

High-performance flexible supercapattery enables by binder-free two-dimensional mesoporous ultrathin nickel-ferrite nanosheets

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Experimental section

Materials

All the chemicals used in this research work are analytical and utilized in the experiments without any purification. Nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), iron chloride ($\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$), sodium acetate (CH_3COONa), potassium hydroxide (KOH), ammonium fluoride (NH_4F), urea ($\text{CO}(\text{NH}_2)_2$), polyvinylalcohol (PVA), carbon cloth (CC), hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) were purchased from Aladdin Chemical suppliers and CC was bought from Shanghai Lishuo Composite Material Technology Company, China.

Growth of NiFe_2O_4 nanoparticles embedded in ultra-thin nanosheets

The direct growth of dual-morphology based on mesoporous nickel ferrite nanoparticles embedded in ultra-thin nanosheets ($\text{NiFe}_2\text{O}_4\text{-NP-NS@CC}$) has been developed by simple hydrothermal process. First, CC was cleaned by deionized water, ethanol and improve the hydrophobicity by immersing it in concentrated nitric/sulfuric acid (50 %: 50 % by volume); after that CC was dried at 60 °C for further use. After the acidification of the carbon cloth, the existence of oxidation functional groups on the surface of CC, some covalent chemical bonds were formed on the surface of activated carbon cloth due to which NiFe_2O_4 nanosheets/particles can easily anchor firmly on the CC substrate. The diffusion distance of electrolyte ions from the electrode material to the substrate is significantly reduced and conductivity of the electrode is enhanced. In a general run, 2.5 mmol of Nickel chloride and 5 mmol of iron chloride were added/dissolved in a mixture of 40 mL DI water and 10 mL of ethanol solution. Subsequently, the solution was kept on stirring for half one hour to get complete dissolution after that 10 mmol of CH_3COONa and 10 mmol NH_4F were added and stirred for further 30 min. In next step, the prepared solution mixture was poured

to an autoclave of 70 mL capacity along with cleaned carbon cloth pieces. The tightly packed autoclave was transferred to an electric oven that was already heated at 180 °C and kept heated for 16 h. After the completion of the hydrothermal process, the autoclaves were left to turn cold at room temperature. Afterwards, the coated carbon cloth pieces were collected and washed three times using ethanol/deionized water and placed in an oven at 90 °C for whole night. In the last step, the coated carbon cloth pieces were annealed in air at 350 °C (ramping rate of 2 °C min⁻¹) for 2 h. The same procedure was followed to produce single morphological architecture by removing the NH₄F from the solution mixture while other conditions remained the same. The fabrication of nitrogen-doped porous carbon (NPC) for the negative electrode was reported in our previous work. The physical and electrochemical characterizations of NPC negative electrodes are elaborated in Fig. S1-S5.

Fabrication of the single electrode and flexible supercapattery

Working electrode assembly: The electrodes assembly as single electrode (for three electrode systems) and working electrode device can be summarized as: Single electrode assembly: the as-prepared NiFe₂O₄-NP-NS@CC were cut into small pieces of 1×1 cm² and directly attached to the Cu wire while using the silver paste. In order to find out accurate results from prepared material, the backside of the electrode was covered with epoxy resin. The LMD (loading mass density) of metal oxide onto the substrate (CC) was found to be ~1.25 mg cm⁻², assessed by subtracting the weight of coated samples to the weight of pristine CC.

Electrolyte preparation: The solution of PVA/KOH electrolyte was prepared as: in the first step 1.5 g of polyvinyl alcohol (PVA) was dissolved into 10 mL of DI water at 90 °C. In second step, solution of KOH was prepared by dissolving 1.12 g of KOH into another 5 mL DI water. Finally,

the above mentioned two solutions (PVA solution and KOH solution) were mixed together and kept on stirring until a clear jelly like solution (PVA/KOH) was obtained.

