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

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Hollow structures of NiAs-type cobalt sulfide have been synthesized by a facile hydrothermal method. These hollow structured cobalt sulfides exhibit excellent electrochemical properties for supercapacitor applications (867 F/g) and respectable hydrogen evolution activity. The symmetrical supercapacitor device fabricated using cobalt sulfide nanostructure showed areal capacitance of 260 mF/cm^2 with good flexibility and high temperature stability. Specific capacitance of the supercapacitor is enhanced over 150 %, when the temperature is raised from 10 to 70 °C.

Over the last few decades, the increasing demand for the energy motivated the scientific community to develop high performance, sustainable, cost-effective and environmentally friendly materials for energy conversion and storage applications[1-4]. Undoubtedly, materials for supercapacitors and hydrogen evolution are among the widely studied ones for these purposes. Supercapacitors are electrochemical energy storage devices primarily appealed for their excellent power density and long cycle life[4-7]. Carbon based electrodes are suitable for delivering the high power density but have low energy density[8]. Nevertheless, in recent years the energy density of supercapacitors has been boosted by the use of metal oxides, which in turn sacrifices the cycle life[4].

Second, energy generation using a cleaner and cheaper method is of high importance due to increasing concerns of carbon emission. Hydrogen generation by splitting water is highly desired. Hydrogen evolution reaction (HER) is one of the key steps in water splitting process[9]. Ideally, the thermodynamic potential for hydrogen evolution reaction should be at 0 V (*vs.* SHE). However, without an efficient catalyst, this reaction occurs at high overpotential[10]. Presently, platinum is the most effective and durable catalyst for hydrogen evolution reaction, but its wide spread use is precluded due to its high cost and limited availability.

At this juncture it is essential to develop cost effective, sustainable and stable materials for both supercapacitor and HER applications. Recently, transition metal chalcogenides have attracted considerable attention for energy applications such as fuel cells, supercapacitors and batteries due to their high abundance, low cost and decent performance[2, 11-15] Wang *et al* have synthesized 3D flower-like MoS_2 nanostructures and were used as an electrode for high-performance electrochemical capacitors[16]. The MoS_2 electrode showed a specific capacitance of 168 F/g and retained 92.6% of capacitance even after 3,000 cycles. Soon *et al* have reported a MoS_2 based supercapacitor having a capacitance of 8 mF/cm^2 [17]. Hierarchically porous nickel sulfide has been synthesized for both HER and oxygen evolution reaction (OER)[18]. The synthesized nickel sulfide showed overpotentials of 60 mV for HER and 180 mV for OER in 1.0 M KOH at a current density of 10 mA/cm^2, respectively. Sharma *et al* have synthesised flower like ZnS for charge storage application[19]. They observed a high specific capacitance (226 F/g) and specific capacitance was observed to decrease by 60 % on increasing the scan rate from 20 to 200 mV/s. Other metal sulfide such as WS_2 is also synthesized for HER, supercapacitors and batteries applications[20-22]. As an important member of the transition metal sulfide family, cobalt sulfide is considered to be one of the promising candidates for such applications. Accordingly, various phases of cobalt sulfides have been synthesized and studied for supercapacitor and HER applications [23,24-29].

Xing *et al* have synthesized octahedron-shaped CoS_2 crystals using a hydrothermal method for their application in supercapacitors[30]. These CoS_2 crystals showed a specific capacitance of 237 F/g at 1 A/g with only a loss of 7.4% in the specific capacitance after 2000 cycles. Sphere like CoS nanostructures were synthesized and used as an electrode material for charge storage applications[31]. These sphere like CoS showed very stable electrochemical performance with only about 13% reduction in charge storage capacity of the available capacitance (363 F/g) on increasing the scan rate by 10 times. Ray *et at* have used a facile electrochemical technique to fabricate titania nanotube-CoS composite electrode for supercapacitor applications[32]. Cyclic voltammetric measurements presented a very high specific capacitance (370 F/g) with great cycle stability in KOH electrolyte. Since various phases of cobalt sulfides

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have been found useful for energy storage and catalytic applications, it is highly desirable to synthesize cobalt sulfide using a facile and efficient method to explore its multifunctionality. Herein, we report a facile one step hydrothermal synthesis of hollow structured NiAs type cobalt sulfide and investigate the material for supercapacitor and HER applications. Our investigations show excellent electrochemical properties for supercapacitor applications with a specific capacitance of 867 F/g and an electrocatalyst for hydrogen evolution reaction (Tafel slope of 97 mV/decade). The high performance of the cobalt sulfide could be due to the unique morphology.

