

RESEARCH PAPER

Using the $[\text{Co}(\text{oct})_2]$ as a New Precursor for Simple Synthesis of CoS_2 Nanoparticles and Kinetics Studies on Photocatalytic Activities Under UV Irradiation

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ABSTRACT

Cobalt sulfide (CoS_2) nanostructures were synthesized via a simple thermal decomposition method using $[\text{Co}(\text{oct})_2]$ as a new precursor. Using the organometallic compound as precursor could synthesize materials in nano-scale because of having the massive structure that acted as capping agent. The products were characterized by various analyses such as X-ray diffraction pattern (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and fourier transform infrared (FT-IR) spectroscopy. Also, the optical properties of this product was investigated by photoluminescence spectroscopy (PL). However, band gap of CoS_2 nanostructures was estimated about 2.2 eV in this work but CoS_2 was considered as a metallic product in the former work. This difference may be related to quantum effects in nanomaterials. The photocatalytic activity of CoS_2 nanoparticles was examined by decolorization of Erythrosine as an organic pollutant under UV irradiation and degradation percent of this dye was reported about 84 %. According to the kinetics studies, the photocatalytic reactions are following the Pseudo first-order model.

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INTRODUCTION

Metal chalcogenide semiconductor nanostructures have received much attention due to their wide range of potential applications as optical devices [1,2] biological imaging, , gas sensors [3, 4] and photovoltaic devices [5-7]. One of the most complicated metal chalcogenides is cobalt sulfides that have considerably received attention because of the unique catalytic, electrical, optical and magnetic properties [8] and potential application in various fields. Cobalt

sulfides have the strong intrinsic absorption coupled with surface morphology effects [9], so are used in photovoltaic objects such as solar cells and photocatalysts. Among cobalt sulfide compounds, CoS_2 with the pyrite structure has extensively investigated due to their electric and magnetic properties [10-12].

Many approaches have been explored to prepare the metal sulfides, including the high temperature solid phase process [13] the hydrothermal and solvothermal method [14]

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arc-discharge method [15] low temperature procedures [16] chemical vapor decomposition [17] and so on [18]. Thermal decomposition is an appropriate method for control shape and size of nanomaterials, in addition it no need any expensive and complicated equipment. Recently, using the complex precursors with massive structures has been a common way for preparation of nanostructures [19, 20]. The massive structures of different organometallic compounds prevent the agglomeration of the as-prepared products. So, the massive precursor can be used as capping agent and starting materials, simultaneously and decrease the using of chemical compounds [21-23].

In this work, CoS₂ nanostructures were synthesized by thermal decomposition of [Co(oct)₂] as a new precursor. The as-prepared products were characterized by different analyses such as XRD, SEM, TEM, FT-IR, and PL and the photocatalytic performance of this product was explored by degradation percent of Erythrosine dye as an organic pollutant under UV irradiation. According to the results, the degradation percent of this dye in presence of this product was about 84 % that can be considered as a good performance for it.

MATERIALS AND METHODS

All the chemicals reagents used in our experiments such as PEG, sulfur (99.95%), absolute ethanol were of analytical grade and were used as received without further purification. In this paper, we reported the synthesis of CoS₂ nanoparticles by thermal decomposition of [bis(octanoat)cobalt(II)] ([Co(oct)₂]) as a new precursor, in the presence of PEG as solvent.

Characterization

XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu K α radiation. Elemental analyses were obtained from Carlo ERBA Model EA 1108 analyzer. Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. Scanning electron microscopy (SEM) images were obtained on Philips XL-30 ESEM equipped with an energy dispersive X-ray spectroscopy. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. Room temperature photoluminescence (PL) was studied on an F-4500 fluorescence

spectrophotometer. Transmission electron microscope (TEM) images were obtained on a Philips EM208S transmission electron microscope with an accelerating voltage of 100 kV.

