Electronic Supplementary Information

ZnO quantum dots-decorated carbon nanofibers derived from electrospun ZIF-8/PVA nanofibers for high-performance energy storage electrodes

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Experimental details

Materials: $Zn(NO_3)_2 \cdot 6H_2O$, 2-methylimidazole (Hmim), poly(vinyl alcohol) (PVA, MW=85000–124000), and polyacrylonitrile (PAN, MW=150000) were purchased from Sigma-Aldrich. All of chemicals were used as received without further purification. Deionized (DI) water was used in all experiment.

Synthesis of ZIF-8 nanocrystals: ZIF-8 nanocrystals were synthesized in aqueous system according to the previous report with a minor modification.[s1] In a typical synthesis, Hmim (22.7 g) was dissolved in DI water (80 ml) with constant stirring. Subsequently, $Zn(NO_3)_2 \cdot 6H_2O$ (1.17 g) in DI water (8 ml) was rapidly poured into the above solution with stirring for another 5 min. Finally, the white powders were collected by centrifugation and washed with DI water several times. As-prepared ZIF-8 nanocrystals were dried at 60 °C under vacuum before the characterization.

Preparation of ZPCNF: ZnO quantum dots-decorated carbon nanofibers (ZPCNFs) were fabricated by carbonization of electrospun ZIF-8/PVA nanofibers. The precursor solutions were prepared by dispersing a given amount of ZIF-8 (2 or 4 wt% of total solution) in a 8 wt% PVA aqueous solution. The electrospinning process was carried out by feeding the above solution through a metallic needle at the rate of 0.36 ml h^{-1}. The needle was placed at a distance of 12 cm from the collector and a high voltage (10 kV) was applied. Subsequently, the resulting ZIF-8/PVA nanofiber mat was carefully peeled off from the collector and transfered to a tube furnace. They were first stabilized in air at 180 °C for 12 h and then carbonized in N_2 atmosphere at 650 °C for 3 h. The carbonized samples were named ZPCNF-2 and ZPCNF-4, respectively, depending on the amount of ZIF-8 used (2 or 4 wt% in precursor solution). Pristine ZIF-8 nanocrystals and PVA nanofibers were carbonized by the same method above to prepare carbonized ZIF-8 nanocrystals (ZIF-8-Cs) and PVA-based carbon nanofibers (PCNFs), respectively, as control samples for comparison.

Preparation of ZIF-8/PAN-C: ZIF-8/PAN-C was prepared by carbonization of electrospun ZIF-8/PAN nanofibers. Electrospinning solution was prepared by dispersing a given amount of ZIF-8 (5 wt% of total solution) in a 10 wt% PAN solution in DMF. The electrospinning process was performed by feeding the precursor solution with injection speed of 0.6 ml h^{-1}. The distance and applied voltage between the needle and the collector were fixed at 12 cm and 10 kV, repectively. Subsequently, the collected fiber mat was stabilized in air at 270 °C for 1 h and carbonized in N_2 atmosphere at 650 °C for 3 h. ZIF-8/PAN-C was fabricated as a control sample to compare the structural properties with ZPCNF.

Characterization: Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were obtained with a JSM-6701F (JEOL) and a JEM-2100 (JEOL), respectively. High-resolution TEM (HR-TEM) images and selected area electron diffraction (SAED) micrographs were acquired with a JEM-3010 (JEOL). Elemental mapping of ZPCNF was conducted by scanning TEM (STEM) mode of Tecnai F20 (FEI). X-ray photoelectron spectroscopy (XPS) was performed with a Sigma probe (VG Scientific) installed at the National Center for Inter-university Research Facilities (NCIRF) at Seoul National University. Raman spectra were recorded with a LabRAM HV Evolution spectrometer (HORIBA) using a laser of wavelength 532 nm. X-ray diffraction (XRD) spectra were obtained with a New D8 Advance (Bruker) at 40 kV and 30 mA (Cu-Kα radiation, λ=0.15418 nm). Thermogravimetric analysis (TGA) was carried out using Pyris 6 thermogravimetric analyzer (PerkinElmer) under ambient condition with a heating rate of 10 °C min^{-1}. N_2 adsorption and desorption isotherms were measured using a ASAP 2000 surface area measurement analyzer (Micromeritics) at liquid nitrogen temperature. The specific surface area and pore distribution of the samples were acquired by applying the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method, repectively. The electrical conductivities of the samples were investigated by four-probe method using a KEITHLY 2400 (KEITHLY). The shear viscosities of sample solutions were examined as a function of the shear rate ranging from 0.01 to 400 s^{-1} using AR2000 Advanced Rheometer (TA Instruments).

