Manganous-Manganic Oxide@Carbon Core-Shell Nanorods for Supercapacitors with High Cycle Retention
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Very few research has focused on MnO2@carbon nanorod-structured materials for supercapacitor electrode. A facile process has been developed to prepare MnO2@carbon core-shell hybrid nanorods for supercapacitor electrode materials. The core MnO2 polycrystals, which are 50 nm in diameter and 500 nm in length, offer faradaic pseudo-capacitance, while at the same time they serve as supporting template for 4.5 nm shell carbon surface, which functions as electrically conductive material and is also beneficial for improving the capacitive performance. It is highly desirable that the hybrid nanorods exhibit an excellent cycle ability with 95% retention after 5000 cycles at 4 A g−1. The hybrid nanorods present a capacitance of 168 F g−1 and good rate capability (125 F g−1 at 5 A g−1). The results indicate that the MnO2@carbon core-shell nanorods may have a promising future in applications which need durable, stable long-lasting power supply.

Sustainable and renewable resources have become more and more important due to climate change and the decreasing availability of fossil fuels. As a result, a continuous and dramatic increase in renewable energy production from wind and sun is observed, as well as the rapid development of vehicles fully powered by electricity with zero carbon dioxide emission. Wind energy and solar power, however, both suffer from instable and inconsistent supply, while a practical car model should be able to run at least a few hours on its own. So large-scale efficient energy storage industry has been flourishing to solve this problem. Batteries and supercapacitors stand at the very front of energy storage industry.1–3

Supercapacitors, also called ultracapacitor, are efficient energy storage units. Those using fast surface redox reaction are called pseudo-capacitors, and those using ion adsorption-desorption are called electrochemical double layer capacitors. They have attracted wide attention around the world over the past decades because of their high power density, longer cycle life, safer working conditions, higher retention, better environment-friendliness and wider range of working temperatures compared with secondary batteries. And their energy density is much higher than those available in conventional electrical double-layer capacitors. It is undeniable that in order to develop an advanced supercapacitor device, high performance electrode material is indispensable. Active carbon materials, conducting polymers and transition-metal oxides are three fundamental candidates for supercapacitor electrode materials.4–6 Unfortunately, none of them are entirely satisfactory. Active carbon materials have long cycle life but low specific capacitance.7 Conducting polymer is well-known for its high flexibility but poor cycle ability.8,9 Transition-metal oxides, such as RuO2 and MnO2 have their unique advantages in their variable oxidation states, good chemical and electrochemical stability, convenience in preparation and high theoretical specific capacitance. However, low porosity, low natural abundance, toxicity and the high cost of RuO2 have made them unlikely candidates for commercialization of supercapacitors.10 In contrast, manganese oxides are somehow attractive due to their low cost, abundance, high theoretical capacitance (about 1370 F g−1 over a potential window of 1.0 V in theory) and environment friendliness.11–13 Unfortunately, pure and bulk MnO2 has a much lower specific capacitance than its theoretical value. According to the charge-discharge mechanism of MnO2 involving:1

\[ \text{MnO}_2 + M^+ + e^- \rightarrow (\text{MnO})^\cdot + M^+ \]

where \( M^+ = \text{Li}^+, \text{Na}^+, K^+ \text{ etc.} \),

In order to improve the electrochemical performance of MnO2, a hybrid of conductive materials and MnO2 has been widely researched, especially those bind-free electrode materials. Bind-free electrode materials come from a nanofabrication which applies MnO2 as a thin film coating on the surface of electrically conductive nanomaterials such as Au,19 Cu,20 Ni,21 Mn,22 SnO2,23 ZnO,24 Co3O4,25 polyaniline,26 three dimensional graphene.27 Of those, carbon/MnO2 hybrid materials have been most intensely investigated, such as carbon@MnO2 core shell nano-spheres,2 carbon nano-tube MnO2 composite6,13 etc. This structure, carbon material with manganese oxide thin film coating, can obtain high specific capacitance for MnO2 electrodes, but their relatively complicated fabrication process (As for the carbon@MnO2 core shell nano-spheres,2 carbon nanospheres are produced from hydrothermal reaction and in order to synthesize carbon@MnO2 nanospheres hydrothermal reaction has to be conducted for a second time. The whole process is slightly convoluted.), relatively common specific capacitance, not high cycle retention may have restricted their industry applications in electric vehicles. Besides MnO2, Mn3O4 is also a potentially and promising electrode material for high performance supercapacitors. Nam synthesized MnO2 film using electrostatic spray deposition.28 Cui prepared multilayer carbon nanotubes/MnO2 composite by dip-coating method.30 Lee obtained graphene/MnO2 composite in hydrothermal.31 Although these electrode materials synthesized with MnO2 showed a certain degree of electrical performance, there is still large room to improve the electrical performance of MnO2 composite electrode materials.