The flexible supercapattery device was assembled in the given steps: the fabricated binder-free NPC@CC was employed as a negative electrode, and the as-prepared NiFe₂O₄-NP-NS@CC with equal dimensions was utilized as the positive electrode. Subsequently, positive and negative electrodes were sandwiched with Whatman filter paper (8 mm) as a separator, whereas, the separator was previously soaked in the PVA/KOH electrolytic solution. Before using the assembled supercapattery device, the device was left overnight for solidification.

Characterizations and Electrochemical Measurements

The detailed morphologies and microstructures of the fabricated samples were investigated by field emission scanning electron microscope (FEG-SEM, FEI Nova 400) with Energy dispersive X-ray (EDX) and transmission electron microscope (TEM, JEOL-2100). The specific surface area and pore size distribution of the prepared materials were estimated by N₂ sorption isotherms (BET, Quantachrome ASIQM0000-5). The crystalline structures of the sample were characterized by X-ray diffraction (XRD) (PANalytical X'Pert Powder with Cu K α radiation). The chemical states and composition of the elements were examined by X-ray photoelectron spectroscopy (XPS, PerkinElmer PHI 5000C).

All electrochemical experiments were conducted at room temperature using an electrochemical workstation (CHI 660D). Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and the galvanostatic charging/discharging (GCD) experiments of the assembled electrodes

were recorded using a three-electrode system in 6 M KOH aqueous solution as the electrolyte, whereas, Ag/AgCl was used as a reference and platinum wire (Pt) as a counter electrode. The EIS experiments were conducted in an open circuit potential at 0.1 V amplitude and 0.01 to 100 kHz of the frequency range. The optimum mass correlation between NiFe₂O₄-NP-NS@CC cathode and NPC@CC as an anode (m^+/m^-) acquired through the charge balance theorem ($Q^+=Q^-$) is about 0.43 to approach the best output. Thus, the electrodes generated were provided with 1.5 mg of NiFe₂O₄-NP-NS and 3.5 mg of NPC. Therefore, the total mass of the active materials for the device was 5.0 mg cm⁻², depending on the following equations ($m^+/m^- = C^-V^-/C^+V^+$). Where, m^+ , C^+ , V^+ denoted the mass, capacitance and potential window of positive electrodes and m^- , C^- , V^- for mass, capacitance and potential window of negative electrodes, respectively.

The specific capacitance of single electrode (C_s), specific capacitance (C_d), energy density (E_d), power density (P_d) and Coulombic efficiency (η) of the NiFe₂O₄-NP-NS@CC//NPC were calculated according to the following equations: [1-2]

$$C_s = \frac{1}{m v (V_f - V_i)} \int_{V_i}^{V_f} I dV \quad (1)$$

$$C_d = \frac{I \Delta t_d}{M (V_f - V_i)} \quad (2)$$

$$E = \frac{1}{2} C_d (V_f - V_i)^2 \times \left(\frac{1000}{3600} \right) \quad (3)$$

$$P = \frac{E}{\Delta t_d} \quad (4)$$

$$\eta (\%) = \frac{\Delta t_d}{\Delta t_c} \times 100 \quad (5)$$

$$\text{Capacity (C g}^{-1}\text{)} = [\text{Capacitance} \times \text{Potential Window}] \quad (6)$$

Where C_s ($F g^{-1}$) is the specific capacitance of single electrode; m (g) is the mass of active material on one CC; ΔV ($V_f - V_i$) is the potential window; ν (mVs^{-1}) is the scan rate; I (A) is the applied current; C_d ($F g^{-1}$) is the capacitance of ASC device, M is the mass of both positive and negative electrodes of ASC device; E ($Wh kg^{-1}$) is the energy density; P ($W kg^{-1}$) is the power density; Δt_d and Δt_c are discharging time and charging time (s) and η is the Coulombic efficiency of ASC device.

