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Short communication

# Preparation of Ag-modified Zn<sub>2</sub>GeO<sub>4</sub> nanorods for photo-degradation of organic pollutants



POWDER

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#### ARTICLE INFO

Article history: Received 17 June 2013 Received in revised form 11 September 2013 Accepted 11 October 2013 Available online 19 October 2013

Keywords: Microstructure Nanocomposites Photo-catalysis Degradation

#### 1. Introduction

Photo-catalytic degradation of organic pollutants by semiconductor photo-catalysts is promising for environmental purification and energy conversion [1-4]. Many organic compounds can be degraded successfully to safer end-products such as CO<sub>2</sub>, H<sub>2</sub>O and mineral acids via photo-catalytic method [5,6]. However, many photo-catalysts reported having a dissatisfactory efficiency for photo-degradation of organic pollutants or water-splitting due to their inherent characteristic including low redox ability, high photo-generated holes-electron pair recombination and serious photo-corrosion [7]. Zinc germanate  $(Zn_2GeO_4)$ , as a ternary oxide with a wide bandgap of 4.68 eV and willemite structure, has attracted great attention for various applications due to its optical and electrochemical properties [8]. It is reported that the UV photodetectors made by Zn<sub>2</sub>GeO<sub>4</sub> materials exhibit high-wavelength selectivity, and carbon dioxide can be reduced to organic matter (e.g. formic acid) [9–11]. A Zn<sub>2</sub>GeO<sub>4</sub> crystal cell is composed of GeO<sub>4</sub> and ZnO<sub>4</sub> tetrahedra. A GeO<sub>4</sub> tetrahedron of Zn<sub>2</sub>GeO<sub>4</sub> is so heavily distorted to generate a dipole moment inside, which is considered to promote the separation of electron-hole pairs generated by light irradiation [12]. Zn<sub>2</sub>GeO<sub>4</sub> can be used as a promising photo-catalyst for the decomposition of organic pollutants and photoreduction of CO<sub>2</sub> due to its intrinsic properties such as stability,

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### ABSTRACT

The Zn<sub>2</sub>GeO<sub>4</sub> nanorod photocatalysts with Ag doping and Ag decorating (Ag-modified Zn<sub>2</sub>GeO<sub>4</sub>) were synthesized by a mild solvothermal method. The as-prepared samples were characterized by field emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectrum (EDS) measurements. The one-dimensional (1D) Ag-modified Zn<sub>2</sub>GeO<sub>4</sub> nanorods exhibited excellent photo-degradation performance using RhB and phenol as model for organic pollutants. The cycle degradation results revealed that Ag-modified Zn<sub>2</sub>GeO<sub>4</sub> nanorods had an excellent chemical stability. The active species trapping experiment suggested that the hydroxyl radicals and superoxide radical were the dominating active species, rather than holes.

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electronic configuration and crystal structure [13]. However, Zn<sub>2</sub>GeO<sub>4</sub> photo-catalysts still cannot meet the requirements of practical application due to their insufficient photo-degradation ability. Therefore, it is promising and indispensable to enhance their photo-catalytic efficiency by modification, such as doping, coupling and supporting [14]. Herein, we developed a facile solvothermal method for the preparation of Ag-modified Zn<sub>2</sub>GeO<sub>4</sub> nanorods. The resultant composites exhibited excellent photo-catalytic activity on the degradation of RhB and phenol.

# 2. Results and discussion

Fig. 1A shows the SEM image of Ag-modified  $Zn_2GeO_4$  phtocatalysts when the  $R_N$  is 0.1. The product is an aggregation of short nanorods. And these nanorods tend to agglomerate to form nanorod bundles, resulting in a larger physical dimension. The TEM image of Ag-modified  $Zn_2GeO_4$  ( $R_N = 0.1$ ) nanorods displays the uniform and small size nanorods with ca. 120 nm in length and 20 nm in diameter (Fig. 1B). The Ag-modified  $Zn_2GeO_4$  nanorods become more slender with increasing  $R_N$  value (Fig. S1). The interplanar distance with well-defined lattice fringes is 0.259 nm which is defined to be the distance of (410) D-spacing in the rhombohedral phase of  $Zn_2GeO_4$  (Fig. 1C). The corresponding SAED image reveals the single-crystalline nature of Ag-modified  $Zn_2GeO_4$  nanorods (Fig. 1D).

