Chem. Mater. **2005,** *17,* 332−336

Morphosynthesis and Ornamentation of 3D Dendritic Nanoarchitectures

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Received September 10, 2004. Revised Manuscript Received November 3, 2004

Complex 3D dendritic nanoarchitectures of copper hydroxide built up of ultrathin nanosheets have been synthesized progressively under nearly sustained supersaturation of impurity-free nutrients that are supplied statically from the natural oxidation of copper metal. Adjacent dendritic nanoarchitectures can further expand and eventually self-organize/merge themselves into impressive bicontinuous networks through the reaction-volume-controlled growth in formamide aqueous solution. When the simplest amino acid, glycine, was used as organic additive, high-order, shell-ornamented dendritic nanoarchitectures can be fabricated accordingly. A clear perspective is shown here that more complex nanostructured materials could be chemically synthesized under nearly sustained supersaturation and further decorated when biological molecules are used as templates.

Introduction

Morphological diversity and complexity of natural minerals reflect a remarkable level of control over high-order organization of inorganic materials in living organisms.[1,2] The finely tuned morphologies or architectures are precisely directed by organized biomacromolecules.[1,2] The bioinspired strategies of using organic ligands, additives, or templates have been developed and widely applied to prepare elaborate inorganic materials.[3−7] Meanwhile, the controlled thermodynamic driving force for inorganic crystallization, i.e., supersaturation, is another most decisive parameter to exert exquisite control over morphologies in biological systems.[8−10] The second prerequisite for biomineralization has been simulated by continuously replenishing the precipitation-consumed inorganic nutrients to maintain a certain level of supersaturation.[8,11,12] However, impressive architectures of inorganic materials have yet to be produced readily by simply retaining constant supersaturation of reaction nutrients with the currently used double-jet method. In this paper, we report a slow and progressive production of 3D intricate nanoarchitectures under nearly sustained supersaturation of impurity-free nutrients, which are supplied statically from the natural oxidation of copper metal. The controllable supersaturation itself has shown its importance for the self-organized growth of ultrathin nanosheets into intricate 3D dendritic architectures of copper hydroxide in the absence of self-assembled templates or matrixes. Highly branched nanoarchitectures, such as inorganic dendritic flowers, have been reproducibly synthesized in aqueous solution of formamide molecules (the simplest model molecule of peptide containing a prototype amide HNC=O peptide linkage). Two or more adjacent dendritic crystals can further expand and eventually self-organize/merge themselves into continuous porous networks. It is noted that impressive shell-ornamented dendritic nanostructures have also been fabricated when the simplest amino acid, glycine, is used as organic additive. The high-order, shell-ornamented nanoarchitectures have not been observed in natural biominerals or synthetic materials. The successful fabrication of hierarchical morphology provides new complex forms with extremely high surface-to-volume ratio for new catalytic or scaffolding applications and sheds new insights to understand the underlying mineralization mechanisms of complex nanoarchitectures in the natural and synthetic world.

Experimental Section

Materials. Formamide (99.8%, Merck) and glycine (99.0%, Aldrich) were used without further purification. Copper foils (99.9%, Aldrich) with a thickness of 0.127 mm were ultrasonically washed with ethanol and deionized water before use.

Preparation of 3D Dendritic Nanoarchitectures. In a typical procedure, a piece of copper foil (7.0 × 7.0 × 0.127 mm) was first laid on the bottom of a 4-mL glass vial containing 1 mL of 9 M formamide aqueous solution (40% formamide in volume), and the mixed reaction solution was left still at room temperature under

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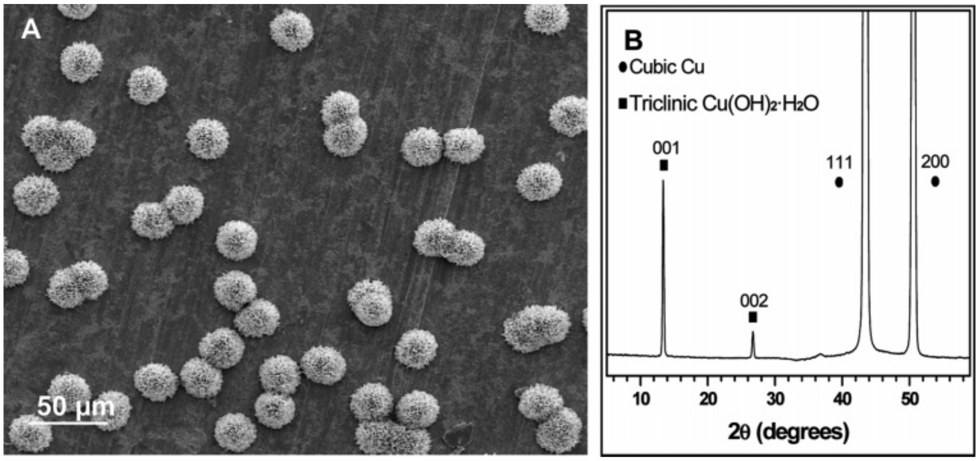

