## Fabrication of Malachite with a Hierarchical Sphere-like Architecture

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Malachite ( $Cu_2(OH)_2CO_3$ ) with a hierarchical sphere-like architecture has been successfully synthesized via a simple and mild hydrothermal route in the absence of any external inorganic additives or organic structure-directing templates. Powder X-ray diffraction, scanning electron microscopy, and Fourier transmission infrared spectrometry are used to characterize various properties of the obtained malachite samples. The hierarchical malachite particles are uniform spheres with a diameter of  $10-20~\mu m$ , which are comprised of numerous two-dimensional microplatelets paralleling the sphere surface. The initial concentration of reagents, the hydrothermal reaction time, and temperature are important factors which dominantly affect the evolution of crystal morphologies. The growth of the hierarchical architecture is believed to be a layer-by-layer growth process. Further, copper oxide with the similar morphology can be easily obtained from the as-prepared malachite.

#### Introduction

Over the past several years, the chemical synthesis of inorganic materials with unusual and novel morphologies has attracted considerable attention because of their potential applications in various fields such as catalysts, medicine, electronics, ceramics, pigments, and cosmetics. <sup>1–4</sup> In particular, the hierarchical structure is one of the important forms among various morphologies, 5,6 which is a structure made up of building units at different levels, with the higher levels having a control or precedence over the lower levels. <sup>7</sup> Among various methods developed for the fabrication of hierarchical structures, the solution-phase chemical synthesis (especially, the hydrothermal synthesis<sup>8,9</sup>) has been considered as one of the most promising routes due to its low cost and potential for large-scale production. 10,11 Generally, there have been two basic templating methods (with either hard or soft templates) for the synthesis of hierarchical structures. Nevertheless, the introduction of surfactants, templates, or other additives into the synthetic route undoubtedly leads to more synthetic procedures and causes impurities in the final products. Therefore, developing simple template-free methods seems to be more promising due to various expected advantages, such as the relatively low cost, high purity, and large-scale production.

As one of the interesting minerals, malachite is a famous and very popular semiprecious stone commonly used in jewelry and is frequently employed in catalysts, coatings, and pigments. <sup>12</sup> It is also used as a copper source to prepare other copper compounds with special morphologies, such as CuO, which has been widely exploited for diverse applications (e.g., heterogeneous catalysts, gas sensors, lithium ion electrode materials, and field emission emitters). <sup>13</sup> Recently, malachite has already attracted extensive interest in various research fields, for example, its crystal structure, IR and Raman spectra, thermal decomposition behavior (from malachite to copper oxide), and quantum magnetic properties have been widely investigated. <sup>14–17</sup>

Meanwhile, different morphologies of malachite, such as the sphere-like, peanut-like, and lamella-like morphologies have been obtained via different synthesis routes. <sup>18–20</sup> However, until now there has been no report on the fabrication of malachite with a novel hierarchical sphere-like architecture by directly employing the simple hydrothermal method.

In this work, we report a simple hydrothermal route (in the absence of any inorganic additives or organic templates) to synthesize malachite with a novel hierarchical sphere-like architecture. Copper oxide with similar morphology can also be obtained by a facile thermal treatment of the as-prepared malachite. To the best of our knowledge, such a novel hierarchical sphere-like architecture has not been reported.

# **Experimental Section**

The starting solutions of analytical grade  $CuSO_4$  and  $K_2CO_3$  were freshly prepared. Synthetic malachite was prepared by the titration of a  $0.5~M~CuSO_4$  solution with a  $0.5~M~K_2CO_3$  solution under vigorous stirring at room temperature for 30 min, then ultrasonication for 10 min. The bluish slurry mixture was transferred to a Teflon-lined stainless steel autoclave of 80 mL capacity, filled up to 70% of the total volume. The autoclave was sealed and heated at 50-180~C for 1-48~h in an electric oven, and the autoclave was then cooled to room temperature naturally. Green precipitates were filtered and washed with deionized water and anhydrous ethanol (respectively) several times, and the final product was dried at 50~C for 5~h.

