

**Editor's note:** A Correction was published on 20<sup>th</sup> August 2020 that affects Fig. S4 of this ESI. This can be viewed online at <https://doi.org/10.1039/D0TA90185G>.

## Supporting Information

### Sulphur-doped Co<sub>3</sub>O<sub>4</sub> Nanowires as Advanced Negative Electrode for High-Energy Asymmetric Supercapacitors

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### Calculations

#### 1 Single Electrode

The areal capacitances of the single electrodes (including Co<sub>3</sub>O<sub>4</sub>, S-Co<sub>3</sub>O<sub>4</sub> and MnO<sub>2</sub> electrodes) were calculated from their CVs based on the following equation:

$$C_a = \frac{Q}{\Delta V \cdot S} \quad (1)$$

Where  $C_a$  (mF/cm<sup>2</sup>) is the areal capacitance,  $Q$  (C) is the average charge during the process of charging and discharging,  $\Delta V$  (V) is the potential window and  $S$  (cm<sup>2</sup>) is the area of these electrodes.

Alternatively, the areal capacitances of these electrodes can also be calculated by galvanostatic charge/discharge method according to the following equation:

$$C_a = \frac{I \times \Delta t}{\Delta V \times S} \quad (2)$$

Where  $C_a$  (mF/cm<sup>2</sup>) is the areal capacitance,  $I$  is the constant discharging current,  $\Delta t$  is the discharging time,  $\Delta V$  (V) is the potential window, and  $S$  (cm<sup>2</sup>) is the surface area

## 2 MnO<sub>2</sub>//S-Co<sub>3</sub>O<sub>4</sub>-ASC devices

The cell (device) capacitance ( $C_{cell}$ ) and volumetric capacitance of the devices were obtained from their CVs based on the following equation:

$$C_{cell} = \frac{Q}{\Delta V} \quad (3)$$

$$C_v = \frac{C_{cell}}{V} = \frac{Q}{V \times \Delta V} \quad (4)$$

where  $Q$  (C),  $V$  and  $\Delta V$  (V) are the average charge during the charging and discharging process, the applied current, the volume (cm<sup>3</sup>) of the whole device and the voltage window respectively. The area and thickness of the MnO<sub>2</sub>//S-Co<sub>3</sub>O<sub>4</sub>-ASC device is about 1 cm<sup>2</sup> and 0.08 cm. Therefore, the whole volume of the MnO<sub>2</sub>//S-Co<sub>3</sub>O<sub>4</sub>-ASC device are about 0.08 cm<sup>3</sup>. It need to mention that the volumetric capacitances were calculated on account of the volume of the device stack, including the active material, the flexible substrate and the separator with electrolyte.

Alternatively, the cell (device) capacitance ( $C_{cell}$ ) and volumetric capacitance of the electrode ( $C_v$ ) was measured by the slope of the discharge curve according to the following equations:

$$C_a = \frac{I \times \Delta t}{\Delta V} \quad (5)$$

$$C_v = \frac{C_{cell}}{V} = \frac{I \times \Delta t}{V \times \Delta V} \quad (6)$$

where  $I$  is the applied current,  $V$  is the volume (cm<sup>3</sup>) of the whole device (the whole volume of the MnO<sub>2</sub>//S-Co<sub>3</sub>O<sub>4</sub>-ASC device is about 0.08 cm<sup>3</sup>),  $\Delta t$  is the discharging time,  $\Delta V$  (V) is the voltage window.

Volumetric energy density, equivalent series resistance and power density ( $P$ ,  $W/cm^3$ ) of the devices were calculated by using the following equations 7 to 9:

$$E = \frac{1}{2 \times 3600} C_V \Delta V^2 \quad (7)$$

$$ESR = \frac{iR_{drop}}{2I} \quad (8)$$

$$P = \frac{\Delta V^2}{4 \times ESR \times V} \quad (9)$$

where  $E$  ( $Wh/cm^3$ ) is the energy density,  $C_V$  is the volumetric capacitance obtained based on Equation (5) and  $\Delta V$  (V) is the voltage window.  $ESR$  ( $\Omega$ ) is the internal resistance of the device.  $P$  ( $W/cm^3$ ) is the power density.

### 3 Charge balance between the negative and positive electrode in ASC device:

As far as a SC is concerned, the charge balance will follow the relationship  $q^+ = q^-$ . The charge stored by each electrode is decided by the capacitance ( $C_s$ ), the potential range for the charge/discharge process ( $E$ ) and the mass of the active materials electrode ( $A$ ) and expressed by the following Equation:

$$q = C_s \times \Delta E \times m \quad (10)$$

In order to meet the requirement of  $q^+ = q^-$ , the area balancing between  $MnO_2$  and  $S-Co_3O_4$  should be calculated according to the following equation:

$$\frac{A_{MnO_2}}{A_{S-Co_3O_4}} = \frac{C_{A_{S-Co_3O_4}} \times \Delta E_{S-Co_3O_4}}{C_{A_{MnO_2}} \times \Delta E_{A_{MnO_2}}} \quad (11)$$

Based on the equation, the calculated areal ration between the MnO<sub>2</sub> electrode and S-Co<sub>3</sub>O<sub>4</sub> electrode is about 5:6.

