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Tailored Nanoscale Interface in Hierarchical Carbon Nanotube Supported MoS_2@MoO_2-C Electrode toward High Performance Sodium Ion Storage

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METHODS

Materials Synthesis: Firstly, CNT-MoS_2 precursor was synthesised using a hydrothermal method. The mixture of 0.2 g Sodium Molybdenum Oxide Dihydrate ($Na_2MoO_4 \cdot 2H_2O$), 0.4g Thiourea (CH_4N_2S), 0.05 g Hexadecyl trimethyl ammonium Bromide (CTAB) and 30 mg acid-multiwalled carbon nanotubes (CNT) were mixed under ultrasonication for 30 min.

The resulting solution was transferred to Teflon-lined stainless steel autoclave and heated to 200 ^{o}C for 24 h. After cooling, the products were washed with ethanol and water for several times. Secondly, the as-prepared CNT-MoS_2 (0.4 g) was added into mixed solution containing 80 ml water and 150 ml ethanol, then 0.3 mg dopamine and 1.2 g of ammonium molybdate were poured into above solution under stir for 20 min. Subsequently, amount of ammonium hydrochloride was dropped to adjusting pH until to 8, the reaction proceeds at room temperature for 3 h. The as-obtained performance was centrifuged and pyrolyzed at 800 ^{o}C for 2h under Ar condition. In order to compare the performance, control CNT-MoS_2 and MoS_2 samples were synthesized using the same condition without MoO_2 and CNT source, respectively.

Material Characterization: The crystal structure of sample was investigated by XRD (Bruker with a Cu Kα X-ray source (λ =1.5418 Å). The morphology of sample were collected by SEM and TEM. The surface chemical state of sample were determined by XPS and Raman spectra. The active ration of sample was analyzed by TGA at a heating rate of 5 °C min^{-1} in air. The surface areas of the samples were performed using the nitrogen adsorption–desorption isotherms.

Electrochemical Measurements: The 2016-type coin cells were assembled using Na metal as reference electrode and electrolyte of 1M $NaClO_4$ in the mixture of EC/PC (1:1). The working electrode was prepared by mixed as-prepared sampled, 10% super P and 10% CMC. The mass loading of active materials is ~1 mg cm^{-2}. Galvanostatic charge-discharge measurements were conducted by a Land battery cycler. CV tests were performed at a scan rate from 0.1 to 5 mV s^{-1} using CHI605D electrochemical workstation. EIS was recorded on

AUTOLAB.

DFT Calculation: Density Functional Theory (DFT) calculation were carried out with the gradient corrected exchange–correlation functional of Perdew, Burke and Ernzerhof (PBE) under the projector augmented wave (PAW) method as implemented in the VASP code. The energy cut-off was set at 450 eV. As for periodic interface model construction, to minimize the lattice mismatch between

MoS_2 and MoO_2, a rather large slab containing p(10×10) MoS_2 and p(7×7) MoO_2 was adopted. [2]All atoms were full relaxed until the force on them was less than 0.01 eV $Å^{-1}$. Both spin-polarized and vander Waals (vdW) calculated by the DFT-D method of Grimme were taken into consideration.[3] The band offset of the junction was obtained by alignment of Fermi level, which was calibrated by the core level of sulfur.

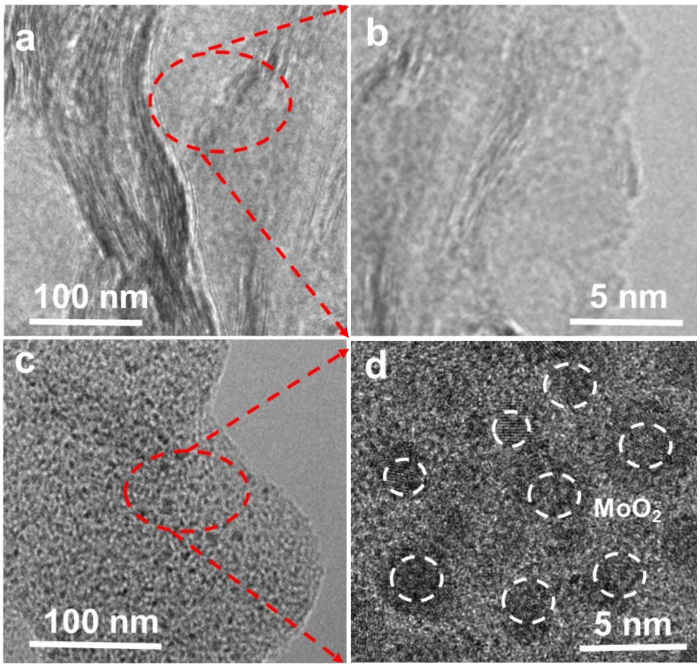

Figure S1 TEM images of CNT-MoS_2 (a-b) and CNT-MoS_2@MoO_2-C (c-d).

