Sandwich-structured MnO₂@N-doped Carbon@MnO₂ nanotubes for high-performance supercapacitors

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Graphical abstract

A **N-doped carbon nanotubes templating method** was developed to synthesize triple-walled MnO₂@N-doped carbon@MnO₂ nanotubes, which can be used for high-performance supercapacitors.

ABSTRACT:

The MnO_2 @N-doped carbon@ MnO_2 triple-walled nanotubes were synthesized by an *in-situ* growing of MnO_2 nanosheets to both the external and internal surfaces of N-doped carbon nanotubes (NCNTs). Thanks to the unique structures of NCNTs, the density of MnO_2 nanosheets were relatively high in the nanocomposite. Because of the NCNTs offered adequate room to accommodate the volume deformation of MnO_2 on/in the nanotubes, the final nanocomposites possessed comprehensive electrochemical performance: high specific capacitance (253.1 F/g at a current density of 1 A/g), good rate capability (83.3 % retention with charge-discharge rate increasing from 1 A/g to 10 A/g), superior reversibility and cycling stability (96.43% capacitance retention after 2000 cycles at 10 A/g). Based on the above features, the nanocomposites were well fitted for high performance supercapacitors.

Keywords: Supercapacitor, Triple-walled, MnO_2 @N-doped carbon@ MnO_2 nanotubes, Electrochemical performance.

1 Introduction

In recent years, supercapacitors have attracted intense interest due to their excellent properties, such as high power density, fast delivery rate, safe operation mode and long cycle life[1-6]. Basis on the energy-storage mechanism, capacitor can be divided into two kinds: one is the non-faradaic electrical double-layer capacitors (EDLCs) which are usually composed of carbon-based materials[7, 8], the other one is the faradaic pseudocapacitors which usually consist of transition metal oxides[9-11]. Since the limitations of the most of carbon-based materials, such as their low capacitance[12-14], low energy density, poor rate capability, and unsatisfactory thermal stability, lots of studies have been stimulated on transition metal oxides with a high reversible capacity and power density[15-17]. Among these transition metal oxides, the MnO_2 is particularly attractive, because of its high theoretical specific capacity (theoretical pseudocapacitance is 1370 F/g), small voltage hysteresis, high abundance and environmental benignity[13, 18-21]. However, the poor conductivity[22] and large volume variation during the discharge/charge processes greatly limits its performance on rate capability and cycling stability. Therefore, many strategies have been developed to address these problems. Especially, the combination of transition metal oxides and carbon-based materials together is an efficient way to improve capacitor performance. Carbon usually effectively enhances the electronic conductivity and sustains a stable structure upon cycling. Very recently, it was reported that N-doped

carbon (N-C) materials could further enhance the electrical properties of carbon materials[23], in addition to improve the specific capacitance and cycling performance for supercapacitors. For example, Li et al. prepared CNT@Nitrogen-doped carbon shell@MnO₂ materials which showed a specific capacitance of 312.5 F/g[13]. Li et al. produced hierarchical hollow MnO₂/nitrogen-doped hollow carbon hybrid with a capacitance of 306 F/g[12]. Recently, a easy and cheap way to obtain carbon/MnO₂ hybrid materials was reported based on the redox reaction: $4\text{KMnO}_4 + 3\text{C} + \text{H}_2\text{O} \rightarrow 4\text{MnO}_2 + 2\text{KHCO}_3 + \text{K}_2\text{CO}_3$ [24, 25]. In this way, MnO₂ nanostructures can be well coated on the carbon materials, thus greatly improve the energy density of the electrode material. Unfortunately, this method led to a compact carbon-MnO₂ structure, which decreased the specific surface area. This situation was unbeneficial for fast electron transfer and electrolyte diffusion[26-28], thus affected the electrochemical performance. To this end, the synthesis of hybrid materials with suitable structure to enhance the electrochemical performance is still a challenging topic.

