

**Supporting Information for**  
**Fabrication of Co<sub>3</sub>O<sub>4</sub>-Reduced Graphene Oxide Scrolls for High-**  
**Performance Supercapacitor Electrodes**

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### **Graphene oxide (GO) Preparation:**

GO was prepared by a modified Hummers method (ref. 7 in main text). Firstly, 5 g of graphite powder was mixed with 3.5 g of  $\text{NaNO}_3$ . Next, 70 mL of concentrated  $\text{H}_2\text{SO}_4$  was added to the mixture and stirred. With the stirring still in progress, 10 g of  $\text{KMnO}_4$  was added slowly, bit by bit, to the mixture to prevent a sudden accumulation of heat that is evolved. After that, the mixture was stirred for 6 days at room temperature. At the end of the 6th day, 100 mL of 5 wt%  $\text{H}_2\text{SO}_4$  was added to the mixture and the mixture was then heated up and refluxed at 98 °C for 2 hours. At the end of the 2nd hour, the temperature of the mixture was decreased to 50 °C and the reaction was terminated by adding 10 mL of 30 wt%  $\text{H}_2\text{O}_2$  to the mixture. To purify the graphene oxide, the mixture was washed with 3 wt%  $\text{H}_2\text{SO}_4$ , ultrasonicated at 140 W, 30 min and then centrifuged at 6000 rpm for 30 min. This purification step was repeated until the pH of the solution was 5~6. GO powder used in this work was obtained after freeze drying of the upper suspension.

### **Synthesis of $\text{Co}_3\text{O}_4/\text{r-GO}$**

1 mmol of sodium dodecyl sulphate (SDS) was first dissolved in 28 mL of ethylene glycol (EG) and water mixed solvents with volume ratio of 13:1. After complete dissolution of SDS under magnetic stirring, 10 mg of as-made GO was added to the above solution, with ultrasonication for 0.5 h. Then, 1 mmol of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was added under vigorous stirring. The addition of 1 mmol of  $\text{H}_2\text{C}_2\text{O}_4$  was proceeded upon the complete dissolution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . The resulting mixture was further stirred at room temperature for 10 h. The solid products were collected by centrifugation and washed several times with ethanol and distilled water. The

precipitate was dried at 60 °C overnight. Co<sub>3</sub>O<sub>4</sub>/r-GO was obtained by annealing the as-obtained precipitate at 450 °C under argon protection for 2 h.

The pure Co<sub>3</sub>O<sub>4</sub> scrolls were made by the same two-step method in the absence of GO while keep other conditions unaltered. Control experiments like without SDS, replacing GO with the same amount of high-temperature hydrogen reduced GO (HRGO) were both carried out according to the conditions above to investigate the growth mechanism. Herein, HRGO was prepared simply by annealing the as-synthesized GO at 950 °C for 3 h under hydrogen atmosphere. Another control experiment was conducted by physically blending pure Co<sub>3</sub>O<sub>4</sub> with commercial carbon black on the purpose of comparing the electrochemical properties with Co<sub>3</sub>O<sub>4</sub>/r-GO. The weight ratio of Co<sub>3</sub>O<sub>4</sub> to carbon black is equal to that Co<sub>3</sub>O<sub>4</sub>/r-GO, which is calculated to be 90:10 according to the initial dosages of the reactants.

## Characterization

The powder X-ray diffraction (XRD) analysis was performed using a D8 Advanced diffractometer with Cu *K*α line. Transmission electron microscopy (TEM) images were recorded by a JEOL JEM-1400F transmission electron microscope with accelerating voltage of 100 kV. Field-emission scanning electron microscopy (FESEM) analysis was conducted with a JEOL JSM-6700F electron microscope. Raman spectra and images were obtained by a WITeck CRM200 confocal microscopy Raman system with a piezocrystal controlled scanning stage. The excitation light is a 532 nm laser. The laser spot size is estimated to be 500 nm. Atomic force microscopy (AFM) was carried out using a Digital Nanoscope V in the tapping mode. An etched silicon tip was used as a probe for imaging the samples.

