Synthesis And Structural Characterization Of FeS_2 Nanoparticles Using Rietveld Refinement

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Abstract. We report the synthesis and characterization of FeS_2 nanoparticles (NPs) in view of their possible applications, which may range from organic and inorganic based hybrid solar cells to the replacements of Lithium Batteries (LIBs). The Polyol method was used to prepare the Iron Pyrite (FeS_2) NPs with reducing reagent Ethylene Glycol (EG) and precursor Thiourea. The crystalline quality and stoichiometry of synthesized FeS_2 NPs were confirmed by X-ray diffraction (XRD) and Raman Spectroscopy, which gave an average crystallite size of 35.4 nm. The Rietveld refinement of the diffraction data revealed the lattice parameters, hkl values, phase, Rp (Profile Factor) etc. of FeS_2NPs through the profile matching routine of FullProf software. The elemental has been investigation has been performed using Energy-Dispersive X-ray Spectroscopy (EDS), where characteristic emission peaks of Fe and S elements were observed. Further, Raman Spectroscopy experiment provided information on chemical bonding and symmetry of molecules for the device possibilities of surfactant coated FeS_2 NPs.

INTRODUCTION

Transition metal dichalcogenides have attracted attention of many researchers because of the interesting properties offered by different compounds of this family. They find applications in optoelectronics, holographic recording systems, switching, infrared generation and detection system [1].Metal dichalcogenides are represented by the general formula ME_2, where M = a transition metal and E = S, Se, Te [2].The most important members of this category are the sulfides. They are insoluble in all solvents and exhibit semiconducting properties. In contrast to traditional metal dichalcogenides, Iron Pyrite is usually described as consisting of $Fe^{2+}$and the persulfido anion S_2^{2-}. FeS_2 has been comprehensively investigated for energy storage, conversion devices etc. in view of its similar electrochemical mechanism as that of metal oxides as well as its abundance in nature along with affordable cost [3, 4].Pyrite Iron Sulfide (FeS_2) has also drawn significant interest because it is a promising anode material for LIBs due to high storage capacity, small environmental impact and low cost compared to that of lithium metal oxides [5, 6]. In the bulk form, pyrite FeS_2 exhibits the band gap energy of 0.95 eV and high optical absorption coefficient of 5×10^5 cm^{-1} [7]. In view of this, FeS_2 has found to possess novel semiconducting properties that may be applicable in various devices such as in photoelectric devices, including photovoltaics because of its low band gap, photo detectors and dye-sensitized solar cells etc.

Such metal sulphide NPs have received remarkable research attention because of their unique physical, chemical and biological properties associated with their broad surface to volume ratio and due to quantum confinement effects [8]. These properties make them useful for the development of novel applications in energy storage, data storage, optical sensing, cosmetic, biology and medicine. Nanoscale FeS_2 is considered one of few potentially transformative

materials for photovoltaics capable of bridging the cost/performance gap of solar batteries and holds promise for energy storage applications.

For the successful operation of resulting devices, it is required that the properties and their correlation is understood at the basic atomic level. Therefore, the main aim of the present work is to obtain pure and stoichiometric FeS_2 NPs and to establish a correlation between its major properties including crystal structure and possible effects on overall performance before their feasibility for device fabrication is tested. Several physical and chemical methods have been used for synthesizing the metallic NPs but Polyol method is one of the best method to prepare the NPs because, it is easy to use, cost effective, less time consuming and reaction temperature is higher. In the present study, Polyol method was used to synthesize FeS_2NPs.As prepared NPs sample was characterized by XRD as well as Raman spectroscopy to understand their basic properties.

