**Facile fabrication of MnO_x and N co-doped hierarchically porous carbon
microspheres for high-performance supercapacitors**

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Abstract

Facile fabrication of manganese oxide (MnO_x , $0 < x < 2$) and nitrogen (N) co-doped carbon microspheres ($\text{MnO}_x\text{-N-CS}$) has been firstly developed by *one-pot* construction of Mn-functionalized melamine-formaldehyde (Mn-MF) resin spheres before pyrolysis. The resulting hybrids bear evenly dispersed MnO_x and N moieties *in situ* anchored on hierarchically porous carbon microspheres formed simultaneously. The capacitive performance is greatly tailored by varying the Mn/melamine molar ratio **in the synthetic mixture** and pyrolysis temperature. It is found that the $\text{MnO}_x\text{-N-CS}$ hybrid (0.008 wt% Mn, pyrolyzed at 800 °C) exhibits the highest specific capacitance up to 258 F g⁻¹ at a scan rate of 1 mV s⁻¹ (in 6 M KOH), and keeps a high capacitance retention ratio of 98% after 5000 cycles. The synergism between MnO_x , N moieties and carbon spheres proves to be responsible for the remarkably improved performance, as compared to the pure carbon sphere and MnO_x (N)-doped carbon sphere. The well-developed $\text{MnO}_x\text{-N-CS}$ hybrids highlight the great potentials for widespread supercapacitor applications.

Keywords: Mn-functionalized melamine-formaldehyde; Carbon microsphere; Manganese oxide; Nitrogen; Supercapacitors

1. Introduction

Development of energy-storage devices with high energy and power **output**, short charging time, and long life span is urgently needed to satisfy the growing demand for electrical energy in our daily life, as well as to relieve the global warming and pollution caused by fossil fuel overuse [1,2]. Among various power-source devices, supercapacitors, also known as electrochemical capacitors, have attracted much attention owing to their higher power density, longer cycle life and faster charge-discharge rate compared with batteries or dielectric capacitors. On the basis of the energy-storage mechanism, supercapacitors are classified as either electric double-layer capacitors (EDLCs) or faradaic pseudocapacitors. EDLCs use carbon-based materials, such as activated carbon, carbon fibers, carbon nanotubes, graphene, carbon aerogels and carbon spheres, to store charge by electrostatic charge separation at the electrode/electrolyte interface [3]. Carbon microspheres with regular morphology and adjustable diameter are unique because they decrease the resistance of ion diffusion, and the package porosity among carbon spheres benefits the generation of ion buffer reservoirs and reduces the ion diffusion distance [4]. However, due to the low capacitance and energy density, these carbon microspheres are severely limited in applications in commercialized supercapacitor devices. To remedy the inability of carbon microspheres to provide sufficient capacitance and energy density, doping carbon spheres with metal oxides or **hetero atoms** is employed to prepare composite electrodes. Manganese oxide is one of the most promising candidates owing to its low cost, environmental benignity and high specific capacitance

(theoretical capacitance up to 1370 F g^{-1}) [5]. Nitrogen-doping is also effective to improve the reversible pseudo-capacitance like metal oxides [6,7]. And recent research has demonstrated that MnO and N codoped carbons, including ultrasmall MnO@N-rich carbon nanosheet and MnO-graphene composite, exert positive effects on the supercapacitors [8,9]. So it can be supposed that co-doping of carbon microspheres with both manganese oxide (MnO_x) and nitrogen (N) would significantly improve the capacitance.