Electrochemical measurements: All the electrochemical measurements were conducted on a three electrode system using platinum wire as the counter electrode and Ag/AgCl as the reference electrode in 1 M Na_2SO_4 electrolyte solution. To prepare the working electrode, as-prepared active materials (1.0 mg) were mixed with polyvinylidene fluoride (PVDF) binder (0.1 mg) in N-methyl-2-pyrrolidone (NMP) solvent, resulting in a homogeneous paste. The resulting paste was subsequently coated onto the stainless-steel mesh, followed by drying in an oven at 80 °C before the measurements. The cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) tests were examined with a WBCS 3000 (Wonatech) at various scan rates and current densities between –1.0 and 0 V. The electrochemical impedance spectroscopy (EIS) measurements were conducted using a ZIVE SP2 (Wonatech) with an AC voltage of 10 mV amplitude in the frequency range from 100 kHz to 10 mHz. ZMAN software was used to obtain significant parameters from the Nyquist plots.

S1. Y. Pan, Y. Liu, G. Zeng, L. Zhao and Z. Lai, *Chem. Commun.*, 2011, **47**, 2071.

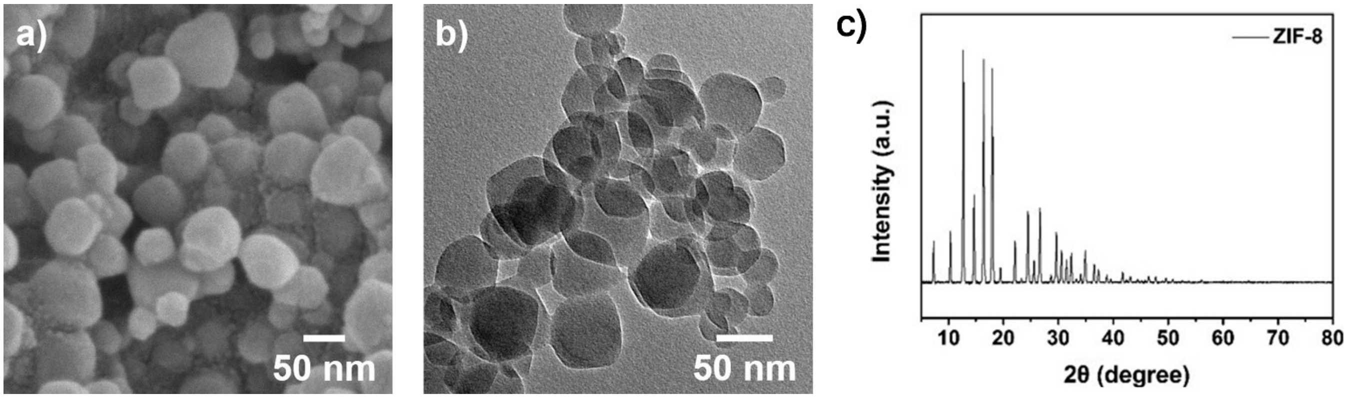

Fig. S1 (a) SEM image, (b) TEM image, and (c) XRD pattern of the synthesized ZIF-8 nanocrystals.

