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Electronic Supplementary Information

CNTs grown on Nanoporous Carbon from Zeolitic Imidazolate Frameworks for Supercapacitors

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21st May 2018 – Note added after first publication:

This Supplementary Information file replaces that originally published on 10th October 2016. In the "Synthesis of materials" on page 2, $Co(CH_3COO)_2{\cdot}4H_2O$ was incorrectly written as $Co(NO_3)_2{\cdot}6H_2O$ 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 $Zn(CH_3COO)_2·2H_2O$ and 26.19 g of $Co(CH_3COO)_2·4H_2O$ (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-Emmett-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 H_2SO_4 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 H_2SO_4 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:

$$C = \frac{I \times \Delta t}{m \times \Delta V} \qquad (1)$$

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:

$$C_{device} = \frac{I\,t}{M\,V} \tag{2}$$

Where C_{device} is the gravimetric capacitance of the symmetric device ($F \cdot g^{-1}$), 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).

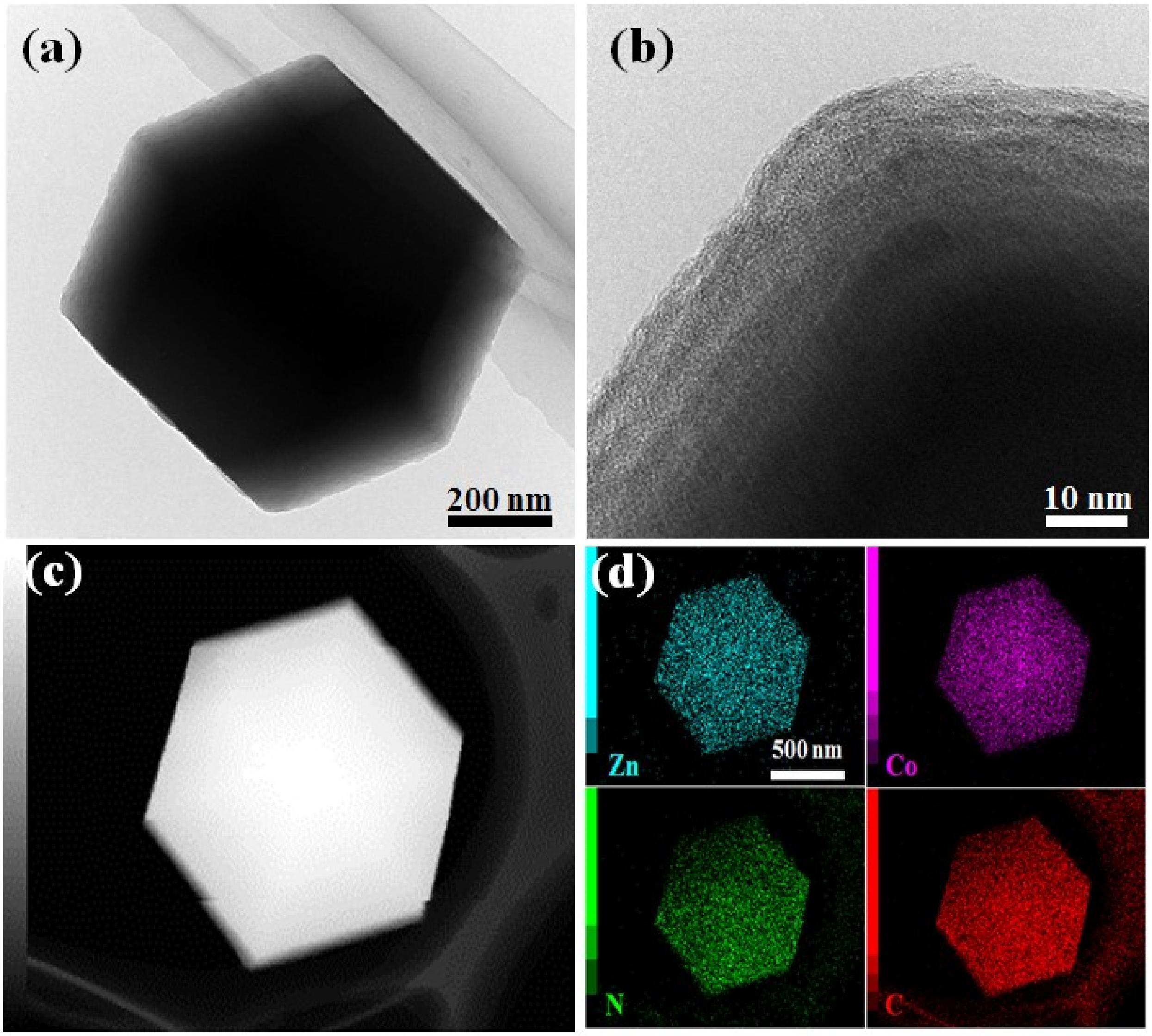

Figure S1. (a-b) TEM images, (c) high-angle annular dark field – scanning TEM (HAADF-STEM) image, and (d) EDS mapping of hybrid Co/Zn-ZIF.

