

Supporting information

Multi-hierarchical Structure of Hybridized Phosphates Anchored on Reduced Graphene Oxide for High Power Hybrid Energy Storage Devices

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Experimental materials

Reagents cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), graphene oxide (GO) colloid (2 mg/mL), ammonium phosphate ($(\text{NH}_4)_2\text{HPO}_4$), ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$) (2 M), potassium hydroxide (KOH) (6 M), polytetrafluoroethylene (PTFE, 1 wt. % water suspension), and absolute ethanol are commercially available with analytical grade. All stock solutions used in this work were prepared with deionized water.

Synthesis of $(\text{Ni},\text{Co})(\text{OH})_2/\text{GO}$ nanocomposites precursor

The cobalt nickel hydroxide/GO $(\text{Ni},\text{Co})(\text{OH})_2/\text{GO}$ nanocomposites were prepared through a simple hydrothermal method. Firstly, 0.432 mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.432 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 35 mL of deionized water, magnetic stirred for fifteen minutes to obtain a light pink solution, then 25 mL GO colloid (2 mg/mL) was added and vigorous ultrasonic stirring for 1h. After this 2 mL ammonia solution (2 mol/L) was dropwise added. The mixed solution was kept at 120°C for 4 h in a Teflon lined autoclave, and then cooled down naturally to room temperature. The dark solid was collected by centrifugation and thoroughly washed with deionized water and ethanol.

Characterizations

Powder X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (Rigaku, $\lambda = 1.5418 \text{ \AA}$). Field emission scanning electron microscopy (FESEM) images were taken with a Hitachi SU-8030 field emission scanning electron microscope at the acceleration voltage of 15 kV, and further confirmed on transmission electron microscopy (TEM) equipped with SAED (Hitachi-7650, 100 kV 10 μA).

Electrochemical measurement

For electrochemical measurements, the working electrode was prepared by mixing the products of NCNP/RGO, acetylene black, and polytetrafluoroethylene (PTFE, 1 wt. % water suspension) binder with a weight ratio of 85:10:5. The slurry was pressed onto a nickel foam current collector, vacuum drying 12 h at 70°C. Each electrode contained about 3.0 mg of electroactive materials with geometric surface area of about 1 cm^2 . A platinum plate and Hg/HgO (1 M KOH) electrode were used as the

counter and reference electrodes, respectively. Cyclic voltammetry (CV) and the electrochemical impedance spectra (EIS) were tested on a CHI660C electrochemical workstation (Chenhua, China) in 6 M KOH electrolyte. Current charge-discharge test was performed on a LAND battery program-control test system (Land, CT2001A, China).

The electrode capacitance (C) was calculated from the following equation:

$$C = \frac{I}{m \frac{dV}{dt}} \quad (\text{eq.1}), \text{ where } I (\text{A cm}^{-2}) \text{ is the discharge current, } m (\text{g cm}^{-2}) \text{ is the mass of}$$

active materials, and $(dV)/(dt)$ (V s^{-1}) is the gradient of discharge curves. The power density (P) and the energy density (E) of HC corresponds the two electrodes were

calculated from the equations: $P = E/\Delta t$ (eq.2) and $E = \frac{1}{2} C \cdot (\Delta V)^2$ (eq.3), respectively,

where ΔV (V) is the potential window of discharge curve, Δt is the discharge time consumed in the potential range of ΔV .

Hybrid Device Fabrication

The hybrid device (NCNP/RGO//HPC) is constructed with appropriate amount of hierarchical porous carbon (HPC) as the negative electrode, the as prepared NCNP/RGO composites as the positive electrode, glass fiber membrane as a septum and 6 M KOH as the electrolyte. Balancing the charges stored at the positive electrode (ΔQ_+) and the negative electrode (ΔQ_-) to build a HC with a high operating voltage and high energy density is very important. Following the relationship of $\Delta Q_+ = \Delta Q_-$, the mass ratio of positive and negative electrodes (m_+/m_-), can be calculated by equation $m_+/m_- = C_- \cdot \Delta E_- / C_+ \cdot \Delta E_+$, where C_+ and C_- represent the specific capacitance values of the positive and negative electrodes, respectively, and ΔE is the potential range. Based on this the loading amount of positive and negative active materials are 1.6 mg cm^{-2} and 4.0 mg cm^{-2} , respectively, with the total loading of 5.6 mg cm^{-2} . Both electrodes were prepared by mixing active materials, acetylene black, and polytetrafluoroethylene (PTFE, 1 wt. % water suspension) with a mass ratio of 85:10:5, which were then pressed on nickel foam and dried at 70°C for 12 h.

