



Synthesis and Photocatalytic Activity of Ag@AgCl Modified ZnO†

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Nano-ZnO was prepared by sol-gel method. Silver chloride was loaded onto the ZnO particles by a precipitation reaction, and some of the AgCl particles were reduced to Ag particles under halogen tungsten lamp irradiation. The structure of Ag@AgCl-modified ZnO was characterized by XRD, TEM and XPS. Its photocatalytic activity was investigated by the photocatalytic degradation of methyl orange. The results show that the size of as prepared ZnO particles is 20-30 nm as photocatalytic agent, Ag@AgCl/ZnO composite has better photocatalytic activity of visible light and can degrade the methyl orange effectively under visible light irradiation.

Keywords: Ag@AgCl, Sol-gel method, ZnO, Photocatalytic activity.

INTRODUCTION

Zinc oxide is a wide band gap semiconductor with an energy gap of 3.37 eV at room temperature. Zinc oxide semiconductor used as photocatalytic degradation materials of environmental pollutant had been extensively studied¹⁻⁴. However, such photocatalytic degradation only proceeded under UV irradiation because of its wide band gap and can only absorb UV light.

Recently, noble metal plasmonic have attracted special attention because of their ability to strongly absorb visible light. In particular, silver plasmonic show efficient photocatalytic activity in the visible region due to their plasmon resonance effect. Wang *et al.*⁵ prepared Ag@AgCl by treating Ag₂MoO₄ with HCl aqueous to form AgCl and subsequently reducing some Ag ions to form silver nanoparticles on AgCl surface by the light irradiation. Yu *et al.*⁶ synthesized Ag@AgCl modified TiO₂ nanotubes. Wen and Ding⁷ prepared TiO₂ nanotubes loading Ag@AgCl by precipitation and photoreduction. Nie *et al.*⁸ prepared Ag@AgCl modified TiO_{(2-x)C_x} by hydrothermal method. Hu *et al.*⁹ prepared Ag@AgBr/TiO₂ by impregnation method, using CTAB, P25 and AgNO₃ as raw material. It has good photocatalytic activity for degrading azo dyes. Although there are many reports about Ag@AgX modified TiO₂, fewer about Ag@AgX modified ZnO.

In this paper, ZnO nanoparticles were firstly prepared by sol-gel method. Then Ag@AgCl modified ZnO was prepared by precipitation-photoreduction. Its photocatalytic activity was

studied by degrading the methyl orange in aqueous solution under visible light irradiation.

EXPERIMENTAL

Preparation of ZnO nanocomposite: Zinc oxide nanocomposite was prepared by sol-gel method. All the chemicals used were analytical grade reagents. Firstly, 0.2 mmol Zn(CH₃COO)₂·2H₂O, 2 mg citric acid were dissolved in 50 mL solution (volume ratio of water and alcohol was 1:1) under vigorous stirring. After dispersed 0.5 h by ultrasonic, added dropwise NH₃·H₂O until pH = 9. The resulting mixture was refluxed 2 h under 80 °C, then ZnO sol had been obtained. After set for 8 h, the sol became gel. Dried the gel 10 h under vacuum, then calcined 4 h under 500 °C. Zinc oxide nanoparticles had been formed.

Preparation of Ag@AgCl modified ZnO: At room temperature, the synthesized ZnO (1 g) powders were dispersed in 30 mL deionized water and sonicated for 20 min. Then 10 mL of 0.1 mol/L AgNO₃ solution was added into the ZnO suspension and sonicated for 20 min. 10 mL of 0.1 mol/L HCl aqueous solution was added dropwise under magnetically stirring. After stirred magnetically for 0.5 h, the resulting suspension was irradiated by a 50 W ultraviolet lamp for 0.5 h to reduce some Ag⁺ in the AgCl particles to Ag⁰. Finally, the attained Ag@AgCl/ZnO powders were collected, washed, filtered and dried at 80 °C for several hours.

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Characterization method: The phase of product was determined by D5005 X-ray diffractometer, with $\text{CuK}\alpha$ radiation. The size and morphology of product was determined by HitachiH-7500 transmission electron microscopy spectrometer. The UV-visible absorption spectroscopy was studied by UV-2100 spectrophotometer. The XPS spectra were observed by PHI-1600x system.