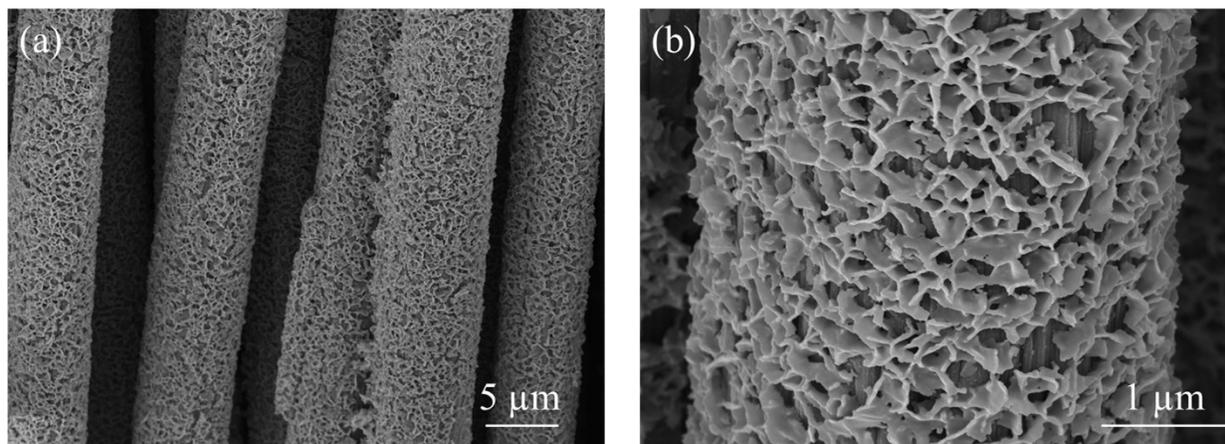


Figure S1: (a-c) Low- and high-resolution SEM images of bimetallic MOF derived ZIF/ZIF-67:50/50 derived N-doped carbon nanosheets at CC substrate after carbonized at 800 °C in N_2 for 2 h.

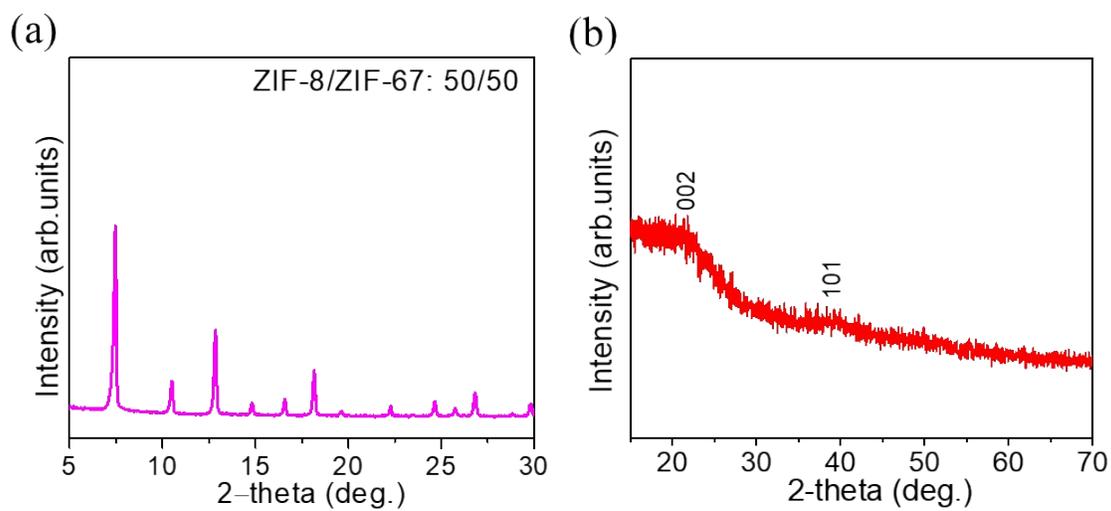


Figure S2: (a) Physical characterization of bimetallic MOF ZIF-8/ZIF-67 (50/50) derived precursor and carbon. (a) XRD pattern of MOF precursors, (b) XRD pattern of MOF derived carbon.

