Electronic Supplementary Information:

Large-scale preparation of hierarchical manganese oxide octahedral molecular sieves (OMS-1) nanoplate microspheres via a facile one-pot reflux method

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Preparation of OMS-1

In a typical synthesis, 18 mmol of Mg(CH₃COO)₂ · 4H₂O and 18 mmol of Mn(CH₃COO)₂ · 4H₂O were mixed with 150 mL distilled deionized water (DDW), then 150 mL of 0.18 mol/L K₂CrO₄ solution was slowly added to the mixture solution. The suspensions were heated to reflux under stirring. After being refluxed for 24 h, the suspensions were cooled to room temperature. The products was washed with DDW until the conductivity of the supernatant was below 2.0 us/cm, and freeze-dried. CH₃COONa and Cu(CH₃COO)₂ · 3H₂O were used to replace Mg(CH₃COO)₂ · 4H₂O in the preparation process to investigate the role of Mg²⁺ in the formation of OMS-1 structure.

Characterizations

X-ray powder diffraction (XRD) was carried out using a Bruker D8 ADVANCE X-ray diffractometer equipped with monochromated Cu Kα radiation (λ = 0.1541 nm) at a tube voltage of 40 kV and a tube current of 30 mA. Both buserite and todorokite have a basal d spacing of about 1 nm. Buserite is not stable and can be transformed to the birnessite (basal d spacing is about 0.7 nm) when heating. However, todorokite has a relatively high thermal stability. For the identification of todorokite, before XRD analysis the oriented slides for the freeze-dried products were heated for 10 h at 110 °C to eliminate the interference of diffraction peaks of buserite. As such, the about 1 nm peak in the diffraction pattern could be attributable to the characteristic peak of todorokite. High-resolution electron microscopy (HRTEM) was performed on sample suspensions dried on a carbon coated grid (200 mesh, 3.05 mm in diameter) with a JEOL JEM 2010 FEF electron microscope operated at 200 kV. Scanning electron microscopy (SEM) images were obtained with a Hitachi S-4800 emission scanning electron microscope. A Quantachrome Autosorb-1 instrument was used to measure the surface areas and micropore size distributions of the materials. Samples were degassed in a vacuum at 250 °C for about 10 h to remove water and other physically adsorbed species. N₂ isothermal adsorption and desorption experiments were performed at relative pressures (P/P₀) from 10⁻⁶ to 0.9916 and from 0.9916 to 0.047, respectively. To investigate the oxidation state of chromium in the framework of the synthetic OMS-1, X-ray photoelectron spectroscopy (XPS) spectra of the OMS-1 were recorded on a PHI Quantum 2000 Scanning ESCA Microprobe spectrometer with an Al Kα incident X-ray beam. The X-ray source
was operated at 35 W, and the spectra were recorded at 15 kV. The analysis chamber pressure was $5 \times 10^{-8}$ Pa. The chemical composition of the OMS-1 was analyzed by a Varian Vista-MPX ICP-OES. Thermogravimetry analysis (TGA) was performed on a NETZSCH TG 209 thermogravimetric analyzer with a 20 mL/min \( \text{N}_2 \) flow from 37 to 800°C at a heating rate of 10°C/min.

**Electrochemical characterization of OMS-1**

The electrochemical characteristics of the synthetic OMS-1 was evaluated by galvanostatic charge/discharge using simulated battery test controlled by a battery testing system (Shenzhen Neware Electronic Ltd., China). The cathode mixtures consisted of 78 wt.% OMS-1 dried at 110°C for 12 h, 15 wt.% acetylene black and 7 wt.% polytetrafluoroethylene binder on the aluminum mesh. The anode and reference electrode were all lithium foils. The electrolyte used in this work was 1 mol L\(^{-1} \) LiClO\(_4\) in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethylmethyl carbonate (EMC) with equal volume. Celgard 2400 membrane worked as a separator. The charge/discharge cycles were carried out between 2.0 V and 3.8 V (vs Li/Li\(^{+}\)) with current density of 20 mA g\(^{-1}\) at 25 ± 1°C. All the operations of this experiment were performed in a simple glove box protected with flooding inert argon.
Fig. S1 N₂ adsorption and desorption isotherms and pore-size distribution (inset) for the as-prepared OMS-1.

Fig. S2 (a) Thermogravity analysis (TGA) and (b) thermal differential analysis (DTA) of as-prepared OMS-1.
Fig. S3 XRD patterns of intermediate products at the different stages of refluxing process.

Fig. S4 FESEM images of the intermediate products at different stages of reflux: (a) 1 h; (b) 3 h; (c) 6 h and (d) 12 h.
Fig. S5 XPS pattern of the Cr 2p for the synthetic OMS-1.
Fig. S6 (a) SEM image of the synthetic OMS-1. (b), (c), (d), (e) scanning SEM elemental distribution mapping for O, Mn, Cr and Mg, respectively.
Fig. S7 XRD patterns of the products for refluxing treatment of K$_2$CrO$_4$, Mn(CH$_3$COO)$_2$ and CH$_3$COONa mixture solutions: (a) 24 h; (b) 48 h; (c) 72 h; (d) refluxing treatment of K$_2$CrO$_4$, Mn(CH$_3$COO)$_2$ and Cu(CH$_3$COO)$_2$ mixture solutions for 24 h.

Fig. S8 FESEM images of as-prepared OMS-1 obtained by hydrothermal treatment at (a) 100 °C, 24 h; (b) 120 °C, 24 h and (c) 140 °C, 24 h (Insets are high-magnification images).