Degradation of methyl orange: Add Ag@AgCl/ZnO nanocomposite to 30 mL methyl orange aqueous solution. After stirred for 20 min, the mixture solution was irradiated by tungsten lamp. Separating the solid by centrifugalization, the absorbance of the resulting solution was determined by UV-2100 spectrophotometer. The degradation rate of methyl orange was calculated according to the formula:

$$R(\%) = \frac{(A_0 - A)}{A_0} \times 100\%$$

A_0 and A , respectively referred to the absorbance of methyl orange before and after irradiation.

RESULTS AND DISCUSSION

The XRD patterns of products are shown in Fig. 1. Curve 1 shows the characteristic peaks of pure ZnO. Curve 2 shows the peaks of ZnO and AgCl, but no peaks of Ag because the content of Ag is low.

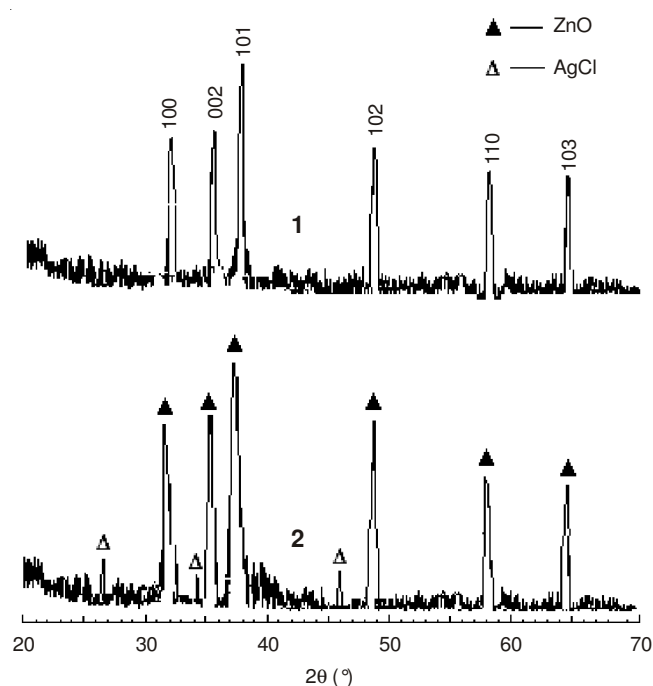


Fig. 1. XRD pattern of samples

TEM images of samples are shown in Fig. 2. The size of ZnO is 20-30 nm with smooth surface. When Ag@AgCl was disposed on the surface of ZnO, the size and morphology of particles have no change because the fewer Ag@AgCl can not change the structure of ZnO.

The XPS analysis of Ag@AgCl/ZnO was showed in Fig. 3. It shows the spectrum of Ag and Cl. The high resolution spectrum of Cl 2p species is showed in Fig. 3a. The peaks centered at 197.52 and 199.43 eV are corresponding to the