In order to simplify fabrication process, to decrease the impedance of electrode materials and to improve electrochemical performance, also considering the fact that very few researches focus on MnO2@carbon nanorod-structured materials for supercapacitors, we came up with a method in preparing powdery MnO2@carbon core-shell hybrid nanorods electrode materials for supercapacitor with improved electrochemical performances. The new structure MnO2@carbon core-shell hybrid nanorods electrode materials exhibit an excellent cycle ability with 95% retention after 5000 cycles at 4 A g−1, a good specific capacitance of 168 F g−1 at 0.1 A g−1, good rate capability (125 F g−1 at 5 A g−1), relatively low combination of electrolyte resistance \( R_e \) (1.5 ohm) and charge-transfer resistance \( R_s \) (2 ohm).

Experimental

Synthesis of MnO2@carbon core-shell composites.— All of chemical reagents were analytically pure and used without any further purification. Firstly, 3.16 g MnO2(Sinopharm Chemical Reagent Co., Ltd) were dispersed in 150 mL deionized water by magnetic stirring for 5 min at room temperature until uniform transparent purple aequous solution was obtained. 1 mL aniline (C6H5NH2) (Sinopharm Chemical Reagent Co., Ltd) was then added dropwise under stirring. The mixture was heated at 100 °C for 5 h. The obtained black product was filtered, washed by deionized water and dried at 60 °C for 12 h. Then, 1 mL 28 wt% hydrochloric acid (Sinopharm Chemical Reagent Co., Ltd) was added to the above black product. The mixture was stirred for another 8 h. Finally, the obtained black product was washed by deionized water until the PH reached 7. The final product was dried at 60 °C for 12 h.

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Chemical Reagent Co., Ltd was added to the above solution by magnetic stirring for 20 min. The dark brown precipitates and puce suspension were isolated by centrifugation at a rate of 10000 r min⁻¹, and then rinsed with deionized water and alcohol respectively. Three deionized water rinsing/centrifugation/alcohol rinsing/centrifugation cycles were carried out till the supernatant became colorless and transparent. The obtained amorphous MnO₂ was dried at 70 °C for 3 h in air. The synthesis of amorphous MnO₂ is based on the redox reaction as below:

\[
2\text{KMnO}_4 + \text{NH}_3 \rightarrow \text{MnO}_2 + 2\text{KOH} + \text{N}_2 + 3\text{H}_2\text{O}
\]

The amorphous MnO₂ was calcinated at 500 °C for 5 hours to obtain MnO₂ nanorods, seen in Fig. 1b. 0.4 g PEO (Polyethylene Oxide) (A Johnson Matthey Company) was dispersed into 80 mL deionized water. To prevent the PEO from aggregating and precipitating, magnetic stirring for 1 h. 0.8 g MnO₂ nanorods were added into PEO solution with stirring for 3 h. The black precipitates and suspension were isolated by centrifugation at a rate of 10000 r min⁻¹ for 60 min. The MnO₂@PEO nanorods were dried at 70 °C for 3 h in air, followed by calcinating at 500 °C for 5 h in argon atmosphere and then Mn₃O₄@carbon nanorods were obtained, seen in Fig. 1c and Fig. 1d.