Hollow structured cobalt sulfide was synthesized by reacting cobalt nitrate with thioacetamide in ethylene glycol under a hydrothermal condition at 180 °C for 12 h (details in ESI). Powder XRD pattern of the black precipitate from the hydrothermal reaction showed diffraction planes, predominantly matching with NiAs-type hexagonal $Co_{1-x}S$ phase of cobalt sulfide (JCPDS file: 42-0826). The diffraction peaks can be indexed to the (010), (011), (012), (120) planes of $Co_{1-x}S$ (Fig. 1a). Scanning electron microscope image of the cobalt sulfide obtained by a hydrothermal reaction exhibited irregular shaped granules (Fig. 1b). The ratio of cobalt to sulfur determined from SEM-EDX was found to be 0.98, close to the expected composition for $Co_{1-x}S$ (Fig. 1S, ESI). To gain morphological insight, TEM imaging was performed. TEM image in Fig. 1c shows nearly uniform hollow ring like structures that are composed of pseudo-spherical nanocrystals. It is widely accepted that the hollow structures are consequence of difference in diffusion rates of constituent elements[33]. A similar hollow structure has also been reported by microwave assisted synthesis of cobalt sulfide[33]. Lattice distance measured from HRTEM image (Fig. 1d) of $Co_{1-x}S$ nanocrystals was close to 0.293 nm corresponding to (010) plane. In addition, we have carried out BET nitrogen adsorption/desorption isotherm measurements to determine the surface area of the sample (Fig. 2S, ESI). The hysteresis loop in the isotherm of the synthesized $Co_{1-x}S$ is the indication of capillary condensation, which arises due to different mechanisms of adsorption/desorption in micropores. The synthesized $Co_{1-x}S$ showed a specific surface area of 23.9 m^2/g which is much higher than commercial samples of CoS (0.39 m^2/g and MoS_2 (3.33 m^2/g).

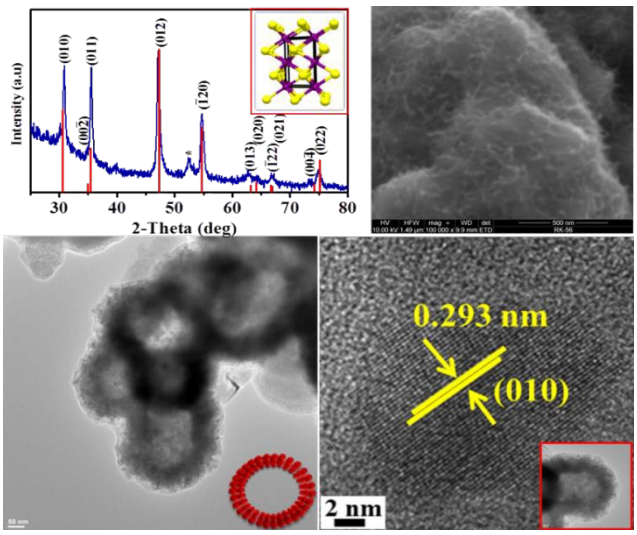

Fig. 1: (a) XRD pattern (Inset: crystals structure of $Co_{1-x}S$, (b) SEM image, (c) TEM image (Inset: Schematic of hollow structure composed of nanocrystals), and (d) HRTEM image of synthesized cobalt sulfide (inset: Low magnification TEM image of hollow structure.

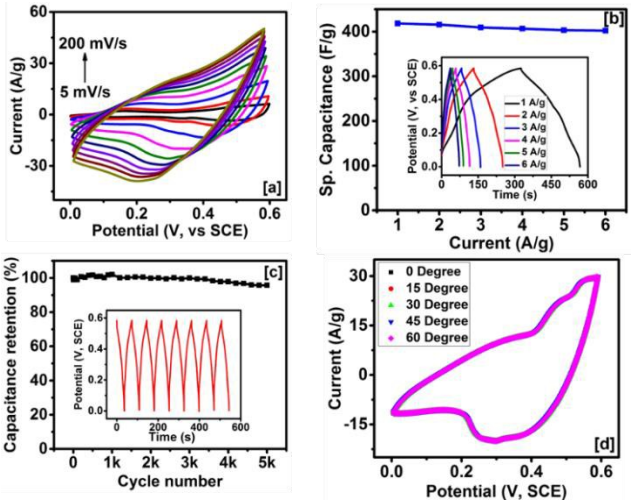

Fig. 2 (a) CV curves at various scan rates, (b) variation of specific capacitance with applied current (inset figure show potential-time curves at different applied currents, (c) capacitance retention as a function of number of charge-discharge cycles (inset figure shows first few cycles of charge-discharge curves), and (d) CV curves at various bending angles of cobalt sulfide electrode.

