Supporting Information

Nitrogen-Doped Carbon Polyhedra Nanopapers: An Advanced Binder-Free Electrode for High-Performance Supercapacitors

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EXPERIMENTAL SECTION

Materials. 2-methylimidazole (MIM), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), methanol, hydrochloric acid (HCl, 37%), sulfuric acid (H_2SO_4, 98%), nitric acid (HNO_3, 68%), hydrogen peroxide (30 wt%), potassium permanganate ($KMnO_4$), potassium persulfate (KPS), phosphorus pentoxide (P_2O_5), potassium nitrate (KNO_3), *N,N*-dimethylformamide (DMF), *N*-methyl pyrrolidone (NMP), ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd. The graphite (325 meshes) was obtained from Alfa-Aesar. All these chemicals were used as received without further purification unless specified.

Preparation of ZIF8. 10 mmol 2-methylimidazole was dissolved in methanol (100 mL) to form solution A, and 4 mmol $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in another 100 mL methanol to form solution B. The above two solutions were mixed under continuous stirring for 10 s, and the mixed solution was kept for 20 h at room temperature. The white precipitate was collected by centrifugation at 10000 rpm, washed with methanol for several times, and dried at 80 °C in vacuum.

Preparation of NC. ZIF8 powder was dispersed in a ceramic boat and then heated to 900 °C at a heating rate of 2 °C min^{-1} under a Ar (100 sccm) atmosphere. The sample was kept at 900 °C for another 2 h before cooled down to room temperature naturally. The obtained black powder was treated with a 2 M HNO_3 solution for 6 h. The resulting products were collected by centrifugation, and repeatedly washed with DI water before being dried at 80 °C to obtain the NC.

Preparation of NC/rGO nanopaper. Graphene oxide (GO) was synthesized

according to a modified Hummers' method. A certain amount of NC powder was added into 7.5 mL DMF and sonicated for 30 min to form dispersion A. The dispersion A was added into 7.5 mL GO dispersion in DMF (2 mg mL^{-1}) to form dispersion B with another sonication for 60 min. The dispersion B was filtrated on a nylon filter and naturally dried in air, resulting in the NC/GO nanopaper, which can be easily peeled off from the filter. The NC/GO nanopaper was then thermally reduced to the NC/rGO nanopaper at 500 °C under a Ar atmosphere. The NC/rGO-1, NC/rGO-2 and NC/rGO-3 were prepared by adding 5, 10 and 15 mg NC, respectively. The rGO nanopaper was prepared by the same method without the addition of NC.

Characterization. Transmission electron microscopy (TEM) characterization was conducted on a Tecnai G2 20 TWIN TEM instrument under an accelerating voltage of 200 kV. Field emission scanning electron microscopy (FESEM) observation was performed by a Zeiss Ultra 55 FESEM instrument at an accelerating voltage of 5 kV. X-ray diffraction (XRD) measurements were carried out using a PANalytical X'pert PRO XRD with Cu K_α radiation (operating voltage, 40 kV; cathode current, 40 mA; λ = 0.1542 nm; scan rate, 5 ° min^{-1}). X-ray photoelectron spectroscopy (XPS) spectra were collected by a VG ESCALAB 220I-XL device. The specific surface area and pore size distributions of the samples were characterized with a belsorp-max surface area detecting instrument (Quantachrome Instruments) by N_2 physisorption at 77 K.