## Electrochemical Measurement

The electrochemical properties of the as-obtained products were investigated under a three-electrode cell configuration at room temperature on a CHI 760D electrochemistry workstation with 6 M KOH aqueous solution as the electrolyte. The working electrode was fabricated by casting Nafion-impregnated catalyst ink onto a glassy carbon disk electrode with diameter of 5 mm (without any other carbon additives).<sup>[1]</sup> Typically, 5 mg of the active electrode material was ultrasonically dispersed into 1 mL of an ethanol solution containing 5  $\mu$ L of a Nafion solution (5 wt % in water, DuPont) for 10 min to form a catalyst ink; 0.2 mL of the as-prepared ink was dropped onto the glassy carbon disk electrode and baked at 80  $^{\circ}$ C for 10 min. Platinum foil and a Ag/AgCl electrode (immersed directly into the electrolyte) were used as the counter and reference electrodes, respectively. Cyclic voltammetry studies were performed within a range of 0 to 0.5 V at scan rates of 5 - 100 mV s<sup>-1</sup>. The specific capacitance (SC) is calculated using half the integrated area of the cyclic voltammogram (CV) curve to obtain the charge (Q), and subsequently dividing the charge by the mass of the active material (m) and the width of the potential window ( $\Delta V$ ):

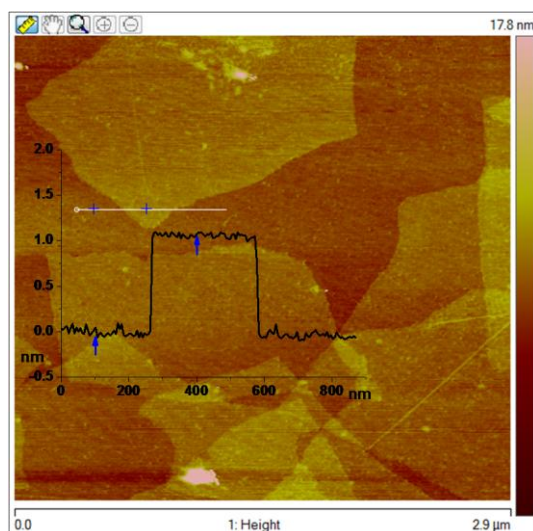
$$C = Q / m \Delta V \quad (1)$$

Galvanostatic charge-discharge measurement was performed at different constant current densities. The SC can also be calculated using galvanostatic charge-discharge curves by the following equation:

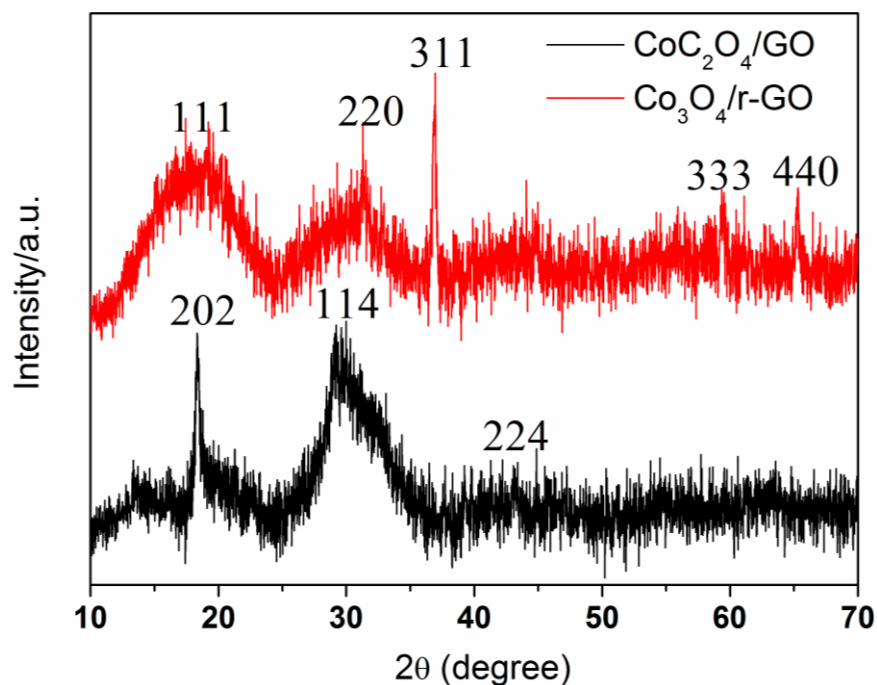
$$C = I (\Delta t) / m (\Delta V) \quad (2)$$