Up to now, fabrication of doped carbon microsphere is widely based on a *multi*-step synthesis. However, the poor dispersion and loose attachment of doped species are often rendered by such a *post*-synthesis. It is reported that MnO_x coupled carbon microspheres [10], and MnO_2 nanosheet combined N-doped hollow carbon spheres [11] display enhanced capacitance to a certain degree, whereas their cycling stability is a concern. Direct conversion of N-containing polymer precursors, like polyaniline and melamine-functionalized polystyrene [12,13], *in situ* creates N-doped carbon spheres bearing homogeneity and firmness, showing both long lifetime and high capacitance. Similarly, MnO_x is recently *in situ* anchored by pyrolysis of Mn-containing carbon precursors, based on the redox reaction between carbon and KMnO_4 [14]. Inspired by these investigations, it can be speculated that by *one-pot* construction of Mn- and N-containing polymeric spheres, the dispersion of MnO_x and N moieties, as well as their tight attachment to the carbon spheres would be guaranteed. In this situation, high-performance MnO_x and N co-doped carbon microspheres could be facilely fabricated.

To facilitate fabrication of **such** high-performance MnO_x and N co-doped carbon microspheres, *one-pot* construction of rigid Mn- and N-containing polymeric spheres is crucial because: (I) The parent sphere could be inherited by pyrolysis of rigid polymeric spheres; (II) The even dispersion of MnO_x **and** N moieties in the final hybrids should be preset in Mn- and N-containing polymeric spheres. However, how to construct such a rigid and homogeneous polymeric sphere remains a challenge. It is well known that the conventional synthesis, including chemical vapor deposition, templating and emulsion fabrication methods [15], is either time-consuming or expensive for carbon sphere or carbon sphere composite synthesis. Direct conversion of organic colloidal spheres like resorcinol-formaldehyde (RF) to carbon spheres innovate the synthetic methodology in terms of both economy and flexibility recently [16]. Considering the similarity of melamine to resorcinol in the reactivity with formaldehyde, melamine-formaldehyde (MF) resin spheres could be fabricated and further converted to N-doped carbon spheres *in situ*. Moreover, the N-rich melamine provides accommodations for metal species based on a coordination interaction. Therefore, if *one-pot* construction of Mn-functionalized MF resin spheres could be realized, the MnO_x and N co-doped carbon microspheres will be facilely fabricated.

To verify this hypothesis, we herein report the facile fabrication of manganese oxide (MnO_x , $0 < x < 2$) and nitrogen (N) co-doped carbon microspheres (MnO_x -N-CS) developed by *one-pot* construction of Mn-functionalized melamine-formaldehyde (Mn-MF) resin spheres before pyrolysis (Scheme 1). The resulting hybrids bear evenly dispersed MnO_x and N moieties *in situ* anchored on

hierarchically porous carbon microspheres formed simultaneously. The capacitive performance is greatly tailored by varying the Mn/melamine molar ratio **in the synthetic mixture** and pyrolysis temperature. It is found that the MnO_x-N-CS hybrid (0.008 wt% Mn, pyrolyzed at 800 °C) exhibits the highest specific capacitance up to 258 F g⁻¹ at a scan rate of 1 mV s⁻¹ (in 6 M KOH), and keeps a high capacitance retention ratio of 98% after 5000 cycles. The synergism between MnO_x, N moieties and carbon spheres proves to be responsible for the remarkably improved performance, as compared to the pure carbon sphere and MnO_x (N)-doped carbon sphere.

2. Experimental

2.1. Chemicals

All chemicals are of analytical grade and used as received without any further purification. Melamine, formaldehyde, potassium permanganate (KMnO₄), ammonia and resorcinol were purchased from Sinopham Chemical Reagent Co., Ltd. Acetylene black, polytetrafluorethylene and ethanol were purchased from Beijing Chemical Works.

2.2. Synthesis of MnO_x and N co-doped carbon microsphere

First, the N-rich melamine combined with formaldehyde was used as the N, C precursors, and KMnO₄ was used as the metal precursor to construct Mn-functionalized melamine-formaldehyde (MF) resin spheres (Scheme 1). In a typical synthesis, 1.2 g of melamine combined with 9.4 g of formaldehyde solution (37 wt%) was added into 19.4 g of deionized water with vigorous stirring at 60 °C for

