Co$_3$O$_4$/MnO$_2$ Core/Shell-Nanostructured Pseudocapacitor Electrode

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Pseudocapacitors have received a great deal of attention as next-generation energy storage systems.$^1$ With high power density, specific capacitance, and the use of low-cost electrode materials, the pseudocapacitor has been considered an ideal system that is capable of bridging the gap between the electrical double-layer capacitor and the Li-ion battery. However, several issues, such as poor rate capability and cyclability resulting from the low electrical conductivity of the active materials, as well as Faradaic redox reactions for charge storage, must be addressed before practical utilization is feasible. A great deal of effort has been devoted to addressing these issues, including nanostructuring active materials, developing a novel electrode substrate, and synthesizing carbon-based nanocomposites.$^2$–$^5$

Among these strategies, utilizing multi-components for electrode materials has become popular due to the synergistic effect from the use of multiple active materials. Various combinations such as Ni(OH)$_2$/MnO$_2$, Co$_3$O$_4$/MnO$_2$, MoO$_2$/Co(OH)$_2$, and Co$_3$O$_4$/RuO$_2$ have been examined.$^6$–$^9$ Among them, MnO$_2$-based nanocomposites have received significant interest due to their abundance, high theoretical capacitance, and availability in a neutral electrolyte of MnO$_2$.$^{10}$

The combination of Co$_3$O$_4$ and MnO$_2$ in particular is considered ideal, as Co$_3$O$_4$ can serve as a conductive scaffold for MnO$_2$ due to its relatively good electrical conductivity, and can also improve the overall capacitance via its own redox reaction.$^7$–$^{11}$ Fan et al. recently reported a Co$_3$O$_4$/MnO$_2$ core/shell array that exhibited high pseudocapacitive performance due to the synergistic effect.$^7$ The synergistic contribution from both materials, however, was somewhat limited from the viewpoint of areal ($C_A$) and gravimetric ($C_m$) capacitances, which is a result of low mass loading. In general, achieving simultaneously high $C_A$ and $C_m$ poses a significant challenge, as increasing $C_A$ via a high mass loading of the active materials often leads to a dramatic decrease in $C_m$ which originates from the large portion of dead material beneath electrode surface.$^{12}$ To address this issue, we designed a new nanoarchitecture, where core/shell-structured Co$_3$O$_4$/MnO$_2$ was conformally deposited on carbon fiber paper (CFP). CFP offers a porous structure, facilitating the access of electrolytes and alleviating the low electrical conductivity of electrode materials.$^{13}$ A thin Co$_3$O$_4$ layer was conformally deposited over CFP via a one-step hydrothermal synthesis, and mesoporous MnO$_2$ nanoflakes were subsequently integrated over the Co$_3$O$_4$ layer to further boost the charge storage capability. By virtue of this rationally-designed electrode, the Co$_3$O$_4$/MnO$_2$ electrode on CFP showed good capacitive performance in terms of both areal and gravimetric capacitances, despite significant electrode material loading.

Co$_3$O$_4$ is typically synthesized via a two-step process involving the synthesis of a Co$_3$O$_4$ precursor such as Co(OH)$_2$, followed by calcination for conversion to Co$_3$O$_4$. To avoid cumbersome post-annealing, Zhang et al. recently reported a new strategy for a single-step deposition of Co$_3$O$_4$.$^{14}$ In this approach, however, a substrate must be treated with HNO$_3$ prior to the reaction; otherwise only non-uniform Co(OH)$_2$ films would be obtained. However, unlike this report we found that CFP was capable of serving as a substrate for one-step hydrothermal deposition of Co$_3$O$_4$ without any pre-treatment. This is advantageous because it not only shortened the reaction time, but also eliminated the need for a strong oxidant.

