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A novel deposition precipitation method for preparation of Ag-loaded titanium dioxide

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Ag/TiO_2 photocatalysts were prepared by a novel deposition precipitation method. Formation of Ag nanoparticles on the surface of TiO_2 was confirmed by XRD, HRTEM and XPS. The photocatalytic activity of Ag/TiO_2 was tested with the photocatalytic degradation of methyl orange and found effectively enhanced. The optimum content of Ag for photocatalytic activity is about 2.0 wt%.

KEY WORDS: Ag; TiO_2; photocatalytic degradation; methyl orange.

1. Introduction

In the past three decades, photocatalysis has attracted much attention owing to its great advantages in the decomposition of organic pollutants in water and air. TiO_2, a chemical stable and nontoxic semiconductor, can effectively mineralize most of the organics to CO_2, H_2O and inorganic ions under UV or solar irradiation. However, the photo-quantum efficiency of TiO_2 is greatly limited because of the recombination of photogenerated electrons and holes. Thus, it is of current interest to develop some techniques to depress the electron-hole recombination in TiO_2. Besides the semiconductor combination, transition metals doping, TiO_2 surface modification with noble metal has been proved as an effective technique to depress the recombination of photogenerated electrons and holes in TiO_2. The noble metals deposited on the surface of TiO_2, such as Au, Pt and Ag, have excellent exhibitions in promoting the organics degradation with TiO_2 under UV irradiation [11–33]. The deposition of Ag on TiO_2 was usually carried out with photocatalytic deposition method [44,55], or some involves calcination method [66,77]. Although it hasn't attracted much attention, another deposition technique, so called deposition precipitation, is also proved to be a competitive method as reported in the preparation of Au/TiO_2 for degrading 4-chlorophenol [88]. In this letter, a novel deposition precipitation (DP) method was developed for deposition of metal Ag on TiO_2. This novel DP method needs no calcination, which is different from traditional deposition precipitation method. Since neither calcination nor long-term UV irradiation is needed in this DP method, the agglomeration of Ag particles on the TiO_2 could be avoided, comparing with others in the preparation of Ag/TiO_2 photocatalyst. The photocatalytic activities of Ag/TiO_2 photocatalysts were tested with the photodegradation of methyl orange under UV irradiation.

2. Experimental

2.1. Catalyst preparation

The bare TiO_2 (anatase, specific area, $\sim$78 m^2/g) sample was synthesized by hydrolysis of tetrabutyl titanate, followed by a temperature programmed calcination (5 K/min, up to 673 K, 2 h, under air). Calculated from the UV–vis diffuse reflectance spectrum, the energy gap of the bare TiO_2 sample is 3.22 eV. The details of this synthesis were as described elsewhere [99]. The preparation of Ag/TiO_2 was carried out by the reaction of Ag^+ ion with hydrogen peroxide in the TiO_2 suspension. The reaction equation is as follow:

$$2Ag(NH_3)_2^+ + H_2O_2 + 2OH^- \rightarrow 2Ag + O_2 + 4NH_3 + 2H_2O$$

To prepare the Ag/TiO_2 catalysts, 0.5 g of TiO_2 was firstly suspended in an aqueous solution (15 mL) containing different amounts of $Ag(NH_3)_2^+$ ion at 293 K and the suspension was then kept stirring for 20 min. Aqueous hydrogen peroxide solution (H_2O_2, 2 wt%) was then added dropwise to the stirred solution. Afterward, the suspension was kept stirring for another 30 min and then filtered. The filtrate was checked with Cl^- ion and no Ag^+ ion was detected, which indicated that all of the Ag^+ ions were transformed to metal Ag by the reaction with H_2O_2. The solid product was

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filtered, washed repeatedly with water, dried in air for 4 h at 353 obtain the final Ag-deposited TiO_2 photocatalyst.

XRD measurements were carried out with a Rigaku D/max 2550 VB/PC apparatus at room temperature using Cu Kα radiation and a graphite monochromator (40 kV, 100 mA). XPS spectra were collected using a Perkin Elmer PHI 5000C ESCA instrument with Al Kα X-rays. The Ag/TiO_2 sample morphology was observed under high-resolution transmission electron microscopy (HRTEM) on a 2100 JEOL microscope (200 kV) using copper grids.

