Materials Letters 123 (2014) 172–175

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Template-free and eco-friendly synthesis of hierarchical Ag_3PO_4 microcrystals with sharp corners and edges for enhanced photocatalytic activity under visible light

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ARTICLE INFO

Article history:
Received 30 December 2013
Accepted 19 February 2014
Available online 11 March 2014

Keywords:
Semiconductor
Hierarchical Ag_3PO_4
Photocatalysis
Template-free
Crystal growth
Solar energy materials

ABSTRACT

Herein, we demonstrate a template-free and eco-friendly strategy to synthesize hierarchical Ag_3PO_4 microcrystals with sharp corners and edges via silver–ammine complex at room temperature. The as-synthesized hierarchical Ag_3PO_4 microcrystals were characterized by X-ray diffraction, field-emission scanning electron microscope (FESEM), UV–vis diffuse reflectance spectroscopy (UV–vis DRS), BET surface area analyzer, and photoluminescence analysis (PL). Our results clearly indicated that the as-synthesized Ag_3PO_4 microcrystals possess a hierarchical structure with sharp corners and edges. More attractively, the adsorption ability and visible light photocatalytic activity of the as-synthesized hierarchical Ag_3PO_4 is much higher than that of conventional Ag_3PO_4.

1. Introduction

In recent years, hierarchical structured materials have been receiving great attention in various fields such as drug delivery systems, gas separation, luminescence, photonic devices, electrochemical capacitors and photocatalysis due to their unique properties including large surface area, light trapping effects, low density and surface permeability [1–4]. Photocatalysis is an important chemical process that underpins the development of clean renewable energy and environmental technologies such as photocatalytic water splitting, low-cost solar cells and water/air purification [5–7]. Hierarchical structured semiconductor materials can offer high photocatalytic activity and better light induced photochemical behavior [8]. A few efforts were made in order to develop hierarchical semiconductor materials such as ZnO, TiO_2, etc., for improved photocatalytic performance [8–10]. The most common method adapted for preparing the hierarchical structures is based on template assisted route [11,12]. Unfortunately this template assisted route involves high cost chemicals, tedious procedures, high temperate or chemical etching which are major obstructions for practical environmental applications. Thus, it is desirable to develop a facile and template-free method for synthesis of hierarchical semiconductor based materials with a unique property to achieve high efficiency for practical applications.

In the present work, we report a facile, template-free and reproducible method to synthesize hierarchical Ag_3PO_4 microcrystals via silver–ammine complex at room temperature. The phase, microstructure, morphology and textural properties were investigated comprehensively by X-ray diffraction, FESEM, UV–vis DRS, PL and BET surface area analyzer. The photocatalytic activity of the as-synthesized hierarchical porous Ag_3PO_4 microcrystals was examined, for degradation of methyl orange (MO) under visible light irradiation.

2. Experimental details

Hierarchical Ag_3PO_4 microcrystals were synthesized by the ion exchange method. In brief, 0.42 g of silver nitrate (Merck, 99.5%) was dissolved in 25 mL of double distilled water and stirred for 10 min at room temperature. To this solution, aqueous solution of NH_3 (Merck, 25%) (0.1 M, 50 mL) was added drop wise for a period of 10 min. Furthermore, aqueous solution of sodium hydrogen phosphate (SISCO, 99.5%) (0.1 M, 50 mL) was added drop wise and stirred for 12 h at room temperature. The powder sample was centrifuged and washed (thrice) with water and ethanol. The as-synthesized Ag_3PO_4 was dried at 100 °C for 1 h. However, for the synthesis of conventional Ag_3PO_4, sodium phosphate tribasic dodecahydrate (SISCO, 99.5%) was directly added to aqueous solution of silver nitrate.

Powder X-ray diffraction studies (PXRD) were carried out on a Bruker D_8 Advance diffractometer using Ni filter to avoid

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http://dx.doi.org/10.1016/j.matlet.2014.02.106
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Cu K_β radiation. FESEM studies of samples were carried out on a FEI quanta 3D FEG-FESEM operated at 10 kV by coating the powder sample with gold. UV–vis diffuse reflectance spectra were recorded on Lambda/20 Instruments. The nitrogen adsorption isotherms were carried out by using a Quanta chrome NOVA 1200e. The photoluminescence (PL) spectra of photocatalysts were recorded on a TSC solutions F96PRO fluorescence spectrophotometer with excitation wavelength of 365 nm.

Photocatalytic activity: The photocatalytic activity of the as-synthesized Ag_3PO_4 samples (25 mg) was examined via degradation of methyl orange (100 mL, 10 mg L^{-1}) under visible light (solar simulator 300 W Xe lamp). Prior to irradiation, solutions suspended with photocatalysts were stirred in dark condition for 30 min to ensure that the surface of catalyst was saturated with methyl orange. The sample was periodically withdrawn (sampling time of 5 min), centrifuged to separate the photocatalyst from solution, and used for the absorbance measurement.