EXPERIMENTS

FeS_2 NPs were synthesized by Polyol method. For this, 1.0 g (3.699 mmol) of $FeCl_3 \cdot 6H_2O$ and 0.25 g (3.2842mmol) of thiourea (NH_2CSNH_2) were dissolved in 50 mL of ethylene glycol (EG). This mixture was taken in a round bottom flask fitted with a thermometer and heated at180°C for 3h. This gave rise to black precipitate due to the formation of FeS_2nanocrystals. This solution was then cooled to 27 °C and washed by adding 20 ml of ethanol. Washing was done 4-5 times to extract NPs. The particles were dried at 60°C and used directly for characterizations such as X-ray diffraction (XRD), Energy Dispersive X-ray spectrometer (EDS) and Raman spectroscopy.

The XRD measurement was done on Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (1.54Å) in the 2θ range of 20°-90°.Further, the data refinement was carried out through the profile matching routine of FullProf 2000 software package.EDS measurement was done on the INCA Oxford machine attached with SEM. Qualitative and quantitative analysis indicated that the atomic percentage ratio of Fe to S in the energy range 0-20 KeV. The investigation of chemical bonds, symmetry of molecules and the vibrational information has been done using Raman spectroscopy [Lab RAM HR Visible instrument (Horiba Jobin Yuvon) equipped with an Ar ion laser with a wavelength of 488 nm at room temperature] in the wave number range from 200 to 500 cm^{-1}.

RESULTS AND DISCUSSIONS

Figure 1represents the structural Rietveld refinement of XRD patterns of as prepared FeS_2NPs. The peaks in the XRD spectra arising from corresponding Bragg's (hkl) planes for various diffraction positions of FCC crystal structure were recorded as (111), (200), (210),(211),(220),(311),(222),(023) and (321) at 2θ values ~ 28.44°, 32.95°, 36.97°, 40.66°, 47.23°,56.12°,58.86°, 61.52° and 64.11° respectively. They are related to FeS_2 pyrite cubic structure [JCPDS file No. 710053]. The crystallite size (L) was determined by standard Sheerer relation:

$$L = \frac{0.9\lambda}{B\cos(\theta)} \quad (1)$$

Where, λ is the incident X-ray wavelength, B=Full width at half maxima of the peak and θ is the Bragg angle. The average crystallite size was found to be~35.4 nm. The observed values of Lattice parameter, Profile factor (R_P), Weighted profile factor (Rwp), Bragg factor (R_B), Crystallographic factor (R_F) and χ^2 by Rietveld refinement were found to be 5.4335(Å), 111, 58.7, 30.71, 19.81 and 1.31 respectively. The chemical content of FeS_2 unit cell was obtained in weight percent as Fe (24.0) + S (32.8) + S (32.8).

