

Research Article

Tunable Cu₂O Nanocrystals Fabricated by Free Dealloying of Amorphous Ribbons

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This work discovers that Cu₂O nanocrystals with controllable structures can be synthesized on surfaces of nanoporous Cu and amorphous ribbons by free dealloying of Cu-based amorphous alloys in acidic solutions. Technological parameters, such as the acid, acid concentration, and dealloying time strongly influence the crystal size, structure and morphology of Cu₂O. Cu₂O nanocubes are fabricated on surfaces of nanoporous Cu in the hydrofluoric acid treated alloy, while various Cu₂O particles are tailored on surfaces of amorphous alloys immersed in hydrochloric acid for different time. The increasing dealloying time and adsorbed oxygen improve the growth rates along the (1 0 0) direction of Cu₂O crystals relative to that of the (1 1 1) direction, which is the key to change the shapes of Cu₂O crystals. The understanding of morphology evolution of Cu₂O nanocrystals in this work is helpful in tailoring Cu₂O particles with designable shapes and controllable properties in application fields.

1. Introduction

Dealloying, which is a phenomenon of corrosion where the less noble metal is selectively removed from an alloy, has recently gained interest for tailoring nanoporous metallic materials [1–4]. Nowadays, Chen et al. [5] found that, instead of formation of nanoporous copper, cuprous oxide (Cu₂O) nanocubes and nanograins can be formed on the ribbon surfaces when electrochemically dealloying a Cu₃₀Mn₇₀ alloy in hydrochloric acid (HCl) solutions. At the same time, octahedral metal oxide nanoparticles, such as Fe₃O₄ and Mn₃O₄, are produced by dealloying binary alloys in NaOH solution [6]. These existing examples clarify that dealloying method can be extended to the fabrication of metal oxide nanostructures with intricate structural properties.

Cu₂O, which is an important p-type semiconductor with a direct band gap of 2.17 eV [7], has been widely studied as a promising material for applications in gas sensors [8], in solar energy conversion [9], as an electrode in lithium ion batteries [10], as a photocatalyst for the degradation of organic pollutants [11] and for the decomposition of water into H₂ and O₂ under visible light irradiation [12]. Therefore, Cu₂O particles with different sizes and morphologies are highly desirable for these applications. So far, Cu₂O has been prepared by several different methods

[13–16], such as sonochemical methods [11], solvothermal [17], and hydrothermal methods [18]. In this paper, we present a new approach to design tunable-structured Cu₂O nanocrystals by free dealloying Cu-based metallic glasses in hydrofluoric acid (HF) or HCl aqueous solutions and investigate the morphology evolution of Cu₂O particles with different conditions. To our knowledge, this is first attempt to select metallic glasses as a precursor and carrier because metallic glasses have high strength, high toughness and free of crystalline defects, which are different from crystalline alloys. In addition, we simplify the fabrication process of Cu₂O by using this route as compared to traditional chemical method [19, 20]. The most important contribution by this work is to produce the amazing compounds with multiple properties which are hopeful to be applied in broad fields in the future. Cu₂O together with its carrier can be stored in solid form, but not in liquid anymore.

2. Experimental

Ternary Cu-Hf-Al ingots with nominal compositions of Cu_{52.5}Hf₄₀Al_{7.5} were prepared by arc-melting Cu (99.99 mass%), Hf (99.99 mass%), and Al (99.99 mass%) metals in argon gas atmosphere and using Ti getters. Thin

ribbons of Cu-Hf-Al alloy about 20 μm thick and 1.2 mm wide were prepared by melt-spinning with a linear velocity of the copper wheel of 40 m/s. Samples of 15 mm in length were cut from ribbons for free dealloying experiments at room temperature. One of the samples was etched in 0.5 M hydrofluoric acid (HF) solution for 4 min. The others were etched in 0.05 M HCl solution for 6 h, 8 h, 14 h, 20 h, and 24 h, respectively. The dealloyed samples were rinsed in deionized water for three times to remove the residual chemical substances and then dried in a vacuum drying oven. The X-ray diffraction (XRD) patterns were identified using a Bruker D8 X-ray diffractometer with Cu-K α radiation. The microstructures of the dealloyed ribbons were characterized by a scanning electron microscope (SEM, Hitachi S-4800) equipped with energy-dispersive spectroscopy (EDS) analysis.

