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Preparation of Ag-sensitized ZnO and its photocatalytic performance under simulated solar light

Feng Peng†, Hancai Zhu, Hongjuan Wang and Hao Yu

The School of Chemical and Energy Engineering, South China University of Technology, Guangzhou 510640, P. R. China
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Abstract−ZnO was prepared rapidly by microwave heating method. The results of scanning electron microscopy show that the leaflike ZnO is composed of self-assembled ZnO particles of 30-50 nm. Ag-sensitized ZnO composite was prepared by UV-photoreduction and glycol reduction, respectively. The composite was characterized by means of scanning electron microscopy, X-ray diffraction and photoluminescence. The ZnO and Ag/ZnO prepared were applied in photocatalytic degradation of phenol and methyl orange as model of organic pollutant in water under simulated solar light. The results show that Ag doping in both methods of UV-photoreduction and glycol reduction can remarkably improve the photocatalytic activity of ZnO under simulated solar light. The utilization ratio of Ag in glycol reduction is high and the optimum content of Ag in Ag/ZnO composite is only 1.33%. Therefore, the glycol reduction is a novel and excellent method for preparing Ag-sensitized ZnO composite with high photocatalytic activity.

Key words: Nanostructures, Photocatalysis, ZnO, Photocatalytic Degradation, Solar Light

INTRODUCTION

Photocatalysis is an efficient method used in energy and environmental protection because of its low energy cost, mild reaction condition and easy operation [1-4]. ZnO is close to being an ideal photocatalyst, due to being relatively cheap, nontoxic and with holes of strong oxidizing power. ZnO has been proven to be very active in the photocatalytic oxidation of different organic compounds, which has received much attention in the degradation and complete mineralization of environmental pollutants [5-7]. ZnO has approximately the same band gap energy (3.2 eV) as TiO_2 and its photocatalytic capacity is anticipated to be similar to that of TiO_2. A drawback of using ZnO as photocatalyst is that it can only be activated by ultraviolet light of wavelength below 385 nm [8]. The ultraviolet light reaching the earth's surface is less than 5% of the solar energy, which is too low to attain significant photodegradation in commercial application. Some interesting approaches have been adopted to extend the photo-response of ZnO toward the visible spectral region, such as implanting transitional metal ions [9-12], doping with nitrogen [13-16] and photosensitization [17,18]. Recently, considerable attempts have been made to use small band gap semiconductors, such as CdS and Cu_2O, to photosensitize TiO_2 or ZnO in the visible light region [19-21]. In fact, metal silver is also a significant visible light photosensitizer, which is stable and nontoxic compared with dye-photosensitizer. Ag is also relatively cheap; thus Ag modification is of great significance for industrial practice. The improvement in efficiency of photocatalytic reactions under visible light is explained as the result of a vectorial transfer of photogenerated electrons and holes from metal to semiconductor. Moreover, ZnO modified by Ag can improve the distribution of surface charges, accept a conduction band generated by solar light irradiation during photo-reaction, prevent the recombination of the photogenerated electron-hole and thereby increase the efficiency of photocatalysis effectively. Some reports also indicate that Ag precipitated onto the ZnO surfaces can greatly improve the photocatalytic degradation activity of ZnO [22,23]. Many researchers reported that ZnO thin film with Ag doping, which enhances ultraviolet emission and improves electrical and optical properties, was prepared by ion-implantation [24], DC magnetron sputtering [25,26] and pulsed laser deposition [27]. But the most of reported methods for Ag doping in ZnO nanoparticles are UV-photoreduction [28-30], that is, Ag ion in aqueous solution was reduced onto ZnO nanoparticles surface under UV irradiation.

We reported here a simple and facile microwave heating method to synthesize the leaf-like ZnO successfully. Ag-sensitized ZnO composite was prepared by two methods of UV-photoreduction and glycol reduction with as-synthesized leaf-like ZnO. Photocatalytic reactions show that Ag doping in both methods can remarkably improve the photocatalytic activity of ZnO under simulated solar light. However, glycol reduction is a novel and excellent method for preparing Ag-sensitized ZnO composite with high photocatalytic activity.