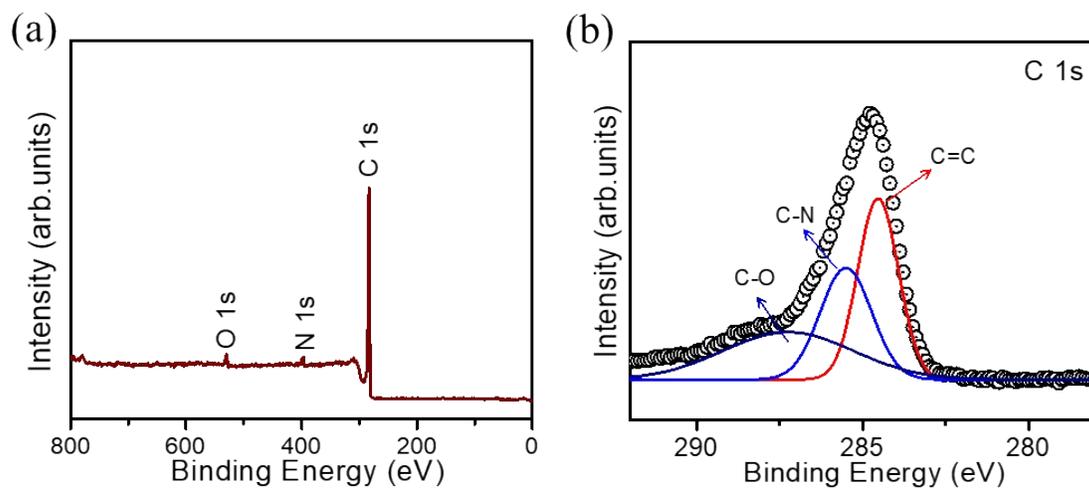


Figure S3: (a) Physical characterization of bimetallic MOF ZIF-8/ZIF-67 (50/50) derived precursor and carbon. (a) XPS full survey and (b) De-convoluted XPS spectrums of C 1s.

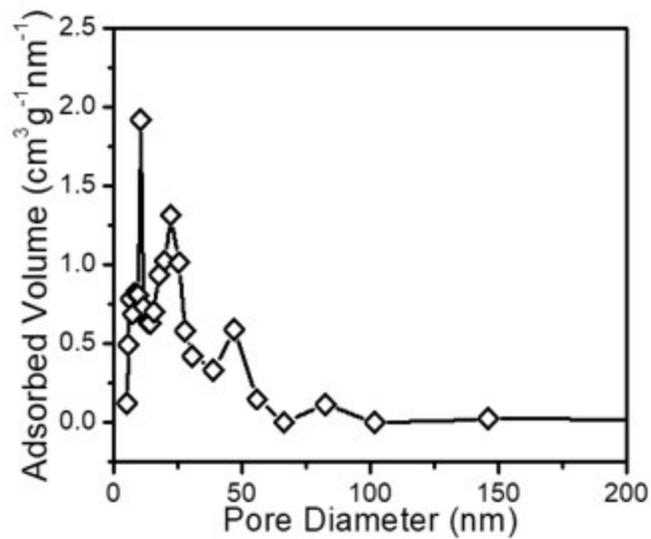


Figure S4: N₂ adsorption-desorption pore size distribution curve derived using BJH method for NPC.

