

Supporting Information

Nano iron pyrite (FeS₂) exhibits bi-functional electrode character

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1. Synthesis of FeS₂ nano-particles: The synthesis of FeS₂ can be divide in two parts first is polysulfide preparation and then synthesized polysulfide used for further FeS₂ nano partical preparation.

1.1. Preparation of polysulfide: We have taken 3.2 gm of sodium hydroxide and mix it with deionized water to make it to 100ml. Then we divided this solution into two equal parts (Part A and Part B). In Part A, a stream of H₂S gas was passed for approximately half an hour and after that we mixed this with part B solution and added 1.28 gm sulfur powder in this solution. Again we have passed H₂S gas for approximately two hour. The color of the sodium polysulfide solution which was formed after the reaction is completed was yellowish orange or dark orange (Figure S1a). Sodium Polysulfide which was formed in this reaction is a mixture of sulfide and polysulfide comprising of H₂S, HS⁻, S₂⁻, S₂²⁻, S₃²⁻, S₄²⁻, and S₅²⁻. The filtered out solution was of orange color and stored it at 4°C.

1.2. Synthesis of FeS₂ from polysulfide¹⁻³: For FeS₂ synthesis, we made a buffer solution by mixing 0.2M Sodium acetate with 0.2M acetic acid in 91: 9 ratios. 100 ml of this buffer solution was mixed with 100 ml of 0.4 M of ferric chloride (turned to bright red) and it was stirred for half an hour in an inert argon atmosphere for removing any oxygen. Then in a drop-wise manner 20 ml of polysulfide is added to this solution and the color which was initially bright red gradually get converted to black because of the formation of unstable ferrous sulfide. Now this solution was stirred further for approximately 6 hour in an inert argon atmosphere at 100-120°C temperature, which resulted in the formation of the grayish black precipitate of FeS₂. The FeS₂ solution was centrifuged, washed with HCl to remove FeS impurity (As FeS₂ is not soluble in HCl), and cleaned with toluene and acetone to remove non-reacted sulfur and other impurities.

This grayish black precipitate of FeS_2 is dried and stored for further experiment. The set up flow of FeS_2 synthesis is given in Figure S1b.

