

Formation of 3D Dandelions and 2D Nanowalls of Copper Phosphate Dihydrate on a Copper Surface and Their Conversion into a Nanoporous CuO Film

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3D dandelion-like porous nanostructures and 2D nanowalls of copper phosphate dihydrate built up of thin nanosheets have been synthesized simply by corrosion of a copper foil with aqueous phosphoric acid under mild conditions. The composition of the nanostructures has been confirmed by XRD, ICP-AES, and Raman spectroscopy. Controlling the ini-

tial concentration of the acid and the conditions of drop drying allows control of the morphology of the nanostructures. The phosphate nanostructures can be converted into nanoporous CuO films by pyrolysis.

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Introduction

Over the past ten years, metal-based nanomaterials have attracted extensive interest due to their promising applications in catalysis, energy storage or conversion, and data storage and memory devices.^[1,2] To date, many interesting zero-dimensional (0D) and one-dimensional (1D) nanomaterials have been synthesized.^[3–5] However, the fabrication of well-controlled two-dimensional (2D) or three-dimensional (3D) nanostructures is usually difficult because control of the nucleation and growth of nanomaterials is still a challenge:^[6–9] simply mixing two incompatible solutions of metal salts will lead to the formation of a polycrystalline deposit with an irregular structure. It is known that a double-jet technique can be used to provide supersaturation conditions by continuously replenishing nutrients. However, the impurity of the counterions often leads to an unpredictable change in the crystal morphology.^[6] Thus, it is important to develop innovative and convenient techniques for fabricating metal-based nanomaterials with 2D or 3D structures under mild conditions and at low cost.

On the other hand, copper phosphates are catalysts for the oxidation of aromatic compounds.^[10–12] Nanostructures of these salts provide high specific surface areas that enhance their catalytic activity and selectivity. Cupric oxide (CuO) and basic Cu^{II} salts with layered structures have also been studied extensively in the past few years.^[13–18] CuO is a p-type semiconductor with a narrow bandgap and its

nanostructures have potential applications in catalysis, superconductors, and the fabrication of sensors and solar cells.^[19–22] Orthorhombic [Cu₂(OH)₃Cl] was the first copper-based biomineral found in living organisms. It exists as polycrystalline nanofibers arranged along the outer contour of the tooth tip, leading to an extraordinary resistance to abrasion.^[23] Galvanic cell corrosion is a general phenomenon in everyday life and it may provide a continuous low concentration of metal ions for controlling the formation of characteristic micro- or nanostructures.^[18] In this paper, we report a 3D dandelion-like nanostructure and a 2D nanowall of copper phosphate dihydrate by simple corrosion of a copper foil with aqueous phosphoric acid. Furthermore, a nanoporous CuO film is also produced by pyrolysis of these phosphate nanostructures.

Results and Discussion

Drying of a drop of aqueous phosphorus acid solution on a copper foil leads to the formation of many pale-blue particles on its surface. Figure 1 shows the typical SEM images of the particles. As shown in Figure 1 (A) nearly all the particles are round with a size in the range of 40 to 50 μm . When two or more particles merge together a peanut-like 3D architecture is formed. When a single particle as shown in part A of Figure 1 was further magnified, a crystalline dandelion-like structure was revealed. This dandelion-like structure is made up of uniform nanosheets and its surface is porous, with pore sizes ranging from several hundreds of nanometers to one micrometer (Figure 1, B). Figure 1 (C) indicates that the dandelion grows at almost the same rate from the core in all directions above the copper surface. A magnified view of the top of the dandelion reveals that the nanosheets are about 35 nm thick (Figure 1,

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D). Figure 1, part E, is the bottom view of a single dandelion. It reveals that there is an obvious core at the center of the dandelion and that the nanosheets grow with their thin face perpendicular to the bottom plane. Figure 1 (F) is a magnified view of the core, the formation mechanism of which is not very clear yet.

