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Electronic Supplementary Information

Highly stable hollow bifunctional cobalt sulfides for flexible supercapacitor and hydrogen evolution

C. Ranaveera[a], Z. Wang[a], E. Alqurashi[a], P. K. Kahol[b], R. Dvornic[a], Bipin Kumar Gupta[c], Karthik Ramasamy[d], Aditya D. Mohite[e], Gautam Gupta[e] and Ram K. Gupta[*a]

Experimental Details:

Synthesis of $Co_{1-x}S$:

Nanostructured cobalt sulfide was synthesized using a facile hydrothermal technique. All the reagents used were of analytical reagent grade and used without further purification. For the synthesis of cobalt sulfide, cobalt nitrate $Co(NO_3)_2.6H_2O$ and thioacetamide (TAA) were used. In typical synthesis, 0.873 g of cobalt nitrate and 0.450 g of thioacetamide was dissolved in 36 ml ethylene glycol. After mixing the solutions for 10 min, 300 mg of PVP was added and the mixed solution was transferred to a 45 mL Teflon line stainless steel autoclave and heated at 180 ^oC for 12 h. After 12 h of reaction at 180 ^oC, the reactor was cooled to room temperature naturally. The obtained black precipitate at the bottom of the Teflon container was filtered out and washed several time with deionized water followed by isopropanol. The obtained powder was dried at 60 ^oC for 10 h.

Structural characterizations:

The structural characterization and morphological examination of the synthesized powder were carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). The XRD spectra was recorded with Shimadzu X-ray diffractometer using the 2θ-θ scan with CuKα1 (λ=1.5406 Å) radiation. The surface morphology and elemental composition were performed using a JEOL 7000 FE SEM equipped with energy dispersive X-ray spectroscopy (EDX). Transmission electron microscopy (TEM) analysis was performed using a FEI-Tecnai, 200 kV transmission

electron microscope equipped with a CCD camera for STEM, HAADF detector, and EDX. TEM image non-linear processing was carried out using Gatan digital micrograph version 3.4. The surface area was determined by the Brunauer−Emmett−Teller (BET) adsorption method (Micrometrics, USA, Tristar II 3020 Models). The samples were firstly degassed for 24 hours at a holding temperature of 60 ^{o}C after that the analysis for nitrogen adsorption was done at liquid nitrogen temperature (-196 ^{o}C).

Electrochemical characterizations:

The electrochemical characterization of the cobalt sulfide was performed using a standard three electrode cells. A Versastat4-500 electrochemical workstation (Princeton Applied Research, USA) was used for the electrochemical measurements. A platinum wire and saturated calomel electrode were used as a counter electrode and a reference electrode, respectively. The working electrode was prepared by mixing 80 wt.% of the cobalt sulfide, 10 wt.% of acetylene black and 10 wt.% of polyvinylidene difluoride (PVdF) in the presence of N-methyl pyrrolidinone (NMP). After thoroughly mixing the components, the slurry was pasted onto nickel foam. The prepared electrode was dried at 60°C under vacuum for 10 h. An aqueous solution containing 3M NaOH was used as an electrolyte. The supercapacitor device was fabricated using two working electrodes separated by ion transporting layer (Celgard, 25μm thick, 39% porosity) in alkaline electrolyte. The charge storage capacity of the electrode and device was tested using cyclic voltammetry (CV) and galvanostatic charge-discharge methods. Electrochemical impedance spectroscopy (EIS) measurements were carried out by applying an AC voltage with 10 mV amplitude in a frequency range from 0.05 Hz to 10 kHz at open circuit potential.

HER polarization curve was measured using Versastat4-500 electrochemical workstation with a three-electrode electrochemical cell equipped with a gas flow controlling system. Graphite rod was used as the counter electrode and Ag/AgCl (saturated KCl filled) as the reference electrode. A glassy carbon electrode with a diameter of 5 mm was used as the working electrode. Typically, 10 mg of CoS (or MoS_2)

was dispersed using bath sonicator in 1 ml water-ethanol (1:1 V/V) solution containing 25 µL Nafion solution (5 wt.%). 10 µL of the solution was drop casted over glassy carbon electrode and dried before electrochemical testing. All the electrochemical measurements were conducted in an N_2 saturated 0.1 M H_2SO_4 electrolyte at room temperature.

