Electrophoretic Deposition of a Thick Film of Layered Manganese Oxide

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Delamination of layered manganese oxide into colloidal nanosheets occurred when manganese oxide intercalated with tetramethylammonium ions was ultrasonically dispersed in acetonitrile organic solution. An oriented layered manganese oxide thick film with (00*l*) plane parallel to the substrate was obtained by electrophoretic deposition of negatively charged manganese oxide nanosheets on ITO-coated glass substrate.

Recently, layered manganese oxides have attracted increasing attention because of their unique adsorptive, catalytic, ion-exchange, and electrochemical properties. Birnessite-type manganese oxide has a two-dimensional layered structure that consists of edge-sharing [MnO_6] octahedra with water molecules and cations occupying the interlayer space to balance negative charges on manganese oxide layers.[1] Great efforts have been devoted to developing synthetic methods for layered manganese oxide films, such as sol–gel spin coating,[2] electrostatic layer-by-layer adsorption technique,[3] and electrochemical deposition.[4,5] However, these methods are limited to prepare thin films (nano- to submicroscale thickness), which may be restricted in practical applications such as battery and supercapacitor because of the low mass loading.[6]

Electrophoretic deposition (EPD) is a promising technique for obtaining uniform films with thickness from nanometer to micrometer scale by the electrophoresis of isotropic particles under the influence of an electric field. Recently, this method has been developed for nanosheets due to the colloidal and charged properties of nanosheets.[6–10] Moreover, it is an effective method to construct oriented films using exfoliated nanosheets, such as α-zirconium phosphate,[6] layered titanate,[7] and high-T_c superconducting $Bi_2Sr_2CaCu_2O_y$.[10] It is reported that the electrochemical decomposition of water prevented films from forming on substrates during the EPD process.[6] Layered manganese oxides have been delaminated in alkylammonium hydroxide–water solution;[11–13] however, the delamination behavior has not been studied in organic solution. Here, we firstly report the delamination of layered manganese oxides in acetonitrile and the preparation of an oriented layered manganese oxide film by the EPD method using manganese oxide nanosheets in acetonitrile solution.

The precursor, birnessite-type layered manganese oxide, was synthesized according to the method reported in the literature.[11] A mixed solution (200 mL) of 0.6 M NaOH and 2 M H_2O_2 was quickly poured into a 0.3 M $Mn(NO_3)_2$ solution (100 mL) and stirred for 30 min. The precipitate was then subjected to hydrothermal treatment at 150 °C for 16 h in a 2 M NaOH solution. The obtained precipitate was acid treated with a 1 M HNO_3 solution for 3 days at room temperature to produce proton-type layered manganese oxide, which was designated as birnessite(H). Birnessite(H) (2 g) was stirred in a 0.16 M aqueous solution of tetramethylammonium (TMA) hydroxide (200 mL) for 7 days at room temperature. After soaking, the suspension was centrifuged at a speed of 10000 rpm for 10 min and washed with 200 mL of water four times to obtain manganese oxide slurry. Then, manganese oxide slurry was ultrasonically dispersed in acetonitrile solution and centrifuged at a speed of 5000 rpm for 30 min to obtain the exfoliated manganese oxide nanosheet colloid. The obtained colloidal suspension was light- to dark-brown, depending on the concentration of manganese oxide nanosheets, and Tyndall light scattering was observed (not shown here).

The electrochemical cell for the electrophoretic deposition was composed of an ITO-coated glass anode and a platinum plate cathode. The anode and cathode were placed parallel with a separation of 10 mm in the manganese oxide nanosheet colloid, and a constant potential of 10 V was applied for 30 min at room temperature. The as-deposited films were dried at 80 °C under ambient conditions. Ultraviolet–visible (UV–vis) spectrum was recorded using a Shimadzu UV-2501PC spectrophotometer equipped with an integrating sphere detection system. X-ray diffraction (XRD) patterns of the obtained films were measured by a Shimadzu XRD-6000 powder diffractometer using Cu Kα radiation source ($\lambda = 0.15405$ nm).

The colloidal suspension of manganese oxide nanosheets in acetonitrile solution exhibits optical absorption with a broad peak centered around 387 nm (Figure 1). Omomo et al. have reported similar optical properties for the exfoliated manganese oxide nanosheets in water solution.[12] The UV–vis absorption of manganese oxide nanosheets is due to quantum confinement effects that arise from the subnano- to nanometer thickness of manganese oxide nanosheets.

Figure 2 shows the XRD patterns of powder birnessite(H) and manganese oxide films electrophoretically deposited on ITO-coated glass substrates. The birnessite(H) has a layered

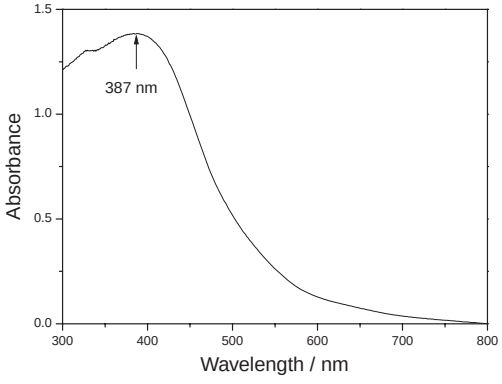

Figure 1. UV–vis spectrum of colloidal suspension of manganese oxide nanosheets in acetonitrile solution.