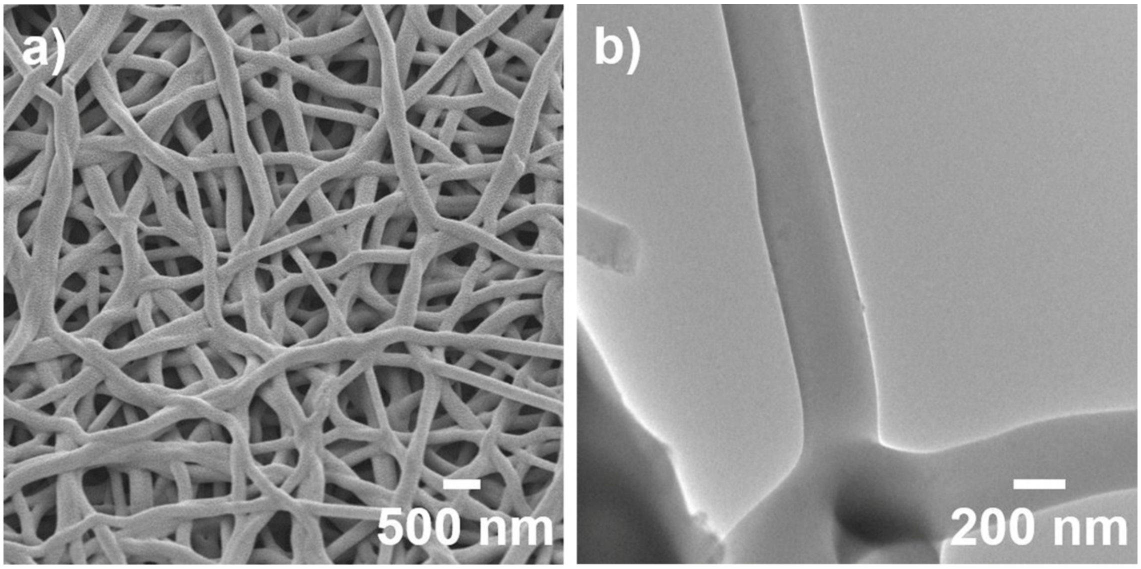

Fig. S2 (a) SEM image and (b) TEM image of PCNF.

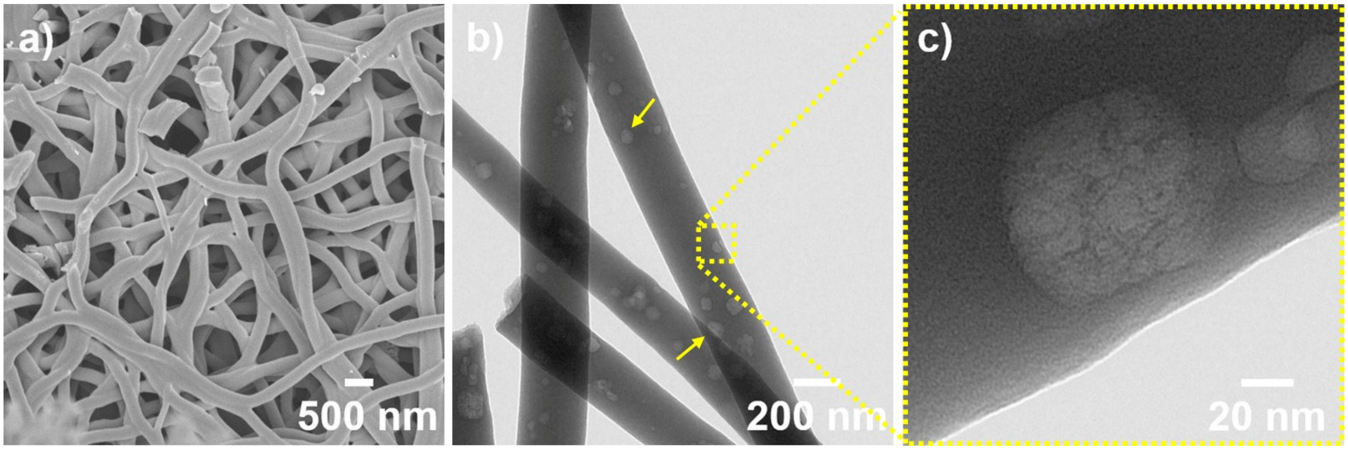

Fig. S3 (a) SEM image and (b and c) TEM images of ZPCNF-2.