3. Results and Discussion

Figure 1 shows XRD patterns of as-spun $\text{Cu}_{52.5}\text{Hf}_{40}\text{Al}_{7.5}$ ribbon, the ribbon dealloyed in 0.05 M HCl solution for 14 h, and the ribbon dealloyed in 0.5 M HF solution for 4 min. The diffraction pattern for the as-spun alloy is broad and has no Bragg peaks, indicating a single homogeneous glassy structure. The XRD pattern of the HCl-treated ribbon exhibits a broad halo peak superimposed on sharp crystal peaks. These crystal peaks match with (111), (200), (220), and (311) crystal planes of Cu_2O (JCPDS number 05-0667) and (111), (200), and (220) crystal planes of Cu (JCPDS number 04-0836), respectively. Moreover, the existence of a broad halo peak reveals that although the surface of the sample is rich in Cu_2O and Cu, the inner part remains metallic glassy structure. Similar XRD patterns are also obtained in other HCl-immersed samples of this study. For the HF-treated ribbon, the amorphous pattern disappears. Only Cu and Cu_2O peaks are identified, which indicates that HF selectively leaches the Hf and Al elements of the alloy, leaving Cu behind.

Figure 2 shows SEM images of the $\text{Cu}_{52.5}\text{Hf}_{40}\text{Al}_{7.5}$ alloy at various dealloying conditions. It was reported that Cu_2O nanocubes with a cube edge of 150–200 nm can be produced on ribbon surfaces when electrochemically dealloying a $\text{Cu}_{30}\text{Mn}_{70}$ alloy in 0.001 M HCl solutions [5]. In this paper, we fabricate Cu_2O nanocubes with a finer size of 60–90 nm by free dealloying of a Cu-based amorphous alloy in 0.5 M HF solutions for 4 min (Figure 2(a)). The inner ribbon shows clear nanoporous Cu structure after selectively leaching the Hf and Al elements of the alloy. Thus, the resultants of the HF treated alloy are Cu_2O nanocubes embedded on nanoporous Cu. On the other hand, various shapes of Cu_2O crystals are synthesized by free dealloying of the $\text{Cu}_{52.5}\text{Hf}_{40}\text{Al}_{7.5}$ amorphous alloy in 0.05 M HCl solutions at different time (Figures 2(b)–2(f)). With the prolonged dealloying time, various Cu_2O crystals are observed on the ribbon surfaces. According to the XRD results, we can see that the final synthetic products of the HCl treated alloy are Cu_2O particles and Cu metal coated on amorphous alloys. As a result, Cu_2O nanoparticles with designable size, structure

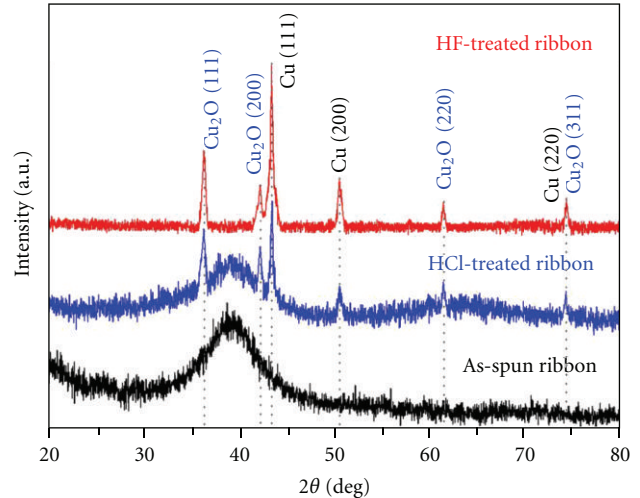


FIGURE 1: XRD patterns of as-spun $\text{Cu}_{52.5}\text{Hf}_{40}\text{Al}_{7.5}$ ribbon (bottom), HCl-treated ribbon (middle), and HF-treated ribbon (up).

and morphology can be tailored by controlling dealloying conditions.

Up to now, a variety of Cu_2O nanostructures have been synthesized. Xu and Xue [21] reported five branching growth patterns in the cubic crystal system of Cu_2O . The five patterns are cube, truncated cube, cuboctahedron, truncated octahedron, and octahedron, respectively. In our work, we successfully synthesize four of them, as shown in Figure 3. It is well known that the growth rate of Cu_2O particles along the $\langle 100 \rangle$ direction relative to that of the $\langle 111 \rangle$ direction, or the value of R , is the key reason to result in the morphology evolution of Cu_2O cubes [21]. For cubic, cuboctahedral, truncated octahedral, and octahedral Cu_2O particles, their values of R are about 0.58, 0.87, 1.15, and 1.73, respectively [21].