Figure 1. (A) Overview SEM image of pale blue spherulites grown on copper substrate (7.0 × 7.0 × 0.127 mm) for 6 days in 1 mL of 9 M formamide aqueous solution. (B) X-ray diffraction pattern of dendritic crystals on copper substrate with a high surface coverage. In addition to the strong diffraction peaks from cubic copper substrate, characteristic diffraction peaks at 13.38° and 26.73° correspond to (001) and (002) planes of monoclinic copper hydroxide, respectively.

atmospheric environment for 10 days. It is known that natural oxidation of copper metal by naturally dissolved oxygen in water is very slow due to the surface oxide layer.[13,14] However, in the presence of formamide, this spontaneous oxidation reaction can be accelerated drastically. Cu^{2+} ions were released continuously from copper foil into formamide solution while oxygen is reduced ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$). The released copper ions can be immediately captured through the coordination with formamide molecules to form copper complex ions as reported in the literature ($Cu + {}^1/_2O_2 + H_2O + 4HCONH_2 \rightarrow [Cu(HCONH_2)_4]^{2+} + 2OH^-$),[15] which will be transformed into 3D dendritic copper hydroxide on substrate slowly. The copper foil was then taken out, followed by washing with ethanol/deionized water, and dried in air before characterization. In addition, a similar synthetic procedure was also used to prepare shell-decorated dendritic architectures in the presence of 0.5 mM glycine.

Characterization. The size and morphology of $Cu(OH)_2$ nanostructures were examined by JEOL JSM-6700 field-emission scanning electron microscope (SEM). The X-ray diffraction pattern of copper hydroxide was recorded by Bruker AXS GADDS X-ray diffractometer. The crystalline structure of nanosheets was analyzed by means of JEOL 3010 transmission electron microscope (TEM). The TEM samples were prepared by dispersing copper hydroxide nanosheets onto TEM copper grids, which were removed tenderly from copper substrates. The growth process of copper hydroxide nanostructures was studied through monitoring the temporal evolution of atomic concentration of copper in reaction solution during the growth period of 10 days. The copper concentrations were measured by inductively coupled plasma−atomic emission spectrometry (ICP−AES; Optima 3000, Perkin-Elmer).

Results and Discussion

Complex biominerals usually consist of the most common Ca-, Si-, and Fe-based minerals.[1,16] The first copper-based biomineral (copper hydroxide chloride) with an extraordinary resistance to abrasion was recently discovered in the worm jaws, which were decorated with a thin capping layer of oriented polycrystalline nanofibers.[17] Since it is difficult to prepare highly crystalline copper hydroxide under normal chemical reaction conditions, we have developed a synthetic approach to complex copper hydroxide minerals that proceeded accordingly by simply immersing a piece of pure copper foil into 9 M formamide aqueous solution. When the reaction solution was left still at room temperature for 6−10 days, the solution color changed gradually from colorless into light blue, indicating the formation of $[Cu(HCONH_2)_4]^{2+}$ complex ions, as was determined in the literature.[15] With increasing reaction time, the resulting formamide−copper complexes can be transformed into copper hydroxide crystals on substrate slowly. Consequently, many pale-blue spherulites grew onto the copper surface over time as revealed by a low-magnification scanning electron microscopy (SEM) (Figure 1A). Single particles have a round shape and a uniform size of ~26 μm, and peanut- or dumbbell-like particles were formed when two particles merged together. Other shapes were also produced by integrating three or more particles altogether. The structure and composition of the spherulites confirmed by means of X-ray diffraction measurement are triclinic layered copper hydroxide hydrate, $Cu(OH)_2 \cdot H_2O$ (JCPDS No. 42-638) (Figure 1B).

