

Sol-gel synthesis of black ZnO/AuNPs nanocomposites for effective photocatalytic activity of methylene blue*

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In this study, we present a facile method for the fabrication of ZnO/AuNPs hexagonal wurtzite structure by sol-gel method. Transmission electron microscope (TEM) results indicate that the synthesized AuNPs have good round shape and uniform size with an average diameter of 15 nm. Scanning electron microscope (SEM) results show that the prepared ZnO/AuNPs nanocomposites are uniform spheroidal nanoparticles with sizes in diameter from 60 nm to 100 nm. The presence of Zn, Au and O elements in those samples is determined by X-ray photoelectron spectroscopy (XPS) analysis. The investigation of photocatalytic ability shows that the ZnO/AuNPs (8 mL) achieve complete degradation of methylene blue (MB) under UV irradiation with 65 min. We can conclude that the presence of AuNPs hybrid ZnO can strongly enhance the photocatalytic performance of MB compared to pure ZnO, which may be attributed to the larger specific surface area and surface plasmon resonance (SPR) effect of AuNPs hybrid ZnO nanocomposites. This method may provide a new way to improve ZnO photocatalysis for water cleaning application.

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Industrialization has led to considerable increase in a number of phenols, pesticides, dye, solvents and other organic pollutants with potentially carcinogenic intermediates in natural resources. Photodegradation of organics in water has attracted much attention^[1,2]. In particular, semiconductors have been emerged as a promising strategy for elimination of environment pollution due to their potential work under solar irradiation without generating harmful substances by product. Among the various semiconductor photocatalysis, ZnO is a promising semiconductor with a band gap of 3.37 eV and a high bound exciton energy of 60 mV^[3,4], which is extensively investigated as a photocatalyst for environmental remediation due to its excellent photoelectric characteristics, favorable morphology and long time stability^[5,6]. However, some drawbacks of conventional ZnO limit its wide application due to the wide band gap (3.37 eV for anatase), which will result in poor absorption. And high recombination rate of photoinduced electron-hole pairs greatly hinders the photocatalytic efficiency of ZnO.

Many methods have been developed to overcome wide band gap of ZnO to get excellent photocatalytic properties. Doping ions have demonstrated better photocatalytic activity and facile, such as doping rare earth, metal and noble metals^[7-9], to improve photocatalytic efficiency by reducing the electron-hole pairs recombination, and to improve light absorption for narrowing the band gap of ZnO. Noble metal nanoparticles have been confirmed to

increase the photoenergy conversion efficiency of semiconductors by contributing the separation of charge carrier and extending the light absorption by surface plasmon resonance (SPR) effect, which is a collective oscillation of the free conduction band electrons at interface among noble metal nanoparticles^[10]. In addition, noble metal nanoparticles act as sinks for the photogenerated electrons leading to suppression of the recombination of photoexcited charge carriers and thereby resulting in the enhanced photocatalytic efficiency of noble metal ZnO hybrid nanostructures. Among noble metals, Au is proved to be a useful material to improve the catalytic properties due to the versatile properties such as the capacity to alter the physicochemical properties, SPR and conductivity. Although considerable efforts have been made on the synthesis of a serious Au/ZnO hybrids, most of the reported nanostructures were formed by ZnO supporter with Au nanoparticles deposited^[6, 10].

To our knowledge, it is rarely reported on the use of sol-gel method to obtain synthesized AuNPs hybrid ZnO for methylene blue (MB) degradation under UV light. On the basis of the above consideration, this work reports the effect of AuNPs on the structures, optical and morphological properties of ZnO by sol-gel method and the photocatalytic activity for MB. The advantages of sol-gel process include the possibility of scaling production,

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easy to handle sample in instrumental operation, cheap and uniform in morphology and size for produced materials. Zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), monoethanolamine (MEA) and Chloroauric acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, 48%—50% Au basis) were purchased from Macklin (China, www.labgogo.com). All the reagents used in this work were of analytical grade without further purification. Deionized water was used throughout the study.

Scanning electron micrographs (SEM) were obtained from an S-4800 scanning electron microscope (Hitachi, Japan). Transmission electron microscopic (TEM) images were obtained from a JEM-2100F transmission electron microscope (Hitachi, Japan). Fluorescence measurements were carried out on an F-4600 spectrophotometer (Hitachi, Japan).

