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Synthesis and Characterization of SiO_2/TiO_2 Pillared Layered Manganese Oxide

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A novel pillaring procedure without alkylamine or tetraalkylammonium pretreatment has been developed to prepare SiO_2/TiO_2 pillared layered manganese oxide with large surface area. SiO_2/TiO_2 pillared layered manganese oxide is prepared by solvothermal treating H-type layered manganese oxide at 220 °C for 12 h in a mixed solution of absolute ethanol, tetraethylorthosilicate, and titanium isopropoxide. The obtained SiO_2/TiO_2 pillared layered manganese oxide is expected to be a selective catalyst or an improved battery material.

Pillared technology has been applied to prepare porous materials from layered inorganic compounds, and the prepared porous materials can be utilized as catalysts, molecular sieves, selective absorbents, and lithium battery materials, etc.[1–3] Among the available layered inorganic compounds, layered manganese oxide is a classical material because it can be used as molecular sieves, catalysts, battery materials, and precursors for synthesizing porous manganese oxides.[4] Meanwhile, TiO_2 is an interesting semiconductor pillar agent due to its unique photocatalytic performance and electrochemical properties.[5] Therefore, silica and titania (SiO_2/TiO_2) hybrid material is expected to be used in catalysts, lithium ion secondary batteries, and selective adsorbents, and many research efforts have been devoted to the pillaring of TiO_2 into the layered manganese oxide.

In general, the layered pillaring manganese oxide materials can be prepared by two conventional methods, ion exchange–intercalation and exfoliation–reassembly.[6,7] By using the two methods, various inorganic pillaring species such as SiO_2, Al_{13} Keggin ion, TiO_2, or SiO_2/TiO_2 have been intercalated into the interlayer space of layered manganese oxides.[6,8–10] However, these preparation methods have obvious disadvantages that are the pre-expanded treatment by alkylamine or the delaminated reaction by tetraalkylammonium hydroxide needed for the precursor layered manganese oxide, which causes a long preparation procedure and restricts the pillaring technology application. Therefore, a simple preparation method for the pillared materials without alkylamine or tetraalkylammonium pretreatment is expected to be developed. In the present work, a simple method is developed to prepare SiO_2/TiO_2 pillared layered manganese oxide.

Layered manganese oxide was prepared as reported in the literature.[11] 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 precipitate was then subjected to hydrothermal treatment at 150 °C for 16 h in a 2 M NaOH solution; Na-type layered manganese oxide was obtained. Na-type layered manganese oxide was treated with a 0.1 M HCl solution at 25 °C for 3 days to produce a proton-type layered manganese oxide, which is abbreviated as BirMO(H). BirMO(H) (0.2 g) was soaked in a mixed solution of 6 mL of absolute ethanol, tetraethylorthosilicate (TEOS, 4.16 mL), and titanium isopropoxide (TIIP, 1.84 mL). The obtained suspension was then transferred into a 20-mL Teflon-lined stainless steel autoclave, which was sealed and maintained at 220 °C for 12 h. The resultant product was filtered, washed several times with anhydrous ethanol, and dried at room temperature for 1 day. SiO_2/TiO_2 pillared layered manganese oxide material was obtained, which is abbreviated as STPMO.

The powder X-ray diffraction pattern was measured on a D/Max-3c X-ray diffractometer with Cu Kα ($\lambda = 1.5406$ Å), using an operation voltage and current of 40 kV and 30 mA, respectively. SEM images were taken using a Quanta 200 environmental scanning electron microscope operated at the accelerating voltages of 20 kV. Nitrogen adsorption–desorption was carried out on a Micromeritics ASAP 2010 surface area and porosity analyzer.

The precursor, BirMO(H) has a layered structure with a basal spacing of 0.73 nm along the *c* axis, with lattice water and exchangeable H^+ ions in the interlayer space.[6] The X-ray diffraction pattern of sample STPMO reveals that the layered structure remains and that its basal spacing is 1.26 nm after the SiO_2/TiO_2 intercalation into the interlayer of manganese oxide. The increase of the basal spacing is ascribed to the SiO_2/TiO_2 incorporation, and the net clearance height is 0.74 nm after subtracting 0.52 nm of manganese oxide nanosheet thickness.[12] In comparison with the basal spacing of the typical pillared composite, the interlayer expansion is relatively small due to the ripening of silicate and titanate polymer to compact SiO_2/TiO_2 particles at the relatively high solvothermal treatment temperature. Meanwhile, the high-order diffraction peaks are weakened due to the incorporation of SiO_2/TiO_2, suggesting that the stacked structure is weakened and no multistacked aggregation existence of homogeneous SiO_2/TiO_2 species in the interlayer spacing of BirMO(H) (Figure 1).

