

## Synthesis of a New Layered Manganese Oxide Nanocomposite through a Delamination/Reassembling Process

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A new layered nanocomposite with propylamine-containing silica between the manganese oxide sheets was synthesized for the first time through a delamination/reassembling process. It had a higher ordered stacked structure than the silica-pillared manganese oxide obtained by the conventional intercalation reaction.

Recently, organic/inorganic nanocomposite materials have been the focus of considerable research interest since these materials are proven to exhibit a variety of unique properties arising from the synergies of the inorganic and organic components.<sup>1-3</sup> Layered manganese oxides are important two-dimensional layered inorganic materials because of their unique adsorptive, catalytic, and electrochemical properties.<sup>4</sup> The organic/inorganic nanocomposites based on layered manganese oxides can be obtained by intercalation of organic alkylamines into the interlayer. They can be used as molecular sieves or precursors to synthesize porous manganese oxides.<sup>5,6</sup> However, there have been relatively few reports on the interlayer compounds of manganese oxide. Since the layered manganese oxides have a higher charge density in the interlayer than other layered materials, the intercalation of bulky guests by the conventional pillarizing method is difficult owing to the strong attractive force between the layers. This limits the formation of interlayer compounds of manganese oxide.

The delamination/reassembling process is an alternative route to the synthesis of an interlayer nanocomposite. This process is expected to form interlayer compounds more freely since the delaminated sheets have a higher degree of freedom than the stacked sheets. Delamination techniques have been developed for several classes of layered materials.<sup>7-11</sup> The subsequent reassembling of the delaminated sheets in the presence of bulky guest ions or molecules has produced novel nanocomposite materials.

We first succeeded in the delamination of layered manganese oxide (birnessite) by intercalation of tetramethylammonium ions ( $\text{TMA}^+$ ) followed by water washing.<sup>12</sup> The delaminated manganese oxide is suitable as a starting material for the preparation of layered compounds with specific functional materials in the interlayer of manganese oxide sheets. The present paper describes the preparation of a manganese oxide nanocomposite with propylamine-containing silica in the interlayer by the new route involving a delamination/reassembling process. This new technology is effective and can be used widely for various kinds of guest ions or molecules to develop novel selective adsorbents or cathode materials for lithium batteries.

The formation process is given in Figure 1. The starting material, proton-type birnessite ( $\text{BirMO(H)}$ ) was prepared by the acid treatment of highly crystallized sodium-type birnessite. It has the chemical composition of  $\text{H}_{3.33}\text{Na}_{0.24}\text{Mn}_{12}\text{O}_{24} \cdot 9.6\text{H}_2\text{O}$  and

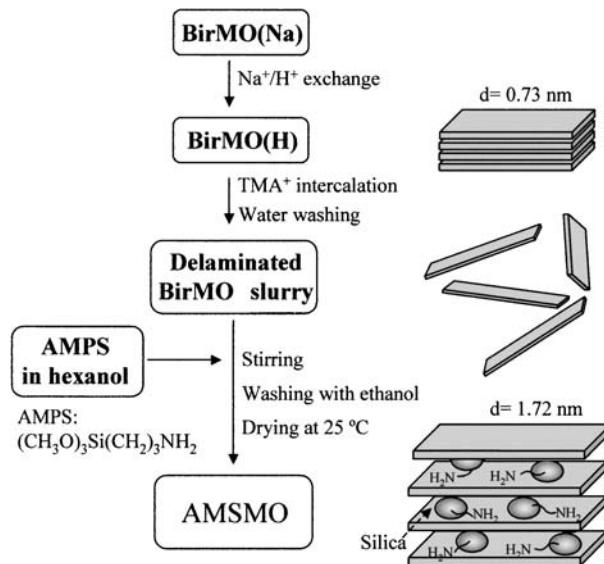


Figure 1. The formation process of nanocomposite, AMSMO.