EXPERIMENTAL SECTION

1. Materials

Zinc acetate ($Zn(OAc)_2$), glycerol, glycol, silver nitrate, ethanol absolute, methyl orange and phenol were used either as the starting material for the preparation of the catalysts or in the measurement of photocatalytic activity. All chemicals were of analytical reagent grade quality and were used as received. The water used was doubly distilled.

2. ZnO Preparation

Certain amount of $Zn(OAc)_2$ was dissolved in a solvent mixture of 80 mL glycol and 40 mL glycerol. After stirring, a transparent solution was obtained. The solution was then placed in a conventional microwave with power of 1,000 W. The experiment was operated for several cycles (35 s as a cycle with 15 s on and 20 s off)

†To whom correspondence should be addressed.
E-mail: cefpeng@scut.edu.cn

until deposition appeared. Five more cycles were executed to make the reaction complete. The resulting mixture was filtered and washed with distilled water and ethanol. The filter cake was then dried at 100 °C for 12 h and further calcined at 400 °C for 2 h to obtain as-synthesized ZnO powder.

3. Ag/ZnO Composite Preparation

UV-photoreduction method: In a typical synthesis, the ZnO powder (0.200 g) is added to a stirred solution of $AgNO_3$ (0.136 g, 0.800 mmol) in distilled water (100 mL). The solution is vigorously stirred for 30 min before irradiation to establish desorption/adsorption equilibrium of Ag^+. A 500 W high-pressure mercury lamp is used as an irradiation source. Irradiation is carried out at room temperature. The resulting powder is washed with distilled water and ethanol, and then dried to form Ag/ZnO-1.

Glycol reduction method: In a typical synthesis, the ZnO powder (0.200 g) and $AgNO_3$ (0.0042 g, 0.0246 mmol) is added to glycol (40 mL). The solution is vigorously stirred for 30 min to establish desorption/adsorption equilibrium of Ag^+. The solution is then placed in a conventional microwave with power of 1,000 W. The experiment is operated for 10 cycles (35 s as a cycle with 15 s on and 20 s off). The resulting powder is washed with distilled water and ethanol, and then dried to form Ag/ZnO-2.

4. Samples Characterization

An X-ray diffractometer (D/max-IIIA, Japan) was used for XRD (X-ray diffraction) analysis. The radiation source was Cu Kα, and the applied current and voltage were 30 mA and 30 kV, respectively. During the analysis, the sample was scanned from 5° to 70°. The surface morphology was characterized with SEM (scanning electron microscopy, LEO1530VP, LEO Company) at an acceleration voltage of 15 kV. The PL (photoluminescence) spectra were obtained from a Hitachi F-4500 spectrophotometer equipped with a Xe lamp as the excitation light source at room temperature. All the filtrate in the preparation process was collected and analyzed by atomic adsorption spectroscopy (Shimadzu AA-6800) to calculate the exact utilization ratio of Ag.

5. Photocatalytic Activity

The photocatalytic reaction was conducted in 200 mL cylindrical glass vessel fixed in the XPA-II photochemical reactor (Nanjing Xujiang Machine-electronic Plant). The reactor was equipped with several accessories, such as magnetic force stirrer, quartz cool trap, condensation tube, which can keep the reaction temperature

