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Photoactivity of Ag/TiO_2 Microsphere by One-Step Hydrothermal Method

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Ag/TiO_2 microsphere photocatalyst was prepared *via* one step hydrothermal method and prepared catalyst was used for photodegradation of rhodamine B under visible light. The Ag/TiO_2 catalyst was characterized through X-ray diffraction (XRD) and scanning electron microscope (SEM). The results showed Ag was uniformly distributed in the titanium matrix. The 6 % Ag doped TiO_2 catalyst had the higher photoactivity than other proportion to degrade rhodamine B 86.6 % within 60 min under visible light. The Ag doped TiO_2 also had the good activity under solar light cut off UV light.

Keywords: Ag doped TiO_2, Microsphere, Hydrothermal method, Photodegradation.

INTRODUCTION

Titanium dioxide (TiO_2), as an interesting semiconductor material, has been extensively investigated the photocatalyst including pure TiO_2, a variety of doped TiO_2. Due to the high activity, TiO_2 and the modified materials were used to remove inorganic and organic compounds from industrial waste waters and polluted air[1].

The band gap[2] of anatase TiO_2 is 3.2 eV, rutile is 3 eV, brookite is 2.96 eV. Because of the high band gap, pure TiO_2 can just absorb UV light, which is the shortage of TiO_2. Many studies have been carried out that the doping and surface modification is an effective way to improve the activity of TiO_2 and increase the absorption of visible light, such as Si, Fe, Cu, Au, Pt, Ag and so on[2-9]. Many reports have proved that the special morphology can also enhance activity, such as nanorodes, nanotubes, nanowires, nanoplates, microsphere, *etc.*[10-13].

Among the above mentioned doped or modifications of TiO_2, Ag has been used as a common metal element. Yu *et al.*[12] prepared the Ag-TiO_2 nano thin film and the composite display excellent antibacterial activity. Cheng *et al.*[13] obtained the Ag@TiO_2 core-shell nanocomposite nanowire *via* a vapor-thermal method and highly photoactivity under UV light irradiation. Liu *et al.*[14] prepared Ag/TiO_2 composite microspheres by combining a hydrothermal and an ultrasonic spray pyrolysis (USP) method. In the present work, the Ag/TiO_2 microsphere has been prepared by one step hydrothermal method and the nanocomposites have been characterized by XRD and SEM. And then Ag/TiO_2 microsphere catalysts were used to photodegradation of rhodamine B under both visible light and solar irradiation in an aqueous solution.

EXPERIMENTAL

Silver nitrate, HNO_3, titanium tetraisopropoxide (TTIP), CH_3CH_2OH, rhodamine B were purchased from China National Medicines Corp. All reagents were analytical grade and used as received without further purification. Ultrapure water was employed in all experimental work. Rhodamine B solution was made at a concentration 6.25 µmol L^{-1}.

Preparation of the Ag/TiO_2 microspheres: Titanium tetra-isopropoxide and silver nitrate were used as a source of titanium and silver respectively. The 12.5 mL ultrapure water, 10 mL absolute ethanol, 0.5 mL HNO_3, 0-0.1077 g $AgNO_3$ (from 0 to 7 %) and 3.9 mL titanium tetraisopropoxide were added and mixed. Then the mixture was heated at 140 °C with constant stirring during 4 h in oil bath. After filtration, the white or light grey product was treated with ultrapure water until pH value close to 7, subsequently, the products was dried and calcined at 400 °C for 4 h.

Photocatalytic activity: In each trial, 10 mg catalyst was added to 60 mL 6.5 µM aqueous RhB solution and adsorbed 3 h under dark and then the mixture was irradiated by a Xe lamp with a filter (UVIRCUT 420) to filter out ultraviolet light. After the allotted reaction time had elapsed, the sample was centrifuged and then the solution was detected by TU-1901 UV-visible spectrophotometer (Beijing Purkinje General Instrument Co. Ltd., China).

Characterization of catalysts: Powder X-ray diffraction patterns of TiO_2 and Ag doped TiO_2 were obtained using XRD (D8 Advance, Bruker AXS, Germany). The surface morphologies of the prepared photocatalyst were obtained using the field emission scanning electron microscope (Hitachi S-4800, Japan).

