

Synthesis, Characterization and Photocatalytic Activity of SnS Nanocrystals

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ABSTRACT

Tin sulfide nanocrystals were successfully synthesized by wet chemical precipitation method. The as prepared SnS nanocrystals are characterized by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), field emission scanning electron microscopy (FESEM), UV-VIS and photoluminescence (PL) study. XRD results show that the phases of obtained nanoparticles are orthorhombic. TEM image shows that the particles are almost spherical shape and the grain size is about 23 nm. UV-VIS absorption spectroscopy study determines the band gap energy of SnS is approximately 2.39 eV. Room temperature PL spectra of as prepared SnS show an emission peak at 630.34 nm (1.96 eV) which is due to various defect level transition. It is clear that as obtained SnS shows a strong photocatalytic activity for the degradation of methyl blue (MB) in visible light radiation. This outstanding photocatalytic performance of SnS is mainly due to smaller crystal size, greater surface area and good absorption coefficient in the range of visible light spectrum.

Keywords: SnS Nanocrystals; X-ray diffraction; TEM; Absorption spectra; PL spectra; photocatalytic

1. Introduction

Due to crisis of energy and different types environment pollution of world, photocatalysts play an important role to explain the problems by solar energy for splitting water for hydrogen generation as well as purifying water and air. TiO₂ shows an excellent photocatalytic activity [1]. But main disadvantages of this material that it has wide band gap energy (3.2 eV) and hence it can absorb only UV light. Different methods have been followed for visible light driven photocatalysts such as (i) doping a wide band gap energy element to the photocatalytic material [2] (ii) doping a narrow band gap material to the photocatalytic material [3] (iii) mixing organic-dye to the original material for better photocatalytic performances so that it can be applied for the fabrication of solar cell [4] and others optical devices. Few promising solar-light-driven photocatalysts have been studied e.g.: InTaO₄ [5], TaON [6], BiFeO₃ [7], and Bi₂WO₆[8] etc.

Photocatalysis is a process in which a semiconducting material can absorb the incident radiation of energy greater than or equal to band gap energy, can excite the electron from valence band to the conduction band [9]. In Such cases charge separation

creates electron-hole pairs which can further generate free radicals. The resulting free-radicals are very efficient oxidizers for organic as well as inorganic materials and can degrade the pollutants [10].

SnS is an important semiconducting materials having band gap energy 1.3eV. It has wide range for visible light absorption. In summary, it has large absorbance coefficient, lower toxicity, low cost, does not hamper the environment. Tin sulfide nanomaterials potentially used as gas sensor [11], Li-ion batteries [12], thin film solar cell [4], photo detectors [13], electrochemical capacitor [14]etc.To prepare different types of morphology most of the workers follow different methods. Here we followed a simple cost effective wet chemical precipitation method [15] using TEA to increase the reaction rate. To transform the organic pollutants into harmless product photocatalytic degradation in visible light is a better method. It is well known that SnS nanomaterials is a narrow band gap semiconducting material and can be employed in solar cell, photodetector and others optical devices for its excellent photorsponse behavior. On the other hand it has wide range of UV-VIS absorbance ranging from 200-900 nm. Both theory and experiments suggest that SnS nanoparticle is a proper material for solar energy conversion [16]. Hence it can be expected that SnS is a good promising materials for visible light driven photocatalytic performance. In this paper, we report the synthesis of SnS nanoparticles by a simple wet-chemical precipitation method at room temperature and its photocatalytic activity in presence of visible light.

2. Experimental

2.1. Preparation of SnS nanocrystals

The SnS nanoparticle is prepared by Precipitation method. In this synthesis process 0.2 M of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (1.80g, 40 ml) and 0.2 M of $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ (0.62g, 40 ml) were used as tin and sulfur sources respectively. Initially tin chloride and sodium sulfide were taken separately in the deionized water of 40 ml taken in a beaker. Stirring was ongoing using a magnetic stirrer until both dispersed well. Then 5 ml of TEA (triethanolamine) was added to the tin chloride solution. Finally, both solutions were mixed together and stirred vigourly at a constant speed. The solution was turned into dark brown black in color. The black solid precipitates were centrifuged and washed with deionized water for many times and dried at room temperature for characterization.