ca. 10 min to form a clear solution, and then the mixture was heated up to 90 °C, and was further stirred for 10 min. Then certain amount of KMnO₄ was added (Mn/melamine molar ratio = 0, 0.001, 0.003, 0.005, 0.008 and 0.010), and further stirred for 10 min. The resulting mixture was sealed in a Teflon-lined autoclave followed by hydrothermal treatment at 180 °C for 6 h. After cooling, the precipitate was collected by centrifugation, washed repeatedly with distilled water and ethanol for several times, and dried overnight, affording MF, 0.001Mn-MF, 0.003Mn-MF, 0.005Mn-MF, 0.008Mn-MF and 0.010Mn-MF, respectively. The 0.003Mn-MF resin sphere was heated in a quartz tube at 400, 600, 800 and 950 °C for 5 h with a heating rate of 1 °C min⁻¹ under N₂ atmosphere, yielding 0.003MnO_x-N-CS-400, 0.003MnO_x-N-CS-600, 0.003MnO_x-N-CS-800 and 0.003MnO_x-N-CS-950, respectively. MF, 0.001Mn-MF, 0.005Mn-MF, 0.008Mn-MF and 0.010Mn-MF were then heated at 800 °C as the same **procedure** mentioned above to produce N-CS-800, 0.001MnO_x-N-CS-800, 0.005MnO_x-N-CS-800, 0.008MnO_x-N-CS-800 and 0.010MnO_x-N-CS-800, respectively.

2.3. Characterization

The infrared spectra of samples were recorded in KBr disks using a Nicolet Nexus 870 FTIR spectrometer. SEM analysis was performed on a FEI-Quanta 200F field-emission scanning microscope operated at 15 kV to determine the morphology of samples. The TEM images, selected area electron diffractions, high angle annular dark field scanning transmission electron microscopy (HAADF-STEM), line scanning and mapping of C, O, N and Mn elements were analyzed using a FEI Tecnai G2 F20

transmission electron microscope equipped with an energy dispersive X-ray spectroscopic analyzer operated at a voltage of 200 kV. Samples were sonicated for 5 min in EtOH, one drop of the suspended sample was dripped in a holey carbon microgrid supported on a 300 mesh copper grid. N₂ adsorption/desorption isotherms were recorded at 77 K using a JW-BK222 static volumetric gas adsorption instrument manufactured by Beijing JWCB Sci. & Tech. Co., Ltd. Before measurements, the samples were de-gassed at 300 °C for 3 h in vacuum. Specific surface area was determined by the Brunauer-Emmett-Teller (BET) method and mesopore size distributions were measured using the Barrett-Joyner-Halenda (BJH) method from the desorption branch of the isotherms. The linearized BET model was used to fit the microporous data within the relative pressure range of $0.001 < P/P_0 < 0.05$. The micropore size distributions were determined by using the Horvath-Kawazoe (H-K) method assuming slit pore geometry. Raman spectra were recorded with a HORIBA Jobin Yvon HR800 with a microscope attachment. The laser wavelength of 633 nm was focused using a diffraction limited spot, and the scan time was 2 s for each sample. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALAB 250Xi X-ray photoelectron spectrometer (employing a monochromated Al-K α) X-ray source ($h\nu = 1486.6$ eV). The C 1s line (284.6 eV) was used as the reference to calibrate the binding energies (BE). Microanalysis for C, H and N were performed at the well-group CE-440. X-ray absorption fine structure (XAFS) was examined on the 12-BM-B beamline of APS at Argonne National Laboratory. The XAFS data were obtained in the fluorescence mode at the Mn K-edge (6539.0 eV).