Preparation of CoS₂ nanoparticles

CoS₂ nanoparticles were synthesized in a three-neck flask under argon atmosphere. In a typical synthesis process: 0.6 g of [Co(oct)₂] as a new precursor was added to 9 ml of PEG as solvent. This solution was transferred to the flask under stirring, then 0.28 g sulfur was added to the above solution. The mixture was heated up to 180 °C for 120 min. The obtained solution was cooled to the room temperature. The products were collected by adding the excess ethanol. After that, precipitates were centrifuged and washed with absolute ethanol and dichloromethane, subsequently. Finally, the products were dried in the vacuum oven at 50 °C.

Preparation of sample for photocatalytic tests

The photocatalytic activity of the as-prepared CoS₂ nanoparticles was examined by degradation of Erythrosine dye as an organic pollutant. The photocatalytic reactions were carried out under ultraviolet (UV) irradiation. The photocatalytic degradation reactions were performed in a quartz photocatalytic reactor and carried out with 1 L of 20 ppm dye solution containing 0.02 g of CoS₂ nanoparticles as the photocatalyst. This mixture was aerated for 30 min to reach adsorption equilibrium. Then, the mixture was placed inside the photoreactor in which the vessel was 40 cm away from the UV and visible source. The quartz vessel and light sources were placed inside a black box equipped with a fan to prevent UV leakage. The photocatalytic tests were done at room temperature and the mixtures were exposed to radiation for certain times (10, 20, 30, 40 and 50 min) and then were analyzed by UV-vis spectrometer.

RESULTS AND DISCUSSIONS

The XRD pattern of the product is shown in the Fig. 1. According to this pattern, all of diffraction lines are correspondent with CoS₂ with cubic phase (JCPDS= 41-1471). No other peak exists in this figure, so synthesis of pure CoS₂ nanostructures were confirmed. The peaks that are placed at 28°, 32.5°, 36.5°, 46.5°, 55.5°, 60.5°, 63° position are belong to (111), (200), (210), (211), (220), (221),

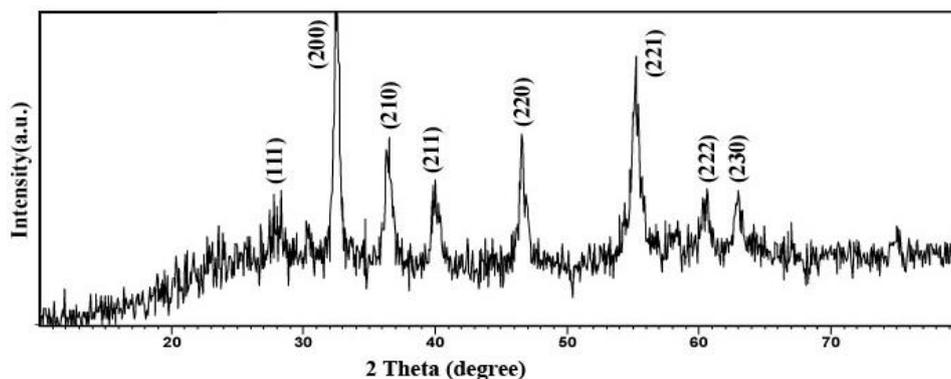


Fig. 1. XRD pattern of CoS₂ nanoparticles.

(222) and (230) miller indices. The broadening of the peaks is mainly due to the nano-scale product.

The particle size and morphology of the product was investigated by SEM and TEM images. According to SEM images that were given in Fig. 2, 30 nm-sized nanoparticles were obtained. As shown, the massive structure of precursor can prevent agglomeration, so nanostructures were

produced that consists of fine particles.

To investigation the particle size and morphology with more details, the TEM image of the product was given in Fig. 3. It can be seen that the product is mainly composed 25 nm-sized particles.