The obtained malachite samples were confirmed by powder X-ray diffraction (XRD, D/Max 2400, Rigaku, by a diffractometer equipped with the graphite monochromatized Cu K $\alpha$  radiation) in the  $2\theta$  angles ranging from  $10^{\circ}$  to  $70^{\circ}$ . The morphologies of malachite and CuO were characterized by using a scanning electron microscope (SEM, JSM-5600LV, JEOL) equipped with an energy-dispersive X-ray spectrometer (EDX). FT-IR spectra were recorded on a Fourier transmission infrared spectrometry (FT-IR, NEXUS) at wavenumbers 400-4000 cm $^{-1}$ .

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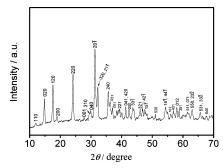
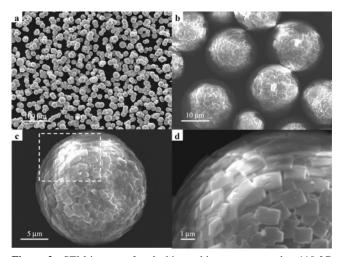


Figure 1. XRD patterns of malachite architecture prepared at 110 °C and 12 h.

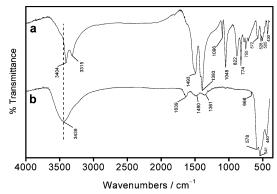


**Figure 2.** SEM images of malachite architecture prepared at 110 °C and 12 h: (a) an overall morphology; (b and c) detailed views on average-sized spheres; and (d) a detailed view on the sphere surface corresponding to (c) indicated by the dashed rectangle.

### **Results and Discussion**

Malachite (Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>) crystallizes in a monoclinic space group  $P2_1/a$  with lattice parameters a = 9.502 Å, b = 11.974Å, c = 3.240 Å, and  $\beta = 98.75^{\circ}$  (Z = 4). <sup>14</sup> All species Cu<sup>2+</sup>,  ${\rm CO_3^{2-}}$ , and  ${\rm OH^-}$  ions occupy  $C_1$  site symmetry. Two crystallographically different  ${\rm Cu^{2+}}$  and  ${\rm OH^-}$  ions and one type CO<sub>3</sub><sup>2-</sup> ion exist in the lattice. Cu(1) is coordinated to two oxygen atoms from CO<sub>3</sub><sup>2-</sup> ions and two OH<sup>-</sup> ions; Cu(2) is coordinated to two oxygen atoms from CO<sub>3</sub><sup>2-</sup> ions and four OH<sup>-</sup> ions, thus forming the elongated octahedron ((4 + 2)) coordination that is connected by edge-sharing, as shown in the crystallographic structure of Figures S1-S4). XRD patterns of the as-prepared malachite sample are shown in Figure 1, and all peaks can be clearly indexed as a pure monoclinic phase of malachite and matched well with the reported data (JCPDS card File No. 76-0660). No other peaks (such as azurite (Cu<sub>3</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>)) or amorphous copper compounds can be observed in XRD patterns, indicating a high purity and crystallinity of the final product.

SEM images of these samples are shown in Figure 2, which exhibit an interesting sphere-like architecture that comprises numerous two-dimensional microplatelets paralleling the sphere surface, while several layers on the sphere surface can be clearly seen (Figure S5). The thickness, breadth, and length of these microplatelets on the sphere surface are in the range of 0.2–0.3  $\mu$ m, 1–2  $\mu$ m, and 2–3  $\mu$ m (the size of two-dimensional microplatelets corresponds to the diameter of spheres as shown in Figure S5f), respectively. It is intriguing to note that malachite platelets can self-aggregate into the sphere-like hierarchical architecture in the absence of any specific ionic additives,



**Figure 3.** IR spectra of samples: (a) malachite prepared at  $110~^{\circ}$ C and 12~h and (b) CuO prepared at  $180~^{\circ}$ C and 48~h.

biological macromolecules, or synthetic organic templates. Under the reported conditions, the malachite products are almost all in this hierarchical morphology with a diameter ranging from 10 to 20  $\mu$ m.