All the reagents were used without any further purification, and the AuNPs were prepared according to our previously reported works by citrate reduction method^[11]. Briefly, 20 mL HAuCl_4 (0.5 mmol/L) was heated up to 90 °C under vigorous stirring for 5 min. Then 20 mL sodium citrate (0.25 mmol/L) was quickly added to the boiling solution with vigorous stirring. After the mixture was stirred vigorously for 30 min, the color of the pale yellow solution changed from faintly gray to claret-red. The solution was cooled down to room temperature and stored at 4 °C in a refrigerator.

The synthesis precursors of ZnO/AuNPs were prepared by dissolving 2.3 g of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in 30 mL mixture solution of deionized water (DI) water, AuNPs and ethanol under vigorous stirring at 65 °C for 10 min. The volumes of DI water, AuNPs and ethanol are 10 mL: 0 mL: 20 mL, 8 mL: 2 mL: 20 mL, 4 mL: 6 mL: 20 mL, 0 mL: 10 mL: 20 mL, respectively. Then 1 mL MEA was added drop by drop into vigorous stirring condition with continuous stirring for 2 h. Finally, the resulting sol was heat-treated in a quartz-tube furnace at 600 °C for 2 h in nitrogen (N_2).

10 mg ZnO/AuNPs were added into 25 mL MB solution (20 mg/L), then the suspension was stirred magnetically in dark for 1 h to establish absorption-desorption equilibrium between the photocatalyst. Then the solution was irradiated by a 300 W Hg light illumination. At a given time interval of irradiation, about 4 mL mixture was withdrawn, then was centrifuged three times with 10 000 r/min for 3 min to remove all the photocatalyst. The concentration of MB was monitored on UV-vis spectrometer and estimated from its maximum absorption wavelength.

Fig.1(a) shows the TEM image of the AuNPs, respectively. Fig.1(a) indicates that AuNPs are uniformly distributed and the synthesized AuNPs have good round shape and uniform size with an average diameter of 15 nm.

Fig.1(b) and Fig.1(c) show the low and high magnification SEM images of ZnO/AuNPs nanocomposites (8 mL), respectively. The presence of ZnO/AuNPs nanocomposites shows uniform spheroidal nanoparticles.

Most of the ZnO nanoparticles are of the size in diameter from 60 nm to 100 nm. But the structure of the ZnO/AuNP nanoparticles is destroyed when the amount of AuNPs is increased to 10 mL.

The X-ray photoelectron spectroscopy (XPS) technique was used to investigate chemical states of elements in ZnO/AuNPs as shown in Fig.2. Au, C, O and Zn can be observed from the survey spectrum in Fig.2(a). Fig.2(b) shows that the core level spectrum of Zn 2p consist of two peaks 1 020.9 eV and 1 044.0 eV, corresponding to Zn 2p_{3/2} and 2p_{1/2}, respectively. The peak separation of 23.1 eV is consistent with that of the standard reference value for pure ZnO. Fig.1(c) shows the XPS spectrum of O 1s. The peak can be fitted well when two Gaussian peaks centered at 529.6 eV and 530.2 eV are used. This corresponds to O²⁻ ions in the wurtzite ZnO surrounded by the ZnO atoms and the deficient O²⁻ ions within the ZnO matrix^[12]. The core level spectrum of Au 4f, as shown in Fig.2(d), is composed of two peaks centered at binding energies of 87.9 eV and 90.6 eV for ZnO/AuNPs (8 mL) nanocomposites, respectively. The position of binding energy at 87.9 eV is consistent with metallic Au. The other of binding energy at 90.6 eV is due to the $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ in the preparation of AuNPs. So we can conclude that the ZnO/AuNPs nanocomposites are composed of Zn, O and Au.

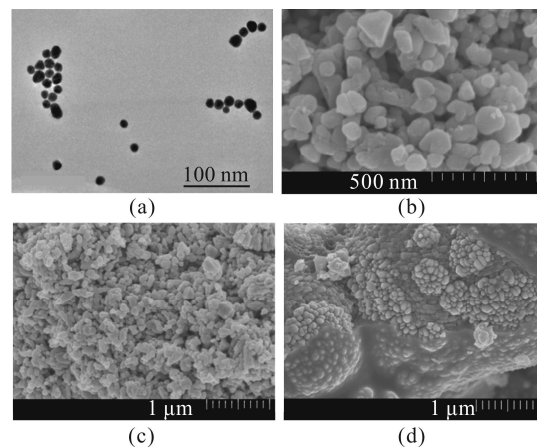


Fig.1 (a) TEM image of synthesized AuNPs; (b) High-magnification SEM image of ZnO/AuNPs (8 mL) nanocomposites; Low-magnification SEM images of (c) ZnO/AuNPs (8 mL) and (d) ZnO/AuNPs (10 mL) nanocomposites