Herein, we demonstrate the uniform loading of ultrafine and loosened MnO₂ nanosheets on NCNTs surfaces. The triple-walled MnO₂@N-doped carbon@MnO₂ nanotubes were obtained by the redox reaction between KMnO₄ and N-doped nanotubes(NCNTs) at both of the external and the internal surfaces. The loading amount of MnO₂ can be easily controlled by tuning the KMnO₄ concentration. The present MnO₂@N-doped carbon@MnO₂

nanotubes exhibited several obvious advantages as electrode materials: (a) the ultrafine and loosened MnO₂ floccules possessed a higher specific surface area, hence endowed the nanocomposites with more electroactive sites. (b) one-dimensional N-doped nanotubes (NCNTs) with high conductivity served as both the backbone and conductive pathway for MnO₂. More significantly, the MnO₂@N-doped carbon@MnO₂ nanotubes exhibited intriguing electrochemical performance with a specific capacitance as high as 253.1 F g⁻¹ in 1 M Na₂SO₄ aqueous solution. Such a structure fully exploited the good electronic conductivity and hollow structure of N-doped carbon tubes to realize the high-density loading of MnO₂ nanosheets, and reduce their charge-transfer resistance simultaneously. As a result, the triple walled MnO₂@N-doped carbon@MnO₂ nanotubes exhibited superior electrochemical performances in terms of cycling stability and capacitance, which were better than that of NCNTs and MnO₂. The excellent performance was related with the aid of NCNTs and triple walled structure, which effectively enhanced the electronic conductivity. More importantly, this method could be extended for other materials built by metal oxides and N-doped carbon nanotubes.

2 Experimental

2.1 Synthesis of the samples

2.1.1 Synthesis of molybdenum trioxide (MoO_3) nanorods.

The MoO_3 nanorods were prepared by a solvothermal method as described previously[29]. In a typical synthesis, 1 g of ammonium heptamolybdate tetrahydrate ($\text{H}_{24}\text{Mo}_7\text{N}_6\text{O}_{24}\cdot 4\text{H}_2\text{O}$, Sigma-Aldrich) was dissolved in a mixed solution of 65% HNO_3 (5 mL) and deionized water (20 mL). After fully dissolved, this reaction solution was transferred into a Teflon-lined stainless steel autoclave (35 mL capacity) and heated at 180 °C in a preheated electric oven for 20 h. After cooling, the white product was harvested by centrifugation and washed thoroughly with deionized water and ethanol before drying at 60 °C overnight.

2.1.2 Synthesis of MoO_3 @PPy nanocomposite.

A typical synthesis was listed as follows. Freshly prepared MoO_3 (0.1 g) nanorods were homogenously dispersed into a mixed solution of 40 mL deionized water and 5 mL anhydrous ethanol with the help of sonication for 1h at ambient temperature. To this vigorously stirred suspension was added 0.1 mL of pyrrole, and stirring was continued for 0.5 h. Then 0.329 g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (dissolved in 5mL of deionized water) was slowly dropped into the above solution, and the polymerization was performed 4.5 h. The black-colored solution was filtration and then dried at 60 °C for 12 h under vacuum to obtain the MoO_3 @PPy nanocomposite.

2.1.3 Synthesis of NCNTs, MnO₂, and MnO₂@NCNTs@MnO₂ composites.

The MoO₃@PPy nanocomposite was treated with ammonia solution to remove the MoO₃ and generate the PPy nanotubes[30]. The details of carbonization of the PPy nanotubes were listed as follows: the thermal treatment was performed under flowing nitrogen in a tube furnace with a heating rate of 2°C/min up to 300°C, which was maintained for 2.5 h, and heating at a rate of 5°C/min up to 600°C, which was maintained for 5 h. 20 mg NCNTs were dispersed into 30 mL of 0.01M KMnO₄ solution under high power ultrasonication for 1h. Then, the mixture was transferred to a Teflon-lined stainless steel autoclave (50 mL capacity) and heated at 180 °C for 1.5h. The product was obtained by centrifugation and dried at 60°C for 12 h. Subsequently, the MnO₂ was obtained by calcining the MnO₂@NCNTs@MnO₂ in air atmosphere with the rate of 1°C/min up to 600°C, which was maintained for 4 h.

2.2 Electrochemical measurements.

The electrochemical tests were carried out at room temperature in three-electrode configurations. The MnO₂@NCNTs@MnO₂ electrode served as the working electrode, and a Pt wire and Ag/AgCl electrode were used as the counter and reference electrode, respectively. The working electrode was prepared by mixing MnO₂@NCNTs@MnO₂ with super P and polytetrafluoroethylene (PTFE) in a weight ratio of 8:1:1. After thorough mixing, the slurry was pressed into thin Ni foam by a rolling method and then dried at

60°C for 12 h. A 1M Na₂SO₄ solution was employed as electrolyte for electrochemical measurements. The specific capacitance values of the electrode were calculated from galvanostatic charge–discharge curves according to Equation,

$$C = I \Delta t / m \Delta V$$

Where I is the response current density, Δt is the discharge time, m is the mass of the active materials on a single electrode and total mass of the active materials on both the positive and negative electrode, and ΔV is the potential range during the charge–discharge measurement.

