

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

Jiasheng Xu and Dongfeng Xue\*

State Key Laboratory of Fine Chemicals, Department of Materials Science and Chemical Engineering, School of Chemical Engineering, Dalian University of Technology, 158 Zhongshan Road, Dalian 116012, P.R. China

Received: May 30, 2005; In Final Form: July 20, 2005

Malachite ( $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ) 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  $\mu\text{m}$ , 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,<sup>5,6</sup> 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.<sup>10,11</sup> 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  $\text{CuO}$ , 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.

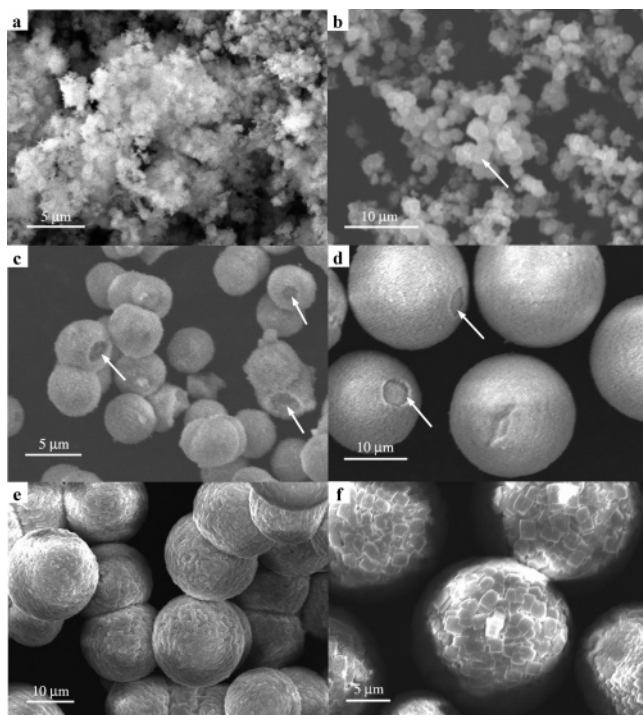
### Experimental Section

The starting solutions of analytical grade  $\text{CuSO}_4$  and  $\text{K}_2\text{CO}_3$  were freshly prepared. Synthetic malachite was prepared by the titration of a 0.5 M  $\text{CuSO}_4$  solution with a 0.5 M  $\text{K}_2\text{CO}_3$  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.

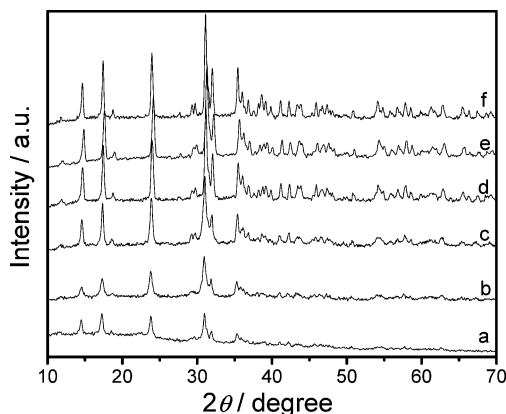
The obtained malachite samples were confirmed by powder X-ray diffraction (XRD, D/Max 2400, Rigaku, by a diffractometer equipped with the graphite monochromatized  $\text{Cu K}\alpha$  radiation) in the  $2\theta$  angles ranging from 10° to 70°. The morphologies of malachite and  $\text{CuO}$  were 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  $\text{cm}^{-1}$ .

\* Address correspondence to this author. E-mail: dfxue@chem.dlut.edu.cn.



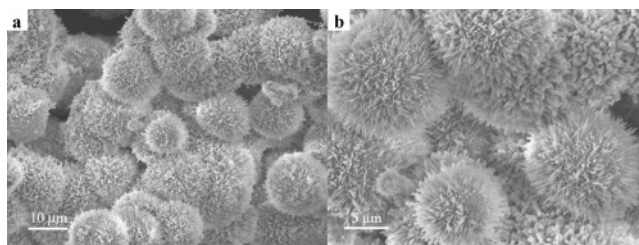


**Figure 4.** SEM images of malachite samples prepared at different reaction stages: (a) stage 1 at 50 °C and 1 h; (b) stage 2 at 50 °C and 1.5 h; (c) stage 3 at 50 °C and 3 h; (d) stage 4 at 70 °C and 4 h; (e) stage 3 at 90 °C and 5 h; and (f) stage 6 at 110 °C and 12 h. Arrows are to aid the eye.



