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Short communication

The highly active saddle-like Ag_3PO_4 photocatalyst under visible light irradiation

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ABSTRACT

Saddle-like Ag_3PO_4 particles of tetrahedron structure were successfully synthesized using a co-precipitation method by mixing H_3PO_4 ethanol solution and $AgNO_3$ ethanol aqueous solution, where the percentage of ethanol in $AgNO_3$ ethanol aqueous solution was varied at 0, 50, 80, 90 and 100% (v/v). The photocatalytic performance of the synthesized samples was evaluated by photodegradation of Rhodamine B (RhB) under blue light irradiation ($\lambda = 455$ nm). The results showed that the morphology of the Ag_3PO_4 particles greatly changed depending on the ethanol content in the reaction solution. Excellent photocatalytic activity was observed at 80% (v/v) of ethanol, where the Ag_3PO_4 showed saddle-like morphology derived from the tetrahedron structure.

1. Introduction

Today, the morphology of silver phosphate has been receiving much attention for its ability to improve photocatalytic activity under visible light irradiation. Researchers have successfully controlled the morphology of Ag_3PO_4 to provide high photocatalytic activity for dye pollutant degradation [1–3] and antibacterial activities [4,5]. Wang et al. [1] synthesized spherical, polyhedral and irregularly shaped Ag_3PO_4 by co-precipitation method using various reactants under different temperatures. The polyhedral Ag_3PO_4 showed the highest photocatalytic activity because the polyhedral sample absorbed more visible light compared to the spherical and irregularly shaped samples. Wu et al. [4] synthesized three different morphologies of Ag_3PO_4, such as rhombic dodecahedron particles of 500 nm in diameter, spherical particles of 100 nm and small particles of 20 nm using the solvent of water, ethylene glycol and dimethyl sulfoxide, respectively. The highest activity could be found in small particles of 20 nm.

The unique morphologies of Ag_3PO_4, which improve photocatalytic activity, were also synthesized [6–8]. Xu and Zhang [6] designed the truncated tetragonal bipyramid hollow microboxes of Ag_3PO_4. This morphology exhibited much higher photocatalytic activity than other morphologies of Ag_3PO_4, such as spherical and rhombic dodecahedral under visible light irradiation. A unique morphology of the flower-like Ag_3PO_4, which exhibited high photocatalytic activity under visible light irradiation was successfully synthesized using a facile aqueous solution route in the presence of polyethylene glycol [7]. The unique of concave trisoctahedral Ag_3PO_4 microcrystals consisting of {221} and {332} facets exhibited high photocatalytic activity [8].

The cubic morphology of Ag_3PO_4 microcrystals which enhanced the photocatalytic activity under visible light irradiation, were easily synthesized [9–11]. The ammonia played a crucial role in the formation of cubic Ag_3PO_4 microcrystal [9]. The cubic Ag_3PO_4 designed using ammonia, exhibited a higher photocatalytic activity, compared to irregularly shaped Ag_3PO_4. The cubic Ag_3PO_4 particles of around 120 nm in diameter, were synthesized in the presence of PVP [10]. This cubic Ag_3PO_4 showed superior photocatalytic activity for the photodegradation of methylene blue (MB) under visible light irradiation due to its larger specific surface area and longer life time of electron–hole pairs. The cubic–type structure could be well-controlled by volume ratio of water/ethylene glycol [11]. With this method, the uniform morphology of Ag_3PO_4 microcrystals could be designed and exhibited higher photocatalytic activities under visible light irradiation. The decomposition rate of RhB using these cubic Ag_3PO_4 microcrystals was three times higher than that of irregularly shaped Ag_3PO_4 microparticles.

