Facile Synthesis of Cu_2O Polyhedral Micro/Nanocrystals in Aqueous Solution of an Amphiphilic Polyvinylacetone

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(Received January 25, 2006; CL-060108; E-mail: zhuqr@ustc.edu.cn)

Cu_2O polyhedral micro/nanocrystals were synthesized in aqueous solution of amphiphilic polyvinylacetone (PVKA) (ketalization degree $D_H = 0.549$) under ambient conditions (20–23 °C), via natural oxidation of copper metal by naturally dissolved oxygen in water.

Over the past several decades, much research has been focused on cuprous oxide (Cu_2O). Cu_2O is an important p-type semiconductor with unique optical and magnetic properties,[1] which make it a promising material in the fields of solar energy conversion, micro/nanoelectronics, magnetic storage devices, catalysis, and biosensors.[2] Nanostructured Cu_2O with morphologies such as wires, cubes, and rods has been synthesized by various methods. Generally, Cu_2O is gained via reduction of Cu^{2+}; Cu_2O can also be obtained via oxidation of pure copper in aerated chloride solutions, in which Cu^+ ions will also form complexes with chloride ions simultaneously, or via oxidation under 0.1 mbar of O_2 at 700 °C.[1–3]

Presently, polyvinylacetone (PVKA) is known to be a hydrolysable polymer, whose hydrolysis time is controlled by both ketalization degree and pH of water.[4] The amphiphilic PVKA is also proved to be a weakly reductant (due to the ketal-ring units) and a colloidal stabilizer (due to the alcohol units).[5,6] Our interests are stemmed from the properties of PVKA. Among the investigations, one focus is the preparation of desirable nanomaterial. For example, we recently reported that silver flowerlike and dendritic nanostructures,[5] and Ag/cross-linked poly(vinyl alcohol) (PVA) cable-like nanostructures[6] could be controlled synthesized utilizing the properties of PVKA. These results indicate the probability of the research of PVKA on structural construction and utilization. Establishing an effective method to prepare desirable nanostructures is an increasing interest in chemistry and nanotechnology, and also a challenge in PVKA study.

In this paper, we report the synthesis of Cu_2O polyhedral micro/nanocrystals via oxidation of copper in aqueous solution of amphiphilic PVKA (ketalization degree $D_H = 0.549$) under ambient conditions. Although neither the size nor morphology of the obtained Cu_2O micro/nanocrystals is uniform and there are certainly much better methods to synthesize well-defined Cu_2O micro/nanocrystals,[1–3] the present study centered on the oxidation of copper by oxygen to yield large Cu_2O particles in aqueous solution of PVKA is interesting, since the oxidation of copper usually yields the thermodynamically more stable CuO phase. The present finding also allows one to explore an effective method for growing Cu_2O onto Cu substrate directly for various applications in optoelectronic devices.[1]

The amphiphilic PVKA ($D_H = 0.549$) used in this study was synthesized as outlined in a previous publication.[4] Copper foils (≥99.8%) with a thickness of 0.1 mm were ultrasonically washed with ethanol and deionized water before use. In a typical procedure, Cu_2O polyhedral micro/nanocrystals were synthesized laying a piece of copper foil on the bottom of a 25 mm × ϕ 40 mm container containing 8 mL of 9.23 g L^{-1} PVKA aqueous solution, which was then left still under ambient conditions (20–23 °C) for 6 days. The copper foil was then taken out, washed with ethanol and deionized water carefully, and dried in air before characterization.

Figure 1a presents typical SEM image of the product synthesized in 9.23 g L^{-1} PVKA aqueous solution. It is clear that the polyhedral micro/nanocrystals have smooth surfaces and distinct edges and corners, and have an edge length in the range of 300–1000 nm. The structure and composition of the product confirmed by the XRD pattern are cubic Cu_2O (JCPDS No. 05-0667) (Figure 2). This is further confirmed by XPS measurements (Figure 3) that the $Cu_{2p3/2}$ binding energy of the products is 932.6 eV, and the Cu_{LMM} kinetic energy is 916.5 eV, which are in good agreement with the literature values.[2d,3a]

As shown in Figures 1b–1d, Cu_2O polyhedral micro/nanocrystals could be also obtained in aqueous solution of different PVKA concentrations (7.01, 4.68, and 2.31 g L^{-1}, respectively). And the morphology of the product is affected by the concentration of PVKA. At a relative lower concentration of PVKA, the polyhedral micro/nanocrystals have a smaller size, and they tend to aggregate, resulting in more or less stacking-like aspect. However, Cu_2O cannot be obtained in any cases in the absence of PVKA or the cases substituting PVA for PVKA. It is possible that PVKA indeed plays a key role in the synthesis.

The synthesis mechanism is also investigated. It is well

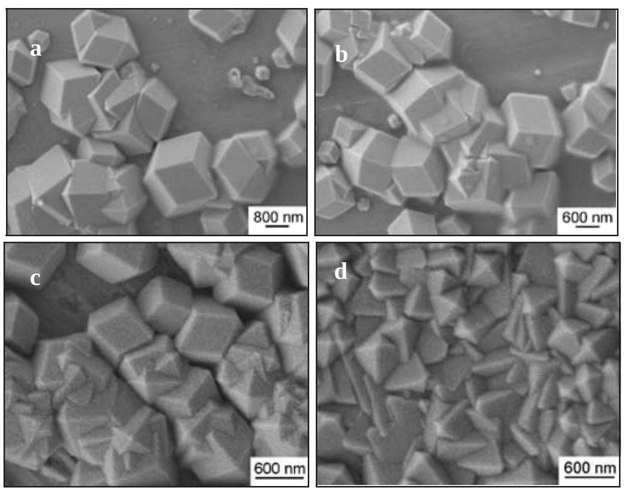

Figure 1. Typical SEM images of the obtained Cu_2O polyhedral micro/nanocrystals, at various PVKA concentrations: (a) 9.23, (b) 7.01, (c) 4.68, and (d) 2.31 g L^{-1}.