It is well-known that the crystal growth and morphology are determined by the degree of supersaturation, diffusion of the reaction, surface energy, and crystal structure, that is, the extrinsic and intrinsic factors (both crystal growth environments and crystal structure) have significant effects on the final morphology.<sup>21</sup> Considering that no additional templates are added into the formation process (without taking into account the media in which crystals are grown), the platelet-like malachite can be thought to have a habit to form this morphology due to its crystal structure (malachite is well-known to have a layered structure, as shown in Figures S1-S4). The framework of malachite crystal structure defines two directions for the orthorhombic Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>, one along [010] and another along [102] owing to Cu(1)-O, Cu(2)-O, C-O, and hydrogen bonds. Both directions define  $(20\overline{1})$  planes, which are parallel to each other and form a layered structure. The layers are connected through the weaker Cu(2)—O bonds (the atom distance between Cu(2) and O is 2.353 and 2.362 Å, respectively, as shown in Figures S1-S4), and the number of bonds between the two layers is fewer than that in the  $(20\overline{1})$  plane.

IR spectra of malachite and CuO are shown in Figure 3, and our spectra coincide well with these reported in the literature. 15 Comparing with the incorporation of OH<sup>-</sup> ions in CuO samples (prepared at 180 °C and 48 h), it is clear that the bands of OH stretching modes in malachite shift to the lower wavenumbers, and split into two bands (as shown in Figure 3 indicated by the dashed line). The bands at 3405 and 3316 cm<sup>-1</sup> are assigned to the OH stretching modes of two crystallographically different OH<sup>-</sup> ions in the malachite crystal lattice. The strengths of these two hydrogen bonds are different, irrespective of the shorter hydrogen bond (O-H) lengths, 22 due to the difference of hydrogen bond acceptors (the longer hydrogen bond (H···O) lengths are 1.908 and 1.775 Å, respectively, as shown in Figure S2). During the hydrothermal process, both kinds of hydrogen bonds in the crystal structure of malachite (on the same  $(20\overline{1})$ plane and in the different directions formed during the crystallization of malachite, which are different from the C-O bonds that have been formed before the crystallization of malachite) may have significant effects on the formation of the plateletlike morphology. When we add ethanol into the solution (20% volume) to affect the formation of hydrogen bonds during the synthetic process, the morphology of malachite is changed drastically (Figure S6); a similar experiment has been employed for evaluating the role of hydrogen bonds in crystal growth. 23

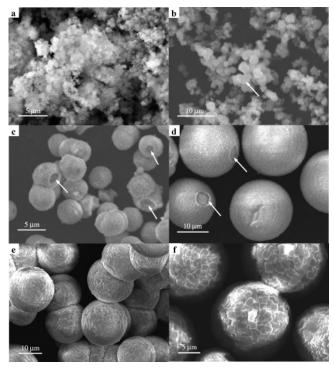


Figure 4. SEM images of malachite samples prepared at different reaction stages: (a) stage 1 at 50 °C and 1 h; (b) stage 2 at 50 °C and 1.5 h; (c) stage 3 at 50 °C and 3 h; (d) stage 4 at 70 °C and 4 h; (e) stage 3 at 90 °C and 5 h; and (f) stage 6 at 110 °C and 12 h. Arrows are to aid the eye.

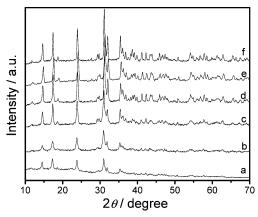


Figure 5. XRD patterns of malachite samples prepared at different reaction stages: (a) stage 1 at 50 °C and 1 h; (b) stage 2 at 50 °C and 1.5 h; (c) stage 3 at 50 °C and 3 h; (d) stage 4 at 70 °C and 4 h; (e) stage 3 at 90 °C and 5 h; and (f) stage 6 at 110 °C and 12 h.

