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Fabrication of floating CdS/EP photocatalyst by facile liquid phase deposition for highly efficient degradation of Rhodamine B (RhB) under visible light irradiation

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ABSTRACT

The cadmium sulfide (CdS) faces photochemical corrosion, and hence, the photocatalytic efficacy decreases with the light-irradiation time. The deposition of suitable content of CdS on the expanded perlite (EP) may prevent the photochemical corrosion and aggregation of CdS nanoparticles. Hence, a series of solid nanocomposites containing CdS nanoparticles on the EP support with different CdS contents were synthesized. CdS/EP buoyant nanocomposites have been successfully prepared by deposition of CdS on the EP using a simple one-step facile liquid phase deposition route at ambient temperature. The as-prepared nanocomposites were characterized by scanning electron microscope (SEM), transmission and high-resolution transmission electron microscopy (TEM, HRTEM), UV–vis spectroscopy, X-ray diffraction, and FT-IR spectroscopy. The XRD and HRTEM results indicated the formation of CdS nanoparticles with the hexagonal cubic phase in the EP. The SEM, TEM and HRTEM results clearly show that CdS nanoparticles have homogenously embedded in the mesopores of EP supports. The photocatalytic activities of CdS/EP nanocomposites with varying CdS contents were examined for the degradation of Rhodamine B (RhB) dye under visible light irradiation. Hence, these results reveal that enhanced catalytic activity arises in novel CdS/EP nanocomposites and significantly, its photocatalytic activity is about two times higher than that of bare CdS. This advanced nanocomposite is expected to provide a new appreciation into the design of floating photocatalysts with excellent recyclability, high efficiency, and good stability.

1. Introduction

In recent years, water pollution especially caused by organic pollutants including pesticides and various dyes used in textile industries have become a global issue, all these precarious activities have hazardous effects on the hydrological cycle [1–4]. The discharges of these organic pollutants from different industries and oil seepage from ship containers have caused severe environmental disasters [5,6]. Various kinds of industries are responsible for these contaminants without suitable treatment [7,8]. Great efforts have been made to remove these organic pollutants from waste water before release to the major water bodies [9]. However, effectual and inexpensive treatment of these organic pollutants in waste water has been a big issue of extensive concern [10]. Therefore, scientists seriously focused on solar light utilizing photocatalytic technology to eliminate the treacherous pollutants and reduce the environmental impact of the human activities [11,12]. To deal with these hazardous contaminants, several novel technologies have been developed, proposed for treatment of toxic and polluted water [13]. Narrow band gap semiconductor nanoparticles, such as bismuth sulfide (Bi_2S_3) [14] and cadmium sulfide (CdS) have attracted keen interest in the past two decades as a promising photocatalyst in both fields of energy and environment due to their high photocatalytic activity, low cost, photostability, and resistance to photo-corrosion [15,16]. Cadmium sulfide is a semiconductor material with ideal structure, electronic and optical properties and colloidal nanocrystals possessing anisotropic shapes for many applications [17]. CdS is a direct band gap semiconductor, the band gap energy of bulk CdS is 2.40 eV [18]. Owing to its distinctive characteristics, CdS is widely used in many applications including physicochemical, photoluminescence and potential applications in many fields [19]. To hinder the easy preferable agglomerations of nanoparticles, several research efforts have been made on using emulsifiers as a stabilizer to control the architecture i.e. both particle size and distribution of nanoparticles [20]. However, CdS nanocomposite has a small band gap, but the

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combination of holes and electrons in the semiconductor have demerit to decompose organic pollutants [21]. Therefore, to prevent the combination of electrons and holes, CdS is combined with different semiconductors [22,23].

Although, the blended of different semiconductors solved the problems of recombination of holes and electrons and also aggregations of the photocatalyst [24]. But still these powdered composite materials have several problems of sink into the water body, application of nanocomposite powder to a continuous flow system, and the accessibility of oxygen and sunlight to the bottom of the water is a really big challenge [25]. To work out these problems, floating photocatalysts have been synthesized [26]. Many techniques have been carefully elaborated for immobilizing CdS catalyst onto a solid surface and different types of substrates have been experienced [27,28]. Liu et al. [29] reported the synthesis of CdS on hematite (α-Fe_2O_3) via a three-step process. Zhang et al. [30] prepared the ternary CdS-graphene-TiO_2 hybrids by through an in-situ strategy on the flat surface of graphene oxide. However, all these photocatalysts preparation required most time, high temperature, costly support and difficult to achieve, which limits their extensive use.

Perlite is siliceous volcanic glass rock lava containing crystal water, its main components are alumina (Al_2O_3) and silica (SiO_2), and also incorporate Na_2O, MgO, CaO, Fe_2O_3 and K_2O [31]. When perlite is heated at a temperature range of 700–1200 °C, it is expanded up to 20 times of its original length, its color is white and transparent and has a low density of 32 kg m^{-3} [32]. It is used in different manufacturers due to the low price, and easy availability [33]. They are composed of different layers and pores, which are considered to be used as the best support due to their corrosion resistance, the absence of toxicity and high-temperature stability [34]. For this reason, expanded perlite (EP) is used as a support to prepare some of the nanocomposites photocatalysts [35]. In the present study, for the first time, CdS component was immobilized on layered expanded perlite as novel CdS/EP visible light photocatalyst. There is no need to control the pH of the solution as this technique is reported without the use of any kind of complexing agent. The photocatalytic activity of CdS/EP photocatalyst was evaluated by the degradation of Rhodamine B (RhB), and its photocatalytic degradation was compared with that of pure CdS photocatalytic activity. The photocatalytic efficacy of CdS/EP nanocomposites is superior for degradation of Rhodamine B to the pure CdS nanoparticles.

