Preparation of Hierarchic Porous Films of $\alpha$-MnO$_2$ Nanoparticles by Using the Breath Figure Technique and Application for Hybrid Capacitor Electrodes

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ABSTRACT: The honeycomb-structured film has advantages such as high wettability and high surface area. This structure and properties are suitable for the capacitor electrode. In this study, the electrode structure is controlled by the synthesis of MnO$_2$ nanoparticles using the breath figure method. The electrode performance was calculated by electrochemical measurements. As a result, the capacitance value was 100.5 F/g at 1 mV s$^{-1}$, which was improved 2.7 times as compared with that without structure control.

1. INTRODUCTION

Energy storage devices with low cost, high power density, and large storage capacity are crucially important for realization of low carbon society. Many types of energy storage devices have been proposed, examined, and developed for this aim. Among them, a supercapacitor is one of the promising energy storage devices with respect to its high power density and long cycle life.1–3 Pseudo-electrochemical double layer capacitors employing redox active metal oxides such as RuO$_2$ as anodes received considerable attention over the last decade because they could achieve high charge densities approaching those of secondary batteries owing to the additional faradic charge.6 For example, Miller et al. have reported a RuO$_2$-based supercapacitor with a high capacitance exceeding 1000 F/g.7 However, wide use of RuO$_2$ devices is difficult because of scarcity and toxicity of Ru.7

Thus, alternative electrode materials other than RuO$_2$ are needed for practical use of supercapacitors. Manganese dioxide (MnO$_2$) is one of the most promising materials with its theoretical capacity second to RuO$_2$.8 Mn is an abundant element and environmentally safe.9 In fact, MnO$_2$-based capacitors have shown excellent cycle stability and storage capacity.10,11 MnO$_2$ is known to exist in several different crystallographic forms such as $\alpha$, $\beta$, $\gamma$, $\delta$, and $\epsilon$-types, achieved by different connections of [MnO$_6$] octahedra.12 Among them, $\alpha$-MnO$_2$ is most interesting in terms of its high chemical stability and long cycle life when used in electrochemical capacitors.13 Some general drawbacks of MnO$_2$ are the low surface area as it tends to form large crystals and low conductivity, both limiting the performance of the capacitor.14,15 Application of MnO$_2$ is therefore hindered due to small Coulombic capacity in its practical use and large energy loss on charging/discharging at high rates.14,15 In order to improve the device performance of MnO$_2$ supercapacitors, we have focused on both improving the electrical conductivities and increasing the surface area of electrodes by introducing hierarchically porous surface structures. In our previous study, the surface of MnO$_2$ particles was decollated with fullerene nanocrystals.16 Capacitors made from such composites exhibited higher capacitance than those of original MnO$_2$. The added fullerene nanocrystals contributed to both improving the conductivity and increasing double layer capacitance.

In the present study, we have examined the usefulness of hierarchic porous structure to be simply achieved by

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connection of nanosized MnO₂ crystals. A method called “breath figure technique” has been employed to construct such a structure. Successful application of the technique has been demonstrated in the preparation of porous polymer films. When solutions of a polymer in solvents nonmiscible with water are cast onto substrates under humid air, droplets of water are co-deposited. Evaporation of both the solvent and the water droplet then leaves a highly open honeycomb structure of the polymer ranging from submicron to micron scale. Because of the high porosity and surface roughness, such a honeycomb polymer showed a high water repellency. The breath figure technique has further been applied in a construction of hierarchic porous films composed of inorganic nanoparticles by replacing the polymer solution with a dispersion of polymer-stabilized inorganic nanoparticles. The wall of the honeycomb is then made with sintered and interconnected inorganic nanocrystals instead of polymer. If such a structure is made from nanocrystals of MnO₂, the layer should be ideally suited as the electrode for capacitors, as a large surface area is achieved while assuring a good conductivity within the well-connected nanoparticles. The large honeycomb pores should facilitate ion transport at the same time to ensure fast charging/discharging.

We have synthesized α-MnO₂ nanoparticles in a narrow size distribution by the previously established method. The surface of the particles was modified with catechol-containing amphiphilic copolymers to help their dispersion in chloroform as a solvent nonmiscible with water. The breath figure technique was then applied to structure a hierarchically porous honeycomb out of interconnected α-MnO₂ nanoparticles. Structural characterizations, as well as electrode performance in supercapacitors, are discussed.

2. RESULTS & DISCUSSION

The process for the preparation of α-MnO₂ nanoparticles is graphically summarized in Scheme 1, whereas the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the product are shown in Figure 1. The MnCl₂ precursor is slowly hydrolyzed and oxidized with atmospheric O₂ to result in nanosized MnO(OH)₂, which is finally converted to MnO₂ by sintering in air. The SEM image shows formation of round particles in an average diameter of about 20 nm. The TEM image also confirms the spherical morphology, without inclusion of particles in other shapes such as rods and cubes.

