Battery-type hollow Prussian blue analogues for asymmetric supercapacitor

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Synthesis of CNT film

A continuous carbon nanotube aerogel was synthesized by a chemical vapor deposition (CVD) method, which fabricated at 1100°C in a horizontal quartz tube using a mixture of nitrogen (150 L/h) and hydrogen (50 L/h) as the reactant and carrier gas. The reaction solution consisted of a carbon source (60.0 wt% ethanol and 37.5 wt% acetone) mixed with ferrocene (1.5 wt%) and thiophene (1.0 wt%). Ferrocene was used as the source of iron catalyst, and thiophene was used as the source of sulfur for catalyst activation. The solution was injected into the reactor at a rate of 210 μL min^{-1}. The CNT aerogel was collected and laid onto a travelling lattice, which formed a macroscopic CNT film.

Calculation

In the three-electrode system, CuO/Co_3O_4/CNT Fe_2O_3/CNT were used as the working electrodes, a platinum electrode was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. Moreover, using 3.0 M KOH aqueous solution as the electrolyte. The specific capacitance (C, mF/cm^{-2}) of the electrodes was calculated from the galvanostatic charge/discharge curves based on the formula:

$$C= I\times\Delta t/(S\times\Delta V) \qquad (1)$$

where I (mA) is the discharge current, Δt is the discharge time, ΔV is the potential range in the discharge process, and S (cm^2) is the surface area of the electrode and/or device. A PVA/KOH gel electrolyte was prepared by dissolving 3.0 g PVA into 30 mL DI water and heating to 95°C under vigorous stirring until it became clear. Then the 10 mL 3 M KOH solution was added in solution under stirring. The two pieces of electrodes were coated with the PVA/KOH three times and dried at 40 ^{o} C, respectively. Then the electrodes were assembled face-to-face, noticing that the PVA/KOH gel electrolyte was used as both the gel electrolyte and separator. After the PVA/KOH gel electrolyte was solidified, a flexible all-solid-state asymmetric supercapacitor (ASC) device could be packed and tested.

The areal energy density and power density of the devices were obtained from the following equations:

$$E=1/2C\times\Delta V^2 \qquad (2)$$

$$P=E/t \qquad (3)$$

Where C is the specific capacitance and ΔV (V) is the voltage window.

Prior to the assembly of the ASCs, the area ratio of the positive and negative electrodes was balanced according to the following equations:

$$Q^+=Q^- \qquad (4)$$

$$C_S^+\times\triangle V\times S^+=C_S^-\times\triangle V\times S^- \qquad (5)$$

$$S^{-}/S^{+} = C_S^{+} \times \Delta V^{+} / (C_S^{-} \times \Delta V^{-}) \qquad (6)$$

where Q^+ and Q^- are respectively the charge stored at positive and negative electrodes, ΔV is the voltage window and C_S is the areal capacitance of each electrode measured in a three electrode configuration. To balance the charges of the two electrodes in this work, the area ratio required was $S^+/S^- = 1$.

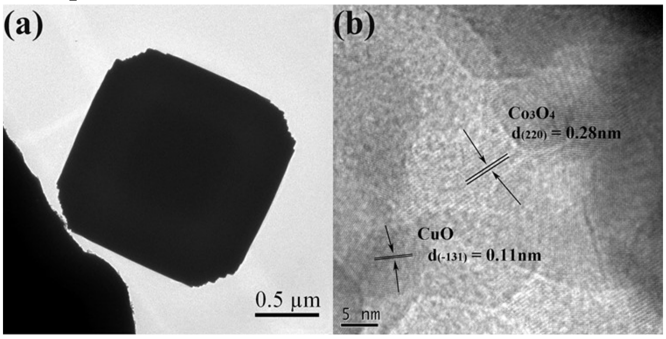

Figure S1 (a) TEM image of CuCo-PBA nanocube. (b) HRTEM image of CuO-Co_3O_4 nanoframes.