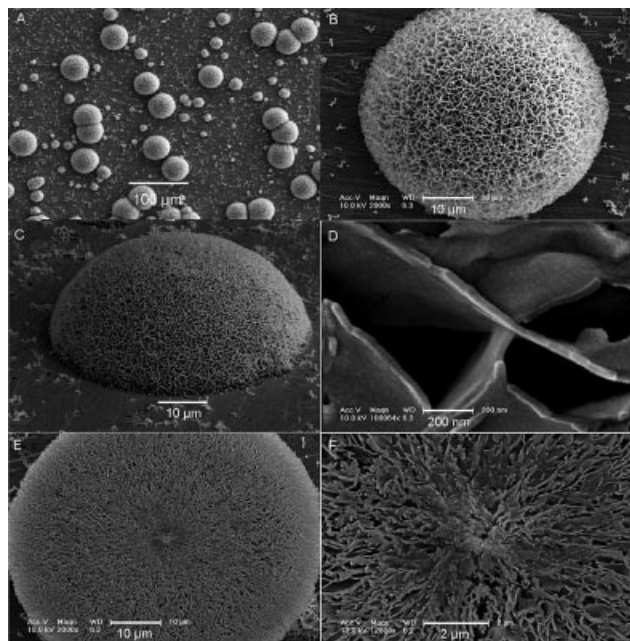


Figure 1. Typical SEM images of $\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ dandelion-like nanostructures formed by drop-drying of 100 μL of 5 mM phosphorus acid on a copper foil surface. A) Overview SEM image of the copper surface. B) A dandelion-like 3D nanostructure. C) Side view of a dandelion. D) Magnified view of a dandelion. E) Bottom view of a dandelion. F) Magnified view of the dandelion bottom.

In order to study the composition of the dandelion-like nanostructures, the blue product was collected and washed repeatedly with deionized water, then dissolved in aqueous HNO_3 solution. The ion concentrations of copper and phosphorus in the solution were determined by ICP-AES and the results confirmed a strict stoichiometric Cu/P ratio of 1.5:1.0. Furthermore, the chemical weight of the blue product was calculated to be 416.60, thus indicating its chemical formula to be $[\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$ (416.67). The formation of crystalline copper phosphate dihydrate $[\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$ was further confirmed by the use of wide-angle X-ray diffraction. Figure 2 shows the XRD pattern of an as-prepared $[\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$ powder sample. The diffraction lines are in agreement with those reported in the literature.^[24] The X-ray photoelectron spectrum (XPS) of a dandelion exhibits peaks at 935.4, 531.5, and 133.4 eV, which are attributed to $\text{Cu} 2p_{3/2}$, $\text{O} 1s$, and $\text{P} 2p_{1/2}$ of $[\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$,^[25] respectively.

The chemical structure of the as-prepared $[\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$ dandelion-like nanostructures was also confirmed by Raman spectroscopy. Figure 3 is the 633-nm-excited Raman spectrum of a dandelion and the inset is its optical microscope image. The band at 994 cm^{-1} is assigned to the PO_3 symmetric stretching vibration, the two bands at 646 and

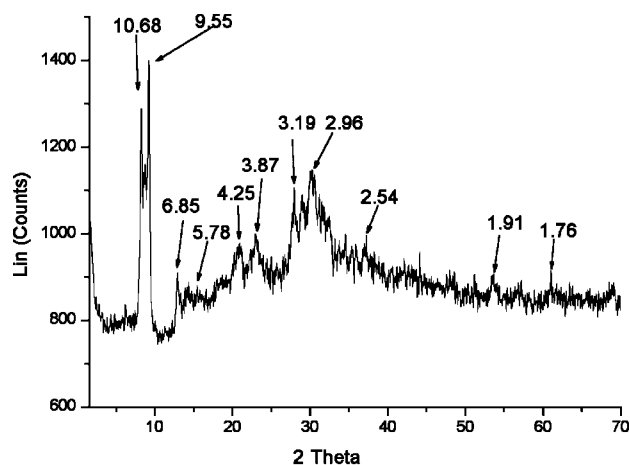


Figure 2. An XRD pattern of an as-prepared $[\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$ powder sample formed by drop drying of a 50 mM H_3PO_4 solution on a copper foil at 15°C and 49% humidity.