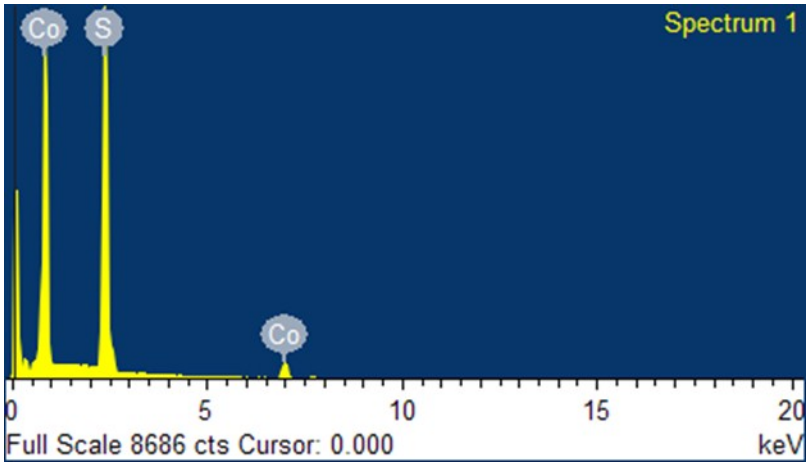

Fig. 1S: EDX patterns of the cobalt sulfides.

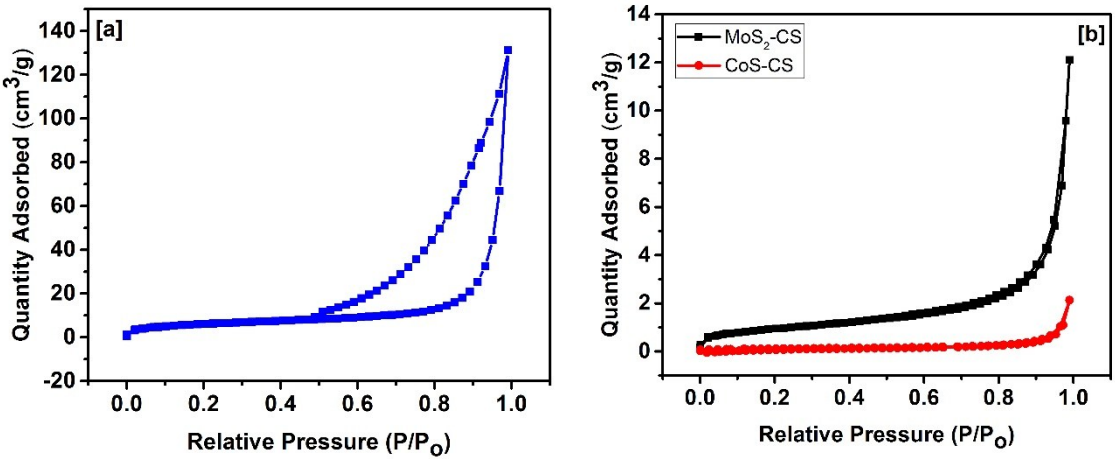

Fig. 2S: Adsorption/desorption isotherm of N_2 (a) for synthesized $Co_{1-x}S$ and (b) commercial samples of MoS_2 and CoS.

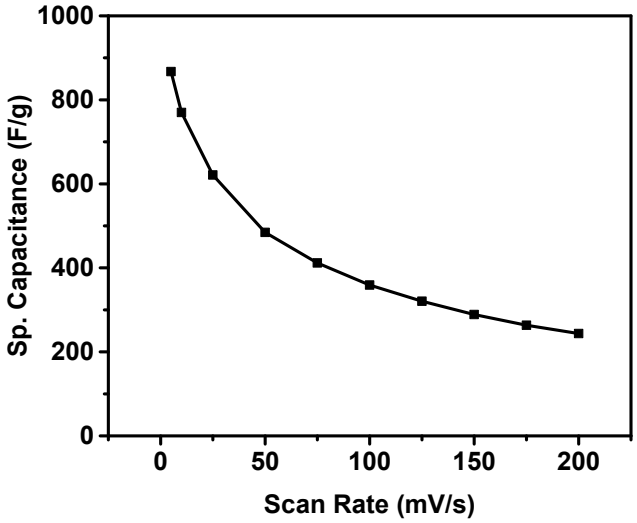

Fig. 3S: Variation of specific capacitance versus scan rate for cobalt sulfide.

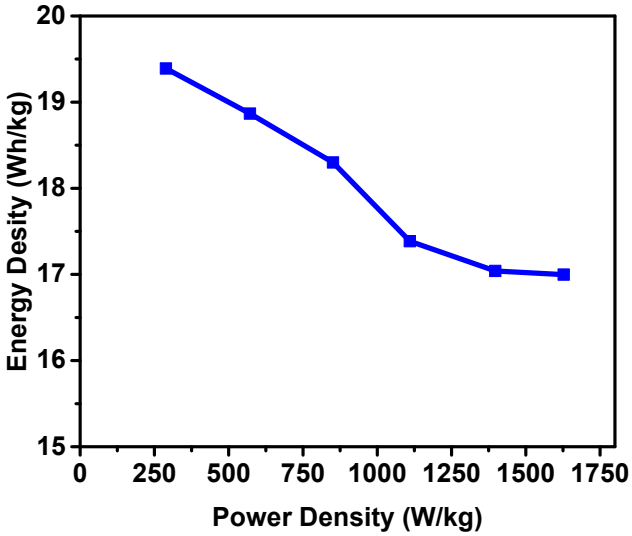

Fig. 4S: Ragone plot for cobalt sulfide.

