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Rational construction of 3D hierarchical $NiCo_2O_4$/PANI/MF composite foam as high-performance electrode for asymmetric supercapacitors

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Experimental detalis

Materials: Aniline (ANI), ammonium persulfate ($(NH_4)_2S_2O_8$, APS), hydrochloric acid (HCl), cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), hexamethylenetetramine (HMTA, $C_6H_{12}N_4$, 99%), ethanol and acetone were commercially available from Sinopharm Chemical Reagent Co. Ltd. All chemicals were of analytic grade and directly used without further purification.

Preparation of $NiCo_2O_4$/PANI/MF: A piece of MF (30×10×3 mm^3) was carefully cleaned through sonication consecutively in acetone, deionized (DI) water and ethanol (10 min each) to remove the impurities. The in-situ polymerization of aniline was performed in an ice bath at 0-5°C. Typically, the cleaned MF was first soaked in HCl solution (1 M, 20 mL) containing aniline for the sufficient adsorption of aniline by MF, then another HCl solution (1 M, 20 mL) containing APS was slowly dropped in the above solution to initiate the polymerization. The 0.03 M aniline was polymerized over 10 h with the molar ratio of ANI/APS fixed at 2/1. The obtained PANI/MF composite foam was then washed with DI water and dried at 60°C.

In a typical one-step hydrothermal procedure for the deposition of $NiCo_2O_4$, the mole ratio of $Ni(NO_3)_2{\cdot}6H_2O$: $Co(NO_3)_2{\cdot}6H_2O$: HMTA was kept as 1: 2 : 4 for all samples. First, $Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, and HMTA were dissolved into a mixed solvent of 20 mL of H_2O and 20 mL of ethanol with magnetic stirring to form a clear pink solution. Subsequently, the as-prepared PANI/MF was immersed into the mixed solution, which was then transferred to a 40 mL Teflon-lined autoclave and heated in an electric oven at 90°C for 10 hours. After reaction, the composite foam was taken out and washed several times with DI water, followed by annealing at 300°C for 2 h with a heating rate of 2°C min^{-1} in air to obtain $NiCo_2O_4$/PANI/MF composite foam. The concentration of $Ni(NO_3)_2{\cdot}6H_2O$ in the hydrothermal reaction was varied as 5 mM, 10 mM and 20 mM to optimize the deposition of $NiCo_2O_4$, obtained three composite foams were denoted as NCO/P/MF-1, NCO/P/MF-2 and NCO/P/MF-3. The mass loading of $NiCo_2O_4$ on PANI/MF was obtained based on the weight change of the PANI/MF composite foam before and after reactions. According to calculation, the mass loading of $NiCo_2O_4$ on NCO/P/MF-1, NCO/P/MF-2 and NCO/P/MF-3 is about 1, 1.2 and 1.4 mg cm^{-2}, respectively. For comparison, pure $NiCo_2O_4$ was also prepared through the same method.

Characterization: The morphology of the samples was investigated by scanning electron microscope (SEM, Hitachi, Japan). Transmission electron microscope (TEM) was recorded on Hitachi H-800. The crystal structure of the products was studied using X-ray diffraction (XRD) on a Bruker D8 diffractometer in the 2θ range of 10-80° at room temperature (Cu Kα radiation, λ= 1.5418 Å). X-ray photoelectron spectroscopy (XPS) was carried out on Kratos AXIS Ultra DLD.

Electrochemical Characterization: The electrochemical measurements were conducted in a standard three-

electrode setup. NCO/P/MF composite foams pressed on the nickel foam were used as the working electrodes. Pt electrode and saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. KOH solution (3 M) was used as the electrolyte. The asymmetric supercapacitor device was assembled using NCO/P/MF composite foam as the positive electrode and the activated carbon (AC) as the negative electrode. The AC electrode was prepared by mixing 70 wt% AC, 20 wt% carbon black and 10 wt% polytetrafluoroethylene (PTFE) binder to form homogeneous slurry, followed by pressing onto nickel foam and drying. 3 M KOH solution was utilized as electrolyte (fabricated device was denoted as NCO/P/MF//AC ASC). Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge-discharge (GCD) measurements were carried out on a Gamry Interface 5000P at room temperature. The specific capacitance (C_s) was calculated from the discharge curves according to the following equation:

$$C_s = I\,\Delta t/(m\,\Delta V) \quad (1)$$

Where I is the constant discharge current, Δt is the discharge time, m is the active mass loadings of working electrode, and ΔV is the discharge voltage. The energy density (E (Wh kg^{-1})) and power density (P (W kg^{-1})) of the asymmetric supercapacitor were calculated based on the following equations:

$$E = (1/2)C(\Delta V)^2 \quad (2)$$

$$P = E/\Delta t \quad (3)$$

Discussion on XRD and XPS

The crystalline structure and phase purity of the as-obtained samples were first examined by XRD analysis. The diffraction peaks in Figure S3 can be assigned to nickel-cobalt hydroxide hydrate. After annealing under 300°C to remove the interlayer water molecule, $NiCo_2O_4$ exhibits a series of characteristic peaks at 18.8, 31.1, 36.7, 38.5, 44.7, 55.6, 59.2 and 65.2° (Figure 4), which can be well indexed to the (111), (220), (311), (222), (400), (422), (511) and (440) plane of the spinel $NiCo_2O_4$ phase (JCPDS Card no. 73-1702). In the spectrum of NCO/P/MF composite foam, all the diffraction peaks of $NiCo_2O_4$ can be observed without the detection of any impurity peaks, demonstrating the synthesis of pure $NiCo_2O_4$ in NCO/P/MF. Additionally, the absence of the PANI signal is ascribed to its relatively low diffraction intensity.

The elemental composition and chemical state of the samples were further analyzed through XPS with results shown in Figure 5. Survey spectrum indicates the individual peaks of Ni, Co, O, and C elements, no other impurity peaks can be detected (Figure 5a). In the Ni 2p spectrum (Figure 5b), the core level spectrum is reasonably divided into four peaks. The signals at 854.2 and 872.3 eV are ascribed to Ni^{2+}, whereas those at 856.1 and 873.1 eV can be indexed to Ni^{3+}. Two strong satellite peaks at the high binding energy of Ni $2p_{3/2}$ and Ni $2p_{1/2}$, i.e. 861.2 and 879.9 eV, are two shakeup peaks of Ni. Meanwhile, two kinds of cobalt can be observed in the core level

spectrum of Co 2p (Figure 5c). The peaks at 779.4 and 794.6 eV are correspond to Co^{3+} and the peaks at 781.2 and 796.2eV can be attributed to Co^{2+}. Two peaks located at 529.4 and 531.1 eV in the O 1s spectrum indicate the metal-oxygen bonds of Co-O and Ni-O in the metal oxide (Figure 5d). These results further confirm the successful synthesis of spinal $NiCo_2O_4$ in NCO/P/MF composite foam, which is in good agreement with XRD results.

