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Photodegradation of *Indigo Carmine* dye by CdS nanostructures under blue-light irradiation emitted by LEDs

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ABSTRACT

Two nanostructured CdS semiconductors were prepared by the precipitation method under ethylenediamine mild synthesis conditions. The ethylenediamine–acetonitrile solvent mixture induces the formation of CdS-1D-flexible nanofibers, whereas the ethylenediamine–ammonia solvent produces 3D-microflower morphology. Similar crystalline structure and optical–electronic properties were obtained by using both solvents; however, the photocatalytic activity strongly depends on both the CdS morphology and textural properties. In comparison with the commercial CdS, the flexible CdS nanofibers showed the highest photocatalytic activity in the photodegradation of *Indigo Carmine* (*IC*) dye by using pure blue light irradiation. The effect of the stirring rate, photocatalyst load and *IC* dye concentration was investigated under either the diffusive or kinetic controlled regime of the photoreaction. The influence of the pH solution and stability cycle on the nanofibers was also evaluated. The blue photoreduction of *IC* dye was also investigated in the presence of hydrazine as O_2 scavenger. The possible oxidation or reduction mechanisms of the *IC* dye by the photogeneration of either the superoxide or hydrazil radicals on the surface of the CdS nanofibers are presented and discussed.

1. Introduction

The *Indigo Carmine* (*IC*) dye is considered as a highly toxic indigoid class of dye which constitutes one of the largest groups of pollutants found in wastewaters from textile and other industries. These compounds are categorized as environmentally hazardous materials because the discharge of this highly colored wastewater into the ecosystem involves problems such as esthetic pollution and perturbation of aquatic life [1,2]. *IC* is released into water from its processing since it is among the most widely used textile dyeing agents; it is also used as an additive in pharmaceutical tablets and capsules, as a redox indicator in analytical chemistry and as a microscopic stain in biology, among other applications [3]. Several chemical and physical processes like precipitation and electrochemical oxidation are currently used for its decomposition. Alternatively, the photocatalytic degradation (oxidation or reduction) of organic dyes using semiconductor materials has resulted to be an efficient method for the degradation of these pollutant compounds [4,5]. One of the paths for the dye photodegradation process is via oxidation, which is based typically on the generation of (OH^*) hydroxyl radicals by the oxidation of the OH^- ions with the holes (h^+) photogenerated during UV light irradiation in the presence of a high content of dissolved O_2 and using photocatalysts such as TiO_2, MgO, Y-CeO_2, $ZnSeO_3$, $SnBu_3Cl$, Sm_2FeTaO_7 and Nb_2O_5 semiconductors [6–15]; however, the broad band gap energy of these materials ($E_g = 3.2–4.5$ eV) requires the aforementioned UV light for their activation. On the other hand, it is known that the holes (h^+) produced under visible light irradiation have a weak oxidation potential ability, and as a consequence, the formation of the powerful OH^* radical is negligible [16].

Semiconductors like CdS or modified CdS, which present narrow band gap energy in the visible region (2.4 eV), have been extensively used as photocatalysts for the photodegradation of diverse organic pollutant dyes, for example, Methyl Orange, Rhodamine B, Methylene Blue, Eosin Y, Orange II, and Safranin O [17–25]. Recently,

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this photodegradation process has been conducted by using a pure blue LED lamp as a photonic energy source [26,27], which provides enough energy for the generation of the powerful hydroxyl (OH^*) o superoxide ($^*O^{2-}$) radicals [28]. The use of a LED lamp has advantages such as high photon efficiency for long time operation, low voltage electrical power source, and cooled emission in a specific spectral wavelength [29,30]. It is known that the *IC* dye has a very slow degradation rate when is exposed to visible light [31]; for this reason, studies about its photodegradation (oxidation and/or reduction) by using a CdS photocatalyst, especially under pure blue light conditions, have not been reported yet. According to the aforesaid, the present research work attempts to be one of the first ones reporting the kinetic study of the photodegradation of the *IC* dye via an oxidation or reduction process.

The use of either naturally dissolved O_2 or hydrazine enabled us to focus on favoring either the dye oxidation or dye reduction, respectively. This was possible by generating either superoxide ($O_2{}^{*-}$) or hydrazil radicals, using nanostructured CdS (fibers or flowers) under a cold light source (blue LED lamp). The effect of the dye concentration, stirring rate, and photocatalyst load using blue-light irradiation emitted by a low-power LED lamp (3 W) was investigated. The prepared CdS nanostructures were well characterized by several techniques like XRD, UV–Vis, EDX, N_2 physisorption, SEM and TEM.