**Structural characterization.**— Transmission electron microscopy (TEM) was carried out on a Tecnai G²20 instrument in bright field at 200 kV. Scanning electron microscopy (SEM) was conducted on a JSM-7001F (JEOL, Japan). The X-ray diffraction (XRD) data were recorded using a Bruker X-ray diffractometer (D8 ADVANCE A25) with Cu Kα (λ = 0.154178 nm) radiation. The diffraction patterns were recorded from 10° to 90° at a scanning rate of 6° min⁻¹. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALAB 250 Xi electron spectrometer from VG Scientific using a l sw e r ep r e p a r e db ym i x i n g t h eM n₃O₄@carbon, acetylene black and polytetrafluoroethylene (PTFE) in a weight ratio of 80:10:10 with ethanol. Then the electrode slurry was coated on nickel foam round sheet (r = 7 mm) and dried at 70 °C for 3 h. The thickness of the tested electrodes are 0.1 mm and typical mass of the loaded Mn₃O₄@carbon electrode materials in each nickel foam sheet is about 5 mg cm⁻².

**Electrochemical measurements.**— The working electrode materials were prepared by mixing the Mn₃O₄@carbon, acetylene black and polytetrafluoroethylene (PTFE) in a weight ratio of 80:10:10 with ethanol. Then the electrode slurry was coated on nickel foam round sheet (r = 7 mm) and dried at 70 °C for 3 h. The thickness of the tested electrodes are 0.1 mm and typical mass of the loaded Mn₃O₄@carbon electrode materials in each nickel foam sheet is about 5 mg cm⁻².

Electrochemical measurements were carried out in a three-electrode system: A Ni foam coated with Mn₃O₄@carbon composites as the working electrode, a platinum foil as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The measurements were carried out in a 0.5 mol L⁻¹ Na₂SO₄ (Sinopharm Chemical Reagent Co., Ltd) aqueous electrolyte at room temperature. Cyclic Voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) were measured by a CHI 760E electrochemical workstation. CV tests were done between 0 and 1.0 V (vs. SCE) at different scan rates of 2, 5, 10, 20, 50, 100, 150 mV s⁻¹. Galvanostatic charge/discharge curves were measured at different current densities of 0.1, 0.2, 0.5, 1, 2, 3 and 5 A g⁻¹, and the electrochemical impedance spectroscopy measurements were performed by applying an AC voltage with 5 mV amplitude in a frequency range from 0.1 Hz to 100 kHz. The specific capacitances were calculated from galvanostatic charge/discharge curves respectively according to the following equation:

\[
C = \frac{I \times \Delta t}{\Delta V \times m}
\]

Where I is the constant discharge current, Δt is the discharging time, ΔV is the potential window, and m is the mass of the Mn₃O₄@carbon electrode materials. Two-electrode system is also used to evaluate the capacitive behavior of Mn₃O₄@C//AC in 0.5 mol L⁻¹ Na₂SO₄ aqueous electrolyte at room temperature. The method of preparing activated carbon (AC) is from former reports.

**Results and Discussion**

The Mn₃O₄@carbon nanorods were synthesized via a series of reactions between KMnO₄, aniline and PEO. Firstly, amorphous manganese oxide was prepared. Fig. 2a shows a typical TEM image of amorphous manganese oxide. It is obvious in Fig. 2a that tiny crystals distribute extensively in the view of sight and the SAED figure on the left-above shows the material is amorphous.

The MnO₂ nanorods showed in Fig. 2b are about 50 nm in diameter and 500 nm in length. The diameter and length of the nanorod are determined by the calcination time of armorphous manganese oxide (Shown in Fig. S2 (a), (b) and Fig. S3). Because when those armorphous manganese oxides were calcinated at 500 °C, the thermodynamic free energy of Mn²⁺ and O₂⁻ ions were raised above their diffusion barrier energy, so Mn²⁺ and O₂⁻ atoms transferred to form MnO₂ monocrystal in order to decrease the whole system energy as...
much as possible. The longer the calcination time, the more unanchored atoms would shift onto the outside surface of crystal nucleus and consequently longer, wider nanorod would form. As we can see, the broadside of the nanorod is polyhedral and each plane of the polyhedral is a lattice plane of MnO₂. The top/bottom edge of the MnO₂ nanorod is rough, because the edge consists of several crystal planes of MnO₂. These monocrystal nanorods can serve as ideal templates for further coating. The high resolution TEM (HRTEM) and selected area electron diffraction (SEAD) methods were also used to characterize structure of the MnO₂ grains. Fig. 2c shows a HRTEM image of one MnO₂ nanorod. Visible lattice spacing was measured to be 0.49 nm in one MnO₂ grain, a perfect match of the distance of (200) plane of MnO₂ (JCPDS 44–0141). For the sake of clarity, Fig. 2e demonstrates a simulation image of Inverse Fast Fourier Transform (IFFT) taken from the red circle region in Fig. 2c. Fig. 2d is a SAED of Fig. 2c, which displays a dot diffraction pattern, a typical character of single crystalline MnO₂ with d-spacing values of various planes. Typical SEM images of MnO₂ nanorods are shown in Fig. S2 (c), (d).