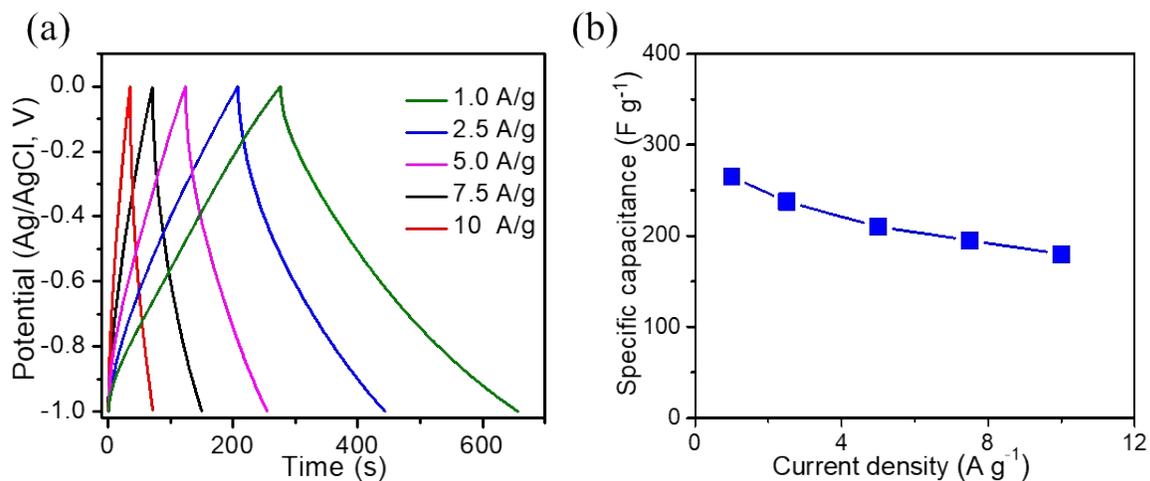


Figure S5: Electrochemical performance of NPC@CC electrode in KOH aqueous electrolyte. (a) GCD curves in potential window of -1.0 to 0.0 V at various current densities, (c) Specific capacitance as a function of current density.

Discussion on negative electrode

The SEM images of the NPC@CC are shown in Figure S1, and corresponding physical characterizations XRD, XPS and BET/BJH pore size distribution are demonstrated in S2-S4, respectively. The surface area of the MOF derived carbon material is 279 m²/g. These characterizations confirm the existence of mesoporous carbon. The electrochemical performance of NPC@CC in KOH aqueous electrolyte is shown in Figure S5. The NPC@CC electrode revealed the high capacitance of 260 F g⁻¹ at 1 A g⁻¹.

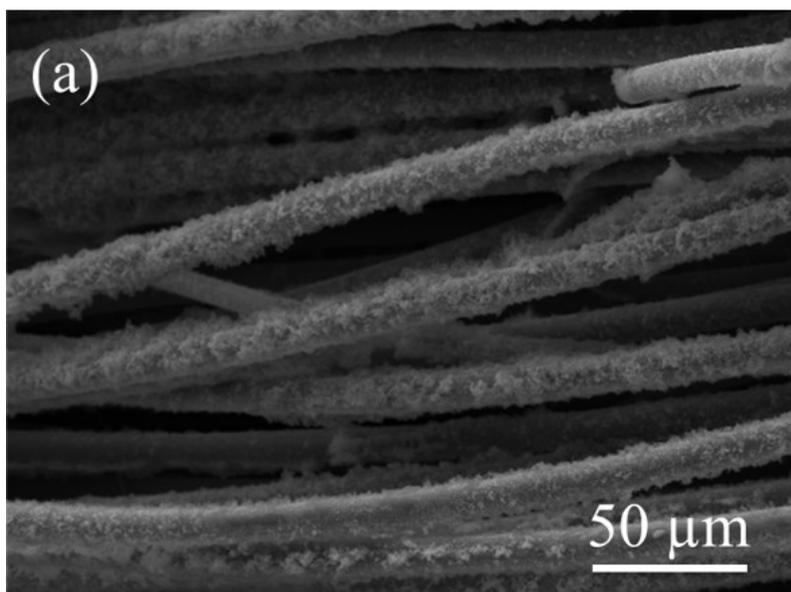


Figure S6: Low resolution SEM images of NiFe₂O₄-NP@CC.

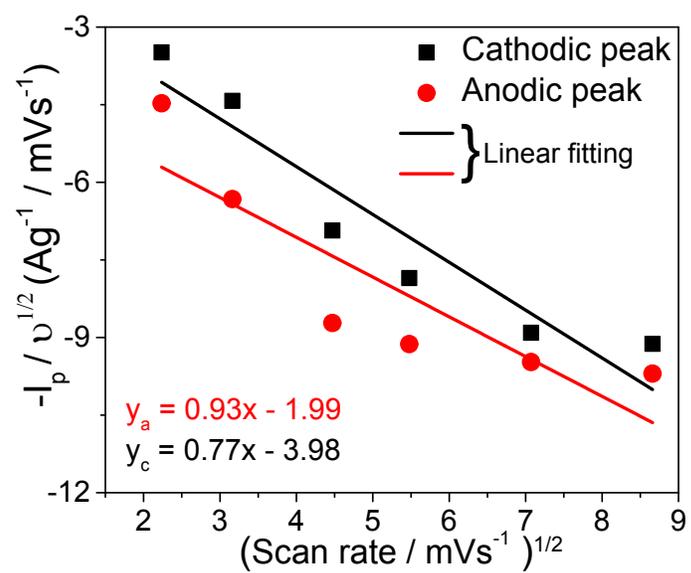


Figure S7: Plot for the calculation of k_1 and k_2 values.