The XAFS data were processed using the Athena software for background removal, post-edge normalization and X-ray absorption near edge structure (XANES) analysis. The oxidation states of the samples were determined by comparing the inflection point of the edge from the sample to that of standards with known oxidation state. The extended X-ray absorption fine structure (EXAFS) was analyzed using Artemis software, which implemented FEFF. The EXAFS data reduction was conducted by utilizing the standard procedures. The EXAFS function, χ , was obtained by subtracting the *post*-edge background from the overall absorption and then normalized with respect to the edge jump step. Subsequently, k^3 -weighted $\chi(k)$ data in k space were Fourier transformed to r space to separate the EXAFS contributions from the different coordination shells. However, fitting Mn local structure doesn't have physical solution, and the error of coordination numbers is always larger than 10%. Therefore, the fitted parameters were not listed and discussed in this study. Metal content was estimated by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis conducted on a Perkin Elmer emission spectrometer. Before, analysis, certain amount of vacuum-dried sample was placed in a crucible and heated at 600 °C for 8 h. The residue was then dissolved in 3 mL of aqua fortis solution, and each solution was filtered through a 0.45 μm polyethersulfone filter and set the constant volume to be 10 mL, and then submitted for metal analysis.

2.4. Electrochemical test

Electrode slurries containing the electrode materials synthesized, acetylene black and polytetrafluorethylene at a weight ratio of 7: 2: 1 were painted on a nickel foam (1

$\times 1 \text{ cm}^2$) to create samples for electrochemical characterization. The coated Ni foam was pressed under a pressure of 3 MPa to enhance the adhesion between the active materials and the Ni foam. A three-electrode cell was used for electrochemical capacitance tests with a Hg/Hg₂Cl₂ reference electrode and a Pt counter electrode and a 6 M KOH-distilled water electrolyte. Cyclic voltammetry (CV, scan rate 1, 2, 5, 10, 20, 50 and 100 mV s⁻¹, and potential window -1.0 ~ 0 V), galvanostatic charge-discharge cycling (specific current 0.25 A g⁻¹, and potential window -1.0~0 V), electrochemical impedance spectroscopy (frequency range 0.01 ~ 100000 Hz) and life-time tests were performed using an electrochemical workstation (CHI660E B14013). The electrochemical gravimetric specific capacitance (C_m) of the electrode material was determined as follows:

$$C_m = \frac{C}{m} = \frac{S}{2UV_m}$$

in which C_m is the gravimetric specific capacitance (F g⁻¹), C is the capacitance (F), m is the mass of electrode material (g), S is the integrated area of the CV curve, V is the scan rate (mV s⁻¹) and U is the potential window (V).

3. Results and discussion

3.1. Morphology and structure study

The obtained polymeric resin 0.003Mn-MF shows monodisperse and regular spheres with an average diameter of 3 μm (Fig. 1a). The image of a magnified sphere indicates the solid configuration (Fig. 1a, inset). These solid spheres are uniform and can be obtained by tailoring the Mn/melamine molar ratio ranging from 0 to 0.008, and they show essentially similar appearance, dimensions and diameters in the range

of 3-5 μm (Fig. S1a-d and Fig. 1a). The FT-IR spectrum of 0.003Mn-MF exhibits two principle linkages formed during the condensation of methylolmelamines, namely ether linkages (-N-CH₂-O-CH₂-N-) at 1193 cm^{-1} and methylene linkages (-N-CH₂-N-) at *ca.* 2948 cm^{-1} , as well as shows the hydroxymethyl moieties at *ca.* 3040 cm^{-1} (Fig. S2). And thus it can be speculated that the melamine was condensed with formaldehyde through a hydroxymethylation reaction, in which the H atoms in NH₂ moieties are substituted by methylol groups (-CH₂OH). The N sites in the hydroxymethylated melamine provide accommodations for MnO₄⁻ ions based on a coordination interaction. Under hydrothermal conditions, the methylolmelanines were cross-linked through methylene linkages to form colloidal nanoparticles, during which the anchored MnO₄⁻ species were engulfed. Further cross-link through the remaining methylol groups yields Mn-functionalized MF resin spheres.