Supporting Figure

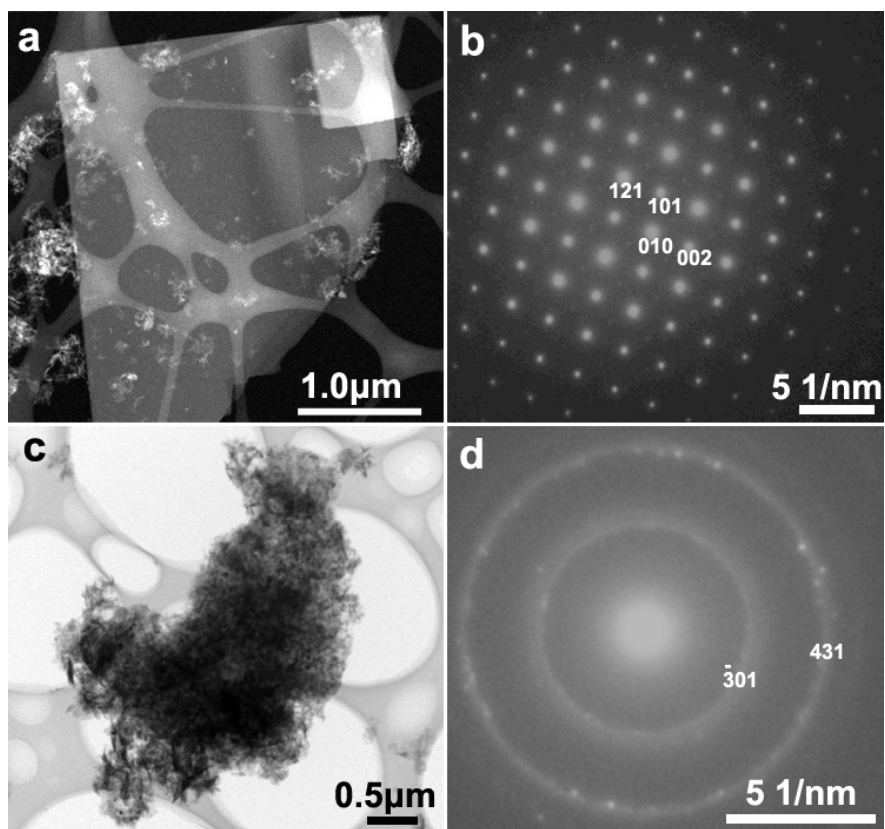


Figure S1. TEM images of NCNP with the structure of micro-sized platelet (a), nanopieces (c), and their SAED patterns (b, d).