The electrochemical properties of electrode prepared using $Co_{1-x}S$ hollow structures were studied using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS). The CV measurements of $Co_{1-x}S$ electrode in alkaline electrolyte (3M NaOH) displayed non-rectangular shape curves with quasi-reversible redox waves in potential range of 0 to 0.6 V (Fig. 2a). The unambiguous appearance of redox waves, confirms the pseudocapacitive behaviour of $Co_{1-x}S$. As evident, the charge-storage mechanism in CoS is significantly Faradic in nature than capacitive type. The Fadadic reaction occurring on the surface of CoS electrode in alkaline media is given below[31]:

$$CoS + OH^- \leftrightarrow CoSOH + e^- \quad \text{..... (1)}$$

$$CoSOH + OH^- \leftrightarrow CoSO + H_2O + e^- \quad \text{..... (2)}$$

The specific capacitance of $Co_{1-x}S$ electrode estimated from CV curves was found to be 867 F/g at 5 mV/s (Fig. 3S, ESI). Further, GCD measurements exhibit symmetrical and non-linear charge-discharge characteristics, confirming the pesudocapacitance behaviour of the electrode (inset of Fig. 2b). The specific capacitance of cobalt sulfide electrode determined from GCD measurements is about 420 F/g at 1 A/g, which is significantly higher than the value obtained for CoS hollow nanosheets and hollow nanoprisms[31, 33]. Interestingly, the specific capacitance value was nearly retained (402 F/g at 6 A/g) even at higher current density (Fig. 2b), suggesting excellent rate stability of $Co_{1-x}S$ hollow structures. In addition, we have evaluated the cyclic stability of the cobalt sulfide electrode using GCD measurements. From Fig. 2c, it can be witnessed that the specific capacitance was almost preserved even after 5,000 charge-discharge cycles, confirming their high electrochemical stability. It is noteworthy that electrode using CoS_2 ellipsoids lost nearly 50 % of specific capacitance within 1,000 charge-discharge cycles[34]. Furthermore, we have tested the flexibility of the cobalt sulfide electrodes by carrying out CV measurements at different bending angles. The shape and size of the CV curves were found to be identical at different bending angles (Fig. 2d), suggesting that $Co_{1-x}S$ hollow structures are exceptional candidates for flexible energy storage devices. The

variation of the specific energy density versus power density (Ragone plot) for cobalt sulfide is shown in Fig. 4S, (ESI). The highest specific energy density of 19.4 Wh/kg and power density of 2644 W/kg was observed.

We fabricated the supercapacitor device by sandwiching an ion transporting layer between two cobalt sulfide electrodes (inset of Fig. 3b). Fig. 3a shows the CV curves of the supercapacitor device at different scan rates. The shape of the voltammogram at various scan rates are similar in nature, suggesting high charge transfer stability of the device even at high scan rates. The near rectangular shape of the CV curves indicates a near ideal capacitive behaviour. The variation of specific capacitance as a function of scan rate for the device is shown in Fig. 3b. The specific capacitance of the device was observed to decrease with increase in the scan rate. The highest areal capacitance of 261 mF/cm^2 was observed at a scan rate of 5 mV/s. It was observed that specific capacitance of the devices decreases with increasing scan rate, which is due to insufficient time for the electrolyte to form an electrochemical double layer capacitor at cobalt sulfide electrode. The galvanostatic charge-discharge measurements were also performed to study the charge storage capacity of the device. The charge storage capacity of the device decreases with increasing current density (Fig. 5S, ESI). A specific capacitance of 60 mF/cm^2 was observed at 2 mA/cm^2 of current density. Further, the effect of temperature on the performance of the supercapacitor device was studied. The CV curves of the device at various temperatures are shown in Fig. 3c. The area under the CV curves increases with increasing temperature, indicating improvement in charge storage capacity of the device. It was observed that the charge storage capacity of the device increases over 150 % by increasing temperature from 10 ^oC to 70 ^oC (Fig. 6S, ESI). The improved performance of the cobalt sulfide based supercapacitor device could be due to activation of the cobalt sulfide sites at higher temperature. In addition, the improvement could be due to and improved mobility of the electrolyte ions and lower series resistance at higher temperature.