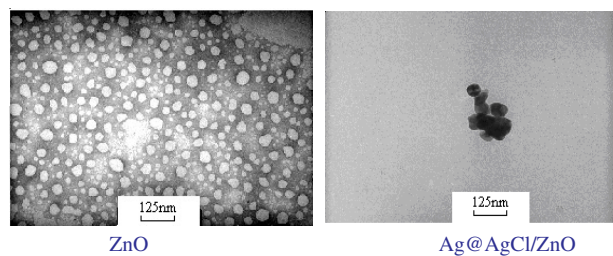


Fig. 2. TEM images of the samples

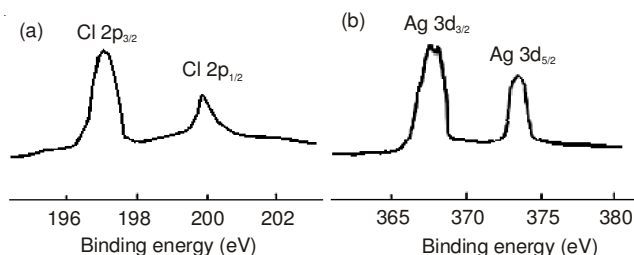


Fig. 3. XPS spectra of Cl 2p and Ag 3d of Ag@AgCl/ZnO

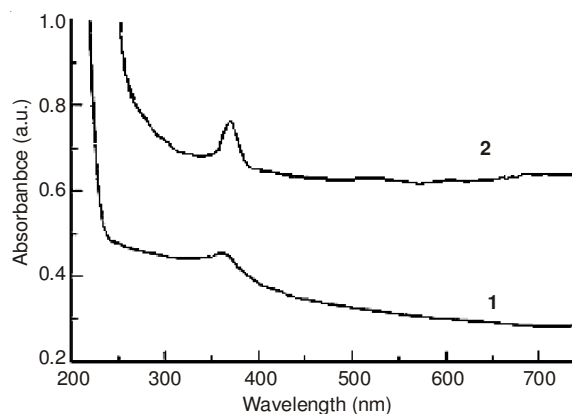


Fig. 4. UV-visible spectrum of samples. 1-ZnO, 2-Ag@AgCl/ZnO

peaks of Cl 2p_{3/2} and Cl 2p_{1/2}, respectively. The high-resolution spectrum of Ag 3d species is shown in Fig. 3b. It consists of two individual peaks. The peak at 373.57 eV is the peak of Ag 3d_{5/2}. The peak of Ag 3d_{3/2} is divided into two peaks, corresponding to Ag⁰TAg⁺, respectively, which shows the coexistence of Ag and AgCl species in the samples.

The room temperature UV-visible absorbance spectra of the samples are given in Fig. 4. Fig. 4 shows that ZnO only has absorption in the violet light area, but Ag@AgCl/ZnO has both absorption in the violet light region and in visible light region. UV-visible analysis shows that Ag@AgCl increases the visible light absorbable range of ZnO significantly because of the surface plasmon resonance effect of AgNPs.

Fig. 5 is degradation rate curve of methyl orange using ZnO and Ag@AgCl/ZnO as photocatalyst, concentration of methyl orange being 20 mg/L, dosage of catalyst being 10 mg. Further, the degradation rate of methyl orange is very low using ZnO as photocatalyst under visible light irradiation. When using Ag@AgCl/ZnO as photocatalyst, the degradation rate of methyl orange greatly increase, being 86.3 % when irradiated 3 h.

When loading Ag@AgCl, absorbable light range of ZnO extend to visible light region because of the surface plasmon resonance effect of AgNPs. When irradiated by visible light, Ag nanoparticles absorb the visible light, producing electron-

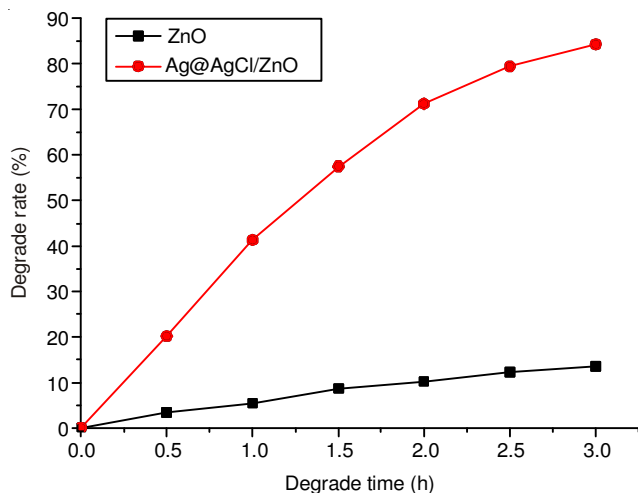


Fig. 5. Photodegradation curves for the methyl orange under visible light irradiation

hole pairs (e^-/h^+ pairs). Electron transferred to the conduction band of ZnO, which prevents the recombination of electron-hole pairs and then reduces the adsorbed oxygen to produce super oxygen anionic free radical ($\cdot O_2^-$). Holes can directly oxidate dyes molecules into various degraded products. At the same time, holes can also combine with Cl^- of AgCl forming Cl^0 . Cl^0 is a kind of strong oxidant. It can oxidate dyes molecules to form Cl^- .

Conclusion

Zinc oxide nanoparticles were prepared by sol-gel method. The size of ZnO particles is 20-30 nm. Silver chloride was loaded onto the ZnO particles by a precipitation reaction and some of the AgCl particles were reduced to Ag particles under halogen tungsten lamp irradiation. The size and morphology of ZnO particles have no change after loading Ag@AgCl. UV-visible analysis shows that Ag@AgCl increases the visible light absorbable range of ZnO significantly. Ag@AgCl/ZnO can degrade the methyl orange effectively under visible light irradiation. The degradation rate of methyl orange is high as 86.3 % when irradiated for 3 h.

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