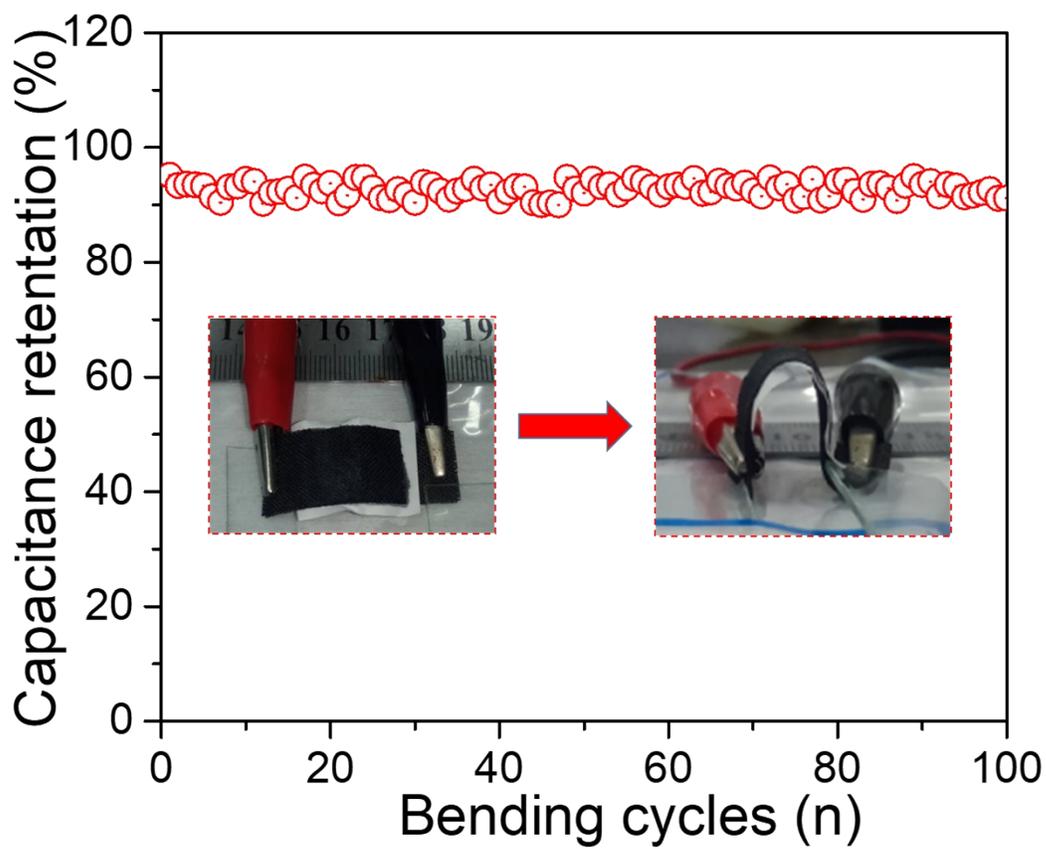


Figure S8: Flexible performance of NiFe₂O₄-NP-NS@CC//NPC up to 100 bending cycles (insets show the one complete cycle from linear state to bent state).

References

- [1] M.S. Javed, C. Zhang, L. Chen, Y. Xi, C. Hu, *Journal of Materials Chemistry A*, 4 (2016) 8851-8859.
- [2] M.S. Javed, H.U. Shah, N. Shaheen, R. Lin, M. Qiu, J. Xie, J. Li, R. Raza, W. Mai, C. Hu, *Electrochimica Acta*, (2018).