Electrochemical measurements. The NC/rGO nanopaper was directly used as the working electrodes. The mass loadings of the NC/rGO-1, NC/rGO-2 and NC/rGO-3 are about 1.5, 2.2 and 2.9 mg cm^{-2}, respectively. Control sample NC was mixed with

carbon black (Super P), poly(vinylidene fluoride) (PVDF) binder at a weight ratio of 80:10:10 in a NMP solvent to form a slurry, followed by dring it on the graphite paper current collector. A two-electrode configeration was utilized by inserting a cellulose fiter paper as the separator between two working electrodes to assemble a symmetric supercapacitor. A 6 M KOH aqueous solution was used as the electrolyte. All the electrochemical mesaurements were conducted on a CHI 660D work station (Chenhua Instruments Co. Ltd., Shanghai). Cyclic voltammetry (CV) curves were carried out from 0 to 1.0 V at a sweep rate of 10 to 200 mV s^{-1}. Galvanostatic charge/discharge tests were performed with a voltage range from 0 to 1.0 V under a current density of 1 to 20 A g^{-1}. Eletrochemical impedance spectroscopy (EIS) was performed in the frequency range from 100 kHz to 0.01 Hz at an open circuit potential. The specific capacitance (C, F g^{-1}), energy density (E, W kg^{-1}) and power density (P, W h kg^{-1}) were calculated based on the following equations:

$$C = \frac{2I\Delta t}{m\Delta V} \quad (1)$$

$$E = \frac{1}{4}C\Delta V^2 \quad (2)$$

$$P = 3600 \times \frac{E}{\Delta t} \quad (3)$$

Where I is the discharge current (A), Δt is the discharge time (s), ΔV is the working voltage range (V) and m is the mass of active materials on each electrodes.

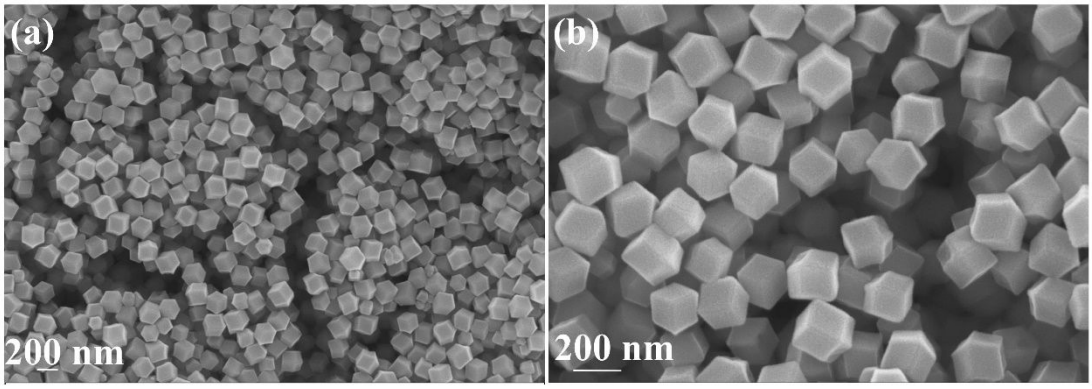

Figure S1. SEM images of ZIF-8 at (a) low and (b) high magnifications, respectively.

