



# A stable, efficient and reusable CdS–SnO<sub>2</sub> heterostructured photocatalyst for the mineralization of Acid Violet 7 dye

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## ABSTRACT

We report the photocatalytic activity of a stable and efficient CdS–SnO<sub>2</sub> composite for the complete degradation and mineralization of Acid Violet 7 (AV 7, 50 ppm) dye. The composite catalyst exhibits higher photocatalytic activity compared to pure CdS and SnO<sub>2</sub>. Fluorescence lifetime study shows that the photogenerated charge carriers have higher lifetime in the composite than that in single phase CdS. The enhanced photocatalytic activity is attributed to the increased lifetime of the photogenerated charge carriers in the heterostructured CdS–SnO<sub>2</sub> catalyst. Total organic carbon (TOC) analysis indicates that there is hardly any organic carbon in the solution after irradiation for 150 min. Characterization of the catalyst before and after photocatalysis does not show the presence of dye in it in the adsorbed form, suggesting complete mineralization of the dye by the photocatalytic reaction. Experiments with different quenchers indicate that photogenerated holes (h<sup>+</sup>), superoxide radical anions (O<sub>2</sub><sup>•-</sup>) and hydroxyl radicals (OH<sup>•</sup>) play significant roles in the degradation reaction. The composite catalyst exhibits good photo stability and there is no significant deterioration of the catalyst up to 6 cycles of photocatalytic reaction. Present study provides insights for improving the photocatalytic activity and stability of CdS photocatalyst.

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## 1. Introduction

Synthetic textile dyes and other industrial dyestuffs are one of the major classes of pollutants which are harmful to the environment, hazardous to human health, and difficult to degrade by natural means [1]. Recently, a lot of attention has been focused on the use of semiconductor (SC) photocatalysis for the removal of organic and inorganic pollutants from aqueous phase. CdS is widely used in various applications such as photocatalysis, gas sensor, detectors for laser and infrared light, solar cells, non-linear optical materials, various luminescence devices and optoelectronic devices [2–4]. CdS can utilize visible light for photocatalytic reaction due to its narrow band gap (2.42 eV) [5–7]. Although, CdS photocatalyst is visible light active, charge carrier recombination is quite fast limiting its photocatalytic activity [8]. Besides, it is prone to photo corrosion in aqueous media containing oxygen during photocatalytic reaction [9]. Therefore, it is important to develop effective

methods to improve the photocatalytic activity of the CdS photocatalyst. Nanocomposites are advantageous over single phase photocatalysts due to the increased surface area and the effective charge separation of photogenerated electrons and holes, if the band potentials are favorable [10–13]. In a composite photocatalytic system, the narrow band gap SC can act as visible light sensitizer and can be excited by visible light. The photogenerated electrons or holes from the narrow bandgap SC can be injected to the wide bandgap SC, thereby increasing the lifetime of the charge carriers [14,15].

Many CdS based composites are reported for the photocatalytic degradation of dyes [16–19]. Self assembled flower like CdS–ZnO nanocomposite is found to be effective for the photocatalytic degradation reaction of Rhodamine B [16]. Li et al. [17] suggest that CdS–TiO<sub>2</sub> composite is suitable for the photo degradation of Rhodamine B under visible light irradiation. Gao et al. [18] report that graphene oxide–CdS nanocomposite is quite effective for the photo degradation of Acid Orange 7 and photo reduction of Cr<sup>6+</sup> under visible light irradiation. A magnetically recoverable CdS–ferrite nanocomposite shows photocatalytic activity for the degradation of Rhodamine B and 4-chlorophenol in the presence of visible light [19]. In all these cases, the reasons suggested for the improved photocatalytic activity of the composite are either the increased surface

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area of catalysts or the increased lifetime of the photogenerated charge carriers.

In the present work, a heterojunction photocatalyst, CdS dispersed on SnO<sub>2</sub>, is synthesized by a facile chemical route with the aim of enhancing the lifetime of photogenerated charge carriers, stability, and photocatalytic activity of CdS. It is expected that the favorable heterojunction formed between CdS and SnO<sub>2</sub> semiconductor particles can facilitate the charge transfer from CdS to SnO<sub>2</sub> and can increase the photocatalytic activity. Besides, the presence of SnO<sub>2</sub> can minimize the aggregation of CdS particles thereby increasing the surface area. With this idea, a series of CdS–SnO<sub>2</sub> nanocomposites are synthesized and studied the photocatalytic activity for the degradation of Acid Violet 7 (AV 7). The photocatalytic property of the composite is correlated with its various physico-chemical properties. Present study highlights the efficiency of this photocatalyst not only for the degradation reaction, but also for the mineralization of AV 7 dye. The stability and reusability of this composite photocatalyst has also been studied.

## 2. Experimental

### 2.1. Materials

Tin metal granules (Qualigens, 99.5%), Cadmium chloride hydrated AR (s.d. fine chem. Ltd. 99.5%), sodium sulfide flakes purified (Merck), thiourea GR (Merck, 99%), urea (Qualigens, 99%), ethylene glycol (Merck 99%), HCl (Fisher Scientific), HNO<sub>3</sub> (Fisher Scientific), Acid Violet 7 (Aldrich, dye content ca. 40%) were used as received without further purification. Millipore water was used in all solutions.