2.2 Characterization

The Structural characterization of the prepared SnS has been characterized by Transmission Electron Microscope JEOL JEM200 at 200KV. XRD image was obtained using Rigaku Mini Flex-II X-ray Diffractometer. FESEM micrograph was obtained from JEOL JSM 5800. Optical measurement of the sample was done by Shimadzu-Pharmaspec-1700 visible and ultraviolet spectrophotometer. PL spectra of the said sample were measured by Perkin Elmer LS55 spectrophotometer.

3. Results and discussions

3.1. X-ray diffraction study

Fig.1 shows the XRD pattern of as- prepared SnS nanocrystals by wet-chemical precipitation method. The XRD peaks are observed at 2θ values of 26.02° , 30.22° , 31.15° , 38.66° , 43.79° , 48.79° , 51.31° , 56.31° , 63.95° corresponding to the planes (120),

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(101), (111), (131), (141), (211), (122), (231) and (080) respectively. All these peaks are closely matched with orthorhombic crystal structure. The lattice parameters of orthorhombic SnS are $a = 4.328 \text{ \AA}$, $b = 11.19 \text{ \AA}$, $c = 3.978 \text{ \AA}$. No impurity peak of SnS has been observed. We can calculate the particle size from the following Scherer's formula:
$$P = \frac{0.9\lambda}{\beta \cos\theta}$$

Where, λ is the wavelength of the incident X-rays which is 1.5405 \AA , β is the full width at half maximum, θ is the Bragg's angle.

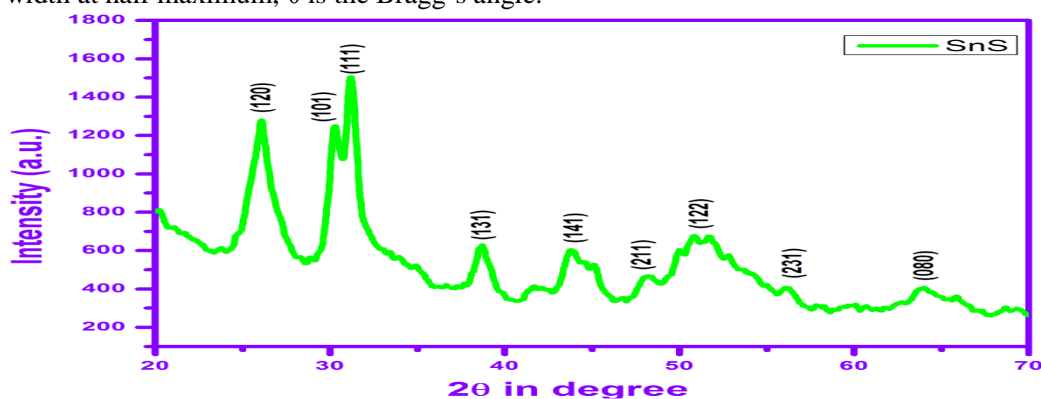


Figure1: XRD pattern of as synthesized SnS NPs.

The (120) plane was used to calculate the size of the SnS nanocrystals. The size of the as synthesized nanocrystals is approximately 29 nm.

3.2. Transmission electron microscopy (TEM) study

The morphology of as prepared SnS was examined by TEM. A typical TEM image and corresponding SAED pattern of as synthesized SnS nanocrystals is shown in fig. 2(a) and 2(b) respectively. The approximate diameter of prepared SnS nanocrystals is about 23 nm. The SAED pattern (insert) confirms well-crystalline nature of SnS nanomaterial and hence TEM and SAED results perfectly matched with the XRD results.

3.3. FESEM study

Particle orientation, shape and size of the surface of SnS nanocrystals was observed by FESEM. Fig. 2(c) shows the surface morphology of the as prepared sample. From the SEM micrograph we observed that the surface particles are in spherical shape.

3.4. Optical absorption spectroscopy study

The UV-VIS absorption spectrum and corresponding band gap energy measurement of as synthesized SnS nanocrystals is shown in fig. 3(a). Optical absorption coefficient is determined in the wavelength region 200–900 nm. The band gap energy of the as-prepared SnS nanocrystal is approximately 2.39 eV is depicted in fig. 3(b). $(\alpha h\nu)^2 = c(h\nu - E_g)$ relation was used to determine the band gap of SnS. where c is a constant quantity. E_g is the band gap of that material and α is the absorption coefficient. Therefore a large blue shift ($\sim 1.09 \text{ eV}$) is observed which is due to quantum confinement effect of the carriers in SnS nanocrystals [17].