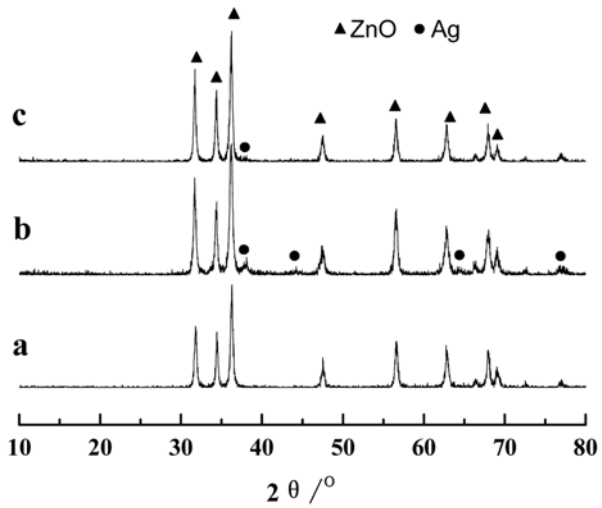

Fig. 1. XRD patterns of ZnO (a), Ag/ZnO-1 (b) and Ag/ZnO-2 (c).

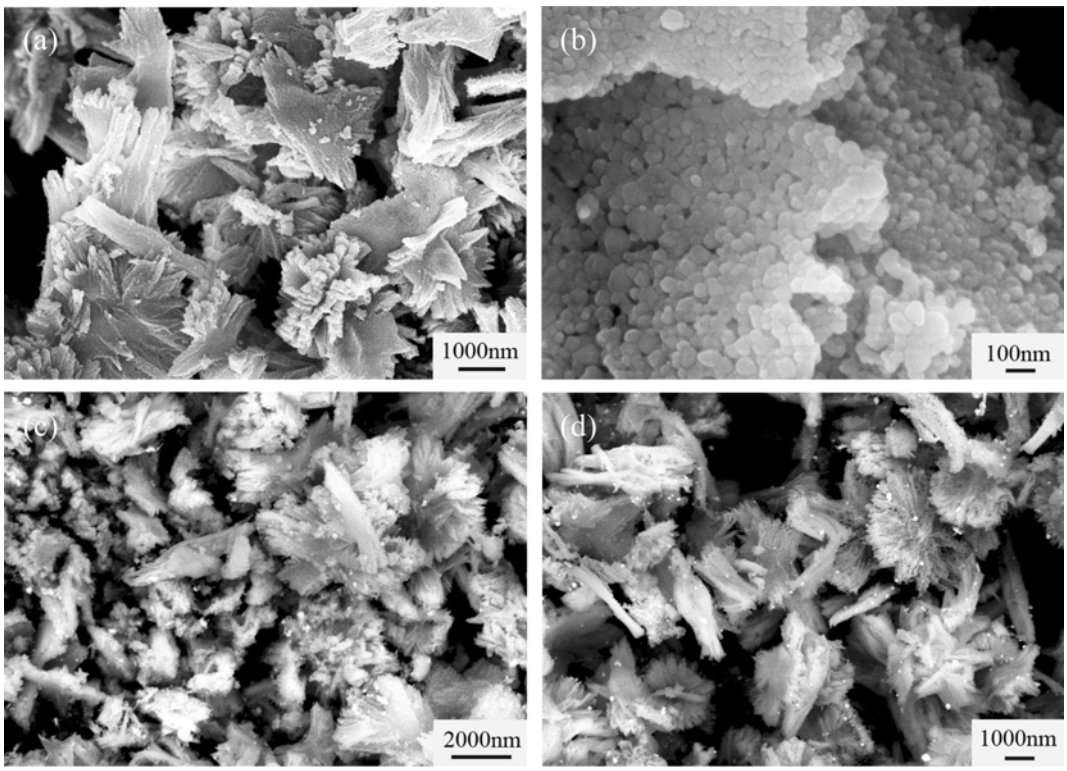

Fig. 2. SEM images of ZnO (a and b), Ag/ZnO-1 (c) and Ag/ZnO-2 (d).

steady and prevent the evaporation of water. A 1,000 W Xe lamp (λ_{max}=600 nm) was used as simulative solar light source. Methyl orange dye (MO) or phenol was used as reactant with a concentration of 20 mg/L. Photocatalyst powder of 20 mg was firstly dispersed in 200 mL reaction solutions by ultrasonication for 15 min to obtain an optimally dispersed system and to reach complete adsorption/desorption equilibration. Subsequently, oxygen was blown into the reaction medium at a flow rate of 100 mL/min during the course of the reaction. At regular intervals, 15 mL of the suspension was sampled and filtered through a 0.2 μm membrane filter. The concentrations of remaining pollutants were measured by their absorbency (A) at 465 nm (methyl orange) or 270 nm (phenol) with a UV-Vis spectrometer (U3010, HITACHI, Japan). The degradation ratio (X) of reactant can be calculated by $X(\%)=100(A_0-A)/A_0$.