2.2. Photocatalytic experiments

Photocatalytic experiments were carried out in an aqueous solution of methyl orange (MO) to evaluate the photocatalytic activity of Ag/TiO_2 samples. A mixture of 50 mg of Ag/TiO_2 powders and 50 mL of MO (40 mg/L) was first sonicated for 10 min and subsequently stirred for 30 min in quartz tube (inner diameter = 2.4 cm, volume = 80 mL) in the dark to reach an adsorption/desorption equilibrium for MO and oxygen on the surface of Ag/TiO_2 powders. The stirred suspension was then illuminated by a 300 W high pressure Hg lamp with major emission at 365 nm. The distance from Hg lamp to quartz tubes is fixed at 25 cm. The light intensity of Hg lamp was measured by a UV Radiometer (Photoelectric Instrument Factory of Beijing Normal University) at wavelength range from 320 to 400 nm. It was found that light intensity was 1.08 mW/cm^2 at the quart tube spot. The quartz tube was opened to air throughout the reaction to make sure that there was enough oxygen dissolved in the solution. At every interval of 30 min, a small amount (3 mL) of the solution was taken out of the tube and analyzed by measuring its maximum absorption with a UV–vis spectrophotometer (Shimadzu UV-260).

3. Result and discussion

3.1. Catalysts characterization

The Ag/TiO_2 particles were brownish in color. The XRD patterns of Ag/TiO_2 and TiO_2 samples are shown in figure 1. The TiO_2 samples exhibit well-crystallized anatase phase. Weak peaks attributed to metal Ag can be found at $2\theta = 44.3°$ (200), 64.4° (220), 77.4° (311). Unfortunately, the intense peak corresponding to metal Ag at $2\theta = 38.1°$ (111) is covered up by peaks attributed to TiO_2 at $2\theta = 37.8°$ (004), 38.6° (112). The intensity of peaks is increased with the increasing of Ag deposited, indicating the increasing Ag particles size.

HRTEM enable identification of the location, distribution and size of Ag deposits on titania surface (figure 2). The size of TiO_2 particle sizes is unchanged as a result of surface modification by Ag particles, comparing with the bare TiO_2 particles (12 nm). The black spots in HRTEM image of the Ag/TiO_2 present the deposited Ag on the surface of TiO_2. The Ag particles of 1.5 wt% Ag/TiO_2 sample are about 10 nm (figure 2a), which is smaller than that of prepared by calcination method [77]. The Ag particle sizes increase as increasing of further Ag loading. The size of Ag particle is increase to about 16 nm for the 4.0 wt% Ag/TiO_2 sample as shown in figure 2b.

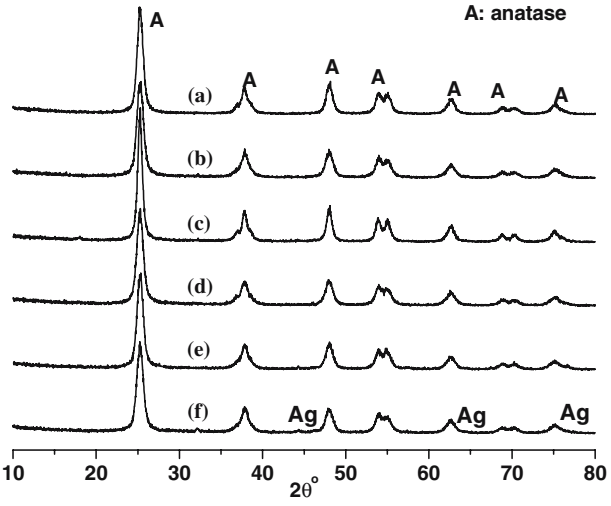

Figure 1. XRD patterns of TiO_2 and Ag/TiO_2 photocatalysts: (a) TiO_2; (b) 1.0 wt% Ag/TiO_2; (c) 1.5 wt% Ag/TiO_2; (d) 2.0 wt% Ag/TiO_2; (e) 2.5 wt% Ag/TiO_2; (f) 3 wt% Ag/TiO_2.

X-ray photoelectron spectroscopy (XPS) experiments were performed to elucidate both the titania structure and the chemical state of Ag particles. Figure 3 shows the XPS survey spectrum of 1.5 wt% Ag/TiO_2 powders prepared by the deposition precipitation method. XPS peaks show that the Ag/TiO_2 powders contain only Ti, O, and Ag elements and a trace amount of carbon. The C element is ascribed to the adventitious hydrocarbon from XPS instrument itself. The evaluation of binding energy values for the Ti 2p and O 1s peaks show that they are in the ranges 458.2–458.8 eV and 530.0–530.2 eV, respectively. These values can be attributed to Ti^{4+} and O^{2-} in TiO_2 [1010]. No Ti 2p peak that attributed to Ti^{3+} was observed.