553 cm^{-1} belong to the PO_3 out-of-plane bending vibrations, and the band at 450 cm^{-1} is attributed to the PO_3 symmetric bending vibration.^[26,27]

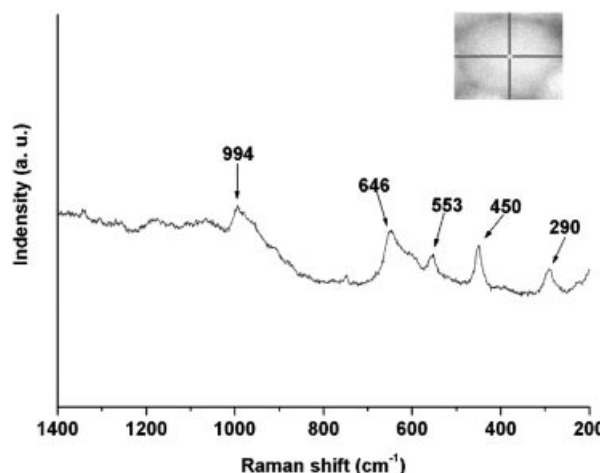


Figure 3. 633-nm-excited Raman spectra of as-prepared $[\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$ dandelion (typically sample) recorded in the region of 200–1400 cm^{-1} ; the inset image is the optical image of the dandelion.

The growth process of the dandelion has been carefully investigated. Figure 4 shows the SEM images of the copper surface recorded at different drying times after removing the residual solutions with a capillary tube. As shown in part A of Figure 4, the heterogeneous nucleation process is very slow, and sheet-like nuclei grow on the copper surface in the initial 60 minutes. When the drying time is increased from 60 to 120 minutes, the sheet-like nuclei form branches on the surface and gradually grow upward into small cores with a size of around $4\text{ }\mu\text{m}$ (Figure 4, B). This small core grows at nearly the same rate in all directions above the surface of the substrate to form a 3D dandelion (ca. $24\text{ }\mu\text{m}$) as the drying time is increased further to 240 minutes (Figure 4, C). Finally, a dandelion with a diameter of about $45\text{ }\mu\text{m}$ is generated after 420 minutes (Figure 4, D).

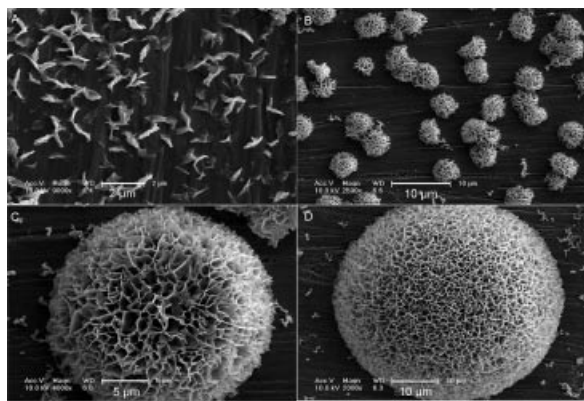
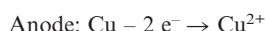


Figure 4. Typical SEM images of the copper surface recorded after drop drying 100 µL of 5 mm phosphorus acid for different times and removal of the residual solutions with a capillary tube: (A) 60 min; (B) 120 min; (C) 240 min; (D) 420 min.

It is known that copper can be corroded easily in a moist atmosphere. Under our experimental conditions, the corrosion mechanism can be simply illustrated by the two half electrochemical reactions



There are a lot of microelectrodes on the corroding copper surface. During the process of corrosion, more and more copper atoms are changed into ions and enter into solution, which results in a high copper(I) ion concentration in anodic domains. Simultaneously, the pH of the solutions in the cathodic domains becomes higher than that of the host solution. The diffusion of copper ions causes the slow crystallization of $[\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$ and leads to the formation of the dandelions. As can be seen from Figures 1 (F), 4 (A), and 5, a core is formed in the initial stage of generation of the dandelion-like nanostructure, and because the cathodic domain is uniformly distributed in the solution, the dandelion grows at almost the same rate in all directions from the core.