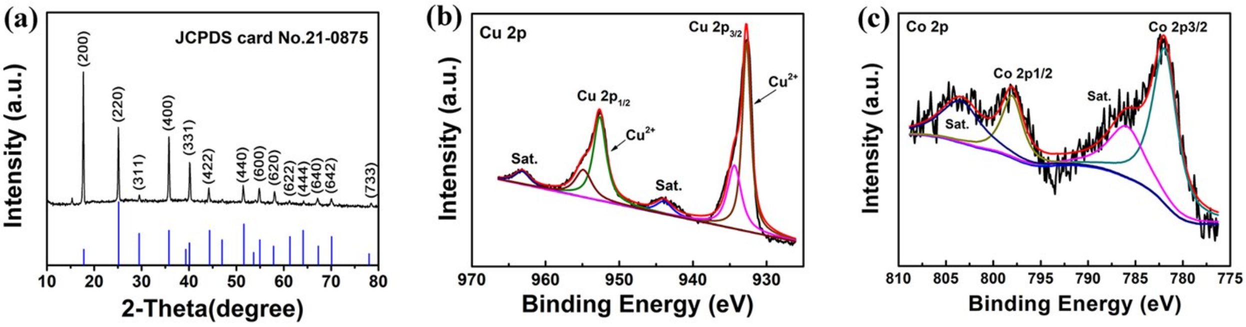

Figure S2 (a) XRD of CuCo-PBA. (b-c) XPS of CuO/Co_3O_4.

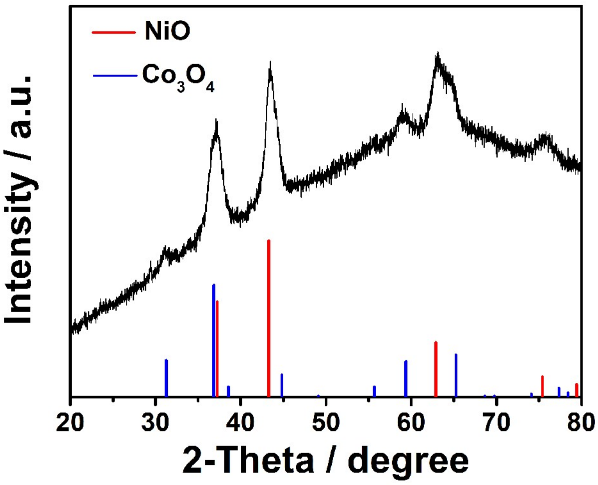

Figure S3 XRD pattern of NiO/ Co_3O_4.

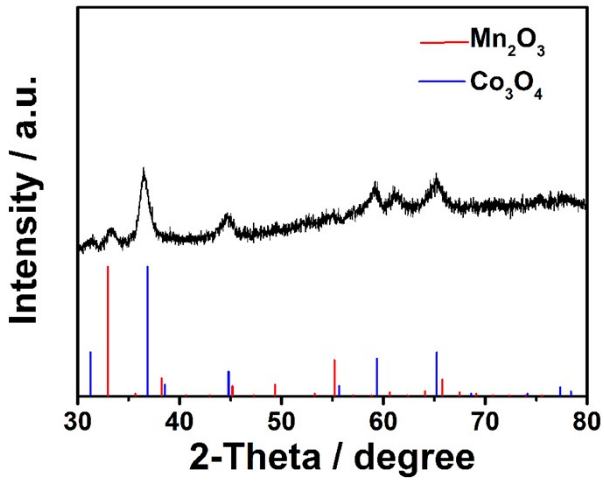

Figure S4 XRD pattern of Mn_2O_3/ Co_3O_4.

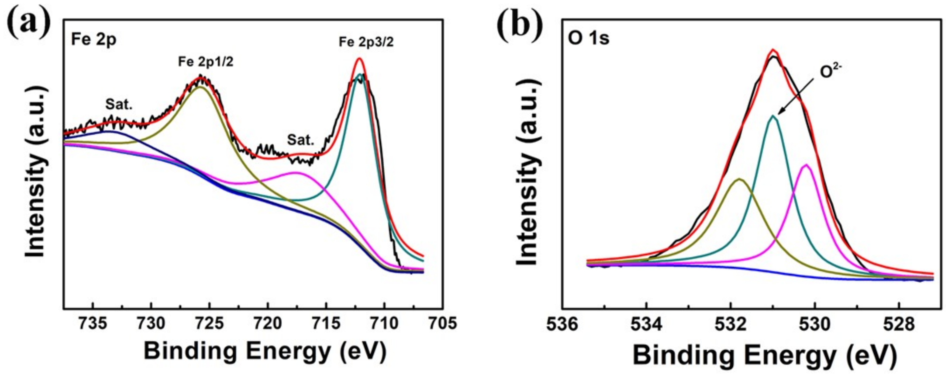

Figure S5 XPS of Fe_2O_3.