RESULTS AND DISCUSSION

Fig. 1 shows XRD patterns of ZnO and Ag/ZnO prepared by different methods. In Fig. 1a, all peaks are regarded as an attributive indicator of hexagonal ZnO wurtzite structure (JCPDS card 5-0644). The average crystallite size of ZnO, evaluated by the Scherrer formula, is about 11 nm. Compared with Fig. 1a, redundant peaks in Fig. 1b correspond to the cubic Ag-related phase (JCPDS card 01-1167) and the intensity of these peaks in Fig. 1c is very weak because the amount of Ag is very small.

In Fig. 2a, it can be seen that the ZnO synthesized by microwave is leaf-like form. Fig. 2b shows the leaf-like ZnO is composed of self-assembled ZnO particles of 30-50 nm. Fig. 2c and Fig. 2d show that Ag-sensitized ZnO prepared by photoreduction or glycol reduction does not cause any change in the morphology compared with pure ZnO. But some newly formed small particles on the surface of ZnO can be observed clearly. These small particles can be considered as Ag by combining with the XRD and flame atomic absorption results.

To Ag/ZnO-1 catalyst, the effects of initial concentration of $AgNO_3$ and UV-photoreduction time on the ratio of the photocatalyzed decomposition of methyl orange are depicted in Fig. 3a and Fig. 3b, respectively. The photocatalytic activity of Ag/ZnO-1 increases rather rapidly initially with an increase of the initial concentration of $AgNO_3$ and the UV-photoreduction time and then reaches a plateau at the $AgNO_3$ concentration of 8 mmol·L^{-1} and a photoreduction time of 60 min. When the initial concentration of $AgNO_3$ is 8 mmol·L^{-1} and the photoreduction time is 60 min, the mass faction of Ag in Ag/ZnO-1 is 9.04%. The utilization ratio of Ag calculated by atomic absorption is about 30%.

We considered the UV-photoreduction mechanisms from the viewpoint of photolysis at ZnO catalyst. Oxidation and reduction occur at the same time in Ag ion photoreduction. In the reduction, the conduction-band electrons generated in the ZnO (e^-(CB)) by UV irradiation can reduce adsorbed Ag^+ ions, giving rise to Ag atoms (Ag^0). The reduced Ag is deposited on the ZnO surface. Photochemical reactions induced by ZnO-light are summarized as:

$$ZnO+h\nu \rightarrow e^-(CB)+h^+(VB) \quad (1)$$

$$Ag^+ + e^-(CB) \rightarrow Ag^0 \quad (2)$$

$$2H_2O+h^+(VB) \rightarrow O_2+4H^+ \quad (3)$$

Fig. 4 shows the effect of the Ag content on the photocatalytic activity of Ag/ZnO-2. The photocatalytic degradation ratio of methyl orange increases rather rapidly initially with the increase of the Ag