**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 μm (Figure 4c) to 10 μm (Figure 4d). Figure 4e shows that prior to the formation of the final hierarchical structure, the diameter of spheres is about 15 μm. It is clear that the



**Figure 6.** Malachite with the urchin-like morphology (prepared at 110 °C and 12 h, the concentration of  $\text{CuSO}_4$  and  $\text{K}_2\text{CO}_3$  is 1.0 M): (a) low magnification view and (b) high magnification view.

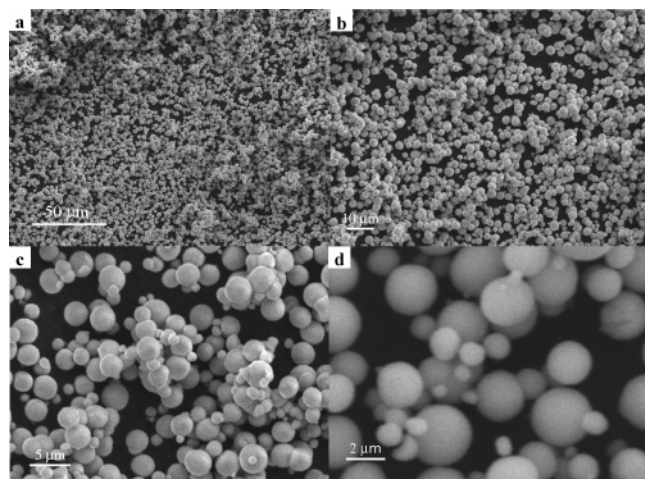
hierarchical structure growth is layer-by-layer and the sphere diameter has a tendency to increase gradually. Meanwhile, from XRD patterns of these samples corresponding to Figure 5, it can be seen that the intensity of peaks of the initial, intermediate, and final stages of samples is gradually enhanced.

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.

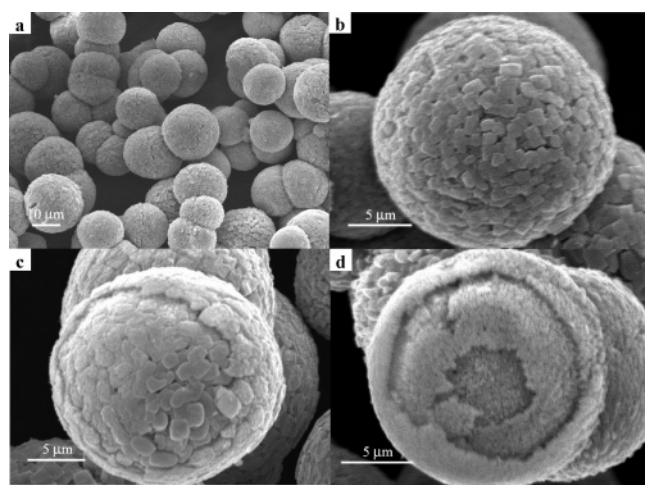
It should be pointed out that during the hydrothermal synthesis of malachite, the final composition and morphology are largely dependent on the synthetic conditions, such as the initial concentration of reagents, temperature, and time. It is well accepted that in the hydrothermal process, the reactant 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  $\text{CuSO}_4$  and  $\text{K}_2\text{CO}_3$  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,<sup>9b</sup> 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:  $\text{Cu}_2(\text{OH})_2\text{CO}_3 \rightarrow 2\text{CuO} + \text{CO}_2 + \text{H}_2\text{O}$ .<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 μm, while the surface of type II CuO is corrugated with the diameter ranging from 10 to 20 μm (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 ( $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ) 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 μm, which consists of numerous two-dimensional 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 as-prepared 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 ( $\text{Cu}_2(\text{OH})_3\text{NO}_3$ ), atacamite ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ), and posnjakite ( $\text{Cu}_4(\text{OH})_6\text{SO}_4 \cdot \text{H}_2\text{O}$ ), etc.

**Acknowledgment.** The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China (NSFC No. 20471012), a Foundation for the Author of National Excellent Doctoral Dissertation of P.R. China (FANEDD No. 200322), and the Research Fund for the Doctoral Program of Higher Education (RFDP No. 20040141004).