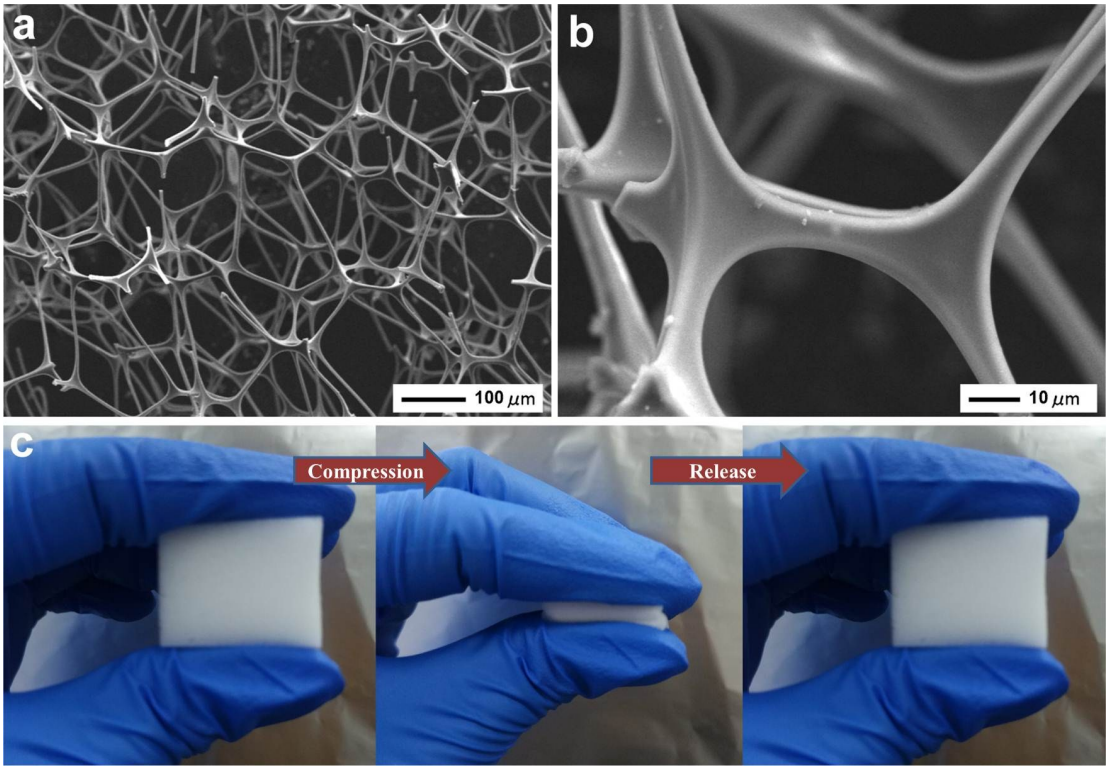

Figure S1. (a-b) SEM images of melamine foam; (c) bending test of melamine foam.

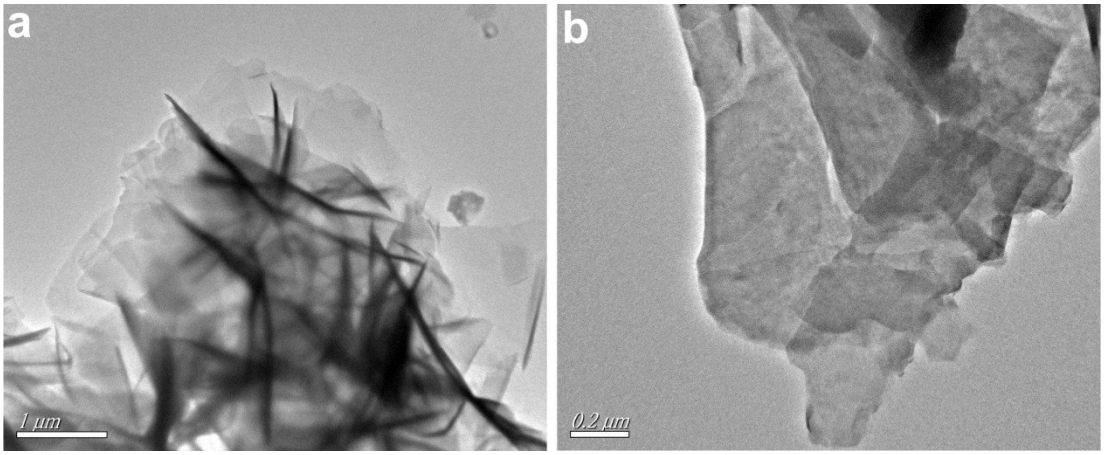

Figure S2. TEM images of $NiCo_2O_4$ scraped off from NCO/P/MF-2.