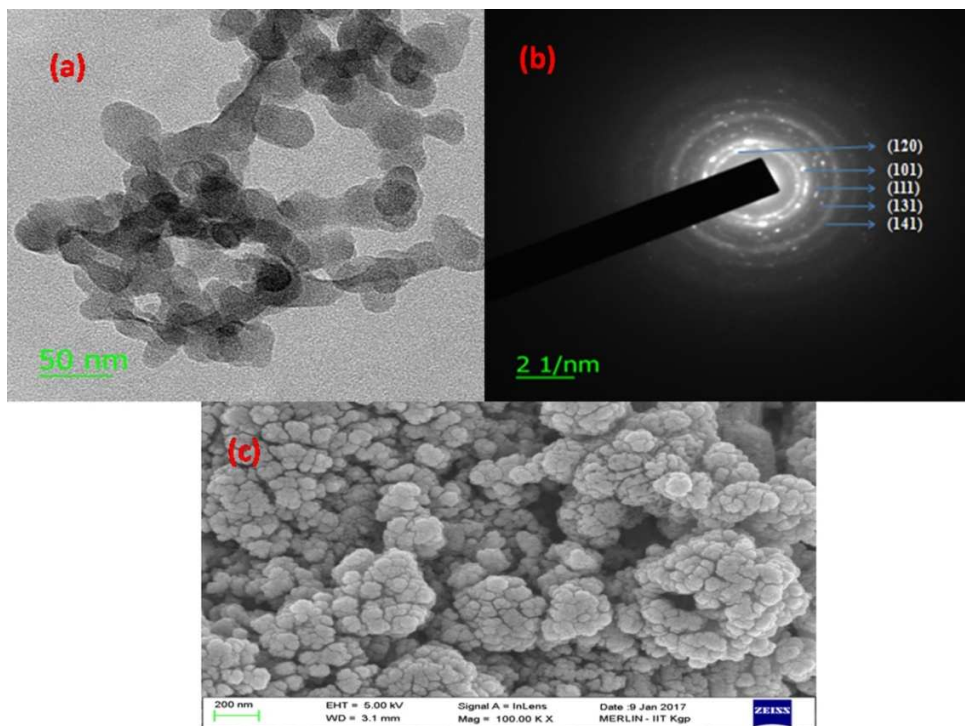


Figure 2: (a) TEM image of SnS NPs (b) SAED pattern of as prepares SnS (c) FESEM image of SnS NPs.

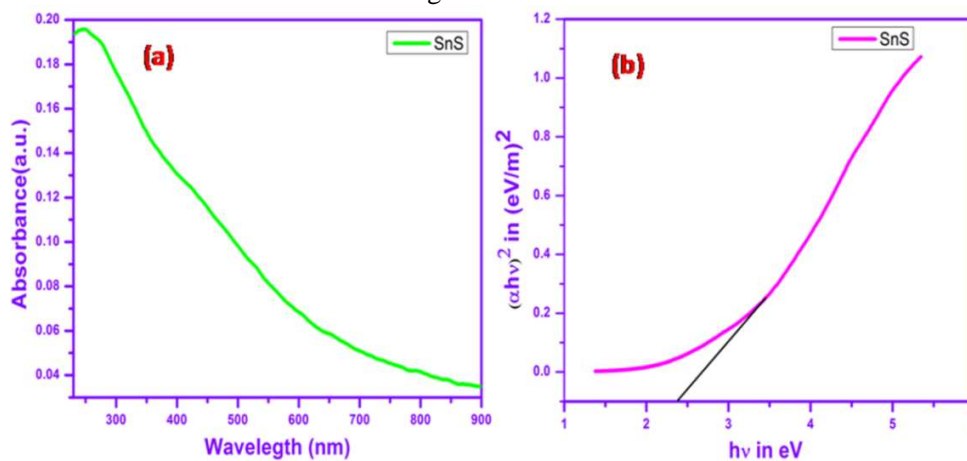


Figure 3: (a) Absorption spectra of as prepared SnS NPs (b) Band gap measurement graph of as-synthesized SnS NPs.

