Electronic Supplementary Information for

Synthesis of amorphous cobalt sulfide polyhedral nanocages for high performance supercapacitors

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Materials. All reagents were of analytical grade and used without further purification.

Synthesis of ZIF-67 nanocrystals. Typically, 249.0 mg (1.0 mmol) of cobalt nitrate hexahydrate and 328.0 mg (4.0 mmol) of 2-methylimidazole were each dissolved in 25.0 mL methanol. The latter clear solution was poured into the former pink solution under stirring with a magnetic bar. Stirring was stopped after combining the component solutions. After 24 h, the purple solid was collected by centrifugation, washed with methanol three times and dried at room-temperature.

Formation of cobalt sulfide nanocages. The as-prepared template was transferred into a round bottomed flask containing 0.187 g thioacetamide (0.1 M) and 25.0 mL ethylene glycol. Then the mixture was refluxed for 1 h under stirring. At last the black product was collected by centrifugation, washed with anhydrous ethanol and dried at 60 °C overnight.

Characterization. The morphology and microstructure of the products were characterized by a transmission electron microscope (TEM, JEOL JEM-1230) with an accelerating voltage of 100 kV, high resolution transmission electron microscope (HR-TEM, JEOL JEM-2100) with an accelerating voltage of 200 kV, and field emission-scanning electron microscope (FE-SEM, ZEISS SUPRATM 55). X-ray diffraction (XRD) patterns were collected on a Rigaku D/Max 2200PC diffractometer with a graphite monochromator and CuKα radiation (λ=0.15418 nm). The X-ray photoelectron spectrum (XPS) was recorded on a PHI-5300 ESCA spectrometer (Perkin Elmer) with its energy analyzer working in the pass energy mode at 35.75 eV, and the AlKα line was used as the excitation source. The binding energy reference was taken at 284.7 eV for the C1s peak arising from surface hydrocarbons. Nitrogen adsorption-desorption data were recorded on a Quadrasorb SI apparatus at liquid nitrogen temperature (T=-196 °C).

Pseudocapacitance performance measurement. The working electrodes were prepared by mixing the as-prepared composites, acetylene black, and polyvinylidene fluoride with the mass ratio 8:1:1. The mixture was grinded adequately to form slurry, then was coated onto nickel foam current collectors (1.0 cm ×1.0 cm), pressed at 10.0 MPa, and dried under vacuum at 60 °C for 24 h. The mass loading is ca.3.0 mg. Cyclic voltammetry (CV) and chronopotentiometry (CP) were performed with a CHI660 electrochemical workstation. All experiments were carried out in a three compartment cell with a working electrode, a platinum plate counter electrode and a Hg/HgO reference electrodes. The electrolyte was 1.0 M KOH aqueous solution.

In order to obtain a well electrochemical performance for the asymmetric supercapacitor, the charge balance between the two electrodes should be followed the relationship $q_+=q_-$, the q is calculated by the formula

$$q=C_S\times\Delta E\times m$$

where the q is the charge stored by electrode, C; Cs is the specific capacitance, $F\cdot g^{-1}$, m is the mass of electrode, g, and ΔE is the potential range for the charge/discharge process, V. According to equation, the ratio of m_+/m_- can be express as follows:

$$m_+/m_-=(C_-\times\Delta E_-)/(C_+\times\Delta E_+)$$

Fig. S1 XRD patterns (a), SEM (b, c) and TEM (d) images of ZIF-67 nanocrystals.

