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Short communication

Facile synthesis of Ag_3PO_4 with the assistance of N, N-dimethylformamid and urea for high performance photocatalysis

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ABSTRACT

Ag_3PO_4 was synthesized with the assistance of N, N-dimethylformamid (DMF) and urea for high performance photocatalysis. The photocatalytic activity of the as-synthesized samples was evaluated by photodegrading rhodamine B (Rh B) under visible light irradiation. As a result, the optimal Ag_3PO_4 synthesized with the assistance of DMF and urea exhibited enhanced photocatalytic activity for Rh B degradation under visible light irradiation. DMF and urea play vital roles in improving the photocatalytic activity of Ag_3PO_4. This study could provide a new perspective for the controllable synthesis of Ag_3PO_4.

1. Introduction

Semiconductor photocatalysis is a green and environmentally friendly technology, and has been extensively researched with potential applications in the field of environmental protection. Various photocatalysts have been investigated, and titanium dioxide (TiO_2) is the most widely studied among them [1]. However, it only absorbs ultraviolet light, which greatly limits its photocatalytic application [2]. Therefore, it is necessary to develop novel photocatalysts particularly with visible light response.

Silver phosphate (Ag_3PO_4) discovered by Ye and co-workers [3] is a new and efficient photocatalyst with visible light response, and exhibits extremely high degradation efficiency toward organic dyes under visible light irradiation. It is well known that the photocatalytic properties of photocatalysts are greatly affected by the morphology [4]. Many efforts have been devoted to further improving and optimizing the photocatalytic activity of Ag_3PO_4 by the morphology control, and notable progress has been made. Up to now, Ag_3PO_4 photocatalysts with various morphologies, including dodecahedron [5], porous microtube [6], cube [7], myriapod [8], nanotube [9], tetrahedron [10], tetrapod [11], branch [12], and truncated tetragonal bipyramid hollow microbox [13], have been prepared by adding single substance, such as hexamethylenetetramine (HMT), polyethylene glycol 200 (PEG200), poly (vinyl pyrrolidone) (PVP), glycine, sodium bicarbonate ($NaHCO_3$), ethanol, urea, DMF, and sodium oxalate. Additionally, limited morphologies of Ag_3PO_4 controlled by two or more additives have been reported. Li et al. [14] reported Ag_3PO_4 crystals with highly-branched structure that was controlled by tetrahydrofuran (THF) and HMT. Dong et al. [15] synthesized tetrahedral Ag_3PO_4 in the presence of DMF and oleic acid. It is observed that the key to the formation of Ag_3PO_4 morphology and improvement of photocatalytic activity is a combination of two additives. Thus, the controlled synthesis of Ag_3PO_4 by combination of different additives is of great importance to enhance its photocatalytic activity.

In this work, Ag_3PO_4 was synthesized with the assistance of DMF and urea for high performance photocatalysis. The photocatalytic activity was evaluated by photodegrading Rh B under visible light irradiation. Moreover, possible activity enhancement mechanism was also discussed.

2. Experimental

2.1. Synthesis of the Ag_3PO_4 with the assistance of DMF and urea

In a typical procedure, DMF (5 mL) and water (15 mL) were mixed together to form a transparent solution. Then, 15 mmoL of urea and 3 mmoL of silver nitrate ($AgNO_3$) were successively added under stirring for 10 min at room temperature. Subsequently, a solution of sodium dihydrogen phosphate (NaH_2PO_4) (1.5 mmoL, 10 mL) was added dropwise. After stirring for 1 h, the obtained precipitate was separated by centrifuge and washed with ethanol and distilled water for several times, respectively. Finally, the product was dried in a vacuum oven at 60 °C for 12 h.

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For comparison purpose, irregular Ag_3PO_4, the Ag_3PO_4 controlled by DMF and Ag_3PO_4 controlled by urea were also synthesized. The preparation details are provided in supplementary material.

2.2. Characterization

The crystalline structure of the samples was characterized by X-ray diffraction (XRD) using a Empyrean diffractometer (PANalytical, Holland) in 2θ range from 10° to 80°. Fourier transform infrared spectra (FTIR) of the samples were collected from a Thermo-Nicolet CCR-1 FTIR spectrometer in the range of 400–4000 cm^{-1}. Scanning electron microscopy (SEM) was carried out in Merlin Compact microscope. UV–visible diffuse reflectance spectra (DRS) were measured within 200–800 nm wavelength range using a Shimadzu UV2600 spectrometer with $BaSO_4$ as a reference. The particle sizes of the samples were analyzed by the Ankersmid Eyetech-Comb laser granulometer.

2.3. Evaluation of photocatalytic activity

The photocatalytic activity was evaluated by photodegrading Rh B under visible light irradiation. Typically, the Rh B solution (8 mg/L, 100 mL) containing 0.1 g of powder was first stirred in the dark for 30 min to establish an adsorption–desorption equilibrium. Then the solution was irradiated with a 500 W Xe lamp equipped with an ultraviolet cutoff filter to provide the visible light (λ ≥ 420 nm). At given time intervals, 4 mL of the suspension was periodically collected and analyzed after centrifugation. The Rh B concentration was determined by its absorption intensity at 554 nm in the UV–vis absorption spectra.