2.3 Characterization

The XRD pattern of samples were recorded with a Shimadzu(Japan) D/Max-2500 diffractometer using a monochromatized X-ray beam with nickel-filtered Cu = K α radiation. N₂ adsorption/desorption was measured at liquid-nitrogen temperature (77 K) by using a Micromeritics ASAP 2460 instrument. The specific surface area was obtained by the BET method, and the pore size distribution was calculated from the desorption branch of the isotherm. The morphology of the samples were observed using a scanning electron microscope (SEM, Hitachi S-8000, Japan) in a secondary electron scattering mode at 5 kV and a transmission electron microscope (TEM). X-Ray photoemission spectroscopy (XPS) data were obtained with an ESCALAB 250Xi instrument equipped with a monochromatic Al anode X-ray gun. Fourier transform infrared spectra (FT-IR) were obtained using a Perkin-Elmer

Spectrum one spectrometer. The electrochemical properties was carried out by a CHI 666D electrochemical workstation.

3 Results and discussion

Scheme1. Schematic illustration for the preparation of MnO₂@NCNTs@MnO₂ composites.

Scheme1 briefly illustrates the synthetic processes of triple-walled MnO₂@N-doped Carbon@MnO₂ nanotubes (MNM). **Firstly**, the MoO₃@PPy nanocables with core-shell structures were fabricated by in-situ oxidative polymerization method. Then, the high-quality PPy nanotubes were obtained by etching MoO₃ cores in ammonia solution under hydrothermal conditions, which were **further** converted into N-doped carbon nanotubes by calcinations in inert atmosphere. Finally, the MnO₂ nanosheets were deposited on **both of**

the external surface and the internal surface of N-doped nanotubes *via* a redox reaction between the NCNTs and KMnO_4 , resulting in a triple-walled $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ nanotubes(MNM).

Fig. 1. XRD patterns of MoO_3 and $\text{MoO}_3@\text{PPy}$ (A), NCNTs and $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ composite (B).

We recorded XRD patterns of MoO_3 , $\text{MoO}_3@\text{PPy}$, NCNTs and $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ to analyze the evolution and crystalline structure. The X-ray diffraction (XRD) patterns of the MoO_3 and $\text{MoO}_3@\text{PPy}$ nanocomposite are shown in Fig. 1A. All the diffraction peaks can be indexed as the orthorhombic MoO_3 phase (JCPDS card no. 05-0508, $a = 3.962 \text{ \AA}$, $b = 13.858 \text{ \AA}$, $c = 3.697 \text{ \AA}$), which are in good agreement with the literature values[31]. Moreover, **due to the semi-crystalline nature of PPy**, the peak intensity of the $\text{MoO}_3@\text{PPy}$ nanocomposite is obviously weaker than that of the virginal MoO_3 nanorods. However, their peak positions are the same as the virginal $\alpha\text{-MoO}_3$ nanorods, fully **indicating** that the MoO_3 cores **are** not changed after PPy coating. Because of the amorphous **nature**, the obvious broad peak about 28° has been observed in the NCNTs product (Fig. 1B). After hydrothermal

reaction in the presence of KMnO_4 , the three peaks (001), (111) and (020) can be indexed to the monoclinic structure of birnessite-type MnO_2 (JCPDS 42-1317, $\delta\text{-MnO}_2$)[28-32]. Moreover, the characteristic peaks for graphitic carbon at 28° and 44° are disappeared, which demonstrates that the MnO_2 nanosheets are uniformly grown on the NCNTs, resulting in the masking of the graphite carbon signal.