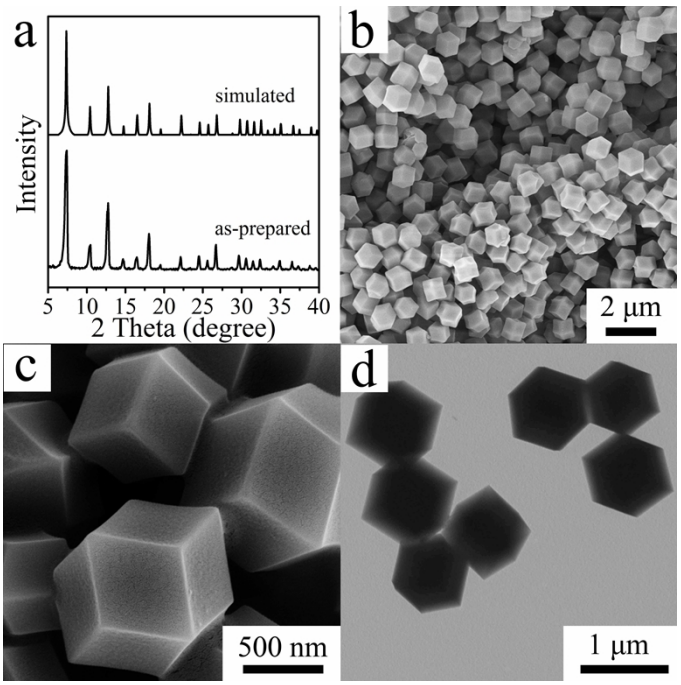

Fig. S2 TEM images of the cobalt sulfide nanocages formed after reaction for 5 mins (a, b) and 20 mins (c, d).

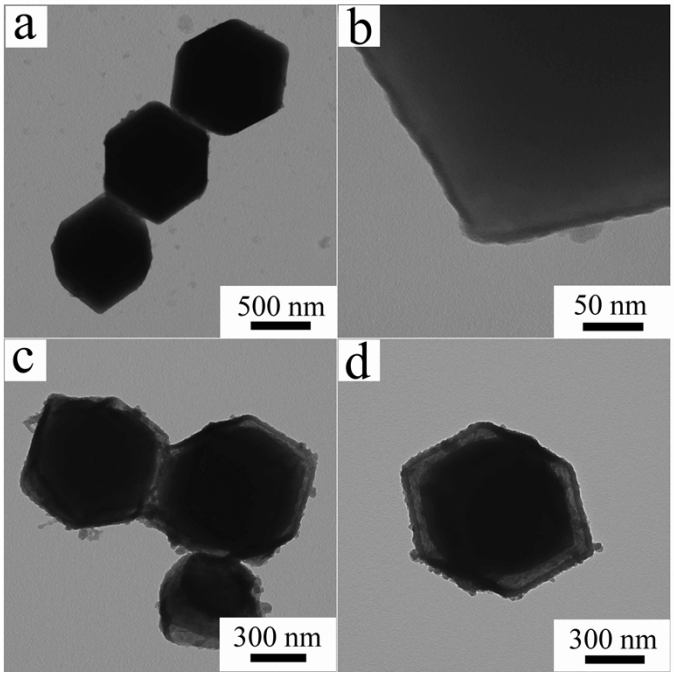

Fig. S3 CoS samples obtained with the thioacetamide-concentration of 0.4 M (a) and 0.02 M (b).

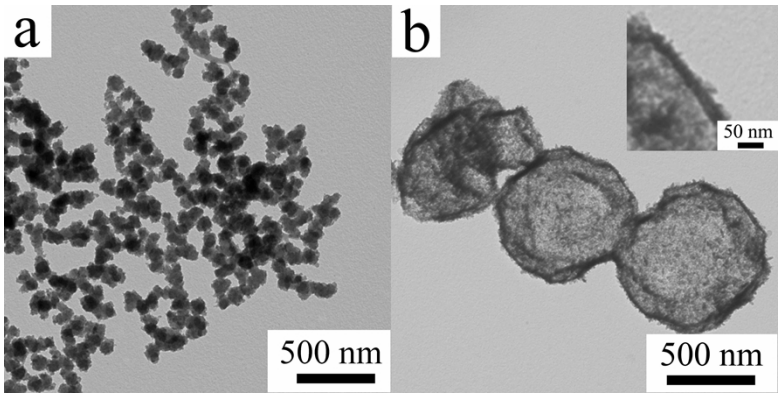

Fig. S4 N_2 adsorption/desorption isotherms (a) and pore-size distribution (b) and CV curves of the three samples (c).