#### 4 Potentiostatic intermittent titration technique (PITT).

The Li ion diffusion for the PITT experiment can be modeled as one-dimensional transport according to Fick's second law, which will follow equation 12:

$$\frac{\partial C_{Li}}{\partial x} = D \frac{\partial^2 C_{Li}}{\partial x^2} \quad (12)$$

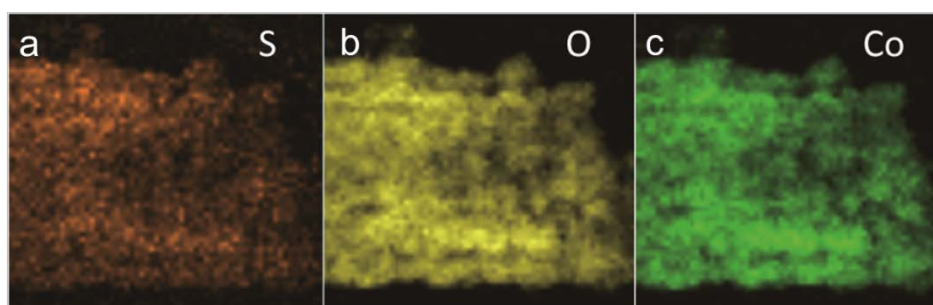
Where  $x$  is the distance of Li ion moving from the electrolyte into the electrode,  $C_{Li}$  is the concentration of Li at  $x$  and time  $t$ , and  $D$  is the chemical diffusion coefficient. In this PITT measurement, a potentiostatic current transient was measured by adding a very small potential step of 10 mV. The transient current versus time during the constant voltage step follows equation 13:

$$I(t) = \frac{2QD}{L^2} \text{EXP}\left(-\frac{\pi^2 Dt}{4L^2}\right) \quad (13)$$

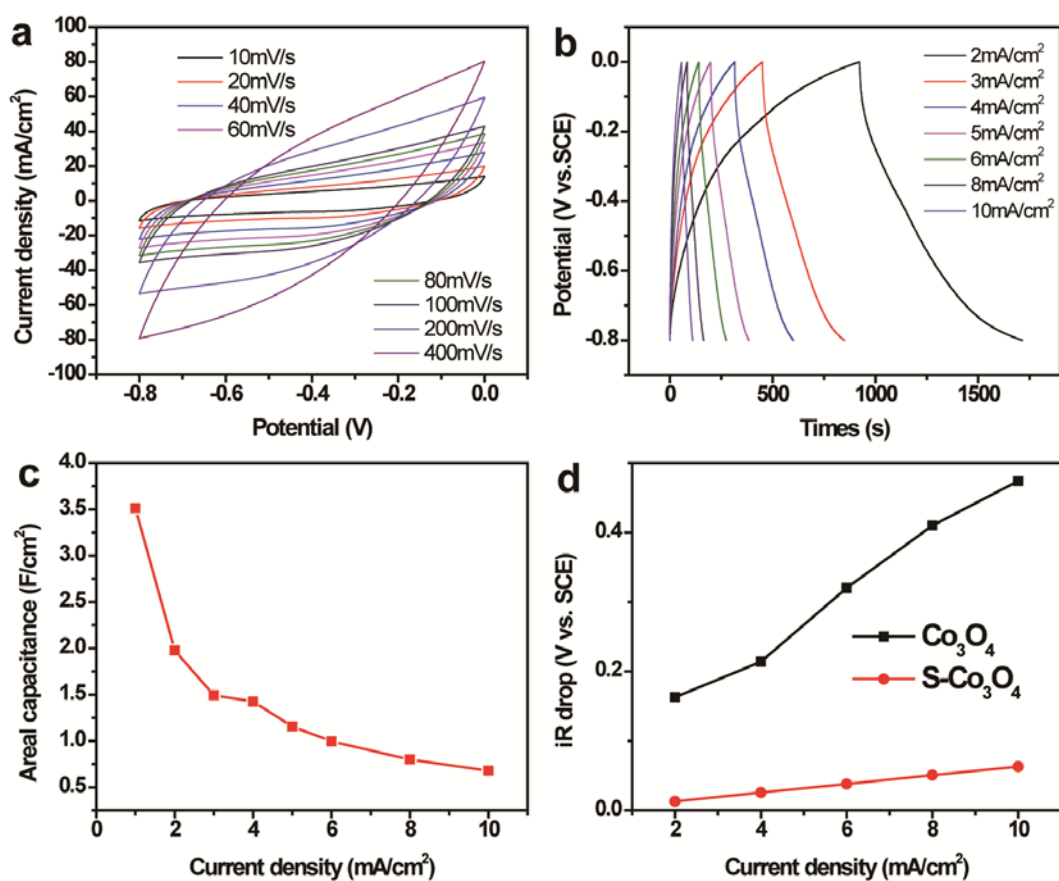
where  $Q$  is the total charge transferred during a potential step and  $L$  is the characteristic thickness of the electrode (0.8  $\mu\text{m}$  for Co<sub>3</sub>O and S-Co<sub>3</sub>O<sub>4</sub> electrodes). The value of  $D$  can be calculated from the logarithmic function of  $I(t)$  (equation 14):

