

Assembling Synthesis of Barium Chromate Nano-superstructures Using Eggshell Membrane as Template

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The branch-like, feather-like BaCrO₄ nano-superstructures were synthesized with bioactive eggshell membrane as directing and assembly template. Studies on the two products revealed that they formed through the self-assembly of nanoparticles, and that the optical properties of the products were different from BaCrO₄ bulk materials.

Key Words : Superstructure, Nanomaterials, Template, Barium chromate

Introduction

Synthesis of inorganic materials with specific size and morphology has recently attracted a lot of interest because of the potential to design new materials and devices in various fields such as catalysis, medicine, electronics, ceramics, pigments and cosmetics.¹⁻⁵ T. Adamski first reported an extra-slow precipitation technique of X-shaped and hexagonal plates and other, more complicated, forms of barium chromate particles as early as 1961.⁶ Later on, higher-ordered BaCrO₄ structures such as long chains and filaments,⁷ funnel-like superstructure,⁸ and nanofibers superstructure^{9,10} have been successfully prepared. These methods employed in the formation of BaCrO₄ crystal with controlled morphologies mainly include AOT reverse micelle^{7,9} method and double-hydrophilic block copolymers (DHBCs)^{8,10} method. But the use of a natural bio-membrane template to prepare barium chromate nano-superstructure has not been reported. Herein, using bioactive eggshell membrane as template, we have prepared branch-like and feather-like BaCrO₄ nano-superstructures. The two products formed through the self-assembly of nanoparticles, and these barium chromate products with such morphologies have not been reported. This research not only provides a novel route for the formation of nano-superstructure, but also has some value for exploring the mechanism of biosynthesis. Furthermore, the products have distinctly different optical properties from BaCrO₄ bulk materials.

Experimental Section

The outer shell of a fresh eggshell was discarded, and the remains were washed with deionized water to obtain the eggshell membrane for use. Then the eggshell membrane was fastened in a container to separate it into two horizontal compartments, into which were added 20 mL of 0.1 mol/L K₂CrO₄ solution and 20 mL of 0.1 mol/L BaCl₂ solution respectively. 0.5-2 wt% C₁₂H₂₅SH was put in two compart-

ments respectively (or C₁₂H₂₅SH was absent). Thereafter, the reaction container was kept at room temperature for 10 hours. The BaCrO₄ products were obtained.

The morphologies of products were observed through transmission electron microscopy (TEM) and scanning electron microscopy (SEM), and optical properties were studied by Fourier transform infrared spectroscopy (FT-IR). The products were dispersed in alcohol to mensurate their UV-Vis and fluorescent properties with Agilent 8453 UV-Vis spectroscopy and Perking Elmer LS-55 fluorescent spectroscopy.

Results and Discussion

Morphologies of Products. When the C₁₂H₂₅SH was absent, the TEM (Figure 1A) images of products showed that they were branch-like nano-superstructures; each small branch was also branch-like, which indicated a self-similar structure.¹ The whole lengths of branch were between 6 μm and 10 μm, consisting of nanoparticles with diameters of 40-70 nm which could be observed from Figure 1B. The electron diffraction (ED) lattice of the selected region suggested that the nanoparticles were single crystals.

When the 0.5-2 wt% C₁₂H₂₅SH was added into the

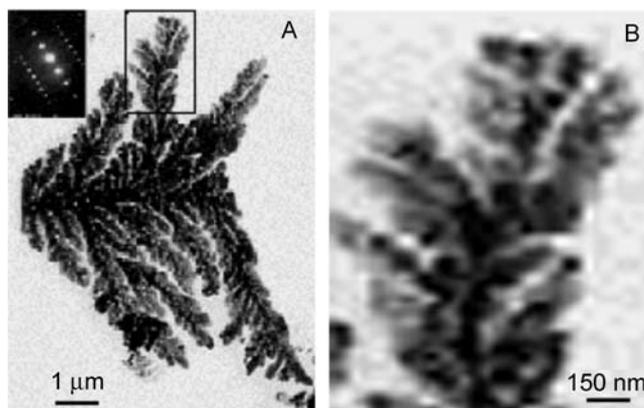


Figure 1. TEM images of branch-like BaCrO₄ nano-superstructure.