The most interesting morphology of Ag_3PO_4 is the tetrahedron which is highly reactive under visible light irradiation [12–16]. Hu et al. [12] reported that the tetrahedral Ag_3PO_4 structure synthesized by directly reacting commercial Ag foil with H_2O_2 and NaH_2PO_4 in an aqueous solution at room temperature, showed higher photocatalytic activity than Ag_3PO_4 cubes, irregular Ag_3PO_4 and N-doped TiO_2. The novel type of regular tetrahedron nanocrystal exposing {111} facets was

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designed by oxidizing Ag with H_2O_2 in the presence of PO_4^{3-} ion [13]. Dong et al. [14] fabricated the Ag_3PO_4 microcrystals with different morphologies, such as tetrahedra with round and sharp corners, short tetrapods, polyhedra, and dendritic long tetrapods via simple and green routes. Among these morphologies, the tetrahedral Ag_3PO_4 with round edges synthesized using KH_2PO_4 as a PO_4^{3-} source showed the highest activity and excellent stability. Zheng et al. [15] synthesized the single–crystalline tetrahedral Ag_3PO_4 microcrystal exposing {111} facet using a facile wet chemical method. This morphology structure showed higher photocatalytic activity compared to those with the {110} and {100} facets. Martin et al. [16] synthesized the tetrahedral Ag_3PO_4 with {111} facets by a novel kinetic control method using starting materials of $AgNO_3$ and H_3PO_4 with the ethanol solution. This tetrahedral crystal showed higher activity for water photo-oxidation than rhombic dodecahedron {110} and cubic {100} structures. The excellent photocatalytic performance was attributed to a synergistic effect of the high surface energy and small hole mass which enhanced the charge carrier mobility and active surface reaction sites.

Based on the above mentioned information, the design of tetrahedral Ag_3PO_4 structure to provide an excellent photocatalyst is very challenging. In the current result, the Ag_3PO_4 sample with the best photocatalytic reactivity, enabled by its saddle-like morphology, derived from the tetrahedron, could be easily prepared using ethanol aqueous solution. It is very important to provide a simple preparation method to be adopted for practical application. This finding could contribute to the improvement of photocatalytic reaction under visible light irradiation.

2. Experiment

The five samples of Ag_3PO_4 were prepared as follows. At first, 0.85 g $AgNO_3$ was dissolved in 50 mL ethanol aqueous solution with an ethanol volume percentage of 0, 50, 80, 90 or 100%. Then, the H_3PO_4 ethanol solution was made by dissolving 0.98 g H_3PO_4 in 50 mL of ethanol, and added to the $AgNO_3$ ethanol aqueous solution drop by drop. The precipitates were separated by 14,000 rpm centrifugation, washed with water three times, and dried in a vacuum over night at 60 °C. The products were designated as E0, E50, E80, E90 and E100, respectively.

The crystal structures of Ag_3PO_4 were characterized using X-ray diffraction (XRD, Bruker AXS D2 Phaser) using graphite-monochromatized CuKα radiation. The absorption spectra of powder samples were analyzed using a UV–Vis NIR spectrometer (JASCO V-670; JASCO Corporation, Tokyo, Japan), giving the output of absorbance in the UV and visible ranges of 200–800 nm with step size of 0.2 nm. The BET specific surface areas (S_{BET}) of samples were determined by nitrogen adsorption (NOVA 4200e). The morphologies were observed by a scanning electron microscope (SEM, Hitachi S-4800). To investigate the binding energy, the X-ray photoelectron spectrometer (XPS, Perkin Elmer PHI 5600) was used.

To evaluate the photocatalytic activities, 100 mg of catalyst was mixed with 100 mL of 10 mg/L Rhodamine B solution, and the solution was stirred at room temperature under dark condition for 20 min. After that, the solution was irradiated by a blue LED lamp (OptiLED, SP-E27BL, 2.5 W, $\lambda = 455$ nm) which is adjusted at 10 cm above the surface of solution. 4 mL of sample solution was withdrawn every 10 min and centrifuged at 14,000 rpm to separate the sample powder, and the concentration of RhB was measured using a spectrophotometer (JASCO V-670; JASCO Corporation, Tokyo, Japan), giving the output of absorbance in the UV and visible ranges of 300–700 nm with step of 0.2 nm [17].

