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# Top-Down Solid-Phase Fabrication of Nanoporous Cadmium Oxide Architectures

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***Abstract:*** In this Article, we have demonstrated one-step solid-phase transformation from high-quality cadmium carbonate microcrystals into highly nanoporous cadmium oxide. The high crystal quality of cadmium carbonate is critical for the successful fabrication of porous nanoarchitectures with predetermined morphology and well-controlled internal structure. This novel strategy has a good potential to prepare nanoporous materials at a large scale by using perfect monolithic carbonate crystals, and it is also useful to synthesize different nanoporous materials on metal-oxide-coated substrates. Meanwhile, this simple thermal transformation of cadmium carbonate into porous structures has further been extended to convert calcium carbonate into such porous structures.

## Introduction

Large complex inorganic nanostructures have been widely synthesized using vapor-phase deposition and liquid-phase templating/self-assembling of subunits via physical, chemical, or biological interactions.[1−4] To simplify their complex synthetic processes, the solid-phase approach could be employed as a simple alternative. In this paper, we have demonstrated one-step solid-phase transformation (thermal decomposition) from cadmium carbonate microcrystals into highly nanoporous cadmium oxide at a micrometer or larger scale while retaining identical outer morphology but with tailored internal nanostructures. It is known that porous solids are of great technological importance and are opening up new opportunities in catalysis and separation technology due to their ability to interact with gases and liquids not only at the surface but also throughout the bulk.[5−7]

The currently used preparation strategies usually involve the initial formation of large assemblies of organic surfactants as templates to make porous inorganic structures for applications.[6,7] In this research, our simple top-down preparation of porous nanoarchitectures from large microcrystals can also be achieved without the aid of such organic templates. Experimentally, a liquid-phase chemical-deposition technique has been introduced first for slow growth of high-quality cadmium carbonate microcrystals, which is a requisite for the successful fabrication of porous cadmium oxide nanoarchitectures with predetermined morphology and well-controlled internal structure. This novel solid-phase fabrication strategy has a good potential to prepare nanoporous bulk materials throughout the entire body by using perfect monolithic carbonate crystals. The highly nanoporous cadmium oxide on substrates/supports is of interest to greatly enhance its surface-to-volume ratios for catalysis and sensing applications or to be potentially used as transparent conducting oxide with extremely large surface area for photovoltaic or electro-optical devices. This novel strategy has also been extended to synthesize porous calcium carbonate for potential applications in bone repair/regeneration.

## Experimental Section

**Materials.** Formamide (99.8%, Merck), cadmium nitrate tetrahydrate (98%, Aldrich), calcium nitrate tetrahydrate (99%, Sigma-Aldrich), sodium carbonate (99.95−100.05%, Sigma-Aldrich), and urea (99.0−100.5%, Sigma-Aldrich) were used as received. Cadmium foils (100 × 100 mm, 99.9%, Aldrich) with a thickness of 0.25 mm were cut into small pieces (7 × 7 mm), which were further ultrasonically washed in absolute ethanol before use. Cadmium oxide films were deposited on glass substrates by a conventional RF magnetron-sputtering system.[8]

**Liquid-Phase Deposition of Cadmium Carbonate Microcrystals on Substrates.** A piece of cadmium foil was laid flat in a 10-mL glass vial containing 3 mL of a 0.2 M formamide aqueous solution. After aerating with carbon dioxide for 10 min, the vial was put in a 250-mL bottle that had been purged with carbon dioxide thoroughly. The system was sealed and then kept in an oven at a constant temperature of 65 °C. After 24 h, the cadmium foil was taken out and washed with ethanol before characterization. In another preparation, one glass substrate (7 × 7 mm) coated with cadmium oxide film was flatly immersed in 3 mL of a 0.2 M formamide aqueous solution in a glass vial in the presence of two cadmium foils (standing vertically against wall), and the remaining procedure followed the same as above.

