In-situ synthesis of europium oxide (Eu_2O_3) nanoparticles in heteroatom doped carbon nanofibers for boosting the cycle stability of the supercapacitors

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1. Experimental section

1.1. Materials

Polyacrylonitrile (PAN, Mw=150 000) and Europium (III) nitrate pentahydrate ($Eu(NO_3)_3 \cdot 5H_2O$) were obtained from Sigma Aldrich. Dimethylformamide (DMF) and Thiourea were purchased from Merck and Labshop41, respectively. All the analytical grade chemicals were used as received without further purification.

1.2. Structural characterization

X-ray powder diffractometer (XRD, PANalytical Empyrean). Samples were also characterized by Raman spectroscopy by employing WITech Alpha 300R with a wavelength of 532 nm. The constituent structures of the materials were characterized and analyzed by an x-ray electron spectrometer (XPS, a Thermo Scientific K-Alpha). The surface morphological structure of the sample materials was visualized using a scanning electron microscope (SEM, Zeiss Sigma 300) with its own energy spectrometer (EDS), a transmission electron microscope (TEM, Hitachi HT7700). N_2 adsorption/desorption isotherms were recorded at 77K (Micrometrics, TriStar II Surface Area and Porosity Analyzer), and the specific surface areas were calculated according to the Brunauer–Emmett–Teller (BET) method.

1.3. Symmetric supercapacitor (SSC) cell assembly and electrochemical measurements conducted in a two-electrode system

Electrochemical measurement was performed using GAMRY Reference 3000 for two-electrode systems. The electrochemical performances of the CNFs were evaluated by cyclic voltammetry (CV) and galvanic charge-discharge (GCD) techniques.

SC cell was assembled by compressing CR2032 button-type cells with an electrical battery closing machine. Two pieces of CNF electrodes (10 mm diameter) and a piece of Whatman separator (19 mm diameter) were cut. Then, they were placed into the button-type CR2032 cell as electrode/separator/electrode in 1 M H_2SO_4, respectively. The CV curves were obtained in the potential range of 0-1.2 V at several sweeping rates. A BST8-MA 8-channel battery analyzer (0.02-10 mA, 5V, MTI Corp.) device was used for GCD tests. The GCD tests were recorded in the potential range of 0-1.2 V at different current densities. 10 000 charge-discharge cycles were performed on SC cells, and the capacity, the specific energy, the

specific power, and the cycle stability of the supercapacitor cells were calculated with the Eqn 2 and 3. The electrochemical impedance spectroscopy (EIS) analysis was implemented in the frequency range of 0.01 Hz-100 kHz. The specific capacitance for the single electrode (C_{sp}) was calculated via Eq. (2).

$$\mathbf{C_{sp} = 2I\times \Delta t / (M \Delta V)} \qquad \mathbf{(1)}$$

where I is the discharge current, Δt is the discharge time, M is a mass of the active materials of working electrodes, and ΔV is the voltage range.

$$\mathbf{E = C_{sp} \Delta V^2 / (8\ X3.6)} \qquad \mathbf{(2)}$$

$$\mathbf{P = 3600 \times E / \Delta t} \qquad \mathbf{(3)}$$

where P and E are the specific power (W/kg) and specific energy (Wh/kg), respectively.