RESULTS AND DISCUSSION

XRD analysis: The XRD was employed to characterize the Ag/TiO_2 catalysts. The data in Fig. 1 indicate the naked TiO_2 and the Ag/TiO_2 catalysts exhibit a pure anatase phase (JCPDS No. 21-1272).

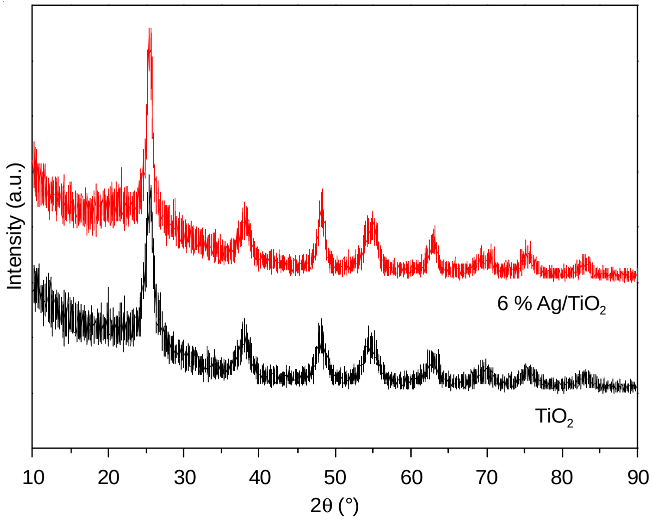

Fig. 1. XRD patterns for the Ag/TiO_2 catalysts

In this work, the TiO_2 and Ag/TiO_2 catalysts have prepared by the hydrothermal method. According to the XRD spectra, there are no obvious Ag peak appears which indicated the Ag is not crystalline phase, also shows the Ag not absorb in the surface of TiO_2, the silver is uniformly distributed in the titanium matrix[12].

SEM images of the Ag/TiO_2 nanospheres: In order to investigate the surface morphology of the Ag doped TiO_2 nanoparticles, the Ag/TiO_2 were examined by SEM and the SEM images are provide in Fig. 2.

The SEM shows the size of the 6 % Ag/TiO_2 nanoparticles is about 20 nm, then the nanoparticles aggregated as microspheres about 1.1 µm. The SEM images suggest the microsphere got in the experiment. The aggregated nanoparticles have the benefit to filter catalyst from reaction solution.

Photocatalystic activity: The degradation ratio of TiO_2 and Ag/TiO_2: the pure TiO_2 and different content of Ag doped TiO_2 catalysts were used to degrade RhB at same conditions. The change of RhB was detected by UV-visible spectroscopy, the degradation ratio get by $A/A_0 \times 100$ %. The result shows in Fig. 3. It shows the degradation rate of catalyst increased from 0 to 3 %, then decreased from 3 to 5 %, but the catalyst including 6 % Ag has the highest degradation rate. The data indicate 6 % Ag doped the TiO_2 have more photoactivity.

Blank trials: The adsorption of rhodamine B on the surface of catalysts and RhB irradiation in absence of catalyst under visible light were carried out as control. 3 mg Ag doped catalysts were, respectively added to 3 mL of a 6.25 µmol L^{-1} aqueous solution of rhodamine B in a 1 × 1 cm quartz cuvette. Then the reaction solutions were determined with a TU-1901 spectrophotometer. The results show in Fig. 4.