Fig.3 shows room temperature PL spectra of as-prepared undoped ZnO and ZnO/AuNP nanocomposites with different amounts of AuNPs under excitation of 325 nm. Two PL peaks can be observed. One is near-band edge emission around 380 nm and the other is a broad emission around 500 nm. The sharp near band edge emission can be attributed to the transition from conduction band to valence band and the free exciton recombination process. The broad yellow emission corresponds to the intrinsic deep level defect emission of

ZnO^[9]. It can be shown that the ZnO/AuNPs nanocomposites exhibit lower PL intensity than the pure ZnO. This indicates that the lower PL intensity is due to lower recombination rate of photo-excited electron and hole pairs, and hence the improved photoactivity in UV light photocatalysis process. In particular, ZnO/AuNPs (8 mL) exhibit lower PL emission than other samples, which means that ZnO/AuNPs have the highest charge transfer efficiency among the ZnO/AuNPs and agrees with the photocatalytic activity. The decrease of PL intensity in Fig.3 for the peak of ZnO/AuNPs at around 500 nm is due to that the high AuNPs incorporated concentration would reduce the distance of the AuNPs. Furthermore, as one pattern of the non-radiative relaxation process, the cross relaxation between the neighbouring AuNPs would take place, which quenches the PL efficiency^[13]. The difference between the PL peak of ZnO/AuNPs (10 mL) and other ZnO/AuNPs results in that the ZnO/AuNPs (10 mL) nanoparticles are destroyed.

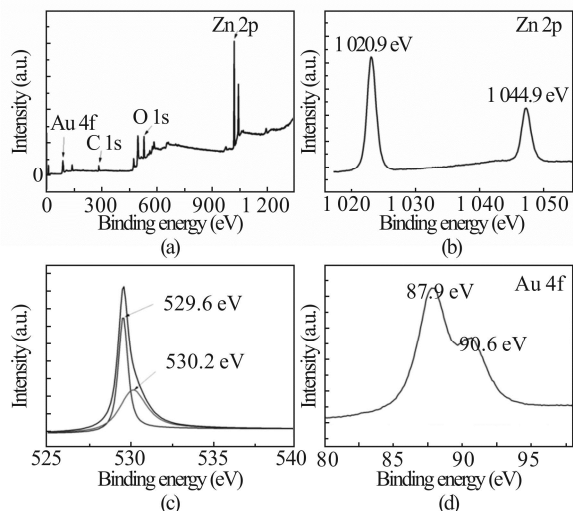


Fig.2 Typical XPS results of the ZnO/AuNPs (8 mL) nanocomposites: (a) Full spectrum; Core level spectra of (b) Zn 2p, (c) O 1s and (d) Au 4f

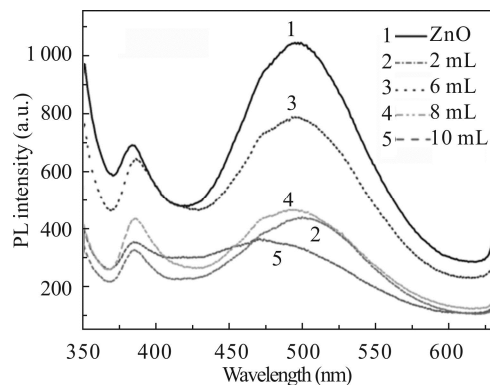


Fig.3 Room temperature PL spectra of ZnO/AuNPs nanocomposites with different amounts of AuNPs under excitation of 325 nm

with different times using ZnO/AuNP (8 mL) nanocomposites. It can be seen that the characteristic absorption of MB at 665 nm decreases progressively with the increase of UV irradiation time and completely disappears after 65 min. As in Fig.4(b), ZnO/AuNPs nanocomposites have higher photocatalytic activity than pure ZnO nanoparticles, which is due to the high specific surface area caused by the smaller diameter of the spheres. Moreover, considering SPR absorption of AuNPs in ZnO/AuNPs nanocomposites, the SPR electrons and holes are generated and then separated. The electrons are transferred to the conduction band of ZnO while the holes are left on Au. These photo-excited holes could oxidize the absorbed water molecules to form hydroxyl radicals, which can result in conductive H₃O⁺ and high charge density on the surface of ZnO/AuNPs nanocomposites^[14].