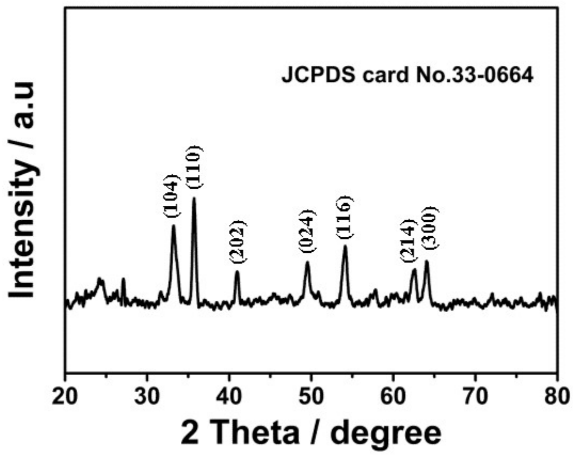

Figure S6 XRD of Fe_2O_3.

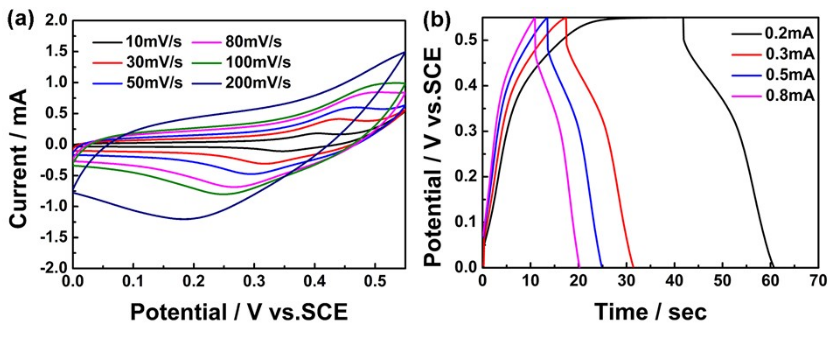

Figure S7 Electrochemical properties of CuO/Co_3O_4-2.

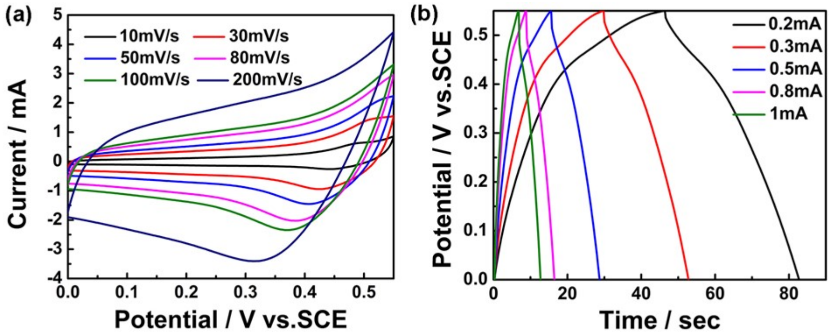

Figure S8 Electrochemical properties of CuO/ Co_3O_4-4.

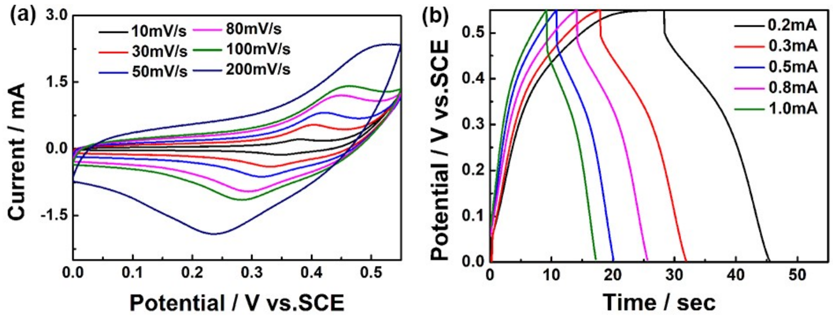

Figure S9 Electrochemical properties of CuO/ Co_3O_4-8.