Fig. 2A shows the XRD patterns of as-prepared samples. All diffraction peaks of the samples can be well-indexed to the rhombohedral phase of Zn<sub>2</sub>GeO<sub>4</sub> (JCPDS: 11-0687). It is worth noting that the intensity of peaks at  $2\theta = 37.8^{\circ}$ , 43.8° and 76.8° increases obviously with improving R<sub>N</sub> value. It can be attributed to the overlap of diffraction peaks between



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Fig. 1. FE-SEM (A), TEM (B), HR-TEM (C) images and SAED pattern of Ag-modified Zn<sub>2</sub>GeO<sub>4</sub> (R<sub>N</sub> = 0.1) (D).

Zn<sub>2</sub>GeO<sub>4</sub> products and face-centered cubic phase of silver (JCPDS: 65-8428) that formed by reducing of Ag<sup>+</sup>. The existence of silver in the products is also confirmed by the EDS analysis (Fig. S2). In order to investigate the Ag valence states, XPS spectra of the Ag-modified Zn<sub>2</sub>GeO<sub>4</sub> (R<sub>N</sub> = 0.1) was measured. As shown in Fig. 2B, the XPS spectrum of Ag 3d indicates that there are two components after solvothermal reaction, corresponding to Ag<sub>2</sub>O (367.4 eV) and Ag<sup>0</sup> (368.1 eV), respectively [15]. According to the peak area of two components, the ratio of Ag<sup>+</sup>/Ag<sup>0</sup> can be estimated as 1.43/1. From the above results, it can be concluded that the Ag doping and depositing is simultaneous during the solvothermal reaction. The Ag-modified Zn<sub>2</sub>GeO<sub>4</sub> (R<sub>N</sub> = 0.1) exhibits the specific surface area and average pore size at 17.84 m<sup>2</sup>/g and 26.7 nm, respectively (Fig. S3).

For explaining the formation of Ag-modified  $Zn_2GeO_4$  products, a group of possible reaction equation that occurred in sequence was exhibited. Firstly, the GeO<sub>2</sub> solid is dissolved in the mixture solvent [Eqs. (1) and (2)] [16]. Secondly, the reaction between zinc ion from  $Zn(CH_3COO)_2 \cdot 2H_2O$  and  $HGeO_3^-$  is taken place under alkaline conditions. Meanwhile, the silver ion from silver nitrate can take part in the reaction of zinc ion and  $HGeO_3^-$  under alkaline conditions [Eq. (3)], and a part of Ag<sup>+</sup> were reduced to Ag attributed to the reducing role of diethanolamine [17]. Thus, the Ag-modified  $Zn_2GeO_4$  materials are generated.

$$[HO(CH_2)_2]NH + H_2O \leftrightarrow [HO(CH_2)_2]NH_2^+ + OH^-$$
(1)

$$\text{GeO}_2 + \text{OH}^- \leftrightarrow \text{HGeO}_3^-$$
 (2)

$$xZn^{2+} + (4-2x)Ag^{+} + HGeO_{3}^{-} + 3OH^{-} \leftrightarrow Zn_{x}Ag_{(4-2x)}GeO_{4} + 2H_{2}O$$
(3)

In order to investigate the photo-catalytic activity of Ag-modified  $Zn_2GeO_4$ , the as-prepared nano-materials with different  $R_N$  values were used for decolorization of RhB under light irradiation. As shown in Fig. 3A, the decolorization rate of RhB is accelerated when the pure