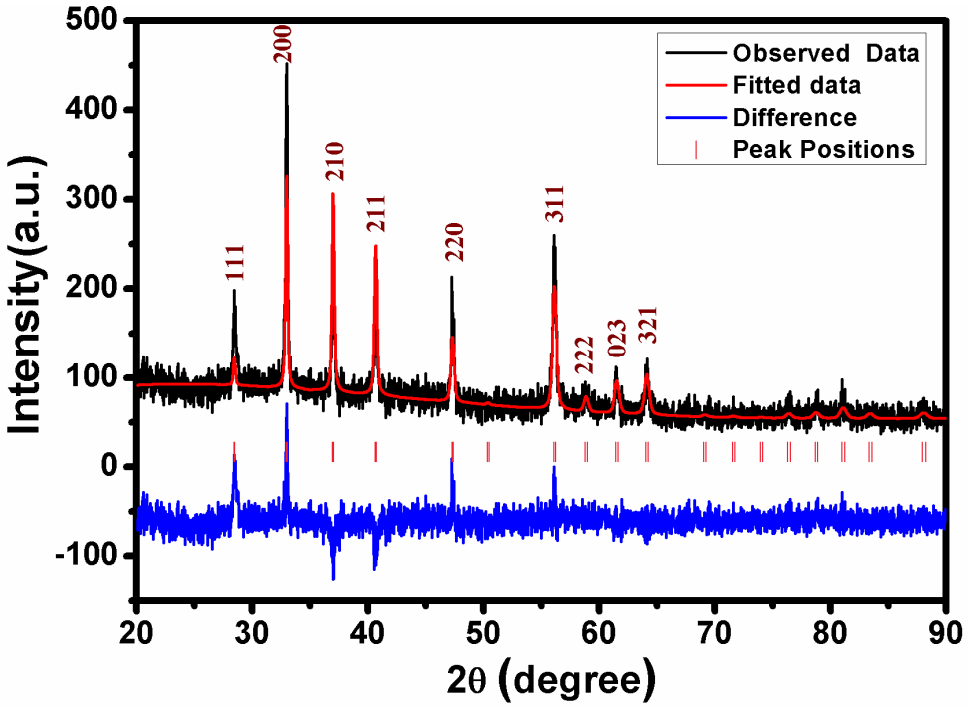

FIGURE 1 Structural Rietveld refinement of XRD patterns of FeS_2 nanoparticles

Figure 2 represents the EDS spectrum of prepared FeS_2 NPs. The EDS spectrum shows the characteristic emission peaks of Fe and S. The quantitative analysis indicates that the atomic percentage ratio of Fe to S of as prepared FeS_2 NPs is 40.59: 59.41, which give thepyrite cubic structure.

In agreement with XRD observations, Raman spectrum also exhibits the pyrite cubic structure. Figure 3 depicts the Raman spectrum of FeS_2 NPs. Three prominent peaks (337.7, 373.8 and 420 cm^{-1}) are observed that are indicative of the presence of S-S bonds and agree well with the literature reports of nanoscale FeS_2 materials [9]. The stretching mode observed near 337.7 cm^{-1} is due to the displacement of S atoms perpendicular to the S-S bond (E_g) and the mode appearing near 373.8 cm^{-1} is due to in-plane stretching vibrations in S-S (A_g).The band at 420 cm^{-1} has been assigned to coupled vibration and stretching (T_g) modes and combinations. However, the peak positions correspond well to the reported peaks of FeS_2 confirming the XRD results that pure FeS_2 has formed, without any crystalline phase impurity. Detection of any atomic impurity will be subjected to further investigation.

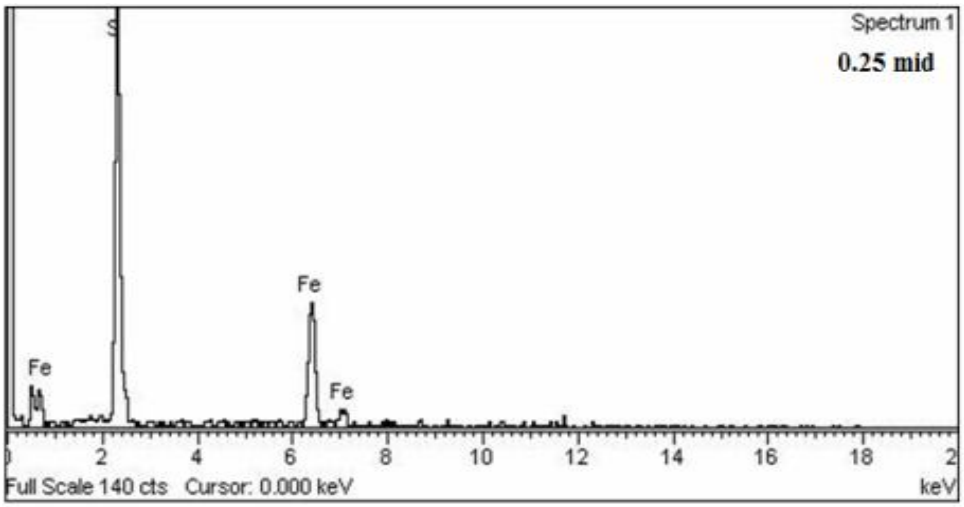

FIGURE 2 EDS of FeS_2 nanoparticles.