Fig. 2. FTIR spectra of the MoO_3 , $\text{MoO}_3\text{@PPy}$, PPy, NCNTs and $\text{MnO}_2\text{@NCNTs@MnO}_2$

The FTIR spectra for MoO_3 , $\text{MoO}_3\text{@PPy}$, PPy, NCNTs and $\text{MnO}_2\text{@NCNTs@MnO}_2$ are displayed in Fig. 2. As can be seen from Fig. 2, the characteristic peaks of $\alpha\text{-MoO}_3$ appear at about 996, 881 and 568 cm^{-1} , belonging to terminal oxygen symmetry stretching mode of Mo=O and the bridge oxygen asymmetry and symmetry stretching modes of Mo-O-Mo respectively[33]. The O-H absorption bands appeared at 3438 and 1633 cm^{-1} can be assigned to the water molecules. By contrast, in the spectrum of

MoO₃@PPy coaxial nanocables, the peaks at 996, 881 and 568 cm⁻¹ shift to 991, 864 and 551 cm⁻¹, respectively, reflecting a mutual interaction between the PPy and original α-MoO₃. Furthermore, the characteristic peaks of PPy also appear in the spectrum of the MoO₃@PPy coaxial nanocables. The peak at 2931 cm⁻¹ and 2854 cm⁻¹ can be attributed to the C-H stretching vibration and the peaks at 1628 cm⁻¹, 1587 cm⁻¹ and 1044 cm⁻¹ are assigned to the C=C, C-C and C-N stretching vibration in the PPy rings, respectively. In addition, the peak at about 1587 cm⁻¹ is assigned to the symmetric stretching vibration of C-C bond in the PPy rings[34]. For the PPy nanotubes, these characteristic peaks of PPy are still existed while the adsorption peaks of MoO₃ are diminished, this fully indicates that the MoO₃ is successfully etched in the ammonia solution. After carbonization, most of the characteristic peaks of organic groups disappears, confirming PPy groups are successfully carbonized[19]. After hydrothermal reaction with KMnO₄, the characteristic peaks at 721, 531 and 475 cm⁻¹ are assigned to the metal-oxygen(Mn-O) vibrations of MnO₆ octahedra[35], indicating that the MnO₂ nanosheets are successfully deposited on the NCNTs.

Fig. 3. SEM and TEM images of MoO₃ template (A, B), MoO₃@PPy(C, D), NCNTs (E, F), MnO₂@NCNTs@MnO₂ (G, H).

SEM and TEM micrographs of the prepared MoO₃ and MoO₃@PPy composites are shown in Fig. 3. The MoO₃ nanorods presents one-dimensional structures with a diameter of ~300 nm and a length of several micrometers(Fig. 3A and B). After PPy coating, a rough and undulating surface morphology is observed (Fig. 3C and D). The distinct core-shell structure indicates that PPy shell is uniformly coated onto the surface of MoO₃, giving an

increased diameter of 350–400 nm. Subsequently, the MoO_3 templates are removed with $\text{NH}_3 \cdot \text{H}_2\text{O}$ (28%) solution at 70 °C for about 4 h to collect the black PPy nanotubes[29]. As the PPy nanotubes are calcined in N_2 at 600°C, PPy gradually carbonized but the structure is carefully kept, producing the hollow N-doped carbon nanotubes (NCNTs). Fig. 3E and F show SEM and TEM images of the NCNTs tubular structure. The nanotubes well copy the morphology of the original 1D shape of MoO_3 nanorods with a thickness of ca. 50 nm. From the cracked tubes, the hollow interior can be observed directly, indicating the formation of tubular structures with inner cavities. It is noted that these NCNTs nanotubes have quite rough surface that it would offer numerous sites for adsorbing MnO_4^- species on the surface during the growth of MnO_2 . Moreover, the good permeability and reaction between NCNTs and MnO_4^- ions are also favorable for MnO_2 growing. These speculations are confirmed by the following SEM and TEM images of the product after the reaction of KMnO_4 . The SEM and TEM image (Fig. 3G, H) shows that both the inner and outer layer of obtained $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ material is gradually covered by MnO_2 during the redox reaction. Here, the hollow NCNTs is applied as both reducing agents and substrates for MnO_2 growth. If the calcination is conducted in air, NCNTs would be burned out, leading to a hierarchical porous structure (MnO_2 nanotubes). (Fig. 4). Without the support of N-doped carbon, MnO_2 nanorods in this structure grow quickly. The obtained products from the pyrolysis on $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ in air can be also used as supercapacitor.

Fig. 4. The SEM and TEM image of the obtained product from pyrolysis of

$\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ composites in air

Fig. 5. XPS spectra of $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ composite: survey spectrum (A),

C 1s (B), N 1s (C) and Mn 2p (D).

XPS analysis is employed to provide further structural information of the $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ hybrid (Fig. 5). The survey spectrum (Fig. 5A) demonstrates that C, O, N, and Mn atoms are present in this hybrid material.