Concerning the formation process of the hierarchical structure, malachite samples prepared at different reaction stages (stage 1 at 50 °C and 1 h, stage 2 at 50 °C and 1.5 h, stage 3 at 50 °C and 3 h, stage 4 at 70 °C and 4 h, stage 5 at 90 °C and 5 h, and stage 6 at 110 °C and 12 h) are respectively studied by SEM and XRD measurements. Several obvious evolution stages can be observed and are shown in Figures 4 and 5. In the initial stage, many small colloid grains with a spherical shape can be formed, as shown in Figures 4a and 4b (the size is less than 1 μm indicated by the white arrow in Figure 4b). Figures 4c and 4d show small spheres, and the sunken circle patterns can be clearly seen on the surface of some spheres (which are indicated by white arrows). The diameters of small spheres increase from  $2 \mu m$  (Figure 4c) to  $10 \mu m$  (Figure 4d). Figure 4e shows that prior to the formation of the final hierarchical structure, the diameter of spheres is about 15  $\mu$ m. It is clear that the

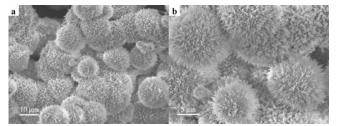


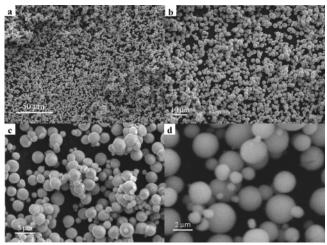
Figure 6. Malachite with the urchin-like morphology (prepared at 110 °C and 12 h, the concentration of CuSO<sub>4</sub> and K<sub>2</sub>CO<sub>3</sub> is 1.0 M): (a) low magnification view and (b) high magnification view.

hierarchical structure growth is layer-by-layer and the sphere diameter has a tendency to increase gradually. Meanwhile, from XRD patterns of these samples corresponding to Figure 5, it can be seen that the intensity of peaks of the initial, intermediate, and final stages of samples is gradually enhanced.

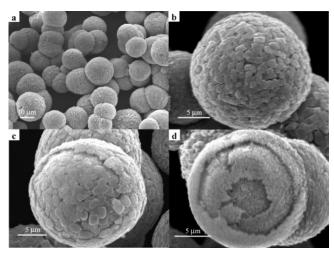
From the observed morphologies and XRD patterns of the samples at different stages, it is possible to interpret the formation process of the hierarchical structure as follows: (1) Malachite colloids are initially formed under the synthetic condition, and the initially formed colloids are aggregated together with a spherical appearance, which indicate a nucleation aggregation mechanism with no room and time for the crystal growth at the high supersaturation level. (2) With the reaction continuing, the concentration of reactants decreases, the reaction rate slows down, the nucleation rate is a dominant step at the high supersaturation level; however, the crystal growth rate is the dominant step at the low supersaturation level. The formation of malachite hierarchical architecture indicates that the nucleation and growth of malachite are well controlled in our present synthetic process. (3) With the reaction temperature and time increasing, samples have a tendency to gradually crystallize (as shown in Figure 5). As a result, the whole synthetic system provides an appropriate crystal growth environment for the formation of novel hierarchical architecture.

It should be pointed out that during the hydrothermal synthesis of malachite, the final composition and morphology are largely dependent on the synthetic conditions, such as the initial concentration of reagents, temperature, and time. It is well accepted that in the hydrothermal process, the reactant concentration exerts an important impact on the crystal nucleation and growth, which is responsible for the morphology of products.<sup>24</sup> When the concentration of reactants is double (i.e., the concentration of CuSO<sub>4</sub> and K<sub>2</sub>CO<sub>3</sub> is 1.0 M), malachite with the urchin-like morphology can be obtained (as shown in Figure 6); XRD patterns are shown in Figure S7. When the temperature is higher than 180 °C and the time is longer than 48 h, we can obtain spherical CuO with the diameter ranging from 1 to 4 μm (as shown in Figures 7 and S8). The surface of CuO spheres is smooth, which is different from that of the dandelion-like morphology reported in the literature,9b even though under similar hydrothermal conditions.

