

A Designed Single-Step Method for Synthesis and Structural Study of Organic–Inorganic Hybrid Materials: Well-Ordered Layered Manganese Oxide Nanocomposites

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Recent studies have indicated that layered materials not only possess interesting properties themselves¹ but also are very important precursors toward synthesizing nanoscale porous materials, nanotubes, and catalysts.² Among these layered materials, intercalated layered manganese oxides (LMOs) have attracted the attention of researchers due to their unique mixed valency of manganese oxide host, tunable pore sizes, and versatile intercalated guest species, such as lithium ion/polycations, TiO₂, polymers, silica, transition metal oxides, and Keggin ions,³ for improved electrochemical performance, photosensitivity, and catalytic activity/selectivity.

Organic–inorganic hybrid layered manganese oxide nanocomposites are important precursors for mesoporous manganese oxides.⁴ In addition, the large interlayer spacing in these materials facilitates additional intercalation processes and also rapid ion exchange.⁵ The development of efficient preparations of these materials is desirable for applications of these systems.

Birnessite⁶ has been widely used as a typical precursor to synthesize pillared or organic–inorganic hybrid LMO nanocomposites. However, due to the high charge density of birnessite, complicated procedures with 3–4 steps were required to make such systems.^{3b,c,7} These conventional methods consequently led to several disadvantages: (1) methods are energy and time consuming (~7–22 days), (2) high pressures and temperatures were used,⁸ and (3) poor ordering of resultant layered structures was observed after numerous synthetic steps.⁹

Here, we designed a single-step method for rapid (1 day) preparation of well-ordered organic–inorganic hybrid LMO nanocomposites under mild conditions. This shortcut not only significantly simplifies the conventional 3–4 steps into one step but allows the possibility of large scale production of these materials due to the mild synthetic conditions, performed without high pressures and temperatures. These syntheses were designed using the following strategies: (1) rapid redox reaction between MnO₄[−] and Mn²⁺ ions under mild conditions; (2) a cetyltrimethylammonium ion (CTA⁺) was chosen due to its well-known self-assembling properties to enhance the degree of ordering of layered structures; and (3) alkali metal ions (e.g., Na⁺, K⁺, or Rb⁺) were totally avoided since these ions might compete with the intercalation of CTA⁺ ions to reduce the order and spacings of layered structures. More importantly, to improve the thermal stability of organic–inorganic hybrid LMO nanocomposites, Keggin ions were introduced in this one-step process to stabilize the layered structure under different thermal conditions.

The X-ray diffraction (XRD) patterns of the as-synthesized hybrid materials are shown in Figure 1. A typical pattern of the layered

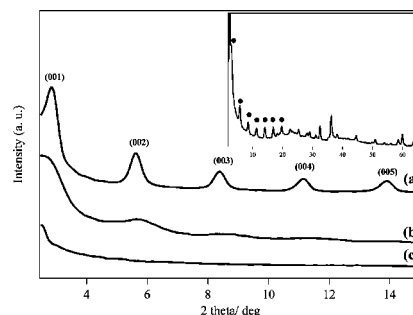


Figure 1. XRD patterns of the as-synthesized organic–inorganic hybrid LMO nanocomposites with pH = (a) 12, (b) 7, and (c) 2. Well-ordered and typical 00 l basal series in (a) were observed from (001) to (005). Insert: Wider angle XRD measurement of (a), showing the 00 l basal series peaks from (001) to (007) as indicated by black dots.

structure with a very well-ordered 00 l basal series is observed in Figure 1a. The peaks can be indexed as (001), 3.08 nm, (002), $d/2$, 1.55 nm, (003), $d/3$, 1.05 nm, (004), $d/4$, 0.79 nm and (005), $d/5$, 0.65 nm, respectively, and the wide angle XRD pattern (insert) indicates a basal series from (001) up to (007). These patterns demonstrate that the well-ordered layered structure can be developed by the rapid redox reaction between Mn²⁺ and Mn⁷⁺ at room temperature. Such ordering in these materials is unprecedented.

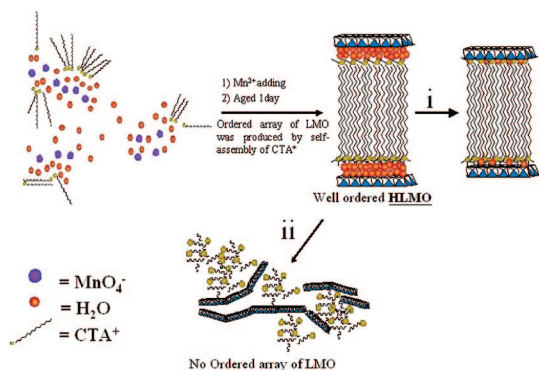
Different pH conditions significantly affect the formation and ordering of layered structures (Figure 1a, b, and c). The XRD patterns demonstrate that the ordering of the layered structure is highly dependent on pH conditions; basic conditions (pH = 12 or higher) are preferred in this process. Although the layered structures prepared at pH < 7 are not as well developed as those at pH = 12, the layered material is indeed produced at pH = 7 by showing a typical but broadened pattern in Figure 1b. However, no layered structure could be obtained under acidic conditions (pH = 2). Based on our previous studies,¹⁰ the critical intermediate, feitknechtite (MnO(OH)), for the preparation of the final layered structure prefers to be formed under basic conditions, which may explain why basic conditions are favorable for the synthesis of these well-ordered hybrid materials (Supporting Information).