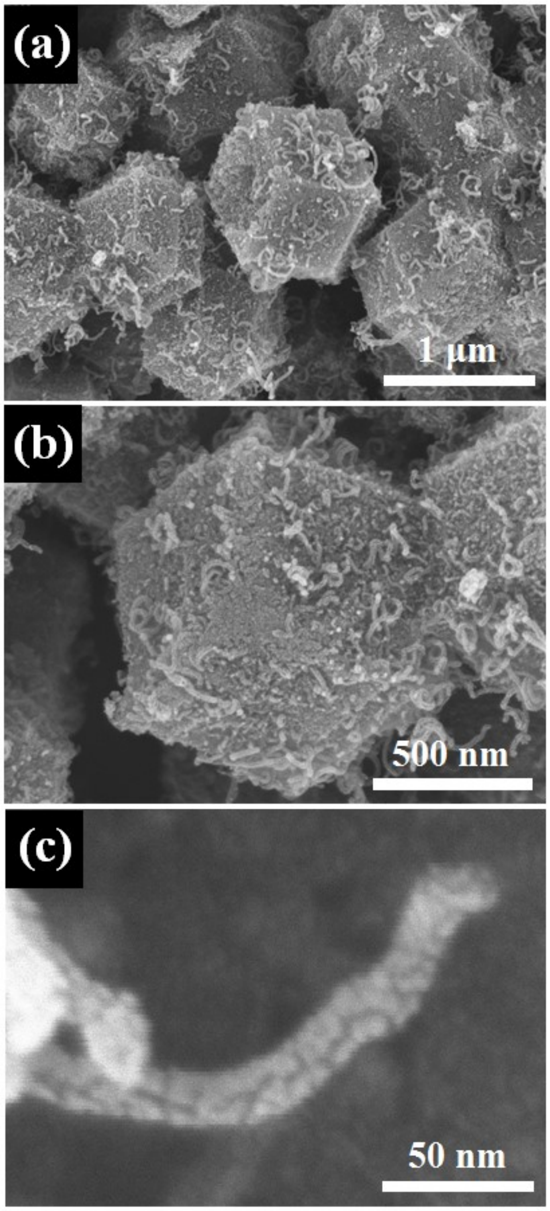

Figure S2. (a-c) SEM images of hybrid Co/Zn-ZIF-derived carbon.