FT-IR analysis was served in order to investigate the existence of PEG on surface of product. As shown in Fig. 4. It can be seen that there are

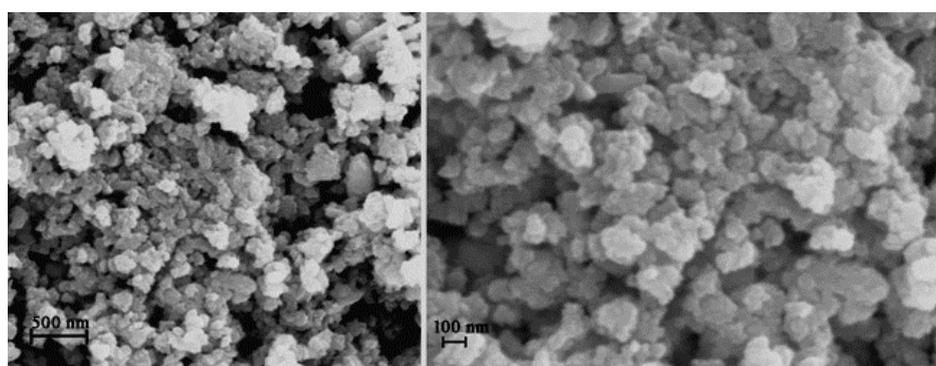


Fig. 2. SEM image of CoS₂ nanoparticles.

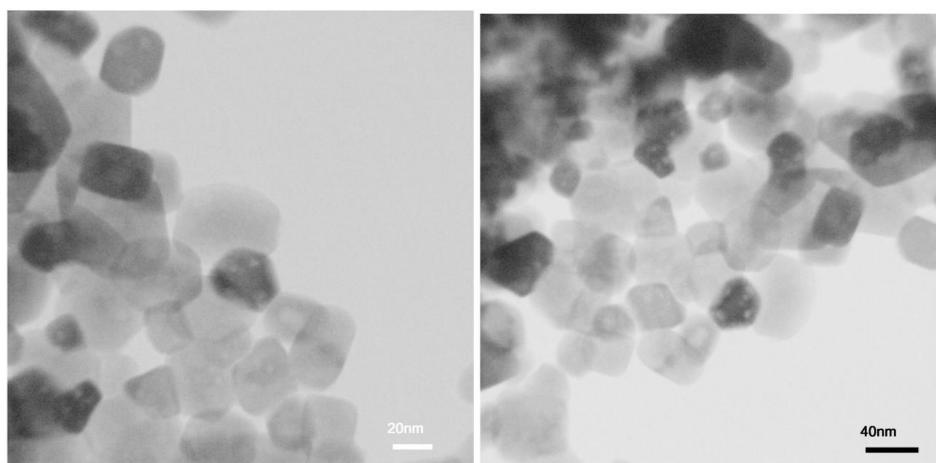


Fig. 3. TEM image of CoS₂ nanoparticles.

some peaks that are not related to the product. It can be observed that a stretch vibration peak located at 1100 cm⁻¹ that is attributed to the C–O stretching model of the PEG. Also two weak stretch vibrations at 2920 and 2885 cm⁻¹ attributing to the C–H stretching models of the PEG carbon chain indicating PEG molecules are absorbed on the surface of nanoparticles.

To study the optical properties of CoS₂ nanoparticles, photoluminescence spectrum (PL)

of the as-prepared product at room temperature was given in Fig. 5. As shown in this figure, an emission at 550 nm is observed. The band gap of this product was estimated about 2.25 eV by this spectrum. According to the reported work, CoS₂ is metallic compound that has no band gap [24]. However, band gap of the product prepared in this work was obtained about 2.2 eV. This difference may be attributed to quantum effect in nanomaterials. The existence of band gap in this

