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Synthesis and structural characterization of magnetic cadmium sulfide–cobalt ferrite nanocomposite, and study of its activity for dyes degradation under ultrasound

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ABSTRACT

Cadmium sulfide–cobalt ferrite (CdS/CFO) nanocomposite was easily synthesized by one-step hydrothermal decomposition of cadmium diethyldithiocarbamate complex on the $CoFe_2O_4$ nanoparticles at 200 °C. Spectroscopic techniques of powder X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), UV–visible spectroscopy, field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX), Brunauer–Emmett–Teller (BET), and magnetic measurements were applied for characterizing the structure and morphology of the product. The results of FT-IR, XRD and EDX indicated that the CdS/CFO was highly pure. SEM and TEM results revealed that the CdS/CFO nanocomposite was formed from nearly uniform and sphere-like nanoparticles with the size of approximately 20 nm. The UV–vis absorption spectrum of the CdS/CFO nanocomposite showed the band gap of 2.21 eV, which made it suitable for sono-/photo catalytic purposes. By using the obtained CdS/CFO nanocomposite, an ultrasound-assisted advanced oxidation process (AOP) has been developed for catalytic degradation of methylene blue (MB), Rhodamine B (RhB), and methyl orange (MO)) in the presence of H_2O_2 as a green oxidant. CdS/CFO nanocomposite exhibited excellent sonocatalytic activity, so that, dyes were completely degraded in less than 10 min. The influences of crucial factors such as the H_2O_2 amount and catalyst dosage on the degradation efficiency were evaluated. The as-prepared CdS/CFO nanocomposite exhibited higher catalytic activity than pure CdS nanoparticles. Moreover, the magnetic property of $CoFe_2O_4$ made the nanocomposite recyclable.

1. Introduction

Semiconductor-based photocatalysis as an enduring research focus and green technology has enough potential to overcome the environmental pollution and energy crisis problems [1]. Among various semiconductor photocatalysts, cadmium sulfide (CdS), an n-type semiconductor with a large direct band gap of 2.4 eV, is one of the most important semiconductors and has been comprehensively studied for different variety of applications, particularly for visible-light-driven photocatalysis during the past decades [2–9]. However, rapid recombination of the excited electron–hole pairs greatly impedes the photocatalytic efficiency of CdS [3]. In addition, CdS is susceptible to producing photocorrosion when the photocatalytic reactions are carried out in aqueous media where CdS itself is oxidized by the photogenerated holes [2,4–7]. To overcome these problems, various approaches have been developed, for instance combination of CdS with other semiconductors [4,8,10], noble metals [11] conductive polymers [12] or carbon nanomaterials [13,14].

In recent years, the combination of CdS with magnetic nanomaterials have proven to be successful in increasing the catalytic activity, antiphotocorrosion, recovery and reuse of CdS catalyst to some extent. For this reason, various approaches have been developed for synthesizing magnetic CdS nanocomposites. Roychowdhury et al. [15] synthesized magnetic CdS–Fe_3O_4 nanocomposites with two step chemical route method. Magnetic measurements revealed the presence of super paramagnetic behaviour in the nanocomposites with smaller particle size (5–7 nm) of Fe_3O_4 nanoparticles whereas the nanocomposite with 12 nm Fe_3O_4 was essentially ferrimagnetic. Liu et al. [16] synthesized the CdS–Fe_3O_4 nanocomposites with sonochemical method which exhibited good magnetic and photocatalytic activity in

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visible light spectrum. Wang et al. [17] reported the epitaxial and non-epitaxial growth of α-Fe_2O_3 and Fe_3O_4 nanoparticles on the surface of CdS nanorods via polymer wrapping technique. Photocatalytic studies revealed that α-Fe_2O_3–CdS completely degrade the methylene blue dye in 7 h. However, only 62% of the dye was degraded using Fe_3O_4–CdS nanocomposite in same time interval. Yu et al. [18] have reported on the synthesis of CdS nanorods/$ZnFe_2O_4$ composite with high efficiency for photocatalytic generation hydrogen. Recently, Xiong et al. [19] have reported the synthesis of CdS/$CoFe_2O_4$ nanocomposite with differing ferrite content via a two-step hydrothermal method. Photocatalytic studies revealed that the nanocomposite completely degrade the RhB dye within 1 h. Very recently, Singh et al. [20] have synthesized CdS nanorods/$CoFe_2O_4$ nanocomposite by using a facile soft chemical method. Photocatalytic results revealed that this nanocomposite degrade about 70% of MB dye albeit after long reaction time of 2 h. However, some of these semiconductor-based photocatalysis methods still are associated with one or more disadvantages, such as use of harmful UV light, prolonged degradation times (≥1 h) and low degradation efficiency. To meet the fast-developing water treatment requirements, it is needed to offer new and innovative technologies and materials for efficient removal of pollutants from the non-transparent wastewater. Semiconductor based sonocatalysis can overcome the disadvantages of photocatalytic technology mentioned above because the ultrasonic wave has a strong ability of penetrating for any aqueous medium [21–25]. It is well known that the sonocatalytic efficiency depends highly on the type of catalyst. Also, novel sonocatalysts development is important to further understanding of the sonocatalytic mechanism as well as promoting the sonocatalysis applications.