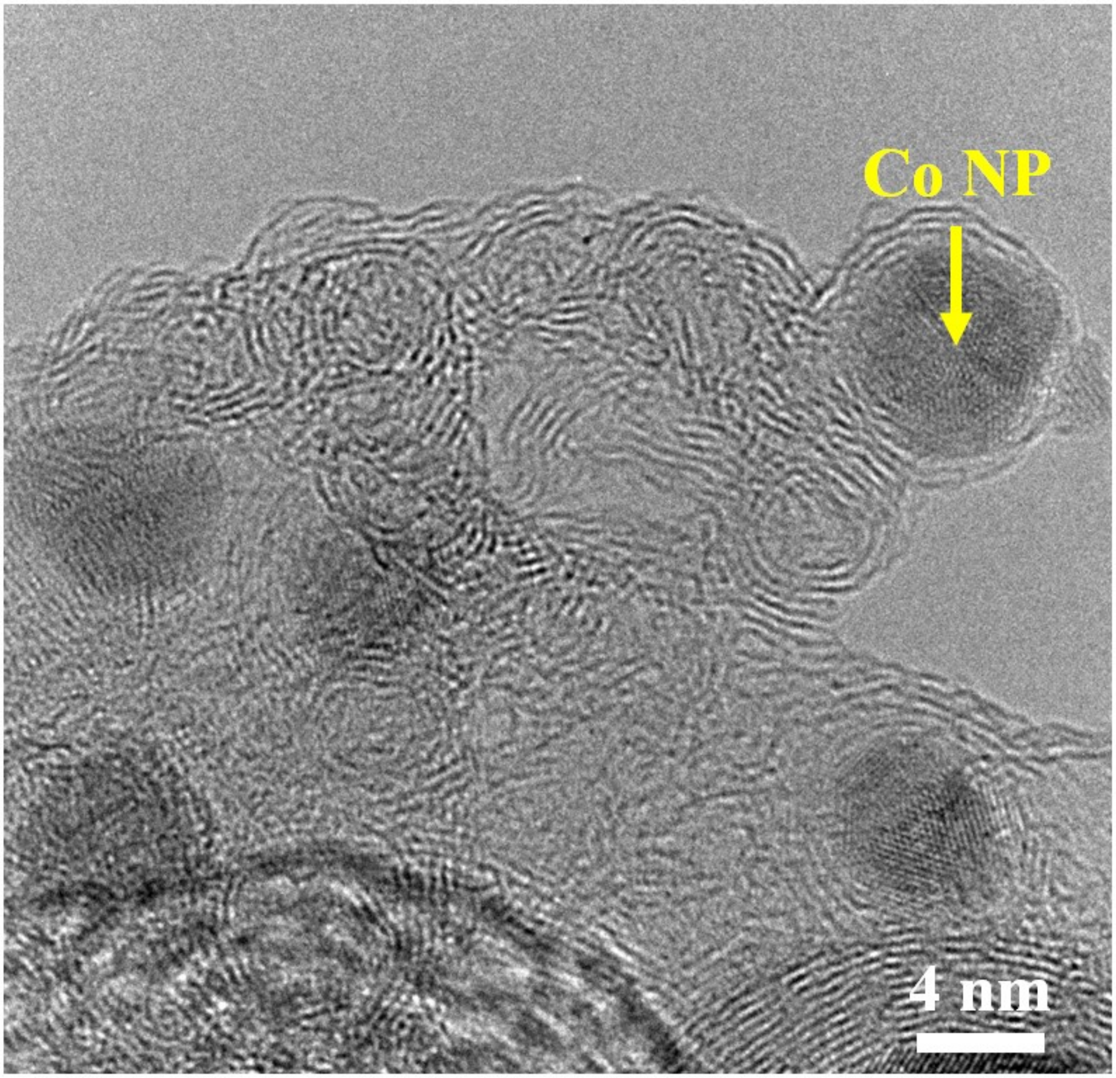

Figure S3. High resolution TEM (HRTEM) image of hybrid Co/Zn-ZIF-derived carbon at edge of particle. The Co nanoparticles are shown with the graphitic carbon structure.