Figure 2 compares the X-ray diffraction (XRD) patterns before and after the sintering. The one before sintering (Figure (a)) shows broadened peaks, indicative of a poorly crystalline material. After sintering (Figure (b)), the peaks become sharper and more intense, suggesting an increase in crystalinity.

Figure 1. (a) SEM image and (b) TEM image of synthesized α-MnO₂ nanoparticles.

Figure 2. XRD pattern of synthesized α-MnO₂ nanoparticles: (a) before sintering and (b) after sintering.
polymer coating and connection of the MnO2 nanoparticles, lateral shrinkage of the layer caused by the removal of the large-sized pores created by the water droplets (some larger than 10 μm diameter) reduce their size after sintering due to interconnections of nanosized MnO2 particles naturally result in mesopores as the primary porous structure, the secondary macropores can be fabricated by the breath figure method (Figure S5), so that hierarchically porous architecture can be made out of a single material.24 Water droplets can be co-deposited with the dispersion of MnO2 in chloroform that is nonmiscible with water. Figure 4 shows the SEM images of thus-prepared honeycomb layers before and after sintering at 400 °C for 10 min (Figures 4a,b, S6, and S7). The unique large-sized pores created by the water droplets (some larger than 10 μm diameter) reduce their size after sintering due to lateral shrinkage of the layer caused by the removal of the polymer coating and connection of the MnO2 nanoparticles, although cracks are apparently not formed. From the high-magnification images provided as insets, the individual particles are not recognized before sintering which become apparent after removal of the polymer coating by sintering. The interconnected MnO2 nanoparticles create a mesoporous structure having a high surface area, essential to achieve a high electrochemical capacitance,22 whereas the macropores made by the breath figure method are expected to facilitate ion transport needed for high current charging/discharging. Figure 5 compares cyclic voltammograms measured at a mesoporous electrode prepared by simple coating of the MnO2 nanoparticles and the hierarchically porous electrode by the breath figure method (Figure S8). The increase of faradic current at the anodic end of the potential scanning can be associated with oxidation of water. When the capacitive current in the broad potential range is compared, it is clearly enhanced by introducing the honeycomb structure, increasing the specific capacitance from 37.0 to 100.5 F g⁻¹. Unfortunately, comparing the capacitance value with previous reports,11,14 our value of capacitance is almost the same. However, there are advantages to constructing a hierarchical electrode structure using nanoparticles such as high surface area, and performance has been further improved by several methods such as coating the conductive polymer by electrodeposition and composite with graphic carbon by dip coating to increase the capacity. In fact, the hierarchic porous structure achieved by our method is

Figure 3. Photographs of dispersion, TEM images of MnO2 nanoparticles coated with amphiphilic copolymer and results of DLS measurement. (a) Photographs of (a-1) before coating and (a-2) TEM image; (b) photographs of (b-1) after coating and (b-2) TEM image; and (c) DLS results show the size distribution of nanoparticles dispersion (1) before coating and (2) after coating with amphiphilic copolymer.

Figure 4. Illustration and SEM and high-magnification SEM images of honeycomb films composed of α-MnO2 nanoparticles (a) before and (b) after sintering.

Figure 5. Cyclic voltammograms of (a) honeycomb film electrode and (b) α-MnO2 nanoparticles without structural control which recorded 0 and 0.8 V vs Ag/AgCl in aqueous 1.0 M Na2SO4 at a sweep rate of 1 mV s⁻¹.
made of well-sintered $\alpha$-MnO$_2$ particles to minimize the infrared (IR) loss, while the large honeycomb pores can facilitate delivery of ions to the mesopores, so that a larger portion of the coated MnO$_2$ nanoparticles can participate in the charging/discharging events than those of the simply coated layer having only tiny mesopores. Thus, usefulness of structure control has been well demonstrated to increase the electrode performance for supercapacitors.

3. CONCLUSIONS

Synthesis of $\alpha$-MnO$_2$ nanoparticles, their dispersion in chloroform by coating with the amphiphilic copolymer, and fabrication of hierarchically porous honeycomb layers by the breath figure method have been successfully achieved. The thus-prepared MnO$_2$ layer exhibited a superior electrochemical performance to a mesoporous MnO$_2$ prepared by simple coating of the same MnO$_2$ particles, increasing the specific capacitance from 37.0 to 100.5 F g$^{-1}$ as determined from cyclic voltammograms. While assuring a high surface area by employing nanosized MnO$_2$ particles as building blocks, the large macropores of the honeycomb structure were found to facilitate ion transport, resulting in the increase of capacitance in the actual use. The present work thus nicely demonstrates the usefulness of structure control to improve full usage of the electrode material in the design of supercapacitors.