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(1) Dai, Z. R.; Pan, Z. W.; Wang, Z. L. *Adv. Funct. Mater.* **2003**, *13*, 9−24.
(2) Sounart, T. L.; Liu, J.; Voigt, J. A.; Hsu, J. W. P.; Spoerke, E. D.; Tian, Z.; Jiang, Y. *Adv. Funct. Mater.* **2006**, *16*, 335−344.
(3) Cölfen, H.; Mann, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 2350−2365.
(4) Kalsin, A. M.; Fialkowski, M.; Paszewski, M.; Smoukov, S. K.; Bishop, K. J. M.; Grzybowski, B. A. *Science* **2006**, *312*, 420−424.
(5) Davis, M. E. *Nature* **2002**, *417*, 813−821.
(6) Lu, A. H.; Schüth, F. *Adv. Mater.* **2006**, *18*, 1793−1805.
(7) Jansen, J. C., Stöcker, M., Karge, H. G., Weitkamp, J., Eds. *Advanced Zeolite Science and Applications*; Elsevier: Amsterdam, 1994.
(8) Yu, H. D.; Zhang, Z. P.; Han, M. Y.; Hao, X. T.; Zhu, F. R. *J. Am. Chem. Soc.* **2005**, *127*, 2378−2379.

10.1021/ja066884p CCC: $37.00

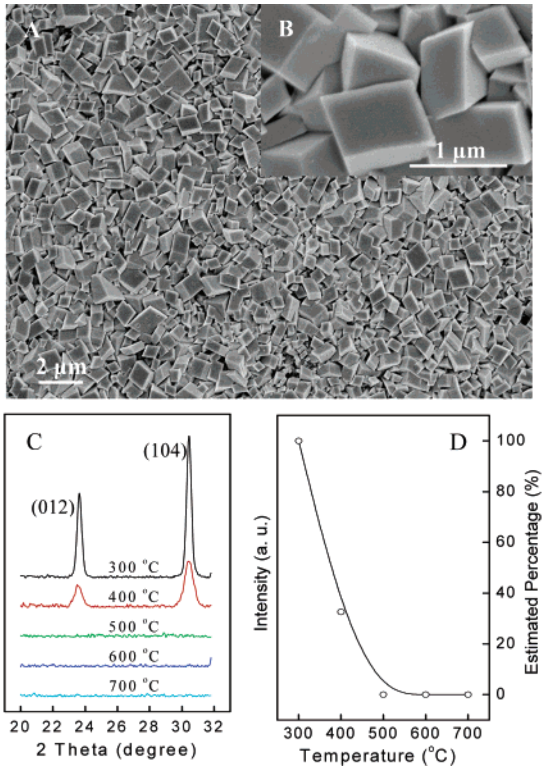

***Figure 1.*** (A) Low-magnification and (B) high-magnification SEM images of closely packed cadmium carbonate microcrystals on a cadmium substrate at 65 °C for 24 h in a 0.2-M formamide aqueous solution in an environment of carbon dioxide. (C) XRD analysis for temperature-dependent decomposition of cadmium carbonate microcrystals at temperatures ranging from 300 to 700 °C. (D) The (104) peak intensity as a function of reaction temperature, indicating the percentage of the remaining cadmium carbonate in thin films after 0.5-h decomposition at different temperatures.

**Liquid-Phase Precipitation of Cadmium Carbonate Microcrystals in Solutions.** A 10-mL glass vial containing 3 mL of a 0.1 M cadmium nitrate aqueous solution was first aerated with carbon dioxide at room temperature for 10 min. The vial was then sealed in a 250-mL bottle filled with carbon dioxide and heated in an oven at a constant temperature of 65 °C for 2 h. After the mixture was cooled to room temperature, white product was collected by centrifugation and further washed twice with water.

Alternatively, 40 mL of a 10 M urea aqueous solution that had been heated at 80 °C overnight was quickly added into 40 mL of a 2 mM cadmium nitrate aqueous solution in a 100-mL beaker. After magnetic stirring for 10 s, the mixed solution was kept in an oven at a constant temperature of 65 °C for 8 h. After the mixture was cooled to room temperature, white product was collected by centrifugation and further washed twice with water.