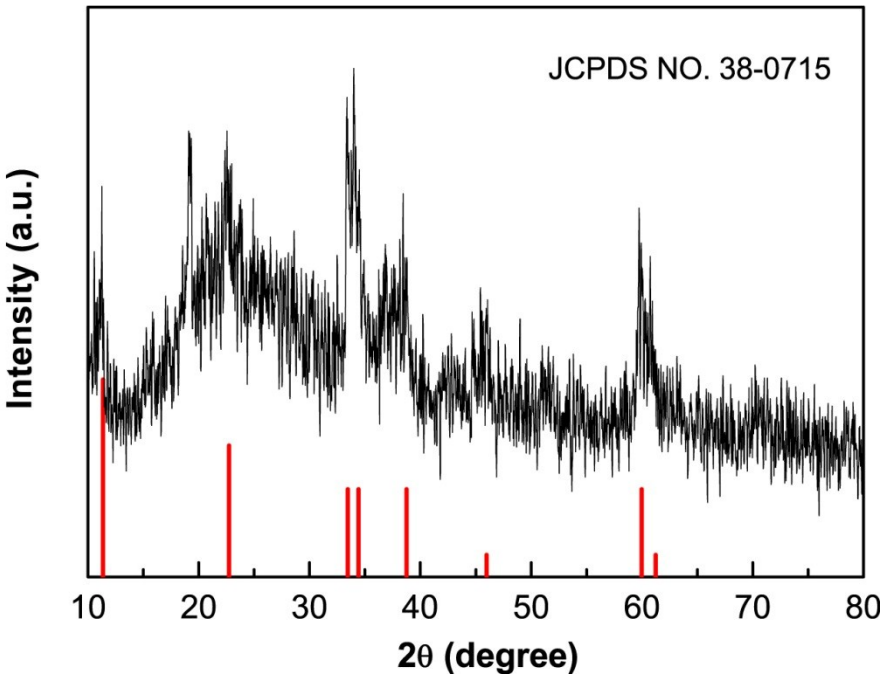

Figure S3. XRD pattern of the as-prepared Ni-Co precursor on PANI/MF.

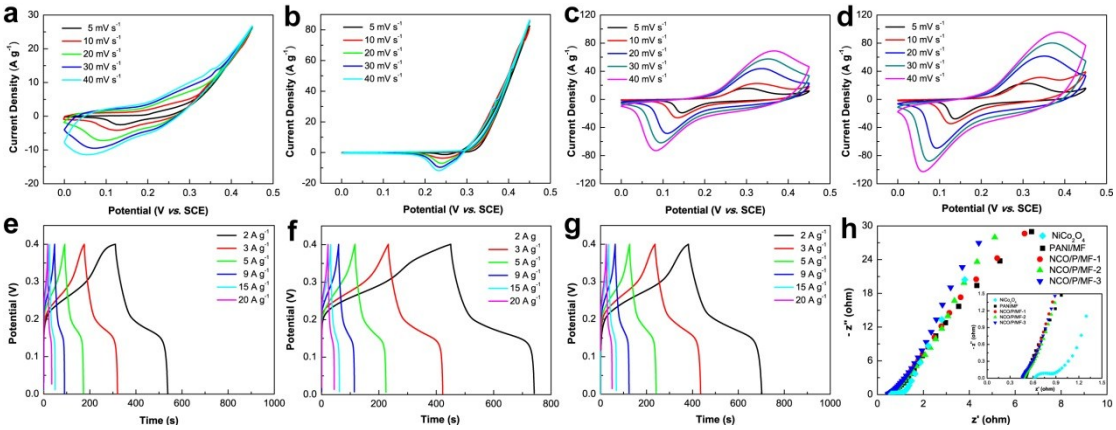

Figure S4. CV curves of samples at different scan rate: (a) $NiCo_2O_4$; (b) PANI/MF; (c) NCO/P/MF-1 and (d) NCO/P/MF-3. Galvanostatic charge-discharge curves of NCO/P/MF electrode at various current densities: (e) NCO/P/MF-1; (f) NCO/P/MF-2 and (g) NCO/P/MF-3. (h) Nyquist plots of PANI/MF, pure $NiCo_2O_4$, and NCO/P/MF electrodes.