Where m is also the mass of electrode material (g),  $\Delta V$  is the potential window (V), I is the discharge current (A) applied, and  $\Delta t$  is the discharge time.

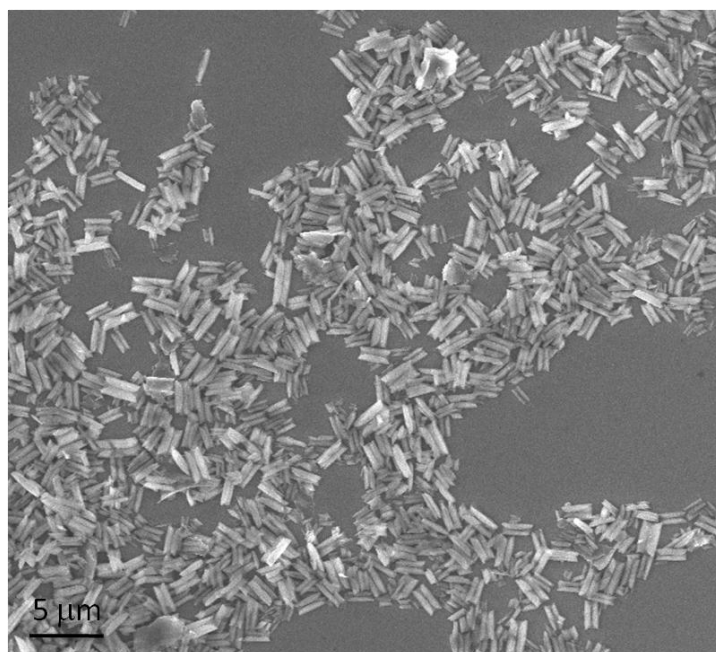
## Supplementary Figures



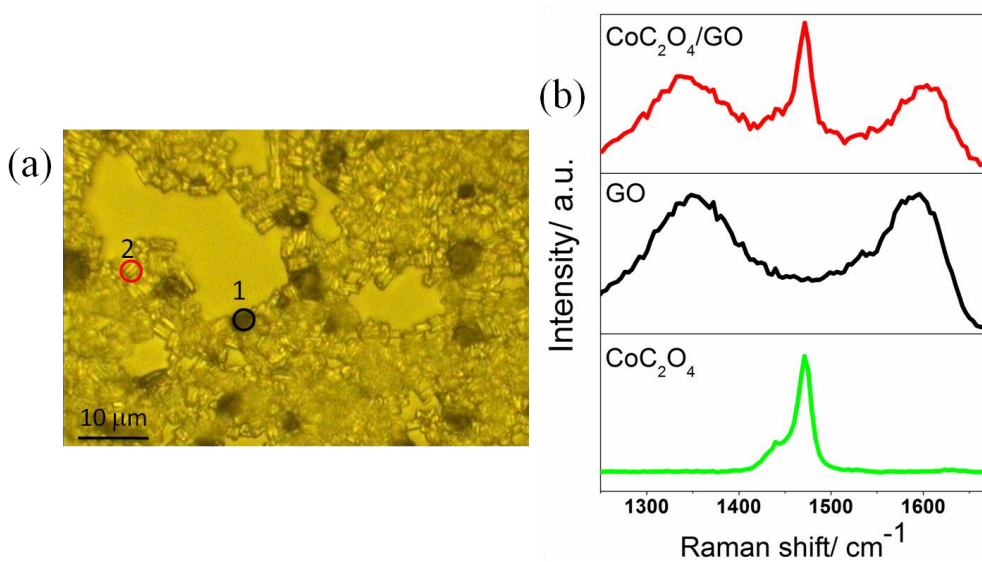
**Figure S1.** AFM image of the as-obtained GO platelets in the upper suspension. Inset is depth profile of the line of interest on the GO platelets, the height difference between two arrows is about 1nm, indicating a single layer GO sheet.