A noticeable evolution of the layered structure of these nanocomposites during various drying times under ambient conditions, defined as “mild drying”, is shown in Figure S-1. These XRD results show a clear trend that the interlayer spacing decreases gradually from 3.08 to 2.64 nm after 2 weeks of drying. Recent work^{3e,7b} reported that the difference between estimated and experimental basal spacings could be a result of the water layers inside the organic pillared LMO (Supporting Information). Gradual evaporation of the interlayer water molecules could cause the interlayer spacing to decrease without a significant effect on the ordered layered

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Scheme 1. Formation Process of Organic–Inorganic Hybrid Layered Manganese Oxide Nanocomposites^a



^a Self-assembly of the CTA^+ ions assists in the formation of well-ordered hybrid LMO via redox reactions. (i) These materials are dried under ambient (mild drying), and the gradual evaporation of water molecules decreases the interlayer spacing. (ii) The “hard drying” (100 °C, 24 h) is applied leading to the collapse of the ordered layered structure.

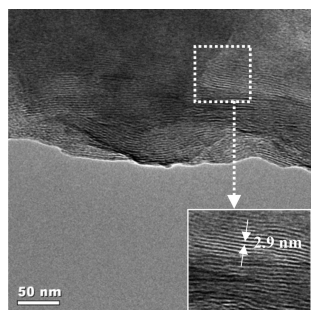


Figure 2. HR-TEM image of intercalated manganese oxide showing a layered structure. The white dashed line square area corresponds to the insert under higher magnification. The insert has an interlayer spacing of 2.9 nm.

structures. In contrast to ambient drying, “hard drying” conditions due to drying at 100 °C for 24 h has been applied to the hybrid material. As shown in Figure S-1e, the collapse of the ordered layered structure is observed under hard drying conditions.

The formation scheme of the hybrid LMO nanocomposites is shown in Scheme 1. Unlike the results of intercalation of primary alkylamines,¹¹ our studies of CTA^+ hybrid material indicate that drying conditions and resultant water-loss rates are important for maintaining the excellent ordering of the layered structure. Under mild drying, the rate of water loss is relatively slow leading to a gradual decrease of the interlayer spacing. However, hard drying gives a faster rate of loss of water causing a rapid decrease in interlayer spacing and a collapse of the ordered layered structure.

To increase the thermal stability of the organic–inorganic hybrid LMO, Keggin ions, $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$, have been introduced to modify this one-step procedure to produce Keggin/ CTA^+ ions intercalated into the layered material. This intercalated material is able to undergo the 100 °C hard drying treatment without any significant change of the well-ordered layered structure and gives an interlayer spacing of 2.87 nm (Figure S-3). The *in situ* XRD studies show stability up to 170 to 205 °C (Figure S-4).

The HR-TEM (Figure 2) images show a layered stacked structure with a 2.9 nm interlayer *d*-spacing, consistent with the corresponding XRD results. The elemental study (Figure S-5) of this material by EDX shows that the sample contains Al, which reconfirms the intercalation of aluminum Keggin ions. The intense carbon signal also indicates that CTA^+ ions could be supporting the pillared structure with Al Keggin ions together.

In summary, well-ordered stable organic–inorganic LMO nanocomposites with large basal spacings were successfully prepared by a one-step, rapid method at room temperature. The synthesis period of the designed method is greatly reduced to 1 day as compared with 7–22 days for conventional methods. The wide synthetic pH ranges (pH = 7–12), ambient pressures, and temperatures are suitable for several environment-sensitive applications, such as protein-intercalation research. Preliminary results of the adsorption/exchange capacity tests on these hybrid materials revealed an adsorption/exchange efficiency of >99% in 2 h using Acid Phosphatase¹² (as adsorbate). These intercalated materials have been simply produced by the modified single-step method, demonstrating a future possibility of mixed intercalated layered materials. Current research in utilizing the as-synthesized hybrid and intercalated hybrid LMO as catalysts or precursors for porous materials is ongoing.

Acknowledgment. We acknowledge the support of the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences for support of this research. We also thank Dr. Frank Galasso, Dr. Xiongfei Shen, and Mr. Craig Calvert for helpful suggestions.

Supporting Information Available: Experimental procedures, chemical equations, and characterization results (XRD, SEM, TGA, and EDX). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) Typical conventional processes were (1) to prepare the birnessites as precursors first (ca. 1–5 days, high temperatures or pressure), (2) use strong acid to protonate the synthesized birnessites several times (ca. 3–10 days), and (3) treat the protonated birnessites with organic amine compounds for several days (3–7 days) to obtain organic–inorganic hybrid LMO.
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- (12) The experiment was performed to test the exchange/adsorption capacity of the organic–inorganic hybrid LMO nanocomposites with protein molecules. The enzyme Acid Phosphatase was used to examine the synthesized hybrid materials as part of a biocatalyst. 1 mL of 2 mg/mL solution of Acid Phosphatase in DI water was added to 50 mg of the hybrid materials. The mixture was shaken for 2 h at room temperature and then centrifuged. The supernatant was taken and Bradford assayed for protein content. The analysis showed that >99% of the protein was adsorbed/exchanged into these hybrid materials.

JA805585V