The resulting Mn-MF resin spheres were pyrolyzed at 800 °C under N₂ flow to obtain doped carbon microspheres. The XRD pattern of the representative 0.003MnO_x-N-CS-800 displays two broad peaks at $2\theta = 23^\circ$ and 46° , assigned to the carbon (002) and (101) diffractions (Fig. S3). These diffractions are different from that at 20° in the parent 0.003Mn-MF, corresponding to the transformation of amorphous Mn-MF polymers to carbonaceous materials. The resultant 0.003MnO_x-N-CS-800 shows uniform spheres with diameters of *ca.* 2 μm (Fig. 1b), implying a total shrinkage of *ca.* 33% occurred after pyrolysis. These spheres are interconnected, and it is the same case for other nMnO_x-N-CS-800 hybrids (n = 0, 0.001 and 0.005) (Fig. S1e-f). It is reasonable that the softening (or melting) of

Mn-MF resin spheres occurred during pyrolysis makes the monosphere reconstruct and interconnect, though the spherical geometry was inherited. However, the spherical shape was completely ruptured when increasing the Mn/melamine molar ratio to 0.008 or higher (Fig. S1g), **implying** the critical role of Mn dosage on the friability of derived carbon microspheres. It is noteworthy that the fragments in 0.008MnO_x-N-CS-800 are dimple shaped, suggesting the hollow spheres. Such a hollow structure also can be observed in 0.003MnO_x-N-CS-800 (Fig. 1b, inset). However, it is difficult to reveal the hollow structure by the TEM observation (Fig. 1c), since the thick carbon shells prevent the penetration of electron beams. **High-magnification TEM** image shows that the formed manganese oxide particles are evenly dispersed on the whole sphere (Fig. 1d). These particles are crystalline, showing diffraction spots in the SAED pattern (Fig. 1d, inset). The high-angle annular dark-field scanning TEM (HAADF-STEM) image (Fig. 1e) along with the compositional line profile across a sphere (Fig. 1f, inset) confirms the hollow structure. **It is noteworthy that the line profile of Mn elements exhibits a low intensity, implying an extremely low concentration. And thereby only C, N and O elements can be clearly observed in the energy-dispersive X-ray spectroscopy (EDS) of 0.003MnO_x-N-CS-800 (Fig. 1f). Whereas it can be observed that these elements are evenly dispersed in the whole sphere, as illustrated in Fig. 1g, further confirming the successful synthesis of uniform MnO_x and N co-doped carbon spheres.**

3.2. Raman spectroscopy

The local structure of **carbons** was analyzed by Raman spectroscopy. As shown in

Fig. 2 and Fig. S4, all 0.003MnO_x-N-CS-t hybrids exhibit “D-band” at 1330-1375 cm⁻¹ attributed to defects and disordered carbonaceous structure, and “G-band” at 1590-1610 cm⁻¹ related to ordered graphitic structure [17]. The integral area ratio of the “D-band” to the “G-band” (I_D/I_G) indicates the degree of graphitic crystalline structure. It is found that 0.003MnO_x-N-CS-800 displays a lower I_D/I_G value of 2.47 than other 0.003MnO_x-N-CS-t hybrids (Table S1), suggesting that more graphitic structure formed when pyrolyzed at 800 °C. In addition, the overlap between D and G peak is so serious that the “A-band” around 1470-1530 cm⁻¹ ascribed to hetero atom-doped amorphous carbon can be fitted and integrated. The integral area ratio of the “A-band” to the “G-band” (I_A/I_G) indicates the proportion of amorphous carbons as well as the oxygen- and/or nitrogen-containing functional groups in carbon microspheres [18]. As illustrated in Table S1, all 0.003MnO_x-N-CS-t hybrids show I_A/I_G molar ratios ranging from 0.17 to 1.05, implying the existence of N- and/or O-containing groups.

