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Supporting Information

Nanoflaky MnO₂/functionalized carbon nanotubes for supercapacitors: an in situ X-ray absorption spectroscopic investigation

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1. N K-edge XAS of N-CNT



Fig. S1 show the N K-edge XAS of N-CNT.

Figure S1 presents the N K-edge XAS of N-CNT. The spectrum reveals the transition from N 1s to unoccupied orbitals with N 2p character. The spectrum exhibits four main features, labeled $A_{S1}\sim D_{S1}$. Feature D_{S1} is associated with the σ^* excitation of C-N bonds [1-3]. Features A_{S1} , B_{S1} , and C_{S1} originate from the pyridinic-like N (C=N π^*) and graphitic-like N, revealing that aminophenyl groups had been successfully attached to the CNT, modifying the surface of the CNT surface during the amine treatment. Hence, the defective site of the CNT that was created by N differs from that of the CNT that underwent oxidative acid treatment, causing the different MnO₂ morphologies to grow on the CNT, resulting in different electrochemical behaviors [1-3].

2. Electrochemical impedance spectroscopy (EIS)



Fig. S2 Nyquist plots of MnO₂/C-CNT-24 and MnO₂/N-CNT-24

Electrochemical impedance spectroscopy (EIS) is a powerful tool for providing information about the conductive behavior of MnO₂/functionalized CNT. Figure S2 compares the electrochemical impedance spectra of MnO₂/C-CNT-24 and MnO₂/N-CNT-24 electrodes in 1 M aqueous Na₂SO₄. The bulk solution resistance (Rs) comprises the resistance of the electrolyte and that of the electrode materials. Both electrodes have an Rs of ~1.5 Ω cm². The Nyquist slope of the MnO₂/C-CNT-24 electrode, indicating that better capacitive behavior of the MnO₂/C-CNT-24 electrode arises from non-Faradaic processes [4]. The semicircle in the figure represents the charge transfer resistance (Rct) that is attributed to the electrode materials. The Rct of MnO₂/C-CNT-24 is much lower than that of MnO₂/N-CNT-24, because the high electrical conductivity of MnO₂/C-CNT-24 materials facilitates the transfer of ions

and charges. These results suggest the MnO_2/C -CNT-24 performs more efficiently as a supercapacitor.

3. Cycling stability



Fig. S3 Cycling stability of MnO₂/C-CNT-24 and MnO₂/N-CNT-24

The cyclic stability of supercapacitors is an important parameter for practical applications. Figure S3 compares the charge–discharge processes of MnO₂/C-CNT-24 and MnO₂/N-CNT-24 electrodes from 0 to 0.8 V in a 1 M NaSO4 aqueous solution over 1000 cycles at a current density of 10 A/g. Approximately 72.8 % of the specific capacitance of the MnO₂/C-CNT-24 electrode is retained after 1000 cycles. However, the capacitance of the MnO₂/N-CNT-24 increases after the first 300 cycles, and then decreases rapidly to a value that is maintained stably as the number of cycles increases. This phenomenon is attributable to the activation of the electrode material

[5]. The results reveal that the long-term electrochemical stability of $MnO_2/C-CNT-24$ exceeds that of $MnO_2/N-CNT-24$.

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