 $Zn_2GeO_4$  and Ag-modified  $Zn_2GeO_4$  nanorods are used as catalyst, and there is no doubt here that photo-catalysis played an important role to decolor RhB. Interesting, the decolorization rate of RhB is not increased with improving amount of modified Ag. Especially, it can be found that the 91% of RhB can be decolored after 30 min when the  $R_N$  is at 0.1 and only 70% of RhB can be removed using pure Zn<sub>2</sub>GeO<sub>4</sub> as the photocatalyst. It may be attributed to an isolated energy level of Ag 3d formed in the band gap of Zn<sub>2</sub>GeO<sub>4</sub> and lower hole–electron pair recombination [18]. Moreover, as shown in Fig. 3B, the photo-catalytic activity of the samples do not exhibit any significant loss which indicates that the Ag-modified materials are stable and effective for the degradation of organics in aqueous solution. To further prove the photo-catalytic activity of the catalysts, the degradation of the phenol is carried out. As observed in Fig. 3C, 95% of phenol can be degraded in the presence of Ag-modified  $Zn_2GeO_4$  ( $R_N = 0.1$ ) catalysts compared with only 1.8% of phenol removed in the absence of catalyst. For detecting the active species of Ag-modified Zn<sub>2</sub>GeO<sub>4</sub> during photo-catalytic reactivity, hydroxyl radicals (\*OH), the superoxide radical  $(O_2^{\bullet-})$ , and holes  $(h^+)$  are investigated by adding 1.0 mM IPA (a quencher of  $^{\circ}OH$ ), BQ (a quencher of  $O_2^{\circ-}$ ), and TEOA (a quencher of h<sup>+</sup>), respectively [18]. After irradiation for 30 min under UV light, the degradation of RhB decreases obviously with the addition of 1 mM IPA or BQ (Fig. 3D). Therefore, it can be concluded that the main active species of Ag-doped Zn<sub>2</sub>GeO<sub>4</sub> are hydroxyl radicals ( $^{\circ}OH$ ) and the superoxide radical ( $O_{2}^{\circ-}$ ), rather than holes. This may be attributed that the high energy of the holes can result into the oxidation of  $OH^-$  to 'OH rapidly.

The plausible schematic diagram of photo-degradation is shown in Scheme 1. The UV-light irradiation will activate the Ag-modified  $Zn_2GeO_4$  to generate electron transition which strongly forms oxidative holes (h<sup>+</sup>) at the edge of valence band and reductive electrons (e<sup>-</sup>) at the edge of conduction band. The potential of edges of valence band ( $E_{VB}$ ) and conduction band ( $E_{CB}$ ) is estimated to be 3.88 eV and -0.8 eV via the Mulliken electronegativity method, respectively



Fig. 2. XRD patterns of as-prepared samples with different R<sub>N</sub> values (A: (a) R<sub>N</sub> = 0, (b) R<sub>N</sub> = 0.1, (c) R<sub>N</sub> = 0.3, and (d) R<sub>N</sub> = 0.5). XPS spectrum of Ag 3d of Ag-modified Zn<sub>2</sub>GeO<sub>4</sub> (R<sub>N</sub> = 0.1) (B).



**Fig. 3.** Photocatalytic degradation of RhB aqueous solution with different photocatalytss (A), cycling runs of Ag-modified Zn<sub>2</sub>GeO<sub>4</sub> (R<sub>N</sub> = 0.1) nanorods for the degradation of RhB aqueous solution (B), degradation of phenol aqueous solution over the Ag-modified Zn<sub>2</sub>GeO<sub>4</sub> (R<sub>N</sub> = 0.1) catalyst (C) and trapping experiments of active species during the photocatalytic reaction (D).

[19,20]. Due to the formation of the isolated energy level of Ag 3d, the photo-generated electrons more readily jump between the valence band and the conduction band. However, the isolated energy level of 3d



**Scheme 1.** Schematic illustration of the photocatalytic mechanism of organic pollutants degradation over Ag-modified Zn<sub>2</sub>GeO<sub>4</sub> catalyst.

is also the recombination centers for holes and electrons. Therefore, when the content of Ag is above the optimal value, metallic silver may act as recombination centers, which is caused by the electrostatic attraction of negatively charged silver and positively charged holes [21]. Furthermore, excessive silver may reduce the number of photons absorbed by the photo-catalyst due to the light-filtering effect, which lowered the apparent photo-quantum efficiency of the photo-catalytic reaction and also decreased the probability of holes reacting with absorbed species on the  $Zn_2GeO_4$  surface. It is the main reason that the photo-catalytic activity decreased with the increasing of  $R_N$  value in the catalysts.