SEM images are used to observe the morphology of the obtained materials. In comparison with the precursor BirMO(H), the plate-like morphology is hardly maintained, and some changes are observed. After intercalation followed by the incorporation treatment of SiO_2/TiO_2 particles, an image with irregularly stacked layered structure is observed. The EDS analysis confirms the presence of silica and titanium in sample STPMO (Figure 2), and the molar ratio of Mn/Si/Ti is 2.0/1.6/1.0. The carbon content is 2.19 mmol g^{-1} in the as-obtained STPMO, and it is mainly derived from ethanol acting as reaction medium. The result indicates that ethanol plays an important role in the expansion of the interlayer gallery. The HR-TEM image

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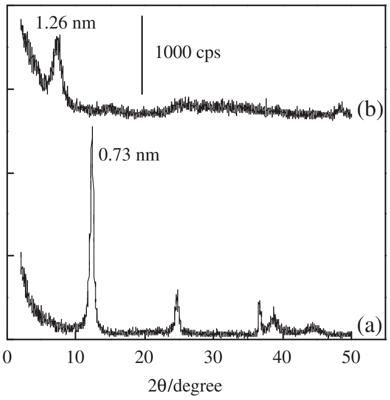
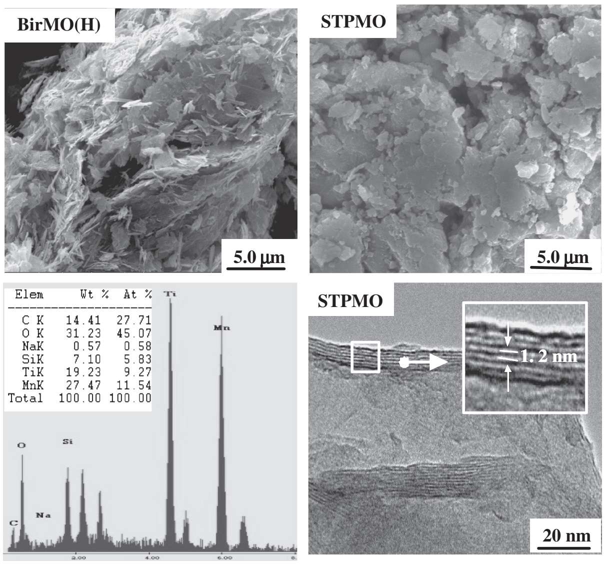


Figure 1. XRD patterns of samples obtained at different stages: (a) BirMO(H) and (b) STPMO.



Elem	Wt %	At %
C K	14.41	27.71
O K	31.23	45.07
NaK	0.57	0.58
SiK	7.10	5.83
TiK	19.23	9.27
MnK	27.47	11.54
Total	100.00	100.00

Figure 2. SEM and TEM images of BirMO(H) and STPMO, EDAX analysis of STPMO.

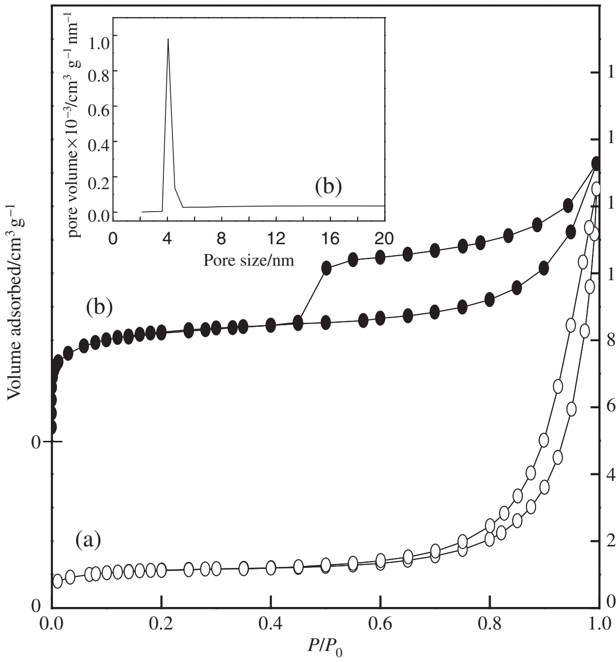


Figure 3. N_2 adsorption–desorption isotherms and BJH pore size distributions (inset) of as-prepared samples (a) BirMO(H) and (b) STPMO.