By dealloying of the Cu-based amorphous alloy in acid solutions, active metals in the alloy are selectively dissolved into the solutions. During this etching process, the relatively inert metal atoms left behind undergo spontaneous oxidation at the metal/electrolyte interface to form metal oxides [6]. Thus, Cu_2O particles are formed by reaction between Cu atoms and dissolved oxygen. As the increase of dealloying time, absorbing more dissolved oxygen on the surface of Cu_2O cubes results in a development in the growth rates along the $\langle 100 \rangle$ direction of Cu_2O crystals relative to that of the $\langle 111 \rangle$ direction and subsequently leads to the morphology evolution of Cu_2O cubes. In this study, the dealloying time is short for HF-treated alloy, whereas it is long for HCl treated alloys. Therefore, Cu_2O cubes show their original morphology in HF-treated alloy but change to various shapes in HCl-treated alloys.

It is worth noting that Hf belongs to a corrosion-resistant element and shows a strong passivating ability in diluted HCl solution but easily dissolves in HF solution [22]. When the Cu-based metallic glass is immersed in diluted HCl solution, the matrix of the alloys can still remain metallic glass structure, in addition to the surface of the samples is occupied by Cu and oxidation products Cu_2O . On the

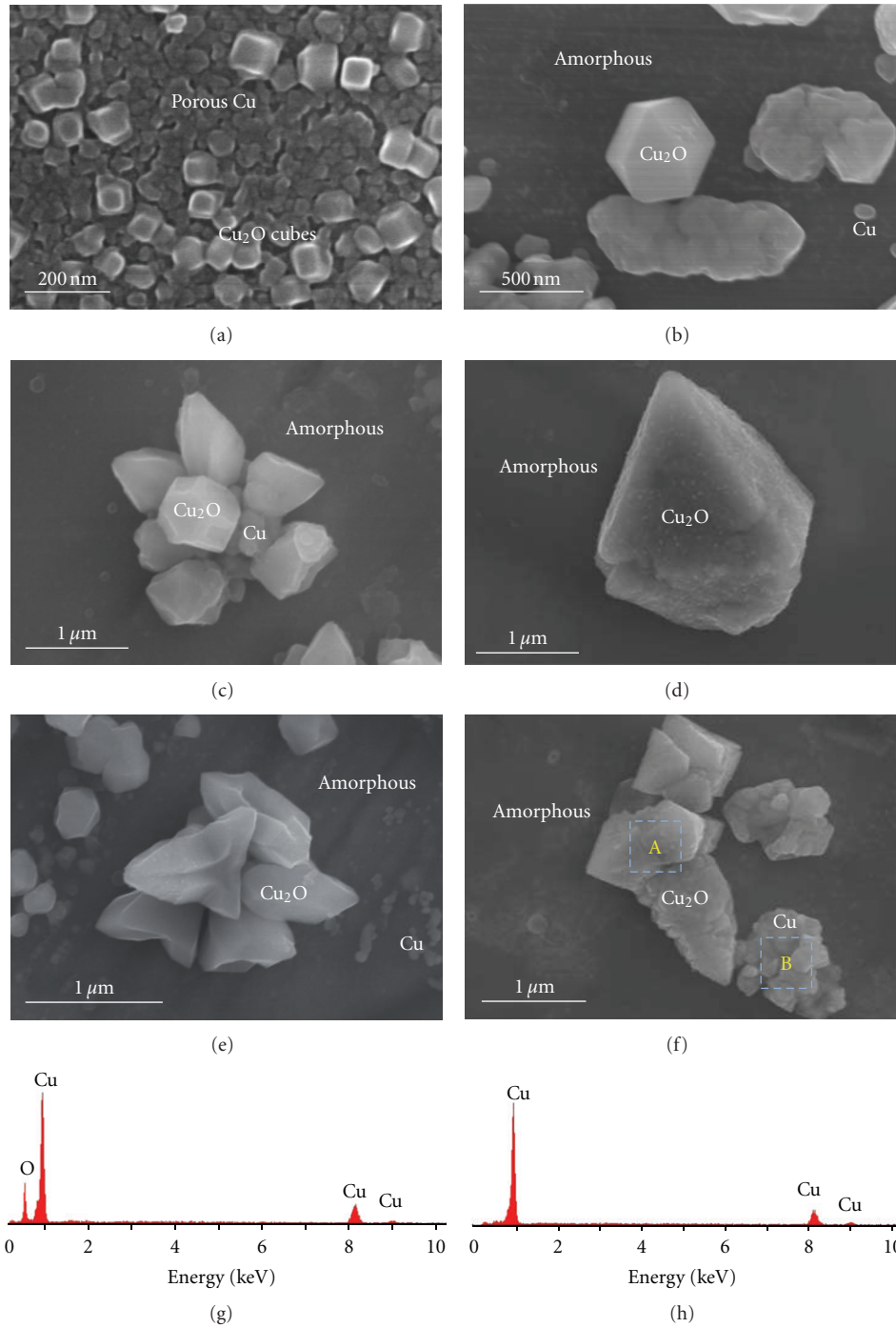


FIGURE 2: SEM images of the $\text{Cu}_{52.5}\text{Hf}_{40}\text{Al}_{7.5}$ amorphous ribbon etched in different acid solutions (a) 0.5 M HF for 4 min; (b–f) 0.05 M HCl for (b) 6 h, (c) 8 h, (d) 14 h, (e) 20 h, and (f) 24 h; (g–h) EDS analysis in (f): (g) point A (h) point B.

contrary, during the immersion in HF solution, as HF strongly leaches constituent elements Hf and Al from the Cu–Hf–Al alloys, nanoporous Cu is formed and subsequent Cu_2O nanocubes grow based on nanoporous Cu surface. In this process, drastic chemical reaction accompanied with a mass of H_2 gas evolution takes place, which shortens the reaction time. That is the reason why the alloys treated by HCl and HF, respectively, show the different XRD patterns.

Figure 4 shows the morphology evolution process of Cu_2O octahedron. It was reported that the six corners of the octahedron represented its six activated corners [21]. These activated corners would grow along their $\langle 100 \rangle$ direction of Cu_2O octahedron. With the increasing dealloying time and adsorbed oxygen, Cu_2O octahedron grows up to hexapods and then develops into dendrite or octahedron-detached hexapods. In general, dendritic Cu_2O crystals can be formed