The formation of Co$_3$O$_4$ was confirmed via X-ray diffraction (XRD) analysis (Figure 1(a)), where the intense diffraction peaks of Co$_3$O$_4$ have been examined.$^6$–$^9$ Among them, MnO$_2$-based nanocomposites have received significant interest due to their abundance, high theoretical capacitance, and availability in a neutral electrolyte of MnO$_2$.$^{10}$

Figure 1. (a) XRD pattern (peaks from CFP are labeled in green), (b) nitrogen physisorption isotherm, and (c and d) SEM images of Co$_3$O$_4$ deposited on CFP.

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associated with narrow, slit-like pores. The Brunauer-Emmett-Teller (BET) surface area was measured to be 43.3 m²/g. The morphology of the deposited Co₃O₄ was examined via scanning electron microscopy (SEM), verifying the conformal deposit of a 400-nm-thick, uniform Co₃O₄ film over the CFP (Figures 1(c) and 1(d)). Narrow, slit-like cracks were sporadically observed along the Co₃O₄ film, which supported the type H4 hysteresis loop observed in the N₂ isotherm. Such conformal a coating with narrow slit-like pores could be beneficial for capacitive performance, as it could fully utilize the CFP surface and minimize dead Co₃O₄ (not exposed to electrolyte), thus maximizing its utilization even with a significant amount of Co₃O₄ loading. The growth of Co₃O₄ was monitored via SEM analysis to elucidate the formation of conformal Co₃O₄ film, as shown in Figure S1. During the initial reaction, no notable changes were observed within a 2 h period in the low-magnification SEM image. After 3 h, however, Co₃O₄ nanoparticles were clearly visible, and more nanoparticles had formed and merged together, gradually filling the gap between the nanoparticles. Each carbon fiber was completely covered with the Co₃O₄ nanoparticles after 8 h reaction time.

MnO₂ was subsequently deposited over the Co₃O₄/CFP electrode via a simple hydrothermal treatment for 30 min. In contrast to the commonly-performed, carbon-assisted reduction (4MnO₂ + 3C + H₂O → 4MnO₂ + CO₂↑ + 2HCO−3)^10 or electrodeposition, our synthesis can quickly produce a thin, porous MnO₂ film without pre-carbon coating or destruction of the structural integrity of Co₃O₄. No noticeable change in pattern was observed in the initial XRD analysis when examining the crystal structure of MnO₂. This may have been due to the intense diffraction peaks from Co₃O₄ and CFP screening those from the thin MnO₂. Raman spectroscopy was then carried out to characterize the MnO₂, revealing the formation of δ-MnO₂ (Figure 2(a)).^18 The formation of δ-MnO₂ was also confirmed via the XRD analysis of MnO₂ directly deposited on CFP (Figure S2). We determined from the type IV isotherm in the N₂ physisorption experiment (Figure 2(b)) that mesoporous MnO₂ was deposited, and its BET surface area was determined to be 130.2 m²/g. The SEM images in Figures 2(c) and 2(d) show that a myriad of thin MnO₂ nanoflakes were vertically integrated on the top of the Co₃O₄, with the morphology of Co₃O₄ preserved. This porous structure could be advantageous for capacitive performance, because it promotes the accessibility of electrolytes to Co₃O₄ covered in MnO₂, and also creates more active sites for the redox reaction occurring on MnO₂. Hence, the contribution from both active materials to the overall capacitance could be maximized.

