



Synthesis, characterization and daylight active photocatalyst with antiphotocorrosive property for detoxification of azo dyes



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ABSTRACT

Utilization of solar energy is an energy efficient process for dye wastewater treatment. Photocatalytic degradation of toxic azo dyes was carried out using modified semiconductors under direct sun light. Concerning this, the different wt% of CdS loaded Ag–ZnO catalysts were prepared by the simple precipitation – thermal decomposition method and used for degradation studies. Cadmium sulfide (CdS) is a kind of semiconductor with fine band gap of 2.4 eV, and its valence electron can be effortlessly evoked to conduction band under solar or visible light illuminations. Among the different CdS prepared catalysts, highly efficient 2 wt% of CdS loaded Ag–ZnO was characterized by different characterization techniques. Metal sulfide loading increases the absorbance of ZnO into the entire visible region. XPS reveals that the presence of metallic silver in the catalyst. The photocatalytic activity of 2 wt% CdS loaded Ag–ZnO was compared with single metal doped, undoped, and other commercial catalysts, especially Degussa P25, a standard bench mark photocatalyst. The photodegradation of RR 120, RO 4, and RY 84 had been analyzed in detail. Mineralization of these dyes has been confirmed by chemical oxygen demand (COD) measurements. A dual mechanism has been proposed for the higher efficiency of CdS–Ag–ZnO at neutral pH under solar light. Antiphotocorrosive study reveals that bare ZnO suffers more dissolution by photocorrosion than our prepared photocatalyst CdS–Ag–ZnO. This catalyst is found to be more stable and reusable.

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1. Introduction

The global energy crisis and related ecological concerns are among the prime technological challenges being confronted by chemists and technologists in the 21st century. The rate of total energy used by all of human civilization reached 15 TW in 2008 and is unsurprising to virtually twice by 2050 due to the emergent global creation and inhabitants [1]. On the contrary, our most important energy resources still instigate from restricted and non-renewable fossil fuels, such as firewood, oil and natural gas. Besides, the combustion of these fossil fuels has caused a succession of critical environmental tribulations, ranging from air and water contamination to worldwide humidity. For this reason, looking for renewable, clean as well as carbon-neutral unusual energy

resources is very quickly needed to replace our dependence on fossil fuels. Solar energy is the primary source of energy for the life on our planet. It's very safe, abundant and carbon neutral. Next to nuclear energy and a combine of other renewables, it is amongst the best options to substitute the fossil fuels, causing environmental problems [2]. On the other hand, solar energy is diffuse, sporadic and its collection, concentration and storage hinder the full utilization of its potential. Plants and organisms have learnt how to use it to exchange plentiful compounds such as water and CO₂ into constructive chemicals for their intensification.

Semiconductor photocatalysis like TiO₂, ZnO and WO₃ have attracted more extensive awareness in current years owing to their immense potential in environmental contaminant degradation and water splitting [3–11]. Among them, ZnO is almost considered to be an excellent sun light receptive photocatalyst material due to its relatively narrow band gap (3.2 eV). Conversely, concerning its application in environmental remediation, there are a number of critical negative aspects to be noted: (i) the separation efficiency

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of photogenerated electrons and holes is very low; (ii) it is prone to photocorrosion in aqueous media containing oxygen during photochemical reaction [12], (iii) it is usually present as fine or ultrafine particles, and it is a challenging and expensive task to separate the catalyst particles from the reaction systems. To overcome these problems, modifying ZnO photocatalysts to enhance light absorption and photocatalytic activity under sun light has been a main research direction in recent years. One of the efficient methods to modify semiconductor surface is by doping noble metals such as Cu, Ag, Ce, Au, and Mg [13–18]. Additionally, the formation of a coupled semiconductor structure can efficiently improve the optical absorption capacity and at the same time reduce the charge recombination under sun light irradiation because they can reimburse for the disadvantages of the individual component, and persuade a synergistic effect [6,7,19–25]. Chalcogenides such as Ag₂S, CdS, CoS₂, ZrS₂ and ZnS have been studied extensively, since they have ideal edge positions of the valence and conduction bands for the redox reactions [26–31]. CdS is an important II–VI semiconductor with direct band-gap energy of 2.42 eV [32], which could be excited by visible light to produce photogenerated electrons and holes. As the conduction band of ZnO is about 0.5 eV more positive than that of CdS, the band position between CdS and ZnO favors the transfer of photogenerated electrons from the conduction band of CdS into that of ZnO efficiently. Furthermore, the improvement in the stability of CdS based photocatalysts utilizing visible range of the spectrum is a great challenge. In the present work, CdS loaded Ag–ZnO composite catalyst was synthesized by direct loading of CdS on Ag–zinc oxalate substrate with simple precipitation – thermal deposition method under mild condition. The photocatalytic activities of CdS–Ag–ZnO were evaluated with azo dyes degradation under solar light.