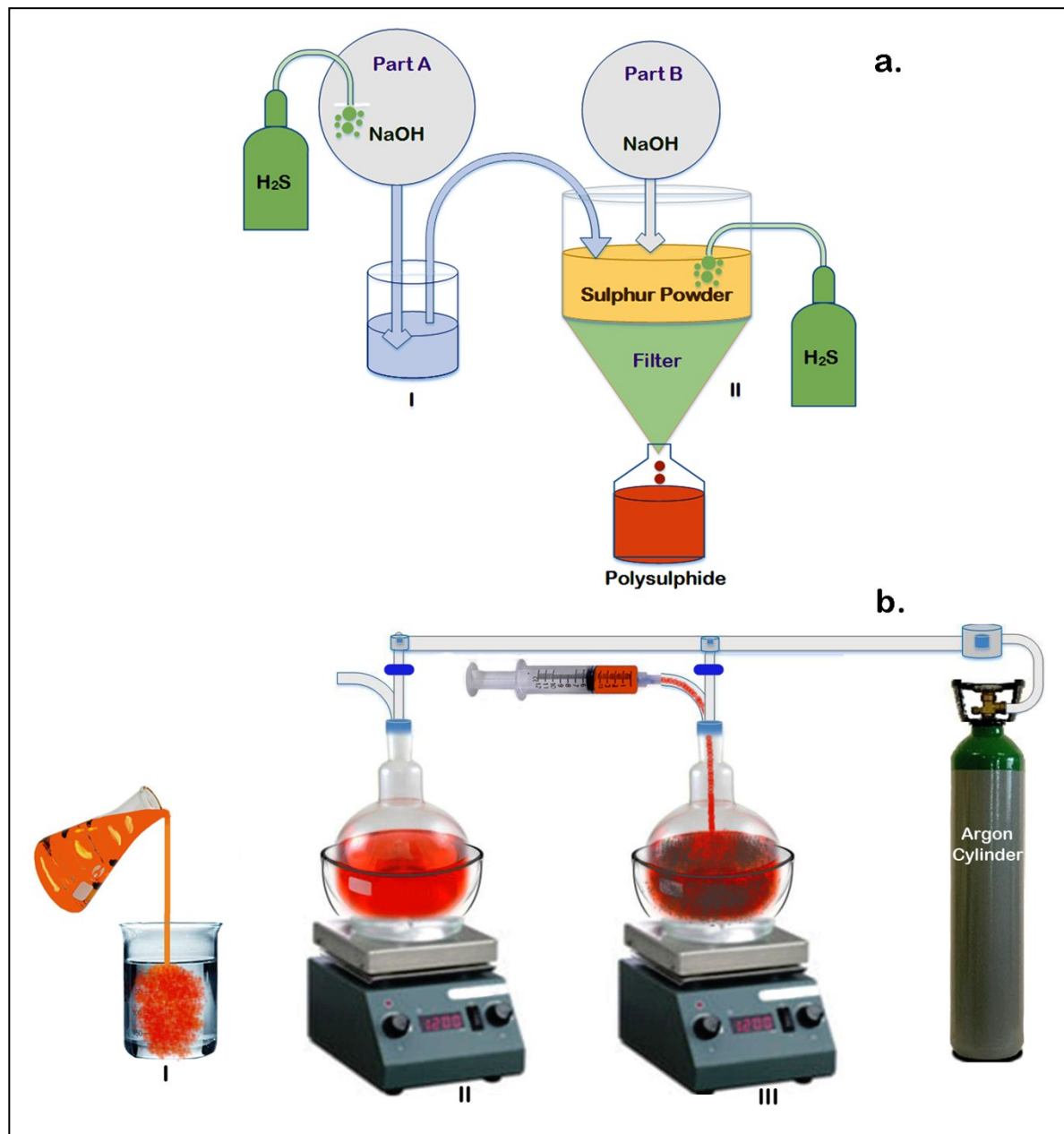


Figure S1. Synthesis of nano FeS_2 . a. Schematic showing the preparation of poly-sulfide solution. b. Step wise synthesis of FeS_2 . I. Buffer mix with FeCl_3 . II. Bright Red solution stirred

and purged in Argon atmosphere III. Mixing of polysulfide in the intermediate solution (that turn blackish color because of FeS formation) at 100-120°C at Argon atmosphere

1.3 Electrode Material FeS₂/PA preparations: The FeS₂/Poly-aniline (PA) composite electrode was prepared by taking 286 mg of sulfosalicylic acid (C₇H₆O₆S·2H₂O) and dissolving it in 30ml of deionized water, and then adding 1.1 ml of sulfuric acid to it and further stirring this solution for 15 minutes. Once this solution was prepared, it was divided into two parts viz., part A and part B. Part A (2/3rd of the solution) was mixed with 0.45 ml of aniline monomer and in part B (1/3rd of the solution) 1gm of ammonium per sulfate, was added. Both these solutions were stirred separately. The resultant Part B solution was placed at -5°C for one hour. In the meanwhile, 5ml of polymerized Part A solution was mixed with 1gm of FeS₂ particles and stirred continuously for 1 hour. Now in this solution, 3ml of cold part B solution was added in a drop-wise manner and continuously stirred to mix thoroughly till the color of the solution become brownish (Figure S2a). This brownish precipitate was the composite of FeS₂ and poly-aniline (PA). It is stored at 5°C for 3 hours. Following this, it was centrifuged, washed multiple times with deionized water and acetone and used for further analysis. PA electrodes were prepared by the same process as described above, without addition of FeS₂.⁴⁻⁶

1.4. Preparation of Electrolyte gel: Electrolyte gel was prepared by mixing 2gm of poly-vinyl alcohol (PVA) powder and 2ml concentrated phosphoric acid (H₃PO₄) in 20ml of deionized water. This solution was heated with continuous stirring at around 85°C for 1 hour till the solution became clear and transparent (Figure S2b).⁷⁻¹⁰

