



Hydrothermal synthesis of porous copper microspheres towards efficient 4-nitrophenol reduction

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ABSTRACT

A facile one-pot approach has been presented to synthesize porous Cu microspheres (PCMs) with diameters of 2–5 μm . The self-organised growth mechanism is proposed according to the product formation order of Cu_2O nanoparticles, Cu nanobranched (CNBs), PCMs, solid Cu microspheres (SCMs) and distorted Cu microspheres. The experimental parameters of reaction time, temperature and reactant amounts can be used to regulate the kinetics of nucleation and crystallization, and further control the morphologies and porosities of the Cu products. Compared with the as-synthesized CNBs, SCMs and the commercial Cu powders, the PCMs show improved catalytic activity for the reduction of 4-nitrophenol to 4-aminophenol, demonstrating the significance of the porous structures. Furthermore, this porous Cu catalyst exhibits superior recycle and long-term air stabilities, which makes it a highly attractive candidate for industrial applications at low cost.

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1. Introduction

The fabrication of porous materials with specific structural features has attracted significant attention in recent decades because of the impact of these features in areas of basic scientific research and potential applications [1–5]. Among them, porous metals including Au, Ag, Pt, Ni, Al and Cu have aroused much interests of researches in various fields due to their great potential applications in catalysts, sensors, electrode materials and surface-enhanced Raman scattering active substrates, as well as their large surface-to-volume ratios and excellent thermal and electrical conductivities [6–12]. As a low-cost coinage metal material with excellent physical and chemical properties, porous Cu has aroused much interest of researchers in various fields [13–15].

To date, a variety of methods have been presented to fabricate porous Cu with different morphologies. The dealloying method is one of the most commons to produce porous Cu film/foams, which has an advantage of facile control of the pore and ligament sizes [16,17]. However, this method easily leads to miscible metals remaining and formation of metal oxides in porous Cu, and also has a side effect of wasting resources for the need of etching other miscible elements away [16]. Gao et al. [18] reported a facile phenol-assisted chemical method to fabricate hierarchically

micro/nanostructured porous Cu. In addition, metal oxide such as Cu_2O and ZnO particles have been used as templates to prepare hollow porous Cu micro/nanostructures [19,20]. Nevertheless, the above methods need porogen or templates to induce the formation of porous structures, which increases the complexity of preparation. Zhang et al. [21] proposed a facile solvothermal method to prepare porous cubic Cu microparticles without using any porogen or templates. The Cu microparticles exhibit cubic morphologies and sizes in the range of 3–6 μm . Compared to the commercial Cu microparticles with irregular morphology and dense internal structure, porous cubic Cu microparticles as catalysts show much higher dimethyldichlorosilane selectivity and Si conversion via Rochow reaction due to the presence of porous structure. However, the growth mechanism suggests that the porous cubic Cu microparticles were formed by the reduction of the dense cubic Cu_2O microparticle intermediates, which results in difficult control of the porosity of the cubic Cu microparticles.

On the other hand, one of the most important applications for micro/nanostructured Cu is as a catalyst for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP), which is very useful in a wealth of applications including analgesic and antipyretic drugs, photographic developers and corrosion inhibitors [18,22]. Zhang et al. [23] introduced a facile approach to synthesize faceted Cu nanocrystals using an inexpensive Cu oxide as a precursor. Sun et al. [24] demonstrated an effective strategy for the fabrication of plate-like Cu catalysts by using NaH_2PO_2 as the reductant.

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Although the Cu nanocrystals have shown excellent catalytic ability for the reduction of 4-NP due to their smaller sizes and higher specific surface areas, they are highly sensitive to oxidation by air, which will result in the degradation of catalytic performance.

Herein, we present a modified hydrothermal approach to synthesize porous Cu microspheres (PCMs). In the preparation of the Cu^{2+} precursor, the sequence for adding ethylene glycol (EG) and sodium hydroxide (NaOH) has been interchanged, and no ethanol was added in the solution compared with the solvothermal method proposed by Zhang et al. [21]. It is found that both the spherical morphology and self-organised growth mechanism of the porous microparticles are different from those of the literature reported porous cubic Cu microparticles. The self-organised growth mechanism of the PCMs indicates that the porosity can be varied by changing the experimental conditions. Additionally, the improved catalytic activity of the PCMs for the reduction of 4-NP has been investigated compared to the as-synthesized solid Cu microspheres (SCMs), Cu nanobranched (CNBs), and the commercial Cu powders. The recycle and air stabilities of the PCMs for the catalytic reactions have been also characterized.

2. Experimental details

2.1. Materials

All chemical reagents used in the experiments were of analytical grade and used without further purification. Deionized water (DIW, 18 M Ω cm) was used throughout all of the experiments. Copper acetate monohydrate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$), NaBH_4 , 4-NP and commercial Cu powders (200 meshes) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). NaOH was obtained from Pinghu Chemical Reagent Company (China). EG and ethanol were purchased from Shanghai Lingfeng Chemical Reagent Company (China) and Changshu Yangyuan Chemical Co., Ltd. (China), respectively.