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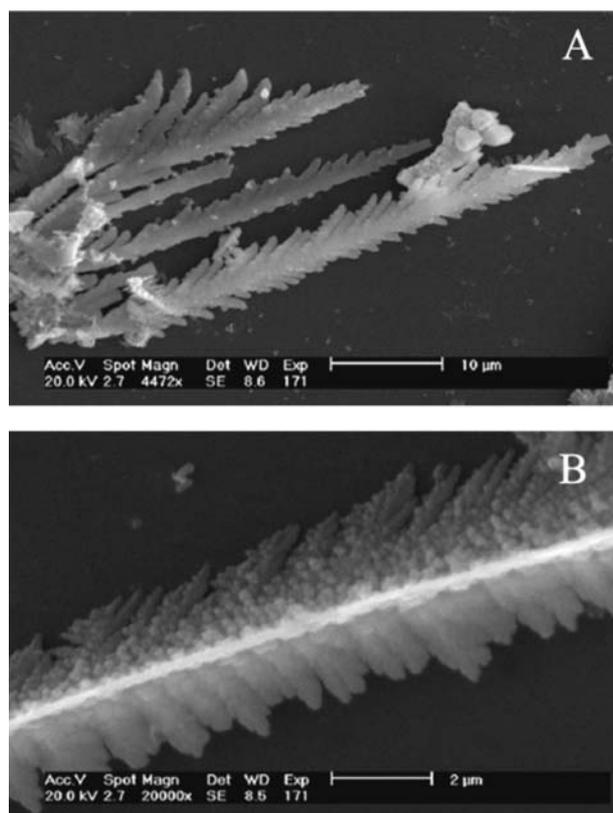


Figure 2. SEM images of feather-like BaCrO₄ superstructures.

solution, the SEM image in Figure 2A showed that the product exhibited a feather-like appearance with numerous bars grown on both sides of a shaft. In general, the feather was between 30 μm and 50 μm in length and ranging from 3 μm to 5 μm in width. The high magnification image in Figure 2B suggested that the product was formed by nanoparticles with diameters of 30-60 nm. The branch-like and feather-like BaCrO₄ superstructures have not been reported by now.

n-dodecanethiol has both hydrophobic and hydrophilic domains, the hydrophilic groups may adhere to eggshell membrane surface through the hydrogen bonding with OH, C=O, NH etc. of eggshell membrane, so it can act together with eggshell membrane. Additionally, the distribution of long hydrophobic carbon chains can also influence the growth of products. So *n*-dodecanethiol was selected as a representative additive organic reagent. In this case, other organic compounds with special groups, such as OH, C=O, NH, can also be used in this system. The suitable concentration of C₁₂H₂₅SH for the formation of BaCrO₄ superstructures ranged from 0.5-2 wt%. Lower concentrations resulted in the reduction of product yield, whereas further increasing the concentration of C₁₂H₂₅SH may strongly hamper ion transfer as no products were obtained. Suitable reaction time was about 10 h. A reaction time below 6 h may result in the incomplete growth of products, as shown in Figure 3A (aging for 3 h), whereas reactions longer than 14 h may lead to the increase in the size of products (in Figure 3B, aging for 16 h) and the breakage of eggshell membrane.