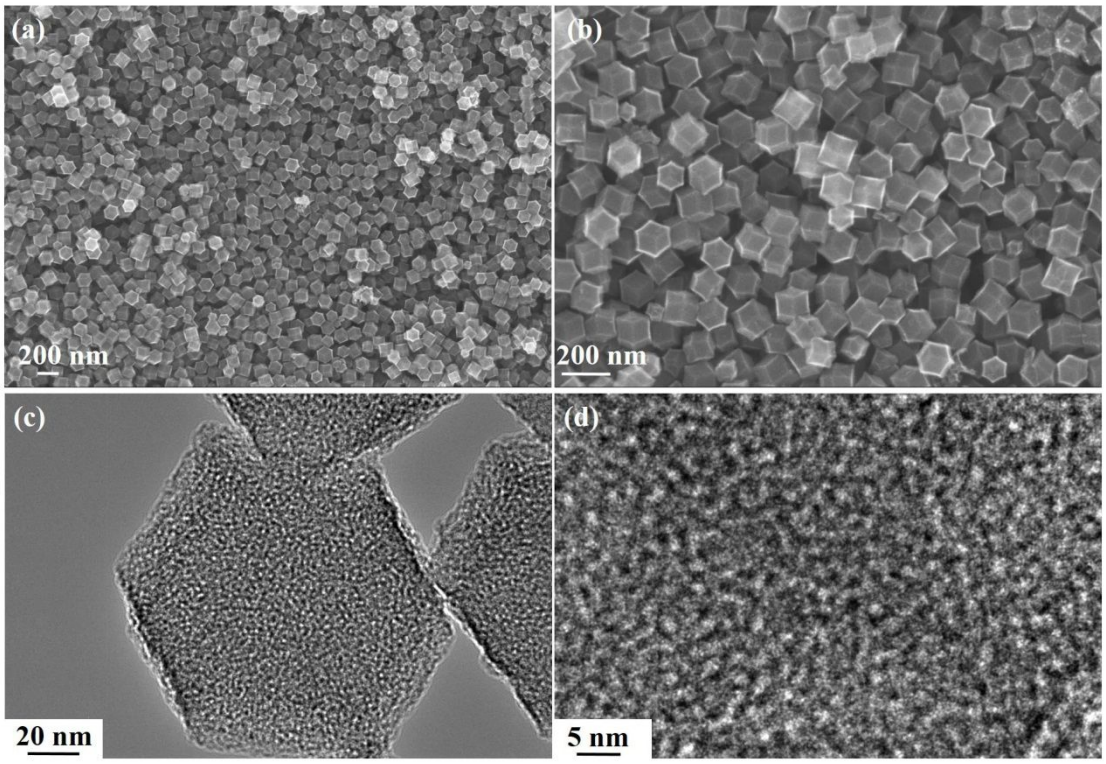

Figure S2. (a, b) SEM and (c, d) TEM images of the NC.