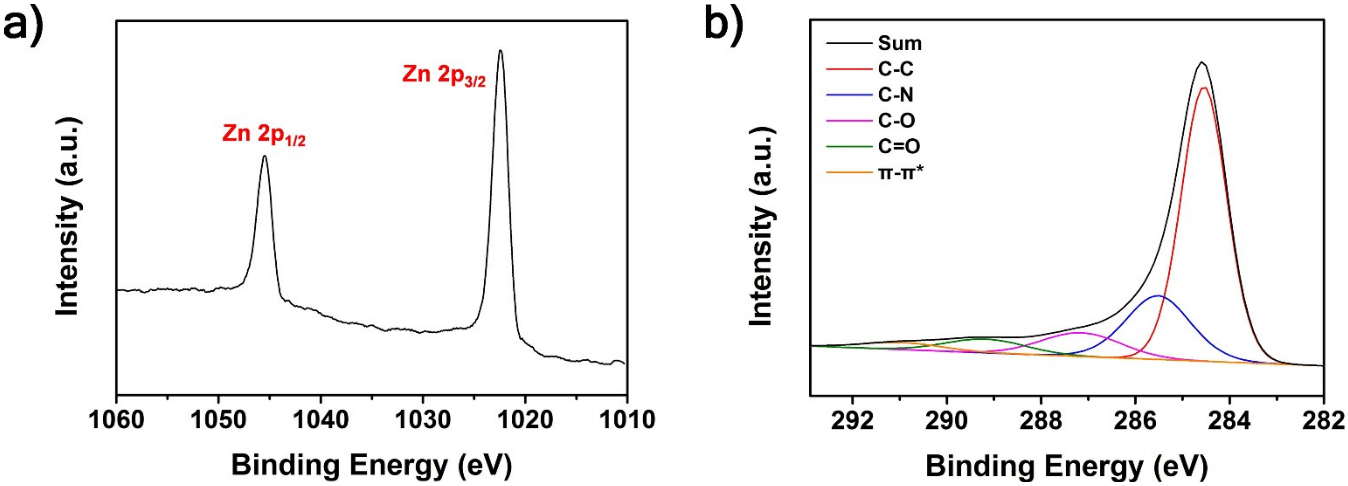

Fig. S4 (a) Zn 2p and (b) C 1s XPS spectra of ZPCNF-4.

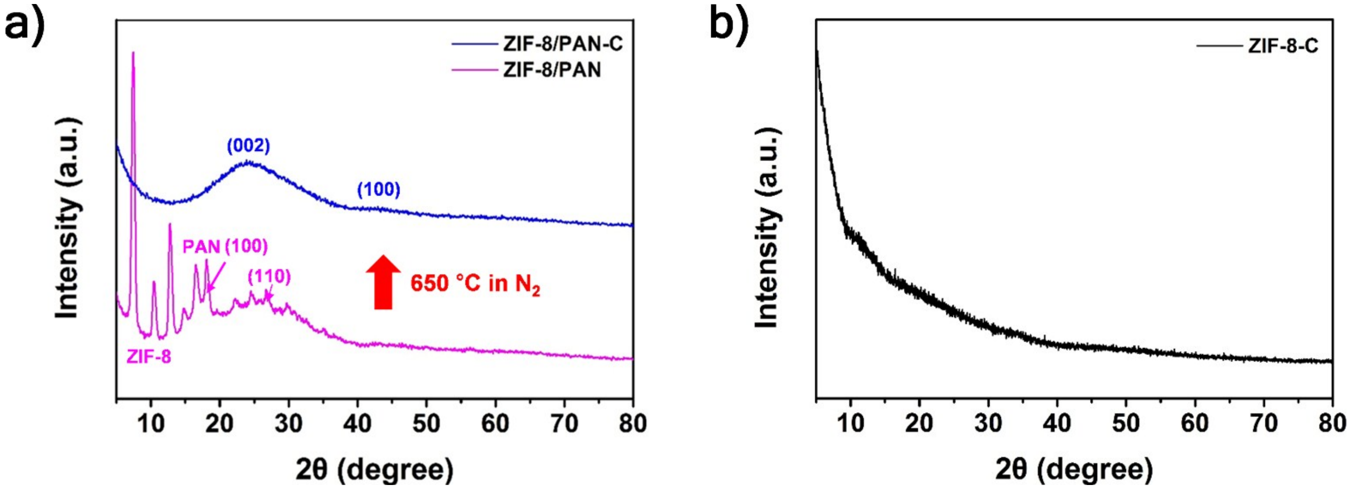

Fig. S5 (a) XRD patterns of ZIF-8/PAN nanofiber and ZIF-8/PAN-C. (b) XRD pattern of ZIF-8-C.