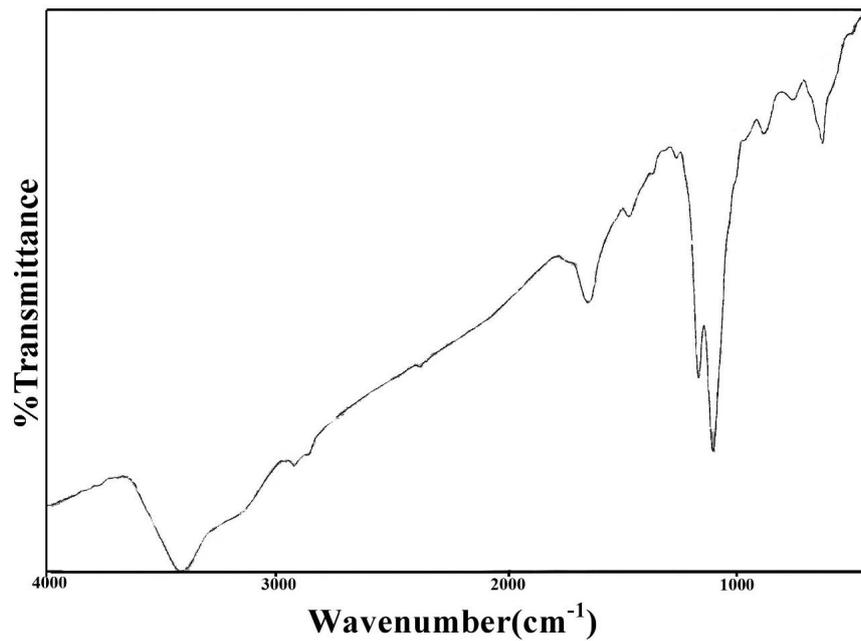


Fig. 4. FT-IR spectrum of CoS₂ nanoparticles.

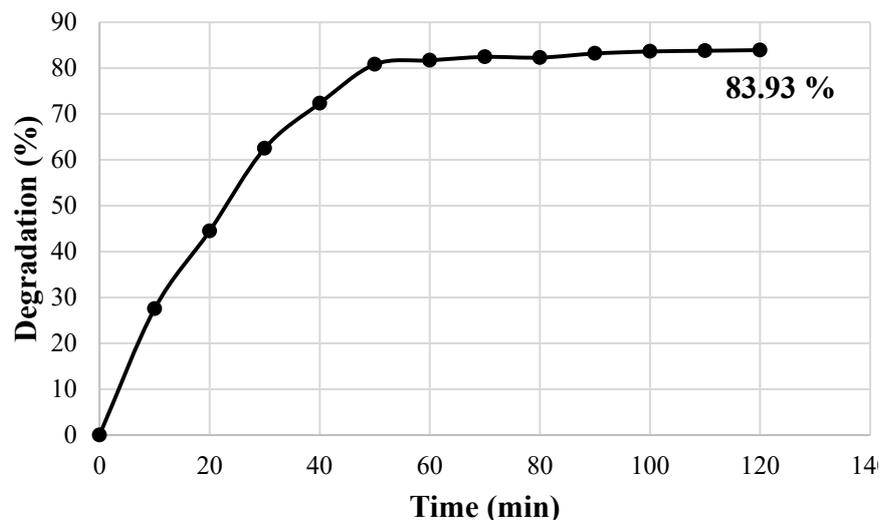


Fig. 5. PL spectrum of CoS₂ nanoparticles.

product can be considered as another reason for synthesis of CoS₂ nanoparticles, successfully.

By considering the estimated band gap for this product, we decided to explore the photocatalytic activity of CoS₂ nanoparticles. Photocatalytic performance was tested using Erythrosine dye as organic pollutant under UV irradiation and the results were given in Fig. 6. As shown, the degradation of this dye in the presence of CoS₂ nanoparticles as photocatalyst during 120 min of UV irradiation was about 83.93 % that can be considered as a good performance for this product. The degradation percent was calculated by the below equation as:

$$\frac{(C_0 - C_t)}{C_0} \times 100$$

where the concentration of dye at t = 0 (initial) and t = t (at the moment) was specified as C₀ and C_t, respectively.