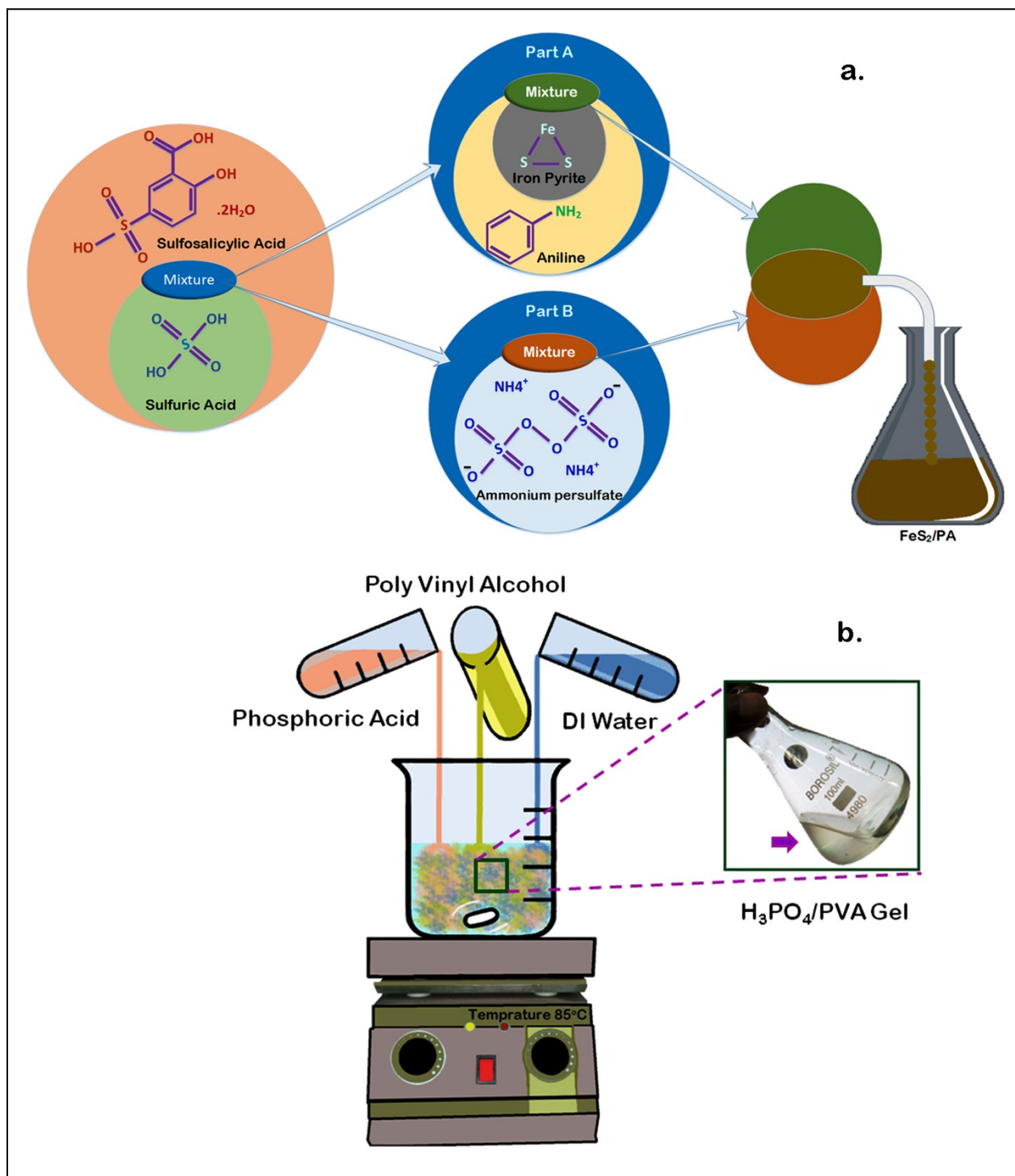


Figure S2. FeS_2 electrode fabrication. a. Outline for the preparation of $\text{FeS}_2/\text{poly-aniline (PA)}$ composite electrode. b. The preparation $\text{H}_3\text{PO}_4/\text{PVA}$ gel for electrolyte.

2. Material Characterization

2.1 Raman Spectra of FeS₂ nanoparticles: We have done Raman spectroscopy of FeS₂ to detect different phases of iron sulfide like FeS, Fe₃S₄, Fe₇S₈, Fe_{1-x}S and FeS₂ for further verify the phase purity of the synthesized sample. The Raman spectroscopy recorded in the wave number range from 200 to 500 cm⁻¹ (Figure S3). In this spectra sharp peaks were observed at 337cm⁻¹ and 379 cm⁻¹, these two-peaks signify the presence of S–S bond in the sample. The Raman peak near 339 cm⁻¹ appeared because of the displacements of the S atoms perpendicular to the S–S bond axis (corresponding to the S₂ libration E_g mode) and that near 378 cm⁻¹ resulting from the in-phase stretching vibrations of the S–S dimer (A_g) in the pyrite FeS₂ crystal.^{11,12} It can be seen that there is one more significant peak at around 432 cm⁻¹ which can be matched to that caused by the third Raman active mode corresponds to the coupled libration and stretching (T_g mode) in a pyrite crystal.^{13, 14}