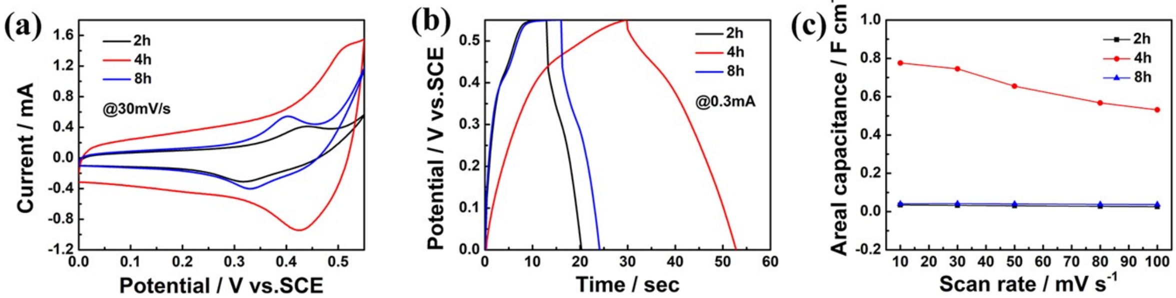

Figure S10 Electrochemical comparison of CuO/ Co_3O_4-*n*.

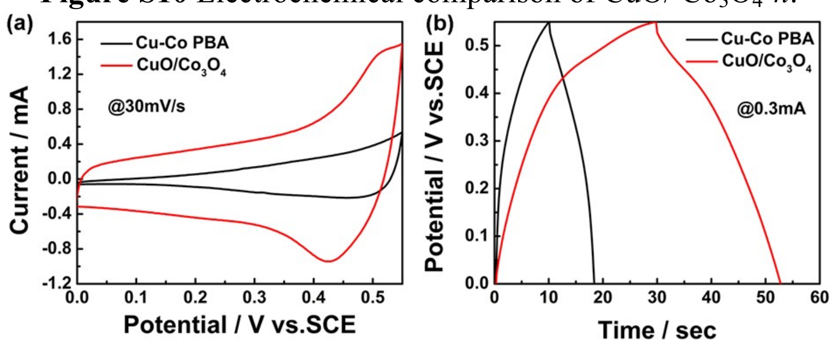

Figure S11 Electrochemical comparison of CuCo-PBA and CuO/ Co_3O_4-4.

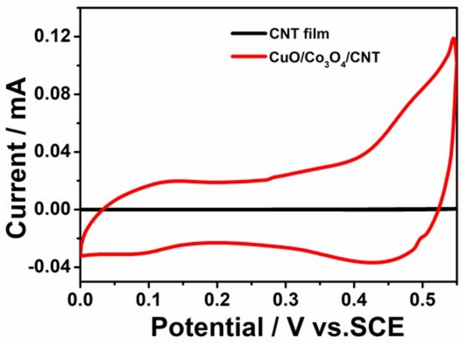

Figure S12 CV comparison of CuO/Co_3O_4-4/CNT and pure CNT film.

The electrochemical properties of the CuCo-PBA and CuO/Co_3O_4 electrodes were investigated in a three-electrode cell with 3 M KOH electrolyte between 0 to 0.55 V. To reach the most favorable electrochemical reaction conditions, we optimized the hydrothermal reaction time with 4 h. The capacitance of CuO/Co_3O_4-n electrodes increase first and then decrease as reaction time increases under 30 mV s^{-1} and 0.3 mA. The areal capacitance of CuO/Co_3O_4-4 electrode is 83.6 mF cm^{-2}.

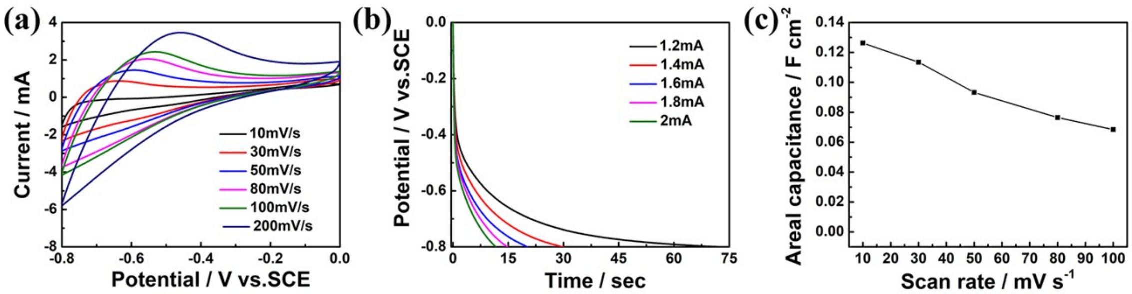

Figure S13 Electrochemical properties of Fe_2O_3.