2. Experimental

2.1. Materials

The commercial azo dyes Reactive Red 120 (RR 120) (Fig. S1, see Supplementary data), Reactive Orange 4 (RO 4), (Fig. S2, see Supplementary data) and Reactive Yellow 84 (RY 84) (Fig. S3, see Supplementary data), from Balaji Colour Company, Dyes and Auxiliaries (Chennai) were used as received. Oxalic acid dihydrate (99%) and zinc nitrate hexahydrate (99%) were obtained from Himedia chemicals. AgNO₃ and CdS from sigma Aldrich, ZnO (Himedia), TiO₂ (Merck) were used as received. A gift sample of Degussa TiO₂-P25 was obtained from Evonik (Germany). It is a 80:20 mixture of anatase and rutile with the particle size of 30 nm and BET surface area of 50 m² g⁻¹. K₂Cr₂O₇ (s.d.fine), Ag₂SO₄ (s.d.fine), HgSO₄ and FeSO₄·7H₂O (Qualigens) were used as such. The double distilled water was used to prepare experimental solutions. The pH of the solution before irradiation was adjusted using H₂SO₄ or NaOH.

2.2. Preparation of CdS loaded Ag–ZnO

CdS loaded Ag–ZnO was prepared by precipitation thermal-decomposition method. Aqueous solutions of 100 mL of 0.4 M zinc nitrate hexahydrate and 100 mL of 0.6 M oxalic acid in deionized water were brought to their boiling points separately. 5 mL of appropriate amount of silver nitrate solution was mixed with zinc nitrate solution. Solution of zinc nitrate and AgNO₃ were mixed with oxalic acid solution. Precipitation of zinc oxalate with Ag occurred (2 wt% Ag related to ZnO, reported concentration refers to the initial concentration of the solution). To this solution 0.054 g of CdS was added and stirred for 1 h at 60–70 °C. The mixed suspension was stirred continuously to attain ambient tempera-

ture. The mixed precipitate of CdS with Ag–zinc oxalate was somewhat fine and homogeneous in dimension. CdS–Ag–zinc oxalate crystals were washed several times with distilled water, air-dried overnight and dried at 100 °C for 5 h. It was calcined in the muffle furnace at the rate of 20 °C min⁻¹ to attain the decomposition temperature of zinc oxalate (450 °C). After 12 h, the furnace was allowed to cool down to room temperature. The CdS loaded Ag–ZnO catalyst was collected and used for further investigation. This catalyst contained 2 wt% of CdS. Catalysts with 1, 3, 4 and 5 wt% of CdS were prepared with this procedure by the addition of appropriate amounts of CdS initially. The pure ZnO was prepared without addition of AgNO₃ and CdS. Ag–ZnO, Ag–CdS and CdS–ZnO were prepared by the same procedure with relevant precursors.

2.3. Analytical methods

Powder X-ray diffraction patterns were obtained using X'Per PRO diffractometer equipped with a Cu K α radiation (wavelength 1.5406 Å) at 2.2 kW Max. Peak positions were compared with the standard files to identify the crystalline phase. For transmission electron microscope (TEM) images, the grids were dried under natural conditions and examined using a TEM Hitachi H-7500. FE-SEM images were taken using a JEOL JSM-6701F field emission scanning electron microscope (FE-SEM). Earlier than FE-SEM analysis, the samples were mounted on a gold platform located in the scanning electron microscope for succeeding analysis at various kinds of magnifications. DRS (diffused reflectance spectra) of the prepared materials were recorded using Shimadzu UV-2450. Photoluminescence (PL) spectra were recorded using a Perkin Elmer LS 55 fluorescence spectrophotometer. The semiconductor material were dispersed in carbon tetrachloride and excited using light of wavelength 300 nm. X-ray photoelectron spectra of the catalysts were recorded in an ESCA-3 Mark II spectrometer (VG scientific Ltd., England) using Al K α (1486.6 eV) radiation as the source. The spectra were referenced to the binding energy of C1s (285 eV). The specific surface areas of the samples were determined through nitrogen adsorption at 77 K on the basis of BET equation using a Micromeritics ASAP 2020 V3.00 H. A Shimadzu (Japan) AA6300 spectra Atomic Absorption spectrometer was used to measure the concentration of Zn²⁺ ions. UV spectral measurements were done using Hitachi-U-2001 spectrometer.

2.4. Photodegradation experiments

Solar photocatalytic degradation was carried out under similar conditions on sunny days between 11 am and 2 pm. An open borosilicate glass tube of 50 mL capacity, 40 cm height and 20 mm diameter was used as the reaction tube vessel. Fifty milliliters of RR 120 (2×10^{-4} M), RO 4 (5×10^{-4} M) and RY 84 (5×10^{-4} M) with the suitable amount of catalyst was stirred for 30 min in dark prior to elucidation in order to achieve utmost adsorption of dye onto the catalyst surface. Irradiation was carried out in the open air with continuous aeration by a pump to provide oxygen and for the complete mixing of reaction solution as well as catalyst. During the illumination time no volatility of the solvent was noted. The temperature of the experimental solution is 32 °C. In all cases, 50 mL of reaction mixture was irradiated. At specific time intervals, 2–3 mL of the sample was withdrawn and centrifuged to remove the catalyst. One milliliter of the sample was suitably diluted and dye concentration was determined from the absorbance at the analytical wavelength (RR 120–285 nm, RO 4–285 nm and RY 84–312 nm). 4-nitrophenol degradation was carried out under both UV and solar sources. For the degradation of 4-nitrophenol by UV-A light (365 nm), a Heber Multilamp-photoreactor HML MP 88 was used [33] (Fig. S4, see Supplementary data).

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