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 CuK\textsubscript{α} radiation (\(\lambda=0.15418\) 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 AlK\textsubscript{α} 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, \( C; C_s \) is the specific capacitance, \( F \cdot g^{-1} \), \( m \) is the mass of electrode, \( g \), and \( \Delta E \) is the potential range for the charge/discharge process, \( V \). According to equation, the ratio of \( \frac{m_+}{m_-} \) can be express as follows:

\[
\frac{m_+}{m_-} = \frac{(C_s \times \Delta E) \times C_+}{(C_s \times \Delta E) \times C_-}
\]

**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** N₂ 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·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 g⁻¹ at 1 A 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 g⁻¹). (c) Power and energy density of the asymmetric capacitor.