Materials Letters 159 (2015) 172–176

Contents lists available at ScienceDirect

Materials Letters

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

Enhanced photocatalytic activity of porous cuprous oxide dodecahedron nanocrystals synthesized by solvothermal method

Lufeng Yang [a,b], Deqing Chu [a,b,*], Limin Wang [b,c,**], Huilou Sun [a], Ge Ge [a]

[a] College of Environment and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300387, PR China
[b] State Key Laboratory of Hollow-Fiber Membrane Materials and Membrane Processes, Tianjin 300387, PR China
[c] College of Material Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, PR China

ARTICLE INFO

Article history:
Received 27 February 2015
Received in revised form
18 May 2015
Accepted 28 June 2015
Available online 30 June 2015

Keywords:
Cuprous oxide
Porous materials
Semiconductors
Crystal growth
Photocatalytic property

ABSTRACT

The porous cuprous oxide (Cu_2O) dodecahedron nanocrystals have been successfully prepared via a solvothermal reduction process at a moderate temperature. The average dimensions of these Cu_2O dodecahedron nanostructures were about 750 nm in diameter. The crystal growth mechanism of the novel architectures has been discussed. And then, the as-prepared Cu_2O samples were used as photocatalysts in the degradation of methylene blue (MB). Due to the porous nature of the products, the photocatalytic performance has been significantly improved. We believe that the current work will offer some ideas for further fabricating porous nanostructures and exploring their applications.

1. Introduction

As an important p-type semiconductor, Cu_2O has a direct small band gap of 2.2 eV [1] and is considered to be a promising material in solar cells conversion [2–4] and photocatalysis areas [5]. Up to now, Cu_2O has been prepared by several different methods, such as electrodeposition [6], thermal relaxation [7], sonochemical methods [8], vacuum evaporation [9], and the liquid-phase reduction [10]. Meanwhile, various morphologies of Cu_2O, such as nanowires [11], octahedral [12], hollow spheres [13], nanocubes [14], and nanorods [15] have been prepared. However, it remains a great challenge to develop simple and feasible approaches for the shape-controlled synthesis of well-defined Cu_2O architectures.

Here we report a new method of the synthesis and characterization of porous Cu_2O dodecahedron crystals. The synthesis was performed using a solvothermal reduction process at a moderate temperature. The adsorption ability and photocatalytic activity of the samples were evaluated by the photocatalytic degradation of MB aqueous solution under UV/visible light illumination.

2. Experimental

A typical synthesis procedure of the porous Cu_2O dodecahedron nanostructures was as follows: 2 mmol (0.3993 g) of copper acetate ($Cu(Ac)_2{\cdot}H_2O$) was dispersed in 25 mL of N,N-dimethylformamide (DMF) under vigorous stirring at room temperature, followed by addition of 1 g of polyvinyl pyrrolidone (PVP). After being stirred vigorously for 10 min, the mixed solution was put into a 50 mL Teflon-lined stainless steel autoclave. The autoclave was maintained at 170 °C for 8 h and then cooled to room temperature naturally. The resulting products were centrifuged, washed several times with distilled water and anhydrous ethanol, and dried at 80 °C in a vacuum for 6 h.

The photocatalytic experiments were carried out by adding 100 mg of Cu_2O samples into 100 mL of MB aqueous solution with the concentration of 10 mg L^{-1}. The suspension was stirred for 30 min in the dark to obtain adsorption equilibrium. Then, the suspension was irradiated with a 365 nm UV-light. As a comparison, the visible-driven photocatalytic experiments were also carried out. The concentration of MB was detected by a UV–vis spectrophotometer.