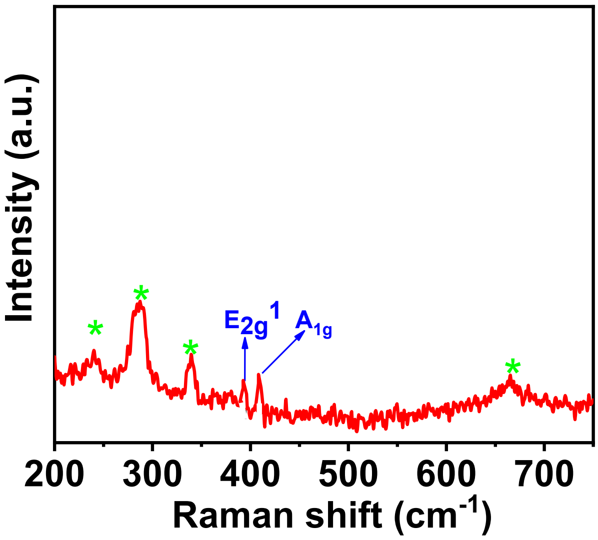

Figure S2. Ranman profile of CNT-MoS2@MoO2-C.

$$m_{CNT} = 27.6\% - 13.8\% = 13.8\%$$

$$m_{CNT+N\text{-doped carbon}} = 31.2\% - 13.8\% = 17.4\%$$

$$m_{MoS2@MoO2} = 100\% - 17.4\% = 82.6\%$$

Figure S3. Calculations of the contents of active materials through TGA.

As shown in Figure S2, the difference of weight losses of the MoS_2 and CNT-MoS2 is the CNT content in the CNT-MoS_2 (~13.8%). And the difference of weight losses of the MoS_2 and CNT-MoS_2@MoO_2-C is the CNT and N-doped carbon contents (17.4%). The active content of MoS_2@MoO_2 in CNT-MoS_2@MoO_2-C is determined to be 82.6%. And the N-doped carbon content is 3.6%.

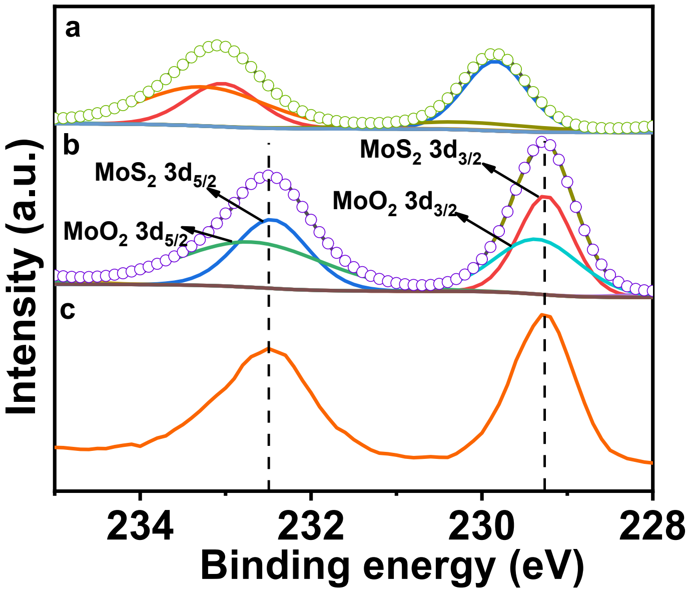

Figure S4. (a) Mo 3d XPS spectra of CNT-MoS_2@MoO_2-C (a), CNT-MoS_2/MoO_2-C (b), and the CNT-MoS_2 (c).

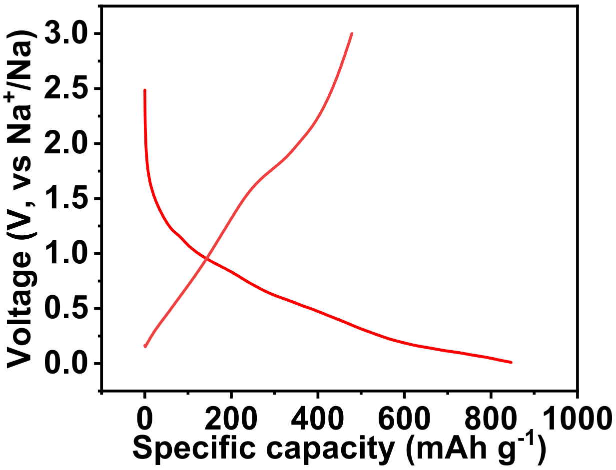

Figure S5. Discharge-charge profiles of CNT-MoS_2 at 0.2 A g^{-1}.