3. Results and discussion

The tetrahedral Ag_3PO_4 was successfully synthesized by the co-precipitation method in ethanol aqueous solutions. Fig. 1(a) shows the XRD profile of samples synthesized using different percentage of ethanol.

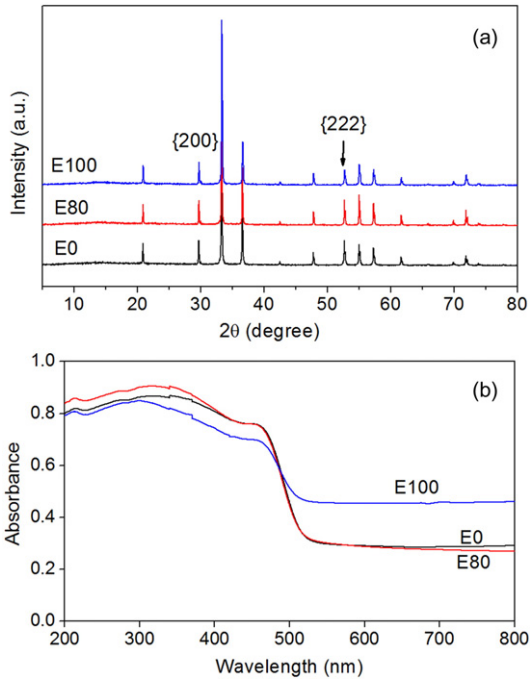

Fig. 1. XRD profiles (a) and diffuse reflectance spectra (b) of the Ag_3PO_4 synthesized by the co-precipitation method in ethanol aqueous solutions of E0, E80 and E100.

The body-centered cubic structure (JCPDS no.06-0505) was observed in all of the samples, similar to other results [18,19]. No impurities were observed on the samples, indicating that the samples were single phase Ag_3PO_4. However, a slightly different {111}/{100} intensity ratio of 1.12, 1.01 and 0.72 were observed in E0, E80, and E100, respectively, indicating that the samples had different facets.

The absorption spectra of E0, E80 and E100 are shown in Fig. 1(b). The absorption spectra of E0 and E80 are similar, whereas significant broad absorption above 500 nm could be found in the sample of E100, indicating that the pure ethanol solution influences the properties of Ag_3PO_4. A high number of defects or deformations of morphology may generate the broad absorption of the sample in the visible region. It could be considered that the defect site of crystal affected the absorption in visible region [20]. The band gap energies were calculated based on the previous reports [17], and listed in Table 1.

Fig. 2 shows that the morphology of Ag_3PO_4 could be controlled by increasing the volume percentage of ethanol. The morphology of the E0 consisted of triangular and irregularly shaped particles. The SEM image of the triangular particles confirmed that the microsized Ag_3PO_4 showed a tetrahedron feature. The tetrahedra are formed by the reaction of H_3PO_4 ethanol solution and $AgNO_3$ aqueous solution. The side edge length of tetrahedron ranges from 1 to 3 μm and that of the irregular shape ranges from 0.5 to 2 μm. The tetrahedron particles appeared in the reaction of H_3PO_4 ethanol solution with $AgNO_3$ ethanol aqueous solution (50% of ethanol). In this step, some of the tetrahedron particles were changed into a unique saddle–like shape of Ag_3PO_4, which has a round shape on one side edge of the tetrahedron feature. With a further increase of ethanol content in $AgNO_3$ ethanol aqueous

Table 1
The BET specific surface areas, band gap energies and rate constants of Ag_3PO_4 synthesized in variation of ethanol aqueous solutions.

Sample	S.S.A. (m^2/g)	Band gap energy (eV)	Rate constant (min^{-1})
E0	8.82	2.40	0.0216
E50	10.30	2.42	0.0352
E80	7.51	2.41	0.0637
E90	12.50	2.38	0.0358
E100	10.74	2.32	0.0300