3.5. Photoluminescence spectroscopy study

Room temperature PL emission spectrum of SnS nanocrystals is shown in fig. 4. PL spectrum shows one strong red emission peak at 630.34 nm (1.97 eV). Since the band gap of SnS as determined from the UV-VIS is 2.39 eV, hence the PL emission does not

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attribute due to the band to band transition. The emission peaks arising from the defect state of SnS nanocrystal. This is probably due to different defect like Schotky, Frenkel etc. as well as sulfur and tin ions vacancies [18]. Therefore alarge blue shift is mainly due to the quenching phenomenon of the carriers of SnS nanostructure.

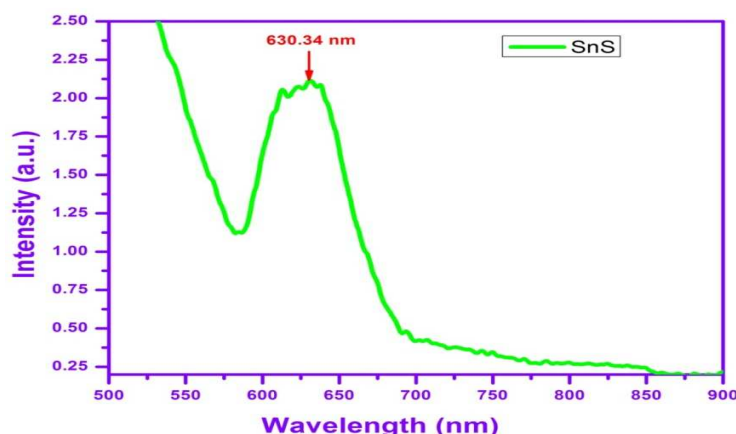


Figure 4: PL spectra of as-prepared SnS NPs

3.6. Photocatalytic activity study

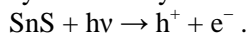
To perform photocatalytic activity of SnS nanomaterials, 50 mg (1gm/L) of the obtained material was dispersed in 50 ml methyl blue (MB) solution (1gm/L). The mixed solution was magnetically stirred under dark condition for 15 minutes to get adsorption and desorption equilibrium condition. Under this condition after 15 minutes a UV-VIS absorbance data has been taken. After that a 45W tungsten lamp as a visible radiation was exposed to the sample for 0-90 min. At a particular time interval 10 ml of the solution was extracted and centrifuged to eliminate the photocatalyst [17]. The photo degradation process was determined by UV-VIS absorption spectrometer (Shimadzu-Pharmaspec-1700 UV-VIS).

Optical absorption spectra of mixed methyl blue dye and synthesized SnS is shown in fig. 5(a). It shows that the absorbance peak of MB decreases with increase of visible light radiation time. After 90 min the as prepared SnS can completely decompose the MB under visible light radiation which indicates that the molecules of MB are degraded by the catalytic. The variation of relative concentration and expose time is depicted in fig. 5(b). According to Lambert–Beer’s law, the concentration of the dilute dye solution is directly proportional to the absorption intensity. Hence $C_t/C_0 = A_t/A_0$ where C_t & A_t is the concentration & absorption intensity of the solution at different times and C_0 & A_0 are initial concentration and absorption intensity of the solution. The photocatalytic rate constant of methyl blue dye degradation can be determined from the following first order plot using the relation:

$$\ln \frac{C_0}{C_t} = kt$$

k is the first order rate constant. Fig. 5(c) shows the plot of $\ln(C_0/C_t)$ vs. time of incident visible light. The calculated value of the first order rate constant (k) was 0.0021. Here SnS absorb the the incident visible light and excited to generate the electron- hole

pair which causes the photocatalytic activity [19]. In traditional photocatalytic theory, the oxidation reaction of the dye is generally initiated by OH^\cdot and $\text{O}_2^{\cdot-}$ radicals [9].