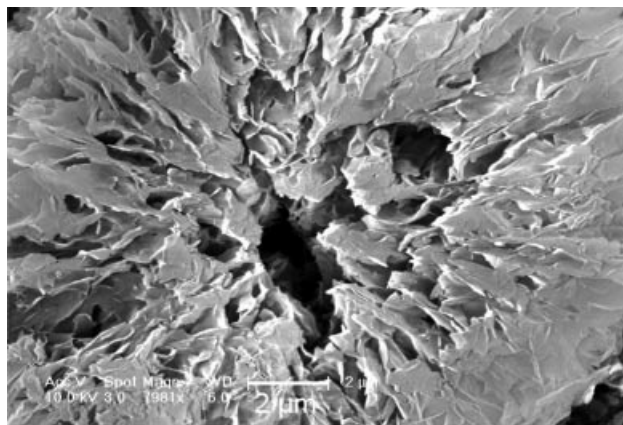


Figure 5. SEM image of a crushed dandelion bottom.

We found that the concentration of phosphorus acid ($C_{\text{p.a.}}$) can strongly affect the morphology of the dan-

delions. As is shown in Figure 6 (A), when $C_{\text{p.a.}} = 0.5$ mm, small particles with sizes of 5–8 µm are formed that cover the copper surface sparsely. The shapes of the particles are irregular and an obvious number density gradient is observed. This is mainly due to the fact that the dioxygen concentration in the edge region is higher than that in the central region of the droplet. As $C_{\text{p.a.}}$ was increased to 2 mm, the structures of dandelions became more regular and their sizes also increased to about 25 µm (Figure 6, B). As described above, the formation of the dandelions depends mainly on the concentration of the phosphate ions. Increasing the phosphorus acid concentration will therefore result in the formation of more and larger dandelions. When $C_{\text{p.a.}}$ is higher than 10 mm, the sizes of the resulting dandelions no longer increase. In this case a large number of “nuclei” are generated and two neighboring dandelions expand and intermesh with each other to form an interconnected porous structure of nanosheets in their boundary region (Figure 6, C).^[6,28,29] A further increase of $C_{\text{p.a.}}$ makes the dandelions cover the whole copper surface compactly to form a lotus-like micro-nanostructure (Figure 6, D).

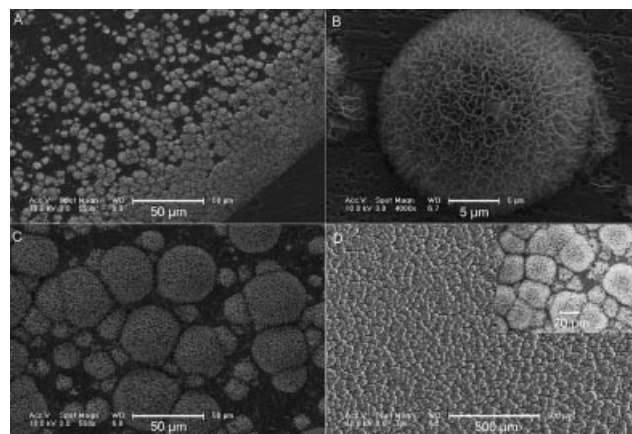


Figure 6. SEM images of the copper surface after drying of different phosphorus acid concentrations: A) 0.5 mm; B) 2 mm; C) 10 mm; D) 20 mm (droplet: 100 µL).