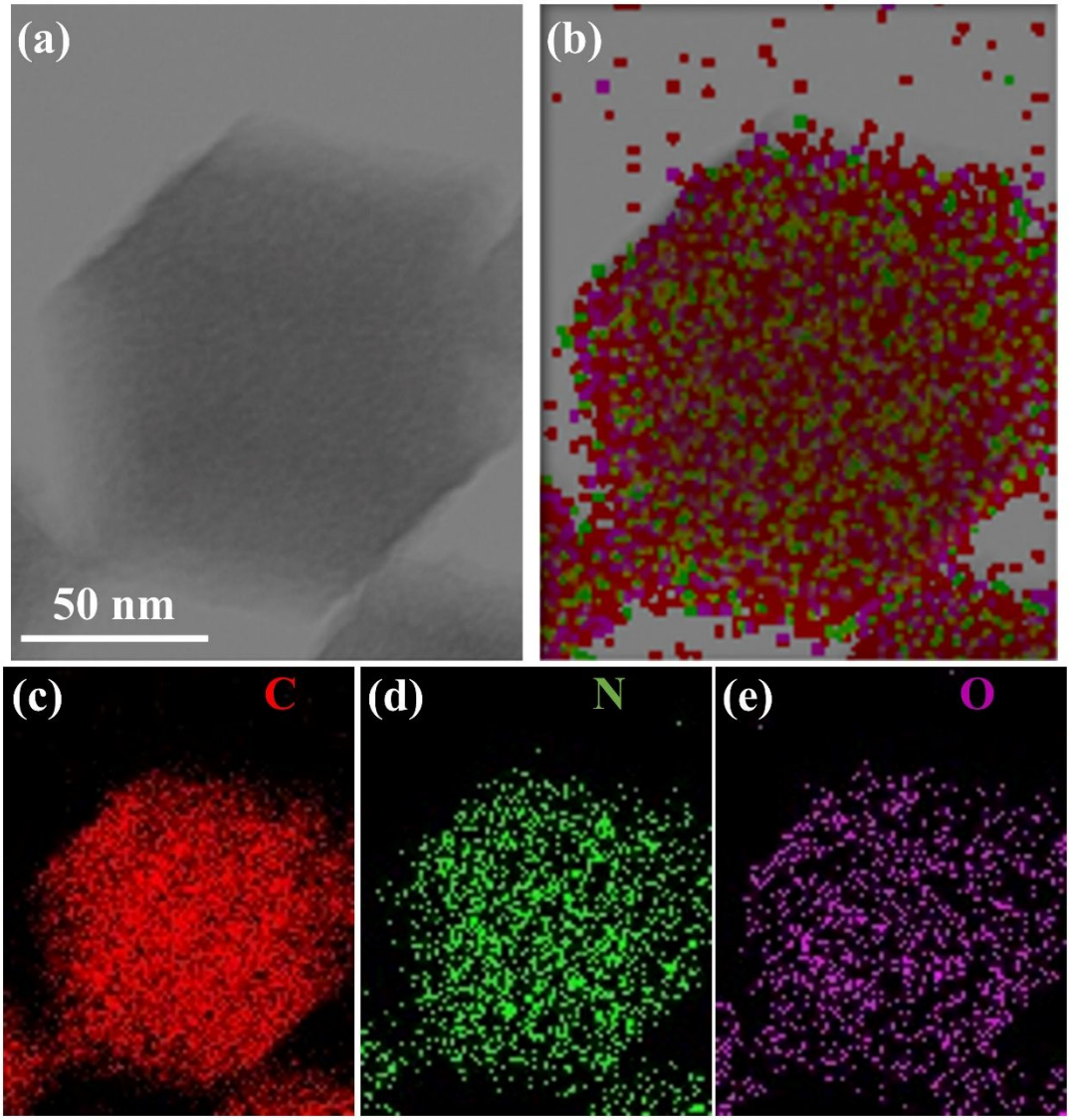

Figure S3. (a) STEM image and EDX elemental mappings of (b) overlapped, (c) C, (d) N and (e) O elements of the NC, respectively.

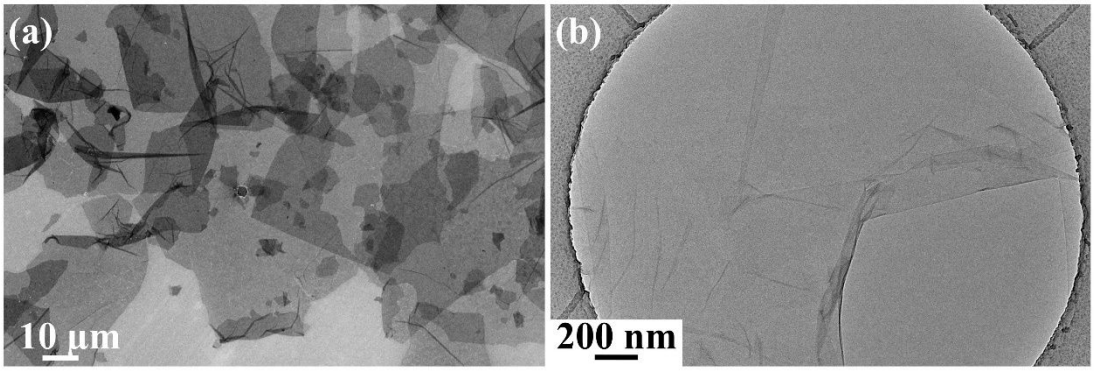

Figure S4. (a) SEM and (b) TEM images of GO.