The effect of temperature on the electrochemical behaviour of the supercapacitor was further investigated using electrochemical impedance spectroscopy (EIS). The variation of real and imaginary

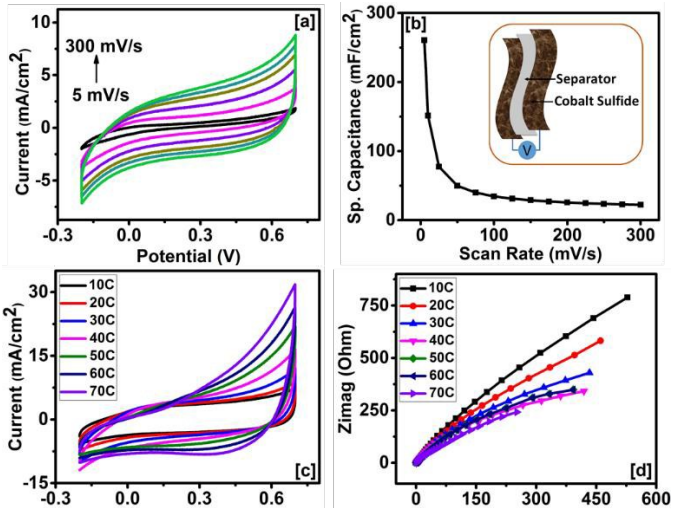

Fig. 3 (a) CV curves of supercapacitor device at various scan rate at room temperature, (b) variation of specific capacitance as a function of scan rate (inset figure show schematic diagram of the supercapacitor device), (c) CV curves of supercapacitor device at different temperature, and (d) Zreal vs. Zimag plots for the device at different temperature.

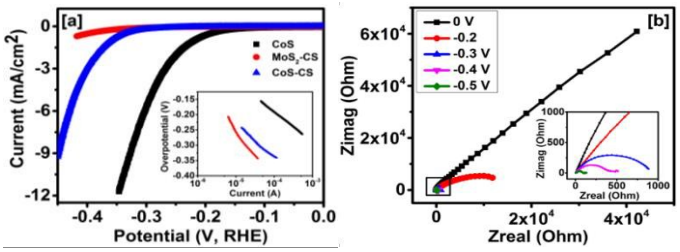

Fig. 4 (a) Polarization curves for synthesized cobalt sulfide (CoS), commercially samples of molybdenum sulfide (MoS_2-CS) and cobalt sulfide (CoS-CS) (inset figure show the Tafel plots) and (b) *Zreal* vs. *Zimag* plots at different potentials for cobalt sulfide.

impedance of the supercapacitor device at various temperatures is shown in Fig. 3d. The real and imaginary impedance of the device decreases with increasing temperature. The equivalent series resistance (ESR) of the supercapacitor device decreases with increasing temperature (Fig. 7S, ESI). The decrease in ESR with temperature could affect the charge storage properties of the device. The increase in the temperature enhances the mobility of the electrolyte ions and thus increases the conductivity of the electrolyte ions[35]. The effect of temperature on the total impedance of the device is shown in Fig. 8S, ESI. It was observed that the impedance of the cobalt sulfide based supercapacitor device decreases with increasing temperature. The total impedance of the supercapacitor device was higher at lower frequency compared to that of at higher frequency. Our observations based on electrochemical characterizations suggest that the cobalt sulfide based supercapacitor device performs even better at elevated temperature than at room temperature.

The HER activity of the synthesized cobalt sulfide was also studied using glassy carbon working electrode with a standard rotating disk electrode instrument. All measurements were performed in 1N H_2SO_4 (aq) electrolyte under continuously purging with nitrogen gas (details in ESI). We have compared the HER activity of commercially available molybdenum sulfide (MoS_2-CS, Sigma, USA) and cobalt sulfide (CoS-CS, Strem Chemicals, USA) with our cobalt sulfide hollow structures. The polarization curves for the samples are shown in Fig. 4a. Cobalt sulfide showed a lower onset potential (0.21 V *vs* RHE) compare to MoS_2-CS (0.31 V *vs* RHE) and CoS-CS (0.35 V *vs* RHE). Our synthesized cobalt sulfide displayed about 60 and 30 times higher current density at 0.30 V (*vs* RHE) compared with MoS_2-CS and CoS-CS, respectively. The HER activity was further analysed using corresponding Tafel plots (inset of Fig. 4a). Tafel slope of 97 mV/decade, 174 mV/decade and 113 mV/decade was observed for synthesized cobalt sulfide, MoS2-CS and CoS-CS, respectively. Lukowski *et al* have reported a Tafel slope of 112 mV/decade for as such synthesized nanostructured MoS_2[36]. A Tafel slope of 75 mV/decade and 90 mV/decade was reported for CoS synthesized using microwave assisted and solvothermal methods, respectively[33]. Sun *et al* have used electrodeposited cobalt-sulfide for HER application and reported a Tafel slope of 93 mV/s in phosphate buffer solution[26]. CoS_2 synthesized using hydrothermal method showed a Tafel slope of 72 mV/s in acidic media[37]. Peng *et al* have synthesized CoS_2/RGO/CNT nanocomposites for HER[38]. A Tafel slope of about 51, 82 and 148 mV/s was observed for CoS_2/RGO/CNT, CoS_2/RGO and CoS_2, respectively. The rate of hydrogen evolution is limited either by proton adsorption onto an active site or evolution of the formed hydrogen from the surface. A high Tafel slope (120 mV/ decade) is indicative of proton adsorption (Volmer step) as the rate-limiting step, while a lower Tafel slope (30 or 40 mV/decade)