**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>.

## References and Notes

- (1) (a) Braun, P. V.; Osenar, P.; Stupp, S. I. *Nature* **1996**, *380*, 325. (b) Mann, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 3392.
- (2) Ohara, P. C.; Heath, J. R.; Gelbart, W. M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1078.
- (3) (a) Duan, X.; Huang, Y.; Agarwal, R.; Lieber, C. M. *Nature* **2003**, *421*, 241. (b) Gates, B.; Mayers, B.; Grossman, A.; Xia, Y. N. *Adv. Mater.* **2002**, *14*, 1749.
- (4) Goldberger, J.; He, R.; Zhang, Y.; See, S.; Yang, H.; Choi, H. J.; Yang, P. *Nature* **2003**, *422*, 599.
- (5) Li, Z. Q.; Ding, Y.; Xiong, Y. J.; Yang, Q.; Xie, Y. *Chem. Commun.* **2005**, *7*, 918.
- (6) Whitesides, G. M.; Grzybowski, B. *Science* **2002**, *295*, 2418.
- (7) Soler-Illia, G. J. de A. A.; Sanchez, C.; Lebeau, B.; Patarin, J. *Chem. Rev.* **2002**, *102*, 4093.
- (8) Cundy, C. S.; Cox, P. A. *Chem. Rev.* **2003**, *103*, 663.
- (9) (a) Chang, Y.; Zeng, H. C. *Cryst. Growth Des.* **2004**, *4*, 273. (b) Liu, B.; Zeng, H. C. *J. Am. Chem. Soc.* **2004**, *126*, 8124.
- (10) Murphy, C. J.; Jana, N. R. *Adv. Mater.* **2002**, *14*, 80.
- (11) Lu, C.; Qi, L.; Yang, J.; Zhang, D.; Wu, N.; Ma, J. J. *Phys. Chem. B* **2004**, *108*, 17825.
- (12) Balitsky, V.; Bublikova, M. *Prog. Cryst. Growth Charact. Mater.* **1990**, *21*, 139.
- (13) (a) Reitz, J. B.; Solomon, E. I. *J. Am. Chem. Soc.* **1998**, *120*, 11467. (b) Chowdhuri, A.; Gupta, V.; Sreenivas, K.; Kumar, R.; Mozumdar, S.; Patanjali, P. K. *Appl. Phys. Lett.* **2004**, *84*, 1180.
- (14) Suesse, P. *Acta Crystallogr.* **1967**, *22*, 146.

- (15) (a) Stoilova, D.; Koleva, V.; Vassileva, V. *Spectrochim. Acta A* **2002**, 58, 2051. (b) Frost, R. L.; Martens, W. N.; Rintoul, L.; Manhmutagic, E.; Klopogge, J. T. *J. Raman Spectrosc.* **2002**, 33, 252.
- (16) (a) Ding, Z.; Frost, R. L.; Klopogge, J. T. *J. Mater. Sci. Lett.* **2002**, 21, 981. (b) Frost, R. L.; Ding, Z.; Klopogge, J. T.; Martens, W. N. *Thermochim. Acta* **2002**, 390, 133. (c) Koga, N. *Thermochim. Acta* **1995**, 258, 145.
- (17) Janod, E.; leonyuk, L.; Maltsev, V. *Solid State Commun.* **2000**, 116, 513.
- (18) (a) Rodriguez-Clemente, R.; Serna, C. J.; Ocana, M.; Matijević, E. *J. Cryst. Growth* **1994**, 143, 277. (b) Astilieros, J. M.; Pina, C. M.; Fernandez-Diaz, L.; Lopez-Andres, S. *Cryst. Res. Technol.* **1998**, 33, 51.
- (19) Zhang, L. Z.; Yu, J. C.; Xu, A. W.; Li, Q.; Kwong, K. W.; Yu, S. H. *J. Cryst. Growth* **2004**, 266, 545.
- (20) Zhu, C. L.; Chen, C. N.; Hao, L. Y.; Hu, Y.; Chen, Z. Y. *Solid State Commun.* **2004**, 130, 681.
- (21) (a) Tang, Q.; Zhou, W.; Zhang, W.; Ou, S.; Jiang, K.; Yu, W.; Qian, Y.; *Cryst. Growth Des.* **2005**, 5, 147. (b) Siegfried, M. J.; Choi, K. S. *Adv. Mater.* **2004**, 16, 1743. (c) Siegfried, M. J.; Choi, K. S. *Angew. Chem., Int. Ed.* **2005**, 44, 3218.
- (22) (a) Schmidt, M.; Lutz, H. D. *Phys. Chem. Miner.* **1993**, 20, 27. (b) Lutz, H. D. *J. Mol. Struct.* **2003**, 646, 227. (c) Libowitzky, E. *Monatsh. Chem.* **1999**, 130, 1047.
- (23) Xu, D.; Xue, D.; Ratajczak, H. J. *J. Mol. Struct.* **2005**, 740, 37.
- (24) Sheldrich, W. S.; Wachold, M. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 206.
- (25) Yan, C.; Xue, D. *J. Phys. Chem. B* **2005**, 109, 12358.