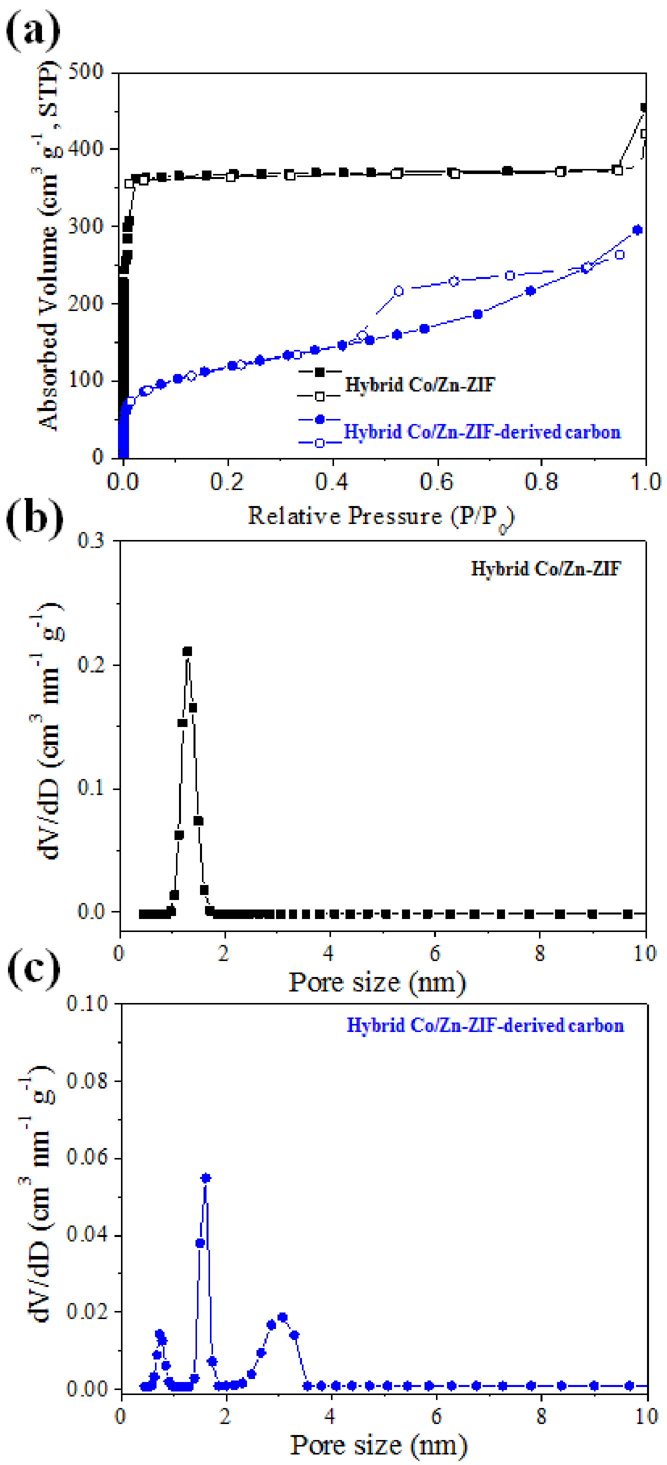

Figure S4. (a) Nitrogen adsorption-desorption isotherms and pore size distributions for (b) hybrid Co/Zn-ZIF and (c) hybrid Co/Zn-ZIF-derived carbon.