cation exchange capacity of 2.70 mmol/g. Delamination of  $\text{BirMO(H)}$  was carried out by the method reported previously.<sup>12</sup>  $\text{BirMO(H)}$  (0.2 g) was treated in a 0.35 M aqueous solution of  $\text{TMAOH}$  ( $50\text{ cm}^3$ ) for 7 days at  $25^\circ\text{C}$ . The amount of  $\text{TMAOH}$  added was 25-fold that of the exchangeable capacity of  $\text{BirMO(H)}$ . After soaking, the suspension was centrifuged and a colloidal sediment was washed with  $40\text{ cm}^3$  of distilled water four times to obtain a delaminated  $\text{BirMO}$  slurry. The delaminated  $\text{BirMO}$  slurry (0.2 g) was added to a mixed solution of 1-hexanol ( $30\text{ cm}^3$ ) and 3-aminopropyltrimethoxysilane ( $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$ , AMPS) ( $4.8\text{ cm}^3$ ) and stirred for one day at  $25^\circ\text{C}$ . The 1-hexanol solution was suitable to suppress rapid hydrolysis/precipitation of AMPS during the reaction with the slurry. The molar ratio of the propylamine group of AMPS to protons of  $\text{BirMO(H)}$  was adjusted to 50. The sediment obtained was washed with ethanol and dried for 2 days at  $25^\circ\text{C}$ . The product was abbreviated as AMSMO.

Total carbon (TC) and total nitrogen (TN) contents of AMSMO were measured by gas chromatography with a Sumigraph NCH-21 analyzer. The propylamine and methoxy group contents could be evaluated from the TC and TN contents. The TC/TN ratio was 3.23, which is close to the carbon to nitrogen molar ratio (C/N = 3) of the propylamine group. The Si content was determined as 3.14 mmol/g by ICP spectrometry. The N/Si molar ratio could be calculated as 1.04 and the C/Si molar ratio as 3.37. The Si/Mn molar ratio was evaluated as 0.62. The chemical analysis data shows that the methoxy groups of AMPS are mostly hydrolyzed while the propylamine groups remain unchanged, being chemically bonded to Si atoms. The hydrolyzed form of

AMPS can be written as  $(OH)_3Si(CH_2)_3NH_2$ , while some of the hydroxyl groups may be condensed to form a polymerized silica material.

The X-ray diffraction analysis was carried out using a Rigaku type RINT 1200 X-ray diffractometer. The XRD patterns of starting BirMO(H), delaminated BirMO slurry, and AMSMO are shown in Figure 2. The starting BirMO(H) has a layered structure with a basal spacing of 0.73 nm. The XRD pattern of the delaminated BirMO slurry gives no clear peaks in its wet state: only an amorphous halo is observed. The broad halo can be interpreted as scattering from the manganese oxide nanosheets with irregular arrangement, similar to the case of layered titanic acid.<sup>9</sup> This indicates that the stacked sheets of layered manganese oxide are delaminated into individual primary sheets by  $TMA^+$ -intercalation/water washing. The AMPS treatment of the delaminated BirMO slurry resulted in the reappearance of a layered structure. The XRD pattern of AMSMO shows a new layered phase with a basal spacing of 1.72 nm. Sharp diffraction lines up to the fifth order indicate a highly ordered stacked structure. The pattern is different from that of silica-pillared layered manganese oxide synthesized by the conventional intercalation reaction, in which only a diffraction line was observed.<sup>13</sup> This shows that the present method is favorable for preparing a manganese oxide composite with higher ordered stacked structure. The interlayer spacing can be evaluated as 1.27 nm on the basis of the thickness (0.45 nm) of manganese oxide sheet. The interlayer spacing agrees comparatively well with that (1.46 nm) of AMPS-treated zirconium phosphate.<sup>14</sup> The expansion of the interlayer indicates the intercalation of organic silicates into the interlayer. These results show that the delamination/reassembling reaction progresses soft-chemically involving the intercalation reaction.

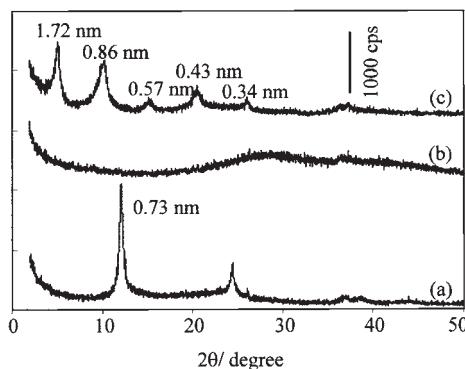


Figure 2. XRD patterns of starting BirMO(H) (a), delaminated BirMO slurry (b), and AMSMO (c).