It has been reported that the thermogravimetry analysis for the thermal decomposition of malachite indicates only a smooth mass-loss trace to give copper(II) oxide: Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> → 2CuO + CO<sub>2</sub> + H<sub>2</sub>O.<sup>16</sup> According to DSC analysis for malachite (prepared at 110 °C 12 h) in a flowing air atmosphere (as shown in Figure S9), our thermal treatment conditions are fixed as follows: (i) the heating rate is 1 °C/min from room temperature to 341 °C, the temperature is then maintained at 341 °C for 3 h and then raised to 500 °C (the heating rate is 1 °C/min) and maintained at 500 °C for 5 h. Thermal decomposition of malachite in air atmosphere leads to the formation of the



**Figure 7.** CuO with the spherical morphology prepared at 180 °C and 48 h: (a and b) low magnification view and (c and d) high magnification view.



**Figure 8.** SEM images of samples: (a and b) CuO after the thermal treatment of malachite under the conditions (i); (c) CuO after thermal treatment of malachite under the conditions (ii); and (d) CuO after thermal treatment of malachite (prepared at 90 °C and 5 h) under the conditions (ii).

hierarchical structure of copper oxide (as shown in Figures 8, S10, and S11); copper oxide with a similar size and morphology can be easily obtained with our thermal treatment conditions (i). With the thermal treatment conditions (ii) (the heating rate is 10 °C/min from room temperature to 500 °C, then the temperature is maintained at 500 °C for 8 h), some two-dimensional microplatelets break off from the large sphere (as shown in Figures 8c and 8d). It is clear that each large sphere is the layer-by-layer hierarchical architecture, which consists of numerous two-dimensional microplatelets paralleling the sphere surface.

There are two types of CuO particles prepared in this work, type I CuO directly prepared at 180 °C and 48 h via the hydrothermal process and type II CuO via the thermal treatment of the as-prepared malachite (as shown in Figures 7 and 8). The major difference of these two types of CuO is their sphere surfaces, diameters, and synthesis methods. The surface of type I CuO is smooth with the diameter ranging from 1 to 4  $\mu$ m, while the surface of type II CuO is corrugated with the diameter ranging from 10 to 20  $\mu$ m (which is prepared via two basic steps, i.e., the hydrothermal synthesis of malachite and the calcination of the as-prepared malachite in air atmosphere). More importantly, type II CuO has a similar hierarchical morphology

as the as-prepared malachite. A similar process to obtain inorganic oxides by the direct calcination of their precursors has also been successfully applied to the synthesis of MgO products with novel morphologies in our recent work.<sup>25</sup>

#### **Conclusions**

In summary, the micrometer-scale hierarchical architecture of malachite (Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>) can be effectively constructed via a simple and mild hydrothermal process. The hierarchical malachite particles are in a uniformly spherical architecture with a diameter of  $10-20 \mu m$ , which consists of numerous twodimensional microplatelets paralleling the sphere surface. The possible formation process of the hierarchical structure has been elucidated by SEM and XRD measurements, which can be ascribed to a layer-by-layer growth process, and the sphere diameter has a tendency to increase gradually with temperature and time increasing. Our present hydrothermal synthetic system provides an appropriate crystal growth environment (the nucleation and growth are well controlled) for the formation of novel hierarchical architecture. Copper oxide with similar morphology can be easily obtained by a facile thermal treatment of the asprepared malachite (in air atmosphere). The simple hydrothermal process does not need any inorganic and organic templates, which can easily avoid introducing impurities into the final product. The present hydrothermal process may also be applicable to the preparation of other basic copper(II) compounds such as gerhardtite (Cu<sub>2</sub>(OH)<sub>3</sub>NO<sub>3</sub>), atacamite (Cu<sub>2</sub>(OH)<sub>3</sub>Cl), and posnjakite (Cu<sub>4</sub>(OH)<sub>6</sub>SO<sub>4</sub>•H<sub>2</sub>O), etc.

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**Supporting Information Available:** XRD, SEM, DSC, and EDX results of the reported samples and the crystal structure of malachite. This material is available free of charge via the Internet at http://pubs.acs.org.

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