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Hydrothermal synthesized stable and reusable tin sulfide filled cellulose photocatalysts and their application in dye degradation

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Abstract

SnS nanostructures were grown using hydrothermal method. Samples were characterized by structural, morphological and optical studies. All the peaks in the x-ray diffractograms are identified and indexed as orthorhombic structure. Scanning electron microscopy studies confirm the formation of orthorhombic structures obtained. EDS confirms the composition of SnS nanoparticles. An optical study shows good luminescence in visible region. Due to strong quantum effect,blue shift is obtained in optical direct and indirect band gap.92 % of methylene red dye removal from waste water.

Keywords: Nanostructures, hydrothermal method, Photocatalyst bag, SnS

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1. Introduction

Semiconductor nanostructures, owing to their particular application in electronic and sensor devices, have gained great research potential interest. The important parameter in the photocatalytic reaction is activation wavelength. The bandgap energy of the photocatalyst should always be equal to or less than the incident photon energy [1]. In the visible and near-infrared regions of the spectrum, metal sulfide semiconductor nanoparticles produce light; therefore, it makes them visible-light-driven photocatalysts [2]. At the nano range, these photocatalytic properties of semiconductors are morphological and structural dependent [3-4].

Tin sulfide (SnS) nanostructure has amphoteric in nature. SnS semiconductor has a direct bandgap between 1.39eV and 2.33, and an indirect bandgap of between 1 eV and 1.5 eV and it is a p-type semiconductor, the obtained bandgap of SnS semiconductor is depend on the preparation method and its heat treatment temperature [5]. Due to the idiosyncratic properties of SnS such as low toxicity, earth abundance, and high chemical stability, it has attracted a large number of research interests [6, 7]. SnS has a good photo-response ability; moreover, it has a complete absorption of visible light during photodegradation [7, 13].

In this paper, we are studying the pH factor of SnS nanoparticles. We are reporting how pH concentrations affect or play important role in the photocatalytic activity of SnS nanoparticles. We will observe the changes in photocatalytic activity of SnS nanoparticles when we manipulate the pH concentration.

2. Materials and methods

2.1. Materials

Ethylene Glycol (EG), Tin (II) chloride (SnCl2.2H2O), and sodium sulfide (Na2S) were taken as solvent, tin, and sulfur sources respectively and used without purification. These chemicals were of analytical grade.

0.1M of SnCl2·2H2O dissolved in 90ml of EG and 0.1M of Na2S in 80ml of EG continuously stirred for 3hour, then kept in ultra-sonicator for other 30 mins at 60°C. 0.1M of Na2S solution was added dropwise into the SnCl2·2H2O solution. After that, the solution is kept in Teflon coated vessel and kept in an oven at 180°C. The precipitated particles were centrifuged and washed with ethanol and distilled water several times. The reusable photocatalyst fillers were prepared by adding SnS nanoparticles in non-woven cellulose paper fillers.

Photocatalytic degradation activity of SnS nanoparticles was performed with anionic methylene red dye in the visible region of the wavelength 400 nm to 700 nm. MR is an anionic dye, maximum absorption is about 464nm. 4ppm Solution of MR dye was prepared. The utmost absorption of MR is 464nm and everyone's reading of absorption is taken on this wavelength by using UV-Vis spectroscopy at continuous time intervals times (150 min). The reaction was carried out in a closed chamber enlighted with a white LED of 36 watts.

The photocatalytic samples were placed inside the solution, the absorption was recorded using a UV-Vis spectrophotometer, at regular intervals of time. The color of the dye decreases as time increases. On the bases of the calculated value of the rate constant (k), and photodegradation percentage, we evaluate the results of SnS nanoparticles. The photocatalytic activity of SnS nanoparticles decreased when the pH of SnS went up from 2 to 10 under the same experimental conditions.2.2. ***Characterizations***

The structural studies of SnS nanoparticles were carried by X-ray diffraction (XRD) measurements (mini Flex 350/600 diffractometer) using the Cu Kα (λ- 1.5406 Å) as a radiation source, scan over the range of 2°-90°. The Photoluminescence were carried by using Perkin Elmer-LS55. The spectral transmittance and absorbance measurements were obtained using UV-VIS spectrometer (Perkin lambda25) in the spectral range of 300 nm to 800nm.