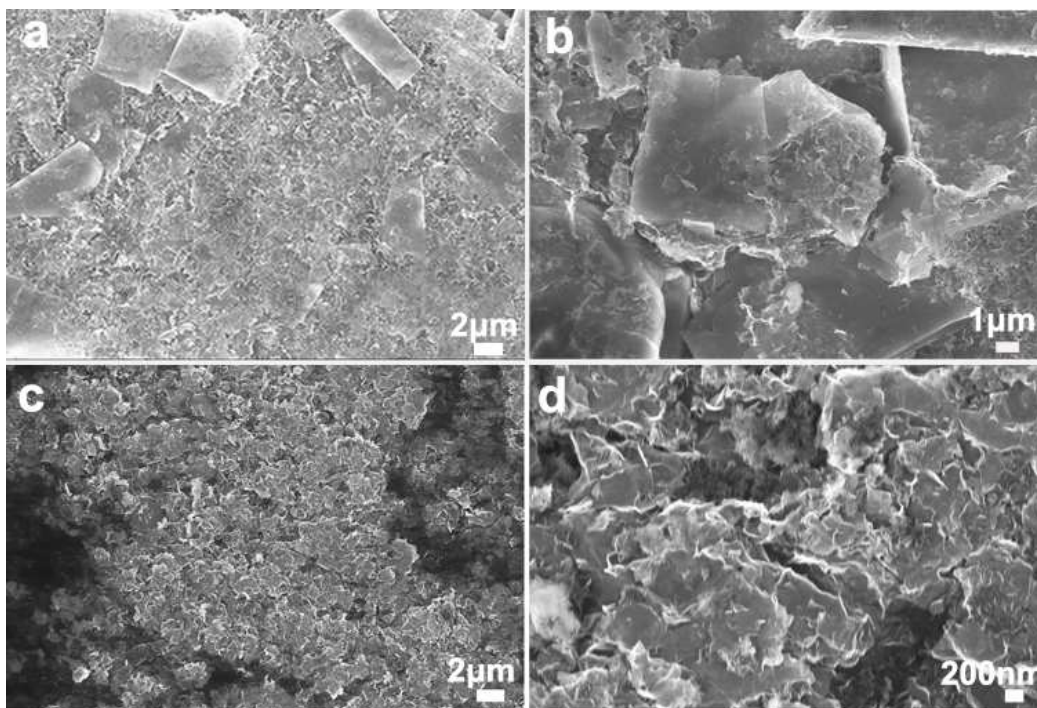


Figure.S2. Typical FESEM images at different magnifications at different magnifications of the (a, b) NCNP/RGO, and (Ni,Co)(OH)₂/GO (c, d).

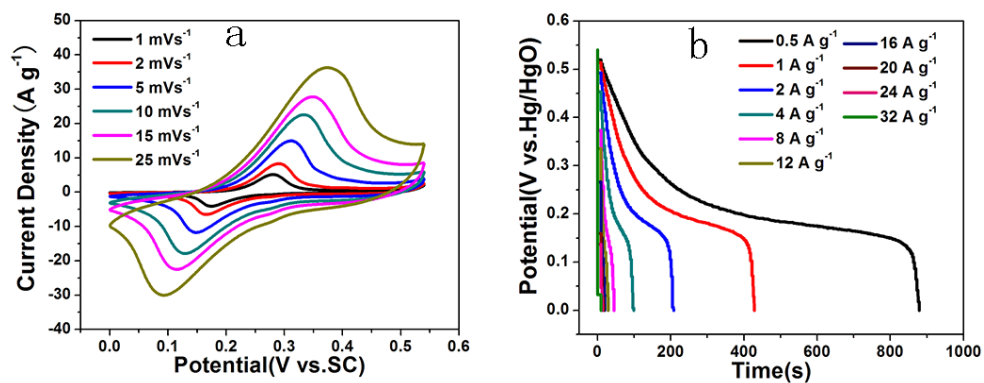


Fig. S3. CV curves at different scan rates of the as prepared (Ni,Co)(OH)₂/GO composites (a). GCD curves at different current densities of the as prepared (Ni,Co)(OH)₂/GO composites (b).