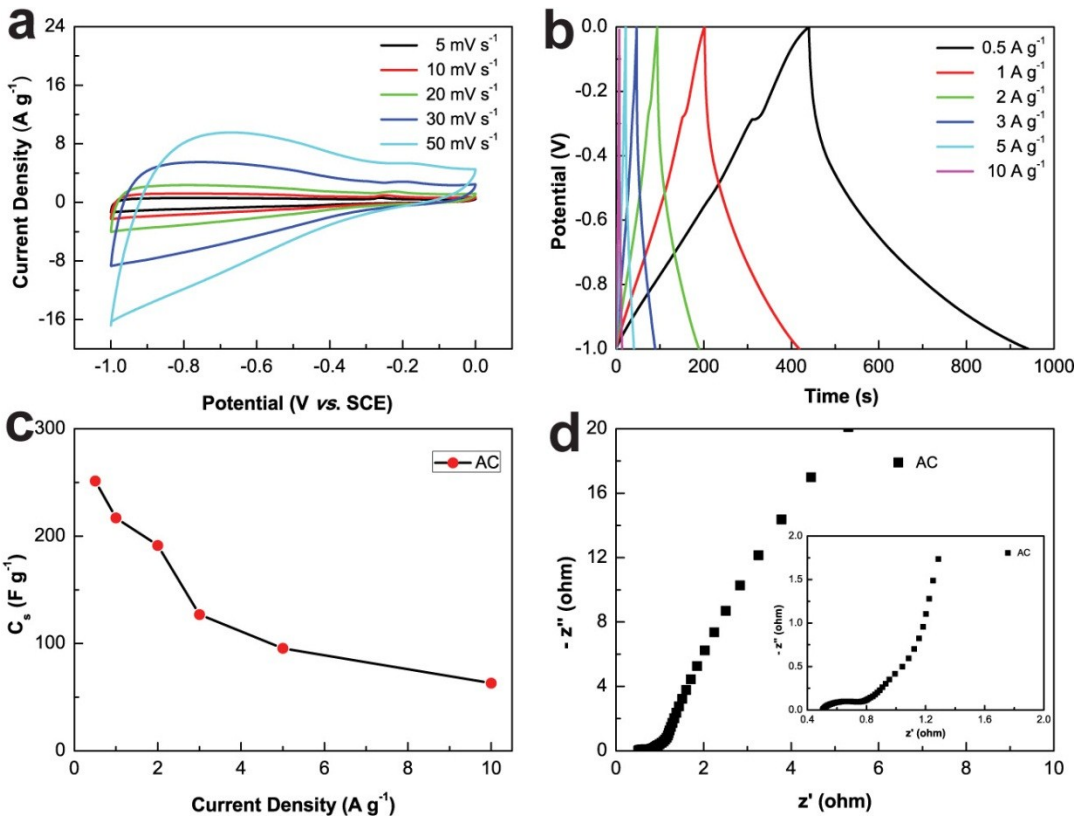

Figure S5. (a) CV curves of AC electrode at different scan rates; (b) galvanostatic charge-discharge curves of AC electrode at various current densities; (c) specific capacitance of ASC electrode at different current densities; (d) Nyquist plots of AC electrode.

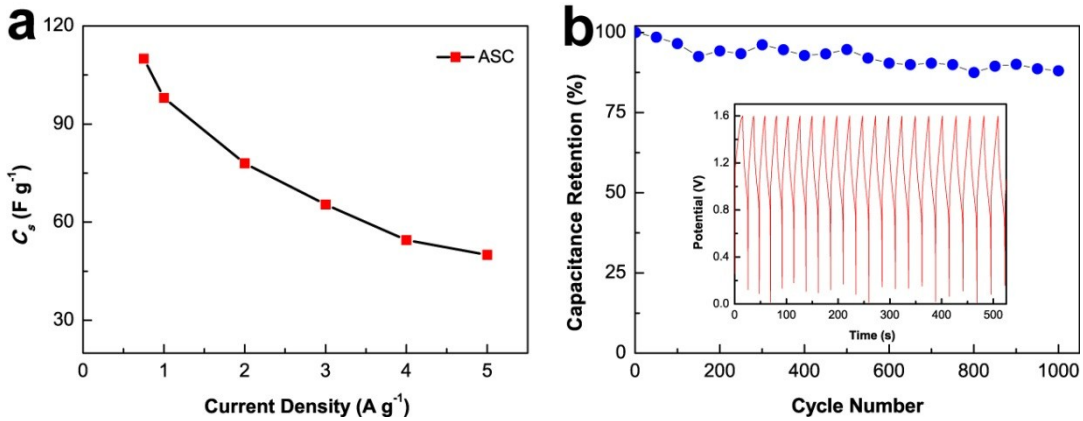

Figure S6. (a) specific capacitances of the ASC at different current densities; (b) long-term stability test of the ASC at 4 A g^{-1} for 1000 cycles. The inset displays the first 23 charge-discharge cycles.