2. Experimental section

2.1. Synthesis

(a) **Preparation of EP.** To get the uniform size of EP, it was first sieved through a 30 mesh screen and then soaked in a 2 L beaker filled with water for 12 h to select only large floating grains and facilitate further photocatalyst treatment. Only the floatable EP was collected and then dried in an oven at 100 °C overnight.

(b) **Preparation of CdS/EP.** A facile liquid phase deposition method was used to synthesize the CdS/EP nanocomposite. In a typical procedure, 0.875, 1.75, and 2.625 mmol of $CdCl_2$•$2.5H_2O$ were dissolved in 30 mL water each and stirred for 5 min, and then 1 g EP was added in each, stirred for 30 min and named solutions A, B, and C respectively. Then equal molar counterpart of 0.875, 1.75, and 2.625 mmol of Na_2S•$9H_2O$ were dissolved in 30 mL water each and stirred for 5 min and named solutions D, E, and F. Then the solutions, D to A, E to B, and F to C were added dropwise with constant stirring. These mixtures were stirred at room temperature for 2 h. After the reaction was completed, the resulting mixtures were filtered and washed with copious amount of distilled water and dried in the oven for 6 h at 65 °C. The final composite materials were labeled as 10-CdS/EP, 20-CdS/EP, and 30-CdS/EP where the number denotes the wt% contents of CdS.

(c) **Preparation of blank-CdS.** For comparison, blank CdS was also synthesized via the same facile low-temperature precipitation process. In detail, 0.5 M of $CdCl_2$ was added to 30 mL distilled water and stirred for 5 min and named solution A. Then 0.5 M of Na_2S was added to 30 mL water and stirred for 5 min and named solution B. Solution B was added dropwise to solution A with constant stirring. The mixture was stirred at room temperature for 2 h. After the reaction was completed the resulting mixture was filtered and washed 3 times with distilled water and dried in the oven for 6 h at 65 °C.

2.2. Characterization

The crystalline phase structure of all samples was observed on a Bruker-D8-Focus powder diffractometer with (Cu Kα irradiation λ = 0.15406 nm) in the range 5–80° (2θ). The morphologies of all samples were observed by transmission electron microscopy (TEM, HITACHI 7700), scanning electron microscopy (SEM, HITACHI S4700), and high resolution transmission electron microscopy (HRTEM, JEOL 3010). The elemental compositions of samples were determined by the energy dispersive spectroscopy (EDS, INCA Energy, Oxford). UV–visible diffuse reflectance spectrometer (DRS, Shimadzu UV3600) was used to study the optical absorption properties of the samples. The Fourier Transform-Infrared spectra (FT-IR) were recorded on Nicolet iS10.

2.3. Photocatalytic activity evaluation

To examine the photocatalytic activity of CdS/EP, the photodegradation of Rhodamine B aqueous solution under simulated sunlight irradiation was conducted. For each cycle, 0.1 g photocatalyst was added to 100 mL Rhodamine B (RhB 10 mg/L). Prior to the photoreaction and to ensure the establishment of adsorption-desorption equilibrium of Rhodamine B dye and photocatalyst, the suspension was stirred for 30 min in the dark. At given time interval of every 15 min, the sample was taken out from the suspension and then immediately centrifuged at 3000 rpm for 20 min to separate the photocatalyst and RhB solution. The concentration of Rhodamine B has measured with an METASH 5100B UV–vis spectrophotometer at a wavelength of 554 nm. According to Beer-Lambert's law, the intensity of RhB character absorption peak is a direct relationship with a concentration of RhB. Therefore, using the following equation the photodegradation efficacy of RhB could be calculated [Rate of degradation (Rd) or residual rate (Rr) %]

$$Rd\% = 100\% - Rr\%$$
$$\mathrm{Rr\%} = (\mathrm{Ct/Co}) \times 100\% \quad (1)$$

Where both, Rd % or Rr % reflects photocatalytic efficacy, C_0 is the initial concentration of RhB, and Ct is the concentration after t min irradiation.

3. Results and discussions

3.1. Morphology of the catalyst (TEM)

The morphology of the composites was depicted by TEM images. In Fig. 1, typical TEM images of EP and as-obtained CdS/EP nanocomposites are displayed, which indicate large pore mesoporous materials with the homogeneity of rotundity and void sizes. In Fig. 1(d) it is seen that CdS nanoparticles are well dispersed in EP matrix. The formation of CdS nanoparticles in EP matrix increases with the increase in the concentration of CdS content, and agglomeration of CdS nanoparticles obviously appears at 30%. Furthermore, the TEM images indicate that the CdS particles were distinguishable, but not well resolved due to the presence of layered EP. Although the CdS particles are in contact with each other, the particles were not aggregated into a big structure. Most of the particles were identical in size and have irregular round shapes.