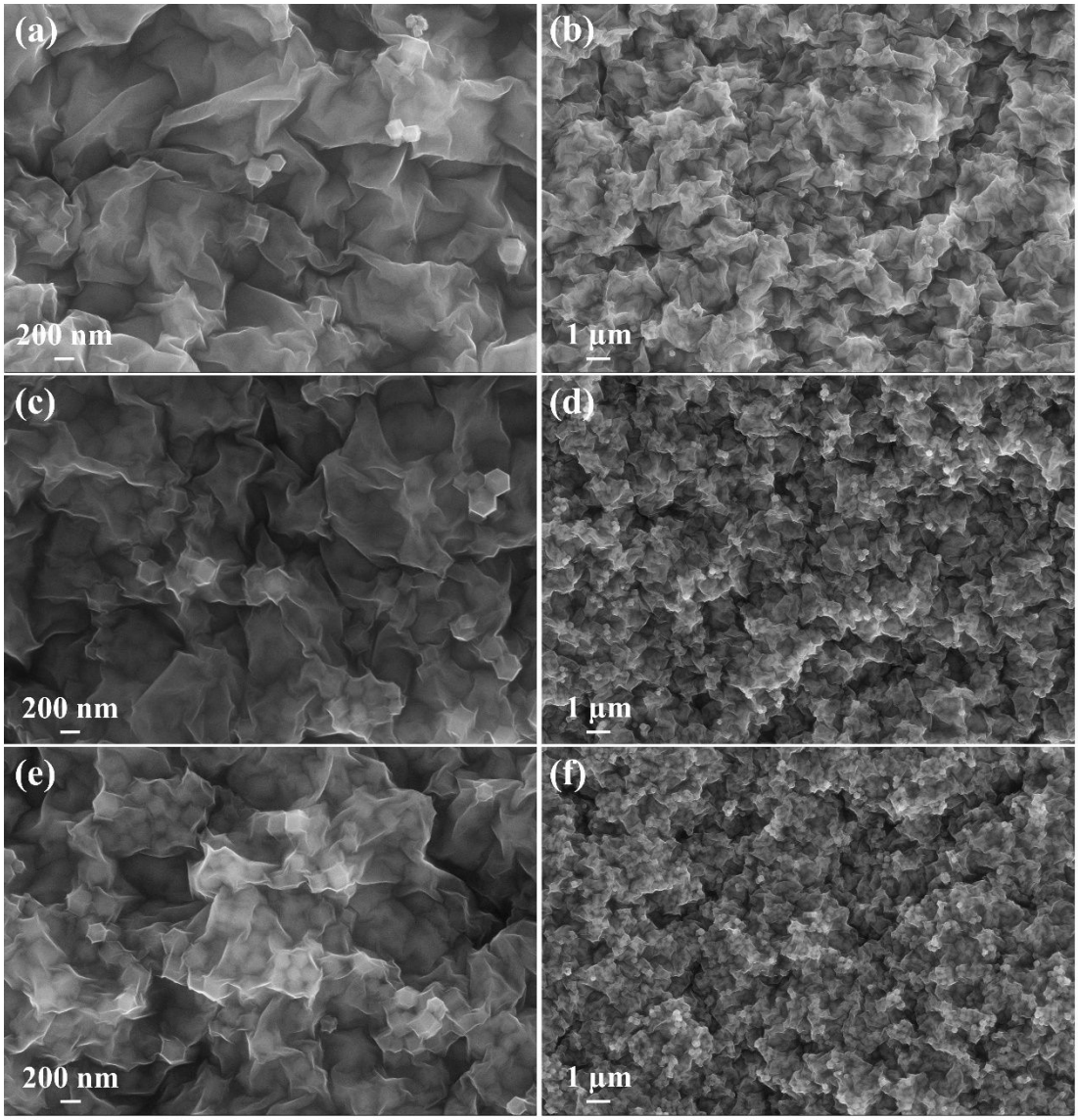

Figure S5. SEM images of the surfaces of (a, b) NC/rGO-1, (c, d) NC/rGO-2 and (e, f) NC/rGO-3 nanopapers.