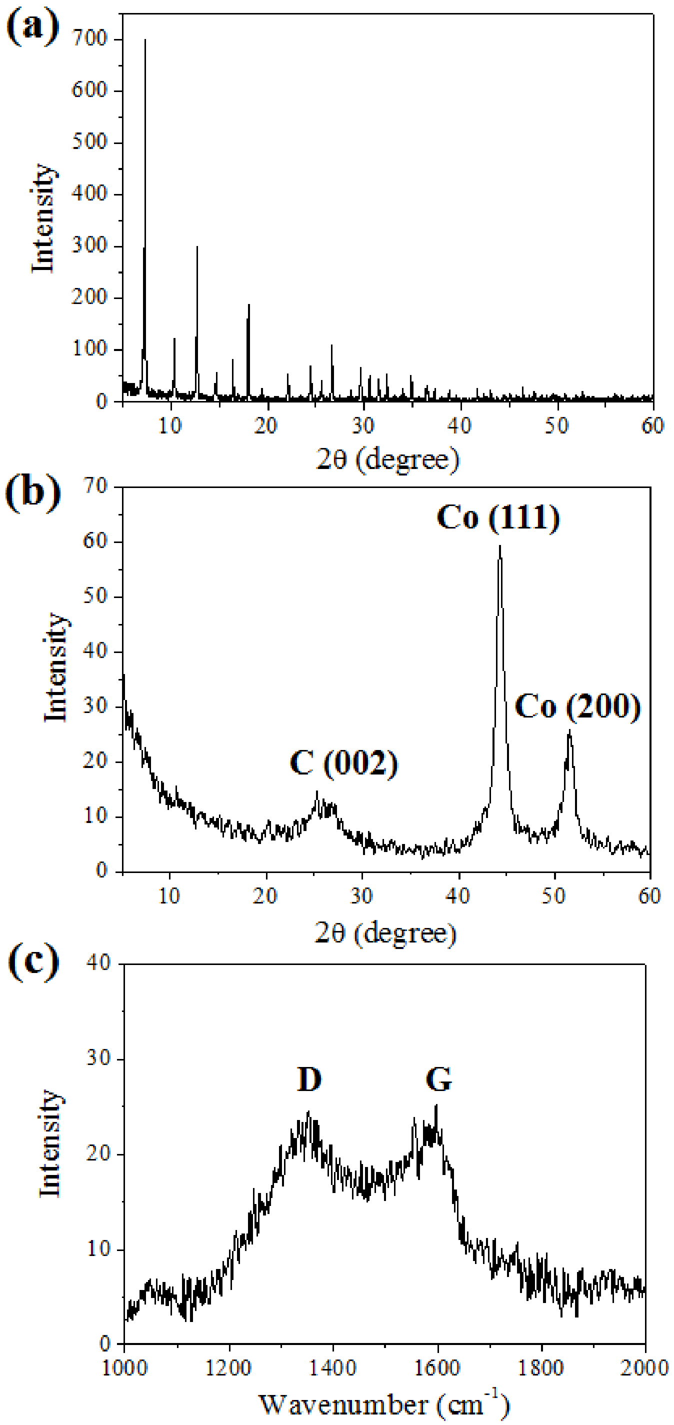

Figure S5. Wide-angle XRD patterns of (a) hybrid Co/Zn-ZIF and (b) hybrid Co/Zn-ZIF-derived carbon. (c) Raman spectrum of hybrid Co/Zn-ZIF-derived carbon (intensity ratio for D and G bands, $I_D/I_G = 0.87$).

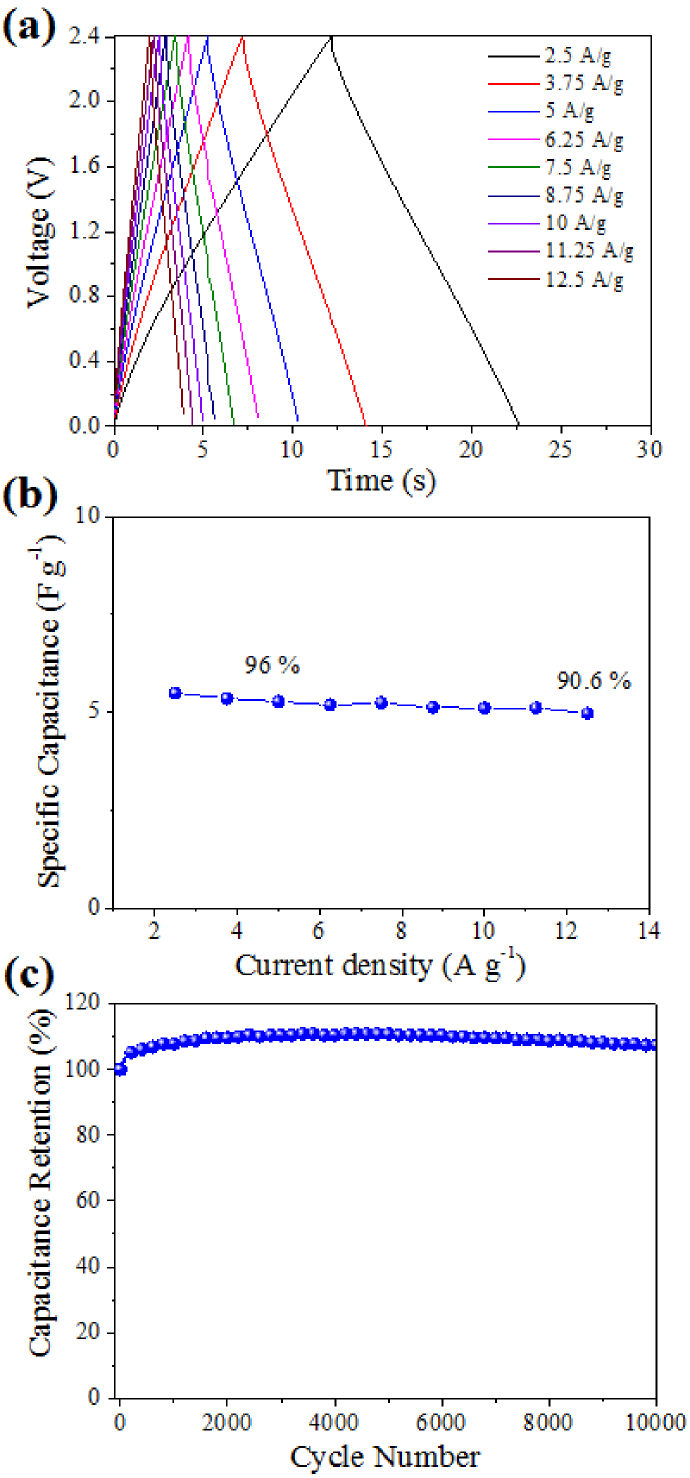

Figure S6. (a) Galvanostatic charge-discharge curves, (b) specific capacitance of device at different current densities, and (c) life cycle test of coin cells using organic electrolyte consisting of 1.0 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) in acetonitrile.