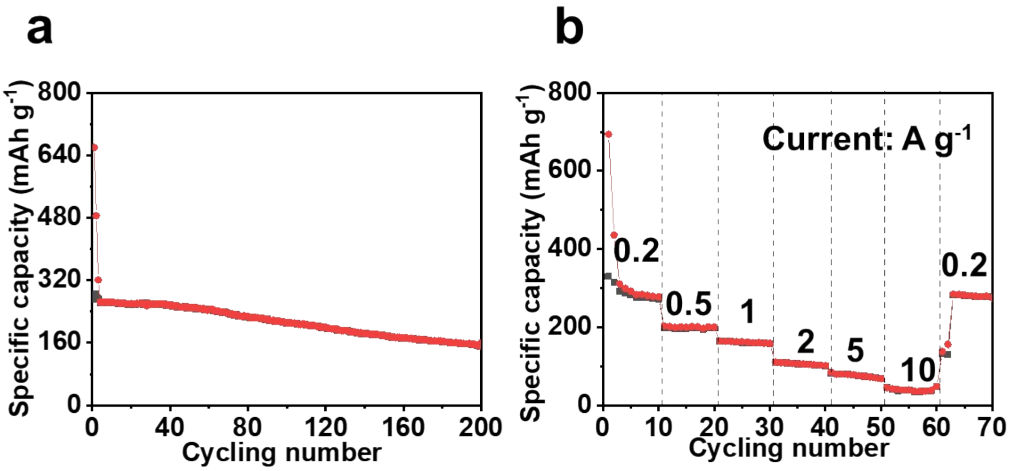

Figure S6 (a) Cycling performance at 1A g^{-1} and (b) Rate capability at various current densities

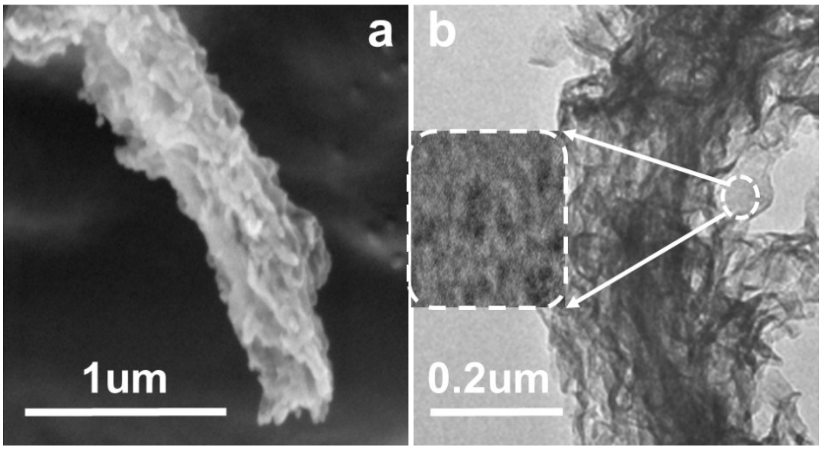

Figure S7 (a) SEM image and (b) TEM image of CNT-MoS_2@MoO_2 electrode after 100 cycles at 1 A g^{-1}.

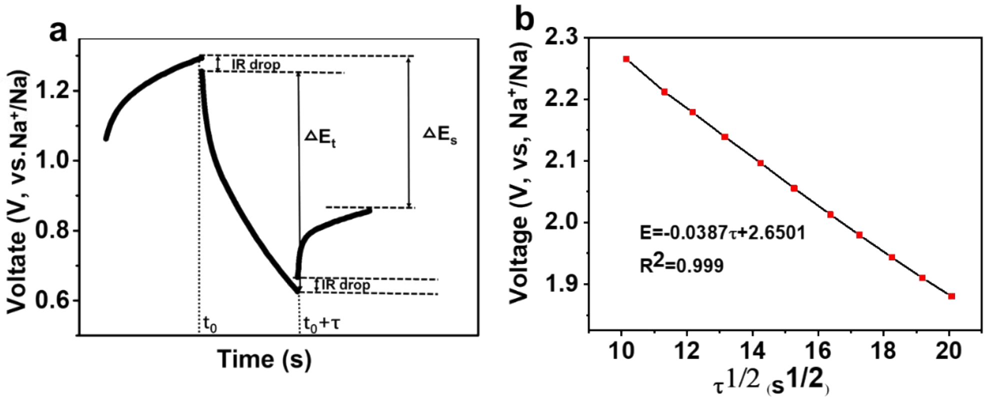

Figure S8. a) Schematic of GITT technique and b) Linear behavior of the E vs $\tau^{1/2}$ relationship.