In this paper, CdS/$CoFe_2O_4$ (CdS/CFO) nanocomposite was prepared, for the first time, by a facile one-step hydrothermal decomposition of cadmium diethyldithiocarbamate ($Cd(Et_2DTC)_2$) precursor over magnetic $CoFe_2O_4$ nanoparticles. Various spectroscopic techniques were used to characterize the CdS/CFO nanocomposite and its application for the degradation of organic dyes pollutants was evaluated under ultrasound irradiation. Also, the effect of different operational parameters such as H_2O_2 dosage, catalyst amount, and dye concentration was investigated on the efficiency of degradation process. In addition, the sonocatalitic activity of CdS/CFO nanocomposite was compared with that of pure CdS nanoparticles under similar conditions. To the best of our knowledge and based on the literature review, there is no report of the rapid sonodegradation of organic dyes by using CdS/CFO nanocomposite especially in the presence of H_2O_2 as an environmental-friendly oxidizing agent.

2. Experimental

2.1. Materials and characterization

Cadmium (II) nitrate ($Cd(NO_3)_2{\cdot}4H_2O$), diethylamine ($C_4H_{11}N$), and carbon disulphide (CS_2) were provided from Sigma-Aldrich. Iron(III) nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), cobalt(II) nitrate ($Co(NO_3)_2{\cdot}6H_2O$), methyl orange (MO, $C_{14}H_{14}N_3NaO_3S$), methylene blue (MB, $C_{16}H_{18}ClN_3S$), and Rhodamine B (RhB, $C_{28}H_{31}ClN_2O_3$) were purchased from Merck Chemical Company. Infrared spectra were obtained using Schimadzu FT-IR 160 spectrophotometer using KBr pellets. The XRD patterns were inscribed on a Rigaku D-max C III, X-ray diffractometer using Ni-filtered CuKα radiation (λ = 1.5406 Å) for the phase determination of the decomposed samples. The powder of CdS/CFO nanocomposite was gold coated in the Desk Sputter Coater-DSR1 auto fine coater for 120 S at 20 mA and then the morphology of coated CdS/CFO nanocomposite was studied by Mira3 Tescan, scanning electron microscope outfitted with energy dispersive X-ray analyzer (EDX) for the elemental analysis of the sample. The size of the nanocomposite particles was measured by a transmission electron microscope (TEM, EM10C) at the accelerating voltage of 100 kV. X-ray photoelectron spectroscopy (XPS, Bestec, German company) measurements were done to study the chemical states of the elements. Optical absorption spectra of nanocatalyst and dyes were obtained from a Cary 100 concvarian UV–Vis spectrophotometer in the wavelength range of 200–800 nm. Formation a homogeneous suspension in ethanol by sonicating for 25 min was done for UV–Vis studies of nanocatalyst. Vibrating sample magnetometer (VSM, Iran Meghnatis Daghigh Kavir Company) was employed to measure the magnetic parameter at room temperature. The Brunauer–Emmett–Teller (BET) surface area was measured by N_2 adsorption measurements at 77.3 K using Nova 2000. An ultrasonic apparatus operating at 37 kHz (Sonic 6MX, output acoustic power 100 W) was used for the degradation of dye solutions.

2.2. Synthesis of the CdS/CFO nanocomposite

Cd(II) diethyldithiocarbamate, CdS and $CoFe_2O_4$ nanoparticles were prepared according to the reported methods [26–28]. The CdS/CFO nanocomposite was synthesized as follows: To 0.16 g $CoFe_2O_4$ nanoparticles dispersing in 30 mL of deioniised water followed by ultrasonicating for 1 h. 0.3 g $Cd(Et_2DTC)_2$ was added to $CoFe_2O_4$ suspension. The suspension was ultrasonicated for 1 h again and was autoclaved at 200 °C for 24 h under autogenous pressure after moving into a 50 mL Teflon-lined stainless steel autoclave. The product was washed five times with water after cooling down to room temperature and then filtered by centrifuging at 4000 r $min^{-1}$for 10 min.

2.3. Sonocatalytic degradation tests

A typical procedure for RhB degradation was applied. The reactions were carried out in an Pyrex glass vessel containing CdS/CFO sonocatalyst (0.5 g/L), H_2O_2 (30 mM), and dyes solution (50 ml, 25 mg/L). Magnetically stirring of the suspensions was performed for 30 min to achieve the adsorption–desorption balance between the dye and catalyst. The experiments were then performed under ultrasonic irradiation. All the tests were carried out at room temperature under atmospheric pressure by using under 37 kHz ultrasonic generators. In the determined time intervals, the samples were taken and the catalyst was separated by an external magnetic field. The residual dye concentrations were determined using UV–vis spectrophotometer. The conversion was calculated by $(C_0-C)/C_0$, where C is the concentration of the reactant after irradiation, C_0 is the concentration of the reactant after adsorption equilibrium. The effect of important parameters, such as the amount of H_2O_2 (0–40 mM), sonocatalyst dosage (0–0.75 g/L), and initial dye concentration (5–35 mg/L), was studied on the sonocatalytic activity of CdS/CFO nanocomposite. Also, the same tests have been used for MB and MO degradation.

3. Results and discussion

3.1. Characterization of the sonocatalyst

XRD pattern of the CdS/CFO nanocomposite is shown in Fig. 1(A). The peaks at 2θ = 24.88, 26.58, 28.25, 43.86, 47.92, 51.97, and 66.97 can be assigned to (1 0 0), (0 0 2), (1 0 1), (1 10), (1 03), (2 0 0), and (2 0 3) planes of hexagonal structure of CdS, which is parallel to the literature values (JCPDS Card no. 41-1049). The peaks at 2θ = 29.96, 35.46, 43.86, 57.05, and 62.47 can be assigned to (2 2 0), (3 1 1), (4 0 0), (5 1 1), and (4 4 0) planes of cubic structure of