3. Results and discussion

3.1. Characterization of photocatalyst

3.1.1. XRD

The phase of the Ag_3PO_4 was characterized by XRD, and the results were shown in Fig. 1. All the diffraction peaks are in accordance with those of body-centered cubic Ag_3PO_4 (JCPDS No. 06-0505) and no impurity phases are found, which implies that DMF and urea have not changed phase structure of the Ag_3PO_4. Compared with irregular Ag_3PO_4, the Ag_3PO_4 synthesized in the presence of DMF, urea, or both, exhibits the higher intensity of diffraction peaks. Notably, DMF and urea make crystallinity of the samples increased. High crystallinity generally means less traps and thereby a stronger photocatalytic activity [16]. Fig. S1 shows the XRD patterns of the Ag_3PO_4 prepared at different volumetric ratios of DMF to water. As the volumetric ratios of DMF to water reduce, a decrease in the intensity of diffraction peaks could be observed, indicating that DMF plays a key role for the formation of Ag_3PO_4 crystals. The XRD patterns of the Ag_3PO_4 synthesized by adding different amount of urea at fixed volumetric ratios (5:15) of DMF to water, as shown in Fig. S2, are almost the same, suggesting that the amount of urea has no effect on crystallinity of the Ag_3PO_4.

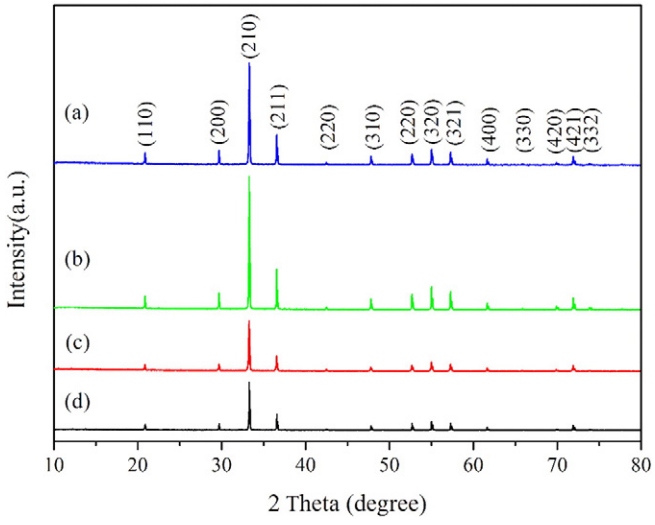

Fig. 1. XRD patterns of (a) the optimal Ag_3PO_4 synthesized with the assistance of DMF and urea; (b) the Ag_3PO_4 prepared by urea; (c) the optimal Ag_3PO_4 prepared by DMF; (d) irregular Ag_3PO_4.

3.1.2. SEM

SEM images of the as-synthesized Ag_3PO_4 were shown in Fig. 2. In water system, every crystal facet is same and in the same growth rate, resulting in the formation of particle with an irregular morphology, as shown in Fig. 2a. Fig. 2b presents the morphology of Ag_3PO_4 controlled by urea, which is similar to that of Ag_3PO_4 prepared in water system. Obviously, urea does not change the general morphology of Ag_3PO_4 in this study. The Ag_3PO_4 synthesized in a mixed solvent of 5 mL DMF and 15 mL H_2O at room temperature displays a rhombic dodecahedral morphology, as shown in Fig. 2c. It is clear that the DMF plays a key role in the formation of rhombic dodecahedral Ag_3PO_4. More specifically, Fig. S3 depicts SEM images of the Ag_3PO_4 prepared at different volumetric ratios of DMF to water. It shows the co-existence of the irregular and rhombic dodecahedral morphologies. In addition, Fig. 2d shows that the morphology of the sample synthesized with the optimized DMF and urea is still irregular and rhombic dodecahedral. The results demonstrate that the main object controlling the rhombic dodecahedral morphology of Ag_3PO_4 is DMF rather than urea. The photocatalytic activity of Ag_3PO_4 is morphology dependent [17]. So the rhombic dodecahedral morphology could contribute to the improvement of photocatalytic activity. The Energy Dispersive Spectroscopy (EDS) patterns of the optimal Ag_3PO_4 synthesized with the assistance of DMF and urea were shown in Fig. 2e. It reveals the elements of O, P, and Ag, suggesting that these morphological features should be assigned to the Ag_3PO_4 crystals [18].

3.1.3. FT-IR

Fig. 3 reveals the FTIR spectra of the as-prepared Ag_3PO_4 by DMF and urea and irregular Ag_3PO_4. The broad absorption at around 3200–3500 cm^{-1} and 1639 cm^{-1} is observed, which could be attributed to the stretching vibrations of O–H and the bending vibration of residual water molecules H–O–H, respectively [19,20]. Besides that, the strong absorption bands are observed at 980 cm^{-1} and 997 cm^{-1}, which are ascribable to P–O stretching vibrations of phosphate (PO_4^{3-}) [12]. The bands at 550 cm^{-1} and 544 cm^{-1} are due to OP–O bending vibration [21]. It turns out that there are no DMF and urea molecules adsorbed on the surfaces of the as-obtained Ag_3PO_4 samples. Furthermore, the structure of the as-prepared Ag_3PO_4 by DMF and urea and irregular Ag_3PO_4 is similar, manifesting that it could not contribute to the improvement of photocatalytic activity.

3.1.4. UV–vis diffuse reflectance spectra (DRS)

The UV–vis diffuse reflectance spectra of irregular Ag_3PO_4 and the optimal Ag_3PO_4 synthesized with the assistance of DMF and urea were displayed in Fig. 4. Both of them exhibit the similar absorption edge around 520 nm. On the basis of the equation listed below [22]: $\alpha h\nu = A(h\nu - Eg)^{n/2}$, where α, ν, A, and Eg are the absorption coefficient, light frequency, proportionality constant and band gap, respectively. The indirect band gap Eg (n = 4) of irregular Ag_3PO_4 and the optimal Ag_3PO_4 synthesized with the assistance of DMF and urea are calculated to be 2.36 eV and 2.39 eV, respectively. It is notable that enhanced visible light absorption was observed for the Ag_3PO_4 synthesized with the assistance of DMF and urea, implying that its synthesis in this study favors better light absorption.