**Thermal Decomposition of Cadmium Carbonate Microcrystals.** The temperature of a furnace (Nabertherm, model N 11/H with a program controller, Germany) was first increased to a predetermined temperature (300−700 °C). After being stabilized for 0.5 h, as-prepared cadmium carbonate microcrystals in a crucible were put into the furnace and then heated for a certain period of time. The as-decomposed product was then taken out of the furnace at the same temperature for further characterization.

## Results and Discussion

**Liquid-Phase Deposition of High-Quality Cadmium Carbonate Microcrystals on Cadmium Substrates.** As shown in Figure 1A, well-faceted microcrystals were densely grown on a cadmium substrate at 65 °C for 24 h in a 0.2-M formamide aqueous solution under an environment of carbon dioxide. The formation of cadmium carbonate microcrystals was confirmed by XRD analysis (Supporting Information). The closely packed microcrystals with flat surfaces and sharp edges/corners are clearly shown in the high-magnification SEM image in Figure 1B. The high-quality cadmium carbonate microcrystals were slowly grown on substrates by slow replenishment of cadmium ions from the source of cadmium foil in the presence of a small amount of basic formamide molecules.[9,10]

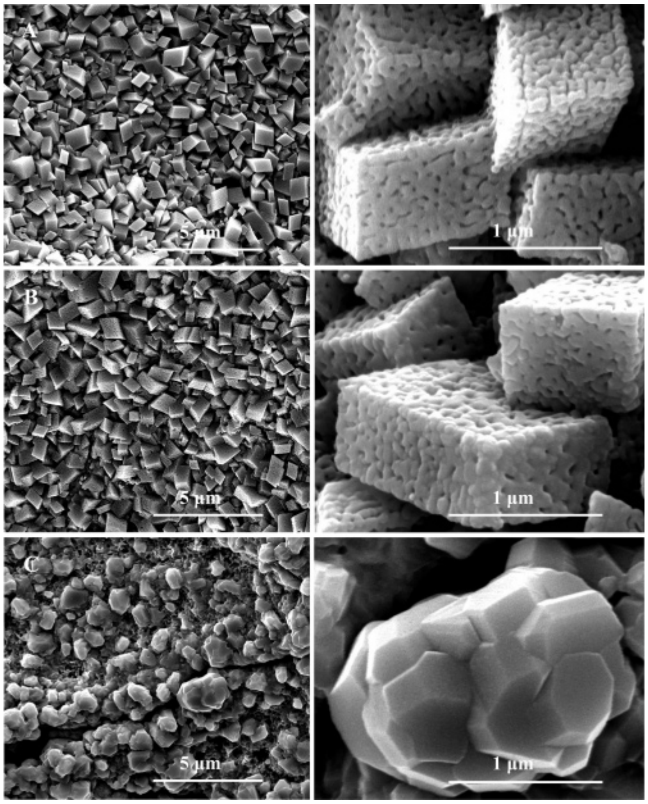

***Figure 2.*** SEM images of as-decomposed cadmium oxide nanostructures after 0.5-h heating at (A) 500, (B) 600, and (C) 700 °C, respectively. The corresponding enlarged structures are shown in the right images.

**Temperature-Dependent Decomposition of Cadmium Carbonate Microcrystals into Nanoporous Cadmium Oxide Architectures.** Figure 1C shows the XRD patterns of the as-decomposed products of the as-obtained cadmium carbonate microcrystals after 0.5-h heat treatment at 300, 400, 500, 600, and 700 °C, respectively. To avoid overlapping of XRD diffraction with cadmium and cadmium oxide, only the two strong (012) and (104) peaks of cadmium carbonate are selected to monitor the temperature-dependent decomposition process. Overall, cadmium carbonate microcrystals are very stable at 300 °C, and they are only partially decomposed at 400 °C after 0.5-h heat treatment. At the temperatures above 500 °C, cadmium carbonate microcrystals can be fully decomposed to cadmium oxide quickly (also refer to the Supporting Information). The above results are also given in Figure 1D by monitoring the (104) peak intensity as a function of temperature, corresponding to the percentage of the remaining cadmium carbonate in thin films after 0.5-h decomposition at different temperatures (calculated on the basis of the changes in peak intensity for

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(9) Zhang, Z. P.; Shao, X. Q.; Yu, H. D.; Wang, Y. B.; Han, M. Y. *Chem. Mater.* **2005**, *17*, 332−336.
(10) Zhang, Z. P.; Yu, H. D.; Shao, X. Q.; Han, M. Y. *Chem.-Eur. J.* **2005**, *11*, 3149−3154.