2. Materials and methods

2.1. Synthesis of CdS semiconductors

The nanostructured CdS materials were synthesized by the precipitation method under mild synthesis conditions (low temperature and short aging time) [32], using 10 vol% of H_2O, 60 vol% of ethylenediamine (*en*, Aldrich) and 30 vol% of a second solvent, which can be either acetonitrile (ACN, Aldrich) or ammonia (NH_3, Aldrich). Through a typical procedure, appropriate amounts of $Cd(NO_3)_2H_2O$ (Reasol) were dissolved at room temperature in acetonitrile or ammonia aqueous solution at constant stirring for 15 min., and then *en* was added. Afterwards, carbon disulfide (CS_2, Aldrich) was added dropwise by maintaining a stoichiometry S:Cd molar ratio of 1:1. The transparent mixed solution was heated up to boiling point (90–110 °C) under vigorous magnetic stirring (800 RPM) for 1 h and subsequently cooled at room temperature at constant stirring. Finally, the resulting yellow precipitate was collected by filtration, washed with an ethanol–water solution and dried at 80 °C for 1 h. The final product was labeled with the name of the second used solvent as ACN and NH_3. For comparison purposes, commercial CdS was supplied from Aldrich.

2.2. Characterization of the CdS semiconductors

The obtained nanostructured CdS materials were characterized by powder X-ray diffraction using a D8 Advance Bruker X-ray diffractometer with Cu kα radiation of 1.5406 A (35 kV, 25 mA). The scanning range was between 10 and 70° (2θ) with a step size of 0.03°/s. For the lattice parameter determination, the Bragg law was used considering a hexagonal structure (see *ESI*). For the crystal size determination, the Debye–Sheerer equation ($\tau = K\lambda/\beta\cos\theta$) was used, where τ is the mean size of the ordered crystalline domains; K is a dimensionless shape factor with a value close to unity (about 0.9); λ is the X-ray wavelength; β is the line broadening at half the maximum intensity (FWHM, in radians); and θ is the Bragg angle. Diffuse reflectance spectroscopy was performed in the range of 190 and 800 nm using a UV–Vis Cary 5000 spectrometer equipped with an integration sphere. The visible band-gap energy (Eg) was calculated using the Kubelka–Munk method, considering a direct transition allowed for CdS. The morphology was determined by means of a transmission electron microscope (TEM) JEOL JEM 1230 operated at 100 keV. The semiquantitative composition of the nanostructured CdS was revealed by field emission scanning electron microscopy (FESEM) using a Helios NanoLab 600i equipped with Advanced DualBeam coupled with an EDS (energy dispersive X-ray spectroscopy) detector. The specific surface area of the semiconductors was determined by the BET method from the nitrogen adsorption–desorption isotherms obtained by using a Quantachrome Autosorb-3B apparatus. Prior to the adsorption procedure, the samples were degassed under high vacuum at 80 °C for 6 h.

2.3. Photodegradation of Indigo Carmine (IC) dye

The photodegradation reactions were performed in an open-air-glass-photoreactor system containing 200 mL of an aqueous solution with 0–40 ppm of *IC* dye and varying the photocatalyst powder load in the 0.025–0.15 g/L range. The exposed-to-air suspension was maintained under magnetic stirring at different stirring rates from 200 to 1000 RPM, at room temperature and without any pH adjustment (natural pH = 8). The system was irradiated by means of a pure blue LED lamp of 3 W (emitting monochromatic light, λ = 450 nm) placed at an average distance of ~7 cm from the suspension. Before irradiating, the suspension was kept under dark conditions for 1 h to ensure the adsorption–desorption equilibrium and during this step, the amount of dissolved O_2 without air bubbling (natural oxidizing condition) was measured by using a Hanna Oxy-Check apparatus to guarantee the oxidation route of the *IC* dye. On the other hand, to ensure the *IC* dye reduction reaction, appropriate amounts of CdS load and hydrazine as reducing reagent or O_2 scavenger were added. The suspension was maintained at 400 RPM, at room temperature in natural alkaline medium without air bubbling, generating reducing conditions.

Once the optimal *IC* concentration (10 ppm) and photocatayst load (10 mg) of the selected CdS semiconductor were established, additional photodegradation experiments, under oxidizing conditions (1000 RPM), were performed: (1) three cycle experiments with the selected CdS semiconductor, recovered by filtration were used again for 5 min; (2) the pH of the *IC* solution was adjusted at 4.5 and 10 with HNO_3 and NaOH, respectively; (3) the *IC* solution in natural pH was bubbled with N_2 varying the stirring rate (see ESI, Fig. S2).

In all cases, the estimation of the *IC* dye concentration was determined by sampling at time intervals and analyzing the samples with UV–Vis spectroscopy on a Varian-Cary 5000 spectrometer through the disappearance of the absorption band at 610 nm for *IC*. The reaction kinetics was established by considering the Langmuir–Hinshelwood kinetic model, usually applicable to describe the photodegradation kinetics on semiconductors. When the adsorption or the reactant concentration is low, the reduction rate (r) can be simplified to the pseudo-first-order kinetics with an apparent first-order rate constant (k_{app}), where the concentration of the reactant after reaching the equilibrium was taken as the initial concentration (C_0), which is expressed as follows: $\ln(c/c_0) = -k_r k_{ads} C = -k_{app} t$ where k_r is the rate constant and k_{ads} is the adsorption equilibrium constant. Plotting $-\ln(C/C_0)$ vs reaction time (t) yields a straight line, and the slope is the apparent rate constant.

3. Results and discussion

3.1. Crystalline structure of CdS

The X-ray diffraction patterns for both CdS samples (Fig. 1) exhibit reflection peaks corresponding to the (1 0 0), (0 0 2) and