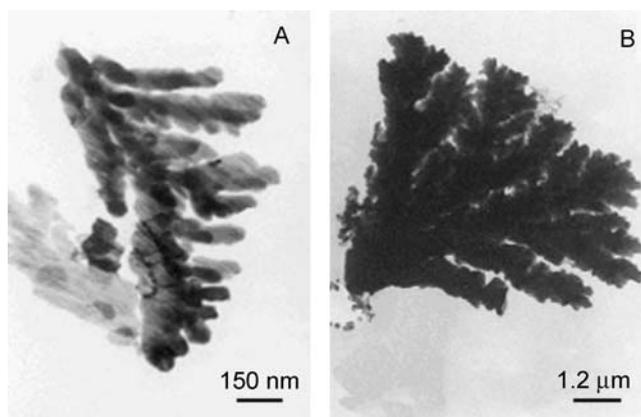


Figure 3. TEM image of BaCrO₄ products at different reaction times (A. 3 h, B. 16 h).

Substituting semipermeable collodion membrane for the eggshell membrane in the absence of C₁₂H₂₅SH, no nano-superstructure was obtained; the obtained products was an irregular large structure, which indicated that the functional groups in eggshell membrane were of great importance to the formation of products.

Discussion of Mechanism. The scanning electron microscope (SEM) of the eggshell membrane is shown in Figure 4A. The eggshell membrane has an interlaced microporous structure. This structure of eggshell membrane can control

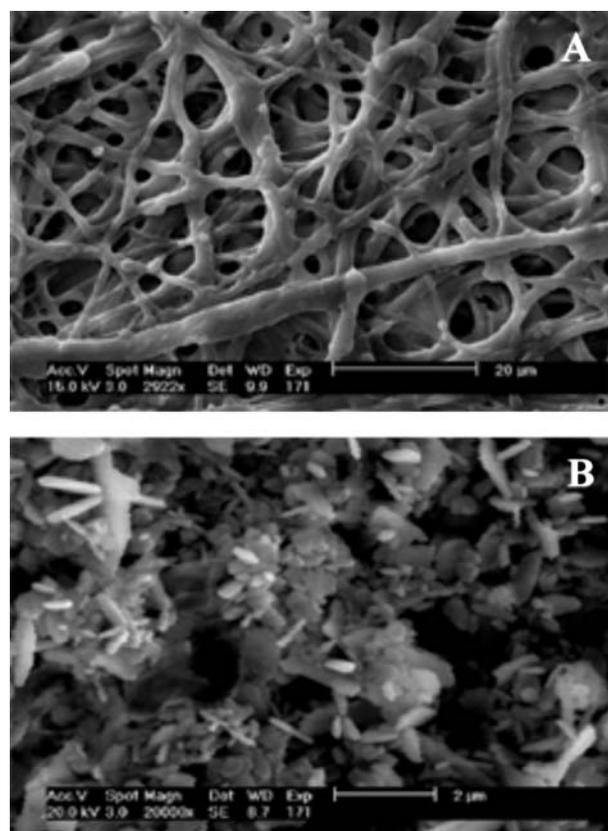


Figure 4. SEM Patterns of eggshell membrane surface (A) and bulk materials (B).

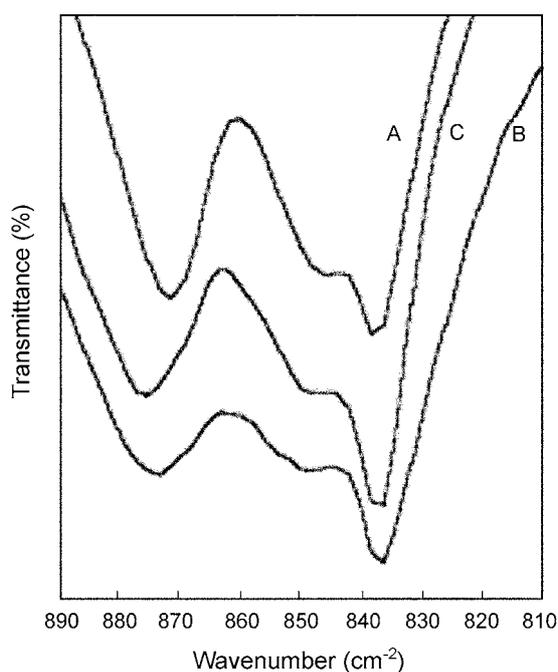


Figure 5. IR spectra of products (A. bulk material; B. branch-like; C. feather-like).

