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S-doping effects on optical properties and highly enhanced photocatalytic performance of Cu_3Se_2 nanoparticles under solar-light irradiation

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ABSTRACT

Undoped and S-doped Cu_3Se_2 nanostructures (NSs) with different sulfur concentrations were synthesized by a green, simple, and cost-effective co-precipitation method in ambient conditions. X-ray diffraction patterns (XRD) of the samples indicated that, all samples had a tetragonal phase of Cu_3Se_2 . Fourier transform infrared spectroscopy (FTIR) results revealed that, some vibration modes were appeared by sulfur. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images showed that, sulfur had a significant role to change of morphology of the products. UV–vis and Photoluminescence (PL) results showed that, the band gap value of the pristine sample was 1.72–1.85 eV, while S-doped (4%) sample had a band-gap value between 1.61 eV and 1.67 eV. On the other hand, further increase of sulfur up to 6% caused band gap value increase in compared to the 4% sulfur doped. In addition, the PL results revealed that, the products had surface-trap states (STS) energy as well as different intrinsic defects such as Cu-vacancy. Furthermore, the PL spectrum of the S-doped sample showed that, sulfur ions caused increase natural donor-acceptor ($\text{D}^0 \rightarrow \text{A}^0$) recombination energy intensity. Finally, photocatalytic measurements showed that, the photocatalytic performance of the samples under solar-light irradiation was enhanced by an increase of sulfur concentration up to 4%.

1. Introduction

The addition of ZnO and TiO_2 , which are the best photocatalytic materials under UV-light irradiation, the other semiconductors with suitable band-gap could be photocatalytic materials with high efficiency under solar-light irradiation. Among different semiconductors that have band-gap value in the visible region of the electromagnetic spectrum, metal-chalcogenide nanostructures can be used as energy conversion devices such as photovoltaic devices as well as photocatalytic activity [1–6]. It is well known, there is a direct relationship between optical properties of these materials and their applications as photocatalytic and photovoltaic materials. Therefore, for developing of these applications, understanding of optical properties of these materials is the most important factor that should be taken into account. For example, recently we investigated a systematic study about optical properties and photocatalytic applications of SnSe nanostructures [7]. We observed that, defect emissions from different impurities had a significant role in optical properties of the products and these emissions could enhance the photocatalytic performance of SnSe nanostructures. Therefore, such study about the other metal-chalcogenide nanostructures that have a potential for photocatalytic activity could be

very important for development of photocatalysis application of semiconductors.

Among different metal-chalcogenide nanostructures, copper selenides compositions (Cu_2Se , Cu_3Se_2 , CuSe , and $\text{Cu}_{1.8}\text{Se}$) with various crystallographic forms are the best suitable materials in solar-cells applications due to their direct band gap, which is able to tune it in the visible region [8,9]. Furthermore, photocatalytic applications of these compounds have recently been considered [10–13]. The band gap value of the copper selenide composites depends on crystal phase [14]. However, the band-gap value of a semiconductor can be tuned by a doping material. Sulfur as an anionic dopant from the same group of Se can substitute with Se easily without any extra phase [13] and it has been used to tune the band-gap of copper selenide nanostructures in the literature [15,16]. However, different results have been obtained for the band gap of copper selenides by sulfur. Ni et al. reported that, the band gap of CuSe nanoflakes was increased by increasing of S concentration [11], while, Wang et al. showed that, the band gap of Cu_2Se was decreased by increasing S/(S+Se) ratio [16]. However, none of these studies showed exact sulfur effects on optical properties of copper selenide nanostructures.

According to above reasons, the current research presents a

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systematic study on optical properties of S-doped Cu_3Se_2 nanostructures with different sulfur concentration, which were synthesized by a simple and cost-effective co-precipitation method by a green surfactant. Optical properties of the products were investigated by a UV-vis and room temperature photoluminescence (PL) spectrometer with different excitation source intensity. Finally, the effects of the optical behavior of the products on the photocatalytic performance of the products were investigated.

2. Experimental

2.1. Materials and synthesis

In the first step, 0.005 mol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99.99%) was dissolved in 50 cc deionized water in a beaker with a magnet stirrer at room temperature to synthesize the pristine copper selenide nanostructures. At the same time, 0.005 mol of Se powder (99.99%) and 0.013 mol of sodium borohydride (NaBH_4) as a reducing agent dissolved in 50 cc deionized water in another beaker with a magnet stirrer at room temperature to prepare a selenium colloids. After that, these solutions were mixed in a 500 cc beaker. A solution of 50 cc deionized water that included 0.005 mol of sodium hydroxide (NaOH) and 0.001 mol of glycine amino acid as a green surfactant was prepared in another beaker and then during approximately 1 h, this solution was added drop by drop to the big beaker. After that, a precipitation was obtained that was washed by deionized water for several times and it was kept in an oven at 70 °C for 24 h to dry completely. After cooling the oven, a soft powder was obtained. The same process was used to synthesize S-doped copper selenide nanocomposites. In this part, 2%, 4%, and 6% of selenium powder was reduced and instead 0.0078, 0.0156, and 0.0234 g of Na_2S was added to copper nitrate solution for doped copper selenide with different percentage of sulfur.