Surprisingly, a beautiful dendritic crystal flower appeared when one of the single spherulites in Figure 1 was further magnified. The highly branched architecture is completely made up of uniform nanosheets, as shown in Figure 2A. A semispherical 3D morphology in the oblique view of the inorganic flower (Figure 2B) indicates the radial and dendritic growth at a similar rate in all directions on substrate (refer to the text hereinafter). Together with the top and lateral views, the cross-section view in Figure 2C confirms that the highly porous structure with ultrathin nanosheets ~40 nm in thickness is identical throughout the dendritic crystal. The highly crystalline nature of the nanosheets is revealed by their straight and parallel lattice fringes with a lattice spacing of 0.34 nm between two adjacent (002) planes, as shown in the high-resolution TEM (HR-TEM) image (Figure 2D). To

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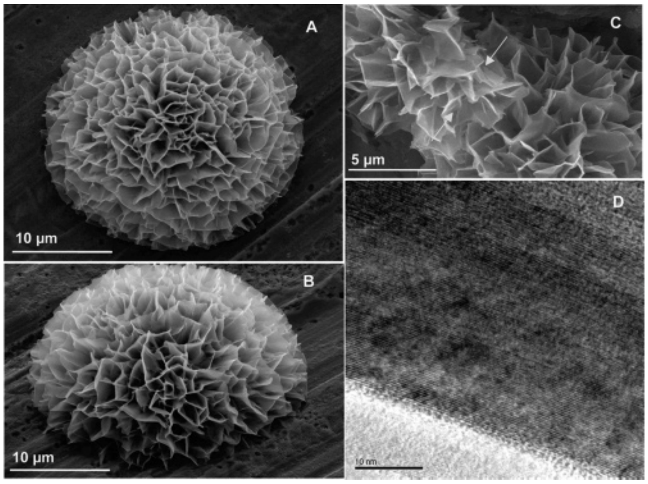

Figure 2. SEM images of 3D dendritic structure of copper hydroxide crystals grown on copper substrate for 6 days in 1 mL of 9 M formamide aqueous solution: (A) top view, (B) oblique view at a tilting angle of 45°, and (C) cross-section view of dendritic crystals. (D) HR-TEM image of a broken nanosheet, which was collected from copper substrate covered with dendritic crystals.

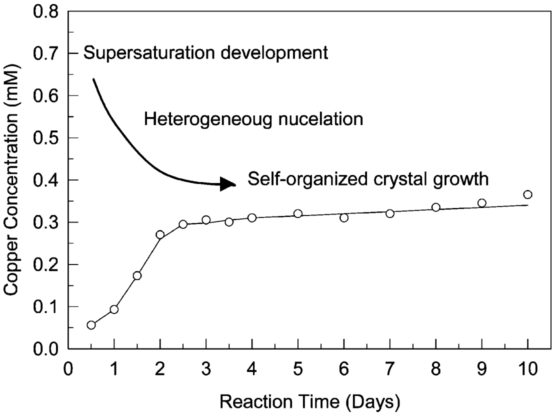

Figure 3. Temporal evolution of copper concentration in 1 mL of 9 M formamide aqueous solution.

the best of our knowledge, this elaborate 3D dendritic nanoarchitecture with high surface-to-volume ratio was first synthesized in the present work.

In the reaction course of 10 days, the temporal evolution of copper concentration in a 1-mL reaction solution was monitored by ICP−AES (Figure 3). The corresponding time-dependent evolution of dendritic crystal morphology was also recorded by SEM simultaneously (Figure 4). As shown in Figure 3, copper oxidation proceeded slowly at early reaction stage by the naturally dissolved oxygen in formamide aqueous solution. As the copper concentration in solution approached 0.30 mM in the first 2 days, very slow heterogeneous nucleation of copper hydroxide took place exclusively, and rodlike nuclei grew on the copper surface sparsely (Figure 4A). A narrow window of copper concentration/supersaturation around 0.30 mM was further maintained in the subsequent process for crystal growth (Figure 3). During the following period from the second to third day, 1D nuclei started branching on the surface and gradually formed 2D dendritic “roots” (∼1 μm in size) as petal rudiment for the following growth of inorganic flowers (Figure 4B). After the slow nucleation process, the 2D dendrites took one more day to grow upward into small dendritic “cores” of ∼8 μm in size (Figure 4C). Upon further increasing time from 5 to 6 to 9 days, the dendritic nanosheets continued to sprout or emanate from the cores and eventually expanded into fully developed 3D dendritic architectures of ∼16, 26, and 38 μm in diameter, respectively (Figure 4D−F). Meanwhile, it should be noted that the heterogeneous nucleation and growth is dominant during the formation of dendritic crystals, because corresponding homogeneous nucleation and growth in solution were not observed by means of TEM. In addition to formamide, organic ligands with bidentate amino groups such as ethylenediamine were also used, but they failed to make regular nanostructures of copper hydroxide due to their strong coordination capability to copper ions. COOH-terminated ligands such as acetic acid were not suitable for growing copper hydrooxide due to the formation of metal carboxylate.

