MnO₂@colloid carbon spheres nanocomposites with tunable interior architecture for supercapacitors

Yuxin Zhang a,b,*, Meng Dong a, Shijin Zhu a, Chuanpu Liu a,**, Zhongquan Wen b

a College of Materials Science and Engineering, Chongqing University, Chongqing 400044, PR China
b National Key Laboratory of Fundamental Science of Micro/Nano-Devices and System Technology, Chongqing University, Chongqing 400044, PR China

1. Introduction

Supercapacitors have attracted intense attention owing to their high power density and long cyclic life [1–3]. Recently, a crowd of materials have been considered as the energy storable materials for supercapacitors electrodes, including transition metal oxides [4–9], carbonaceous materials [10] and conducting polymers [11]. Among them, manganese oxides were attractive due to their high theoretical specific capacitance, low cost and environmental friendliness [12–14]. Yet, the poor electrical conductivity and low specific area of manganese oxide electrodes hampered the emission of capacity. The electrochemical properties of MnO₂ were mainly dependent on their sizes, structures and crystallinity [15]. There were two major charge storage mechanisms that have been widely accepted. One was the surface adsorption–desorption of cations:

\[(\text{MnO}_2)_{\text{surface}} + \text{Na}^+ + e^- \rightarrow (\text{MnONa})_{\text{surface}}\]  \hspace{1cm} (1)

Another one was based on the intercalation/deintercalation of cations in the bulk [16]:

\[(\text{MnO}_2) + \text{Na}^+ + e^- \rightarrow (\text{MnONa})_{\text{surface}}\]  \hspace{1cm} (2)

Ultrathin, ultrafine or amorphous MnO₂ nanostructures [17–20] was expected to have larger specific area and deliver better charge storage performance because of the efficient utilization of surface- and bulk-redox reactions. Lee et al. [21] described the pseudocapacitive behaviors of amorphous manganese oxides with a capacitance of about 200 F g⁻¹. Zhao et al. [22] investigated the capacitive performance of rattle-type MnO₂ on carbonaceous sphere exhibited a capacitance of 184 F g⁻¹ at a current density of 125 mA g⁻¹. Wang et al. [23] reported that novel bushy MnO₂ nanocomposites could be obtained by using KMnO₄ to corrode onion-like carbon, leading to a low capacitance of 189 F g⁻¹ at a discharging rate of 0.2 A g⁻¹. To date, there were few reports using carbon spheres (CSs) as the cores to fabricate MnO₂ nanocomposites with tunable interior architecture to improve electrochemical performance for supercapacitor electrodes.

Herein, we reported a facile redox route to fabricate the ultrathin MnO₂ nanofilms on colloid carbon spheres with a tunable interior architecture in acid conditions. By fine-tuning the preparative conditions (e.g., concentration, process temperature), core–shell, yolk–shell, and hollow nanostructures were obtained, and their electrochemical performances for supercapacitors were examined.
2. Experimental

2.1. Preparation of CSs

Carbonaceous spheres were synthesized via a simple hydrothermal method [24]. Typically, glucose (6 g) was dissolved in 35 mL of distilled water; the solution was sealed in a 50 mL Teflon-lined stainless autoclave, and put in an electric oven at 190 °C for 4 h. Afterwards, the solid CSs precipitates were collected, washed with distilled water and ethanol for several times, and dried at 60 °C for 12 h.

2.2. Preparation of MnO2@CSs core–shell nanostructures

The CSs (5 mg) were dispersed in 20 mL of distilled water. The slurry was dispersed under ultrasonication for 5 min, followed by the addition of KMnO4 solution (5 mL). Afterwards, the precipitates were washed with distilled water and ethanol for several times, followed by centrifugation and drying at 60 °C. The solid samples were designated as S-C5, S-C10, and S-C20, implying the different KMnO4 concentrations of 5, 10, and 20 mM.

2.3. Preparation of MnO2@CSs yolk–shell nanostructures

The CSs (5 mg) were dispersed in 20 mL of distilled water. The slurry was dispersed under ultrasonication for 5 min, followed by the addition of KMnO4 solution (5 mL, 20 mM) and H2SO4 solution (0.8 mL, 50 mM). Afterwards, the precipitates (yolk–shell nanostructures) were washed with distilled water and ethanol for several times, followed by centrifugation and drying at 60 °C.

2.4. Preparation of hollow MnO2 nanostructures

The CSs (5 mg) were dispersed in 20 mL of distilled water. The slurry was dispersed under ultrasonication for 5 min, followed by the addition of KMnO4 solution (5 mL, 50 mM) and H2SO4 solution (0.8 mL, 0.5 M). Afterwards, the precipitates (hollow nanostructures) were washed with distilled water and ethanol for several times, followed by centrifugation and drying at 60 °C.

