Synthesis and Characterization of Fe(II) Doped CdS Nanoparticles and Photodegradation of Acid Blue – 29 (AB-29) Dye

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1. Introduction

II-VI semiconductor nanostructures have been investigated widely and demonstrated for potential applications in solar cells, light emitting diodes, IR photodetectors, electrically driven lasers, optical limiters and luminescent materials. Metal-doped wide-band gap sulfide semiconductor nanoparticles have been considered to achieve a significant breakthrough in the field of the visible-light-driven photocatalyst, especially with respect to the photocatalytic water splitting reactions [1,2]. Most of the efforts are focused on equal valence charge doping. Recently, transition metal ions doped II-VI nanoparticles have attracted keen interest because transition metal ions incorporated into II-VI nanoparticles can improve significantly the optical properties of nanoparticles. The optical properties of doped nanomaterials differ from the corresponding host nanomaterials [3-7]. Doped semiconductor are extensively investigated to obtain basic information on impurity states in quantum dots and to examine their potential applications in novel light-emitting devices [8-10]. In the present study a novel method was designed to synthesize copper doped cadmium sulphide nanoparticles. In this work a series of Fe(II) doped CdS were prepared by a cost-effective colloidal chemical precipitation method and characterized by XRD and HRTEM techniques. The band gap, crystal phase and the morphology of CdS nanocrystals were not found to be affected noticeably by Fe(II) doping, there was an optimal Fe(II) doping content of wt.4%. The present study mainly incorporated with the composition, structure, morphology and photoluminescence behaviors of the prepared samples.

2. Experimental Methods

2.1 Preparation Technique

Three different molar ratios of cadmium acetate to iron (II) acetate, 1:0 (Sample CD-I), 9:1 (Sample CD-II), and 8:2 (CD-III) were prepared. About 20 mL of EDTA (PVP MW 55,000) solution in methanol (0.5 M) was added to 30 mL of the aqueous solution of Cd - Fe mixture solution with vigorous stirring followed by the addition of 0.5 M of Na2S aqueous solution and was allowed to stir vigorously for 2 hr. After stirring precipitate particles were isolated from the solution by centrifugation. Na2S solution was used as a source of S2- ions. The product was washed by water and absolute ethanol through multiple cycles of centrifugation and redispersion. The yellow precipitate of CdS samples was air dried to get dry powder.

2.2 Characterization Techniques

The crystal structure was determined by powder XRD (Table Top XRD MiniFlex 600, RIGAKU-Japan) using Cu-Kα radiation (λ=1.5405 Å) in a 2θ range of 5–60°. XRD patterns were compared with the standard anatase X-ray diffraction patterns. The shape and sizes of the particles were obtained through high resolution transmission electron microscope (HRTEM) Philips Tecnai 20, Holland with an accelerating voltage of 100 kV.

2.3 Photocatalytic Activity

The degradation of the dye molecules was evaluated using ultraviolet and visible absorption spectroscopy. An absorbance spectrum of the dye solution was taken using UV-VIS spectrophotometer in the range of 200 to 800 nm. The λmax of AB-29 was found to be 470 nm. The photocatalytic reaction experiments were carried out in the presence of direct sunlight. The standard (0.1 M) dye solution was prepared in distilled water and investigated for its degradation by using synthesized CdS samples as catalyst at different dosages and pH levels (ranging from 4 to 10). The pH of the dye solution was adjusted by using dilute hydrochloric acid and sodium hydroxide solution. At each pH level the catalyst concentration of 25 ppm was taken and catalyst dosages of 0.1 to 0.4 g/L were added for the color degradation efficiency studied under direct sunlight.

3. Result and Discussion

3.1 X-Ray Diffraction Study

XRD is a very important experimental technique that has long been used to address all issues related to the crystal structure of solids. The prepared Cd1-xFe,S x samples were characterized by X-ray diffraction and the results are compared with that of CdS and shown in Fig. 1. The reflection peaks of synthesized powders can be indexed to cubic phase, has three main peaks at 30.63°, 51.33° and 62.10°, which is corresponding reflections of (111), (220) and (311) planes. The results are good in agreement with the standard JCPDS value (card no. 80-0019). No other impurity peaks were detected in the spectra, this result suggests that Fe dopant is distributed homogeneously without clustering or segregation [11]. The broadening can be attributed to a very small grain size of the particles. The reflection peaks of as synthesized powders can be indexed to cubic phase, with JCPDS data card no. 800019. Moreover, with increase of the doping percentage, the XRD peak position shifts slightly towards higher angle relative to that of the pure CdS powders. Similar XRD patterns were observed by Kim et al. [12].
The crystallite size of the Cd₃FeS₄ nanoparticles calculated using Scherrer formula \[d = \frac{K\lambda}{\beta\cos\theta}\], where \(d\) is the mean crystallite size, \(K\) is the shape factor taken as 0.89, \(\lambda\) is the wavelength of the incident beam, \(\beta\) is the full width at half maximum and \(\theta\) is the Bragg’s angle. The average crystalline size was calculated as 20.20 nm, 18.11 nm and 13.45 nm for pure and Fe doped CdS nanoparticles (Table 1). This result suggests that due to doping of Fe into Cd-site grain growth is reduced significantly.

3.2 Transmission Electron Microscopic Studies

More details of synthesized CdS samples were investigated by HRTEM images. Fig. 2 shows the HRTEM image of the sample CD-III. The HRTEM image shows a mixture of spherical-shaped and rod-like nanoparticles, with particle size in the range of 5-25 nm.