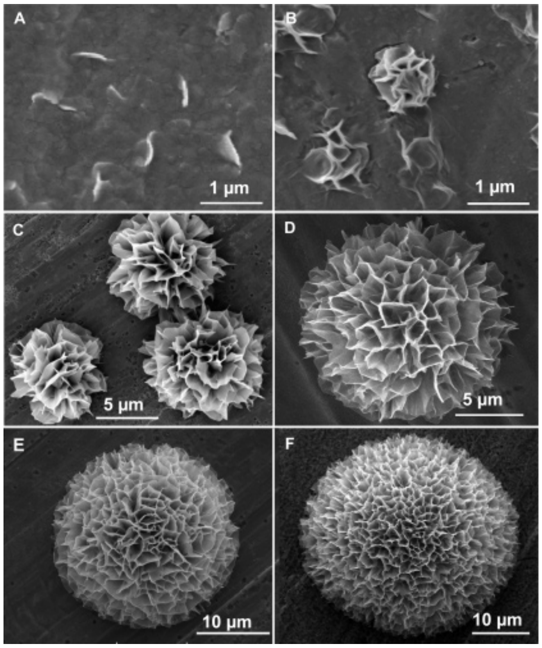

Figure 4. Time-dependent evolution of dendritic crystal morphology at different growth stages for 2 days (A), 3 days (B), 4 days (C), 5 days (D), 6 days (E), and 9 days (F), respectively.

Well-controlled complex morphologies are usually difficult to be produced by directly mixing two incompatible solutions of metal salts because of a rapid decrease in supersaturation and further depletion of reaction nutrients in a short period of time. For example, when equimolar sodium hydroxide was mixed with a copper salt like $CuCl_2$ in a reaction solution, immediate fast precipitation of copper hydroxide with highly reduced growth rate results in a rapid formation of poorly controlled morphology. It is known that double-jet methods can be used to retain sustained supersaturation by continuously replenishing nutrients. However, the continuous disturbance of the reaction solution and the continuous introduction of the impurity of the counterions of the copper ions from copper salts often leads to an unpredictable change in crystal morphology. In the present synthetic approach, pure copper ions can be supplied statically to retain sustained supersaturation via the natural oxidation of metal copper during a long period of time, up to 10 days. As opposed to the previous solution-based synthesis, the high rate of crystallization and continuous environmental distur-

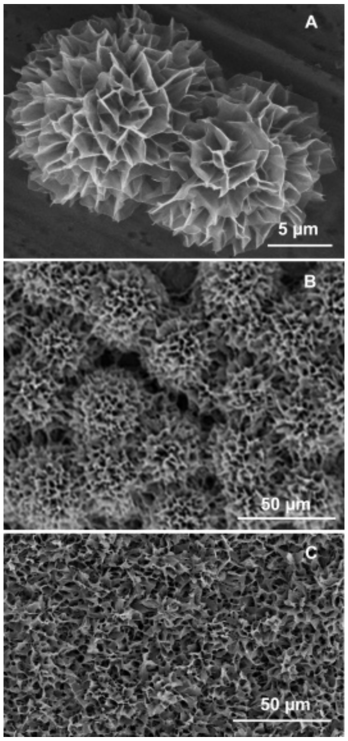

Figure 5. Reaction-volume-controlled self-organized growth of highly porous dendritic architectures. (A) SEM image of a dumbbell-like dendritic crystal produced in the 1-mL reaction system after 6 days. (B) SEM image of dendritic porous network produced in the 0.5-mL reaction system after 6 days. Upon increasing time up to 10 days, a bicontinuous filmlike inorganic scaffold was gradually formed while the contour of the dendritic crystals disappeared, as revealed in the SEM image (C).

bance can be avoided for the slow and progressive growth of elaborate nanoarchitectures. On the other hand, as copper ions prefer square coordination with hydroxyl ions, the resulting extended chains can be connected into 2D layers through the coordination of hydroxyl ions to d$_{z^2}$ orbitals of copper atoms, which can be further stacked into layered copper hydroxide through the interaction of hydrogen bonds.[19] As formamide molecules can coordinate with copper atoms on the crystal surface, the growth is inhibited in the direction perpendicular to the (001) crystal surface, resulting in flexible nanosheets that could readily intermesh each other to form a 3D dendritic porous structure.[20]