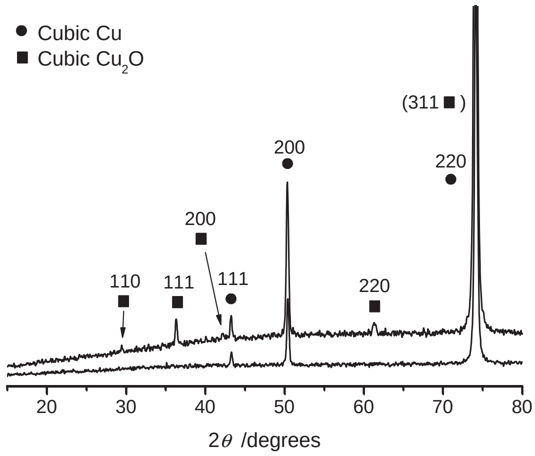

Figure 2. XRD patterns of the copper foil (down) and the product (top).

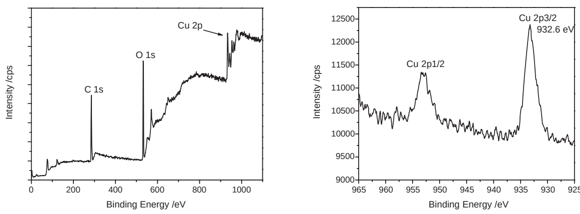

Figure 3. XPS survey spectrum of the product (left) and higher resolution spectrum of Cu 2p region (right).

known that natural oxidation of copper metal by naturally dissolved oxygen in water is very slow,[7] and usually transforms into Cu(II) but very difficult into Cu(I) in neutral solution, according to electrochemical theory;[8] for example, usually CuO or other compounds of Cu(II) is obtained, but not Cu_2O, when copper is oxidized in a humid environment. It has also been demonstrated that the amphiphilic PVKA is a weak reductant (due to the ketal-ring units) and a colloidal stabilizer (due to the alcohol units).[5,6] In the present study, though the structure of PVKA molecules is not changed (see below), the presence of PVKA possibly changes the microenvironment for the electrochemical reaction; therefore, the spontaneous oxidation reaction of copper metal is accelerated drastically, and transforms into Cu_2O, while oxygen is reduced.

Furthermore, the pH value climbed slightly from 6.2 for the starting initial solution to 6.9 for the residual solution after reaction in the synthesis process, which also may be looked as the same within the experimental error. These results imply that PVKA did not hydrolyze under the present experimental conditions, because PVKA can only hydrolyze in the acidic solution;[4] that is PVKA does not participate in the reaction directly, which is further confirmed by the FTIR spectrum (Figure 4). The FTIR spectrum of the residual solution after reaction in the synthesis process is almost the same as that of pure PVKA, which shows several absorption peaks corresponding to ν_{CH2} (2991.5 cm^{-1}) and $\nu_{C\text{-}O\text{-}C}$ (1200.7 cm^{-1}) of the ketal-ring unit, and those corresponding to ν_{OH} (3381.2 cm^{-1}), ν_{CH2} (2942.5 cm^{-1}), $\nu_{C\text{-}O}$ (1103.2 cm^{-1}) and γ_{CH2} (851–818 cm^{-1}) of the alcohol unit. ^{1}H NMR spectrum (data not shown), another useful tool, also confirms that the ketalization degree of PVKA in the residual solutions ($D_H = 0.536$) is nearly the same as that of pure PVKA

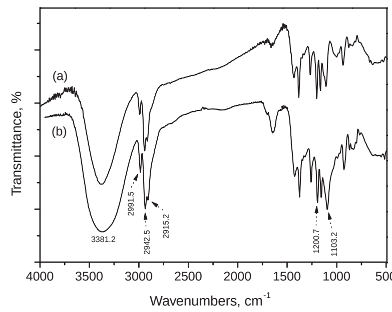

Figure 4. FTIR spectra. (a) Pure PVKA ($D_H = 0.549$). (b) The residual solution after reaction.

engaged, within the experimental error.

On the basis of the above analysis, the reaction that occurred in the synthesis process may be illustrated as follows:

$$4Cu + O_2 \xrightarrow[H_2O]{PVKA} 2Cu_2O. \quad (1)$$

In summary, this study has successfully developed an effective and facile method for synthesis of Cu_2O polyhedral micro/nanocrystals in aqueous solution of an amphiphilic PVKA ($D_H = 0.549$) under ambient conditions, via natural oxidation of copper by naturally dissolved oxygen in water. The PVKA is proved to play a key role in this process. The present oxidation of metallic Cu by oxygen to yield large Cu_2O particles in air-saturated aqueous solutions of PVKA is interesting, also allows one to explore an effective method for growing Cu_2O onto Cu substrate directly for various applications.[1]

This work was supported by the Open Foundation of Structural Research Laboratory of USTC, and the Innovation Foundation of USTC for the Postgraduate.

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Published on the web (Advance View) April 29, 2006; doi:10.1246/cl.2006.574