the transport of ions, making Ba^{2+} and CrO_4^{2-} diffuse to the other side respectively. The membrane plays a pivotal role in the biomineralization of eggshell. The eggshell membrane mainly consists of collagen, glycoprotein and proteoglycan.¹¹⁻¹³ These macromolecules contain ionic hydrophilic and hydrophobic domains. The hydrophilic ends may adsorb Ba^{2+} ions and provide suitable sites for the nucleation and the growth of BaCrO_4 nanoparticles. The intermolecular and intramolecular non-chemical effects among the macromolecules, such as hydrogen bonding and the electrostatic effect, could orientate these macromolecules, this may lead to extend these macromolecules and then induce the assembly of nanoparticles. The *n*-dodecanethiol was adhered to the eggshell membrane surface through hydrogen bonding with OH, C=O, NH etc. of eggshell membrane. As a result, the assembly of nanoparticles was influenced. In other words, BaCrO_4 nanoparticles was formed firstly, and then assembled to BaCrO_4 feather-like nano-superstructure through the orientation direction effect of eggshell membrane and *n*-dodecanethiol.¹³⁻¹⁶ Finally, the products were formed around the channel of eggshell membrane and fell off from the eggshell membrane by the effects of some interaction forces such as gravitation.

Optical Properties of Products. When the excitation wavelength was 310 nm, the emission wavelength of bulk materials was 440 nm (Figure 6A), but the branch-like product emitted at 435 nm while feather-like products emitted at 425 nm (Figure 6B, C). UV-Vis spectra of products were also different from bulk materials. The absorption wavelength of bulk materials was at 426 nm (Figure 7A), whereas branch-like and feather-like products absorbed respectively at 381 nm and 374 nm (Figure 7B, C),

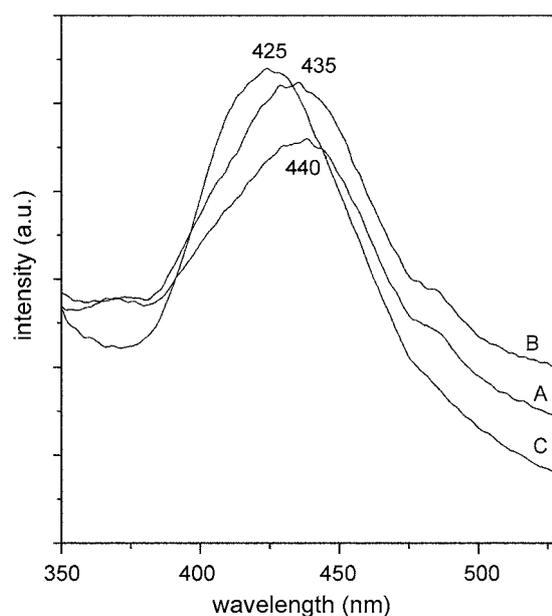


Figure 6. Spectra fluorescence of products (Excitation wavelength at 310 nm, A. bulk material; B. branch-like structure; C. feather-like structure).

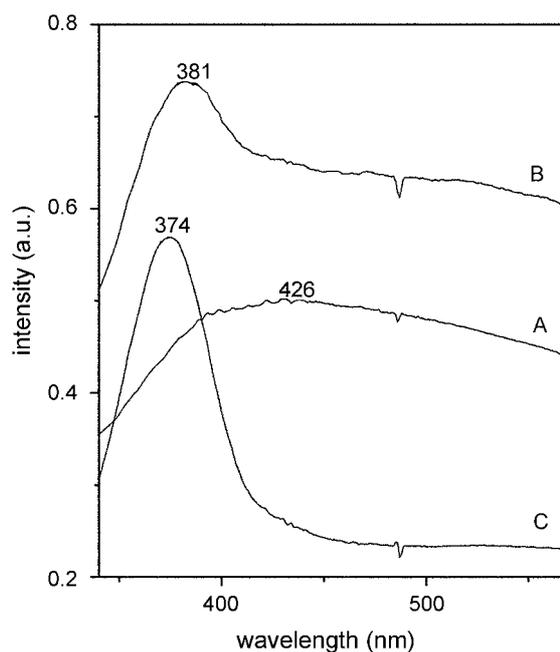


Figure 7. UV-Vis Spectra of products (A. bulk material; B. branch-like structure; C. feather-like structure).