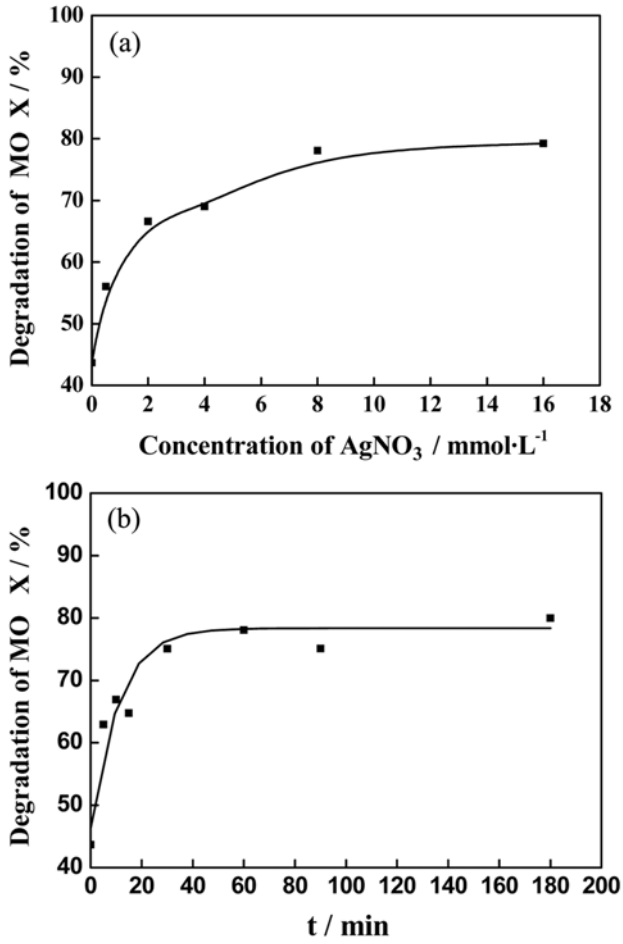

Fig. 3. The effects of initial concentration of $AgNO_3$ (a) and the UV-photoreduction time (b) on the photocatalytic activity of Ag/ZnO-1; photocatalytic reaction time of 30 min.

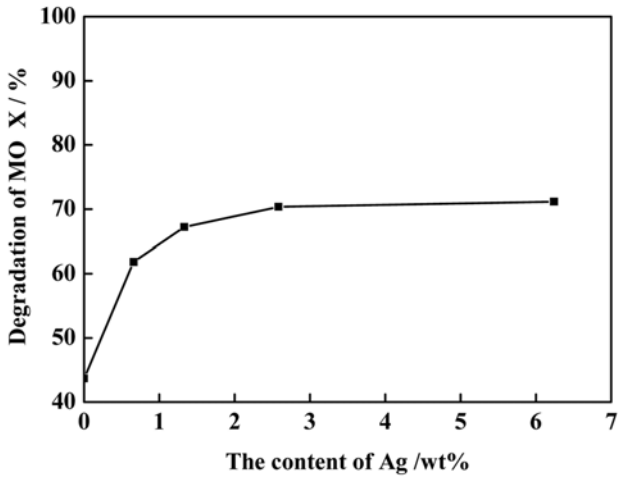

Fig. 4. The effect of the Ag content on the photocatalytic activity of Ag/ZnO-2; photocatalytic reaction time of 30 min.

content and reaches a plateau at the Ag content of 2.58%. But considering the price of $AgNO_3$ and only 3.14% increase of photocatalytic degradation ratio by increasing the Ag content from 1.33% to 2.58%, the optimum content of Ag in Ag/ZnO-2 catalyst is 1.33%. The utilization ratio of Ag calculated is about 95% for glycol reduction method.

Compared with the major reducing agents reported to date for the preparation of metal nanoparticles, ethylene glycol is an environmentally benign material. Ethylene glycol and diols can be used as a reducing agent to prepare metal particles through the so-called polyol process at high temperatures. EG is used not only as the reducing agent, but as solvent as well. In this study, dispersions of colloidal silver have been prepared rapidly by the reduction of silver nitrate by using a microwave technique; the reduced Ag is deposited on the ZnO surface. The reduction of Ag^+ to Ag by EG is denoted as:

$$HO\text{-}CH_2CH_2\text{-}OH+2Ag^+ \rightarrow HO\text{-}CH_2CHO+2Ag^0+2H^+ \quad (4)$$

