New Approach to the Delamination of Layered Manganese Oxide

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A new method for the delamination of layered manganese oxide is successfully developed in a low-concentration solution of tetramethylammonium hydroxide by an ultrasonic treatment.

Recently, nanosheets derived from functional layered materials have attracted extensive attentions because of their wide applications in the field of nanoscience and nanomaterials, which can be obtained by disintegrating a layered compound into the constituent single layers.[1] The obtained unilamellar crystallites have a thickness of the order of nanometers or smaller, with lateral dimensions of submicro- to micrometer, and they are expected to be used as building blocks for the construction of various functional nanocomposites or nanostructures. Up to date, many functional layered materials such as clay minerals,[2] graphite oxide,[3] phosphates,[4] layered titanates,[5] layered double hydroxides, etc.[6] have been delaminated to their constituent nanosheets with a lot of soft chemical methods. Using the delaminated nanosheets, a wide range of nanoscale materials with various properties and morphologies have been constructed.[7]

Layered manganese oxides are important two-dimensional layered functional materials and are subjected to delamination because the delaminated manganese nanosheets are attracted much attention owing to their unique optical properties associated with a quantum effect and their potential as precursors for thin film devices.[8] We were the first to succeed in the delamination of the layered manganese oxide by intercalation of tetramethylammonium ions followed by water washing.[9] The origins of swelling and the delamination were discussed in terms of attractive and repulsive forces by electrostatic interaction, hydration of interlayer cations, and interlayer hydrogen bonding. Gao et al. reported that nanometer-sized manganese oxides were formed in the intercalation process.[10] Omomo et al. reported the swelling and exfoliation behavior of layered manganese oxide in a solution of tetrabutylammonium hydroxide and the formation and characterizations of unilamellar two-dimensional crystallites of MnO_2.[11] But these delamination methods have a main disadvantage, which is the delamination process from the stacked materials to the colloid nanosheets needs time longer than a week and high concentration of the swelling reagents. Here, we report a new simple approach to delamination of layered manganese oxides, which can be carried out only taking 20 min by an ultrasonic treatment of layered manganese oxide in a low-concentration solution of tetramethylammonium hydroxide.

The precursor, layered manganese oxide, was prepared by the method reported in the literature.[12] A mixed solution of 0.6 M NaOH and 2 M H_2O_2 was poured quickly into a 0.3 M $Mn(NO_3)_2$ solution and stirred for 25 min. The precipitation was then subjected to hydrothermal treatment at 150 °C for 16 h in a 2 M NaOH solution. The obtained precipitate was treated with a 0.1 M HCl solution at 25 °C for 3 days to produce proton-type layered manganese oxide, which had a chemical formula of $Na_{0.02}H_{0.34}Mn_{0.94}O_2 \cdot 0.63H_2O$ and was abbreviated as BirMO(H). BirMO(H) was monitored by X-ray power diffraction (XRD) using a D/Max-3c X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å), using an operation voltage and current of 40 kV and 40 mA, respectively. The obtained BirMO(H) had a layered structure with a basal spacing of 0.73 nm (Figure 1a). BirMO(H) (0.30 g) was treated in a 0.25 M aqueous solution of tetramethylammonium hydroxide (TMAOH), where the amount of tetramethylammonium hydroxide added was five fold that of the exchangeable capacity for BirMO(H) ($TMA^+/H^+ = 5$). The mixed solution was treated for 20 min by ultrasonic treatment (300 W, 40 kHz), a colloid suspension of manganese oxides was obtained. The colloid suspension was collected by centrifugation; the delaminated BirMO slurry was obtained. XRD pattern gives no clear peaks but only an amorphous halo in contrast to that of BirMO(H) (Figure 1b). The absence of BirMO(H) reflections indicates the loss of the original crystalline structure, suggesting that the stacked manganese oxide plates are delaminated to the individual primary plates. The delaminated BirMO slurry was freeze-dried in a liquid nitrogen system by using an ALPHAl-2-type freeze-dried instrument. The restacking of the delaminated manganese oxide nanosheets was occurred accompanied with the freeze-drying process. Because of the intercalation of TMA^+ ions into the interlayer of manganese oxide nanosheets with a single TMA^+ layer, a layered structure with a basal spacing of 0.96 nm reappeared. (Figure 1c). The similar behavior has been observed in our report[9] and Omomo and co-