3. Result and discussion

Evolution of hierarchical Ag_3PO_4 microcrystals: Synthesis of hierarchical Ag_3PO_4 microcrystals was shown by schematic diagram with photographs in Fig. 1.

$$AgNO_3 + 2NH_3 \cdot H_2O \rightarrow [Ag(NH_3)_2]NO_3 + H_2O \quad (1)$$

$$3[Ag(NH_3)_2]NO_3 + 6Na_2HPO_4 \rightarrow Ag_3PO_4 + 2(NH_4)_3PO_4 + 3Na_3PO_4 + 3NaNO_3 \quad (2)$$

As shown in Eq. (1), $[Ag(NH_3)_2]NO_3$ complex is formed when aqueous NH_3 solution was added drop wise to aqueous solution of silver nitrate at room temperature. The as-obtained $[Ag(NH_3)_2]NO_3$ complex served as both soft-template and reactant source, which not only mediated the morphology of the product but also served as modifier for the growth of Ag_3PO_4 microcrystals at the beginning stage of the evolution process. The Ag_3PO_4 nuclei were formed by surface reaction and a subsequent crystal growth process. Since PO_4^{3-} ions could be released slowly from Na_2HPO_4 in aqueous solution (Eq. (2)), and the free Ag^+ ions have been gradually released from $[Ag(NH_3)_2]^+$ complex through the neutralization reaction between H^+ from Na_2HPO_4 and NH_3 from $[Ag(NH_3)_2]^+$, which subsequently reacted with PO_4^{3-} anions to form Ag_3PO_4. More specifically, Na_2HPO_4 could rationally control the release rate of Ag^+ ions and the growth rate of Ag_3PO_4, which may promote the formation of hierarchical Ag_3PO_4 microcrystals via the Ostwald ripening and self-assembly process [13].

Catalysts characterization: The PXRD patterns of Ag_3PO_4 and hierarchical Ag_3PO_4 are shown in Fig. 2a. Both Ag_3PO_4 and hierarchical Ag_3PO_4 are well indexed (JCPDS#840193). The strong and sharp diffraction peaks indicate the highly crystalline nature of the samples. The average crystallite size of sample was calculated from the line broadening study using the Debye–Scherrer equation. The estimated average crystallite size was 124 nm for hierarchical Ag_3PO_4 and 83 nm for Ag_3PO_4.

The UV–vis diffuse reflectance spectra of the as synthesized Ag_3PO_4 and hierarchical Ag_3PO_4 are shown in Fig. 2b. Hierarchical Ag_3PO_4 has a strong absorption edge at 520 nm, typically in visible region as compared with Ag_3PO_4. This may be due to the hierarchical structure of Ag_3PO_4 microcrystals that could allow multiple scattering of light, resulting higher optical path length for light transporting through their bodies. Fig. 3a shows typical FESEM images of the as-synthesized hierarchical Ag_3PO_4 microcrystals. As can be seen in Fig. 3a, the as-synthesized Ag_3PO_4 microcrystals possess a hierarchical structure with sharp corners and edges. Moreover, the magnified FESEM images (Fig. 3b) reveal the surface porosity of the hierarchical Ag_3PO_4 microcrystals. The calculated particle size range of the hierarchical Ag_3PO_4 microcrystals is from 0.5 to 2.0 μm and the estimated average pore size of these microcrystals is about 65 nm which is well in agreement

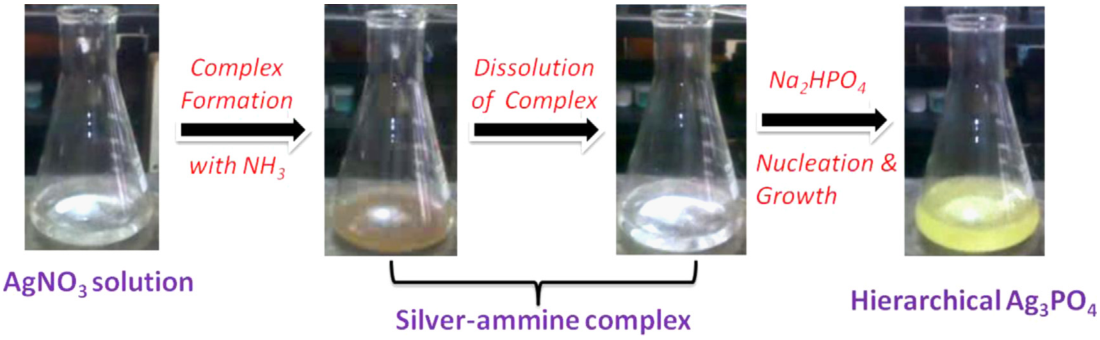

Fig. 1. Schematic diagram with photographs for synthesis of hierarchical Ag_3PO_4 microcrystals.