3.3. XAFS study

The Mn dosage ranges from 0.002 to 0.020 wt% in nMnO_x-N-CS-800 hybrids (Table S2), and such an extremely dosage makes it impossible to be studied by lab characterization techniques. The elemental specific X-ray absorption fine structure (XAFS) based on the synchrotron radiation bears high flux and intensity, showing advantages for investigating the transition and local structure of low concentrated Mn species. As illustrated in Fig. 3A, the 0.003Mn-MF shows higher white line intensity as compared to KMnO₄, implying the coordination of N atoms to MnO₄⁻ ions took

place. Upon pyrolysis, the 0.003MnO_x-N-CS-800 exhibits a negative shift in the adsorption edge position, suggesting that the Mn species were partially reduced. The reduced Mn species carry less positive charges than MnO₂, because they show a negative shift of edge position as compared to MnO₂ [19]. Fourier transform (FT) of Mn K-edge $k^3\chi(k)$ spectra are shown in Fig. 3B. The radial distribution of 0.003MnO_x-N-CS-800 exhibits one prominent peak at 1.30 Å from Mn-O pairs and another peak at 2.60 Å from Mn-Mn contributions [20], **confirming** the formation of MnO_x species.

3.4. N₂ adsorption study

N₂ adsorption study reveals a type II isotherm without hysteresis loops for all nMnO_x-N-CS-800 hybrids (Fig. 4A), indicating the macroporous materials [21]. The mesopore size distribution calculated by the BJH method ranges from 2.3 to 3.4 nm, and the micropore size distribution estimated by the H-K method is in the range of 1.1-1.7 nm (Fig. 4B). These results suggest that the pyrolysis of resin spheres proceeded with reorganization into **hierarchically porous** structures with micro-, meso-, and macropores. However, it is observed that the surface area and pore volume vary depending on the Mn dosage. Increasing the Mn dosage leads to a decline first in the surface area and micropore volume from 17 m² g⁻¹ and 0.0064 cm³ g⁻¹ for N-CS-800 to 6 m² g⁻¹ and 0.0013 cm³ g⁻¹ for 0.003MnO_x-N-CS-800, respectively, and then an increase to 10 m² g⁻¹ and 0.0024 cm³ g⁻¹ for 0.008MnO_x-N-CS-800; while the total pore volume varies in an irregular way (Table S2).

The findings obtained above help us understand the transformation of Mn-MF

resin spheres to MnO_x-N-CS hybrids. Gradual loss of hydrogen, oxygen, nitrogen and carbon occurred when heated, and the polymeric melamine-formaldehyde resin spheres were converted to N-doped hollow carbon spheres with a small fraction of **nitrogen** retained. The anchored MnO₄⁻ species were *in situ* reduced in the presence of liberated gas (H₂, CO, *etc.*) and carbon, which were further agglomerated to MnO_x particles. Meanwhile, the gas release and microsphere stacking during pyrolysis lead to hierarchically porous MnO_x-N-CS hybrids.

3.5. Electrochemical performance

Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) curves were used to characterize the capacitive properties of MnO_x-N-CS hybrids. Figure 5a shows the CV curves of 0.003MnO_x-N-CS-t hybrids. The rectangular-like shape and the appearance of humps in the CV curves indicate **that** the capacitive response comes from both EDLCs and redox reactions [22], which **relates** to the MnO_x and N functionalities in carbon microspheres. Accordingly, the GCD curves are less symmetrical, showing inflections to some extent at -0.4 V (Fig. 5b). The specific capacitance increases from 37 F g⁻¹ for 0.003MnO_x-N-CS-400 to 230 F g⁻¹ for 0.003MnO_x-N-CS-800 at the scan rate of 1 mV s⁻¹, and then decreases to 129 F g⁻¹ for 0.003MnO_x-N-CS-950. The 0.003MnO_x-N-CS-800 shows the highest capacitance, linking to the excellent conductivity originated from the most graphitic carbons. To explore the effect of N-doping, the pure carbon sphere (CS-800) and MnO_x-doped carbon sphere (0.003MnO_x-CS-800) were also prepared and examined for comparison (Supporting Information). It is found that they exhibit **a** smaller capacitance of 174