Cyclic voltammetry (CV) measurement was conducted at various scan rates to investigate the electrochemical behavior of Co₃O₄ and Co₃O₄/MnO₂ electrodes (Figures 3(a) and 3(b)). Both CV showed an ideal capacitive behavior with no distinctive redox peaks, signifying that they were charged and discharged at a pseudo-constant rate. Figure 3(c) displays the Cₓ and Cₓ of Co₃O₄ and Co₃O₄/MnO₂ electrodes at various scan rates. The Co₃O₄/MnO₂ electrode was superior to the Co₃O₄ electrode in terms of Cₓ and Cₓ (319 F/g and 1.14 F/cm² at 1 mV/s), which was attributed to the synergic effect of the two active materials. Even when compared with the MnO₂/CFP electrode, the Co₃O₄/MnO₂ electrode exhibited a better performance, particularly at high scan rates (Figure S3). This indicates that the poor rate capability of the MnO₂/CFP electrode was improved by depositing MnO₂ over the Co₃O₄. While the deposition of MnO₂ over Co₃O₄ gave rise to an increase in electrical resistance, its capacitive loss was less than the benefit gained from the capacitive contribution of the Co₃O₄. The long-term stability of the Co₃O₄/MnO₂ electrode was examined via continuous potential sweeping at a scan rate of 100 mV/s (Figure 3(d)). No degradation in capacitance was observed, proving the excellent

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**Figure 2.** (a) Raman spectrum, (b) nitrogen physisorption isotherm, and (c and d) SEM images of the Co₃O₄/MnO₂ deposited on CFP.

**Figure 3.** Cyclic voltammograms of (a) Co₃O₄ and (b) Co₃O₄/MnO₂ electrodes at various scan rates, (c) gravimetric capacitance of Co₃O₄ and Co₃O₄/MnO₂ electrodes at various scan rates (inset: areal capacitance), and (d) cycling performance of the Co₃O₄/MnO₂ electrode.
stability of the Co$_3$O$_4$/MnO$_2$ electrode.

In conclusions, a core/shell-structured Co$_3$O$_4$/MnO$_2$ electrode on CFP was rationally designed to simultaneously achieve high $C_m$ and $C_A$. A facile hydrothermal approach enabled the conformal deposition of a thin nanocomposite film on the CFP. The multiple-component electrode was superior to its single-component counterparts in terms of both $C_m$ and $C_A$, a result of the synergic effect of the two active materials.

**Experimental**

For Co$_3$O$_4$ deposition, a piece of bare CFP (SGL Technologies, 1 cm × 5 cm) was soaked in a 100 mL, Teflon-lined, stainless steel autoclave that was filled with a solution containing cobalt nitrate hexahydrate (0.2 M) and 0.1 M ammonium nitrate dissolved in ammonium hydroxide solution (9 wt %). The autoclave was heated to 90 °C for 8 h, and then naturally cooled. To deposit MnO$_2$, the black-colored CFP was thoroughly washed with deionized water, dipped again in the autoclave filled with an aqueous solution (40 mL) containing 71.2 mM KMnO$_4$ and HCl (1 mL), and heated at 140 °C for 30 min. The amounts of Co$_3$O$_4$ and MnO$_2$ deposited on CFP were 2.0 and 2.3 mg/cm$^2$, respectively.

Co$_3$O$_4$ and MnO$_2$ were identified using an X-ray diffractometer (Rigaku D/Max-2500/PC) and a Renishaw 2000 confocal Raman microscope. The Brunauer–Emmett–Teller (BET) surface area was determined from the nitrogen adsorption/desorption isotherm measured using a BELSORP MINI II (BEL JAPAN). A scanning electron microscope (SEM, Hitachi S-4800 FESEM) was employed to examine the surface morphology of the electrodes. The electrochemical performance of the electrodes was investigated via a three-electrode system with an Ag/AgCl reference electrode and Pt counter electrode in 0.5 M Na$_2$SO$_4$ electrolyte. $C_A$ and $C_m$ were determined via cyclic voltammetry (CV) at various scan rates using the following equation: $C_A = \frac{l}{dI/dV \times S}$ and $C_m = \frac{l}{dI/d(V \times M)}$, where $l$ is the oxidation/reduction current, $dt$ is the time differential, $\Delta V$ is the potential window, $S$ is the geometrical area of the electrode, and $M$ is the mass of the active material.

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**Supporting Information.** XRD pattern of MnO$_2$ deposited on CFP; CVs and $C_m$ and $C_A$ of MnO$_2$ electrode at different scan rates.

**References**