In order to determine the optimum method of preparing Ag/ZnO, we chose both samples prepared in the optimum conditions to carry out photocatalysis experiments. The details are as follows: the mass faction of Ag in Ag/ZnO-1 is 9.04% for photoreduction method and the mass faction of Ag in Ag/ZnO-2 is 1.33% for glycol reduction method. In Fig. 5a, it can be seen that the photocatalytic degradation ratio of methyl orange is 69.5% after 60 min irradiation for ZnO catalyst. However, the photocatalytic degradation ratio of methyl orange can be up to 99.5% for both Ag/ZnO-1 and Ag/ZnO-2 catalysts. The activity of the Ag/ZnO-1 prepared by UV-photoreduction is a little better than that of the Ag/ZnO-2 prepared by glycol reduction. From Fig. 5b, it can be found that the photocatalytic degradation ratio of phenol for ZnO catalyst is only 17.3% and 54.1% after 60 min and 120 min irradiation, respectively. However, under the same photocatalytic reaction time, the photocatalytic degradation ratios of phenol reach 50.6% and 95.0% for Ag/ZnO-1 and 53.1% and 90.1% for Ag/ZnO-2. It suggests that the Ag-sensitized ZnO composite has much higher photocatalytic activity for phenol degradation than that of the pure ZnO under the simulated solar light. Incorporating Fig. 5a and Fig. 5b, it can be found that the photocatalytic activities of Ag/ZnO composites prepared by photoreduction and glycol reduction are very close. But the utilization ratio of Ag in glycol reduction is high and the optimum content of Ag in Ag/ZnO composite can be as low as 1.33%. Therefore, glycol reduction is a novel and excellent method for preparing Ag-sensitized ZnO composite with high photocatalytic activity.

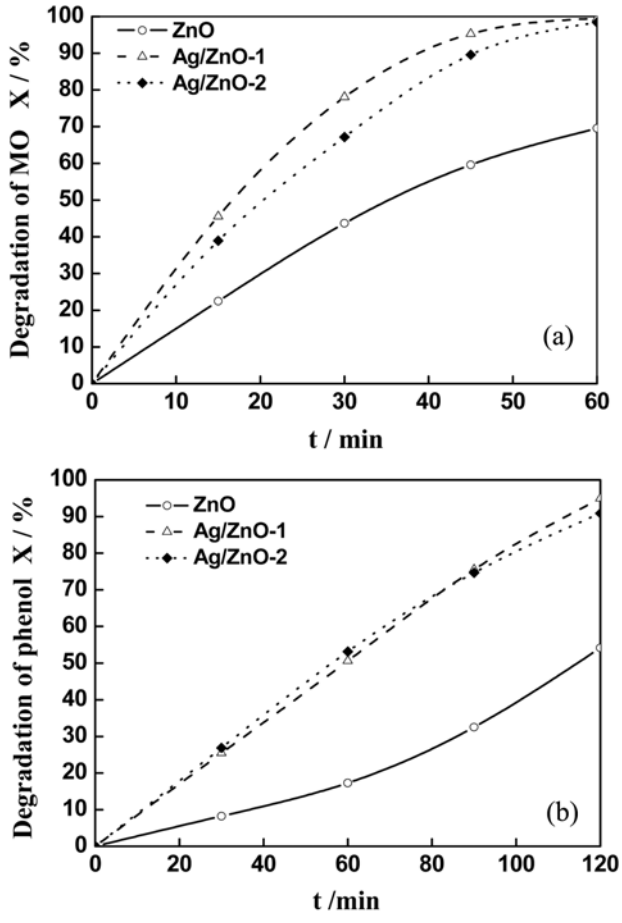

Fig. 5. Photocatalytic activity of ZnO and Ag/ZnO for degradation of methyl orange (a) and phenol (b).