2.5. Characterization

The structures and morphologies of as-prepared nanostructures were measured by focused ion beam scanning electron microscopy (ZEISS AURIGA FIB/SEM) and high-resolution transmission electron microscopy (HRTEM, ZEISS LIBRA 200). The crystallographic information and chemical compositions of as-prepared nanostructures were established by powder X-ray diffraction (XRD, D/max 1200, Cu Kα), Fourier transform infrared spectroscopy (FTIR, Nicolet 5DXC) and thermogravimetric analyzer-differential scanning calorimeter (TGA-DSC NETZSCH STA 449C). The specific surface area was confirmed by N2 adsorption/desorption isotherm at 77 K, and the pore size distributions were calculated from the adsorption curve by the Barrett–Joyner–Halenda (BJH) method.

2.6. Electrochemical measurement

The electrochemical properties of as-prepared core–shell (S-C20), yolk–shell and hollow nanostructures were carried out by a CHI 660D electrochemical workstation in Na2SO4 (1 M) solution. In a typical measurement, the electrochemical cell had three-electrode configuration with as-prepared nanostructures powders electrode as the working electrode, a Pt plate as the counter electrode and a saturated calomel electrode as the reference electrode. The working electrode was prepared by mixing active materials, carbon black (Super P), and polyvinylidene fluoride (PVDF) with a mass ratio of 70:20:10. The slurry of above mixture was painted evenly on the foamed nickel as a current collector. The coated mesh was dried at 120 °C in vacuum oven overnight to remove the solvent and water. The mass of active material on the working electrode was in the range of 0.3–0.4 mg cm−2.

Cycle voltammetry (CV) measurements were performed in the voltage between 0 and 1.0 V at different scan rates. Galvanostatic charge–discharge experiments were enforced to reflect the rate ability at varied current densities. EIS measurements were carried out by applying an AC voltage with 5 mV amplitude in a frequency range from 0.005 Hz to 100 kHz at the open potential.

3. Results and discussion

Fig. 1 showed the XRD patterns of three typical samples with core–shell, yolk–shell, and hollow nanostructures. All the peaks of each sample can be indexed to amorphous birnessite-type MnO2 (JCPDS 42-1317), consisting of a large amount of water molecules between the layers [25,26]. The diffraction peaks of MnO2 were
broad and weak, indicating the poor crystalline nature. The characteristic peaks for MnO$_2$ was intensified with the increase of the MnO$_2$ content in the composites [23]. The TGA measurement also verified that the as-prepared MnO$_2$ consisted of a large amount of water (Fig. S1). Exactly, the first weight loss with slightly decrease below 100 °C resulted from the removal of physically absorbed water. A steep decrease around 250 °C indicated the removal of interlayer water and crystalline water, followed by the loss of colloid carbon spheres around 300 °C.

The FT-IR spectrum was used to investigate the functional groups of representative samples. As presented in Fig. 2a, the peaks in the 1000–1450 cm$^{-1}$ region resulting from the vibrations of –C–O stretching and –OH bending vibrations indicated a large number of residual hydroxyl groups on the surface of the CSs [27]. The bands at 1701 and 1628 cm$^{-1}$ were attributed to C=O and C=C vibrations respectively, implying the immature aromatization of glucose during the hydrothermal treatment. Besides, the bands at approximately 2900 cm$^{-1}$ corresponded to stretching vibrations of C–H. The surface functional groups played an important role to form the MnO$_2$@CSs core–shell structure, due to the weaker oxidizability of KMnO$_4$ in neutral solution at room temperature. Nevertheless, after reaction with KMnO$_4$ (Fig. 2c and d), the band at
about 2900 cm\(^{-1}\) was assigned to stretching vibrations of aliphatic C–H, and the band at 1701 cm\(^{-1}\) (assigned to C=O vibrations) disappeared, implying that some organic groups on the surface of the CSs were oxidized. Furthermore, the broad peak ascribing to the Mn–O vibrations of manganese oxides in the range of 450–650 cm\(^{-1}\) occurred. Additionally, the bands at about 1113, 1386 and 1630 cm\(^{-1}\) were consistent with the coordination of Mn–O–H [28,29], whereas the bands at approximately 3430 cm\(^{-1}\) corresponded to the O–H stretching vibration, indicating a large amount of water, in agreement with the XRD result.