FE-SEM observation was carried out with a JEOL-type JSM-890 high-resolution scanning electron microscope, as is shown in Figure 3. The reassembled layered structure with a flaky appearance was readily observed for the AMSMO sample. The expanded FE-SEM image inset in Figure 3 shows the layer-by-layer assembled structure. No colloidal particles corresponding to silica particles were observed. SEM and EDAX results showed that Mn and Si elements were distributed homogeneously over the AMSMO particles, and silica-rich particles were not observed obviously. These results suggest that the reassembling process takes place smoothly by air-drying the mixture only. Most of the silicate compound may exist in the interlayer to form a

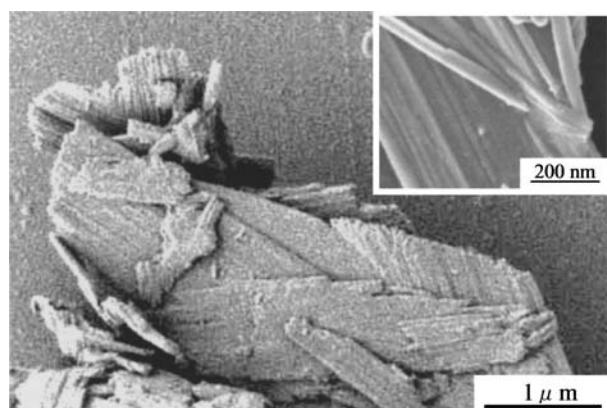


Figure 3. FE-SEM photograph of AMSMO.

nanocomposite.

TG-DTA analysis for AMSMO (on MAC Science thermal analyzer system 001, TG-DTA 2000) showed a broad exothermic peak between 150 and 350 °C, which corresponds to the decomposition of organic materials. The total weight loss between 30 and 400 °C was 32.9%, which was caused by both the weight loss (12.2%) of water molecules existing in the interlayer and the weight loss (20.7%) of the organic materials. The weight loss of the organic materials was close to the amount of the propylamine groups (19.4%) in the interlayer. The presence of propylamine groups is also supported by IR analysis. Bands corresponding to  $NH_2$  deformation vibration ( $1558\text{ cm}^{-1}$ ) and C–N stretching vibration ( $1129\text{ cm}^{-1}$ ) were observed, indicating the presence of propylamine groups in  $NH_2$  form.<sup>14</sup> Stretching frequencies of the O–Si–O bond around  $1038\text{ cm}^{-1}$  and  $CH_2–CH_2$  group vibration around  $1218\text{ cm}^{-1}$  were also observed.

In conclusion, the delamination/reassembling process provides a new simple route to synthesize novel layered manganese oxide nanocomposites with higher ordered stacked structure. The delaminated manganese oxide sheets can form nanocomposites easily by a self-assembling mechanism. The new method is promising for the syntheses of many kinds of functional manganese oxide materials since it can be used for widely different kinds of guests involving bulky ions and molecules.

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#### References and Notes

- 1 J. H. Fendler, *Chem. Mater.*, **8**, 1616 (1996).
- 2 C. Sanchez, G. J. de A. A. Soler-Illia, F. Ribot, T. Lalot, C. R. Mayer, and V. Cabuil, *Chem. Mater.*, **13**, 3061 (2001).
- 3 N. Sukpirom and M. M. Lerner, *Chem. Mater.*, **13**, 2179 (2001).
- 4 Q. Feng, H. Kanoh, and K. Ooi, *J. Mater. Chem.*, **9**, 319 (1999).
- 5 Q. Gao, O. Giraldo, W. Tong, and S. L. Suib, *Chem. Mater.*, **13**, 778 (2001).
- 6 S. Yamanaka, K. Kunii, and Z.-L. Xu, *Chem. Mater.*, **10**, 1931 (1998).
- 7 P. H. Nadeau, M. J. Wilson, W. J. McHardy, and J. M. Tait, *Science*, **225**, 923 (1984).
- 8 G. Alberti, M. Casciola, and U. Costantino, *J. Colloid Interface Sci.*, **107**, 256 (1985).
- 9 T. Sasaki and M. Watanabe, *J. Am. Chem. Soc.*, **120**, 4682 (1998).
- 10 M. M. J. Treacy, S. B. Rice, A. J. Jacobson, and J. T. Lewandowski, *Chem. Mater.*, **2**, 279 (1990).
- 11 F. Leroux, M. Adachi-Pagano, M. Intissar, S. Chauvière, C. Forano, and J.-P. Besse, *J. Mater. Chem.*, **11**, 105 (2001).
- 12 Z.-h. Liu, K. Ooi, H. Kanoh, W. Tang, and T. Tahei, *Langmuir*, **16**, 4154 (2000).
- 13 Z.-h. Liu, K. Ooi, H. Kanoh, W. Tang, X. Yang, and T. Tahei, *Chem. Mater.*, **13**, 473 (2001).
- 14 L. Li, X. Liu, Y. Ge, L. Li, and J. Klinowski, *J. Phys. Chem.*, **95**, 5910 (1991).