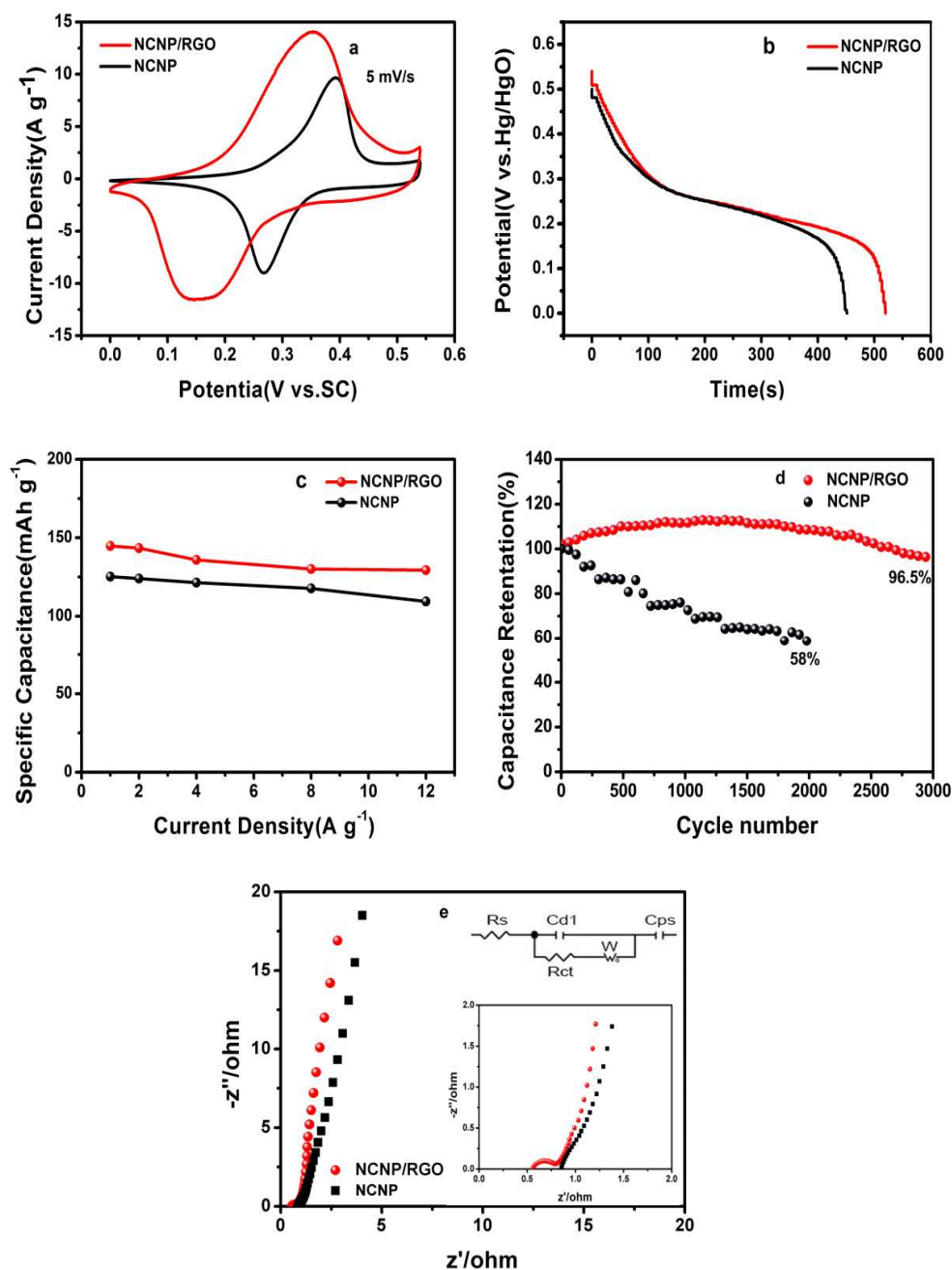


Fig. S4. CV curves of the NCNP/RGO and NCNP at a scanning rate of 5 mV s⁻¹ (a). GCD plots of NCNP/RGO and NCNP at 1 A g⁻¹ (b). The specific capacity calculated from different samples at different current densities (c). Cycling performance of NCNP/RGO and NCNP at a current density of 5 A g⁻¹ (d). The Nyquist plots (e).