FIB/SEM image (Fig. 3a) revealed the carbonaceous spheres with a uniform size of about 400 nm. The entirely sphere with a smooth surface indicated the perfect polymerization of glucose during the hydrothermal treatment. The core–shell nanostructures with different content of MnO\(_2\) were shown in Fig. 3b–d. Clearly, the products looked like a large amount of thin nanofilms enironing the carbon spheres with diameters of around 500 nm, testifying the formation of MnO\(_2\) and the reaction between the surface functional groups of CSs and KMnO\(_4\). With the increased concentration of KMnO\(_4\), the shell changed from scattered nanofilms to integral nanosweater. Whereas, Fig. 3e and f presented that the products were loose nanospheres assembled from a large amount of interconnected small nanofilms, which enhanced the superficial electroactivity. And the cores, safely wrapping themselves in the nanofilms, stayed inside the spheres. TEM images also confirmed the ultrathin nanofilms with a typical thickness of 2–3 nm, in agreement with the XRD result. Nevertheless, with the H\(_2\)SO\(_4\) introduction, the structure transformed from core–shell to yolk–shell nanostructures (Fig. 4a and b). The interior architectures with smooth surface were surrounded by a sweater, indicating the reaction between complete aromatization section and MnO\(_2\) in acidic solution. The thickness of MnO\(_2\) shell was calculated to be 120–130 nm, further probing the etching reaction. With the increased concentration of KMnO\(_4\) and H\(_2\)SO\(_4\) (e.g., 0.05 M and 0.5 M respectively), a hollow nanostructure was obtained (Fig. 4c, d). Apparently, MnO\(_2\) nanostructures possessed hollow cores of ~400 nm in diameter and uniform shells with a thickness of ~150 nm. These findings demonstrated that the morphology and structure of MnO\(_2\)@CSs could be deeply affected by amounts of KMnO\(_4\) and H\(_2\)SO\(_4\) synergistically.

Fig. 5 displays the nitrogen adsorption and desorption isotherms and the corresponding Barrett–Joyner–Halenda (BJH) pore-size distribution of three kinds of samples. A distinct hysteresis loop at a relative pressure of ca. 0.45–1.0 could be observed, which indicated a fingerprint of mesoporous feature. It was believed that colloidal carbon spheres contributed a little for specific area of nanostructures (Fig. S3), owning to their smooth surface with few micropores [30]. Compare to core–shell structure (44.8 m\(^2\) g\(^{-1}\)) and yolk–shell structure (137.3 m\(^2\) g\(^{-1}\)), hollow structure showed the highest specific area of 159.0 m\(^2\) g\(^{-1}\). The pore-size distributions (Fig. 5) revealed the pore diameter of about 11.1, 7.1 and 7.0 nm, respectively, confirming the mesoporous nature. Electrochemical properties were surely influenced by the porosity and the rough surface of the electrode materials [31]. The high BET surface area and mesoporous features of these nanocomposites could provide the possibility of efficient transport of electrons and ions, which led to the good electrochemical behavior of these materials.

Cycle voltammetry and galvanostatic charge-discharge measurement were carried out in a three-electrode configuration in 1 M Na\(_2\)SO\(_4\) to investigate the capacitive properties of the samples with different structures. Fig. 6a showed the CV curves of the three kinds of structures at a scan rate of 5 mV s\(^{-1}\). All the CV curves exhibited rectangular shapes, without any other distinct sharp redox peaks, indicating the ideal pseudocapacitive. This may be attributed to the ultrathin films assembled from hierarchical porous nanostructure. The ultrathin films provided a greater access of the electrolyte to the surface of active materials. Fig. 6b showed the charge–discharge plots of three kinds of structures at a current density of 0.2 A g\(^{-1}\). Obviously, the charge curves were symmetric to their corresponding discharge counterparts, implying a fast and reversible Faradic reaction between alkali cations (Na\(^+\)) and the ultrathin MnO\(_2\) nanofilms [32]. The specific capacitances of the three kinds of structures were calculated to be 154.2, 273 and 188.4 F g\(^{-1}\) at a current density of 0.2 A g\(^{-1}\), according to Eq. (3) as below:

\[
C_s = \frac{\Delta t}{m \Delta V}
\]