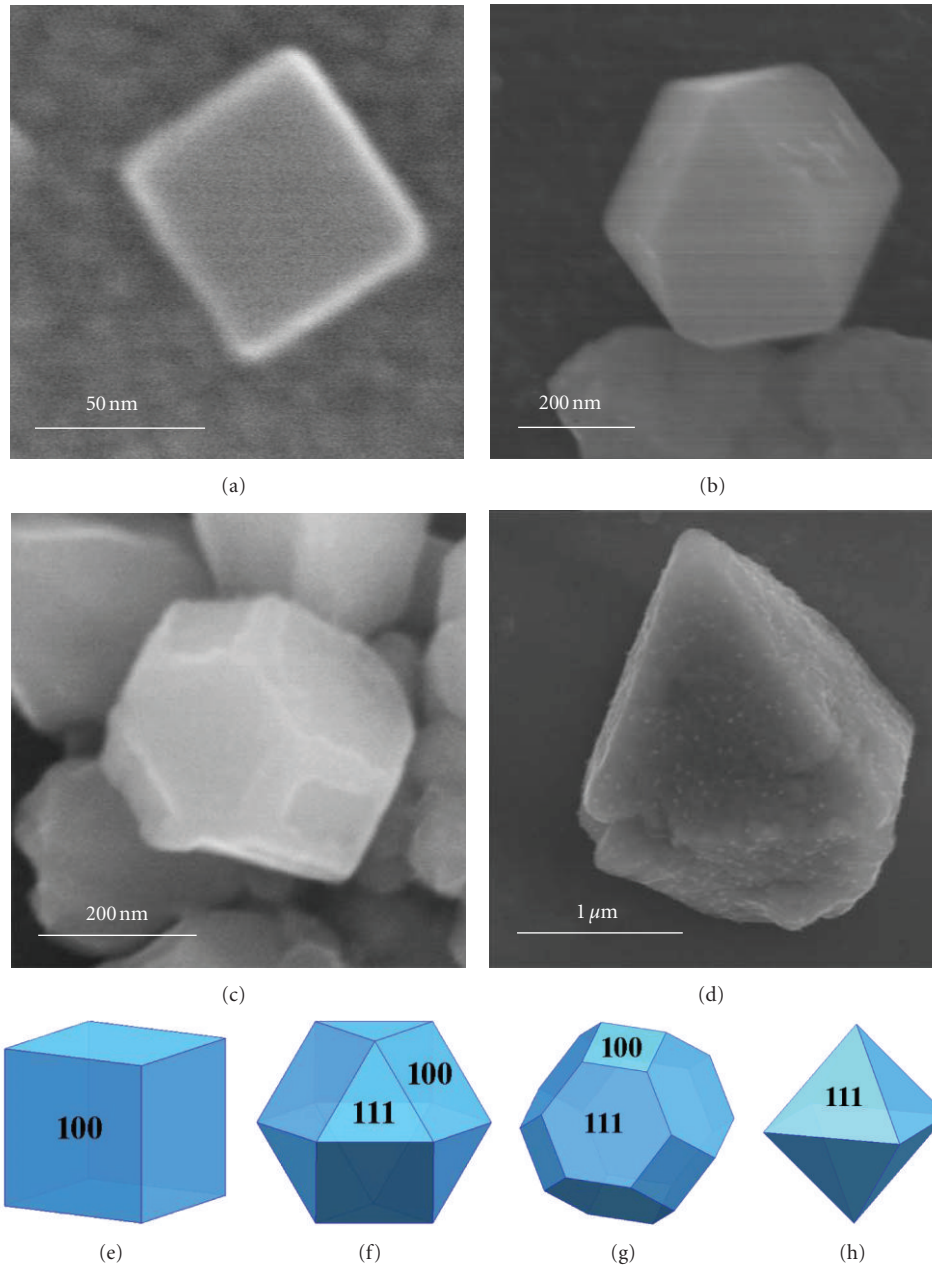


FIGURE 3: Cu_2O crystals with various morphologies: (a–d) SEM images. (a) Cube, dealloyed in 0.5 M HF for 4 min, (b) cuboctahedron, dealloyed in 0.05 M HCl for 6 h, (c) truncated octahedron, dealloyed in 0.05 M HCl for 8 h, (d) octahedron, dealloyed in 0.05 M HCl for 14 h. (e–h) are their corresponding three-dimensional models.

on a long-time-eroded ribbon surfaces. However, if the conditions in six growth directions are the same, a peculiar octahedron-detached hexapods can be synthesized.

Characteristics of Cu_2O crystals produced by free dealloying and spontaneous oxidation are listed in Table 1. Though the area percentage of Cu_2O crystals compared to the whole area of sample is low, there are also some points of advantage by using this method compared with traditional chemical method [19, 20]. Firstly, this route is simpler with no need for extraction of craft from solutions, which is often used in traditional method. Secondly, considering uniform compositions and many good properties [23],

amorphous alloys are selected for first time as carriers of Cu_2O particles. Thus, the dilute HCl-dealloyed ribbon can still possess good ductility which cannot be obtained from crystal materials. Thirdly, two kinds of products, Cu_2O nanocubes embedded on nanoporous Cu and Cu_2O crystals covered on amorphous alloys, are prepared in this study. We can gain multiple properties by tailoring the area percentage of Cu_2O particles from these amazing compounds with undiscovered properties in the future. Moreover, these solid products are easy to store or collect, which can promote their applications. Many promising work are worth doing in the future.

