



Hierarchical P/YPO₄ microsphere for photocatalytic hydrogen production from water under visible light irradiation

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ARTICLE INFO

Article history:

Received 9 December 2011
Received in revised form 3 March 2012
Accepted 9 March 2012
Available online 19 March 2012

Keywords:

Hydrogen production
Photocatalyst
Red phosphorus
Visible-light-driven
Yttrium phosphate

ABSTRACT

Hierarchical P/YPO₄ hollow microspheres are prepared by the reaction between amorphous red P and YCl₃ aqueous solution via a hydrothermal method. The final product consists of crystalline YPO₄ nanosheets and amorphous red phosphorus. Photocatalytic hydrogen formation measurements indicate that the P/YPO₄ composites exhibit higher activity than the individual components. The composite with 53 wt% YPO₄ is up to 6 times more active than red phosphorus under visible light irradiation. The formation mechanism of hierarchical microspheres and the enhanced photocatalytic activity are discussed.

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1. Introduction

The depletion of fossil fuel reserves is one of the most urgent issues facing modern society. Solar-induced photocatalytic hydrogen production from water has been considered as a promising way to alleviate this problem [1–3]. For effective utilization of solar light, numerous attempts have been devoted to the exploration of novel visible-light-driven photocatalysts. These include non-metal or metal ion(s) doped metal oxides, oxynitride, oxysulfide photocatalysts, polymeric photocatalysts, and sensitized systems [4–6]. Red phosphorus has been discovered recently as a visible-light-driven photocatalyst for H₂ formation from water [7]. An attractive property of red phosphorus is a wide visible light absorption band. The absorption band edge is all the way to ~700 nm. However, the photocatalytic efficiency for H₂ formation over red P is relatively low, mainly due to a rapid recombination of photogenerated electrons and holes.

By coupling two different semiconductors together to form a composite, interesting and desirable properties can be obtained [8–10]. For photocatalytic applications, the interface(s) between different components could lead to effective separation of photogenerated carriers [11–14]. Generally, the composites are fabricated by the sequential growth of a second semiconductor on the active seeding photocatalysts [15,16]. For red phosphorus, it

reacts with metal compounds to form phosphates or phosphides under suitable conditions [17,18]. This allows the development of a series of interesting red P based functional composites.

In this work, hierarchical P/YPO₄ hollow microspheres are fabricated by the reaction between red P and YCl₃ aqueous solution via a hydrothermal method. The hierarchical microsphere product is assembled by crystalline YPO₄ nanosheets and amorphous red P. The formation mechanism is investigated by time-dependent experiments. Photocatalytic H₂ formation measurements show that the composites exhibit higher activity than the individual components.

2. Experimental

2.1. Sample preparation

Commercial red phosphorus was purified to remove surface oxidation before use. Typically, red P was dispersed in D.I. water. The suspension was put into a Teflon-lined stainless autoclave and maintained at 200 °C for 12 h. YCl₃·6H₂O (≥99.999%, w/w, Sigma–Aldrich) was used without further purification. P/YPO₄ hierarchical microspheres were fabricated by a hydrothermal method. In a typical synthesis, 0.3 g of YCl₃·6H₂O was dissolved in 15 mL of D.I. water, and then 0.3 g of purified red phosphorus was added. After ultrasonic for 5 min, the prepared solution was transferred into a preheated 200 °C oven for 20 h. After the reaction, resulted products in suspension were washed with D.I. water and ethanol. Finally, the products were dried under vacuum at 60 °C. Pure YPO₄

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was prepared via the same procedure as P/YPO₄ composites with an excess amount of YCl₃·6H₂O.

2.2. Characterizations

The XRD patterns of the products were recorded by powder X-ray diffraction (XRD) with a Bruker D8 Advance diffractometer using Cu K_{α1} irradiation (λ = 1.5406 Å). The general morphologies of the products were characterized by scanning electron microscopy (SEM, Quanta 400) and transmission electron microscopy (TEM) images (TEM, Tecnai F20 microscope) coupled with an energy-dispersive X-ray (EDX) spectrometer (Oxford Instrument). UV–vis diffuse reflectance spectra were collected by a UV–vis spectrophotometer (Cary 100 scan spectrophotometers, Varian). The Brunauer–Emmett–Teller surface areas were determined by nitrogen adsorption and desorption with a Micromeritics ASAP 2010 analyzer. X-ray photoelectron spectroscopy (XPS) spectra were recorded by a PHI 5600 multi-technique system with a monochromatic Al K_α X-ray source (Physical Electronics). All the binding energies were referenced to the C1s peak at 284.8 eV of the surface adventitious carbon. The percentages of red P in P/YPO₄ composites were determined by a thermogravimetric analyzer (TGA6, Perkin-Elmer) under N₂ flow (20 mL/min) with a heating rate of 10 °C/min.

2.3. Hydrogen production tests

The photocatalytic H₂ formation experiments were carried out in a Pyrex reaction cell connected to a closed gas circulation with an evacuation system. 50 mg of the sample were dispersed in 100 mL of aqueous solution containing 5 vol% methanol as a hole sacrificial agent. The suspension was purged with argon to remove dissolved air before irradiation. 1% Pt was loaded onto all samples by photoreduction of H₂PtCl₆ [19,20]. The amount of Pt was measured by an XPS analyzer (Fig. S1). The suspension was irradiated by a 300 W xenon lamp with a 400 nm cut-off filter and a water filter. The amounts of hydrogen generated from photocatalytic water reduction were measured by a Techcomp GC7900 gas chromatography with a TCD detector and a capillary column (Molecular Sieve 5 Å). High purity nitrogen gas was used as a carrier gas.

