



# A high-performance flexible solid-state supercapacitor based on Li-ion intercalation into tunnel-structure iron sulfide



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## ABSTRACT

A flexible solid-state supercapacitor based on iron sulfide (FeS<sub>2</sub>) nanospheres supported on carbon-paper is fabricated, which exhibits excellent electrochemical performance such as, high capacitance of 484 F g<sup>-1</sup> at a scan rate of 5 mVs<sup>-1</sup>, good rate capability, and excellent cycling stability (95.7% after 5000 cycles). The supercapacitor achieves high energy density of 44 Wh kg<sup>-1</sup> at power density of 175 W kg<sup>-1</sup> with high coulombic efficiency (97%). Three charged supercapacitors connected in series can power 12 green-color light-emitting-diodes (LED, 3.0 V, 20 mA) for 5.5 minutes. To understand the detailed electrochemistry, we have carried out both experimental and theoretical investigations. The pseudocapacitive characteristics of the FeS<sub>2</sub> nanospheres are systematically investigated by a single electrode in aqueous electrolyte. According to our structural analysis, the FeS<sub>2</sub> nanospheres have orthorhombic structure, where Fe atoms are surrounded by 6 S atoms to form a FeS<sub>6</sub> octahedron. These octahedrons are connected to form a network structure, which provide tunnels (2.55 × 4.77 Å). With all the evidence, we believe that the FeS<sub>2</sub> nanospheres could be a promising material for supercapacitor electrodes.

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## 1. Introduction

Among the various energy storage devices, supercapacitors (SCs) are considered as one of the most important green energy storage devices with advantages of high power density, good operational safety and long life span [1,2]. Nanostructure electrode materials provide better accommodation of strains during ion intercalation/de-intercalation in Faradaic process, which enhances the performance of supercapacitors. Additionally, porous or nano-network structure would increase electrode-electrolyte contacting area and promote ion diffusion [3]. These effects surely improve rate capability and capacity of various materials, leading to better performance of supercapacitors. Therefore, developing nanostructured electrode materials with superior electrochemical performance is highly desirable. Recently, nanostructured transition metal chalcogenides (TMCs) have attracted more attention as a new class of electrode material for supercapacitors. TMCs have achieved better performance comparing with the carbon or transition metal oxides (TMOs) based materials [4,5].

Experimental investigations have revealed that the redox reactions among different valence states of metal ions in TMCs are similar to the transition metal oxides (TMOs) [4–6]. The mixed-valence chalcogenides are of significance as most of them exhibit interesting electrical or magnetic properties, such as metallic conductivity [7,8] and superconductivity [9]. As the size of S<sup>2-</sup> and Se<sup>2-</sup> is larger than that of O<sup>2-</sup>, the polarization of anion framework is larger; this benefits the mobility of cations in overcoming deformation from the ion intercalation. The other advantage is the higher charge negativity of the anion framework, which can enhance the cation density and promote ion conductivity. There are many reports on the supercapacitors based on different types of TMCs, such as copper sulfide [4], nickel sulfide [10], zinc sulfide [11], cobalt sulfide [12], molybdenum sulfide [13] and nickel-cobalt sulfide [14] and so on. Wan et al. reported hydrothermal synthesis of cobalt sulfide (CoS) nanotubes, which exhibits a specific capacitance of 285 F g<sup>-1</sup> in 6 M KOH aqueous electrolyte [12]. Dai et al. reported hydrothermal synthesis of C/KCu<sub>7</sub>S<sub>4</sub> wires based symmetric SC, which shows excellent electrochemical performance with specific capacitance of 469 mF cm<sup>-2</sup> in LiCl-PVA solid electrolyte [15]. Ratha et al. reported hydrothermal synthesis of layered tungsten disulfide/reduced graphene oxide

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composite, which exhibits a high capacitance of  $350 \text{ F g}^{-1}$  in 1 M of  $\text{Na}_2\text{SO}_4$  aqueous electrolyte [16].