Fig. 5B and 5C shows the high-resolution C 1s and N 1s spectrum, respectively. The Mn 2p_{3/2} peak centered at 642.2 eV and Mn 2p_{1/2} peak at 654.0 eV with a spin-energy separation of 11.8 eV (Fig. 5D) are in good accordance with the data of Mn 2p_{3/2} and Mn 2p_{1/2} in the previous reports[36], which further confirms the successful assembly of MnO₂ nanosheets on the surface of NCNTs. The N1s peak (Fig. 5C) can be resolved into three components centered at 398.6, 399.8, and 400.3 eV, corresponding to pyridinic (N-6), quaternary (N-Q), and graphitic types of nitrogen, respectively[37, 38] [39]. It is reported that the nitrogen atoms can improve the wettability of active materials in the electrolyte and thus favor the ion transport[40]. Moreover, the presence of N-Q and N-6 is beneficial to the conductivity and extra pseudocapacitance of carbon materials[41]. The O1s peak observed at 529.5 eV is indexed to the oxygen bonded with manganese (O-Mn) in α -MnO₂ (see Fig. 5D). All these spectrum informations and peak energies agree well with the previously reported results of MnO₂, confirming the presence of α -MnO₂ and indicating a 4+ oxidation valence state of Mn. Raman spectrum was also measured to analyze the carbon quality in NCNTs and MnO₂@NCNTs@MnO₂ hybrid. As shown in Fig. 6, two strong peaks can be found at 1348 and 1595 cm⁻¹, corresponding to the disordered D band and graphitic G band, respectively. The intensity ratio I_D/I_G is calculated to be 0.85, indicating a high graphitization of NCNTs. For the MnO₂@NCNTs@MnO₂ hybrid, the two strong peaks are centered at 1367 and 1569 cm⁻¹, respectively.

Meanwhile, peak centered at 645 cm^{-1} is also found, which is attributed to the new generated MnO_2 in the $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ composites. The intensity ratio I_D/I_G is calculated to be 0.87, indicating that the high graphitization of NCNTs is still kept after hydrothermal reaction with KMnO_4 .

Fig. 6. Raman spectra for (A) NCNTs and (B) $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ samples.

Fig. 7. N_2 adsorption/desorption isotherm and the corresponding pore size distribution (inset) of $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ composites.

Surface area and pore-size distribution are two influence factors for the properties of a supercapacitor[40-42]. Fig. 7 shows the specific area and porosity of the $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ composites and NCNTs, which are characterized by N_2 adsorption/desorption measurements. The isotherm can be classified as type IV according to the profile of a hysteresis loop in relative pressure (P/P_0) range of 0.4–1.0, revealing that the $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$

composite owns a typical meso-porous structure. The BET surface area is calculated to be 213.3 m²/g with a uniform pore size distribution of 12.6 nm. For the NCNTs, the BET surface area is only 60 m²/g(Fig. 7). Therefore, such an intriguing configuration is reckoned to achieve high electrochemical performance: the ultrafine and loosened MnO₂ cores and shell layer are beneficial for fast faradic reaction, which would enable high specific capacitance. The NCNTs nanotube serves as a fast conductive path for electron transport, which would enable a high power density. The high surface area and appropriate pore size distribution of MnO₂@NCNTs@MnO₂, not only accommodate abundant superficial electrochemically active sites to participate in the faradaic redox reactions, but also benefit to provide the possibility of efficient transport of electrons and ions in the electrode[43]. Both of them enhance the electrochemical properties.

Fig. 8. CVs (A) at scan rates from 5 to 100 mV/s and GCD curves measured at various discharge currents (B) of MnO₂@NCNTs@MnO₂ composite.

In order to evaluate the electrochemical performance of the optimized MnO₂@NCNTs@MnO₂ composite, cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) measurements were analyzed for MnO₂@NCNTs@MnO₂ electrode, which was conducted in a three-electrode

cell in 1M Na₂SO₄ electrolyte with Ag/AgCl as reference electrode and Pt as counter electrode. Fig. 8A shows the CV curves of MnO₂@NCNTs/MnO₂ composite, and the scan rate from 5 to 100 mV/s. Their shapes are similar which indicates that the electrode system has low contact resistance. As shown in Fig. 8B, the charge/discharge test of MnO₂@NCNTs/MnO₂ composite at different densities in the voltage window from 0 to 1.2 V is also provided. All charging curves are almost symmetrical to their discharge counterparts and exhibit good linear voltage–time characteristics, implying small equivalent series resistance, excellent reversibility, and high coulombic efficiency.