3. Results and discussion

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) provided insight into the morphology of the

* Corresponding author at: College of Environment and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300387, PR China. Fax: +86 22 83955762.
** Corresponding author at: State Key Laboratory of Hollow-Fiber Membrane Materials and Membrane Processes, Tianjin 300387, PR China.
E-mail addresses: dqingchu@163.com (D. Chu), wanglimin@tjpu.edu.cn (L. Wang).

http://dx.doi.org/10.1016/j.matlet.2015.06.098
0167-577X/

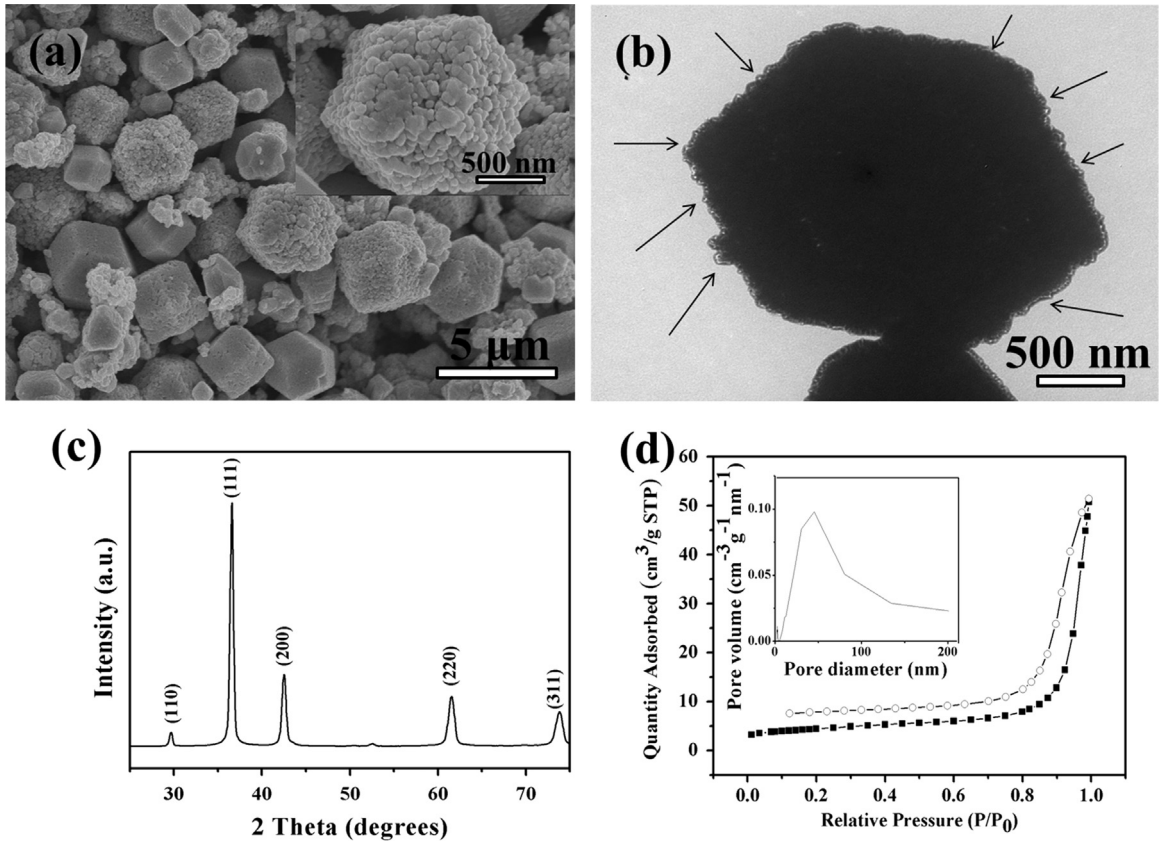

Fig. 1. (a) SEM images of the porous Cu_2O dodecahedron nanocrystals (the inset shows the close observation of the product); (b) TEM image of the Cu_2O nanostructure; (c) a representative XRD pattern recorded for Cu_2O dodecahedron architectures; and (d) N_2 adsorption–desorption isotherm and BJH pore size distribution plots (inset) of the porous Cu_2O dodecahedron nanostructures.