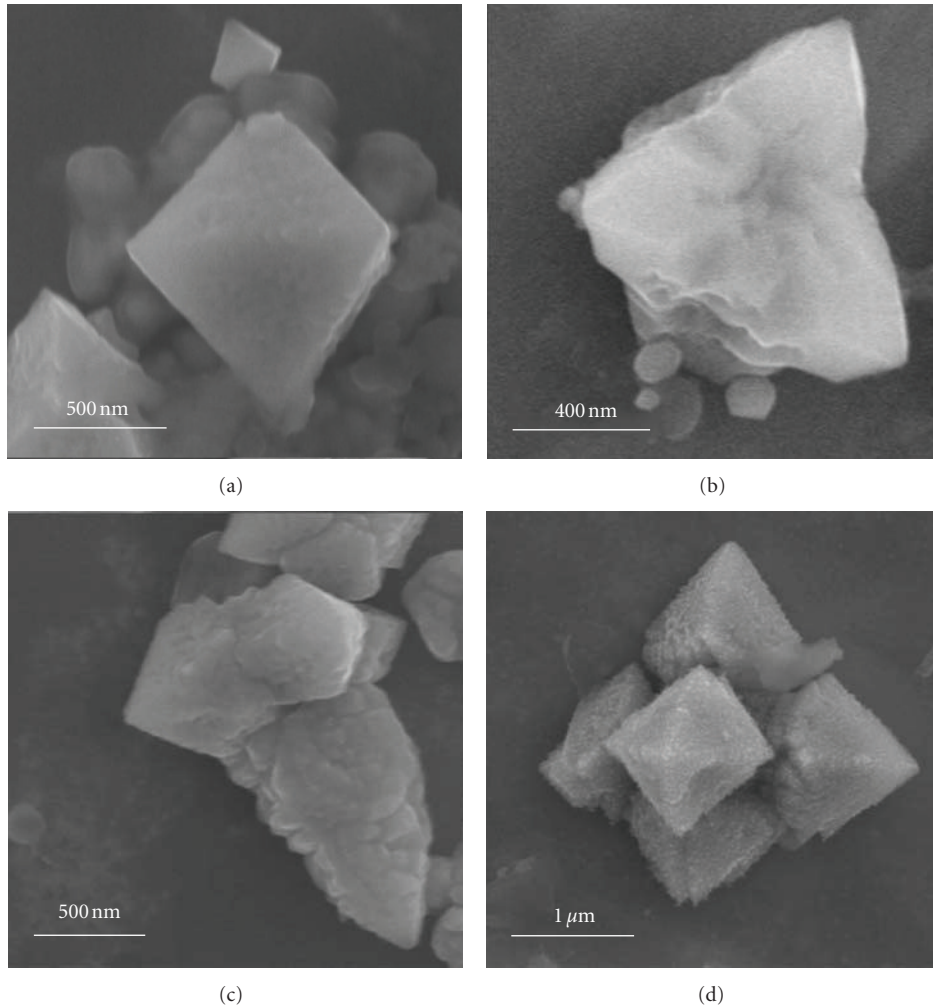


FIGURE 4: Morphology evolution of Cu_2O octahedron. (a) Octahedra, dealloyed in 0.05 mol/L HCl solutions for 14 h and (b) hexapods, dealloyed in 0.05 mol/L HCl solutions for 20 h. (c) and (d) dealloyed in 0.05 mol/L HCl solutions for 24 h: (c) dendrite and (d) octahedron-detached hexapods.

TABLE 1: Characteristics of Cu_2O crystals produced by free dealloying.

Corrosion media	Dealloying time	Morphology	Edge length	Area percentage (%)
HF	4 min	Cube	~90 nm	26.5
	6 h	Cuboctahedron	~300 nm	12.2
	8 h	Truncated octahedron	~150 nm	13.9
HCl	14 h	Octahedron	~1.2 μm	15.8
	20 h	Hexapods	~500 nm	14.4
	24 h	Dendrite	~1.4 μm (dendrite length)	14.3
		Octahedron-detached hexapods	~1.1 μm	5.5
				Total 19.8

4. Conclusions

Cu_2O nanocrystals with morphological control are successfully synthesized on surfaces of nanoporous Cu and amorphous ribbons by free dealloying of a $\text{Cu}_{52.5}\text{Hf}_{40}\text{Al}_{7.5}$ amorphous alloy in acidic solutions. Acids, acid concentration and dealloying time have significant effects on the particle size, structure and morphology of Cu_2O . Differing

from traditional powders products, the resultants of the HF treated alloy are Cu_2O nanocubes embedded on nanoporous Cu materials, while the synthetic products of HCl-treated alloys are Cu_2O particles and Cu metal covered on amorphous alloys. Additionally, various morphologies of Cu_2O are presented on the ribbon surfaces in HCl solution by controlling dealloying time. The increasing dealloying time and adsorbed oxygen improve the growth rates along the

(1 0 0) direction of Cu_2O crystals relative to that of the (1 1 1) direction, which is the key to change the shapes of Cu_2O crystals. Cu_2O octahedron is able to grow up to special shapes, such as dendrite and octahedron-detached hexapods. Furthermore, two kinds of compounds produced in this paper are hopefully to be applied in broad fields for their multiple properties.

Acknowledgments

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