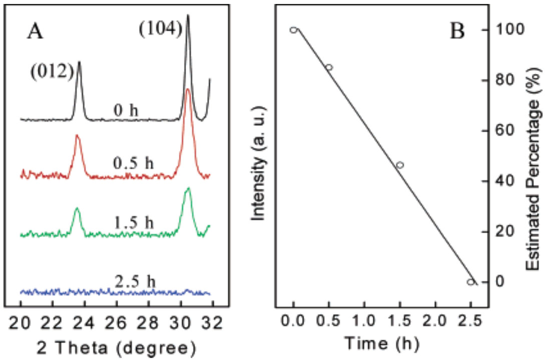

***Figure 3.*** (A) XRD analysis for time-dependent decomposition of cadmium carbonate microcrystals at 400 °C up to 2.5 h. (B) The (104) peak intensity as a function of reaction time and the percentage of the remaining cadmium carbonate in thin films after decomposition at different reaction times.

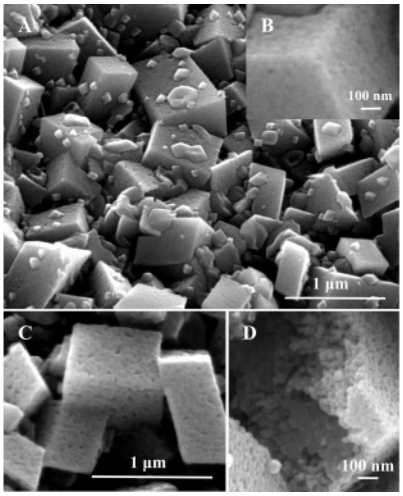

***Figure 4.*** SEM images of as-decomposed product after heating at 400 °C for (A,B) 0.5 h and (C,D) 2.5 h, respectively.

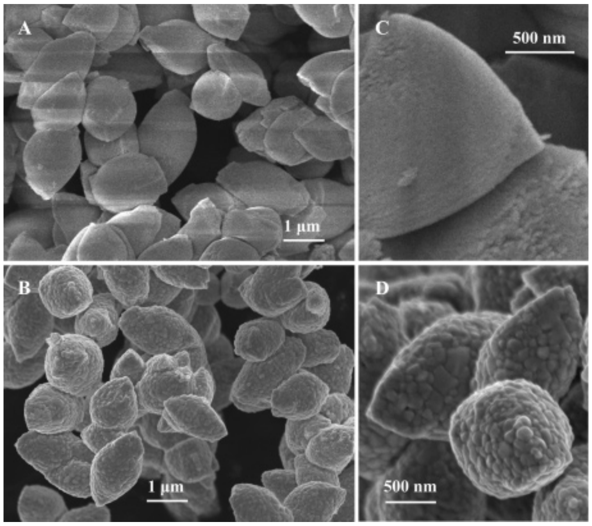

***Figure 5.*** SEM images of (A) cadmium carbonate precipitate in a solution saturated with carbon dioxide and (B) their as-decomposed product after 0.5-h heating at 500 °C. The corresponding enlarged structures are shown in (C) and (D).

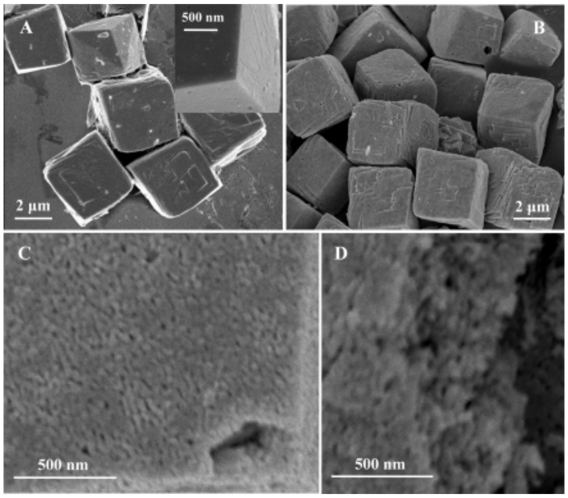

***Figure 6.*** SEM images of (A) cadmium carbonate precipitate in a solution of urea and (B) their as-decomposed product after 0.5-h heating at 500 °C. (C) A high-magnification SEM image of the as-decomposed product with a cross-section view as shown in (D).