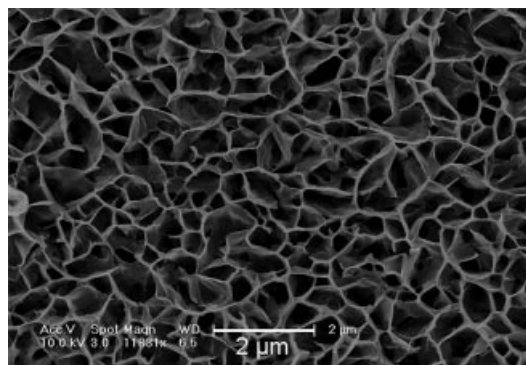


Figure 7. SEM images of the nanowalls. (100 µL of 2 mm aqueous phosphorus acid solution was dropped onto the surface of a piece of copper foil in a sealed box filled with oxygen gas at a temperature of 15–17 °C and humidity of 100% for 48 h. The foil was dried at 15 °C with a humidity of 30%).

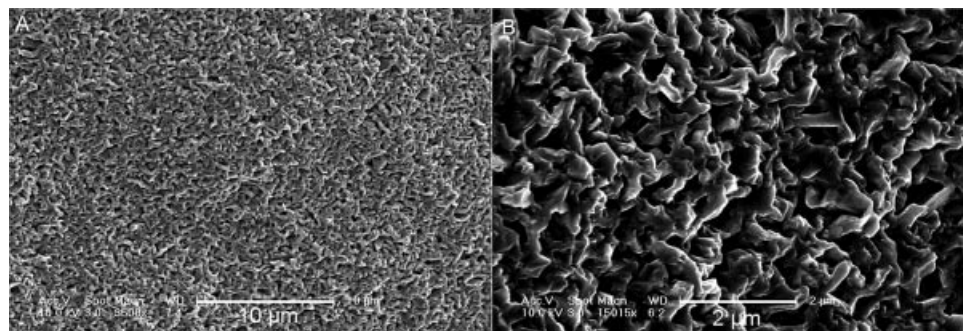


Figure 8. SEM images of the copper foil prepared from 50 mm H_3PO_4 heated at 650 °C for 6 h under nitrogen: A) overall view; B) magnified view.

It was interesting to find that control of the evaporation conditions can also change the morphology of the copper surface from 3D dandelions to 2D nanowalls. Figure 7 shows a typical image of copper phosphate dihydrates nanowalls formed by drop-drying 5 mm phosphoric acid on a copper foil surface in an environment with a humidity of 100% and at a temperature of 15–17 °C. As can be seen from this figure, the nanosheets grow with their surfaces perpendicular to the copper surface and have a thickness of about 35 nm. The nanosheets intermesh with each other to form a porous film with a pore size ranging from 100 to 400 nm. In this case, the drying time is much longer than those described above and more nuclei are generated to form nanowalls.

When the film prepared from 50 mm H_3PO_4 was heated at 650 °C for 6 h under nitrogen and then cooled naturally to room temperature a nanoporous CuO film was produced. Figure 8 shows the SEM images of the as-prepared CuO film. Rod-like CuO particles intermesh with each other to form a porous film. It is clear from this figure that the original walls of the $[\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$ nanostructures have collapsed. This is mainly due to the decomposition of copper phosphate dihydrate in the reaction that can be simply expressed as follow: $[\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}] \rightarrow 3\text{CuO} + 2\text{H}_2\text{O} \uparrow + \text{P}_2\text{O}_5 \uparrow$. The release of water and phosphorus

pentoxide at temperatures higher than 400 °C destroys the framework of the copper phosphate dihydrate and results in the formation of a porous CuO film. The composition of the CuO film was confirmed by its EDS spectrum (Cu/O = 1:1; no phosphorus peak was observed). The composition of the film was also supported by its Raman spectrum (Figure 9): the bands at 301, 348, and 630 cm^{-1} correspond to the Ag, Bg⁽¹⁾, and Bg⁽²⁾ modes of CuO crystals.^[30]

Conclusions

In summary, 3D dandelion-like porous nanostructures and 2D nanowalls of copper phosphate dihydrate built up of thin nanosheets can be fabricated by automatic drop-drying an aqueous solution of phosphoric acid on the surface of a copper foil under mild conditions. Controlling the initial concentration of the acid and the conditions of drop-drying can modulate the morphology of the nanostructures. The complex structure reported here brings new insights into understanding the mineralization mechanisms of nanostructured natural minerals. This work develops a simple, template-free method for fabricating high surface-to-volume ratio complex 3D nanostructures of metal-based materials. We believe this technique could be extended to fabricate 3D nanostructures of other materials by changing the solute or the substrate.