2.2. Synthesis

In a typical procedure, 0.8 g $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and 1.6 g NaOH were dissolved into 35 ml DIW with continuous magnetic stirring. With adding 5 ml EG, the above pale blue emulsion solution gradually changed to dark blue, followed by stirring for 30 min. The mixture was then transferred into a Teflon-lined stainless steel autoclave, sealed and maintained at 200 °C for 6 h and cooled to room temperature in the oven. The products on the bottom of Teflon autoclave were washed using DIW and ethanol, then dried in a vacuum oven at 70 °C.

2.3. Characterization

The crystallinities of the samples were characterized by X-ray diffraction (XRD) using an advanced X-ray diffractometer (D8 ADVANCE, Bruker, Germany) in the diffraction angle range of $2\theta = 20\text{--}80^\circ$, using $\text{Cu K}\alpha$ radiation ($\lambda = 0.154056$ nm) at voltage of 40 kV and current of 40 mA. The morphologies were observed by field emission scanning electron microscope (FE-SEM, Carl Zeiss Ultra 55, Germany) operating at 5 kV. Transmission electron microscopy (TEM, JEM-2100, JEOL, Japan) operating at 200 kV was used to observe the microstructures of the samples.

2.4. Catalytic characterization

The catalytic reduction of 4-NP by Cu catalysts in the presence of NaBH_4 was carried out to examine the catalytic performance. In a typical process, 1.0 ml NaBH_4 solution (30 mM) was added to

0.5 ml 4-NP solution (1.0 mM) in a quartz cuvette, followed by the addition of 0.05 mg Cu catalyst and 1.5 ml DIW, and the mixture was quickly subjected to UV-vis measurements (Lambda 950, PerkinElmer, USA). For the recycling experiment, the catalysts were collected, washed with DIW, and reused in the next reaction.

3. Results and discussion

3.1. Structures and Micro Morphologies of PCMs

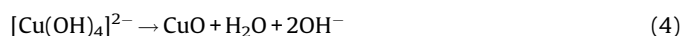
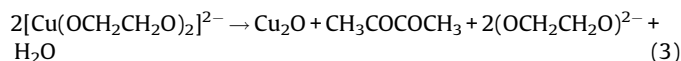
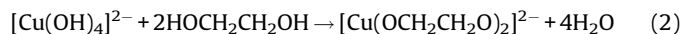
Fig. 1a shows the XRD pattern of the as-synthesized PCMs. It is found that all diffraction peaks can be well matched with the face-centred cubic Cu (JCPDS 04-0836, space group, Fm3m) [16,25], implying that phase-pure Cu can be obtained under this synthetic condition. These peaks at $2\theta = 43.3, 50.4$ and 74.1° correspond to the crystal faces of (111), (200) and (220) of crystalline Cu, respectively. According to the Scherrer formula ($D = K\lambda/(\beta\cos\theta)$) from the full width at half maximum (FWHM), the average crystalline size of PCMs was calculated to be ~ 20 nm.

The low-magnification SEM image (Fig. 1b) indicates that the PCMs are uniformly distributed and exhibit diameters in the range of 2–5 μm (inset, Fig. 1b). The typical SEM images of PCMs (Fig. 1c and d) show that many pores with sizes in the range of 100–500 nm can be observed on the spherical surfaces of PCMs. The High resolution TEM (HRTEM) image of the edge of a PCM (Fig. 1e) demonstrate the polycrystallinity of the porous Cu, and the spacing distance of 0.21 nm can correspond to the distance of the (111) plane of the metallic Cu cubic symmetry.

3.2. Growth mechanism of PCMs

In order to investigate the growth mechanism of PCMs, the time-dependent experiments were carried out. The corresponding XRD patterns (Fig. 2) indicate that impurity phases of Cu_2O and CuO can be detected for sample obtained with the reaction time of 2 h, and products with pure Cu phase could be obtained when the reaction time was prolonged to more than 4 h. The results suggest that the CNBs were formed by the reduction of the organised Cu_xO nanoparticle intermediates (Fig. 3b). As shown in Fig. 3c, CNBs with an average ligament size of ~ 500 nm were obtained with the reaction time of 4 h. As the reaction time was extended to 6 h, PCMs (Fig. 3d) formed on the bottom of the reactor. With the continuous increase of the reaction time, PCMs with smaller pore sizes (Fig. 3e), SCMs (Fig. 3f) and distorted Cu microspheres (Fig. 3g) were prepared under the reaction time of 8, 12, and 16 h, respectively. As illustrated in Fig. 3a, a PCM might be formed by the organisation of CNBs, which were obtained by the reduction of the organised Cu_xO nanoparticles. The results also indicate that the porosity of PCMs can be controlled by the reaction time.

From the product evolution from Cu_xO nanoparticles to CNBs, and then to PCMs, a self-organised growth mechanism for the PCMs has been proposed, as illustrated in Fig. 4. The possible chemical reactions can be expressed in Eqs. (1)–(7) [21,25–27].



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