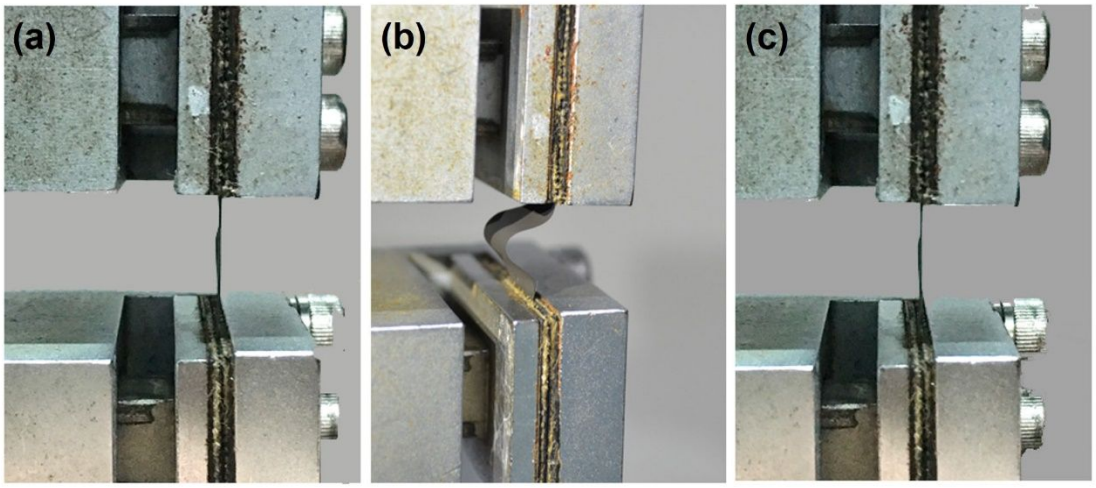

Figure S6. The NC/rGO-2 nanopaper under bending tests, showing its mechanical flexiblility under (a) Initial state, (b) bending state, (c) recovery state.

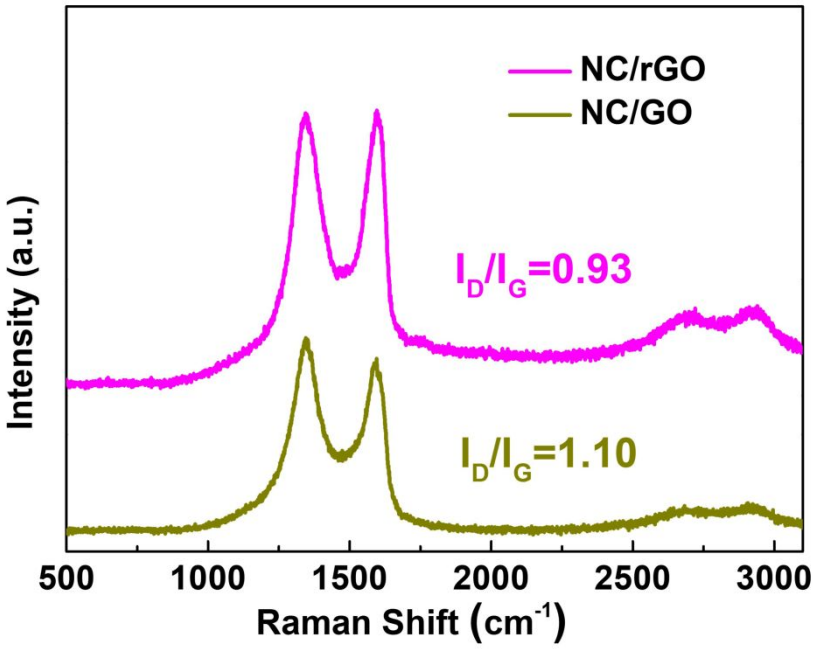

Figure S7. Raman spectra of NC/GO and NC/rGO.

