



Spontaneous growth of CuO nanoflakes and microflowers on copper in alkaline solutions



Jinhang Fan, Dingding Tang, Dihua Wang*

School of Resource and Environmental Sciences, Wuhan University, Wuhan 430072, PR China

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ABSTRACT

CuO with different nano-architectures was synthesized by spontaneous corrosion of copper in alkaline aqueous solutions without any additives. CuO nanoflakes were obtained by simply immersing a copper foil in NaOH solution, while flower-like architectures constructed with nanopetals were produced in Na_2CO_3 solution, indicating the pH value and the anions have a significant impact on the morphology and structure of CuO. The growth rate slowed down with the decrease of the alkalinity of the solution. In a more concentrated NaOH solution (1 M), polyhedron-like Cu_2O was observed at the early stage before transforming into CuO nanoflakes. Based on these findings, massive production of nano-structured CuO powders was successfully realized by using copper powder as the precursor. The growing mechanism of flower-like CuO could be explained by the oriented attachment. The extensive sources of feedstock, the simple synthetic method and the uniform architecture of the products enable CuO to be utilized in a large scale.

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1. Introduction

CuO has attracted considerable interest in various fields, including gas sensors and field emission emitters [1–3], lithium ion batteries and solar cells [4–6], heterogeneous catalysis for CO oxidation [7] and supercapacitors, photodetectors as well as pollutants absorbents [8–10]. The performance of CuO is strongly dependent on its morphologies and structures [11]. There are a variety of different dimensional and morphological CuO reported synthesized by different process. Gao et al. reported the synthesis of CuO nanorods by hydrothermal method and the influence of temperature on the structure of CuO [12]. CuO nanoribbon was obtained by heat treatment of $\text{Cu}(\text{OH})_2$ formed in alkaline solution using CuCl_2 or $\text{Cu}(\text{NO}_3)_2$ as feeding material [13,14]. Liu et al. [15] obtained CuO with different morphologies such as flower-like and spherical architectures by oxidizing Cu foil in low concentration of alkaline solution (NaOH and $\text{NH}_3 \cdot \text{H}_2\text{O}$) at 60 °C for 20 h. Preparation of platelet-like and chrysanthemum-like nano-structured CuO was also reported by immersing Cu into NaOH aqueous solution with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ at room temperature [16]. Furthermore, hierarchical microcabbage of CuO was fabricated on

Cu foil via a solution process at room temperature [17]. Flower-like CuO was synthesized on Cu plate in KOH solution [18]. These investigations suggest that the alkalinity of solution, concentration of oxidant, surfactant in the solution and temperature has an important effect on the morphology of the CuO product.

For massive production of CuO in a more environmentally friendly way, a process using air as oxidant at room temperature without any surfactant is more preferential. Based on the E-pH diagram of copper, spontaneous oxidation/corrosion of Cu will take place in alkaline solution in air. The alkalinity as well as the ions in the solution could affect the corrosion process, thereby affect the morphology of the corrosion product. To the best of our knowledge, there is rare report in literature on the morphology investigation of CuO formed over a wide range of alkalinity under air atmosphere. In this paper, the effect of the concentration of NaOH and Na_2CO_3 on the morphology and structure of CuO growing on copper foil was systematically investigated at room temperature. Based on the optimized growing condition, massive production of nano-structured CuO powder was synthesized using copper powder as feeding stock.

2. Experimental

All chemicals were of analytical grade and purchased from Sinopharm Chemical Reagent, Shanghai, China. The solutions of

* Corresponding author.

E-mail address: wangdh@whu.edu.cn (D. Wang).

sodium hydroxide and sodium carbonate were prepared by dissolving NaOH and Na_2CO_3 in deionized water, respectively. Copper foil, powder with >99.5% purity was used as received. A piece of fresh copper foil or several grams of copper powder was immersed in the NaOH or Na_2CO_3 aqueous solution at room temperature for different time. And then the samples were taken out of the solution and washed with water and dried in a vacuum oven at 80°C for 4 h. The detailed synthesis conditions are summarized in Table 1.

The obtained products were characterized by a Shimadzu XRD-7000 X-ray diffraction analyzer (XRD). The size and morphology of the samples were observed by FEI sirion field emission scanning electron microscope (SEM). Their chemical composition was analyzed on KRA TOSXSAM800 with Al K α ionization source and Confocal Raman Microspectroscopy (Renishaw, RM-1000) at an excitation wave-length of 514.5 nm.

3. Results and discussions

3.1. Synthesis of nanostructured CuO on Cu foil

3.1.1. CuO growth in NaOH solution

A piece of copper foil was immersed into NaOH aqueous solution with different concentration. No oxide film formed on the copper surface in the solution of pH < 10, consistent with previous report [19] at which additional oxidant was added. When the concentration of NaOH was higher than 0.1 M, a black film on copper was observed after certain reaction time (inserted photos in Fig. 1). The solution remained colorless, demonstrating no detectable copper ions in the solution. SEM image showed that the black film consists of uniform nanoflakes (Fig. 1a) of CuO as evidenced by the XRD patterns of the film (Fig. 1c). The morphology of CuO obtained in 0.3 M solution was similar to the product obtained at 0.1 M, but the size of the nanoflakes grew larger (Fig. 1b and c). The specific weight of CuO to CuO@Cu was 6.982 mg/g after 48 h of immersion in 0.1 M aqueous NaOH solution, 8.307 mg/g in 0.3 M aqueous NaOH solution.