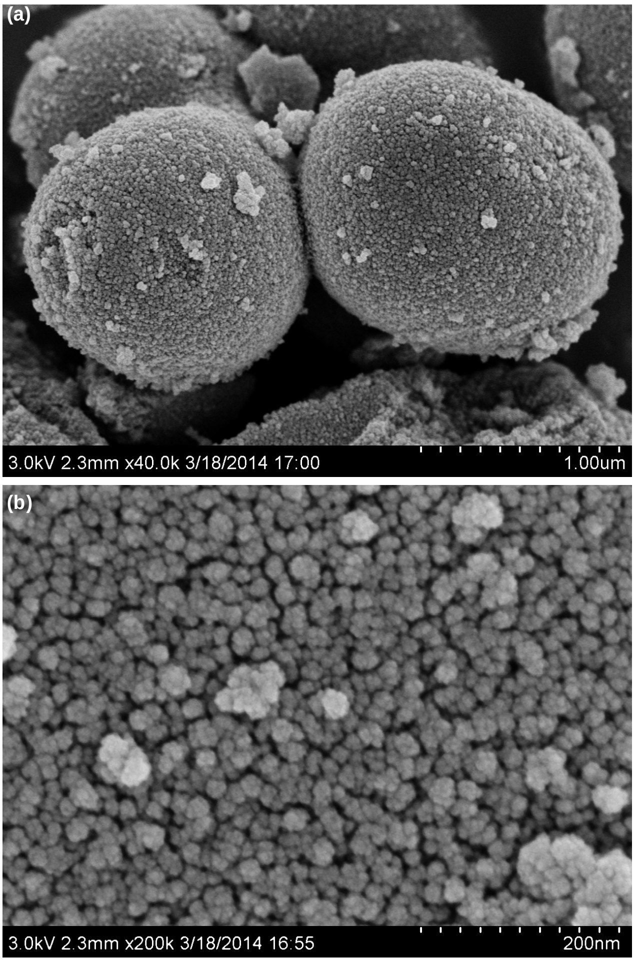

Fig. 2. SEM images of 6 % Ag/TiO_2 nanosoheres

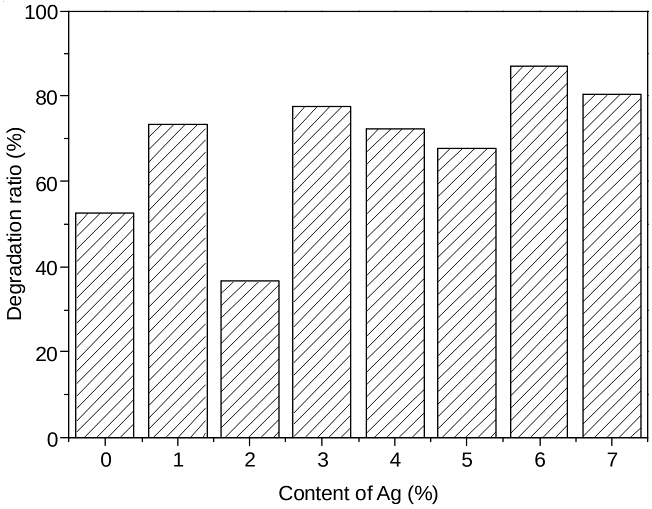

Fig. 3. Photoactivity of the different concentration Ag-TiO_2 catalyst

Fig. 4a shows that the catalyst degraded the rhodamine B under irradiation with visible light and the absorption peak of rhodamine B is drop from 0 to 60 min, the peak also is blue shift after 20 min, we can observe two peaks, which are 546 and 502 nm, appeared at 20 min and the color of the rhodamine B

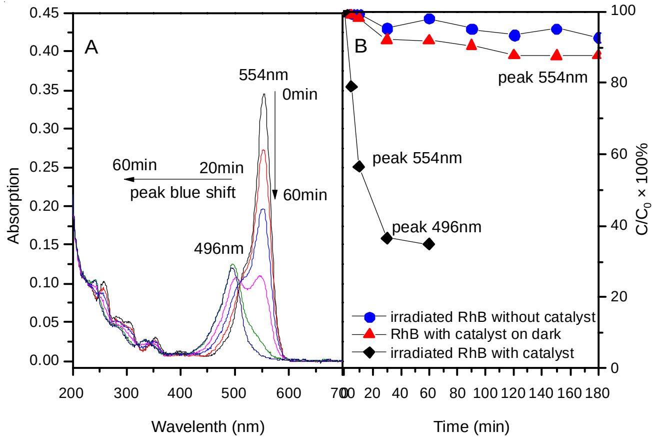

Fig. 4. Blank experiment results; (a) is the photodegradation experiment in presence of 6 % Ag/TiO$_2$ catalyst under irradiation; (b) shows the plot of the peak 554 nm with time under different conditions

solution changing from an initial red color to a light green-yellow. Fig. 4b indicates the 6 % Ag/TiO$_2$ catalyst can absorb about 12.4 % rhodamine B within 180 min.