3. Results and discussion

3.1. Structural studies

The obtained X-ray diffraction peaks of hydrothermally synthesized SnS are shown in Fig. 1. According to JCPDS card number 39-0354, all pattern of peaks confirms the SnS peaks which are closely matched to those of orthorhombic. The diffraction peaks at 16.5°, 21.15°, 25.91°, 26.94°, 30.09°, 31.42°, 38.91°, 45.09° and 50.41° ,the corresponding planes related to obtained peaks are indexed to (1 1 0), (1 2 0), (0 2 1), (1 0 1), (1 1 1), (1 3 1), (0 0 2) and (1 1 2) planes of SnS, respectively. The crystallite size of SnS was calculated using equation1 Debye-Scherer formula [15]. The size of SnS Nanoparticles is varied from (12nm, 10nm, 24nm, and 26nm).

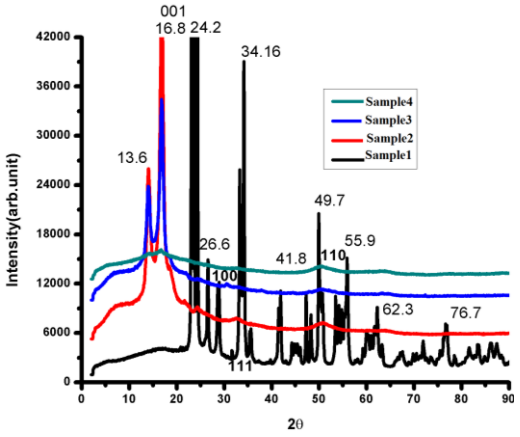

Fig. 1: X-ray diffraction patterns of SnS nanoparticles.

3.2. Morphological studies

The surface morphology of tin sulfide nanoparticles is shown in Fig.2. The size of particles obtained with the help of image j software is very small (nano range), but has the surface area. The grain-sized particles are uniformly cover the whole surface as shown in fig.2.

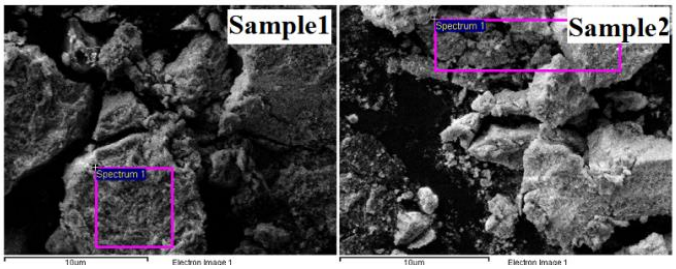

Fig. 2: Micrographs of different pH SnS nanoparticles

3.3. Photocatalytic degradation of methyl red dye (Anionic dye)

In Fig. 3 the anionic dye, the adsorption is bigger at an occasional pH2 value and reduces, because the pH increases because more charged sulfonate groups are present within the MR dye. About 92% of degradation is occurring within 60 minutes.

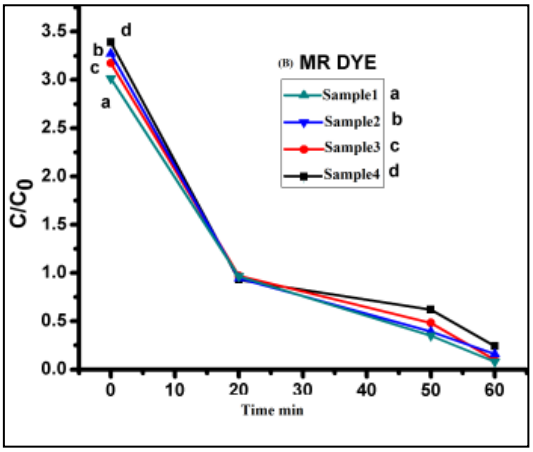

Fig. 3: The rate of concentration of MR dye in the degradation process in 60 min in the first cycle (A) Sample1 (B) Sample2 (C) Sample3 (D) Sample4.

4. Conclusions

This work presents the hydrothermal growth of SnS nanoparticles and inclusions in now oven cellulose fibers to be used as photocatalyst. The crystallinity decreases as the pH values increase. The SnS material shows excellent 92% degradation of dyes and stability up to three cycles as a photocatalyst.

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