where \(I\) (A) is the charge–discharge current density, \(\Delta t\) (s) is the charge or discharge time, \(m\) (g) is the mass of active material, and
\( \Delta V \) (V) is the potential windows during the charge or discharge process. The yolk–shell nanostructures exhibited a promising capacitance, which was better than that of bulk MnO\(_2\) nanorods (180 F g\(^{-1}\)) [32], nanotubes (220 F g\(^{-1}\)) [33], nanoflowers (125.1 F g\(^{-1}\)) [34] and that of some MnO\(_2\)/carbonaceous sphere composites [22, 18], due to the reasonable MnO\(_2\) content and its novel structure. The high specific capacitance originated from the contribution of MnO\(_2\). However, the conductivity of the materials played an indispensable role in their capacitances. Although hollow structure samples were composed exclusively of MnO\(_2\), the corresponding specific capacitance was lower than that of yolk–shell nanostructures. A distinct tendency reflecting the internal resistance of the electrode materials (Fig. 6c) presented that the slopes of linear correlation between the IR drop and discharge current density were linked to the internal resistance of the electrode materials [35–37]. Clearly, the yolk–shell structure possessed a minimal gradient, implying the minimum resistance. The resistance of the electrode was decreased with the decrease of the MnO\(_2\) content. However, the effect of the inner electrolytic reservoir of composites should not be ignored, since yolk–shell structure samples revealed the greatest capacitance performance. Fig. 6d showed the specific capacitances of different structures at different current densities, indicating a slight decrease with the increase of current density, which was contributed to the reduced surface area accessed by the electrolyte at a high current density. Nevertheless, the specific capacitance of yolk–shell structure remained as high as 219 F g\(^{-1}\) at a current density of 2 A g\(^{-1}\), which exceeded those reported for MnO\(_2\)/graphene composites [38]. About 70% of the specific capacitance retention was observed when the discharge rate increased from 0.1 A g\(^{-1}\) to 2 A g\(^{-1}\) [22]. The good rate performance of the yolk–shell nanostructures electrode was surely attributed to the ultrathin MnO\(_2\) nanofilms, providing a possibility of efficient transport of electrons and ions and its unique nanostructure with an electrolytic reservoir inside.

All the Nyquist plots (Fig. 7) exhibited a nearly semicircle over the high frequency range, followed by linear part in the low frequency region [7]. The equivalent circuit model for analyzing these impedance spectra was shown in the inset of Fig. 7. Specifically, the circuit included the ohmic resistance of electrolyte and the internal resistance of the active materials \( R_\text{e} \), the interfacial Faradic charge transfer resistance \( R_\text{ct} \), a capacitance of the double layer and a finite-length diffusion Warburg impedance \( Z_\text{w} \) associated with electrolyte ions diffusion/transport throughout the electrode. The values of \( R_\text{e} \) for core–shell, yolk–shell and hollow structure were 1.13, 1.66, and 3.23 \( \Omega \), respectively, which indicated the relatively good conductivity of the electrolyte. The
large semicircle were consistent with high interfacial charge-transfer resistance, owing to the poor electrical conductivity of materials, while the better verticality revealed an ideal capacitive behavior of the electrode materials [39]. The values of $R_s$ for core-shell, yolk–shell and hollow structure were calculated to be 5.83, 10.56, and 36.46 $\Omega$. The electrode of yolk–shell nanostructures expressed a smaller interfacial charge-transfer resistance and more approaching Faradic capacitive, which was corresponded to the rate performance test and IR drop verdict. In accordance with the largest semicircle, the poor supercapacitive behavior and severe attenuation in capacitance against current density of hollow structure MnO$_2$ would be attributed to the high resistance of charge transfer.

Fig. 8 presented the cycle stability in specific capacitance of the three kinds of structures at a scan rate of 2 A g$^{-1}$ for up to 1000 cycles. The specific capacitance of the samples with yolk–shell structure was decreased more slightly, compared to the core–shell structure and hollow structure, although all the cycling stability of the products decreased throughout the cycle time. After 1000 cycles, the former discharge capacities still retained 187.9 F g$^{-1}$ with 14.1% deterioration of initial available specific capacitance, while the yolk–shell and hollow nanostructures displayed charge/discharge stability with 24% and 20.5% loss, respectively. These findings demonstrated that the yolk–shell nanostructures could be a promising electrode material for high-rate charge/discharge operations in supercapacitors.

4. Conclusions

In summary, a facile and cost effective strategy has been developed to fabricate MnO$_2$/colloid carbon spheres with tunable interior architectures, including core–shell, yolk–shell, and hollow interior structure. Among the three typical structures, the yolk–shell nanostructures exhibited the excellent pseudocapacitance performance, revealing a specific capacitance of 273 F g$^{-1}$, good rate ability and cycling stability, owing to its unique structure and the poor crystallinity of MnO$_2$ nanofilms. In principle, this facile synthetic strategy could be useful to design and fabricate structure tunable materials, potentially applied in supercapacitors.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.materresbull.2013.09.030.

References