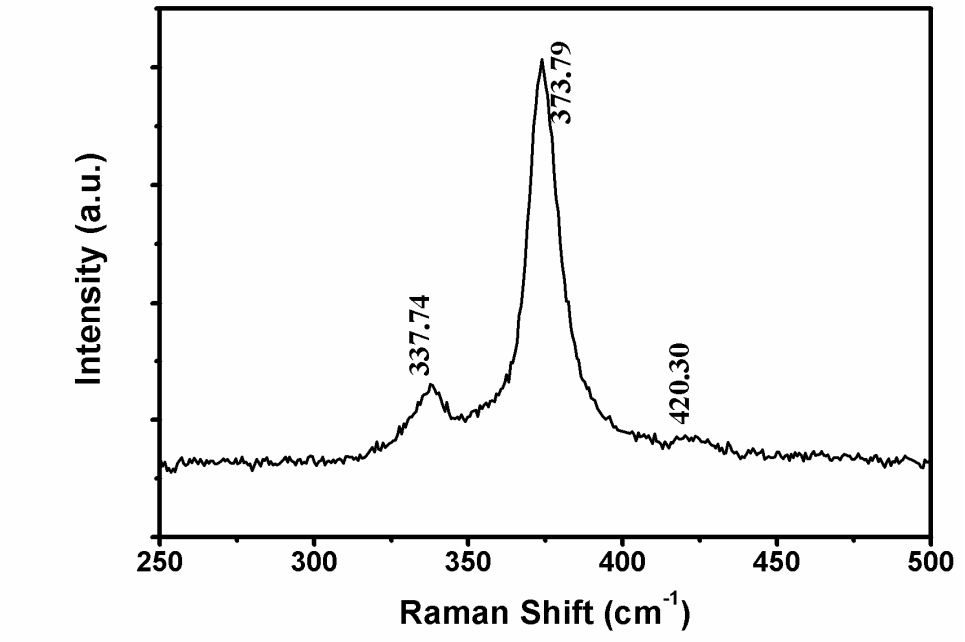

FIGURE 3 Raman spectra of FeS_2 nanoparticles

CONCLUSIONS

FeS_2 NPs with average crystallite size of ~ 35.4 nm were prepared by Polyol methods with the help of reducing reagent Ethylene Glycol (EG) and precursor Thiourea. The chemical content of FeS_2 unit cell was obtained in weight percent as Fe (24.0) + S (32.8) + S (32.8) by Rietveld analysis. Further, EDS result had revealed that the atomic composition ratio of Fe and S equal to ~ 1.46, which supported the pyrite cubic structure. Raman results also confirmed that pure FeS_2 has been formed. The results suggest the utility of Polyol method for preparing FeS_2nanoparticles and will further be utilized for preparing the NPs for advanced measurements.

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REFERENCES

1. J.A. Wilson & A.D. Yoffe, Advances in Physics, 18, 193-335(1969).
2. A.F. Wells, Structural Inorganic Chemistry (Oxford: Clarendon Press, Oxford, England, UK, 1984).
3. Z.Gao, N. Song, Y. Zhang and X. Li, NanoLett.15, 8194−8203 (2015).
4. C. H.Lai, M.Y. Lu and L.J. Chen, J. Mater. Chem. 22, 19−30 (2012).
5. Z. Hu, Z. Zhu, F. Cheng, K. Zhang, J.Wang, C. Chen, J.Chen, Energy Environ. Sci.8, 1309−1316 (2015).
6. S. S.Zhang, J. Mater.Chem. A, 2015, 3, 7689-7694(2015).
7. A.Ennaoui, S.Fiechter, H.Goslowsky, H.Tributsch, J. Electrochem. Soc.132, 1579−1582 (1985).
8. M.Vaseem, A.Umar, Y.B. Hahn (American Scientific Publisher: New York, NY, USA, pp. 1–36, 2010).
9. L.Li, M. Caban Acevedo, S. N. Girard, S. Jin, 6, 2112–2118(2014).