3.3 Photocatalytic Activity

Acid Blue-29 (AB-29) dye solution was prepared and stirred in dark for 20 minutes attain equilibrium. Synthesized cadmium Sulphide was then added to the dye solution in order to catalyze the photocatalytic degradation. The solution with the catalyst was stirred in the dark for 30 minutes for the solution to attain equilibrium so that the loss of compound due to adsorption can be taken into account. It was then irradiated with visible light. The photodegradation process was continued for 2 hours in order to achieve complete degradation. Samples were removed at regular time intervals of 30 minutes in order to measure the decrease in concentration of dye. The absorbance and concentration of the samples were checked using a UV-Visible spectroscopy at the maximum wavelength of the dye. The concentration of the dye was 25 ppm.

3.3.1 Effect of Catalyst Loading

Before checking the photocatalytic activity of the synthesized samples, we have determined the absorbance of AB-29 dye on spectrophotometer at room temperature. It was found that, initially the absorbance of dye solution is 0.80. Now as the time moves ahead, the absorbance of dye solution decreases for the different catalyst doses as shown in Table 2. The results of effect of sample CD-II loading is summarized in Table 3 and illustrated in Fig. 3. The percent removal increases as the CdS dose increases. The optimum concentration of synthesized CdS samples required for the decolorization of 25 ppm AB-29 solution was examined with the catalyst amount from 0.1-0.4 g/L. The results summarized in Table 1 indicate that the required photons, when the concentration of CdS sample CD-III increased to 0.4 g/L, were thoroughly absorbed. This shows that with increase in the amount of catalyst to the level consistent with the optimized level of light absorption increases the percent of dye degradation.

| Table 2 | Absorbance of AB-29 solution with irradiation time |
|---------|--------------------------------------------------|
| Catalyst dose (g/L) | Absorbance of dye solution  |
|          | 0 min | 30 min | 60 min  | 90 min  |
| 0.1      | 0.80  | 0.63  | 0.45  | 0.31  |
| 0.2      | 0.80  | 0.54  | 0.36  | 0.22  |
| 0.3      | 0.80  | 0.40  | 0.18  | 0.11  |
| 0.4      | 0.80  | 0.20  | 0.04  | 0.01  |

| Table 3 | Dye Degradation% with irradiation time |
|---------|---------------------------------------|
| Catalyst dose (g/L) | Dye Degradation%  |
|          | 0 min | 30 min | 60 min  | 90 min  |
| 0.1      | 21.25 | 43.75  | 61.25  |
| 0.2      | 32.50 | 55.00  | 72.50  |
| 0.3      | 50.00 | 77.50  | 86.25  |
| 0.4      | 75.00 | 95.00  | 98.75  |

3.3.2 Effect of Initial Dye Concentration

The influence of initial concentration of the dye solution on the photocatalytic degradation is a significant aspect of the study. The initial concentrations of AB-29 dye solution were selected in the range of 25-125 ppm and it was revealed that the percentage of photodegradation decreased as initial concentration of the dye solution increased, as shown in Fig. 4. One possible explanation of such circumstances is that as initial concentration increases, the catalyst surface gets saturated with the dye molecules.

3.3.3 Effect of pH

Wastewater containing dyes are discharged at different pH. Therefore, it is important to study the role of pH on decolorization of dye. The decrease of pH from neutral condition has decreased the decolorization efficiency at lower dosages of catalyst. To study the effect of pH on the decolorization efficiency, experiments were carried out at various pH values, ranging from 4 to 10 for constant dye concentration (25 ppm) and catalyst loading (0.4 g/L). Fig. 5 shows the color removal efficiency of AB-29 dye solution as a function of pH. It has been observed that the decolorization efficiency increases with increase in pH exhibiting maximum rate of degradation at pH 8. Similar results were reported in our earlier work [14].

The effects of pH on the efficiency of the photocatalytic degradation process are very difficult to interpret because of it is governed by multiple factors. First, it is related to the acid base property of the catalyst surface and can be explained on the basis of zero-point charge. The adsorption of water molecules at surficial metal sites of the catalyst is followed by the dissociation of OH- charge group leading to coverage with chemically equivalent metal hydroxyl groups [15].

Fig. 1 XRD pattern of pure and copper doped CdS powders

Fig. 2 HRTEM micrographs of sample CD-III

Fig. 3 Effect of catalyst dose (CD-III) on photocatalytic degradation of AB-29 dye

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In this study, the preparation of Fe(II) doped CdS nanoparticles with different Fe concentration (0–0.4) was carried out by the colloidal chemical precipitation method. The results of the present investigation proved that, the synthesized CdS nanoparticles with molar ratios of cadmium acetate to Iron (II) acetate 8:2 (sample CD-III) is found to be an efficient photocatalyst for the complete decolorization of AB-29 dye solution under solar radiation. The degradation of dye was maximum at the alkaline pH (pH 8) for 25 ppm of AB-29 dye. This protocol is an effective technique in decolorizing the AB-29 dye solution and can be employed effectively in the treatment of textile dye effluents which are hazardous to the environment. It is concluded that Fe(II) doped CdS acts as a better photocatalyst to degrade the AB-29 dye solution under the present experimental conditions.

4. Conclusion

In this study, the preparation of Fe(II) doped CdS nanoparticles with different Fe concentration (0–0.4) was carried out by the colloidal chemical precipitation method. The results of the present investigation proved that, the synthesized CdS nanoparticles with molar ratios of cadmium acetate to Iron (II) acetate 8:2 (sample CD-III) is found to be an efficient photocatalyst for the complete decolorization of AB-29 dye solution under solar radiation. The degradation of dye was maximum at the alkaline pH (pH 8) for 25 ppm of AB-29 dye. This protocol is an effective technique in decolorizing the AB-29 dye solution and can be employed effectively in the treatment of textile dye effluents which are hazardous to the environment. It is concluded that Fe(II) doped CdS acts as a better photocatalyst to degrade the AB-29 dye solution under the present experimental conditions.

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