Previous studies show that the Ag $3d_{5/2}$ binding energies for the Ag, Ag_2O and AgO are 368.2, 367.8 and 367.4 eV, respectively [1111]. Figure 4 shows the high-resolution XPS of the Ag 3d region of the 1.5 wt% Ag/TiO_2 sample. The XPS curve of the Ag/TiO_2 can be well fitted with a distribution of which there are two peaks centered at 368.5 eV and 374.5 eV corresponding to Ag $3d_{5/2}$ and Ag $3d_{3/2}$, respectively. No peak corresponding to Ag_2O (367.8 eV) or AgO (367.4 eV) was observed in the XPS spectra of Ag/TiO_2. XPS spectra of other Ag/TiO_2 samples with different contents of Ag loading such as 1.0, 2.0, 2.5, 3.0 and 4.0 wt% also exhibit that the Ag

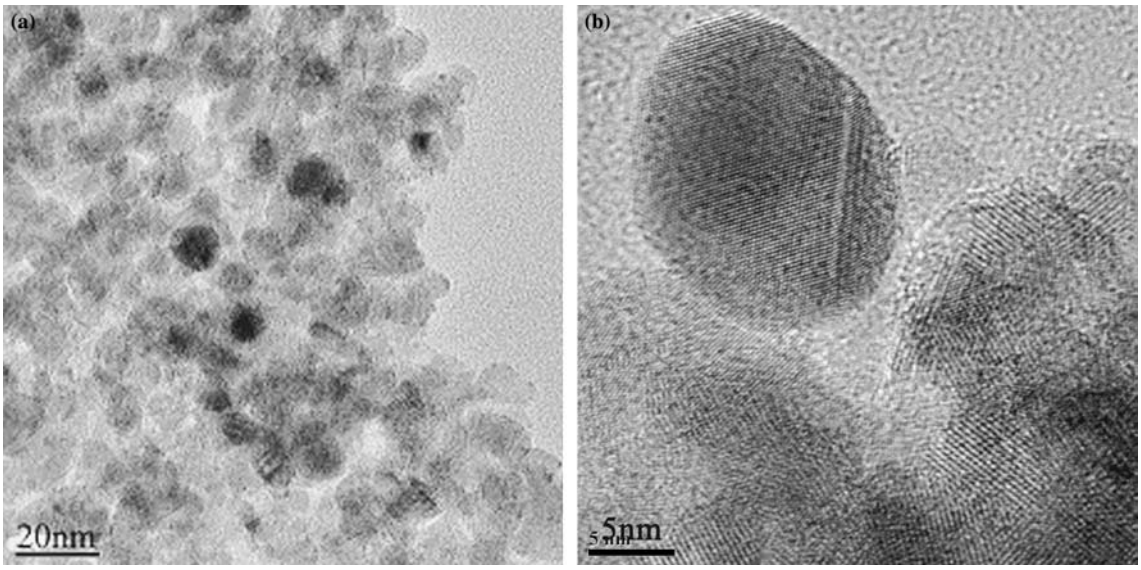

Figure 2. HRTEM image of 1.5 wt% (a) and 4.0 wt% (b) Ag/TiO_2 photocatalysts.

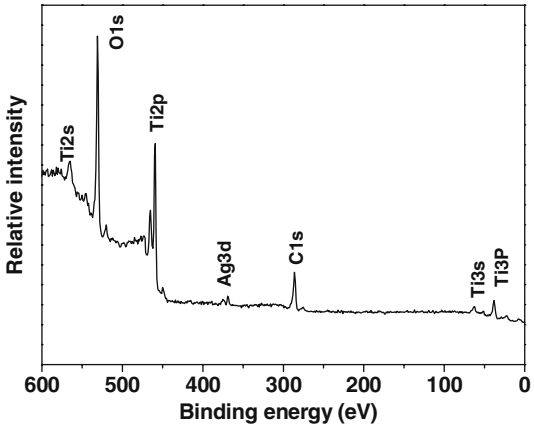

Figure 3. XPS survey spectrum of 1.5 wt% Ag/TiO_2 photocatalyst.

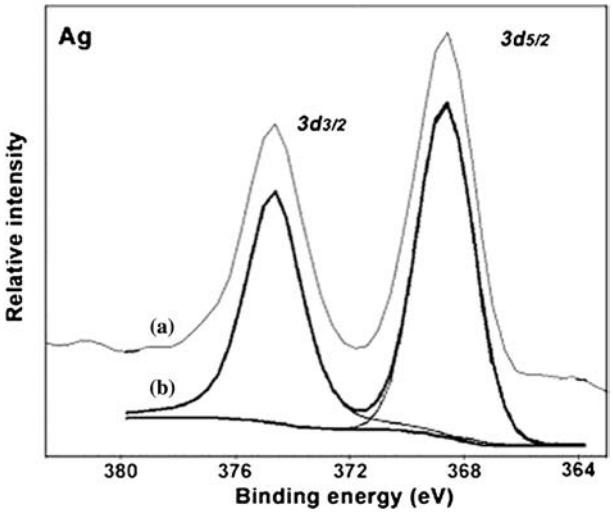

Figure 4. Ag 3d high-resolution XPS spectrum of 1.5 wt% Ag/TiO_2 photocatalyst: (a) orginal curve; (b) fitted curves.