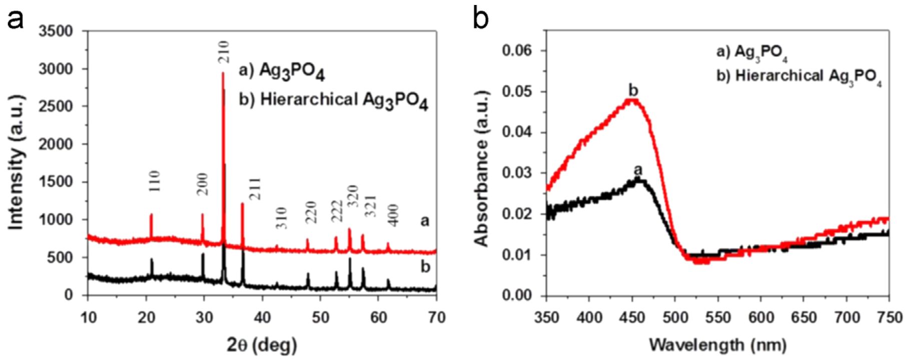

Fig. 2. XRD pattern (a) and UV–vis DRS of the as-synthesized conventional Ag_3PO_4 and hierarchical Ag_3PO_4 photocatalysts.

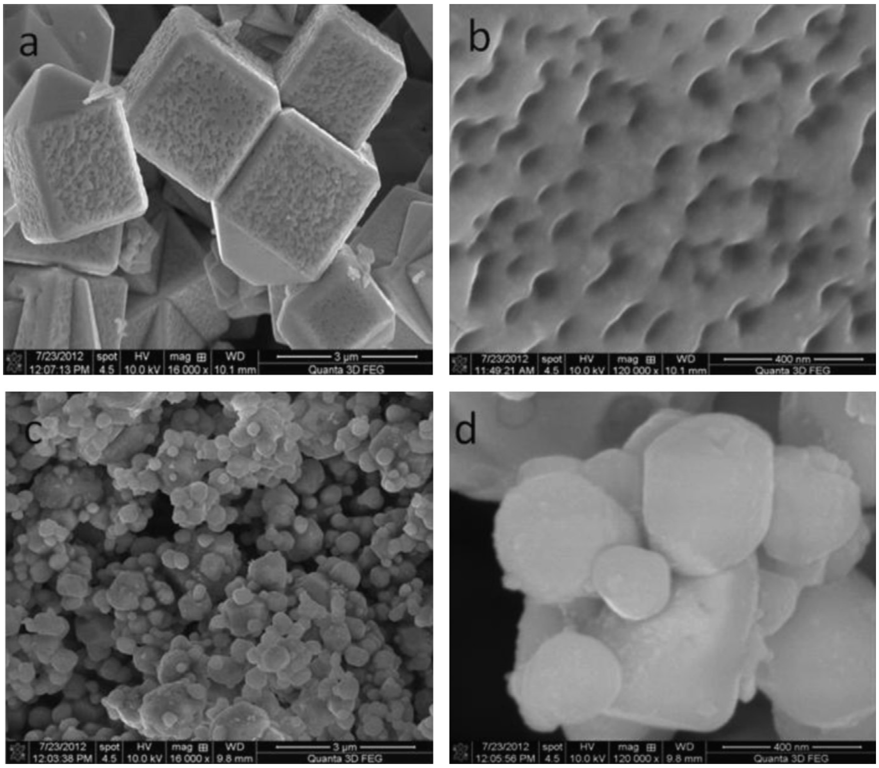

Fig. 3. FESEM images of the photocatalysts: (a) hierarchical Ag_3PO_4, (b) hierarchical Ag_3PO_4 (magnified), (c) conventional Ag_3PO_4 and (d) conventional Ag_3PO_4 (magnified).