Surprisingly, different phenomena were observed when copper foil was immersed into more concentrated NaOH solution (1 M). The metallic luster of Cu foil disappeared within 6 h, different from that in the diluted NaOH solution in which copper surface remained almost unchanged in a short time. A gray-blue film precipitated on the Cu surface. As shown in Fig. 1d, the gray-blue layer consisted of polyhedron shape particles with an anomalous size distribution. With prolonging immersion time (48 h), the surface color turned into purple gray and some black spots were observed (Fig. 1e). The diffraction peaks of Cu_2O were observed in the XRD patterns of the sample (Fig. 2a), demonstrating that the polyhedron was Cu_2O . The morphology of Cu_2O (Fig. 1e) shows that the average size of the polyhedron particles with irregular shape decreases comparatively. Interestingly, some petals with $0.5\text{--}1\text{ }\mu\text{m}$ in length and 500 nm in

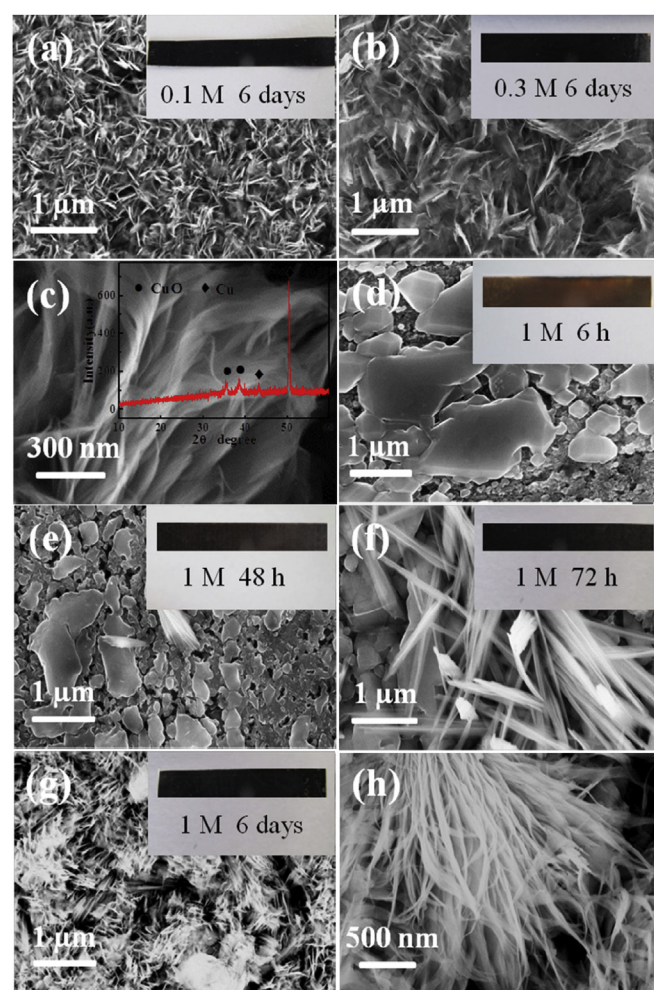


Fig. 1. SEM images of CuO on copper foil prepared in NaOH solution under different concentrations and duration: (a) 0.1 M (b, c) 0.3 M; (d) 1 M (6 h); (e) 1 M (48 h); (f) 1 M (72 h); (g, h) 1 M (6 days).

width formed on the surface of the polyhedron. As the immersion prolonged to 72 h, the copper foil was completely covered with black spots and more petals with increased length ($\sim 2\text{ }\mu\text{m}$) were observed (Fig. 1f). The black spots were ascribed to CuO crystals as evidenced of two characteristic peaks at 35° and 40° in the XRD pattern of the sample as shown in Fig. 2b. After immersion for 6 days, the foil surface turned into black completely and large scale of micro-flowers that composed of nano-flakes were observed (Fig. 1g). No Cu_2O peak but CuO was monitored in the XRD pattern

Table 1

The experimental parameters and the features of the products synthesized under different conditions.

Substrate	Alkaline solutions	Concentration (mol L^{-1})	Time (h)	Product morphology
copper foil	NaOH	0.1–0.3	144	nanoflakes
copper foil	NaOH	1	6–48	polyhedron-like
copper foil	NaOH	1	72	polyhedron-like/needle-like
copper foil	NaOH	1	144	ultrathin flakes-based microflowers
copper foil	Na_2CO_3	0.1	48	sheets-based microflowers
copper foil	Na_2CO_3	0.2	12	sheets
copper foil	Na_2CO_3	0.2	24	sheets/microflowers
copper foil	Na_2CO_3	0.2	48–96	sheets-based microflowers
copper foil	Na_2CO_3	0.5–0.8	48	sheets
copper powder	NaOH	0.05–1	144	ultrathin sheets-based microflowers
copper powder	Na_2CO_3	0.2	144	sheets-based microflowers

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