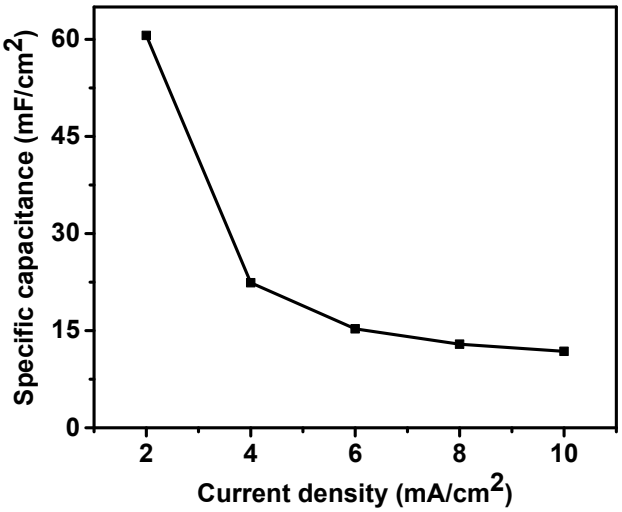

Fig. 5S: Variation of specific capacitance versus scan rate for cobalt sulfide based supercapacitor.

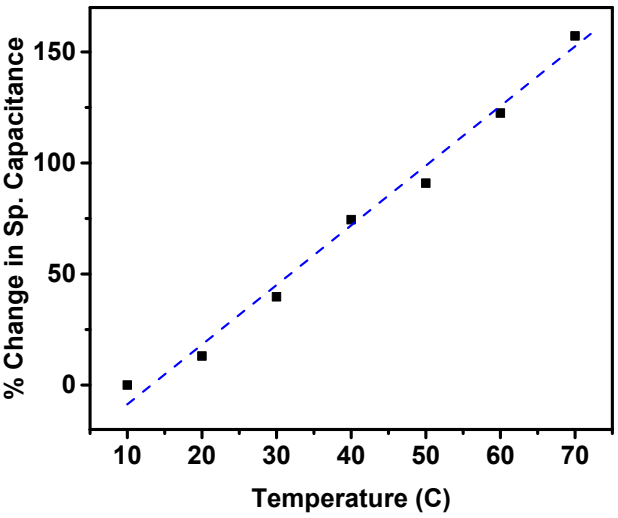

Fig. 6S: % change in specific capacitance as function of temperature for cobalt sulfide based supercapacitor.

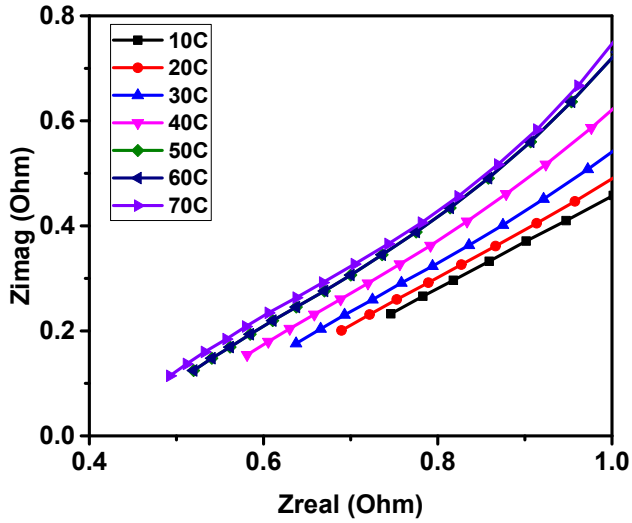

Fig. 7S: Zreal vs. Zimag plots at different temperature for cobalt sulfide based supercapacitor.

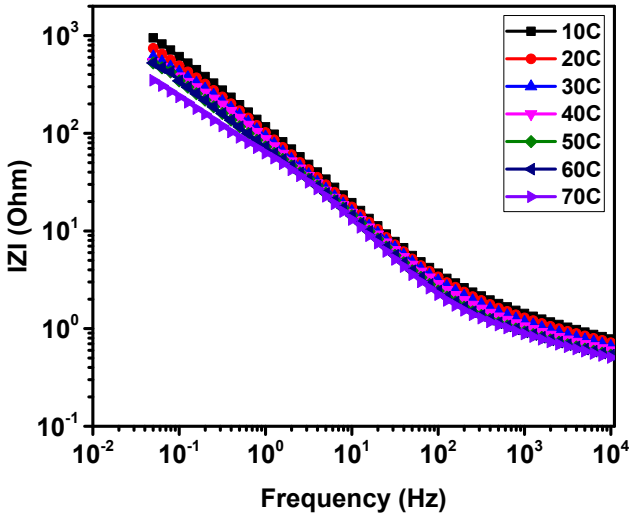

Fig. 8S: IZI versus frequency plot at different temperature for cobalt sulfide based supercapacitor.