which “blue-shifted” 45 nm and 52 nm respectively compared with bulk materials. These may be formed by the quantum size effect and the bandgap change of nanoparticles that constituted branch-like and feather-like structure.¹⁷ Furthermore, the shapes of UV-Vis absorption spectrum were consistent with the size distribution of nanoparticles,¹⁸ indicating that the sizes of the nanoparticles were comparatively uniform.

Conclusion

In summary, the research reveals that, by the cooperative control and directing of the eggshell membrane and organic reagents, BaCrO₄ biomimetic nano-superstructures with branch-like and feather-like morphologies are obtained, and the products show different optical properties from bulk materials. Although it requires in-depth research on the formation mechanism of BaCrO₄ nanoparticles and the final different morphologies, the method is simple and controllable, and this paper provides a novel biomimetic synthesis method for the formation of interesting superstructures of other inorganic materials.

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References

1. Yu, S. H.; Cölfen, H.; Antonietti, M. *J. Chem. Eur.* **8**, 2937, 2002.
 2. Sun, X. M.; Li, Y. D. *J. Chem. Eur.* **9**, 2229, 2003.
 3. Peng, Q.; Dong, Y. J.; Deng, Z. X.; Li, Y. D. *Inorg. Chem.* **2002**, *41*, 5249.
 4. Kim, F.; Kwan, S.; Akana, J.; Yang, P. *J. Am. Chem. Soc.* **2001**, *123*, 4360.
 5. Gao, F.; Lu, Q. Y.; Zhao, D. Y. *Nano Lett.* **2003**, *3*, 85.
 6. Adamski, T. *Nature* **1961**, *190*, 524.
 7. Li, M.; Schnablegger, H.; Mann, S. *Nature* **1999**, *402*, 393.
 8. Yu, S. H.; Antonietti, M.; Cölfen, H.; Hartmann, J. *Nano Lett.* **2003**, *3*, 379.
 9. Li, M.; Mann, S. *Langmuir* **2000**, *16*, 7088.
 10. Yu, S. H.; Cölfen, H.; Antonietti, M. *Adv. Mater.* **2003**, *15*, 133.
 11. Ajikumar, P. K.; Lakshminarayanan, R.; Ong, B. T.; Valiyaveetil, S.; Kini, R. M. *Biomacromolecules* **2003**, *4*, 1321.
 12. Yang, D.; Qi, L. M.; Ma, J. M. *Adv. Mater.* **2002**, *14*, 1543.
 13. Hincke, M. T.; Gautron, U. J.; Panheleux, M. J.; Garcia-Ruiz, M. D.; McKee, Y. N. *Matrix Biol.* **2000**, *19*, 443.
 14. Fernandez, M. S.; Moya, A.; Luis, L.; Luis, A. J. *Matrix Biol.* **2001**, *19*, 793.
 15. Shi, H. T.; Qi, L. M.; Ma, J. M.; Cheng, H. M. *J. Am. Chem. Soc.* **2003**, *125*, 3450.
 16. Shi, H. T.; Qi, L. M.; Ma, J. M.; Cheng, H. M. *Chem. Commun.* **2002**, *16*, 1704.
 17. Peng, Q.; Dong, Y. J.; Deng, Z. X.; Li, Y. D. *Inorg. Chem.* **2002**, *41*, 5249.
 18. Pesika, N. S.; Stebe, K. J.; Searson, P. C. *Adv. Mater.* **2003**, *15*, 1289.
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