cadmium carbonate before and after 0.5-h thermal decomposition). After the complete decomposition at the temperatures of 500 and 600 °C, the well-faceted cadmium carbonate microcrystals were fully transformed into nanoporous cadmium oxide architectures with no significant changes in the overall morphology, as shown in Figure 2A and B. At the higher temperature of 700 °C, the carbonate microcrystals cannot be transformed into nanoporous structures (Figure 2C) due to recrystallization during the decomposition of cadmium carbonate into cadmium oxide.

**Time-Dependent Decomposition of Cadmium Carbonate Microcrystals into Nanoporous Cadmium Oxide Architectures.** As cadmium carbonate can be decomposed slowly at its decomposition temperature (~400 °C), it is thus appropriate for one to continuously monitor thermal decomposition intermediates for understanding the formation of nanoporous cadmium oxide architectures. The time-dependent decomposition of cadmium carbonate at 400 °C in Figure 3A shows that the (104) XRD peak intensity of as-decomposed product decreases slowly and eventually disappears with the increase of time from 0, 0.5, 1.5, to 2.5 h. A linear relationship between the peak intensity and reaction time in Figure 3B indicates a continuous decomposition with a constant rate. Correspondingly, the time-dependent morphology evolution was monitored as well. After 0.5-h decomposition, some small cadmium carbonate crystals appeared on the intermediate product (Figure 4A and B) due to the incomplete decomposition of cadmium carbonate and the obvious shrinkage of cadmium carbonate to cadmium oxide by releasing carbon dioxide. The remaining undecomposed cadmium carbonate clearly stands on the surfaces rather than the corners or edges of product, indicating that the sharp corners/edges of cadmium carbonate microcrystals are more reactive to be transformed into cadmium oxide. After 2.5 h, the cadmium carbonate microcrystals were fully transformed to nanoporous cadmium oxide (Figures 4C and 3). Figure 4D reveals the inner nanoporous structure of cadmium oxide throughout the whole microparticle, consisting of numerous nanoparticles.

**Crystal-Quality-Dependent Decomposition for Solid-Phase Fabrication of Nanoporous Materials.** A different cadmium source, cadmium nitrate rather than cadmium foil, was used to prepare cadmium carbonate in aqueous solution that had been aerated/saturated with carbon dioxide. Grain-like cadmium carbonate microparticles (Figure 5A) were produced quickly, and they were further thermally transformed into cadmium oxide

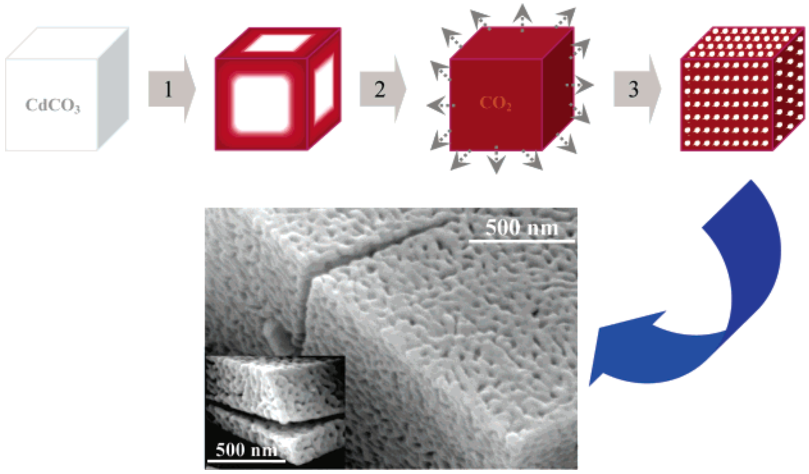

***Figure 7.*** A schematic illustration for the formation of nanoporous cadmium oxide architectures through one-step thermal decomposition of high-quality cadmium carbonate microcrystals. It involves the initial formation of cadmium oxide at active edges/corners (1), continuous growth of cadmium oxide from outer to internal of cadmium carbonate microcrystals (2), and eventual formation of nanoporous cadmium oxide architectures (3). The lateral and transverse cross-section SEM images of nanoporous network of cadmium oxide prepared at 500 °C for 0.5 h.