and 184 F g^{-1} than N-CS-800 (183 F g^{-1}) and $0.003\text{MnO}_x\text{-N-CS-800}$ (230 F g^{-1}), respectively (Fig. S5), indicating the significant role of N-doping. The nitrogen content is 15.0 wt% in $0.003\text{MnO}_x\text{-N-CS-800}$ estimated by CHN elemental analysis, and these **nitrogen species** are embedded into the carbonaceous network in the form of pyridinic (397.9 eV), pyrrolic (399.9 eV) and quaternary (400.6 eV) configurations (Fig. 6) [23]. On the other hand, the specific capacitance of $0.003\text{MnO}_x\text{-CS-800}$ and $0.003\text{MnO}_x\text{-N-CS-800}$ was improved by 10 and 25% compared with that of CS-800 and N-CS-800, respectively. Therefore, the introduction of MnO_x species improves the specific capacitance, and the synergism between MnO_x , N moieties and carbon spheres renders highly efficient $0.003\text{MnO}_x\text{-N-CS-800}$ hybrid. Figure 5c shows the CV curves of various $n\text{MnO}_x\text{-N-CS-800}$ hybrids at a scan rate of 1 mV s^{-1} . The specific capacitance increases from 183 F g^{-1} for N-CS-800 to 230 F g^{-1} for $0.003\text{MnO}_x\text{-N-CS-800}$, and then decreases to 163 F g^{-1} for $0.008\text{MnO}_x\text{-N-CS-800}$, indicating the effect of Mn dosage on the capacitance. Correspondingly, the charge time changes as the same manner (Fig. 5d), indicating a much larger charge capacity of $0.003\text{MnO}_x\text{-N-CS-800}$ electrode. The pseudo-capacitance based on manganese(IV) oxide (C_{MnO_2}) decreases from 437673 F g^{-1} for $0.001\text{MnO}_x\text{-N-CS-800}$ to 89848 F g^{-1} for $0.005\text{MnO}_x\text{-N-CS-800}$ (Table S3). The largest pseudo-capacitance is nearly 320 times of the theoretical specific capacitance of manganese(IV) oxide (1370 F g^{-1}). The highly dispersed MnO_x can be fully utilized due to their extremely low loading. And thus in such a hybrid configuration, manganese oxides offer an extremely high specific capacitance.

The GCD curves of 0.003MnO_x-N-CS-800 at different specific currents are shown in Fig. S6. The potential-time profiles maintain a triangular shape at high specific currents, implying that the 0.003MnO_x-N-CS-800 is suitable for application in supercapacitors in which the rapid charge-discharge is required. The specific capacitance of 0.003MnO_x-N-CS-800 decreases from 230 to 104 F g⁻¹ as the sweep rate increases from 1 to 100 mV s⁻¹, linking to the mesoporosity (Fig. S7). The relationship between the capacitance retention ratio and potential scan rate is plotted (Fig. S8). The minimized capacitance at high scan rates originates from the decreased ion accessible surface area. The capacitance retention ratios at a sweep rate of 100 mV s⁻¹ are above 55% for all nMnO_x-N-CS-800 hybrids, implying that the hierarchically porous structure is suitable for quick ion transportation.

The conductive behavior of nMnO_x-N-CS-800 hybrids were tested by electrochemical impedance spectroscopy (EIS, Fig. 5e). It is clearly that N-CS-800, 0.001MnO_x-N-CS-800 and 0.003MnO_x-N-CS-800 display a smaller diameter of semicircular in the high frequency region than 0.005MnO_x-N-CS-800 and 0.008MnO_x-N-CS-800, implying better charge transfer was achieved by using nMnO_x-N-CS-800 hybrids (n = 0-0.003). The equivalent series resistance (R_s) corresponding to the high frequency intercept at the real axis, is estimated to be 0.65, 0.66, 0.67, 0.70 and 0.71 Ω for N-CS-800, 0.001MnO_x-N-CS-800, 0.003MnO_x-N-CS-800, 0.005MnO_x-N-CS-800 and 0.008MnO_x-N-CS-800, respectively, suggesting the influence of Mn dosage on the conductivity. The EIS spectrum of 0.003MnO_x-N-CS-800 was simulated and shown in Fig. S9. The diffusion

resistance, which can be interpreted using the Warburg element (W), is a crucial factor to understand ion movements, while the interfacial resistance (R_{int}) shows the kinetic characteristics between electrodes and electrolytes at double-layer regions.

