HYDROTHERMAL SYNTHESIS OF TERNARY CHALCOPYRITE CuFeS$_2$ NANOPARTICLES

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Abstract - The synthesis of nanostructured semiconductors had gained momentum due to the shape-dependent properties they offer. Among the ternary semiconductors, the I-III-VI$_2$ compound, CuFeS$_2$ is worth exploring due to the novel optical properties it exhibits. In the present study, CuFeS$_2$ nanoparticles were synthesized using a promising hydrothermal reaction route with copper chloride dihydrate, ferric chloride and thiourea precursors at 200°C for 6 hours. The characterizations of X-ray diffraction and transmission electron microscopy reveal the structural and morphological properties of the blended CuFeS$_2$ nanoparticles. The diffuse reflectance graph aided the estimation of the optical band gap using the Kubelka-Munk plot. The sample showed photocatalytic degradation efficiency towards Rodamine B dye.

Key Words: CuFeS$_2$, hydrothermal, optical, semiconductor, Rhodamine B

1. INTRODUCTION

Tremendous efforts on the investigation of the intriguing properties of ternary chalcogenide compounds have been seen to be mounting in the recent times because of the wide range of applications they offer. CuFeS$_2$, one of the significant ternary semiconductors, with its novel structural and optical properties has attracted the attention of material scientists. It has a very narrow optical absorption edge of 0.5 – 0.6 eV in the bulk form [1-4] which can be varied in the nano regime and utilized for various applications, synthesis of CuFeS$_2$ with varying morphologies such as nanoparticles, nanorods were reported using various physical and chemical methods, [5-7] In the present work, CuFeS$_2$ nanoparticles were synthesized by hydrothermal method since it provides high product homogeneity and narrow particle size distributions in a contamination-free environment. Further, the structural and optical properties of the as-synthesized nanoparticles were studied and its photodegradation efficiency was tested for Rhodamine B dye.

2. EXPERIMENTAL PROCEDURE

Appropriate amounts of copper chloride dihydrate, ferric chloride and thiourea were weighed in stoichiometric ratio of 1:1:2 and dissolved in 50 ml of double distilled water each. Under constant magnetic stirring, the solutions were mixed together by drop-wise addition. The obtained solution was transferred into a Teflon-lined stainless steel autoclave of 200 ml capacity and filled upto 80% of the total volume. The autoclave was then closed tightly and placed in a muffle furnace for 6 h at an optimized temperature of 200°C. After 6 hours the autoclave was removed from the furnace. After cooling down to room temperature, the obtained precipitate was washed several times with double distilled water and ethanol. The product was subsequently dried overnight at 80°C and ground well to obtain CuFeS$_2$ nanoparticles.

3. RESULTS AND DISCUSSION

3.1 Structural analysis

The structural analysis of the as-synthesized CuFeS$_2$ nanoparticles was observed by powder X-ray diffraction using a GE Inspection technology 3003 TT X-ray diffractometer with CuKα radiation ($\lambda=1.540598$ Å) with an operation voltage of 40 kV and 30 mA in the 20 range 20-70°. Fig. 1 represents the x-ray diffractogram of the CuFeS$_2$ nanoparticles. The diffraction peaks may be indexed to the standard JCPDS card number 37-0471 of tetragonal chalcopyrite CuFeS$_2$ along with minor peaks of covellite CuS. The average crystallite size of the attained nanoparticles were calculated to be 27 nm using the Scherrer’s formula

$$D = \frac{k \lambda}{\beta \cos \theta}$$

where $D$ is the grain size in nm, $k = 0.89, \lambda = 1.5406$ Å which is the wavelength of CuKα, $\beta$ is the full width at half maximum (FWHM in radians) and $\theta$ is the Bragg's angle in degrees. The lattice parameters $a$ and $c$ of the as-synthesized CuFeS$_2$ nanoparticles were calculated using the equation
The estimated values $a = 5.3601\text{Å}$ and $b = 10.2115\text{Å}$ are very close to the ones in the standard JCPDS pattern for chalcopyrite CuFeS$_2$.

3.2 Morphological analysis

The morphology of the CuFeS$_2$ nanoparticles was studied using transmission electron microscopy (TEM) image recorded. The TEM micrograph (fig.2) reveals a heterogeneous morphology of particles. The particles appear to be aggregated. The crystalline nature of the sample is emphasized by the presence of concentric rings in the SAED pattern given as inset.

3.3 Optical analysis

The UV-visible absorption reveal the optical properties of the as-synthesized CuFeS$_2$ nanoparticles. Fig.3.a evidences that the CuFeS$_2$ nanoparticles have broad absorption in the visible light region. The optical bandgap, one of the important characteristics of semiconductor nanoparticles, was estimated to be $1.27\text{ eV}$ using the Kubelka-Munk plot. Since the band gap of the prepared CuFeS$_2$ is higher than $0.6\text{ eV}$ (band gap of bulk CuFeS$_2$), we can confirm that the synthesized CuFeS$_2$ is in the nano region.12
3.4 Photocatalytic degradation of CuFeS$_2$ nanoparticles

The photocatalytic degradation efficiency of the as-synthesized CuFeS$_2$ nanoparticles was tested using Rhodamine B (RhB) dye solution in water in the presence of mercury vapour lamp (125 W) as a light source. 10 mg of the nano photo catalyst was dispersed to 50 ml of the aqueous dye solution taken from the standard solution (100 mg/L). In order to ensure sound adsorption-desorption process the solution was maintained under constant magnetic stirring for 30 minutes. The solution was then placed under illumination with addition of 2 ml of H$_2$O$_2$ and the degradation process was monitored by removing 3 ml of the solution at fixed intervals. The solutions were centrifuged to remove the photo catalyst and analyzed using a UV-visible spectrophotometer to evaluate the breakdown of the RhB peak at 554 nm which showed 97% degradation efficiency in 60 minutes. The percentage degradation of the RhB was calculated using the formula

$$\% \text{ disintegration of RhB} = \frac{C_{0_{\text{RhB}}}-C_{x_{\text{RhB}}}}{C_{0_{\text{RhB}}}} \times 100 \quad (2)$$

where, $C_{0_{\text{RhB}}}$ is the initial concentration of RhB in the solution and $C_{x_{\text{RhB}}}$ is the concentration of RhB at time $x$.

In order to inspect the recyclability of the nano photo catalyst, the nanoparticles were extracted by centrifugation, dried and utilized for 5 consecutive cycles. The stability in the obtained results advocate that the as-synthesized CuFeS$_2$ nanoparticles can be used for effective degradation of dye contaminants in water.

4. CONCLUSIONS

In the present work, ternary chalcopyrite CuFeS$_2$ nanoparticles were blended using an effective hydrothermal method. The process saw the formation of a mixture of spherical CuFeS$_2$ nanoparticles and nano rods. The XRD diffractograms confirm the formation of CuFeS$_2$ nanoparticles and the optical direct band gap was estimated from the UV spectrum. Moreover, the synthesized nanoparticles show 97% degradation efficiency of Rhodamine B dye in water in a short span of 60 minutes. This manifests that the nano CuFeS$_2$ can be utilized in waste water management.

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