As shown in Figure 5A, two neighboring dendritic crystals can further expand themselves and eventually intermesh with each other to merge into an interconnected porous structure of nanosheets in their boundary area.[3,16] No separate or isolated nanosheets were observed in the boundary as well. Meanwhile, a higher density of crystal flowers was further developed on copper substrate by reducing the volume of the reaction solution. When the solution volume was reduced from 1.0 to 0.5 mL, a much denser array of dendritic crystals with a uniform size of $\sim$35 μm covers the surface of copper substrate after the self-organized crystal growth for 6 days (Figure 5B). This indicates that the density level of dendritic crystals on the copper surface is dependent on the reaction volume. With a relative smaller volume, solvated Cu^{2+} species can reach the supersaturation level necessary for spontaneous heterogeneous nucleation in a much shorter period of time (much less than 2 days). This shortened induction time for nucleation can lead to the formation of a relative larger number of nuclei on substrate, which can result in a higher density array of dendritic crystals on substrate accordingly. With further increasing time, the contour of dendritic spheres gradually disappears, leading to a uniform film with a bicontinuous porous network (Figure 5C).

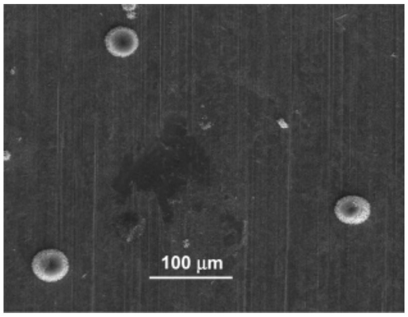

Figure 6. SEM image of shell-ornamented, dendritic spherulites of copper hydroxide grown on copper substrate for 8 days in 1 mL of 9 M formamide aqueous solution containing 0.5 mM glycine.

Meanwhile, it is known that the biomolecules for determining or controlling the morphologies and microstructures of copper-based mineral phase (copper hydroxide chloride) are specific proteins, which are dominated by two major amino acids, glycine (63.2%) and histidine (32.5%), as reported.[17] In the present work, the simplest amino acid, glycine (99.0%, Aldrich), was thus chosen to further control and modulate the crystal growth behavior of dendritic copper-based crystals. After a piece of copper foil was immersed into 9 M formamide aqueous solutions containing 0.5 mM glycine, the metal copper was oxidized slowly by naturally dissolved oxygen in solution at room temperature. With the increase of reaction time, solution color changed gradually from colorless into light blue, indicating the formation of copper complexes.[15,18] Once copper concentration/supersaturation was reached and stabilized at $\sim$0.4−0.5 mM as determined by ICP−AES, complex dendritic copper hydroxide began to crystallize on copper substrate. After crystal growth for 8 days, it is surprising that shell-capped dendritic nanoarchitectures ($\sim$38 μm, Figure 6), instead of the dendritic structure itself, were produced on copper substrate, indicating that the glycine molecules strongly modified the morphology.

Morphology development of the high-order, shell-ornamented nanoarchitectures at different growth stages was monitored by SEM as shown in Figure 7A−C. In the presence of glycine, 3D dendritic architectures with highly porous network structure of nanosheets (Figure 7A) can also be grown on substrate after the growth for 6 days. However, there is an obvious modification effect on the structure of the obtained 3D dendritic crystals in the presence of glycine. The resulting branched nanosheets ($\sim$20 nm in thickness) are much thinner than the ones produced in the absence of glycine ($\sim$40 nm in thickness). Obvious scrolling or curling effects at the edge of the flexible nanosheets were observed