3. Experimental results and discussion

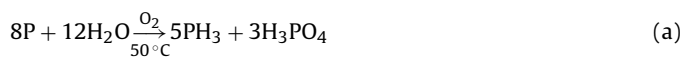
The powder X-ray diffraction (XRD) pattern provides crystallinity and phase information for the P/YPO₄ composite. All the diffraction peaks are readily indexed to the tetragonal YPO₄ (JCPDS No. 11-0254), as shown in Fig. 1a. The existence of red P in the composite can be confirmed by UV–vis diffuse reflectance spectra, colors of products and XPS spectra. As shown in Fig. 1b, pure YPO₄ is a white powder with no absorption in the visible range. The composite is a red powder with an absorption edge at about 700 nm. The chemical composition of the samples and the oxidation states of phosphorus are obtained from XPS analysis. The survey XPS spectrum reveals that the microspheres are composed of Y, P and O, as shown in Fig. 1c. In the high-resolution P 2p XPS spectrum, two peaks at the binding energies of ~134.7 eV and ~129.8 eV are observed (Fig. 1d), corresponding to the characteristic of P⁵⁺ in YPO₄ and elemental P, respectively [21,22]. No red P peak is observed in the XRD pattern, suggesting the amorphous structure of red phosphorus in the composite. These results indicate the prepared composite is composed of crystalline YPO₄ and amorphous red P.

The morphology and microstructure of the P/YPO₄ composite were recorded by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 2a indicates that the product is composed of a large quantity of microspheres. The mean

diameter of the microspheres is ~750 nm. The high-magnification SEM image shows all microspheres have a hierarchical architecture (Fig. 2b). TEM images in Fig. 2c and d clearly show the hollow nature of microspheres and suggest that the hierarchical structure is built from nanosheets. The average thickness of the sheets is about 15 nm. High-resolution TEM (HRTEM) image indicates the single crystallinity of the nanosheets, as shown in the inset of Fig. 2d. The periodic fringe spacing of ~3.5 Å corresponds to the interplanar spacing between the (0 1 2) planes of the tetragonal YPO₄. This agrees with the XRD results. However, it is difficult to show the distribution of red phosphorus in the microsphere by the conventional mapping method. This is due to the overlapping of the binding energy of P with that of Y (Fig. S2). Time-dependent experiments were carried out to understand the distribution of red P and the formation mechanism of the hierarchical microspheres.

Fig. 3 shows the SEM and TEM images of products obtained with different reaction times. They reveal a clear trend of morphology evolution. Microspheres are formed after reacting for 30 min, as shown in Fig. 3a and b. The microspheres are mainly composed of P as indicated by EDX analysis (data not shown). When the reaction proceeds to 1 h, needle-like YPO₄ is observed on the surface of the microspheres (Fig. 3c and d). As the reaction goes on, more YPO₄ are formed and the hollow structure could be seen (Fig. 3e and f). At last, hierarchical P/YPO₄ microspheres with sheet-like YPO₄ are formed (Fig. 3e and f). It is noted that the size of microspheres is different at different reaction stages. The size of microspheres is ~1050 nm at 0.5 h and increases to ~1450 nm at 1 h, beyond which it decreases. At the end of the reaction, the size of microspheres is ~750 nm. Besides, the evolution processes of the hierarchical P/YPO₄ composites also show that the amorphous red phosphorus mainly distribute in the inner layer of microspheres and connects with the crystalline YPO₄ nanosheets to form hierarchical microspheres.

Concerning the morphology evolution of the P/YPO₄ microspheres, the reaction between YCl₃ and P should have played a key role, because no other templates and surfactants are used in our reaction system. The formation of P/YPO₄ composite can be understood by the following equations:



It is known that red P has a disproportionation with the formation of phosphine and phosphate acid in the presence of O₂ and moisture at elevated temperatures (Eq. (a)) [23,24]. In the presence of YCl₃, the H₃PO₄ formed in the first reaction could be consumed immediately with the formation of YPO₄ precipitated (Eq. (b)). Accordingly, the dissociation of red phosphorus is promoted. At last, the P/YPO₄ composite is obtained with an excess amount of red phosphorus.

Scheme 1 shows a formation mechanism for the hierarchical structure. The whole growth process follows an interfacial liquid–solid reaction between red P and YCl₃ aqueous solution. Initially, smooth spheres are formed from red phosphorus particles, which may be related to the synergetic effect of the shear stress from water and the reaction between YCl₃ and P. And then, needle-like YPO₄ is observed on the outer layer of the microspheres. As more YCl₃ solution diffuses into the sphere, the YPO₄ needles gradually evolve to sheets. Meanwhile, the hollow structure is formed with the consumption of red phosphorus. The growth process continues until YCl₃ is depleted, resulting in hierarchical hollow spheres composed of YPO₄ nanosheets and unreacted amorphous red phosphorus. The different microsphere sizes at different reaction times can be understood by the competition between the diffusion of YCl₃ and the consumption of red P. At the initial

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