$$D_{PITT} = -\frac{d \ln I(t)}{dt} \frac{4L}{\pi^2} \quad (14)$$

## Supplementary Figures

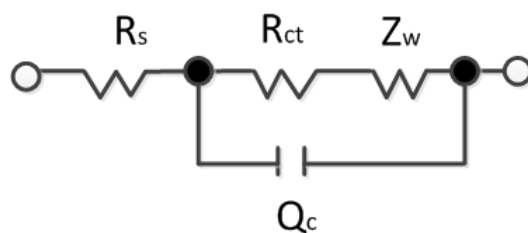


**Figure S1.** Energy dispersive X-ray spectroscopy mapping of S-Co<sub>3</sub>O<sub>4</sub> nanowire. (a) S, (b) O and (c) Co.

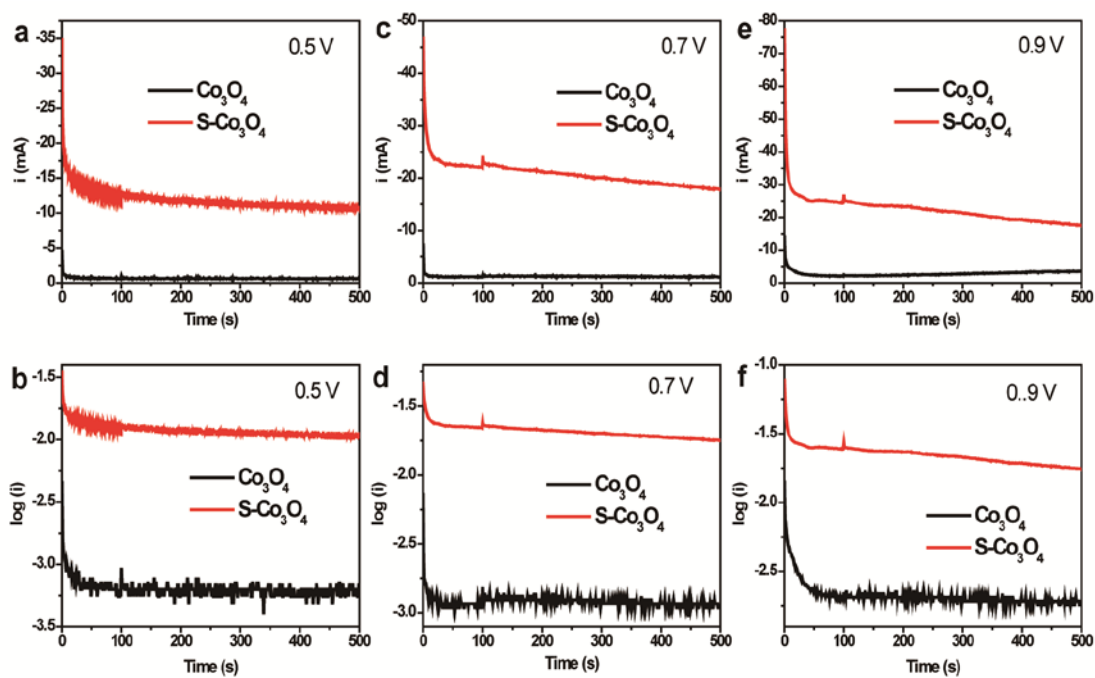


**Figure S2.** (a) CV curves collected for S-Co<sub>3</sub>O<sub>4</sub> electrode at various scan rates. (b) Galvanostatic charge-discharge curves of the S-Co<sub>3</sub>O<sub>4</sub> electrode collected at different current densities. (c) Areal capacitance of the S-Co<sub>3</sub>O<sub>4</sub> electrode collected from galvanostatic charge discharge curves as a