**Figure S2.** XRD patterns of the as-obtained CoC<sub>2</sub>O<sub>4</sub>/GO (JCPDS No. 25-0250) and Co<sub>3</sub>O<sub>4</sub>/r-GO (JCPDS No. 42-1647) scrolls.

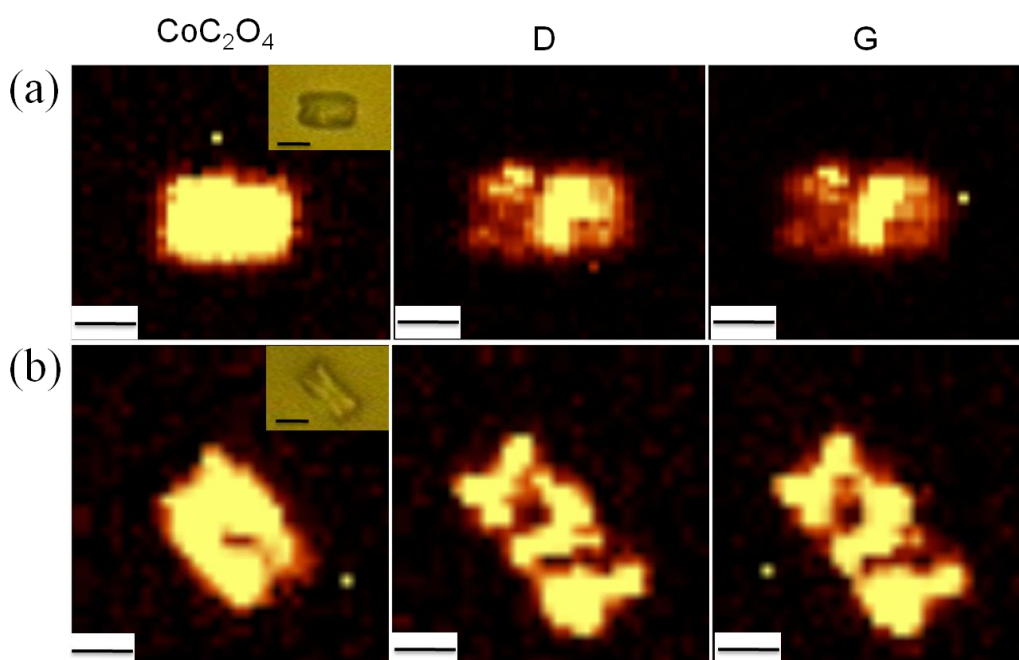


**Figure S3.** Low-magnification SEM image of the  $\text{CoC}_2\text{O}_4/\text{GO}$  scrolls, indicating the high yield and uniformity.

