces: principles, mechanisms and selected results', *Chem. Rev.*, 1995, **95**, (3), pp. 735–758
- [11] Cai Y., Fan H.Q., Xu M.M., *ET AL.*: 'Rapid photocatalytic activity and honeycomb Ag/ZnO heterostructures via solution combustion synthesis', *Colloids Surf. A, Physicochem. Eng. Aspects*, 2013, **436**, pp. 787–795
- [12] Ren C., Yang B., Wu M., *ET AL.*: 'Synthesis of Ag/ZnO nanorods array with enhanced photocatalytic performance', *J. Hazard. Mater.*, 2010, **182**, (1), pp. 123–129
- [13] Zhou G., Deng J.C.: 'Preparation and photocatalytic performance of Ag/ZnO nano-composites', *Mater. Sci. Semicond. Process.*, 2007, **10**, (2–3), pp. 90–96
- [14] Deng Q., Tang H.B., Liu G., *ET AL.*: 'The fabrication and photocatalytic performances of flower-like Ag nanoparticles/ZnO nanosheets-assembled microspheres', *Appl. Surf. Sci.*, 2015, **331**, pp. 50–57
- [15] Zhang Z.F., Liu H.R., Zhang H., *ET AL.*: 'Synthesis of spindle-like Ag/ZnO heterostructure composites with enhanced photocatalytic performance', *Superlattice Microstruct.*, 2014, **65**, pp. 134–145
- [16] Liang Y.M., Guo N., Li L.L., *ET AL.*: 'Facile synthesis of Ag/ZnO micro-flowers and their improved ultraviolet and visible light photocatalytic activity', *New J. Chem.*, 2016, **40**, pp. 1587–1594
- [17] Li J.F., Lu G.Z., Wang Y.Q., *ET AL.*: 'A high activity photocatalyst of hierarchical 3D flowerlike ZnO microspheres: synthesis, characterization and catalytic activity', *J. Colloid Interface Sci.*, 2012, **377**, (1), pp. 191–196
- [18] Yu X., Meng D., Liu C., *ET AL.*: 'Enhanced photocatalytic activity of Fe-doped ZnO nanoparticles synthesized via a two-step sol–gel method', *J. Mater. Sci. Mater. Electron.*, 2014, **25**, (9), pp. 3920–3923
- [19] Lu Y.H., Xu M., Xu L.X., *ET AL.*: 'Enhanced ultraviolet photocatalytic activity of Ag/ZnO nanoparticles synthesized by modified polymer-network gel method', *J. Nanoparticle Res.*, 2015, **17**, (9), pp. 1–15
- [20] Cao X.B., Chen P., Guo Y.: 'Decoration of textured ZnO nanowires array with CdTe quantum dots: enhanced light-trapping effect and

- photogenerated charge separation', *J. Phys. Chem. C*, 2008, **112**, (51), pp. 20560–20566
- [21] Ghaedi M., Ghaedi A.M., Abdi F., *ET AL.*: 'Principal component analysis-artificial neural network and genetic algorithm optimization for removal of reactive orange 12 by copper sulfide nanoparticles-activated carbon', *J. Ind. Eng. Chem.*, 2014, **20**, (3), pp. 787–795
- [22] Abbass A. E., Swart H.C., Kroon R.E.: 'Non-plasmonic enhancement of the near band edge luminescence from ZnO using Ag nanoparticles', *J. Lumin.*, 2017, **182**, pp. 263–267
- [23] Gao S.Y., Jia X.X., Yang S.X., *ET AL.*: 'Hierarchical Ag/ZnO micro/nanostructure: green synthesis and enhanced photocatalytic performance', *J. Solid State Chem.*, 2011, **184**, (4), pp. 764–769