The long-term cycling stability of 0.003MnO_x-N-CS-800 was examined at a specific current of 5 A g⁻¹ (Fig. 5f). The specific capacitance remains almost constant with slight fluctuations, and 98% of the initial capacitance is retained up to 5000 cycles. Our cycling performance is much better than those of previously reported MnO₂-NiO hybrid array (12% loss after 1500 cycles) [24], MnO₂ coaxially coated on a CNT array (decreased by *ca.* 11% after only 500 cycles) [25], and electrodeposited MnO₂ film (13% loss after 2000 cycles) [26]. All the above results clearly reveal the exceptional capability of 0.003MnO_x-N-CS-800 to meet the requirements for high capacitance, good rate capability and long cycling life, which are crucial factors for high-performance energy-storage devices.

4. Conclusions

In conclusion, a facile and scalable synthetic methodology was successfully developed to prepare MnO_x and N co-doped hierarchically porous carbon microspheres *in situ* by construction of Mn-functionalized MF resin spheres before pyrolysis. Such an integrated preparation is economic and flexible, facilitating the control of MnO_x dispersion and dosage. The elaborately fabricated 0.003MnO_x-N-CS-800 hybrid exhibits the highest specific capacitance and long life span, which can be ascribed to the synergism between MnO_x, N moieties and carbon spheres. This study not only indicates that it is vital for the reaction systems to match

with doped porous carbon microsphere, but also offers a new fabrication strategy to prepare high-performance electrode materials that can be used in energy-storage devices.

Acknowledgements

The authors gratefully acknowledge financial support from National Natural Science Foundation of China (21303229, 21173269, 91127040, 51471187), Beijing Natural Science Foundation (2152025, 2152026), and Science Foundation of China University of Petroleum, Beijing (2462013YJRC018, 2462013YJRC005). Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, supported by the U.S. DOE under Contract No. DE-AC02-06CH11357, is also acknowledged.

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Figure 1

Fig. 1. SEM image of (a) 0.003Mn-MF resin sphere and (b) 0.003MnO_x-N-CS-800, TEM image (c), high-magnification TEM image (d), HAADF-STEM image (e), TEM-EDX and line scanning profile (inset) (f) and elemental maps (g) of 0.003MnO_x-N-CS-800.

Figure 2

Fig. 2. Raman spectrum of 0.003MnO_x-N-CS-800.

Figure 3

Fig. 3. Mn K-edge XANES spectra (A) and Mn K-edge EXAFS spectra (B) of (a) KMnO_4 , (b) 0.003Mn-MF, (c) 0.003MnO_x-N-CS-800, (d) MnO_2 and (e) Mn foil.

Figure 4

Fig. 4. N₂ adsorption/desorption isotherms (A) and the corresponding pore size distribution curves (B) of (a) N-CS-800, (b) 0.001MnO_x-N-CS-800, (c) 0.003MnO_x-N-CS-800, (d) 0.005MnO_x-N-CS-800 and (e) 0.008MnO_x-N-CS-800.

Figure 5

Fig. 5. Capacitive performance: CV curves at 1 mV s⁻¹ (a) and GCD curves at 0.25 A g⁻¹ (b) for 0.003MnO_x-N-CS-t hybrids, CV curves at 1 mV s⁻¹ (c), GCD curves at 0.25 A g⁻¹ (d), and Nyquist plots (e) for nMnO_x-N-CS-800 hybrids, and cycling test (f) of 0.003MnO_x-N-CS-800 at a specific current of 5 A g⁻¹.

Figure 6

Fig. 6. XPS spectrum of N1s for 0.003MnO_x-N-CS-800.

Scheme 1

Scheme 1 Illustration of the MnO_x-N-CS hybrid fabrication process.