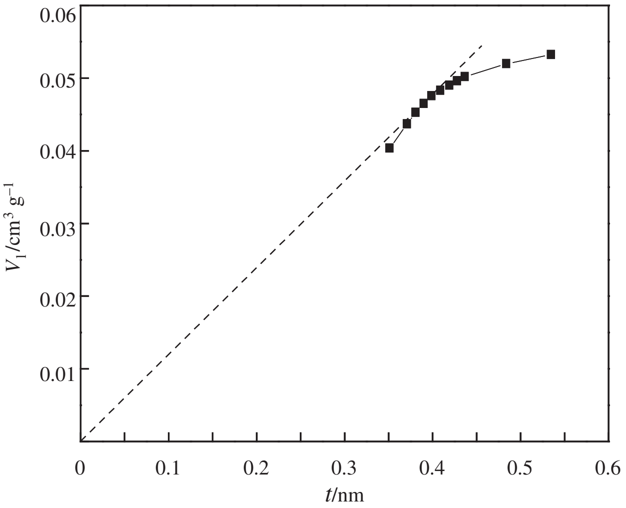


Figure 4. V_1–t plots from nitrogen adsorption data of STPMO.

of STPMO shows that the nanosheets were supported by SiO_2/TiO_2 pillars, forming an ordered multilamellar architecture. It is observable that the nanosheets are parallel to each other, and the basal spacing of SiO_2/TiO_2 pillared manganese oxide was estimated to be 1.20 nm, which is consistent with that estimated from the XRD analysis.

The nitrogen desorption–adsorption isotherms of as-prepared samples are shown in Figure 3. The isotherm for precursor BirMO(H) belongs to BDDT type II with a small hysteresis loop, which corresponds to nonporous or macroporous structures. The Brunauer–Emmett–Teller (BET) surface area is about $33\,m^2\,g^{-1}$. The isotherm for STPMO is of the type IV with a large hysteresis loop, showing a characteristic of mesoporous material.[13] The specific surface area from BET measurement is approximately $113\,m^2\,g^{-1}$. These results suggest that the incorporation of SiO_2/TiO_2 species into the interlayer of manganese oxide causes a mesoporous structure formation and increases the specific surface area. The Barrett–Joyner–Halenda (BJH) method was used for the analysis of the pore size distribution, and the pore size distribution curve was obtained by analyzing the desorption branch and presented in the inset of Figure 3, which indicates the precursor is composed by mesopores and macropores. The pore size of STPMO is centered mainly at 4.1 nm, suggesting that mesoporous structure is formed after BirMO(H) is heat-treated in the solvent of TEOS and TIIP.

The V_1 vs. t curve can be used to determine the ratio of the external surface and inner surface of the porous sample.[14] The corresponding V_1 vs. t curve for sample STPMO is shown in Figure 4, which is carried out with the curve by Lecloux.[15] The V_1 vs. t plot shows a downward deviation from the straight line around $t = 0.4$ nm. This shows the formation of narrow micropores with a pore diameter around 0.4 nm. The curve gives a total surface area (S_t) of 121 $m^2 g^{-1}$ and external surface area (S_{ext}) of 39 $m^2 g^{-1}$; the proportion of micropore surface area reaches 68%. This indicates that the solvothermal treatment results in mainly the production of micropores.

In summary, SiO_2/TiO_2 pillared layered manganese oxide was successfully synthesized via a simple solvothermal treatment of BirMO(H) in a mixed solution of ethanol, TEOS, and TIIP. Its specific surface area from BET measurement is approximately 113 $m^2 g^{-1}$. A direct method is developed to synthesize pillared materials, and layered materials are not pre-expanded or delaminated by alkylamine and tetraalkylammonium. It is expected to be used as a molecular sieve, selective absorbent, or lithium ion secondary battery material.

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