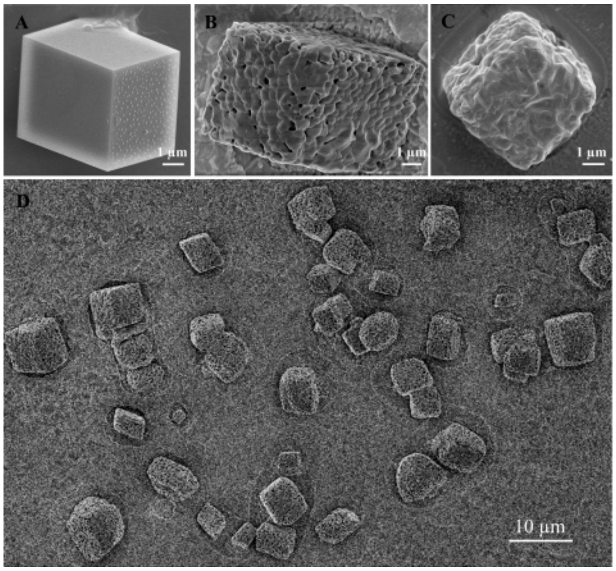

***Figure 8.*** SEM images of calcium carbonate microcrystals (A) before and after 0.5-h heat treatment at (B) 900 °C and (C) 1000 °C, respectively. (D) Low-magnification SEM image of calcium carbonate microcrystals after heat treatment at 900 °C.

with unchanged shape (Figure 5B) at 500 °C, while their smooth surfaces were changed to rough ones that were surrounded with many small particles (Figure 5B and D). However, it is not what we expected because no porous structure was formed. Similarly, cadmium nitrate was also used to prepare cadmium carbonate, while carbon dioxide was slowly replenished by the thermal decomposition of urea in an aqueous solution. As shown in Figure 6A, cubic cadmium carbonate microcrystals were slowly produced at 65 °C after 8 h. After thermal decomposition of cadmium carbonate microcrystals at 500 °C, nanoporous cadmium oxide was produced as we expected (Figure 6B and C). The nanoporous structure is also throughout the whole cadmium oxide microparticles as revealed in the cross-section view of as-decomposed products (Figure 6D). Thus, we can summarize that quick precipitation cannot produce well-faceted cadmium carbonate microcrystals, and the resulting grain-like cadmium carbonate with poor crystal quality may be the major reason not to form nanoporous cadmium oxide architectures.

Thermal decomposition of low-quality cadmium carbonate microcrystals cannot form nanoporous cadmium oxide, indicating the resulting shrinkage itself from cadmium carbonate to cadmium oxide by releasing carbon dioxide is not the only reason to produce the nanoporous structures. On the contrary, the thermal decomposition of high-quality cadmium carbonate microcrystals can readily form nanoporous cadmium oxide architectures, and it is explained by the controlled release of carbon dioxide ($CdCO_3 = CdO + CO_2\uparrow$). As illustrated in Figure 7, high-quality cadmium carbonate microcrystals can be thermally decomposed to form cadmium oxide from more active sharp corners/edges to flat surfaces of cadmium carbonate crystals with increasing time. The newly formed cadmium oxide layer is very densely coated on the perfect cadmium carbonate microcrystals, and it can effectively block the release of internally born carbon dioxide. This is just like that carbon dioxide is sealed in a box, and more and more carbon dioxide can be gathered in the box until the pressure is increased to a certain point to break the box for the formation of a small void/pore. Many such processes can concurrently/continuously occur from the outer to inner part of the crystals until continuous channels are eventually formed, while cadmium carbonate is completely decomposed to cadmium oxide. For poor-quality cadmium carbonate microparticles, there are many defects throughout the whole body. Once carbon dioxide is born during thermal decomposition of cadmium carbonate, it can be released through these defects easily, resulting in no porous structures.