# 3. Conclusion

The Ag-modified  $Zn_2GeO_4$  nanorods were successfully synthesized by a solvothermal route. The Ag-modified  $Zn_2GeO_4$  photo-catalysts exhibit higher photo-catalytic activity than that of the pure  $Zn_2GeO_4$ . The active species trapping experiment suggested that the hydroxyl radicals and superoxide radical were the dominating active species, rather than holes. This material will be a very promising photocatalyst for degradation of organic pollutants.

### Acknowledgments

This work was financially supported by the "521 Talents Training Plan" in ZSTU, the National Natural Science Foundation of China (51373155, 51133006), the Natural Science Foundation of Zhejiang Province (LY13B030009) and the Public Technological Research Project of Zhejiang Province (2012C21098). B. T. thanks the Innovative Program for Graduate Students of Zhejiang Sci-Tech University through Grant 2013YSPY15.

# Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.powtec.2013.10.018.

## References

- [1] T. Lee, V.-D. Le, D. Lim, Y.-C. Lin, G.M. Morris, A.L. Wong, et al., J. Am. Chem. Soc. 121 (1999) 1145-1155.
- R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 293 (2001) 269–271.
  Z. Zou, J. Ye, K. Sayama, H. Arakawa, Nature 414 (2001) 625–627.
- [4] Bai, L. Wang, Y. Zhu, ACS Catal. 2 (2012) 2769–2778.
- [5] G. Jiang, X. Zheng, Y. Wang, T. Li, X. Sun, Powder Technol. 207 (2011) 465–469.
  [6] R. Wang, G. Jiang, Y. Ding, Y. Wang, X. Sun, X. Wang, et al., ACS Appl. Mater. Interfaces 3 (2011) 4154–4158.
- [7] G. Jiang, X. Wang, Z. Wei, X. Li, X. Xi, R. Hu, et al., J. Mater. Chem. A 1 (2013) 2406–2410.

- [8] M.M. Jumidali, K.M. Sulieman, M.R. Hashim, Appl. Surf. Sci. 257 (2011) 4890-4895.
- [9] C. Yan, N. Singh, P.P. Lee, Appl. Phys. Lett. 96 (2010) 053108–053112.
  [10] C. Yan, P.P. Lee, J. Phys. Chem. C 114 (2010) 265–268.
- [11] Q. Liu, Y. Zhou, J. Kou, X. Chen, Z. Tian, J. Gao, et al., J. Am. Chem. Soc. 132 (2010) 14385-14387.
- [12] J. Sato, H. Kobayashi, K. Ikarashi, N. Saito, H. Nishiyama, Y. Ioue, J. Phys. Chem. B 108 (2004) 4369-4375.
- [13] Q. Liu, Y. Zhou, Z. Tian, X. Chen, J. Gao, Z. Zou, J. Mater. Chem. 22 (2012) 2033–2038. [14] G. Jiang, R. Wang, X. Wang, X. Xi, R. Hu, Y. Zhou, et al., ACS Appl. Mater. Interfaces
- 4 (2012) 4440-4444.
- [15] M.A. Thomas, W.W. Sun, J.B. Cui, J. Phys. Chem. C 116 (2012) 6383–6391.
- [16] Y. Sun, L. Yu, P. Rao, J. Cryst. Growth 347 (2012) 73-76.
- [17] J.F. Rusling, P. Zuman, Anal. Chem. 52 (1980) 2209–2211.
- [18] R. Liu, P. Wang, X. Wang, H. Yu, J. Yu, J. Phys. Chem. C 116 (2012) 17721-17728.
- [19] L. Ye, J. Liu, C. Gong, L. Tian, T. Peng, L. Zan, ACS Catal. 2 (2012) 1677–1683.
- [20] M.A. Butler, D.S. Ginley, J. Electrochem. Soc. 125 (1978) 228-232.
- [21] Z. Jia, K. Peng, Y. Li, R. Zhu, Trans. Nonferrous Met. Soc. China 22 (2012) 873-878.