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Solvent-induced structural regulation over Ni_2P/CNTs hybrids towards the boosting performance for supercapacitors

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Chemical Reagents

Anhydrous ethanol (CH_3CH_2OH, 99.7 wt%), methanol, formic acid (HCOOH, 88 wt%), and methylamine water solution (CH_3NH_2, 40 wt%) were purchased from Zhiyuan Chemical Plants (Tianjin). Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 98%), and sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$, 99%) was purchased from Yong sheng Fine Chemical Company (Tianjin). Surfactant polyvinylpyrrolidone K30 (PVP K30) was purchased from Tokyo Chemical Industry Co., Ltd. The commercial active carbon (AC YP-80F) was purchased from KURARAY (Japan). Of note, all the chemicals were of analytical grade and used without further purification.

Structural characterizations

The surface structure and elemental composition of samples were examined by field-emission scanning electron microscopy (FESEM; Hitachi S-4800 microscope) attached with energy dispersive X-ray spectrometry (EDX). Powder X-ray diffraction (PXRD) texted by Bruker D8 advance diffractometer with Cu Ka radiation and high-resolution transmission electron microscopy (HRTEM; Hitachi H600 microscope) were used to analyze crystal phase and porous features of products. Surface element state was measured using X-ray photoelectron spectroscopy (XPS) performed on Escalab 250 Xi system.

Electrochemical measurements

A CHI760E working station was applied to carry out the electrochemical technologies including cyclic voltammetry (CV) with a ranging potential from 0 to 0.6 V for the three-electrode system and 0 to 1.6 V for the asymmetric supercapacitor, respectively, galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS, 10 to 100000 Hz) tests. All electrochemical performances were measured in 6 M KOH electrolyte. At first, a standard three-electrode configuration was designed to access to partial performance information, where a saturated Hg/HgO electrode (in 1 M KOH) and platinum electrode were used as the reference electrode and counter electrode, respectively. The synthesized products were employed as the working electrodes, which were prepared by coating a homogenous slurry containing the 2.25 mg prepared samples, 0.25 mg carbon black and polytetrafluoroethylene (PTFE, 5 wt%) onto a nickel foam (1× 1 cm^2), together with a mass ratio of 9:1:1. Then, the nickel foam was dried at a vacuum oven before pressed under 10 MPa. Moreover, an asymmetric supercapacitor (ASC) was also assembled by using 3D flower-like Ni_2P/CNTs hybrid as positive electrode and commercial active carbon (YP-80F) as negative electrode, where the mass of the positive and negative electrodes is 2.25 and 5.82 mg, respectively. The mass loading of the two electrodes satisfies the following charge balance equation [1-3]:

$$m_+ / m_- = c_- \Delta V_- / c_+ \Delta V_+ \qquad (1)$$

Where m_+ and m_- represent the mass loadings of the anode and cathode, respectively. c_+ and c_- are the corresponding specific capacitance (F /g). ΔV_+ , ΔV_- refer to Voltage window (V) of positive and negative electrodes, respectively. C_+ or C_- can be evaluated from the galvanostatic discharge process based on the following relation:

$$C = I\Delta t / m\Delta V \qquad (2)$$

In which m (g) is the mass of the active materials, I (A), Δt (s), and ΔV (V) represent galvanostatic discharge current, time and potential window of the three-electrode system. For ASC device, the specific capacitance (C_m) also can be calculated with the same principle but M (g) refers to the total mass of two active materials as follows (3):

$$C_m = I\Delta t / M\Delta V \qquad (3)$$

The energy density (E, Wh /Kg) and power density (P, W/ Kg) of ASC device can be determined according to the equations (4) and (5):

$$E = C_m \Delta V^2 / 2 \times 3.6 \quad (4)$$

$$P = 3600E/\Delta t \quad (5)$$

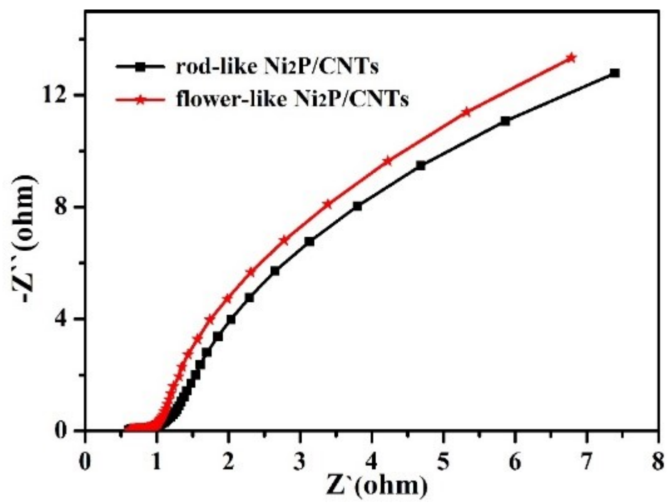

Fig. S1. Nyquist plots of the prepared samples.