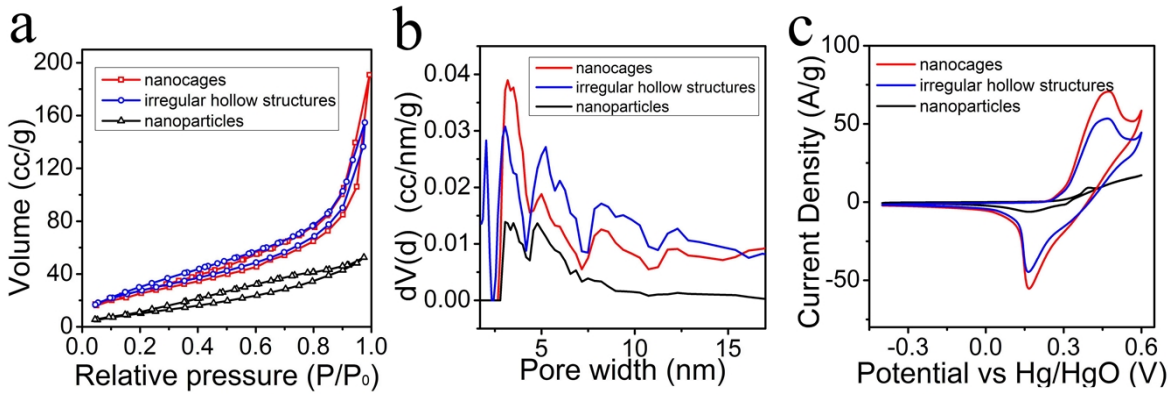

Fig. S5 The cycling performance of the nanocages at 10 $A \cdot g^{-1}$.

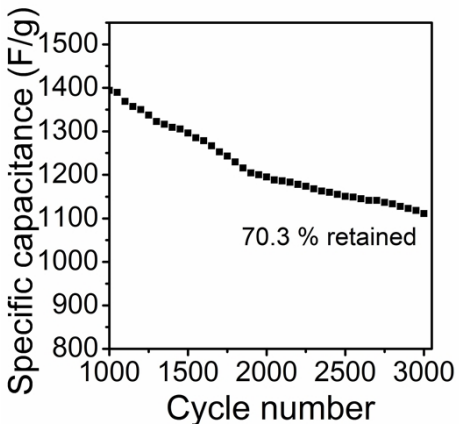

Fig. S6 TEM images of the nanocages (a) and the irregular hollow structures (b) after cycling test.

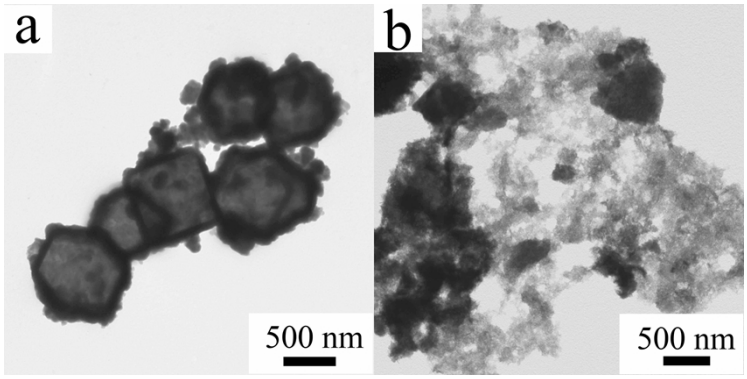

Fig. S7 Electrochemical characterization of the active carbon electrode. (a) CV curves, (b) charge-discharge curves and the specific capacitance is 126.2 $F \cdot g^{-1}$ at 1 $A \cdot g^{-1}$.

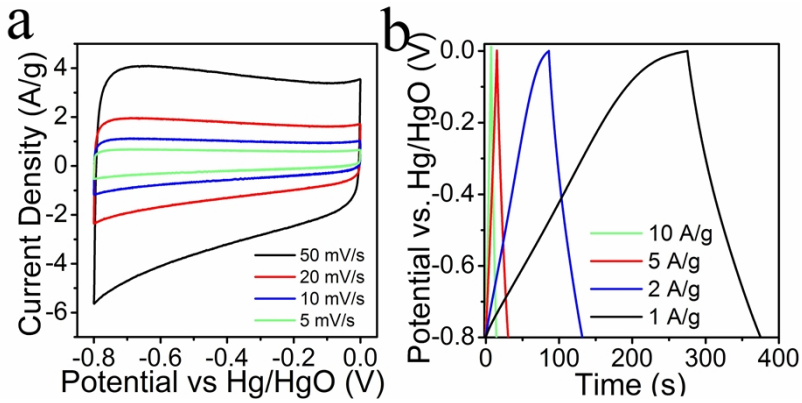

Fig. S8 Electrochemical characterization of asymmetric capacitor. (a) CV curves of the amorphous cobalt sulfide nanocage-active carbon-based asymmetric capacitor at various scan rates in 1M KOH. (b) Charge-discharge curves of the capacitor at various current densities (ranging from 1 to 10 $A \cdot g^{-1}$). (c) Power and energy density of the asymmetric capacitor.