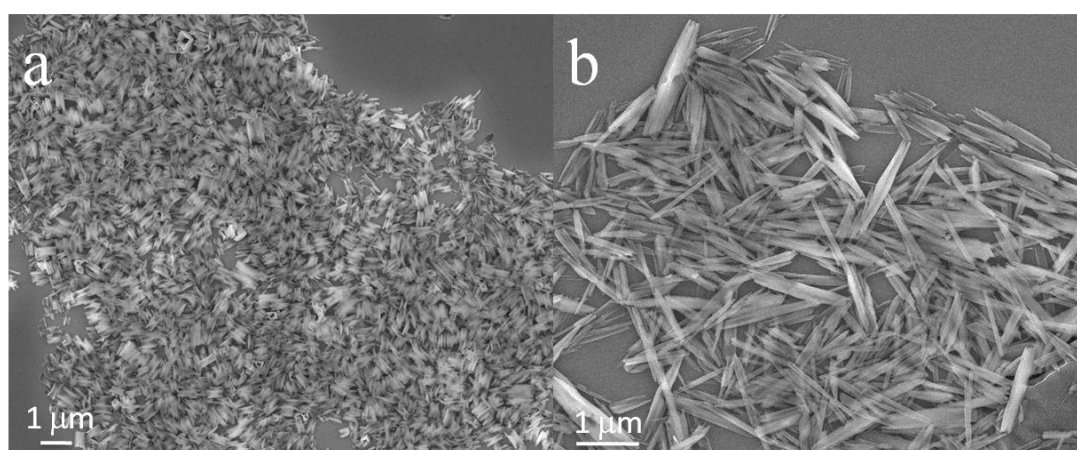


**Figure S4.** (a) Optical image of typical  $\text{CoC}_2\text{O}_4/\text{GO}$  scrolls. (b) Raman spectra of pure  $\text{CoC}_2\text{O}_4$  (for reference), GO [obtained from spot 1 in (a)], and single  $\text{CoC}_2\text{O}_4/\text{GO}$  scroll [obtained from spot 2 in (a)], respectively.

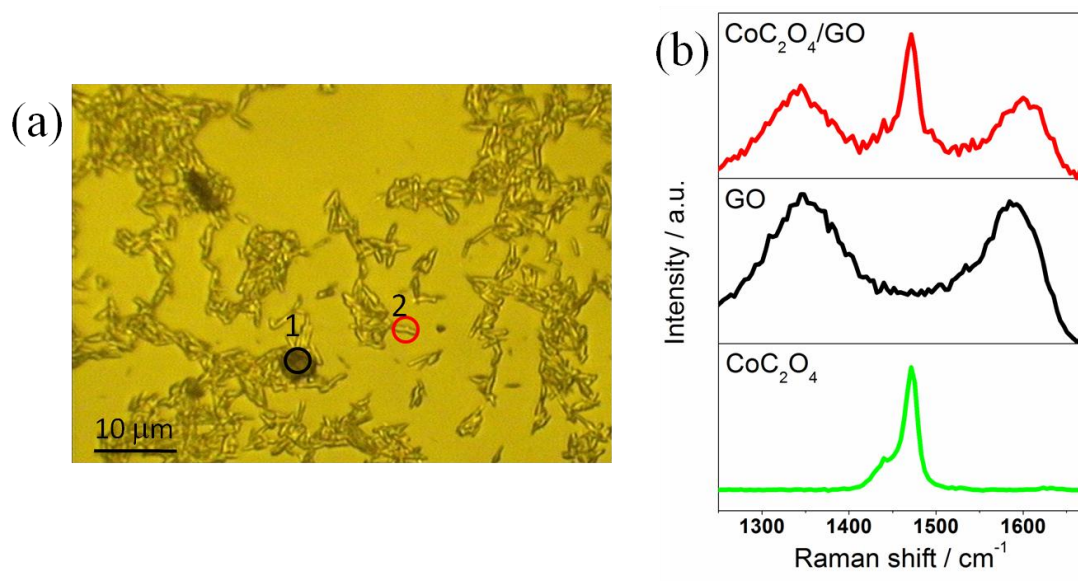




**Figure S5.** Raman mapping images of CoC<sub>2</sub>O<sub>4</sub>, and D, G bands of GO for different CoC<sub>2</sub>O<sub>4</sub>/GO scrolls, indicating the size of GO in every single scroll is equal (a) to or even larger (b) than that of pure CoC<sub>2</sub>O<sub>4</sub> scroll. The scale bars of the optical images and Raman images are 1  $\mu\text{m}$ .