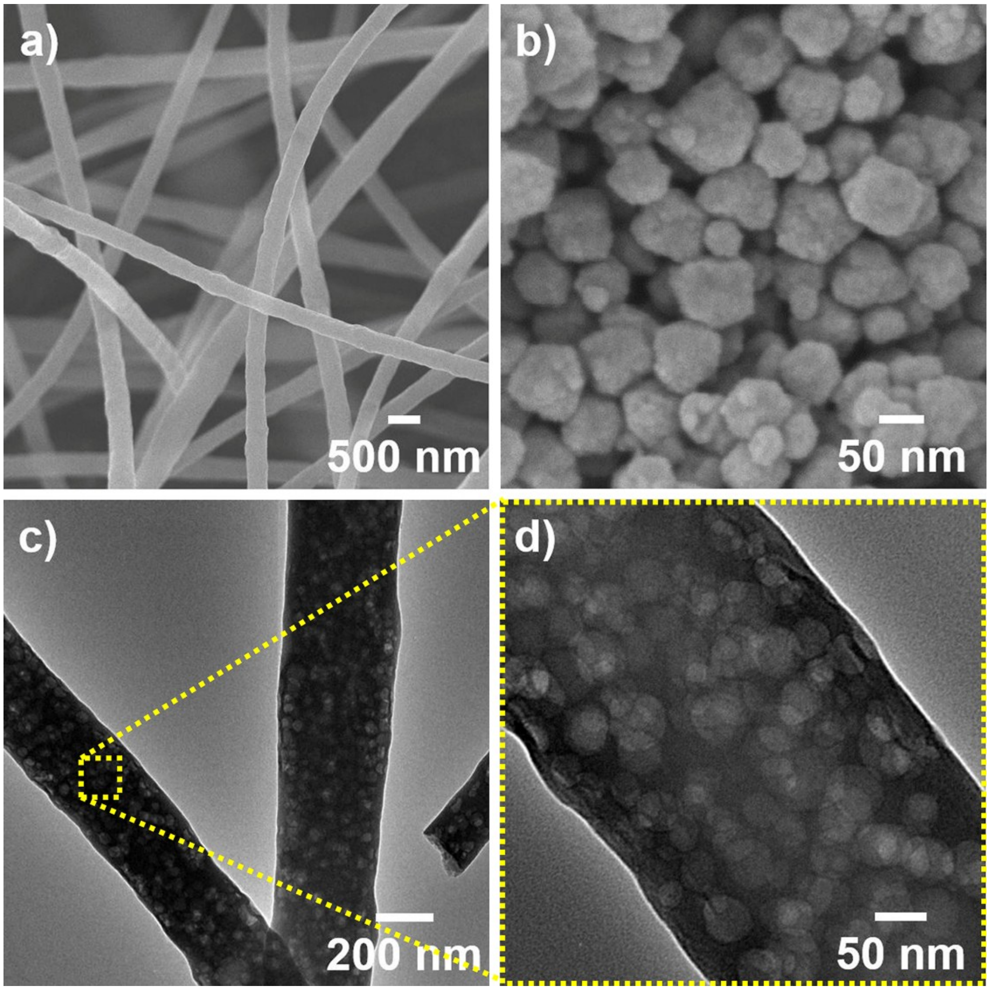

Fig. S6 (a) SEM image of ZIF-8/PAN-C, (b) SEM image of ZIF-8-C, and (c and d) TEM images of ZIF-8/PAN-C.