indicates that the evolution of molecular hydrogen from the catalyst is rate limiting (Heyrovsky or Tafel step, respectively). Tafel slope of 97 mV/decade for $Co_{1-x}S$ suggest typical Volmer–Tafel route with the Volmer step as the rate determining step[39]. Electrochemical impedance spectra of the cobalt sulfide were recorded at various potentials (Fig. 4b). As seen in the EIS spectra, the arc at zero potential converges to a semi-circle at negative potentials. A decrease in semi-circle diameter is observed with increase in negative potential. The charge-transfer resistance determined from the semicircle registered at low frequencies was found to be overpotential-dependent. Similar observation was reported for molybdenum phosphide[9].

In conclusion, we have synthesized nanostructured cobalt sulfide by a facile hydrothermal method. The charge storage capacity and hydrogen evolution reaction activity were investigated using electrochemical methods. The highest specific capacitance of 867 F/g was observed at scan rate of 5 mV/s in cyclic voltammetry measurements. Cobalt sulfide showed a very stable electrochemical behaviour up to 5,000 cycles of charge-discharge study with highly flexible nature. The symmetrical supercapacitor device showed an areal capacitance of about 260 mF/cm^2 which improved over 150 % on raising the device temperature from 10 to 70 °C. The HER activity of cobalt sulfide was observed to be better than commercially available molybdenum sulfide. Our study suggests that cobalt sulfide could be used for high temperature operable flexible energy storage devices and an electrocatalyst for hydrogen evolution reaction.

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Author contributions

RKG designed the experiments, run some structural and electrochemical characterization of the devices, interpret and analyze the data, and prepared the manuscript. CR, CZ, and EA helped in synthesis and performed some electrochemical characterizations. KR performed TEM measurement. GG and AM guided the hydrogen evolution studies. PK, PD, KR, BKG and GG reviewed the manuscript. All the authors reviewed and commented on the manuscript.

Additional information

The authors declare no competing financial interests. Requests for materials should be addressed to RKG.

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Graphical abstract

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

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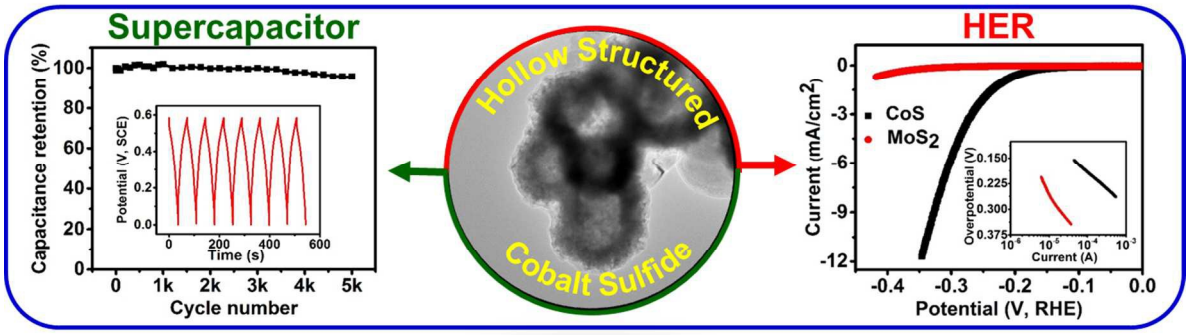

Hollow structured cobalt sulfide exhibits excellent electrochemical properties for highly stable flexible supercapacitor and hydrogen evolution reaction (HER).