Cu_2O crystals. A panoramic morphology of the product is displayed in Fig. 1(a), indicating the high yield and uniformity. A magnified SEM image showing the close observation of the nanostructures is given in the illustration in Fig. 1(a). It reveals that the detailed morphology of Cu_2O product is well-defined porous dodecahedron with diameters of 750 nm and the surface of Cu_2O nanostructures are made of numerous nanoparticals. As shown by the arrows in Fig. 1(b), the surface of the Cu_2O nanocrystal was covered with lots of pores.

The crystal phase of Cu_2O is characterized by XRD, and the data are shown in Fig. 1(c). The characteristic peaks of the cubic phase of Cu_2O crystals (JCPDS 05-0667) were observed. No peaks of impurity are detected in the XRD pattern, indicating the formation of pure Cu_2O under these experimental conditions.

To further confirm the surface architectures of the as-prepared Cu_2O samples, N_2 adsorption and desorption measurements were performed. As shown in Fig. 1(d), the isotherm of the Cu_2O samples exhibit a hysteresis loop at p/p_0 range of 0.8–1.0. This phenomenon clearly indicates that the Cu_2O samples exhibit a large textural porosity [12]. The pore size distribution of the Cu_2O shows that a narrow peak appeared in the pore size region from 2.1 to 200.8 nm. The material had an average pore size of 20.6 nm. The Brunauer–Emmett–Teller (BET) surface area of the Cu_2O nanocrystals was calculated to be 15.4 $m^2\ g^{-1}$, which is much higher than that of the Cu_2O intermidates (5.3, 7.9, 8.6, and 10.3 $m^2\ g^{-1}$ after solvothermal treatment for 2, 4, 6, and 10 h, respectively).

Fig. 2 illustrates the morphology evolution of Cu_2O at different stages. Initially, Cu^{2+} is reduced by DMF to generate Cu_2O particles, and then Cu_2O nanospheres (Fig. 2(a) and (b)) are grown by self-assembly of small primary nanoparticles through an oriented-attachment mechanism after solvothermal treatment for 2 h. In this stage, the morphology evolution of Cu_2O nanostructures had not been completed, meanwhile some Cu_2O crystallites grew along their specific crystallographic planes and eventually evolved into the original polyhedral nanostructures (as shown in the black dotted bordered rectangles of Fig. 2(a)). Seed particles continuously adsorb onto these nanospheres to allow further growth through a ripening process. Then the intermediate structures develop into structurally well-defined dodecahedron nanostructures (Fig. 2(c) and (d)) via a surface reconstruction process in 4 h. The growth control of Cu_2O crystals by adsorption of PVP has been extensively studied [16]. The PVP molecules should be adsorbed preferentially on the {111}, which helps to form unique structure of Cu_2O. After conducting the reaction for 6 h, Cu_2O dodecahedron with rough surface were constructed (Fig. 2(e)). A close-up view of Cu_2O nanostructure in Fig. 2(f) demonstrates that the surfaces of Cu_2O crystals present many tiny holes. Further prolonging the solvothermal time to 8 h, we got perfect porous Cu_2O dodecahedron nanostructures (Fig. 1(a)). It is well known that the structures of products prepared by solution reactions depend on the rate of nucleation and growth of the reaction products. The results show that the rate of growth of Cu_2O is faster than that of its nucleation. Due to the preferential growth of Cu_2O in a certain direction, the porous dodecahedron-like products were obtained. Further observation (inset in Fig. 1(a) and (b)) revealed that a large amount of irregular pores of tens of nanometers was randomly distributed in the nanocrystals, as a result of the dissolution-recrystallization process. Surprisingly, with the extension of the reaction time to 10 h, lots of broken dodecahedron-like Cu_2O particles can be discerned from Fig. 2(g) and (h), which is the result of increasing rate of the dissolution of Cu_2O nanocrystals, probably.

To evaluate the photocatalytic activity of the products, we