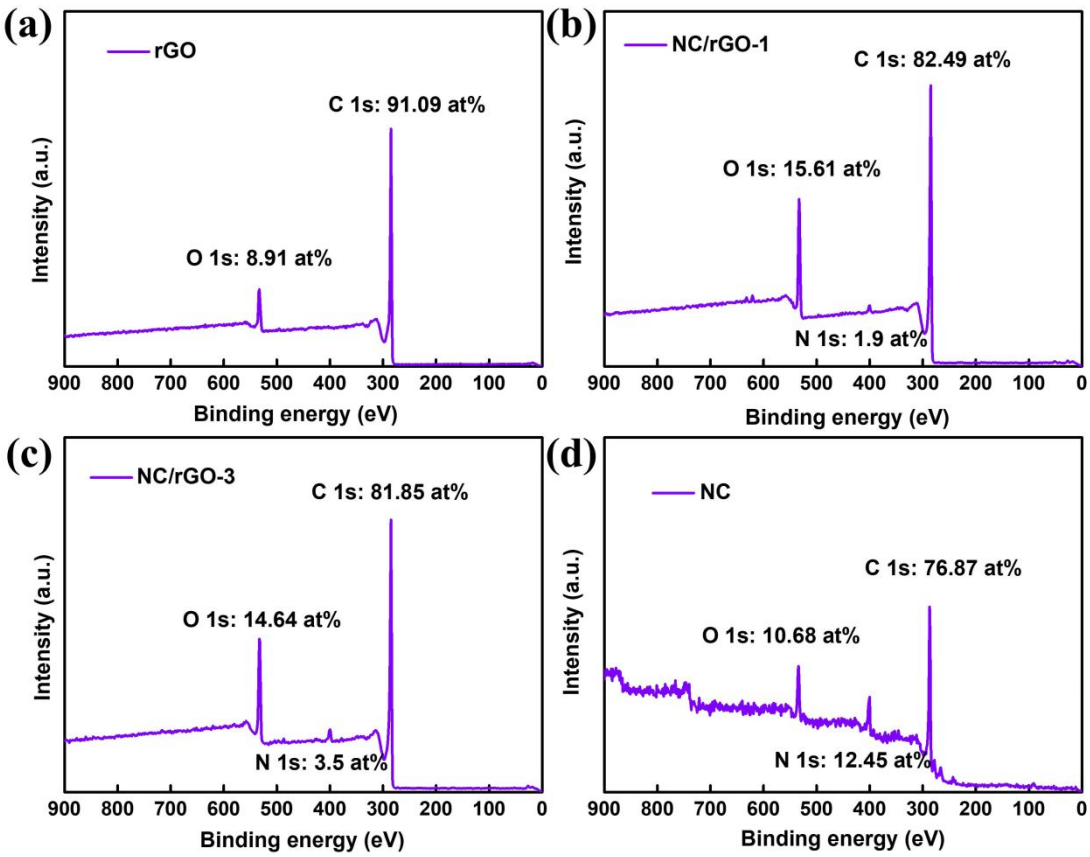

Figure S8. XPS spectra of (a) rGO, (b) NC/rGO-1, (c) NC/rGO-3 and (d) NC.

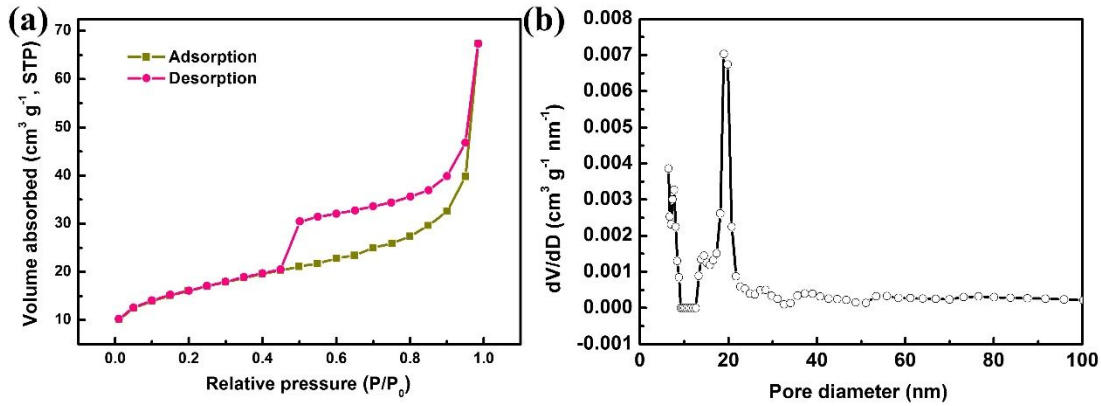

Figure S9. (a) Nitrogen adsorption/desorption isotherms and (b) pore size distribution of NC/rGO-2.