Fig. 9. A) Cyclic voltammograms at 30 mV/s, B) current-density dependence of the specific capacitance, C) Nyquist plots of the EIS and equivalent circuit(inset), and D), and cycling performance of NCNTs, MnO₂ and MnO₂@NCNTs/MnO₂.

Fig. 9A shows the CVs of NCNTs, MnO₂ and MnO₂@NCNTs/MnO₂ electrodes collected from 0 to 1.2 V at a same scan rate of 30 mV/s. Usually, the integral area of CV curves at the same scan rate is proportional to specific

capacitance. Obviously, the $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ electrode has higher current density than the NCNTs and MnO_2 electrodes. The CV curve of the approximately rectangular shape is indicating the ideal supercapacitor behavior[44]. According to Equation of $C = I \Delta t / m \Delta V$, the specific capacitance can be calculated on the basis of discharge time. Fig. 9B shows that the calculated specific capacitance as a function of discharge current density from 1 to 10 A/g for NCNTs, MnO_2 and $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ electrodes. Obviously, all specific capacitances of the $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ electrode are much higher than NCNTs and MnO_2 electrode, which is consistent with the CV tests. With increasing of current density, the specific capacitance all decreases, due to the high current prevents the accessibility of electrolyte ions from the bulk to the sample surface. The specific capacitance of $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ is 253.1F/g at a current density of 1 A/g and 210.8 F/g at a current density of 10 A/g, that is, 83.3% of its capacitance is retained. The improvement on specific capacitance and rate capability can be ascribed to the interconnected porous of NCNTs and the excellent electrochemical properties of MnO_2 . As comparison, the NCNTs have a specific capacitance of 85.24 F. g^{-1} , while the MnO_2 exhibits a specific capacitance of 124.32 F/g (Fig. 9B). It is clear that the unexpectedly large increase in specific capacitance is due to the loading of MnO_2 on both the outside and inside surface of the NCNTs. This demonstrates the strong synergistic effect of the combined pseudo-capacitive contributions from the sandwich type $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$.

Electrochemical impedance spectroscopy (EIS) was tested for understanding the kinetics of the interaction between electrode and electrolyte. As shown in Fig. 9C, the frequency range from 10^{-2} to 10^5 Hz at open-circuit voltage. Each nyquist plot displays a semicircle in high-frequency and a straight line in the low-frequency region, which indicates light electrochemical polarization and good capacitive property[41-45]. The intercept on the real axis reveals the equivalent series resistance (R_s), and the diameter of the semicircle corresponds to the charge transfer resistance (R_{ct}) at the electrode/electrolyte interface. In addition, the $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ electrode have small $R_s(1.74\Omega)$ and $R_{ct} (2.03\Omega)$, suggesting that the $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ has lower diffusive resistance to electrolyte and faster ion transport speed than the MnO_2 . The “knee frequency” of the $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ is about 1.5 Hz, showing that a pure capacitive behavior can be obtained and most of its stored energy is accessible at frequencies below this frequency[46]. Also, the cycle stability is critical for the practical application (Fig. 9D), which is investigated with a charge-discharge current density of 10 A/g for 2000 repetitive cycles, The $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ electrode exhibits a capacitive retention of 96.43%, which is much better than that of the NCNTs(83.10%) and MnO_2 (75.60%). This means that the $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ electrodes have excellent long-term electrochemical stability even at high current density. Finally, it can be concluded that the excellent stability combined with the low resistance and

unique structures make the $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ composites to be a good candidate for energy-storage applications.

4 Conclusions

In summary, $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ nanocomposites have been synthesized by **an** in situ growth of MnO_2 nanosheets on the internal surface and outside surface of N-doped hollow carbon nanotubes. Because of the synergy effect between N-doped hollow carbon nanotubes and MnO_2 nanosheets, the $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ electrode shows high comprehensive electrochemical performance: high specific capacitances, good rate capability, excellent reversibility and superior cycling stability. The specific capacitance of $\text{MnO}_2@\text{NCNTs}@\text{MnO}_2$ composites exhibits 253.1F/g at 1A/g and 210.9F/g at 10A/g, besides it still retains 96.43% of the initial capacitance after 2000 cycles. More importantly, this work shows the great potential to other materials built by metal oxides and N-doped carbon nanotubes **and** further work is underway.

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