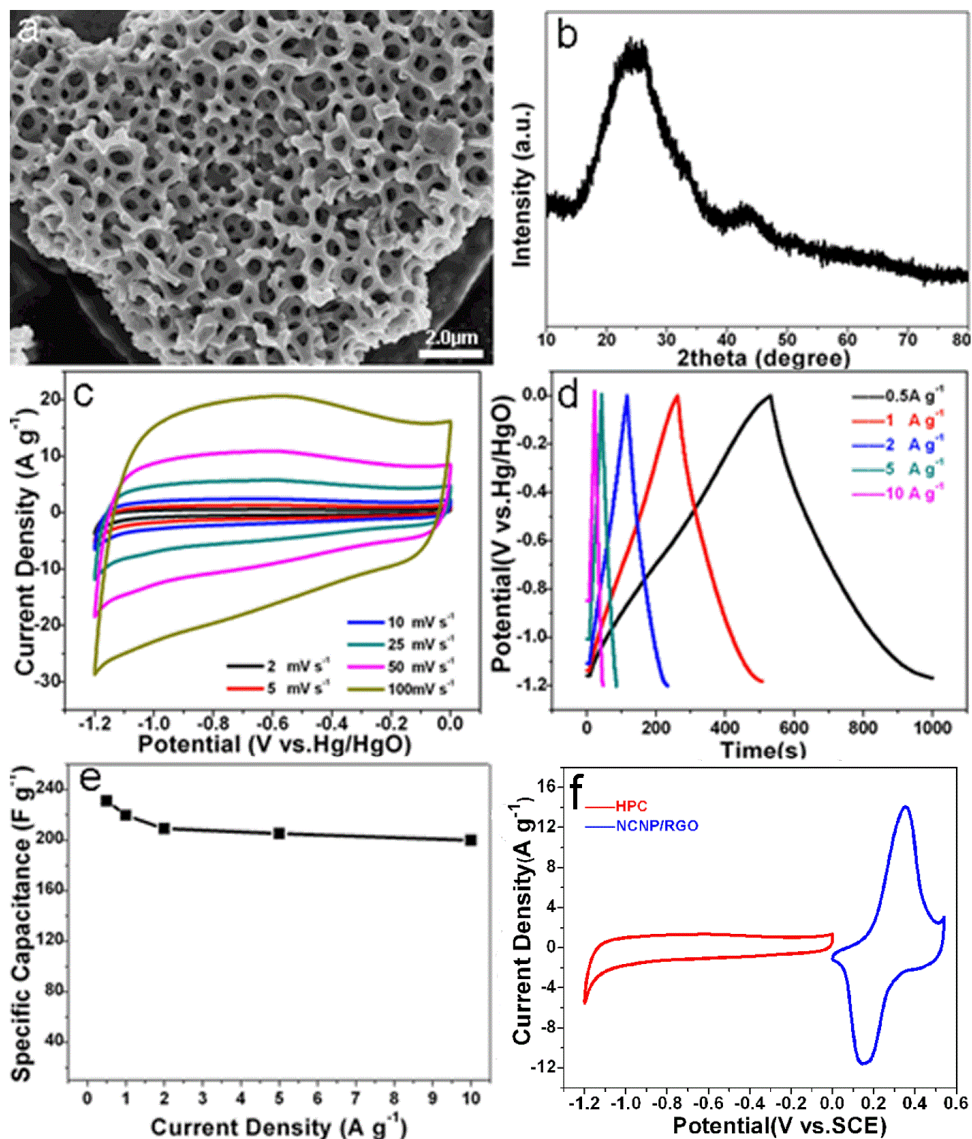


Fig. S5. FESEM image (a), XRD pattern (b), CV curves at different scan rates (c), (d) GCD curves at different current densities. SC as a function of discharge current densities of HPC (e), CV curves of NCNP/RGO and HPC at 5 mV s⁻¹ (f).