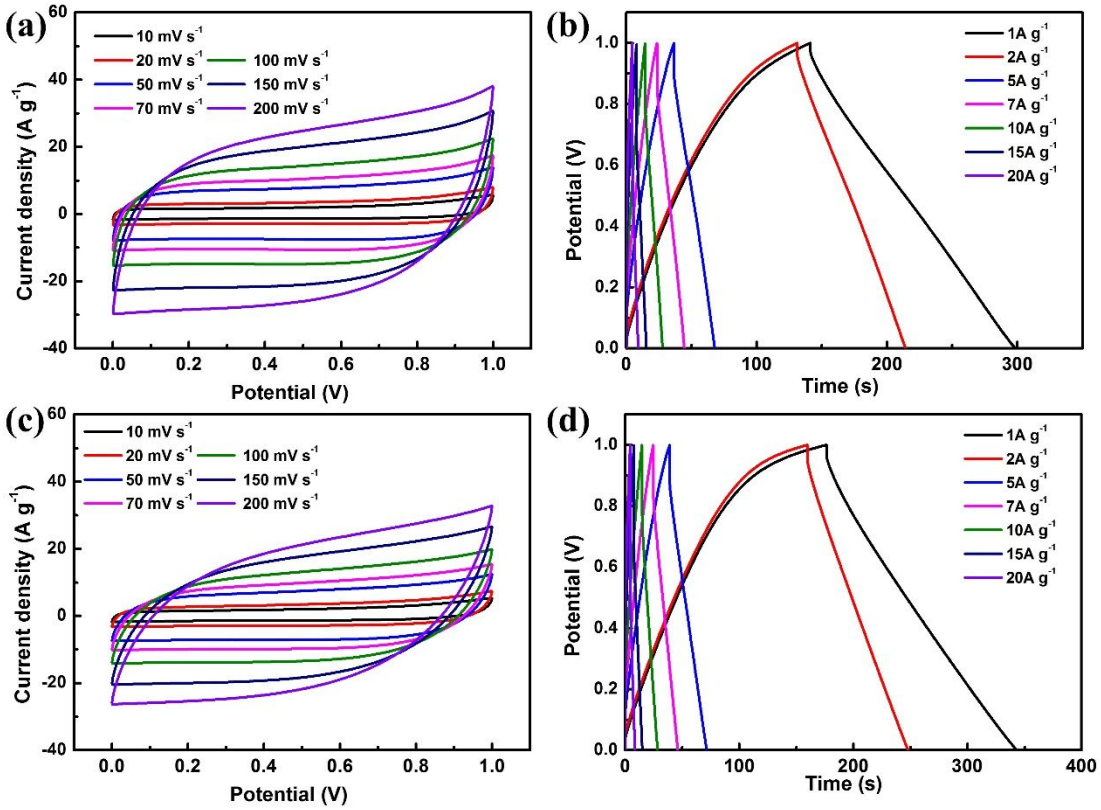

Figure S10. CV and galvanostatic charge/discharge curves of (a, b) NC/rGO-1 and (c, d) NC/rGO-3.

Table S1. BET Surface Areas and Pore Volumes of Related Samples

sample	S_{BET} [m^2 g^{-1}]	total pore volume [mL g^{-1}]	micropore volume [mL g^{-1}]	mesopore volume [mL g^{-1}]
NC	983.2	0.92	0.89	0.03
NC/rGO-1	400.3	0.59	0.22	0.37
NC/rGO-2	489.3	0.73	0.36	0.37
NC/rGO-3	289.5	0.55	0.32	0.23
rGO	17.1	0.01	~0	0.01