The oxidative and reductive reactions are written as:

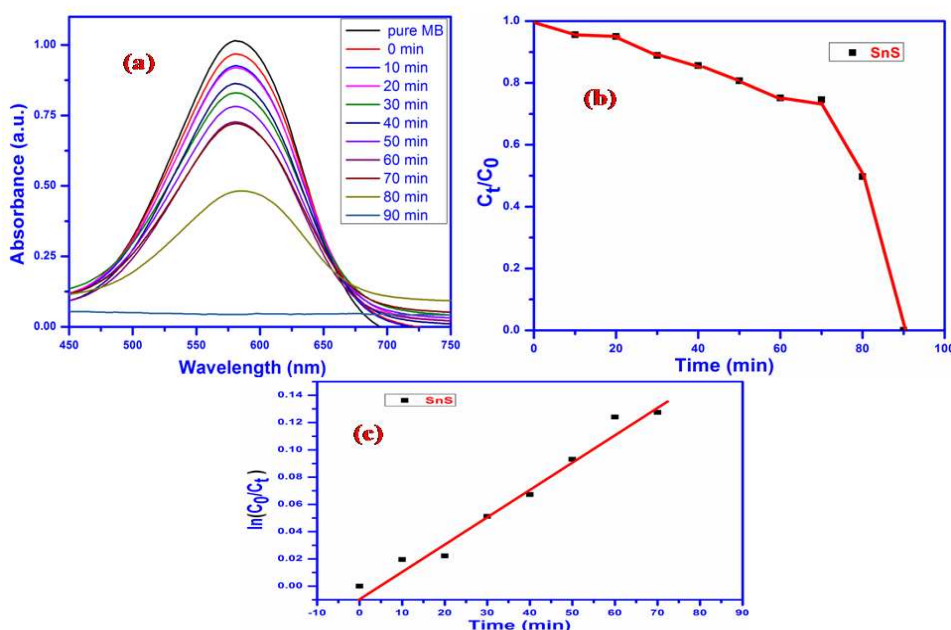
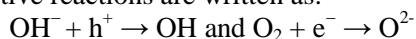


Figure 5:(a) Variation of absorption spectra and photodegradation of MB aqueous solution degraded by SnS nanoparticles under visible light (b) Photocatalytic decomposition graph of MB under visible light. (c) Logarithmic graph of relative concentration changes of MB with incident visible light radiation time to determine the first order rate constant.

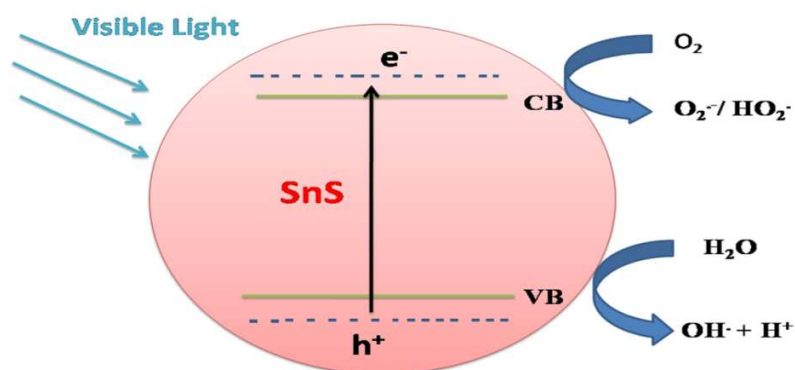


Figure 6:Mechanism of the visible light-induced photo degradation of methyl blue (MB) with SnS nanocrystals.

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On the other hand to get good results of photocatalytic activity surface area of the as prepared sample must be large. Not only larger specific surface area but also effectively separation efficiency of the electron-hole pairs must be required. In a word, the excellent photocatalytic performance of SnS nanocrystals results from their larger specific surface area, wide range visible light absorption, smaller size [20] and chain like pattern in TEM image.

4. Conclusion

SnS nanocrystals have been synthesized successfully by proper precipitation method. XRD results shows that orthorhombic crystal structure have been formed. Particles are almost spherical shape and a chain-like pattern is observed in TEM picture. The crystal size is about 23 nm as observed from TEM image using image-J tools. Optical absorption measurement determines the band gap of SnS is approximately 2.39 eV. PL spectra of as prepared SnS show an emission peak at 630.34 nm. This peak is arising from defect state of SnS nanocrystals. It is clear that as obtained SnS shows a strong photocatalytic activity for the degradation of methyl blue (MB) in visible light radiation. This excellent photocatalytic performance of SnS is mainly due to smaller size of the crystals, large surface area and wide range of visible light absorption.

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