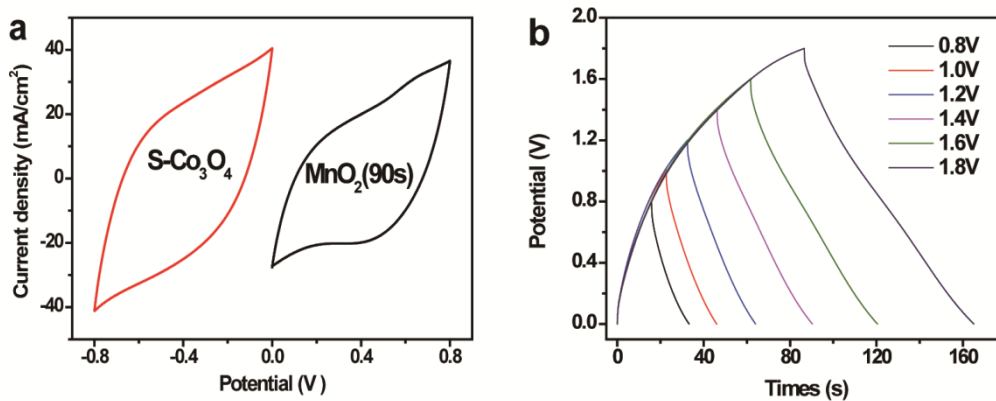
function of current density. (d)  $iR$  drop of the  $\text{Co}_3\text{O}_4$  and  $\text{S-Co}_3\text{O}_4$  electrodes measured at different current densities.



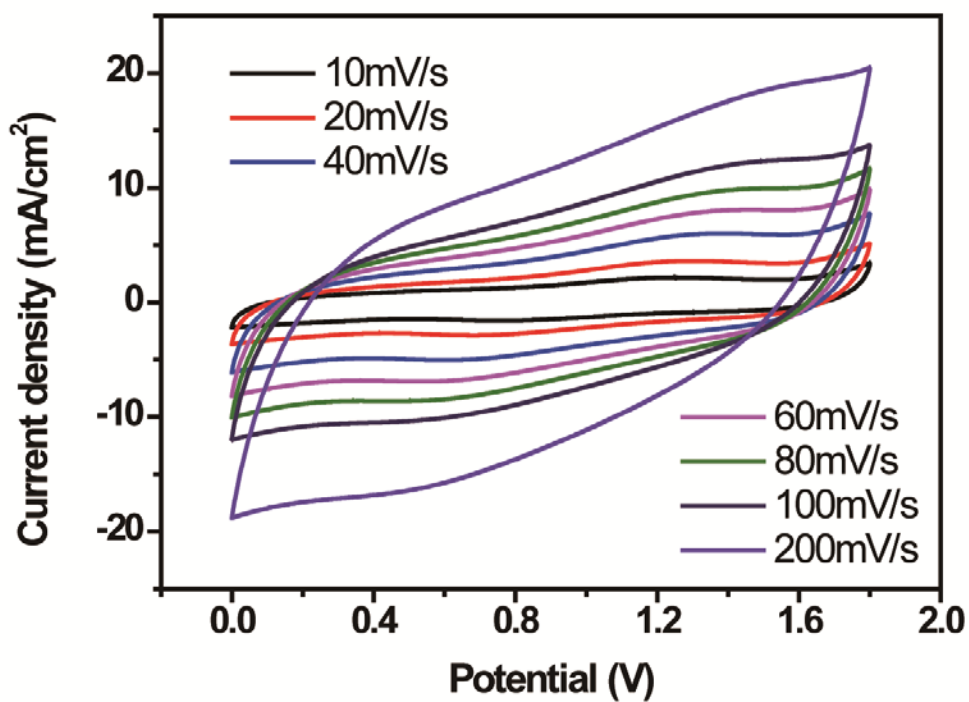
**Figure S3.** The equivalent circuit diagram of the electrochemical impedance spectroscopy (EIS)



**Figure S4.** Transient  $i-t$  curves of the  $\text{Co}_3\text{O}_4$  and  $\text{S-Co}_3\text{O}_4$  electrodes collected at (a)  $-0.5\text{V}$ , (c)  $-0.7\text{V}$ , (e)  $-0.9\text{V}$  upon an addition of a potential of  $10\text{ mV}$ . (b, d, f) The corresponding semi-logarithmic plots of a, c and e.



**Figure S5.** (a) CV curves collected for MnO<sub>2</sub> and S-Co<sub>3</sub>O<sub>4</sub> electrodes at a scan rate of 100 mV/s. (b) Galvanostatic discharge-charge curves of MnO<sub>2</sub>//S-Co<sub>3</sub>O<sub>4</sub>-ASC device collected at different potential windows



**Figure S6.** CV curves of the MnO<sub>2</sub>//S-Co<sub>3</sub>O<sub>4</sub> ASC-device collected at different scan rates.