4. EXPERIMENTAL METHODS

4.1. Chemicals. Manganese(II) chloride tetrahydrate (MnCl$_2$·4H$_2$O, 99.99%) was purchased from Sigma-Aldrich. N,N-Dimethylformamide (DMF, 99.5%), sodium hydroxide (NaOH, 97.0%), ethanol (EtOH, 99.5%), and chloroform (CH$_2$Cl$_2$, 99.0%) were purchased from Wako. All chemicals were used without further purifications. The amphiphilic copolymer, PDMA-γ-PDA, was synthesized from N-(3,4-dihydroxyphenethyl)methacrylamide and N-dodecylacrylamide by free radical polymerization.$^{18,26-29}$

4.2. Synthesis of $\alpha$-MnO$_2$ Nanoparticles. Nanoparticles of $\alpha$-MnO$_2$ were synthesized according to the method proposed by Ramarajan et al.$^{23}$ A precursor solution was prepared by dissolving 450 mg of MnCl$_2$·4H$_2$O in 45 mL of deionized water and stirring at room temperature for 15 min. After complete dissolution, 150 $\mu$L of DMF was added as a surfactant and a total of 45 mL of 0.05 M NaOH was dripped very slowly taking 2 h under stirring. Precipitated solid mass was centrifugally separated at 10 000 rpm and washed four times with ethanol by applying repeated centrifugation. The product particles were then dried at 35 °C under vacuum for 12 h. The nanoparticles were finally sintered at 400 °C under air for 2 h for crystallization to $\alpha$-MnO$_2$ film preparation.

4.3. Preparation of $\alpha$-MnO$_2$ Dispersion and Honeycomb Film Structuring by the Breath Figure Technique. Hydrophobic dispersion was prepared by adding $\alpha$-MnO$_2$ (85 mg) to CH$_2$Cl$_2$ (1.5 mL). The mixture was ultrasonicated for 5 min and then a 1 mL of CH$_2$Cl$_2$ containing 10 mg PDMA-γ-PDA was added dropwise to promote dispersion of the MnO$_2$ particles. It was ultrasonicated for another 1 min and was allowed to stand for 1 h to precipitate large aggregates of MnO$_2$. Supernatant obtained after centrifugal separation at 12 000 rpm containing the dispersion of the surface modified MnO$_2$ was diluted by adding 500 $\mu$L of CH$_2$Cl$_2$ to which another 50 $\mu$L of chloroform was added to support cross-linking of the particles in the honeycomb film.

Fluorine-doped SnO$_2$ (FTO) coated conductive glass (Asahi-DU, 10 $\Omega$/sq) used as the substrate was cut into 20 × 35 mm. A strip of a masking tape (Nitto Denko N-300) of 20 mm long and 15 mm wide was pasted perpendicularly to the FTO glass, leaving 15 mm on one end to regulate the area for coating as 20 × 15 mm, while the other end of 5 mm wide was left for making an electrical contact. A cooling stage controlled at 11 °C was placed in a home-made closed chamber connected to a humidifier (an air pump connected to a gas washer containing deionized water). When the chamber was closed and humidified air was pumped through, a temperature of 23 °C and a humidity of 60% were typically read by the probe put in the chamber. The FTO glass substrate was flat laid on the stage and a 100 $\mu$L of the MnO$_2$ dispersion was cast onto the substrate. Then, the chamber was closed to allow condensation of water droplets on the coated wet film for 1 min. The film was taken out of the chamber to dry the film under air, and then put in a furnace to sinter the film at 400 °C for 10 min to yield the honeycomb-structured MnO$_2$. Film preparation according to this procedure resulted in average quantity of MnO$_2$ coating as 0.9 mg cm$^{-2}$.

4.4. Characterization. SEM (JEOL JSM-6700F) was used to observe the synthesized particle and morphology of the honeycomb-structured film. TEM (JEOL JSM-2100F) images were obtained to observe the state of dispersion of MnO$_2$ nanoparticles by coating with the amphiphilic PDMA-γ-PDA polymer. The crystallinity of the synthesized particles was checked by powder XRD on a Rigaku SmartLab employing Cu Kα radiation. The particle size distribution was measured by DLS employing a Zetasizer Nano ZS (Malvern ZEN3600). Electrochemical measurements at the honeycomb MnO$_2$ working electrode were carried out in a conventional three-electrode single compartment electrochemical cell with a 1.0 M Na$_2$SO$_4$ aqueous solution as the electrolyte and employing an electrochemical measurement system (Hokuto Denko HSV-110) for record of cyclic voltammogram. A Pt-wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03381.

Experimental section and results of FT-IR; thermogravimetric/differential thermal analysis; photographs of dispersions, electrodes, and results of DLS measurement; illustration of the breath figure technique; contact angle measurement; SEM; and electrical measurements (PDF)

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Notes
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