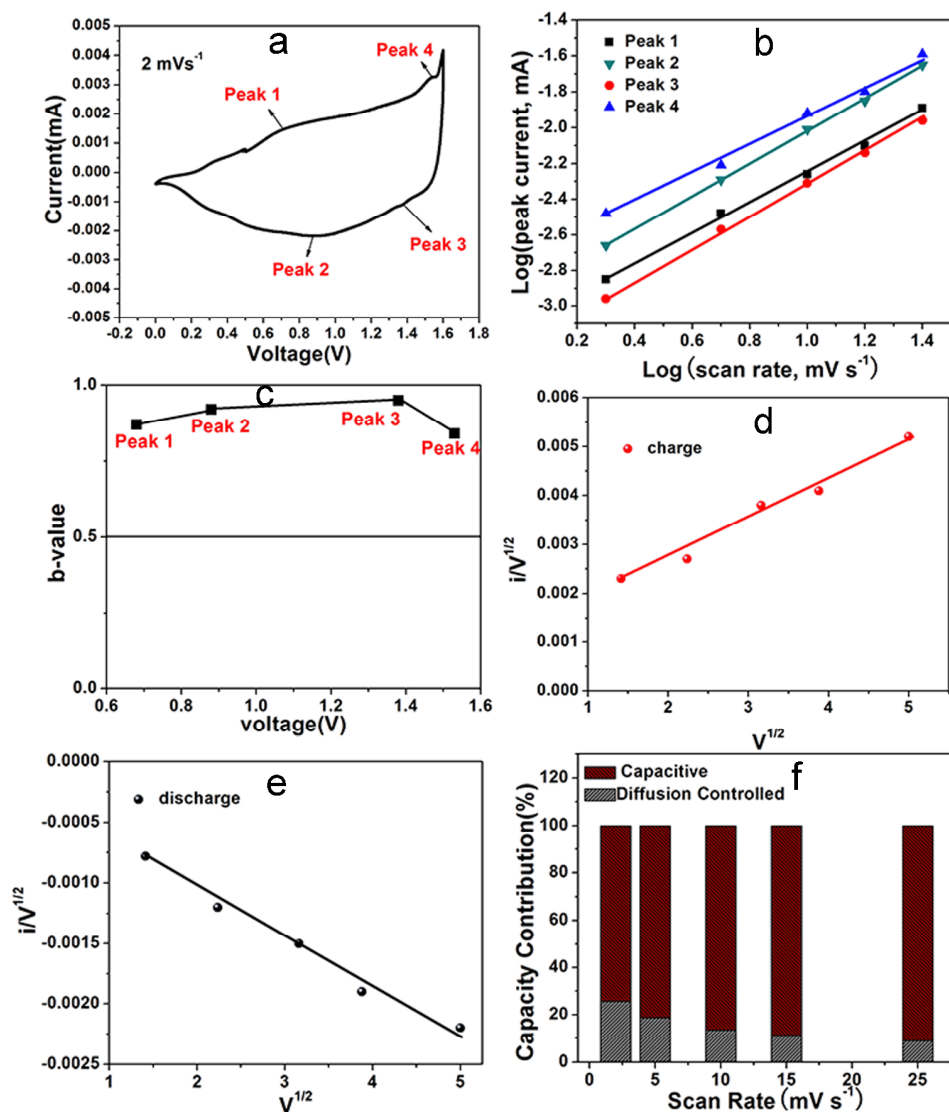


Fig. S6. Cycle voltammetry curve of NCNP/RGO//HPC at a scan rate of 2 mV s⁻¹ (a), Slope of the peak current versus the potential scan rate in a logarithm scale at different anodic and cathodic peaks position (b), the b-values corresponding to different electrochemical centers in the hybrid. “Linear behavior of $i(V)/v^{1/2}$ as a function of $v^{1/2}$ (c), charge process (d), discharge process. This is used to determine the slope (k_1) and intercept (k_2) of the equation 4 (e), the capacity contribution at different scan rate (2, 5, 10, 15, and 25 mV s⁻¹) (f) .

The high capacity can be divided into capacitive-controlled and diffusion-controlled capacity. In other words, the total current is contributed by two types of mechanism: the capacitive-controlled behavior which includes both the

non-Faradaic electrical double layer capacitance (EDLC) and the surface pseudocapacitance, and the diffusion-controlled Faradaic reaction^{S1}. Previously, Zhao et al^{S2} used the following method to further quantify the capacitive and diffusion limited contributions to the total capacity, in which the current response (i) at a certain voltage (V) is regarded to be contributed from capacitive (k₁) and diffusion (k₂) controlled process:

$$i(V) = k_1V + k_2V^{1/2} \quad (\text{eq.4})$$

Here k₁ and k₂ represent the contributions from the capacitive behaviours and the diffusion-controlled Faradaic intercalation process, respectively. **Fig. S6a** shows cycle voltammetry curve of NCNP/RGO//HPC at a scan rate of 2 mV s⁻¹, the different anodic and cathodic peaks were chosen for further analysis. A linear plot of i (V)/versus (**Figure S6 d-e**) was adopted to calculate the slope (k₁) and intercept (k₂). Following this we can estimate the fraction of the current due to each of these contributions at specific voltages.

Table S1. Performances comparison of as-made NCNP/RGO with pure NCNP

Subject	Power density (Wh kg ⁻¹)	Energy density (Wkg ⁻¹)	Specific capacitance (mAh g ⁻¹)	Cycling stability (%)
NCNP	4400	30.9	109.3 (12 A g ⁻¹)	58 (2000 cycles)
NCNP/RGO	14000	32.9	129.3 (12 A g ⁻¹)	97 (3000 cycles)

References

(S1) Sathiya, M.; Prakash, A. S.; Ramesha, K.; Tarascon, J. M.; Shukla, A. K. V₂O₅-anchored Carbon Nanotubes for Enhanced Electrochemical Energy Storage. *J. Am. Chem. Soc.* **2011**, 133, 16291-16299. (DOI:10.1021/ja207285b)

(S2) Zhao, K. N.; Liu, F. N.; Niu, C. J.; Xu, W. W.; Dong, Y. F.; Zhang, L.; Xie, S. M.; Yan, M. Y.; Wei, Q. L.; Zhao, D. Y.; Mai, L. Q. Graphene Oxide Wrapped Amorphous Copper Vanadium Oxide with Enhanced Capacitive Behavior for High-Rate and Long-Life Lithium-Ion Battery Anodes. *Adv. Sci.* **2015**, 2, 1500154. (DOI:10.1002/advs.201500154)