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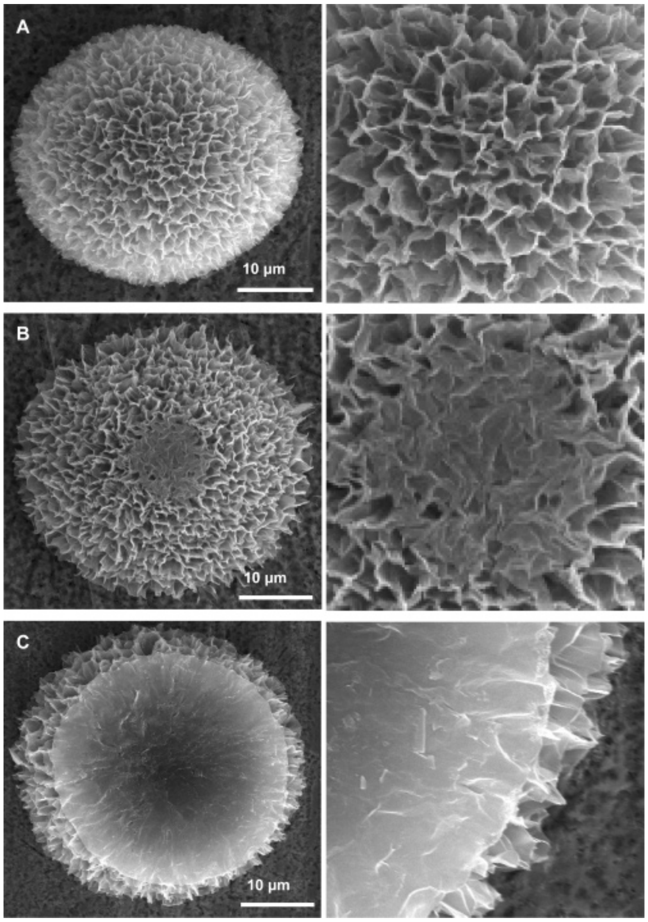

Figure 7. Temporal evolution of dendritic crystal morphology by SEM at different growth time of 6 days (A), 7 days (B), and 9 days (C), respectively. Corresponding enlarged structures are shown in the right images.

clearly due to the ultrathin nature of the dendritic nanosheets.[20] Another visible modification can be seen from the higher density of nanosheets and the smaller size of pores within dendritic architectures. Upon further increasing the growth time up to 7 days, interestingly, a thin layer of round membrane started to grow at the top of dendritic sphere (Figure 7B). The membrane thickness is much thinner than that of the nanosheets in the underlying dendritic sphere. The ultrathin membrane looks almost transparent, so we can clearly see the pores in the dendritic sphere. By continuously prolonging the growth time, the membrane extended itself to form shell-ornamented dendritic architectures along the curved surface, which can also be confirmed by the thickness gradient of shell from center (thick) to edge (thin) as indicated by the image contrast (Figure 7C). It is noted that the surface-capped shell and the underlying radial nanosheets of dendritic sphere were combined and merged altogether.

Copper hydroxide is well-known to have a layered structure. Due to the binding affinity of formamide molecules to copper atoms on the crystal surface,[15,17] the growth is largely inhibited in the direction perpendicular to the (001) crystal surface to form ultrathin nanosheets of ~40 nm in thickness (Figure 2). As compared with formamide ($HCONH_2$), glycine molecules with two functional groups (NH_2CH_2COOH) have higher binding affinity to copper atoms,[18] leading to the formation of much thinner nanosheets. When nanosheets become thin enough (~20 nm in thickness), they start scrolling naturally at the edge of the nanosheets to further decrease the branching growth rate of the nanosheets. After 7 days, secondary nucleation and crystal growth subsequently occurred on the top of the dendritic architecture as “substrate” to form a thin layer of shell-like film. The current results emphasized that glycine molecules can exhibit a significant modifying effect on the branching growth of crystals. The ability to perform such morphological transformations holds promise for creating more complex nanostructured materials.

In conclusion, a progressive production of 3D dendritic nanoarchitectures built up of ultrathin nanosheets has been demonstrated in the absence of self-assembled templates or matrixes. Adjacent dendritic crystals can further expand themselves and eventually merge into continuous porous networks. High-order shell-ornamented dendritic nanoarchitectures can also be fabricated when simple glycine molecules are used as organic additives. Although the formation mechanism of 3D dendritic crystals has yet to be fully understood, this present work shows a perspective that the elaborate self-organized dendritic structures may be chemically synthesized and further decorated into shell-ornamented dendritic crystals under nearly sustained supersaturation. This novel, facile strategy reported herein is being further explored to create complex forms with extremely high surface-to-volume ratio for new applications and brings new insights into the underlying mineralization mechanisms of complex nanoarchitectures in the natural and synthetic world. In addition, dendritic structures of copper hydroxide can also be converted at elevated temperature into copper oxide that could show some unique catalytic properties in many reactions of industrial importance.

Acknowledgment. This work was supported by the Institute of Materials Research & Engineering and the National University of Singapore.

CM048436R