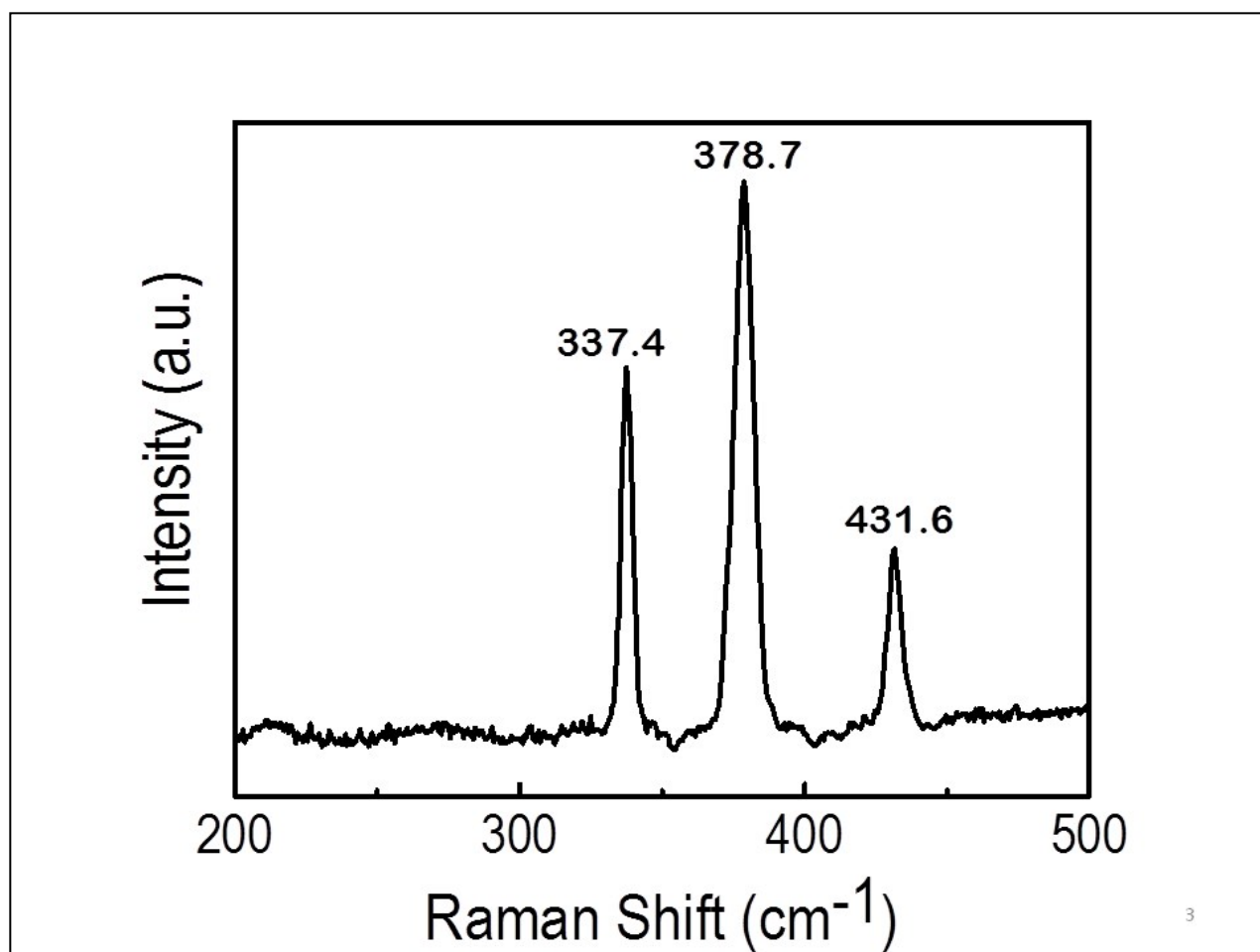


Figure S3. Raman Spectroscopy of FeS₂ nanoparticles

FTIR spectroscopy: The spectra of the samples were obtained from on a Bruker fourier transform infrared spectrometer (Vector 22 model). The model consists of a global lamp source, a KBr beam splitter, and DTGS/KBr detector. The spectra recording was done in the solid state in KBr pellets. In the current configuration, it is possible to cover a range from 400–4,000 cm⁻¹ range with a resolution of 4 cm⁻¹.

References and Notes:

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