Fig. 6 shows room-temperature PL spectrum of ZnO and Ag/ZnO composite at the excitation wavelength of 205 nm. For ZnO catalyst, three weak luminescence bands including a blue emission at about 467 nm and two blue-green emissions at about 495 nm and 550 nm were observed. In general, this blue emission might be attributed to the intrinsic defects (O and Zn vacancies or interstitials and their complexes) in ZnO [31,32], such as the transition between the vacancy of oxygen and interstitial oxygen [33]. But the mechanism of blue emission is not clear now. It is commonly accepted that the two weak emission peaks in the blue-green band might originate from the shift of the ionized oxygen vacancies to the valence band [34]. It is understandable that the higher the oxygen vacancy and defect content is, the stronger the PL signal is. During the process of photocatalytic reaction, oxygen vacancies and defects can become centers to capture photo-induced electrons, so the recombination of photo-induced electrons and holes can be effectively inhibited [34]. Moreover, oxygen vacancies can facilitate the adsorbed O_2 to capture photo-induced electrons, simultaneously producing $\cdot O_2$ radical groups. Thus, it can be deduced that oxygen va-

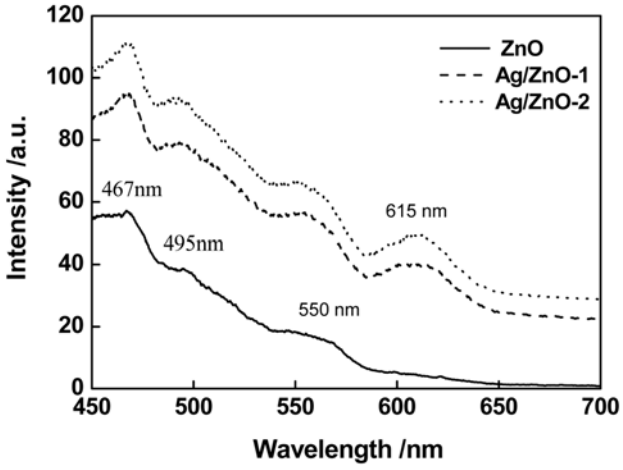

Fig. 6. Room-temperature PL spectrum of ZnO and Ag/ZnO.

cancies and defects are in favor of photocatalytic reaction, and the stronger the excitonic PL spectrum is, the larger the content of oxygen vacancy or defect, and the higher the photocatalytic activity [35]. In Fig. 6, it can also be seen that the emission intensities at about 467, 495 and 550 nm for both Ag/ZnO-1 and Ag/ZnO-2 are higher than that of the ZnO catalyst. The improvement of the PL sensitivity is due to the increase of oxygen vacancy or crystal defects, which can explain why their photocatalytic activities are higher than that of the pure ZnO. Moreover, the Ag-sensitized ZnO composites prepared by the two methods both exhibit a new and unusual PL phenomenon at 615 nm; there is the possibility of the formation of a new surface state. The dopant Ag has a great effect on the separation and recombination process of photo-induced charge carriers of ZnO, which can further influence PL performance. It indicates that the photoluminescence mechanism of Ag/ZnO is very complex and further research is needed.

CONCLUSION

In summary, leaf-like ZnO was successfully synthesized by a simple microwave heating method. Ag-sensitized ZnO composites were prepared by two methods of UV-photoreduction and glycol reduction with as-synthesized leaf-like ZnO. Photocatalytic reactions show that Ag doping in both methods of UV-photoreduction and glycol reduction can remarkably improve the photocatalytic activity of ZnO under simulated solar light. The utilization ratio of Ag in glycol reduction is high and the optimum content of Ag in Ag/ZnO-2 composite can be as low as 1.33%. Therefore, glycol reduction is a novel and excellent method to prepare Ag-sensitized ZnO composite with high photocatalytic activity. The PL spectrum results show that Ag-sensitized ZnO composite not only has higher emission intensities at about 467, 495 and 550 nm than that of the ZnO catalyst, but also exhibits a new and unusual PL phenomenon at 615 nm, indicating that the dopant Ag has great effects on separation and recombination processes of photo-induced charge carriers of ZnO.

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