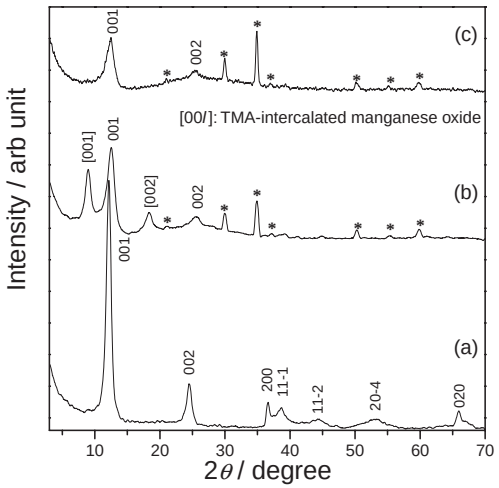

Figure 2. XRD patterns of (a) powder birnessite(H) and manganese oxide films electrophoretically deposited from manganese oxide nanosheets in acetonitrile solution on ITO-coated glass substrates: not centrifuged (b) and centrifuged 5000 rpm for 30 min (c). (*: ITO substrate)

structure with a basal spacing of 0.73 nm, as shown in Figure 2a for comparison. Acetonitrile has a high relative permittivity (37.5), which is usually applied as solvent to provide the electrostatic screening effect for exfoliated nanosheets. Its high vapor pressure and low viscosity (0.325 mPa s) also favor the formation of highly oriented, crack-free films.[6,7] When 30 mg of manganese oxide slurry dispersed in 60 mL of acetonitrile for the electrophoretic deposition, the layered manganese oxide film with two series basal spacing of 0.98 and 0.71 nm is obtained (Figure 2b), suggesting that the delamination is not completed and that some products of tetramethylammonium-intercalated manganese oxide are reserved. After being centrifuged at 5000 rpm for 30 min, the film with a single birnessite-type layered manganese oxide structure is obtained (Figure 2c). The peaks at 12.5 and 25.3° are indexed to the (001) and (002) reflections of birnessite-type manganese oxide, respectively, with an interlayer distance of 0.71 nm. The (001) reflection peak is broad and slightly asymmetric toward the low-angle side, expecting for an oriented, turbostratically restacked film of exfoliated nanosheets.[6] The absence of the (*hkl*) reflections with $h \neq 0$ or $k \neq 0$ indicates that the layered manganese oxide film is oriented with (00*l*) plane parallel to the substrate.[14] FT-IR spectrum shows that the water and acetonitrile molecules are codeposited into the interlayer of layered managense oxide during the EPD process. The interlayer H_3O^+ species may maintain the charge neutrality in the manganese oxide film.[15]

The typical SEM (Hitachi S4700 scanning electron microscope) images of the surface of a film obtained by the EPD of exfoliated manganese oxide nanosheets are shown in Figures 3a and 3b, indicating plate-like sheets uniformly stacked parallel to the substrate. The thickness of the film depends on the deposition time. The cross-sectional SEM image reveals that the thickness of the film is about 80 μm after deposited for 30 min (Figure 3c).

In summery, an oriented layered manganese oxide thick film with (00*l*) plane parallel to the substrate was prepared by electrophoretic deposition of exfoliated manganese oxide nanosheets in

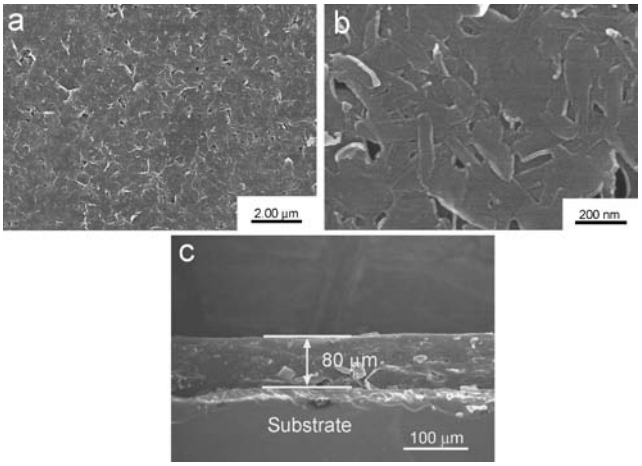

Figure 3. SEM images of layered manganese oxide film electrophoretically deposited from manganese oxide nanosheets in acetonitrile solution on ITO-coated glass substrate: (a) top view, (b) a high-resolution image of (a), and (c) cross-sectional image.

acetonitrile organic solution on ITO-coated glass substrate. The layered manganese oxide film is expected to be used as electrode for lithium ion battery or supercapacitor.

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