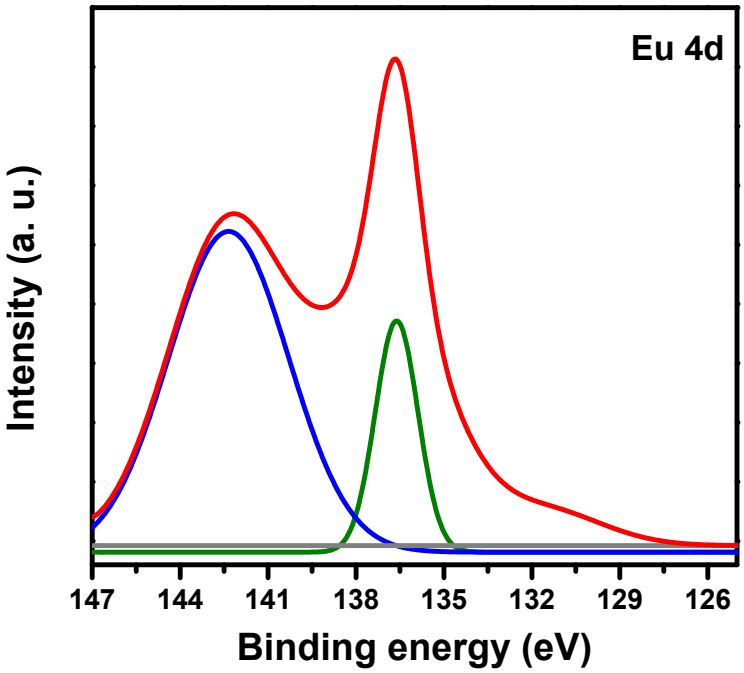

Fig. S1. XPS spectra of Eu 4d of the CNF/Eu_2O_3-1.