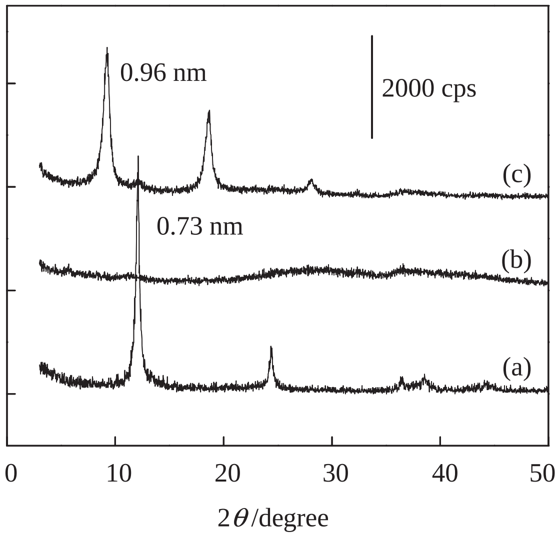

Figure 1. XRD patterns of (a) BirMO(H), (b) delaminated BirMO slurry, and (c) sample (b) freeze-dried.

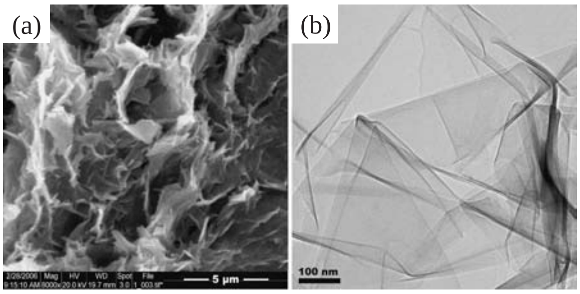

Figure 2. (a) SEM image of freeze-dried delaminated sample, (b) TEM image of the delaminated BirMO slurry.

workers' work,[11] suggesting that the ultrasonic treatment is a fast and effective method for the delamination of layered manganese oxide.

The morphology nature of delaminated and followed by freeze-dried sample was confirmed by SEM (Quanta 200 environmental scanning electron microscopy) imaging. A film-like solid with a glossy surface can be observed (Figure 2a), which is different from that of the precursor BirMO(H),[9] supporting the occurrence of delamination. The transmission electron microscope (TEM) image of the delaminated BirMO slurry shown in Figure 2b also confirms that the delamination has occurred, which is taken with a JEM-3010 transmission electron microscope. Thin transparent platelets of width less than 0.5 μm are easily observed, which is comparable to the crystal dimensions of BirMO(H). The submicrometer- to micrometer-sized nanosheets are contrasting to the "nanosized manganese oxide" with lateral dimensions below 50 nm that has been derived by delamination of birnessite.[10] TEM result indicates that the delamination has occurred at the layer level without destroying the nanosheets by an ultrasonic treatment.

The size of the exfoliated nanosheets was also examined by AFM.[13] The AFM image shows that two-dimensional ultrathin sheets with average lateral dimensions of about 0.5 μm are obtained, although fragments are also observed in small amounts. Some small nanosheets with lateral dimensions of <0.16 μm are occasionally encountered, indicating some breakage or fracture of sheets during the delamination process.

In conclusion, the layered manganese oxide can be simply delaminated in a low-concentration solution of tetramethylammonium hydroxide by an ultrasonic treatment without destroying the layered structural frameworks. This new approach to the delamination of layered manganese oxide has a less time and less pollution, which has the potential to be developed as a general method for the delamination of layered inorganic materials. The delamination process described here opens up a range of possible applications in the preparation of nanocomposites with novel properties and morphologies.

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References and Notes

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13 See Supporting Information.

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