To determine the most active species in photocatalytic procedure, three photocatalytic experiments were carried out in presence of iso-propyl alcohol (0.5 mM), 10 ml of EDTA (0.01 M) and Ar gas as scavengers of hydroxyl radicals, holes and anion radical superoxides, respectively. As shown in Fig. 7, the degradation percent of dye in presence of the EDTA, iso-propyl alcohol and Ar atmosphere decreased as 5.5, 55.73 and 10.53 %, respectively. So, it seems that hydroxyl radicals were more active agent than the others in decolorization process during the photocatalytic reactions. The photocatalytic reactions and the role of different species in degradation of

pollutants can be written as follows [22]:



- Catalyst = Semiconductor

Diverse models were studied to designate the kinetics of reactions. By considering the correlation coefficient R² (0.96) that shown in Fig. 8, it was found that these reactions were following the Pseudo first-order model.

When the concentration of dye is low, the rate expression is given by:

$$-\frac{dC}{dt} = \frac{k_T k_e C}{1 + k_e C} \quad (1)$$

where k_T reflects the apparent reaction rate constant, k_e the apparent equilibrium constant for the adsorption of the dye on to illuminated photocatalyst and C dye concentration at time t (mg/L).

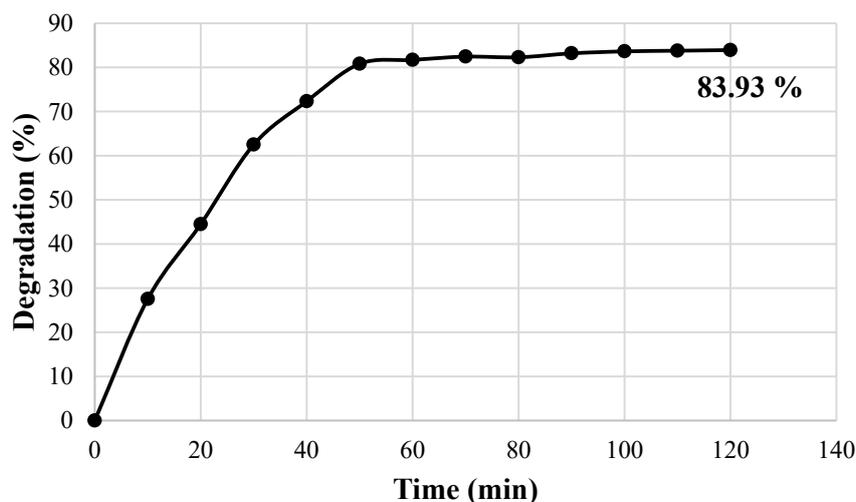


Fig. 6. Plot of dye degradation versus time for Erythrosine dye under UV irradiation in presence of CoS₂ nanoparticles as photocatalyst.

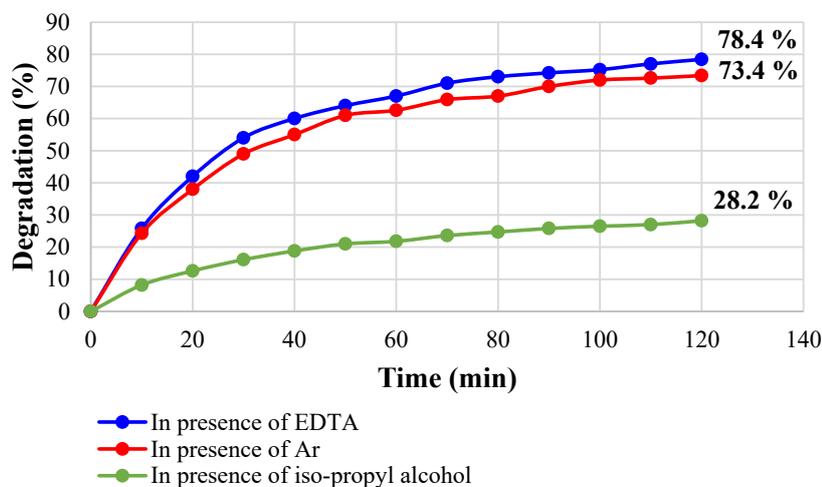


Fig. 7. Curves of dye degradation versus time for Erythrosine dye under UV irradiation in the presence of CoS₂ as photocatalyst and EDTA (78.4%), iso-propyl alcohol (28.2%) and Ar (73.4%) as scavengers.