species deposited on TiO_2 powders are all in metal Ag, but not in Ag_2O or AgO. The increase of Ag particle size deposited on TiO_2 decreased the XPS peak width of Ag $3d_{5/2}$ [1212]. The Ag $3d_{5/2}$ fwhm of 1.0, 1.5, 2.0, 2.5, 3.0 and 4.0 wt% Ag/TiO_2 samples are 2.42, 2.34, 2.38, 2.29, 2.23 and 2.22 eV, respectively. It is the main trend that the peak fwhm width of Ag $3d_{5/2}$ decreases with the increase of the Ag loading, indicating the growth of Ag particle size. This result is found to in agreement with that observed from HRTEM images.

3.2. Photocatalytic activity in MO degradation

Figure 5 shows the percentage of MO decomposed after irradiated with Ag/TiO_2 for 1.5 h. A set of Ag contents, such as 1.0, 1.5, 2.0, 2.5, 3.0 and 4.0 wt%, were chosen to investigate the relationship between the Ag content and the photocatalytic activities of Ag/TiO_2. It can be seen from figure 5 that decomposition of MO

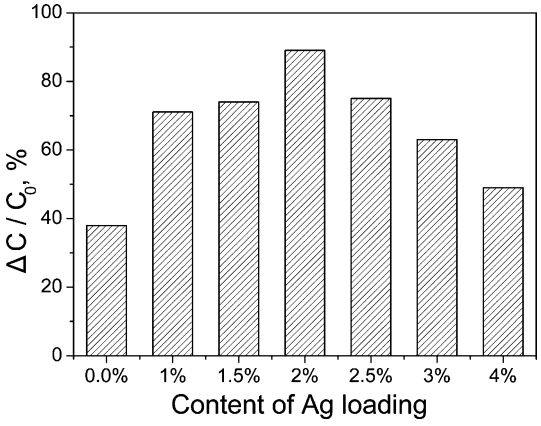

Figure 5. Percentage of methyl orange decomposed after irradiated with Ag/TiO_2 photocatalysts for 1.5 h.

increases significantly with the increasing of Ag load from 0.0 to 2.0 wt%, reaches a maximum at 2.0 wt%, and then decreases with the further increasing of Ag loading. Thus, the optimum Ag content is 2.0 wt%. The photocatalytic activity of 2.0 wt% Ag/TiO_2 is about 2.3 times as that of unmodified TiO_2. In comparison with the DP method, the Ag/TiO_2 photocatalysts were also prepared using the same bare TiO_2 sample by the photocatalytic deposition method. The results indicate that the photocatalytic activities of Ag/TiO_2 catalysts with various content of Ag loading prepared by the DP method are higher than that of prepared by the photocatalytic deposition method. The photocatalytic activity of 2.0 wt% Ag/TiO_2 (the optimum Ag loading) prepared by DP method is about 2.3 times as that of unmodified TiO_2. However, it is only 1.9 times for 2.5 wt% Ag/TiO_2 (the optimum Ag loading) prepared by photocatalytic deposition method. Metal Ag islands contact with TiO_2 leads to the formation of a Schottky barrier [1313]. Therefore, the photogenerated electron in TiO_2 would transfer from TiO_2 into Ag island, which acts as a electron trap promoting charges separation in the TiO_2. Thus, deposition of Ag on the surface of TiO_2 leads to an enhancement of the photocatalytic activity for TiO_2. However, the photocatalytic activity of Ag/TiO_2 begins to decrease when loading of Ag is increase to more than 2 wt%. There are three reasons that may cause this decrease of the photocatalytic activity [1414]: (1) Although Schottky barrier favors electrons flow from TiO_2 to Ag island, the electrostatic interaction from negatively charged silver sites will also attract positively charged holes. Therefore, there is an increased probability for the capture of holes by the large number of silver particles at high metal loads, which is adverse to the photocatalytic activity of TiO_2. (2) Excessive coverage of Ag to TiO_2 increases the reflection of the incident light. This reduces the number of photons absorbed by TiO_2 and thus lowers the apparent photo-quantum efficiency of photocatalytic reaction. (3) Excessive coverage of Ag particles on the surface of TiO_2 may also decreases the probability of holes reacting with adsorbed species at the TiO_2 surface.

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