Experimental Section

Materials: Copper foil (99.9%, Shanghai Chemical Reagent Co. Ltd., Shanghai, China) with a thickness of 0.1 mm was polished with abrasive paper (1200 mesh), then cleaned with deionized water repeatedly and dried before each experiment. Phosphorous acid (analytical grade, Beijing Chemical Co. Ltd., Beijing, China) was used as received.

Preparation of $[\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$ 3D Dandelions: Typically, in a sealed box (the bottom of the box was covered with allochroic silica gel) filled with dioxygen gas, 100 μL of aqueous phosphorus acid solution was dropped onto the surface of a piece of copper foil and dried automatically at a temperature of 15–17 °C. After the reaction, the copper foil was washed with deionized water and dried under vacuum at 40 °C overnight before characterization.

Preparation of $[\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$ 2D Nanowall Films and CuO Nanoporous Films: Typically, a $[\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$ 2D nanowall film

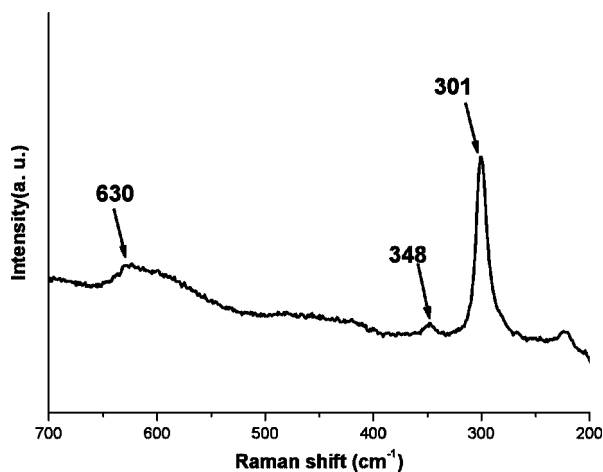


Figure 9. Raman spectrum of the as-prepared CuO film excited at 785 nm.

was synthesized by putting a copper foil in an sealed box filled with dioxygen gas at a humidity of 100% and then dropping 100 μL of 2 mm aqueous phosphorus acid solution onto the foil surface and drying at a temperature of 15–17 °C for 48 h. Finally, the foil with the nanostructures was dried at 15 °C in an environment with a humidity of 30%. The CuO nanoporous film was produced by putting the copper foil covered with $[\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$ nanostructures (fabricated from 50 mm H_3PO_4) into a furnace, heating to 650 °C for 6 h under nitrogen, and cooling naturally to room temperature.

Characterizations: Scanning electron micrographs (SEM) were taken with a FEI Sirion 200 or a S530 (Hitachi) scanning electron microscope. Ion concentrations were measured by using an inductively coupled plasma-atomic emission spectrometer (ICP-AES) model Vista-MP (Varian). X-ray diffraction (XRD) patterns were obtained with a D8 Advance (Bruker) X-ray diffractometer. X-ray photoelectron spectra (XPS) were recorded with an AEM PHI5300 (PE) photoelectron spectrometer. Raman spectra were recorded with a RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC., England) employing a 633- or 785-nm laser beam and a CCD detector with 4 cm^{-1} resolution. The spectra were obtained by focusing a 10- μm laser spot on the sample using a 20 objective and accumulated three times for 30 s each. The powers were always kept very low (≈ 0.05 mW) to avoid destruction of the samples.

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