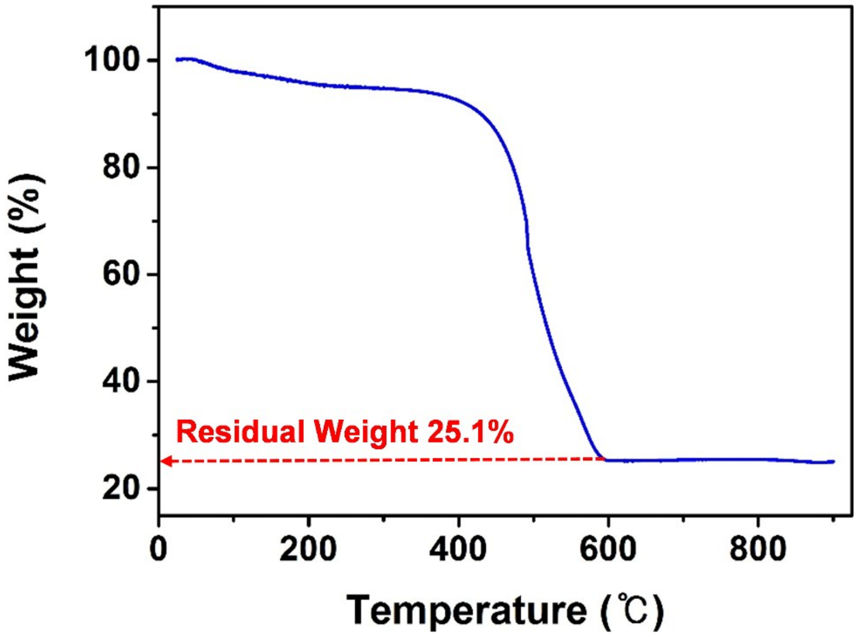

Fig. S7 TGA thermogram of ZPCNF-4 at air atmosphere.

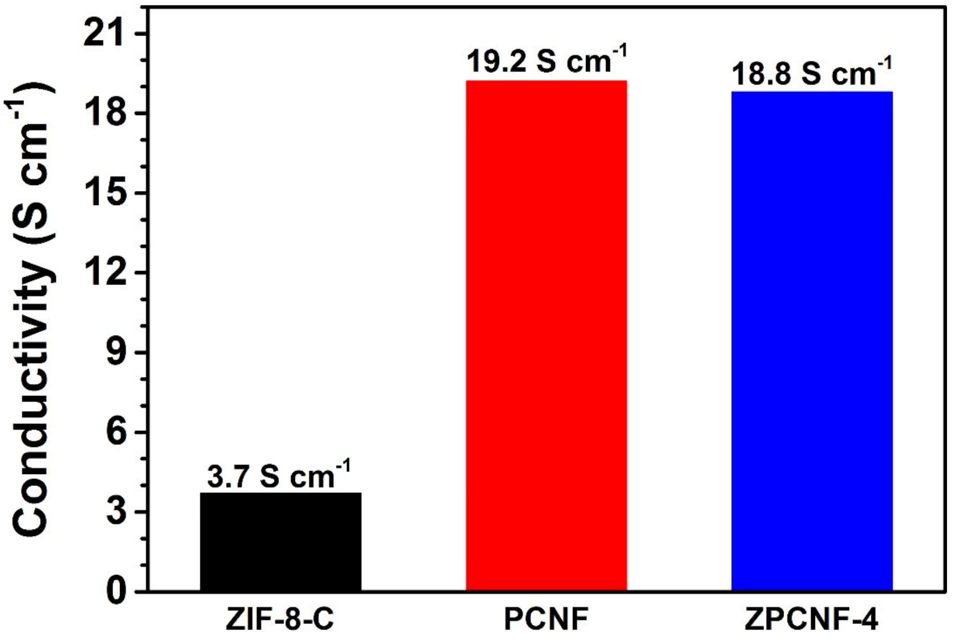

Fig. S8 Electrical conductivities of ZIF-8-C, PCNF, and ZPCNF-4.