Effect of solar light: The solar light was also used to investigate the photo-degradation in this work and compared the degradation rate with Xe lamp. The glass was used to cut UV light under solar irradiation in each trial (Fig. 5).

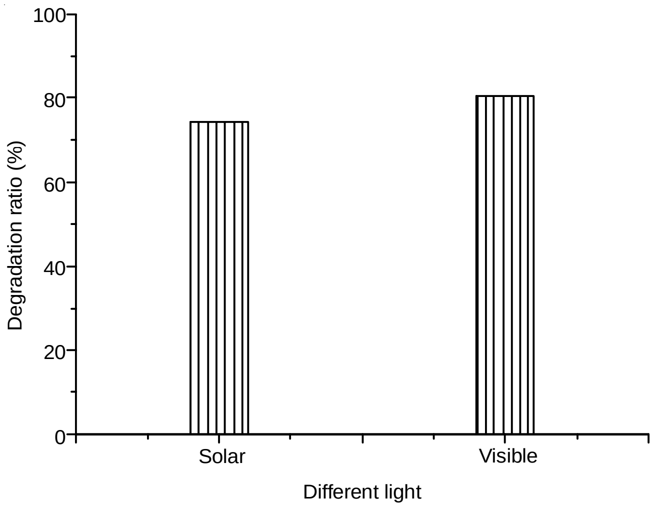

Fig. 5. Effect of different light source

Fig. 5 shows the catalyst can degrade the RhB under solar light, but the degradation rate lower than Xe lamp slightly. The reason is because that the light intensity of solar can't control and the intensity lower than Xe lamp in this experiments.

Recycling experiment: The catalyst recycling trials were used to investigate the stability of Ag/TiO$_2$. Following the initial reaction, the 6 % Ag/TiO$_2$ catalyst was separated and dried at 80 °C before being applied to a subsequent degradation reaction. Fig. 6 shows the degradation rates of the recycling experiments. It is evident that the catalyst maintains practically the photoactivity within three recycle, but after third cycle the photoactivity descent. Which is the catalyst didn't calcine and maybe the photo-corrosion happened.

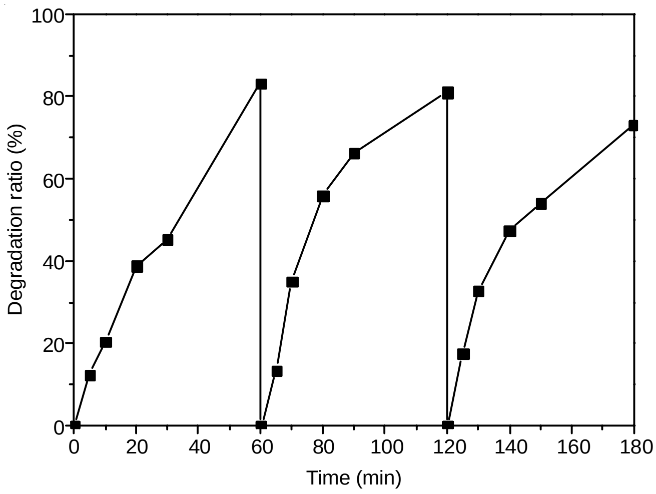

Fig. 6. Recycle and reuse of photocatalytic degradation of RhB

Conclusion

The Ag/TiO$_2$ microsphere photocatalyst was successfully prepared by one step hydrothermal method. The prepared catalyst was characterized by XRD and SEM. The Ag/TiO$_2$ nanoparticles were about 20 nm and relatively uniform, then the nanoparticles aggregated as microspheres about 1.1 µm. The 86.6 % degradation efficiency of rhodamine B (6.25 µmol L^{-1}) was observed within 60 min (6 % Ag doped TiO$_2$) under visible light irradiation. The catalyst was reused up to three runs and found to descent slightly.

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