The MnO₂ nanorods were dispersed in PEO aqueous solution to form coating on the surface of nanorods. TEM images of MnO₂/PEO are presented in Figs. 2g, 2h. The as-resulted Mn₃O₄@carbon nanorods were fabricated when MnO₂@PEO nanorods were calcinated at 500°C for 5 h in argon atmosphere. It is apparent that there is a thin carbon coating on the surface of MnO₂ nanorod which has been pointed out in Fig. 2f, and this denotes that most precursor may has been changed into Mn₃O₄@C. Typical SEM pictures of MnO₂, Mn₂O₃ nanorods and Mn₃O₄@carbon nanorods are presented in Fig. S2 and Fig. S3, which could provide more morphological information.

Fig. 3a is a XRD pattern of the MnO₂ nanorod samples. For MnO₂ samples, the four strong and sharp peaks at 2theta 37°, 28°, 12°, 18° can be ascribed to the (211), (310), (110), (200) planes of MnO₂. It is apparent that these diffraction peaks can be readily indexed to the MnO₂ (JCPDS 44–0141) and sharp profile reveals good crystallinity. Fig. 3b is a XRD pattern of Mn₃O₄@carbon samples. It is also apparent that the diffraction peaks can be readily indexed to the MnO (JCPDS 07–0230) and sharp profile reveals good crystallinity. Meanwhile, the three sharp peaks at 2theta of 35.2°, 40.6°, 58.6° match the characteristic peaks of MnO and these diffraction peaks can be indexed to the MnO (JCPDS 07–0230). It is obvious that after calcination in argon the pure MnO₂ crystals turned into a mixture of Mn₃O₄ and MnO. The fundamental reason for this phenomenon may derive from the following reaction

\[
(3a + b) MnO₂ + \frac{2a + b}{x} C \xrightarrow{\text{Calcination}} aMn₃O₄ + bMnO + \frac{2a + b}{x} CO_x
\]

where \(a\), \(b\) and \(x\) are three parameters in reaction equation (\(x \neq 0\)). The PEO was converted into amorphous carbon which is attached firmly.