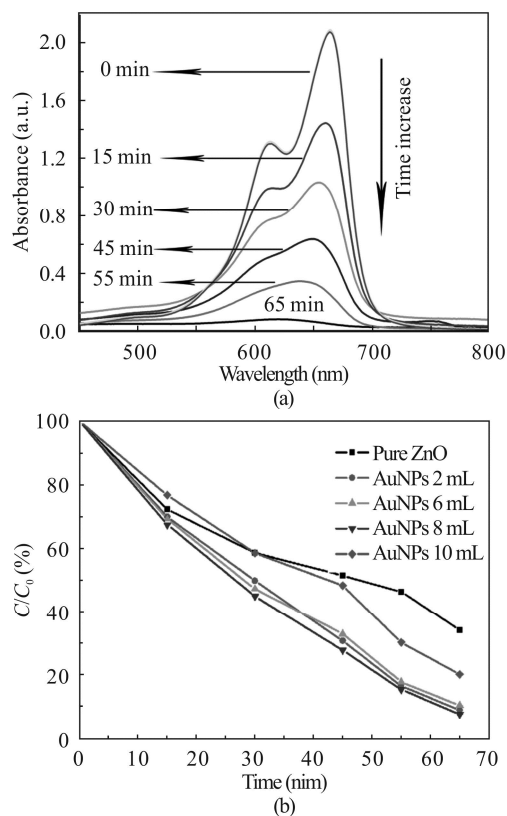


Fig.4 (a) Time-dependent optical absorbance spectra for photocatalytic degradation of MB dye under UV light irradiation using ZnO/AuNPs (8 mL) as photocatalysts; (b) The degradation rate of MB over ZnO/AuNPs with different amounts of AuNPs

ZnO/AuNPs nanocomposites with smaller size and high uniformity have been successfully obtained by sol-gel method. The amount of AuNPs plays an important role in the morphology of ZnO hexagonal wurtzite structure. The ZnO/AuNPs nanocomposites significantly improve MB photodegradation ability compared to pure ZnO under UV irradiation, which may be at-

Fig.4(a) shows the absorption spectra of MB solution

tributed to large specific surface area and SPR effect of AuNPs hybrid ZnO nanocomposites.

References

- [1] S. Wei, R. Wu, X. Xu, J. Jian, H. Wang and Y. Sun, *Chemical Engineering Journal* **299**, 120 (2016).
- [2] S. Girish Kumar and K.S.R. Koteswara Rao, *Applied Surface Science* **391**, 124 (2017).
- [3] J. W. Cai, J. P. Xu, X. S. Zhang, X. P. Niu, T. Y. Xing, T. Ji and L. Li, *Optoelectronics Letters* **8**, 4 (2012).
- [4] LI Yong-fu, ZHANG Ya-guang, LIU Jun-liang and WANG Qing-pu, *Optoelectronics Letters* **11**, 260 (2015).
- [5] M. Kwiatkowski, R. Chassagnon, O. Heintz, N. Geofroy, M. Skompsk and I. Bezverkhyy, *Applied Catalysis B: Environmental* **204**, 200 (2017).
- [6] S. Kuriakose, K. Sahu, S. A. Khan, A. Tripathi, D. K. Avasthi and S. Mohapatra, *Optical Materials* **64**, 47 (2017).
- [7] J. Z. Huang, S. Y. Liu, N. N. Yao and X. J. Xu, *Optoelectronics Letters* **10**, 161 (2014).
- [8] X. Yu, X. M. YU, J. J. Zhang and H. J. Pan, *Optoelectronics Letters* **11**, 329 (2015).
- [9] M. H. Li, X. M. Chen, J. Xu, X. S. Zhang, Y. Y. Wu, P. Li, X. P. Niu, C. Y. Luo and L. Li, *Optoelectronics Letters* **8**, 241 (2012).
- [10] W. P. FENG, A. H. Jing, J. H. Li and G. F. Liang, *Optoelectronics Letters* **12**, 195 (2016).
- [11] H. Y. Zhang, J. Lv and Z. H. Jia, *Sensors* **17**, 1078 (2017).
- [12] S. Wu, Z. Chen, T. Wang and X. Ji, *Applied Surface Science* **412**, 69 (2017).
- [13] L. F. Koao, B. F. Dejene, H. C. Swart, S. V. Motoloung and T. E. Motaung, *Optical Materials* **60**, 294 (2016).
- [14] T. Liu, W. Chen, Y. Hua and X. Liu, *Applied Surface Science* **392**, 616 (2017).