### 2.2. Synthesis of photocatalyst CdS–SnO<sub>2</sub>

SnO<sub>2</sub> nanoparticles were prepared by Polyol method. Briefly, Sn metal was dissolved in dil. HCl containing a few drops of HNO<sub>3</sub>. The volume was reduced by evaporation (50 ml) and taken into 500 ml round bottom flask (RB) followed by the addition of 50 ml of ethylene glycol (EG) to the solution. The mixture was refluxed at 100 °C for 1 h and added urea (molar ratio, Sn:Urea = 2.5) dissolved in 25 ml EG. The temperature of the reaction mixture was raised upto 180 °C and maintained for 4 h. The precipitate obtained was separated by centrifugation, washed and dried in a vacuum oven at 90 °C for 5 h followed by calcination in air at 500 °C for 4 h. CdS was loaded (% by weight of SnO<sub>2</sub>) on SnO<sub>2</sub> by an impregnation method. Calculated concentrations of aqueous cadmium chloride solution were stirred with 0.5 g of SnO<sub>2</sub> powder and evaporated to dryness (80–90 °C). The cadmium chloride adsorbed on SnO<sub>2</sub> was heated with an aqueous solution of thiourea (Cd:thiourea = 1:4 ratio, at 80–90 °C). The resultant mixture was evaporated to dryness followed by heating the powder at 350 °C for 2 h. Concentration of CdS on SnO<sub>2</sub> was varied by changing the concentration of CdCl<sub>2</sub> solution and the different composites synthesized are denoted as xCdS–SnO<sub>2</sub> where x = 28, 40, 49 and 70%.

Pure CdS was prepared by the reaction of cadmium chloride with sodium sulfide in ethylene glycol medium [20]. Cadmium chloride (4 g) dissolved in water was mixed with EG (total volume = 50 cm<sup>3</sup>, water:EG = 1:1 by volume) and refluxed at 100 °C for 15 min. At this stage, sodium sulfide (2 g) dissolved in water and EG (50 cm<sup>3</sup>, water:EG = 1:1 by volume) was added to the solution and refluxed at 120 °C for 4 h. The precipitate obtained was separated by centrifugation, washed with acetone and methanol and dried in an oven at 90 °C for 5 h followed by calcination in air at 350 °C for 2 h.

### 2.3. Photocatalytic experiments

The photocatalytic activity of the samples was studied for the degradation of AV 7 (50 ppm) using a photo-irradiator consisting of 100 W fluorescent lamps (12 lamps) arranged vertically and equidistantly in a rectangular chamber provided with air circulation. The radiation from the lamp contained mainly visible light along with <3% UV radiation [21,22]. The average light flux measured by a digital lutron lux meter (model LX-101) was found out to be 60,000–65,000 lx. Photocatalytic experiments were performed in a beaker containing 125 ml AV 7 solution (50 ppm) in which 0.35 g of catalysts was dispersed. Prior to illumination, the suspension was magnetically stirred in darkness for 30 min to establish adsorption–desorption equilibrium at room temperature. During irradiation, stirring was maintained to keep the mixture in suspension. Control experiments with just dye solution without catalyst and a dark experiment using dye solution with catalyst were done to ensure that the degradation reaction is occurring photocatalytically. During a photocatalytic experiment, a small volume of the clear supernatant solution was extracted every 15 or 30 min and analyzed by a UV-visible spectrophotometer (Shimadzu, UV-1800). The concentration of AV 7 was determined by tracking the absorbance peak around 523 nm.

Stability of the catalyst was tested by reusing the catalyst for repeated cycles of experiment after a photocatalytic reaction. Before each cycle of experiment, the used catalyst was removed from the solution by centrifugation, washed it three times with water and three times with acetone followed by drying in vacuum oven at 90 °C for 2 h. The degradation efficiency of AV 7 was calculated by using following equation.

$$\% \text{degradation} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where  $C_0$  and  $C_t$  are the concentration of AV 7 at time  $t$  and 0 respectively. The reaction rate ( $k$ ) was calculated from the slope of straight line obtained by plotting  $\ln C/C_0$  versus illumination time, ( $t$ ) as

$$\ln \frac{C}{C_0} = -kt \quad (2)$$

where  $t$  is the irradiation time,  $k$  is the first-order rate constant of the reaction,  $C$  and  $C_0$  are concentration of dye at time  $t$  and 0 respectively.

Total organic carbon (TOC) of the illuminated solution having a dye concentration 50 ppm at different time intervals was analyzed with the TOC analyzer (Shimadzu, L-series). TOC was calculated by finding the difference between the total carbon and the inorganic carbon.

### 2.4. Characterization

Powder X-ray diffraction (XRD) patterns of all samples were recorded on X'Pert PRO PANalytical X-ray diffractometer (Philips, Holland) using Cu K $\alpha$  radiation (Wavelength = 1.5418 Å). Total surface area was measured by Brunauer–Emmet–Teller (BET) method using Micromeritics ASAP 2020 V3.04 H surface area analyzer and nitrogen adsorption at 77 K was found out to determine the surface area. Transmission electron microscopy (TEM) images were taken using a FEI Tecnai T-20 electron microscope operating at 300 kV. UV–vis diffuse reflectance spectra (UV–vis DRS) of all samples were recorded using a Jasco (model V-670) spectrophotometer equipped with an integrating sphere accessory. Barium sulfate was used as reference for the reflectance spectra. Photoluminescence (PL) spectra were recorded using FLSP 920 (Edinburgh Instruments) equipped with a 450 W Xe arc lamp as the excitation source and a red sensitive Peltier element cooled Hamamatsu R2658 PMT as the detector. Excited state lifetimes of the charge carriers were

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