Figure 2. (a) Typical TEM image of manganese dioxide; (b) Typical images of MnO₂ nanorod; (c) HRTEM image of MnO₂ nanorod; (d) SAED pattern of one MnO₂ crystal rod; (e) The simulation image of inverse fast Fourier transform (IFFT) taken from the red circle region in c; (f) TEM image of a cluster of Mn₃O₄@carbon nanorods; (g), (h) TEM images of MnO₂/PEO (before pyrolysis).
Figure 3. (a) XRD pattern of the MnO$_2$ nanorod samples; (b) XRD pattern of the Mn$_3$O$_4$@carbon samples; (c) Typical HRTEM image of Mn$_3$O$_4$@carbon nanorod; (d) A HRTEM image of the selected area taken from the red circle in c; (e) EDS pattern of the selected area taken from the red rectangular frame in c; (f) XPS spectra of Mn 2p region; (g) XPS spectra of Mn 3s region of the Mn$_3$O$_4$@carbon samples; (h) XPS spectra of survey scan of the Mn$_3$O$_4$@carbon samples; (i) TG-DSC curves of the Mn$_3$O$_4$@carbon composite.
to the surface of MnO\(_2\) nanorod. The carbon coating, partially oxidized into CO\(_2\), with a strong reducibility can easily reduce MnO\(_2\) into Mn\(_2\)O\(_3\) and MnO. Manganese in MnO\(_2\) is present in two oxidation states: +2 and +3, and the formula could be written as MnO \cdot Mn_2O_3. A mixture of MnO\(_2\) and MnO also contains two different kinds of manganese: Mn(II) and Mn(III), so when it comes to an electrochemical reaction which focuses on the oxidation state of elements, the MnO\(_2\) and MnO mixture may be ascribed as MnO\(_x\). Fig. 3e presents the energy-dispersive X-ray spectroscopy (EDS) of the selected area taken from the red rectangular frame in Fig. 3c, where the atomic ratio of C: O: Mn: Cu is calculated to be about 18: 33.6: 29.9: 18.5. Elements Cu was also detected, which comes from Cu grid probably. Fig. 3d is an HRTEM image of the selected area taken from the red circle in Fig. 3c. The carbon atom layers show various kinds of orientation and the thickness of this carbon coating is about 4.5 nm. A cluster of MnO\(_{2}\)@carbon nanorods is given in Fig. 3d and it is easy to distinguish a thin, uniform carbon coating surrounding the MnO\(_2\) nanorods. In Fig. 3c, visible lattice spacing was measured as 0.49 nm on one MnO\(_2\) grain, well matching the distance of (101) plane of MnO\(_2\) (JCPDS 24-0734). Meanwhile, the manganese oxidation state is confirmed by XPS. As is shown in Figs. 3f and 3g, in the Mn 2p region, the binding energy of 642.01 eV and 635.51 eV corresponds to Mn2p\(_{1/2}\) and Mn2p\(_{3/2}\), respectively. The splitting width of 11.50 eV is in good agreement with earlier reports on MnO\(_2\).\(^{24}\) In the Mn 3s region in Fig. 3g, the spin-energy separation of 5.04 eV is well in accordance with reported data.\(^{26}\) XPS spectra of survey scan is presented in Fig. 3h. In Fig. 3i, the weight loss from 25\(^{\circ}\)C to 100\(^{\circ}\)C is probably caused by evaporation of moisture. It could be calculated that the carbon content in the MnO\(_2\)@carbon composite is approximately 11.8\% (100\% to 366\%) and the weight of the MnO\(_2\)@carbon composite remains steady which is 85\% when the temperature is higher than 366\(^{\circ}\)C.

Cyclic voltammetry (CV), galvanostatic charging-discharging (GCD) and electrochemical impedance spectroscopy (EIS) measurements were tested in a three-electrode system. Fig. 4a shows typical quasi-rectangular and symmetric CV curves at low scan rate and CV curves are still symmetric at high scan rate (150 mV s\(^{-1}\)), indicating that the MnO\(_2\)@carbon nanorods electrode material has a good electrical double-layer capacitive behaviour. Cations could penetrate carbon coating easily during charging and discharging process and redox reaction can take place beneath the porous and amorphous carbon coating in MnO\(_2\) active materials. Curves in Fig. 4b demonstrate fairly linear slopes, electrochemical reversibility and capacitive behavior. In Figure 4b (especially at 0.1 A g\(^{-1}\)) and Figure 4d (inset graph), the IR drops are clearly observable. The voltage (IR) drop caused by the gradual activation process of the MnO\(_2\) aggregates. From 250 cycles to 2700 cycles, the capacitance retention drops from 101.5\% to 97\%. After that, between 2700 cycles to 3000 cycles, retention begins to go up again to 97.5\% and this may be a second time activation process. During the first time activation process, not all of the aggregated MnO\(_2\) are contacted with Na\(_2\)SO\(_4\) aqueous electrolyte thoroughly; however, with the increasing number of cycling, those MnO\(_2\) which are firmly activated may be totally activated. When the activation process is completed, the retention performs a steady state from then on. With the whole system getting into a stable state after 3500 cycles, 95\% of initial specific capacitance can be finally retained and the shape of charge/discharge curves for the last thirteen cycles still remain nearly symmetric, which indicates the excellent electrochemical stability of the MnO\(_2\)@carbon nanorods electrode materials.