Among different crystal structures, layered and tunnel structures would be the best option for high performance pseudocapacitors [8,17] and have recently attracted much attention. These structures provide efficient pathways for ions insertion or extraction, which enhance total charge storage of electrodes [9]. Electrode materials with tunnel structures such as  $\alpha$ ,  $\beta$ - $\text{MnO}_2$  [18],  $\text{Mn}_3\text{O}_2$  [19] and  $\text{KCu}_7\text{S}_4$  [17] have one-dimensional tunnels and exhibit excellent electrochemical charge storage performance. Similarly, iron sulfide ( $\text{FeS}_2$ ) possesses a network structure by  $\text{FeS}_6$  octahedrons. In orthorhombic  $\text{FeS}_2$ , Fe atom is surrounded by 6 S atoms to form  $\text{FeS}_6$  octahedron, and these  $\text{FeS}_6$  octahedrons are connected to form network structure. Such network structure of the octahedrons could provide fast electron transmission and the tunnels along c direction with cross-section size could offer diffusion paths for the ion intercalation/de-intercalation during the charging/discharging process [20]. Therefore, it should be an interesting work to investigate the supercapacitor behaviors of the nanostructured iron sulfide.

In this study, the iron sulfide nanospheres ( $\text{FeS}_2$ ) assembled by nanoparticles are synthesized by the hydrothermal method. The  $\text{FeS}_2$  nanospheres supported on carbon paper (CP) exhibits the large specific capacitance of  $852.3 \text{ F g}^{-1}$  in LiCl liquid electrolyte at a scan rate of  $10 \text{ mVs}^{-1}$  with excellent stability. The  $\text{FeS}_2$ -CP is directly served as binder free electrode in symmetric flexible solid-state supercapacitors. The  $\text{FeS}_2$ -CP solid-state supercapacitor exhibits large specific capacitance of  $484 \text{ F g}^{-1}$  at scan rate of  $5 \text{ mVs}^{-1}$  with good stability. A maximum energy density of  $44 \text{ Wh/kg}$  at a power density of  $175 \text{ W/kg}$  is attained with 97% of coulomb efficiency. Three supercapacitors connected in series can charged up to 3 V and power 12 green color light-emitting-diodes (3.0 V, 20 mA) effectively for 5.5 minutes. This work indicates that the  $\text{FeS}_2$  is promising material for supercapacitors due to the specific tunnel structure of  $\text{FeS}_2$  and the nanoparticle aggregated spheres.

## 2. Experimental and calculation

### 2.1. Synthesis of $\text{FeS}_2$ nanospheres

The  $\text{FeS}_2$  nanospheres is synthesized by simple hydrothermal process, in a typical experiment, 2 mmol of iron nitrate hydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) was first mixed in 20 mL of distilled water under constant stirring for 10 min to get a clear solution. Then 1 mL of ethylenediamine (EN) was added into the solution drop-wise and the solution turned to dark red under stirring for 30 min. Finally, 1 mL of carbon disulfide ( $\text{CS}_2$ ) was introduced into the above solution as a sulfur source and further stirred for another 30 min. After that, the solution was transferred into a Teflon-lined stainless autoclave of 50 mL capacity and then Teflon autoclave was put into  $200^\circ\text{C}$  preheated furnace for 24 hours. After completing reaction, the autoclave was cool down to room temperature naturally and the precipitates were washed with ethanol and deionized water. The final product was dried in an electric oven at  $60^\circ\text{C}$  for 6 hours. The schematic demonstration of the synthesis process for the  $\text{FeS}_2$  nanospheres is illustrated in Fig. S1A.