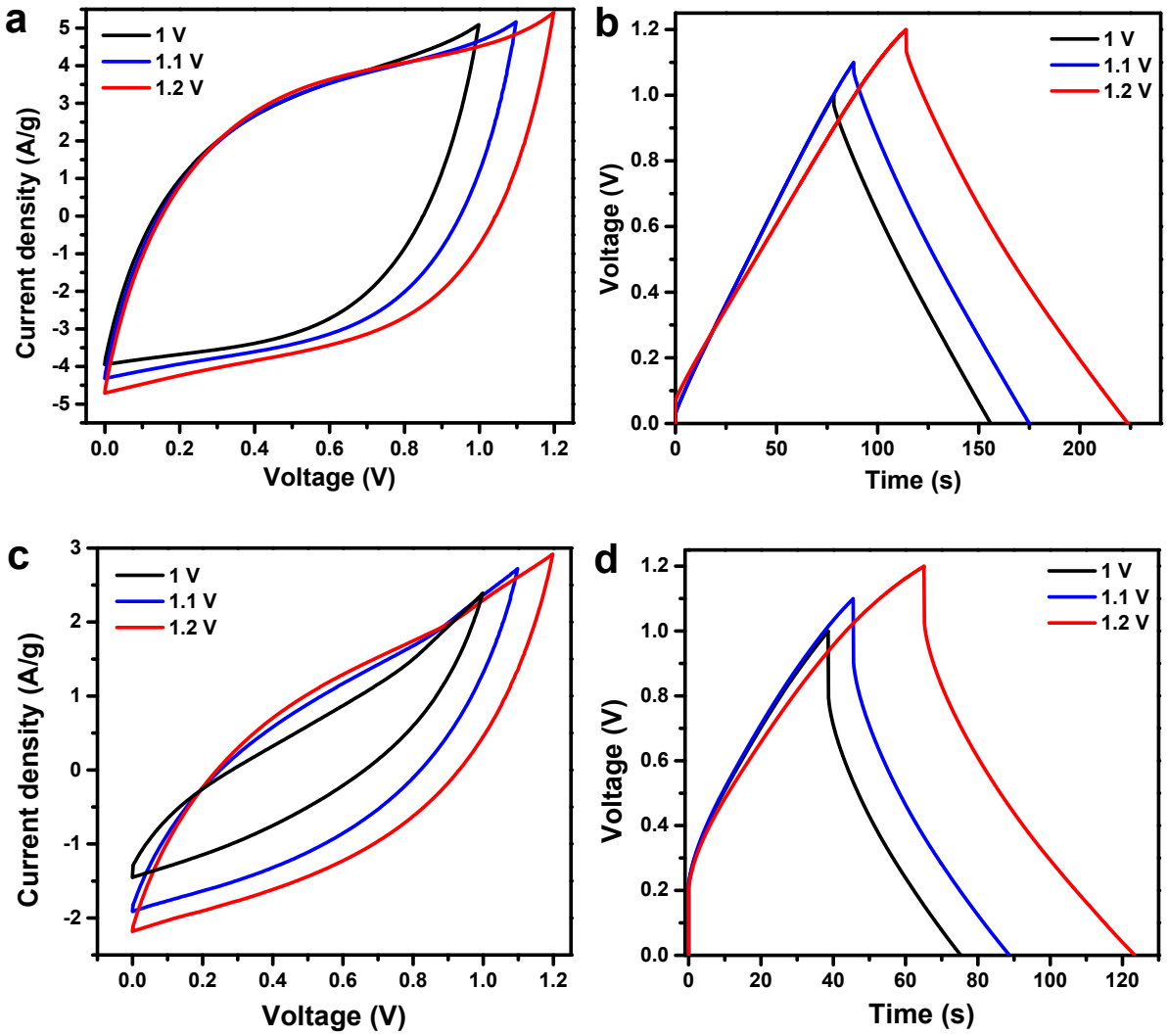

Fig. S2. (a, c) CV curves at 50 mV/s and **(b, d)** GCD curves at 1 A/g of the CNF/Eu_2O_3-1 and CNF/Eu_2O_3-2 for different voltages, respectively,

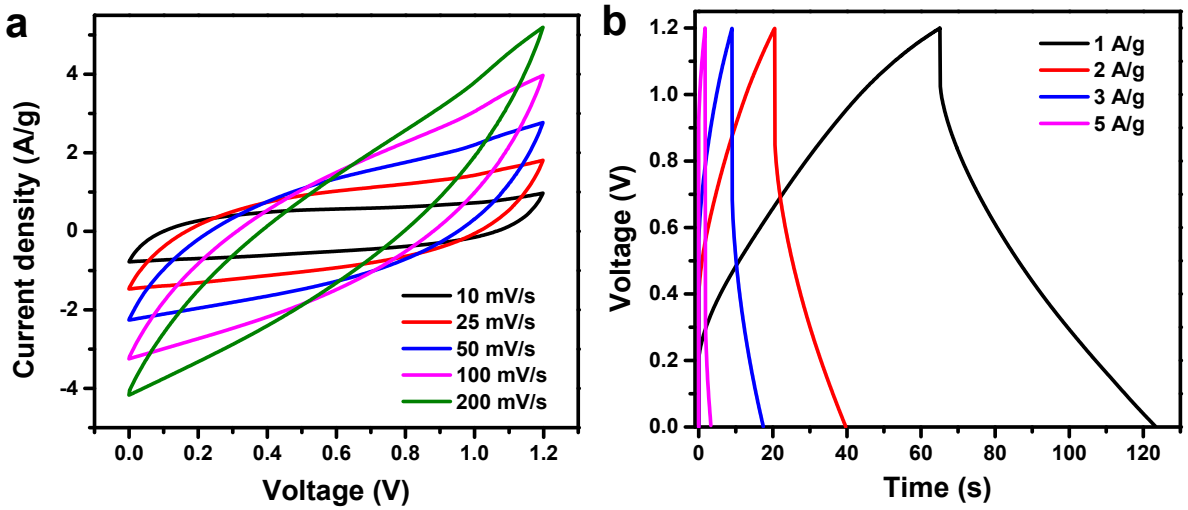

Fig. S3. (a) CV curves at different scan rates and **(b)** GCD curves at different current densities of the CNF/Eu_2O_3-2.

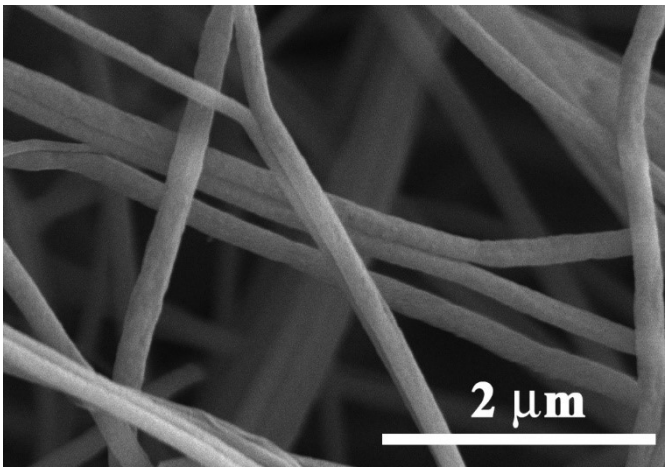

Fig. S4. SEM analysis was performed after 10 000 GCD cycles of CNF/Eu_2O_3-1.