**Liquid-Phase Deposition of Cadmium Carbonate Microcrystals on Cadmium Oxide-Coated Substrates and Solid-Phase Fabrication of Nanoporous Cadmium Oxide.** Besides cadmium substrate, cadmium carbonate microcrystals can also be grown on various substrates that are coated with a thin layer of cadmium oxide. Practically, two pieces of cadmium foils were used to slowly release cadmium ions into a 0.2-M formamide aqueous solution for subsequent growth of cadmium carbonate microcrystals on the surface of a cadmium oxide-coated substrate. Cadmium carbonate microcrystals were densely grown on the entire glass substrate, and they were further decomposed to nanoporous cadmium oxide architectures with unchanged shape after heating at 500 °C for 0.5 h (Supporting Information). It is of technological interest to coat nanoporous cadmium oxide on various substrates such as catalyst supports and semiconductors for catalysis and electronic applications, respectively.

**High-Temperature Transformation of Calcium Carbonate Microcrystals into Nanoporous Calcium Carbonate Architectures.** In addition, highly crystallized calcium carbonate microcrystals can also be grown readily by following the liquid-phase precipitation procedure of cadmium carbonate microcrystals (Supporting Information). The resulting calcium carbonate crystals can be thermally decomposed into calcium oxide at a temperature that is somewhat higher than the decomposition temperature of calcium carbonate, ~825 °C (while releasing carbon dioxide). After 0.5-h heat treatment at 900 °C, the calcium carbonate microcrystals were successfully transformed (Figure 8A to B) into porous nanostructures as revealed in Figure 8B and D. It is interesting to know that the resulting porous nanostructures are calcium carbonate as characterized by XRD (Supporting Information, calcite-type structure before and after heat treatment). This is because calcium oxide can be formed at a higher temperature than the decomposition temperature of calcium carbonate; however, after the heat-treated sample was taken out of the furnace, the reactive calcium oxide started to react with carbon dioxide in air during the subsequent cooling process, and eventually transformed into porous calcium carbonate nanostructures. The one-step thermal transformation of high-quality calcium carbonate crystals into porous calcium carbonate structures offers a simple way to make bone fillers/porous scaffolds or improve porous coatings of implants for bone regeneration/repairing with great integration of tissues.[11,12] Meanwhile, when the temperature was increased to 1000 °C, the resulting calcium carbonate through the intermediate state of reactive calcium oxide was recrystallized to form nonporous structures (Figure 8C), and this is consistent with the studies of cadmium carbonate microcrystals.

## Conclusion

A novel solid-phase fabrication approach has been developed to prepare highly nanoporous cadmium oxide architectures via one-step thermal decomposition of high-quality cadmium carbonate microcrystals, which can be slowly grown on cadmium substrates or cadmium oxide-coated substrates of any kind. The slow liquid-phase synthesis of high-quality carbonate microcrystals is a requisite for the subsequent successful fabrication of nanoporous cadmium oxide. The crystal-quality-dependent fabrication of nanoporous cadmium oxide has been tested with cadmium carbonate microcrystals with different crystal qualities. This simple solid-phase fabrication provides an alternative to synthesize different porous nanostructures with specific predetermined morphology and well-controlled internal structure. The one-step thermal transformation of cadmium carbonate into porous structures has also been extended to convert calcium carbonate into such porous structures. Importantly, it has a good potential for large-scale fabrication of highly porous nanomaterials.

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**Supporting Information Available:** XRD patterns of cadmium carbonate and calcium carbonate microcrystals before and after decomposition. SEM images of cadmium carbonate microcrystals before and after decomposition. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Petite, H.; Viateau, V.; Bensaid, W.; Meunier, A.; de Pollak, C.; Bourguignon, M.; Oudina, K.; Sedel, L.; Guillemin, G. *Nat. Biotechnol.* **2000**, *18*, 959−963.

(12) Sachlos, E.; Gotora, D.; Czernuszka, J. T. *Tissue Eng.* **2006**, *12*, 2479−2487.