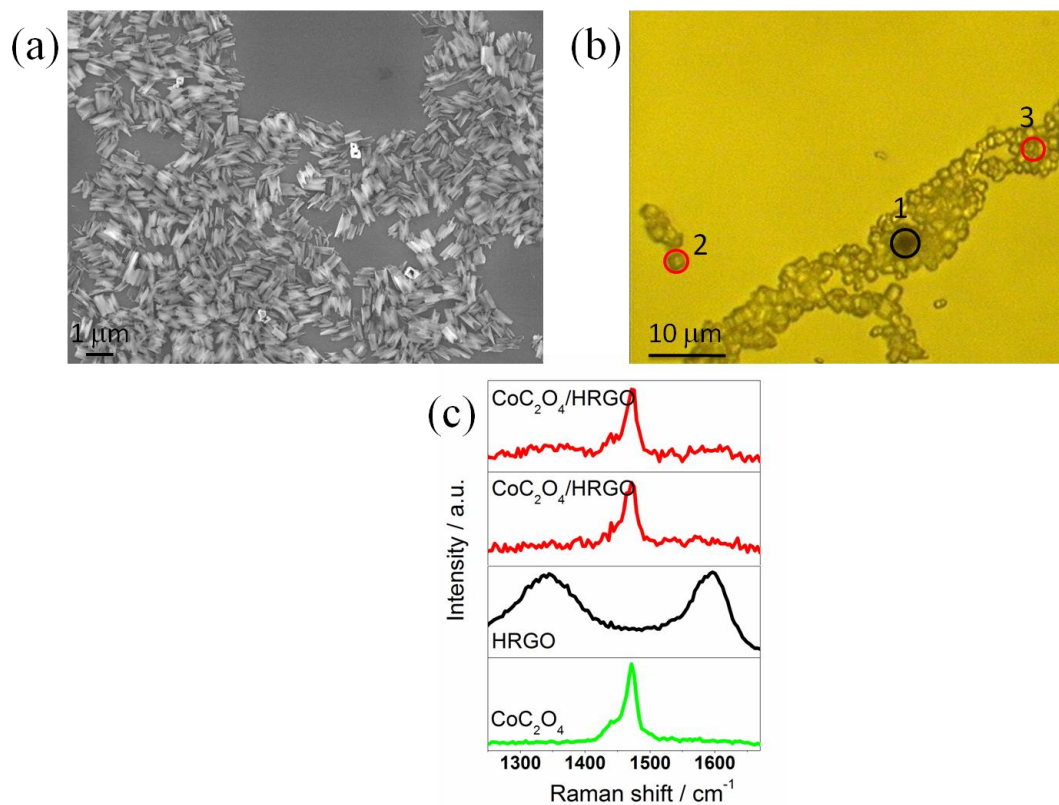


**Figure S6.** SEM images of the samples obtained from the control experiments: (a) in the absence of GO, (b) in the absence of surfactant (SDS).



**Figure S7.** (a) Optical image of the sample obtained in the absence of SDS. (b) Raman spectra of pure CoC<sub>2</sub>O<sub>4</sub> (for reference), GO [obtained from spot 1 in (a)], and single CoC<sub>2</sub>O<sub>4</sub>/GO scroll [obtained from spot 2 in (a)], respectively.