The electrochemical properties of the Fe_2O_3 electrode was investigated in a three-electrode cell with 3 M KOH electrolyte between -0.8 to 0 V. The areal capacitance of Fe_2O_3 electrode is 195 mF cm^{-2}.

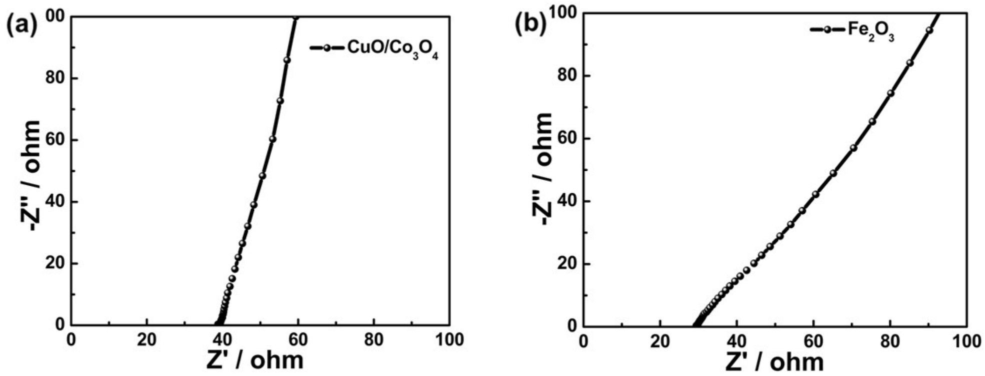

Figure S14 (a) the enlarged plots of Figure 5g at high frequency. (b) the enlarged plots of Figure 5h at high frequency.

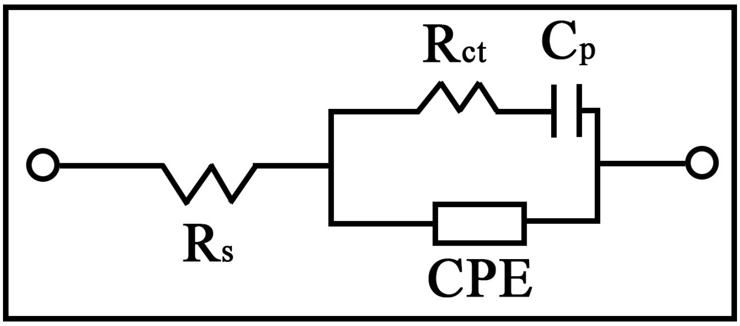

Figure S15 Equivalent circuit diagram of EIS date.

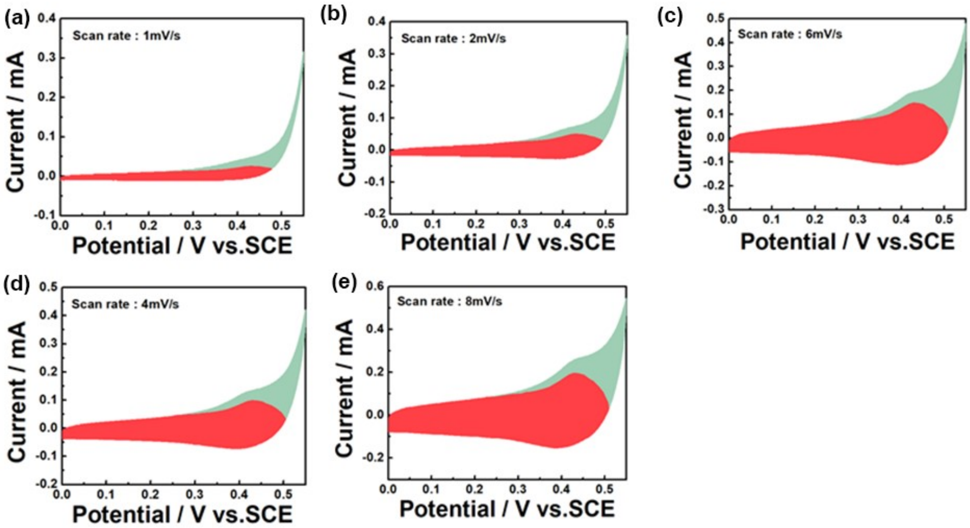

Figure S16 Electrochemical properties of CuO/ Co_3O_4.