In addition, electrochemical impedance spectroscopy (EIS) was employed to detect the properties of charging and ion transfer in the MnO\(_2\)@carbon and MnO\(_2\) nanorods electrode. Fig. 4e shows the Nyquist plots for MnO\(_2\)@carbon nanorods electrode. Fig. 4f is the Nyquist plots for MnO\(_2\) nanorods electrode, the inset is well-fitted equivalent circuit, in which C\(_{eq}\) is double layer capacitance, R\(_{eq}\) is bulk solution resistance, R\(_{f}\) is the Faradic charge-transfer resistance and Z\(_{eq}\) is the resistance. The sectional semicircle reveals the combination of electrolyte resistance R\(_{eq}\) and charge-transfer resistance R\(_{f}\). The slope of the line indicates the Warburg impedance which represents the diffusion behaviors of the electrolyte in electrode pores and ions in active material. It is clear that the MnO\(_2\)@carbon has a slightly smaller semicircle diameter than the MnO\(_2\) electrodes in high-frequency region, implying smaller resistance from the electrochemical system and charge transfer. From Fig. 4f, it could be estimated that the...
Figure 4. (a) Typical CV curves of the Mn$_3$O$_4$@carbon nanorods at different scan rate; (b) Galvanostatic charge-discharge curves of the Mn$_3$O$_4$@carbon nanorods at various current densities; (c) Specific capacitance of MnO$_2$ and Mn$_3$O$_4$@carbon as a function of current density derived from their galvanostatic charge-discharge curves; (d) Specific capacitance of Mn$_3$O$_4$@carbon nanorod as a function of cycle numbers at 4 A g$^{-1}$, the inset graph shows the galvanostatic charge-discharge curves for the last thirteen circles; (e) Nyquist plots for MnO$_2$ nanorods electrode; (f) Nyquist plots for Mn$_3$O$_4$@carbon nanorods electrode, the inset is well-fitted equivalent circuit.

The combination of electrolyte resistance $R_s$ and charge-transfer resistance $R_{ct}$ of Mn$_3$O$_4$@carbon are 1.5 ohm and 2 ohm respectively. Meanwhile, the difference among the slopes of the lines in low-frequency region indicates that the diffusive resistance of the Mn$_3$O$_4$@carbon is much smaller than that of MnO$_2$. The reason for smaller resistance of Mn$_3$O$_4$@carbon than MnO$_2$ may be caused by the outside amorphous carbon coating. When the electrochemical tests are performed in three-electrode testing system, 0.5 mol L$^{-1}$ Na$_2$SO$_4$ aqueous electrolyte at room temperature is used for all tests. The mobility of ions in electrolyte would maintain at a same level for all electrochemical tests. The difference lies in the transfer ability of ions in bulk material. Ions could transfer easier in Mn$_3$O$_4$@carbon than MnO$_2$ nanorod, because the thin carbon film is conductive and the poly-crystal Mn$_3$O$_4$ structure would also facilitate the transportation of ions in bulk material. The
Mn$_3$O$_4$@carbon nanorods in contact with each other in amorphous carbon coating makes charges easier to transfer, and consequently, the charge transfer resistance can become smaller than that of MnO$_2$. A smaller diffusive resistance of Mn$_3$O$_4$@carbon than MnO$_2$ could be induced by Mn$_3$O$_4$ polycrystals, because these small grains make the whole system more porous and provide more defects, Fig. 3c can illustrate the polycrystalline structure. As for MnO$_2$, seen in Fig. 2c, the degree of crystallinity is high and this leads to a condensed bulk with less defects than MnO$_2$@carbon which may increase the diffusive resistance of MnO$_2$.

Conclusions

In summary, a facile and low-cost preparation of Mn$_3$O$_4$@carbon core-shell hybrid nanorods for supercapacitor electrode materials has been developed. The average thickness of amorphous carbon coatings is 4.5 nm. The diameter and length of inner Mn$_3$O$_4$ nanorods are about 50 nm and 500 nm respectively. Electrochemical measurements show that the Mn$_3$O$_4$@carbon nanorods exhibit a good electrochemical performance: a high specific capacitance of 168 F g$^{-1}$ at the current density of 0.1 A g$^{-1}$, a good rate capability with 125 F g$^{-1}$ at 5 A g$^{-1}$ and an excellent cycle ability with 95% retention after 5000 cycles at the large current density of 4 A g$^{-1}$. Considering the efficiency, low cost, good controllability of the synthesis process and superior electrochemical performance, the Mn$_3$O$_4$@carbon core-shell nanorods have a promising future in applications where durable, stable and long-lasting power supply is needed. Due to the large size of Mn$_3$O$_4$ nanorod, the specific capacitance of Mn$_3$O$_4$@carbon nanorod is not outstanding. We still believe that the performance of electrode materials based on Mn$_3$O$_4$ still can be further improved, so future researches shall focus on fabricating a smaller-sized Mn$_3$O$_4$ nanorod electrode materials.

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