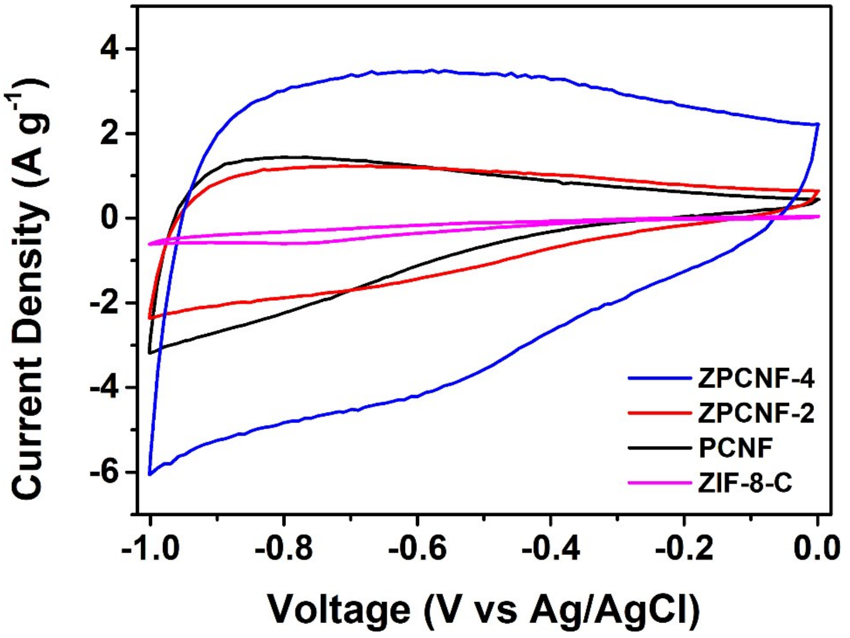

Fig. S9 CV curves of ZIF-8-C, PCNF, ZPCNF-2, and ZPCNF-4 at a scan rate of 10 mV s^{-1}.

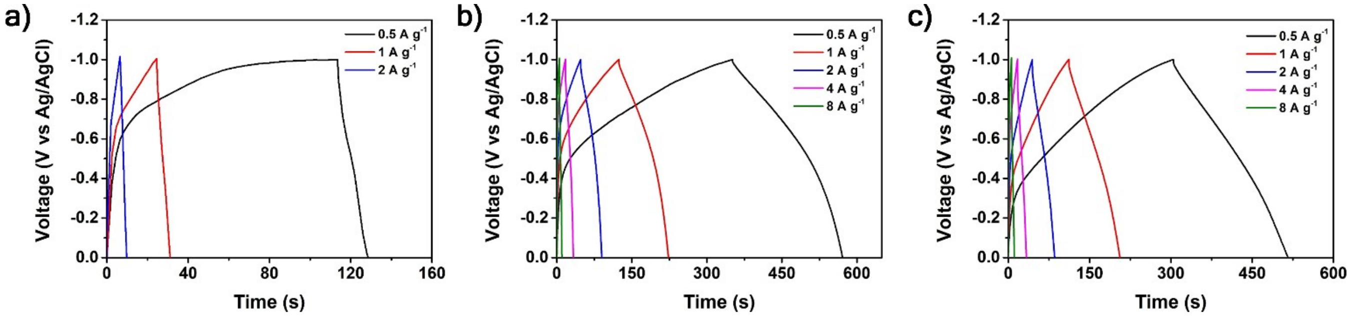

Fig. S10 GCD curves of (a) ZIF-8-C, (b) PCNF, and (c) ZPCNF-2 with different current densities.

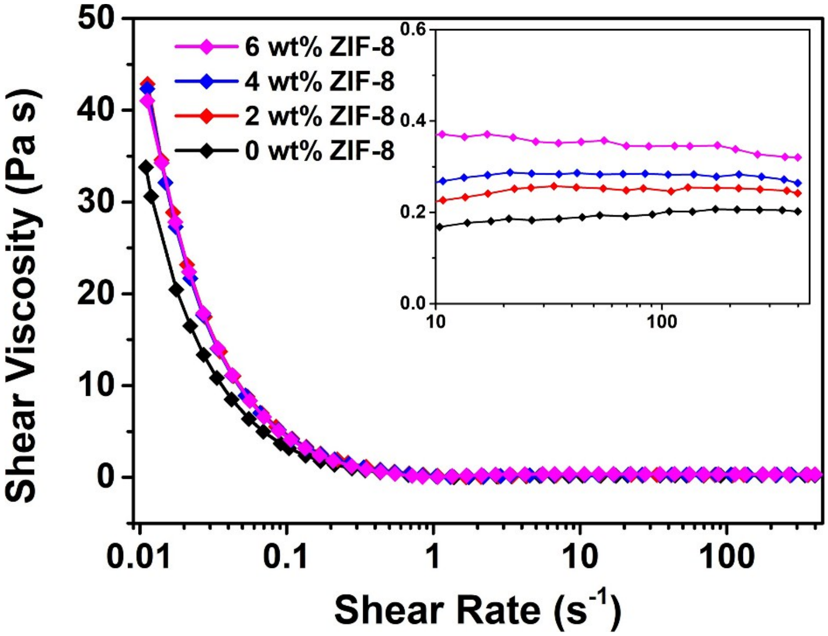

Fig. S11 Shear viscosity as a function of the shear rate for electrospinning solutions containing different amounts of ZIF-8 (inset: magnified data in the high shear rate range).