Electronic Supplementary Information

CNTs grown on Nanoporous Carbon from Zeolitic Imidazolate Frameworks for Supercapacitors


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This Supplementary Information file replaces that originally published on 10th October 2016. In the “Synthesis of materials” on page 2, Co(CH₃COO)₂·4H₂O was incorrectly written as Co(NO₃)₂·6H₂O in the original version.
Experimental Section

Synthesis of materials

Preparation of hybrid Co/Zn-ZIF (Co:Zn= 2:1): All chemicals were purchased from Aldrich and used without further treatment. In a large scale synthesis, 9.855 g (44.9 mmol) of Zn(CH$_3$COO)$_2$·2H$_2$O and 26.19 g of Co(CH$_3$COO)$_2$·4H$_2$O (89.9 mmol) were dissolved in 1350 mL of methanol to form a clear solution, followed by the addition of 2-methylimidazole (88.56 g, 1.07 mol) dissolved in 450 mL of methanol. After thoroughly mixing by continuous stirring for 10 min at 1000 rpm, the mixed solution was kept at 25 °C for 24 hours. The ZIF particles were then collected from the solution by centrifugation at 7000 rpm, thoroughly washed with methanol several times, and dried at 60 °C under vacuum. After drying, 3.5 g of hybrid Co$_2$/Zn$_1$-ZIF powder was obtained.

Carbonization of hybrid Co/Zn-ZIF (Co:Zn = 2:1): The powder sample was kept under an N$_2$ atmosphere for 30 min in a furnace before increasing the temperature. Then, the crystal powder was thermally converted into nanoporous carbon with graphitic carbon nanotubes on the surface through carbonization under flowing N$_2$ at 800 °C for 5 hours with a heating rate of 2 °C·min$^{-1}$. The nanoporous carbon was washed several times with hydrogen fluoride (HF) solution (10 wt%) to remove the Zn and Co species. The obtained carbon powder was dried at 60 °C under vacuum for 24 h.
**Structural Characterization**

The surface morphology of the as-prepared nanostructures was studied using scanning electron microscopy (SEM, Hitachi S-4800) at an accelerating voltage of 5 kV and transmission electron microscopy (TEM, JEM-2100F operated at a voltage of 200 kV). The crystalline structures of the samples were characterized using a powder X-ray diffraction (XRD, Rigaku 2500) system equipped with Cu Kα radiation (λ = 0.15406 nm). Raman spectra were obtained using a Micro-Raman spectrometer (Horiba-Jovin Yvon T64000). The nitrogen adsorption-desorption isotherms were measured on a BELSORP-max (BEL, Japan) at 77 K. The surface areas and pore volumes were obtained by the Brunauer-Emmet-Teller (BET) method, the t-plot method, and the non-localized density functional theory (NLDFT) method.

**Electrochemical measurements**

**Three-electrode preparation and measurement:** The electrochemical measurements were carried out by using an electrochemical workstation (CHI 660e, CH Instruments) for a three-electrode system. For the three-electrode measurements, Ag/AgCl and platinum (Pt) wire electrode were used as the reference electrode and the counter electrode, respectively. The working electrode was prepared by coating a slurry containing the hybrid Co/Zn-ZIF nanoporous carbon, polyvinylidene fluoride binder (PVDF), and N-methyl-2-pyrrolidone on graphite electrode (1 cm x 1 cm). All the electrochemical measurements were carried out using 0.5 M H₂SO₄ aqueous electrolyte.
Coin cell preparation and measurement: The electrodes were prepared by coating a slurry containing the hybrid Co/Zn-ZIF nanoporous carbon (0.4 g, 80 wt.%), a conducting agent (0.05 g, Super-P, 10 wt.%), polyvinylidene fluoride binder (PVDF, 0.05 g, 10 wt.%), and 0.95 g of N-methyl-2-pyrrolidone on Al foil. The electrodes were dried at 120 °C for 12 h in a vacuum oven and were then pressed under 1500 kg cm⁻². The electrochemical performance of the symmetric supercapacitors was examined by assembling CR2032 coin-type cells with a glass fiber membrane in a dry room. The loading level was 1.4 mg·cm⁻². The electrolyte used was 0.5 M H₂SO₄ aqueous solution. The cells were galvanostatically charged and discharged at different current densities (room temperature).

Calculations:

In the three-electrode measurements, the gravimetric capacitance values were calculated using the galvanostatic charge-discharge method according to the following equation:

\[ C = \frac{I \times \Delta t}{m \times \Delta V} \quad (1) \]

Where \( C \) is the gravimetric capacitance (F·g⁻¹), \( m \) is the mass (g) of active material on the working electrode, \( V \) is the potential window (V), \( I \) is the current (A), and \( t \) is the discharge time (s).

In two-electrode measurements, the gravimetric capacitance values of the symmetric device were calculated using the galvanostatic charge-discharge method according to the following equation:
\[
C_{\text{device}} = \frac{I \cdot t}{M \cdot V}
\]  

(2)

Where \(C_{\text{device}}\) is the gravimetric capacitance of the symmetric device (F·g\(^{-1}\)), \(M\) is the total mass (g) of active material on the electrodes, \(V\) is the potential window (V), \(I\) is the current (A), and \(t\) is the discharge time (s).
Figure S1. (a-b) TEM images, (c) high-angle annular dark field – scanning TEM (HAADF-STEM) image, and (d) EDS mapping of hybrid Co/Zn-ZIF.
Figure S2. (a-c) SEM images of hybrid Co/Zn-ZIF-derived carbon.
Figure S3. High resolution TEM (HRTEM) image of hybrid Co/Zn-ZIF-derived carbon at edge of particle. The Co nanoparticles are shown with the graphitic carbon structure.
Figure S4. (a) Nitrogen adsorption-desorption isotherms and pore size distributions for (b) hybrid Co/Zn-ZIF and (c) hybrid Co/Zn-ZIF-derived carbon.
Figure S5. Wide-angle XRD patterns of (a) hybrid Co/Zn-ZIF and (b) hybrid Co/Zn-ZIF-derived carbon. (c) Raman spectrum of hybrid Co/Zn-ZIF-derived carbon (intensity ratio for D and G bands, $I_D/I_G = 0.87$).
Figure S6. (a) Galvanostatic charge-discharge curves, (b) specific capacitance of device at different current densities, and (c) life cycle test of coin cells using organic electrolyte consisting of 1.0 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in acetonitrile.