### 2.2. Preparation of single electrode and all-solid-state-supercapacitors

Carbon paper (CP) and all other chemicals were purchased from Aladdin and used without any further processing. CP is used as a substrate for the fabrication of single electrode and all-solid-state supercapacitor. The as-prepared  $\text{FeS}_2$ -nanospheres were deposited into a piece of CP ( $2 \text{ cm}^2$ ) by vacuum filtration pump and dried at  $60^\circ\text{C}$ . In the fabrication process of all-solid-state supercapacitor; first, the CP was cut into pieces of  $4 \times 2 \text{ cm}^2$  and  $\text{FeS}_2$  nanospheres

were deposited on the pieces of CP using a simple vacuum filtration pump and dried for 1 hour at  $65^\circ\text{C}$ . The active mass of  $\text{FeS}_2$  nanosphere on the CP was approximately  $1.0 \text{ mg cm}^{-2}$ , carefully weighted by an electronic balance before and after the deposition. The two pieces of  $\text{FeS}_2$ -nanospheres coated CPs were face-to-face sandwiched with a separator and thin layer of LiCl-PVA solid electrolyte. The PVA-LiCl electrolyte has a thick layer of 0.45 mm in in supercapacitor device and its ionic conductivity is  $0.15 \text{ S cm}^{-1}$ . PVA-LiCl gel electrolyte was simply prepared as follow: 12.6 g LiCl was mixed with 60 mL deionized water and then 6 g PVA powder was added. The whole mixture was heated to  $85^\circ\text{C}$  under vigorous stirring until the solution becomes clear. The schematic demonstration of the fabrication method of flexible all-solid-state supercapacitor based on the  $\text{FeS}_2$ -CP is shown in Fig. S1B.

### 2.3. Material Characterizations

The crystallographic structure of the as-prepared  $\text{FeS}_2$ -nanospheres was characterized by X-ray powder diffraction (XRD) (PANalyticalX'Pert Powder, Cu  $\text{K}\alpha$  radiation). The surface morphology of the  $\text{FeS}_2$  product was investigated by field emission scanning electron microscope (FEI Nova 400 FEG-SEM) and a transmission electron microscope (TEM, TECNAI20 Philips). The BET surface area was calculated using the multipoint Brunauer-Emmett-Teller (BET) method at 77.0 K with a quantachrome (NOVA4200e). The Nitrogen absorption and desorption isotherms were used to investigate the pore size distribution by Barrett-Joyner-Halenda (BJH).

### 2.4. Electrochemical Measurements

The cyclic voltammetric analysis (CV) and galvanostatic charge-discharge (GCD) measurements were conducted using an electrochemical workstation (CHI 660D). The electrochemical impedance spectroscopy (EIS) measurements were carried out at open circuit potential in the frequency range of 100 mHz to 100 kHz. The electrochemical performance of  $\text{FeS}_2$ -nanospheres based electrode was investigated using three electrode system in 1 M LiCl liquid electrolyte. The as-fabricated  $\text{FeS}_2$ -CPs, platinum foil and saturated calomel electrode were used as working electrode, counter electrode and reference electrode, respectively.

### 2.5. Theoretical calculation

In order to investigate the possible  $\text{Li}^+$  intercalations in orthorhombic  $\text{FeS}_2$ , first principles calculations based on density functional theory (DFT) were carried out. All calculations are accomplished using a plane wave basis set and the projector augmented wave (PAW) method as implemented in the Vienna Ab initio Simulation Package (VASP) [17]. The Perdew-Burke-Ernzerhof (PBE) of the spin-polarized generalized gradient approximation (GGA) was used for the exchange-correlation function [21,22]. A cutoff energy of 500 eV was employed for the plane wave basis set and the geometry optimizations were converged to a force cutoff of  $0.01 \text{ eV/\AA}$ .

## 3. Results and discussion

### 3.1. Morphological characterizations

The morphology of the active material directly influences the performance and stability of the supercapacitor. The FE-SEM image of the as-synthesized  $\text{FeS}_2$ , which is composed of well-dispersed spheres with average diameter of about  $1.3 \mu\text{m}$  as depicted in Fig. 1A. The high resolution FE-SEM image is shown in Fig. 1B, which confirms that the surface of spheres is composed of

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