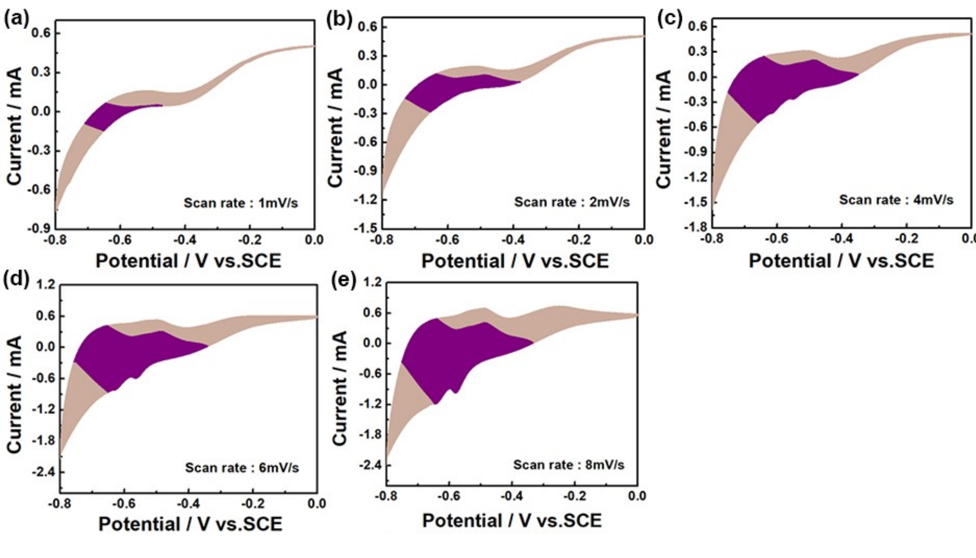

Figure S17 Electrochemical properties of Fe_2O_3.

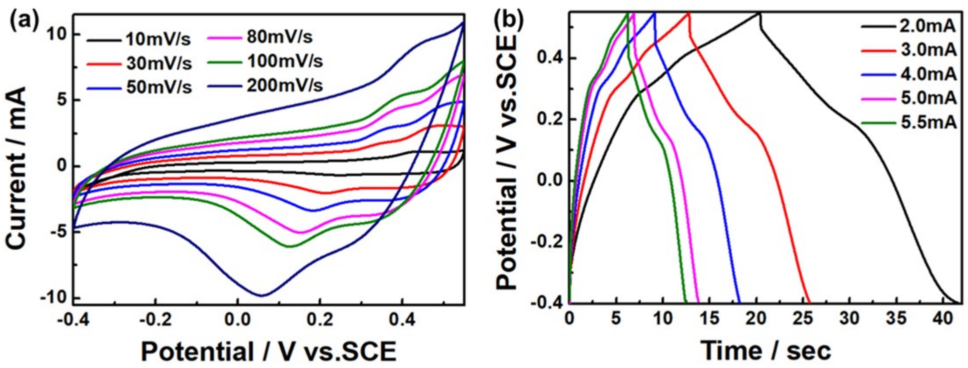

Figure S18 Electrochemical properties of NiO/ Co_3O_4.

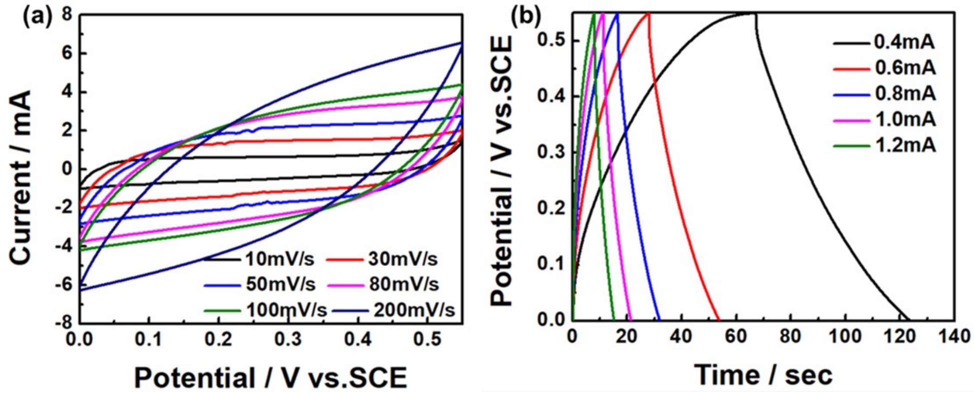

Figure S19 Electrochemical properties of Mn_2O_3/ Co_3O_4.