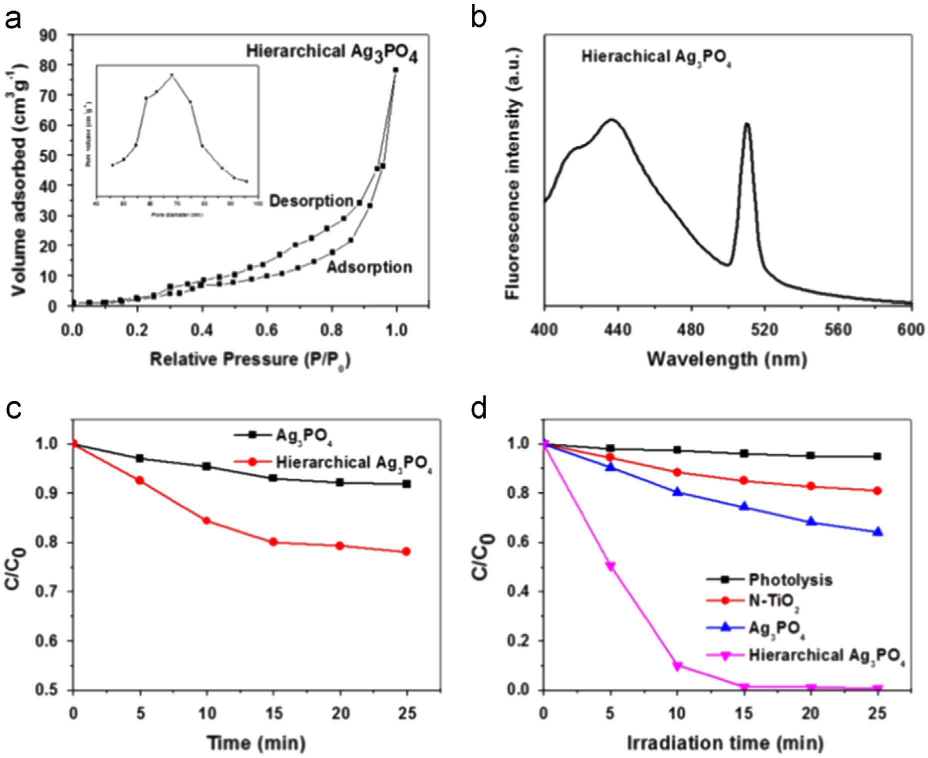

Fig. 4. Nitrogen adsorption–desorption isotherm of hierarchical Ag_3PO_4 (a), photoluminescence spectra of hierarchical Ag_3PO_4 with excitation wavelength of 365 nm at room temperature (b), adsorption studies of MO in aqueous solution over conventional Ag_3PO_4 and hierarchical Ag_3PO_4 microcrystals (c), photocatalytic degradation of MO over conventional Ag_3PO_4 and hierarchical Ag_3PO_4 photocatalysts (d).

with the average pore size calculated from the BET plot in this section. However, the low- and -high magnification FESEM images (Fig. 3c and d) of the conventional Ag_3PO_4 indicate that the product consists of submicron particles.

The typical adsorption–desorption isotherms and pore size distributions of hierarchical Ag_3PO_4 microcrystals are shown in Fig. 4a, which demonstrate that the hierarchical Ag_3PO_4 exhibits high surface area ($18.52\ m^2g^{-1}$) compared to conventional

Ag_3PO_4 (0.89 m^2g^{-1}) [14]. The pore size distribution is determined by the BJH method. The average pore diameter is 67.8 nm for Ag_3PO_4 microcrystals.

Photocatalytic activity: The photocatalytic activity of the as-synthesized hierarchical Ag_3PO_4 was examined for degradation of methyl orange (MO) under visible light irradiation as shown in Fig. 4d. The hierarchical Ag_3PO_4 photocatalysts exhibited much higher photocatalytic activity for degradation of MO under visible light irradiation compared to conventional Ag_3PO_4 as well as commercial N-TiO_2. This might be the synergetic effect of crystal facets [15]. However, the adsorption ability of the as-synthesized catalyst in dark condition was also examined under same experimental conditions. Hierarchical Ag_3PO_4 microcrystals showed good adsorption ability towards MO compared to conventional Ag_3PO_4 (Fig. 4c) which is also beneficial for enhancing the photocatalytic activity as it is the first step of a photocatalytic process.

4. Photoluminescence

Photoluminescence measurement of the as-synthesized hierarchical Ag_3PO_4 was performed at room temperature, with the excited wavelength at 365 nm, as shown in Fig. 4b. The hierarchical Ag_3PO_4 has an emission band centered at about 520 nm and another broad emission band located in the blue region centered at around 435 nm.

5. Conclusion

In summary, we have demonstrated a template-free and reproducible method to synthesize hierarchical Ag_3PO_4 microcrystals via silver–ammine complex at room temperature. More attractively, the photocatalytic activity of hierarchical Ag_3PO_4 microcrystals for degradation of MO under visible light is much higher than that of conventional Ag_3PO_4 and commercial N-TiO_2. This idealizes versatile hierarchical Ag_3PO_4 microcrystals prepared from a cost-effective and environment friendly process would be useful for various applications, including drug delivery systems, gas separation, luminescence, photonic devices, electrochemical capacitors, photodynamic therapy.

Acknowledgment

The corresponding author thanks the Department of Science and Technology, Government of India for financial support (SR/FT/CS-096/2009). Santosh Kumar thanks the Ministry of Human Resource Development, Government of India for providing fellowship.

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