The diffusion coefficient can be expressed as the following equation[1]:

$$D_{Na+} = \frac{4}{\pi}\left(\frac{m_B V_M}{M_B A}\right)^2 \left(\frac{\Delta E_s}{\tau(dE_\tau)/d(\sqrt{\tau})}\right)^2 \quad (\tau \ll L^2/D_{Na+}) \qquad (1)$$

In this equation, τ(s) is the constant current flux time, m_B (g) is the active mass of the electrode, V_M (cm^3 mol^{-1}) is the molar volume of the electrode, M_B (g mol^{-1}) is the molecular weight, A (cm^2) is the surface area of the electrode, L (cm) is the thickness of the electrode, E_S (V) is the total change in cell voltage during a single step and $E\tau$ (V) is the voltage change in the steady state during a single step.

If E versus $\sqrt{\tau}$ shows a linear behavior during the current pulse, the equation can be transformed into:

$$D_{Na+} = \frac{4}{\pi}\left(\frac{m_B V_M}{M_B A}\right)^2 \left(\frac{\Delta E_s}{\Delta E_t}\right)^2 \quad (\tau \ll L^2/D_{Na+}) \qquad (2)$$

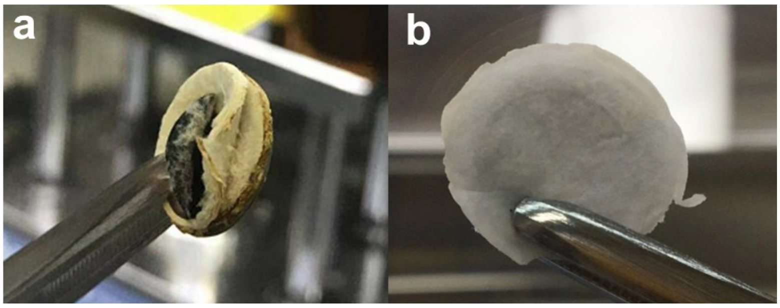

Figure S9. The image of CNT-MoS_2 and CNT-MoS_2@MoO_2-C electrode after extended cycles.

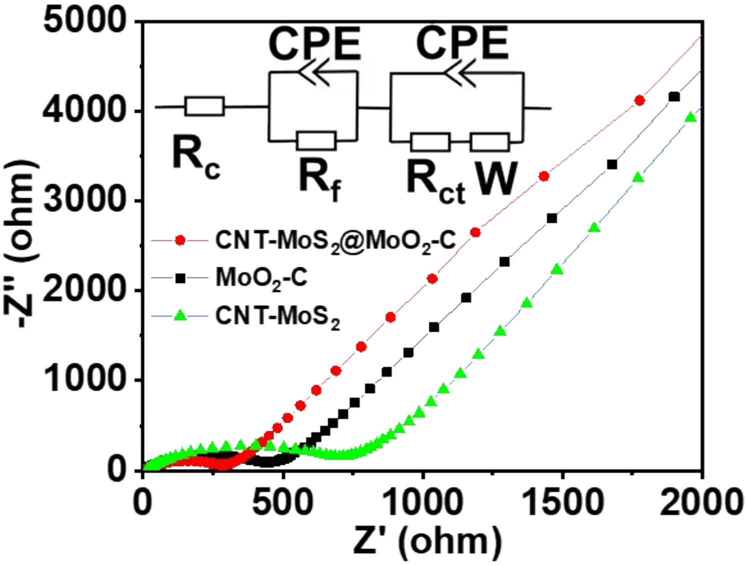

Figure S10. Nyquist plots of the CNT-MoS_2@MoO_2-C, CNT-MoS_2, and MoO_2-C electrodes (inset: Randles equivalent circuit model. R_c, R_f and R_{ct} are the current collector/electrolyte resistance, surface process resistance and the charge-transfer resistance, respectively. CPE1, CPE2 and W are the constant phase element, double layer capacitance and Warburg impedance, respectively).

Reference:

(1) Weppner, W., and Robert A. Huggins. *J. Electrochem. Soc.* **1977**, *124*, 1569-1578.

(2) Grimme, S., n-Alkane Isodesmic Reaction Energy Errors in Density

Functional Theory Are Due to Electron Correlation Effects. *Organic Letters* **2010,** *12*, 4670-4673.

(3) Moellmann, J.; Grimme, S., Importance of London Dispersion Effects for The Packing of Molecular Crystals: A Case Study for Intramolecular Stacking in A Bis-Thiophene Derivative. *Physical Chemistry Chemical Physics* **2010,** *12* (30), 8500-8504.