2.2. Characterizations

The crystal phase, morphology, and microstructure of the product were characterized using X-ray powder diffraction (XRD, Philips, X'pert, system using $\text{CuK}\alpha$ radiation), Fourier transform infrared spectrometry (FTIR, Perkin-Elmer System 2000 series spectrophotometer (USA) by the KBr method), transmission electron microscopy (TEM, Hitachi H-7100), and scanning electron microscopy with Energy-dispersive X-ray spectroscopy (SEM and EDX) to check the quality of the powders obtained. Optical properties of the products were investigated by a room temperature photoluminescence spectrometer (UniRam PL spectrometer) with a He-Cd laser as the source with the power of 40–200 mW and an excitation wavelength of 325 nm and UV-visible spectrometer (Perking-Elmer, Lambda 950).

2.3. Preparation of photocatalytic degradation samples

The photocatalytic application of the powder obtained was examined by degradation of MB dye solutions under solar-light irradiation. Detailed photocatalyst process was similar with our previous work [17]. The MB solutions were made by a concentration of 10. Thereafter, 10 mg of the powders obtained was added to 30 ml of the MB solutions and the mixed suspension was stirred for 30 min under a dark condition to reach an adsorption-desorption equilibrium by a stirrer. The degradation processes were measured by the absorption of MB the filtrate at 664 nm, using a UV-vis absorption spectrometer.

3. Results and discussion

Fig. 1 shows XRD patterns of the pristine copper selenide and S-doped samples with different S concentrations. These peaks belong to tetragonal Cu_3Se_2 phase (JCPDS Card no. 00-008-0279). There is no any extra peaks such as Cu_3S_2 or $\text{Cu}_3\text{Se}_{2(1-x)}\text{S}_{2x}$. Therefore, the XRD

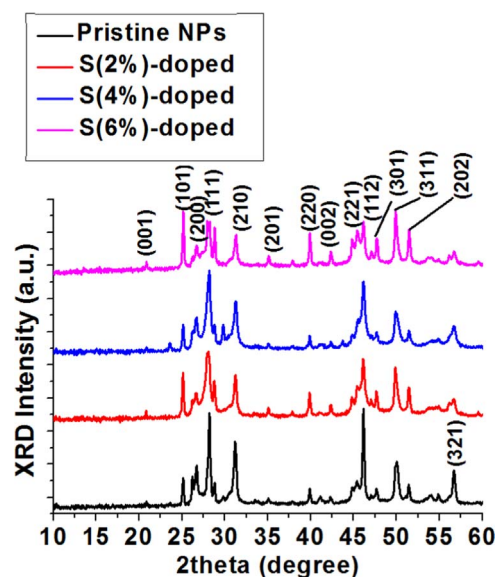


Fig. 1. XRD patterns of the pristine samples and S-doped samples with different sulfur concentration.

results indicate that, Se atoms were substituted by S atoms, successfully. In addition, full width at half maximum (FWHM) of the peaks is enlarged by the increasing of the S concentration that is a sign of a decrease in crystallite size.

Effects of S-doping on vibration modes of the products were investigated by FTIR spectroscopy. Fig. 2 reveals the FTIR spectra of the products. It can be seen, peak at 2908 cm^{-1} , which is appeared in the pristine Cu_3Se_2 , significantly was decreased in S-doped samples. On the other hand, peaks, which are placed between 600 cm^{-1} and 1600 cm^{-1} , have been enhanced by S-doping. Therefore, the FTIR results show that, S ions have different behavior in the Cu_3Se_2 structure in compared to Se ions. It could be due to the different chemical bond length of Cu-Se and Cu-S. In addition, ionic radius of S ion is different in compared to Se ion resulting this difference leads to change vibration modes intensity.

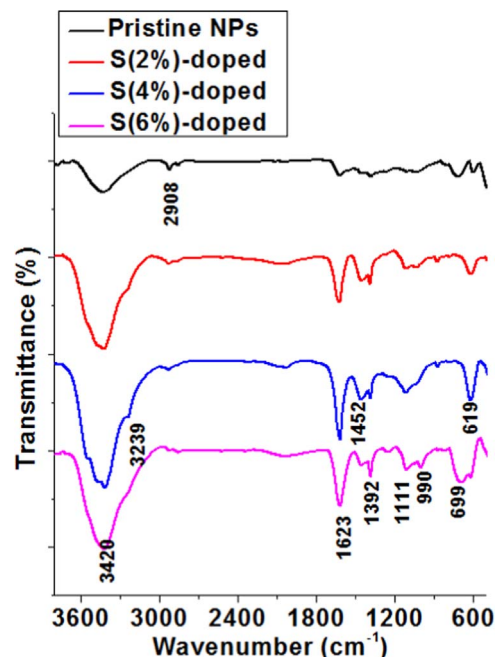


Fig. 2. FTIR spectra of the pristine samples and S-doped samples with different sulfur concentration.

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