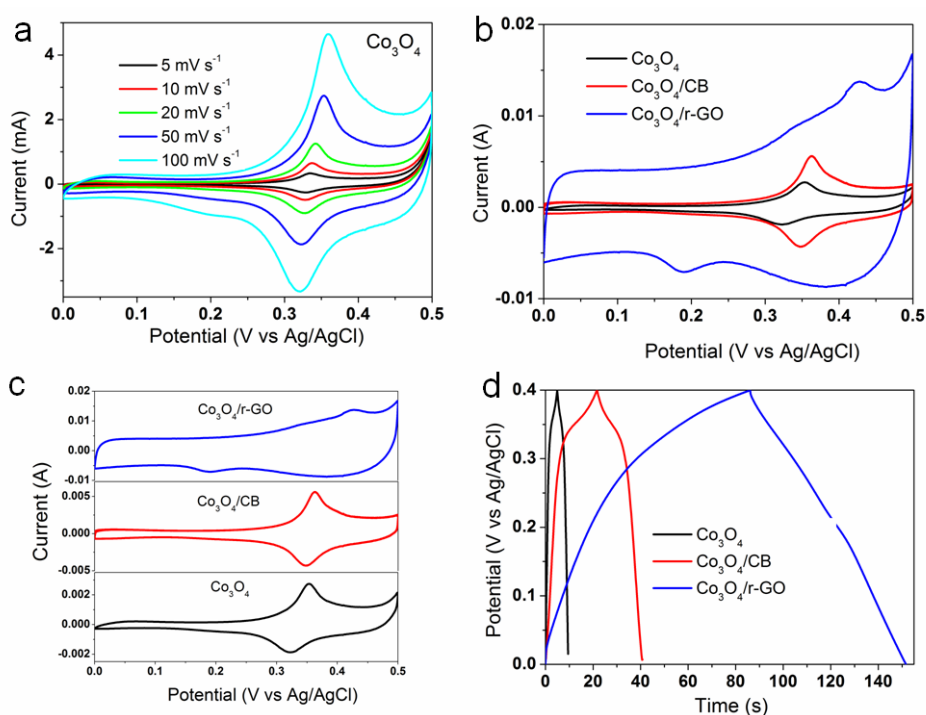




**Figure S8.** SEM (a) and optical (b) images of the product obtained by replacing GO with HRGO. (c) Raman spectra of pure CoC<sub>2</sub>O<sub>4</sub> (for reference), HRGO [obtained from spot 1 in (b)], single CoC<sub>2</sub>O<sub>4</sub>/HRGO scroll [obtained from spot 2 in (a)], and several CoC<sub>2</sub>O<sub>4</sub>/HRGO scrolls [obtained from spot 3 in (a)], respectively.

**Table 1.** The specific capacitances for  $\text{Co}_3\text{O}_4$  and  $\text{Co}_3\text{O}_4/\text{r-GO}$  at different scan rates.

	$5 \text{ mV s}^{-1}$	$10 \text{ mV s}^{-1}$	$20 \text{ mV s}^{-1}$	$50 \text{ mV s}^{-1}$	$100 \text{ mV s}^{-1}$
$\text{SC}_{\text{Co}_3\text{O}_4} (\text{F. g}^{-1})$	14.9	14.7	14.1	12.9	12.2
$\text{SC}_{\text{Co}_3\text{O}_4/\text{GO}} (\text{F. g}^{-1})$	159.8	156.0	151.5	131.2	130.7



**Figure S9.** (a) CV curves of the  $\text{Co}_3\text{O}_4$  electrode in a KOH (6 M) electrolyte at different scan rates. (b, c) CV curves of the  $\text{Co}_3\text{O}_4$  (for comparison),  $\text{Co}_3\text{O}_4/\text{carbon black (CB)}$ , and  $\text{Co}_3\text{O}_4/\text{r-GO}$  electrodes at a scan rate of  $50 \text{ mV s}^{-1}$ . [c is used for clear observation of the initial and final current responses for each kind of materials.] (d) Galvanostatic charge-discharge curves of the  $\text{Co}_3\text{O}_4$  (for comparison),  $\text{Co}_3\text{O}_4/\text{carbon black (CB)}$ , and  $\text{Co}_3\text{O}_4/\text{r-GO}$  electrodes at a current density of  $1 \text{ A g}^{-1}$ .

Reference:

- [1] K. Zhang, L. L. Zhang, X. S. Zhao, and J. S. Wu, “Graphene/Polyaniline Nanofiber Composites as Supercapacitor Electrodes”, *Chem. Mater.* 2010, **22**, 1392–1401.