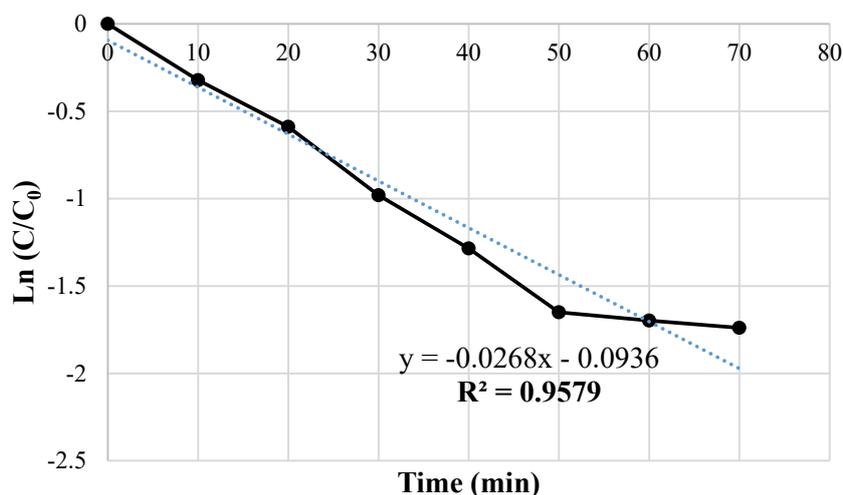


Fig. 8. The effect of photocatalyst on rate constant of the degradation reaction of Erythrosine under UV irradiation.

The integrated form of Eq. (1) is given in below:

$$t = \frac{1}{k_e k_T} \ln \frac{C_0}{C} + \frac{1}{k_T} (C_0 - C) \quad (2)$$

The above equation could be expressed as follows:

$$\ln \frac{C}{C_0} = k_T k_e t = k' t \quad (3)$$

where C₀ and C are the initial dye concentration (mg. L⁻¹) and dye concentration at time t (mg. L⁻¹), t is reaction time (min) and k' is the first-order rate constant (min⁻¹) [25- 27].

CONCLUSION

In this experimental work CoS₂ nanostructures were successfully synthesized using [Co(oct)₂] as a new precursor by simple thermal decomposition method. The product was characterized by various analyses such as XRD, SEM, TEM and FT-IR. The fine particles and high purity of product showed that this method can be considered as a facile method for preparation of CoS₂ nanostructures. The optical properties of this product was studied by PL and band gap of it was estimated about 2.2 eV. According to the reported work, CoS₂ was introduced as a metallic compound without band gap. This difference can be

related to the quantum effect in nanomaterials. So, band gap estimated in this work by PL spectrum could be another evidence for synthesis of this product in nano-scale. By considering CoS₂ nanostructures as a semiconductor with band gap 2.25 eV, photocatalytic performance of it was investigated by degradation of Erythrosine dye as an organic pollutant under UV irradiation. The degradation percent of this dye was obtained about 84 % that can be considered as a good photocatalytic performance. Kinetics studies confirmed that the photocatalytic reactions following by Pseudo first-order model. On the other sides, it should be noted that this method as a simple and inexpensive method can be used to preparation of the other sulfide compounds with various applications.

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CONFLICT OF INTEREST

The author declares that there is no conflict of interests regarding the publication of this manuscript.

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