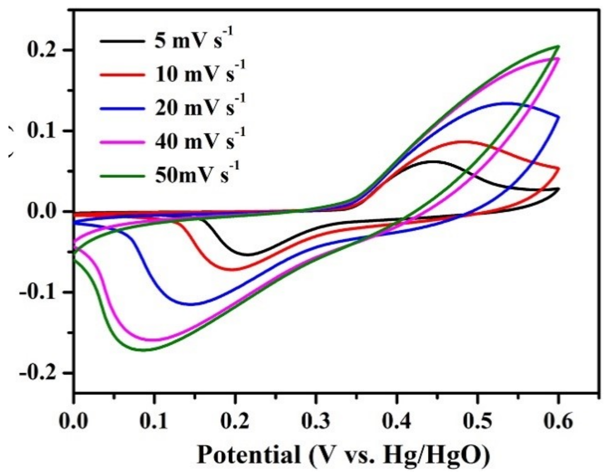

Fig. S2. CV curves of 3D flower-like Ni_2P/CNTs hybrid at different scan rates.

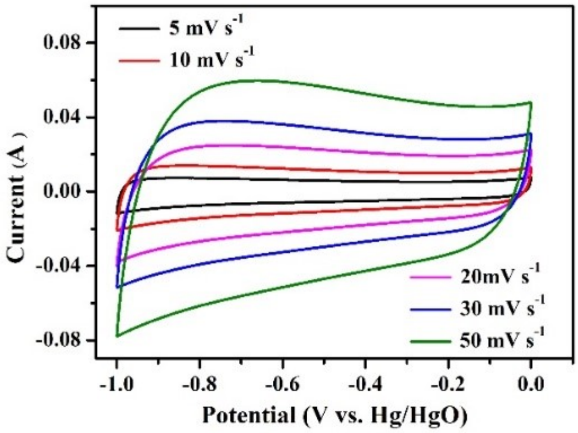

Fig. S3. CV curves of AC(YP-80F) at different scan rates.

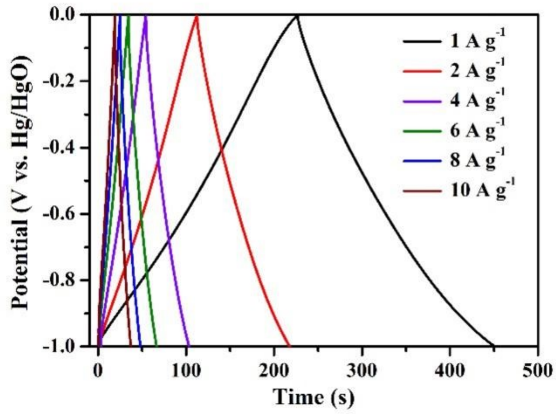

Fig. S4. GCD curves of AC(YP-80F) at different current densities.

References

[1] Q. Wang, J. Su, H. Chen, D. Wang, X. Tian, Y. Zhang, X. Feng, S. Wang, J. Li, H. Jin, Highly conductive nitrogen-doped sp^2/sp^3 hybrid carbon as a conductor-free charge storage host, Adv. Funct. Mater., 2022, **32**, 2209201.

[2] X. Jiao, J. Wang, Z. Yuan, C. Zhang, Smart current collector for high-energy-density and high-contrast electrochromic supercapacitors toward intelligent and wearable power application, Energy Storage Mater., 2023, **54**, 254-265.

[3] R. Patil, N. Kumar, S. Bhattacharjee, H. Wu, P. Han, B. Matsagar, C. Wu, R. Salunkhe, A. Bhaumik, S. Dutta, Influence of catalase encapsulation on Cobalt@Nanoporous carbon with multiwall shell for supercapacitor and polyurethane synthesis using carbon dioxide, Chem. Eng. J., 2023, **453**, 139874.