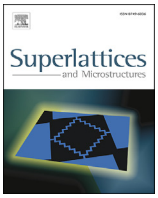
Superlattices and Microstructures 98 (2016) 86–95

Contents lists available at ScienceDirect

Superlattices and Microstructures

journal homepage: www.elsevier.com/locate/superlattices



Synthesis of ZnS/CQDs nanocomposite and its application as a photocatalyst for the degradation of an anionic dye, ARS

Sharanjit Kaur [a], Shelja Sharma [b], Sushil Kumar Kansal [a, *]

[a] *Dr. S.S. B. University Institute of Chemical Engineering and Technology, Panjab University, Chandigarh 160014, India*
[b] *Department of Chemistry, Centre of Advanced Studies, Panjab University, Chandigarh 160014, India*

ARTICLE INFO

Article history:
Received 7 August 2016
Accepted 11 August 2016
Available online 15 August 2016

Keywords:
ZnS
Semiconductor
Carbon dots
Photocatalysis
ARS
Degradation

ABSTRACT

Novel carbon quantum dots (CQDs)-modified ZnS nanocomposite was prepared via a fast and facile chemical precipitation technique and was employed for the first time as a photocatalyst for the degradation of Alizarin red S (ARS) dye under visible light irradiation. The structural, morphological and optical properties of the prepared ZnS/CQDs nanocomposite were characterized by multiple analytical techniques such as X-ray diffraction, X-ray photoelectron spectroscopy, Fourier-transform infrared spectroscopy, thermogravimetric analysis, photoluminescence spectroscopy, transmission electron microscopy, field emission scanning electron microscope equipped with energy dispersive spectroscopy and UV–vis diffuse reflectance spectroscopy. Impact of affecting parameters on the photocatalytic activity of the ZnS/CQDs was studied and optimized. The results showed that the ZnS/CQDs exhibited excellent photocatalytic activity for the degradation of ARS dye i.e. 89% within 250 min, higher than that of the bare ZnS (63%). This enhancement in photocatalytic activity of ZnS/CQDs was attributed to the introduction of CQDs, which could absorb visible light efficiently, suppressing the recombination of electron–hole pairs and improving charge separation. Moreover, various scavengers have been used to study the role of reactive species in the photocatalytic degradation process.

1. Introduction

The breakthrough towards the evolution for designing competent photocatalysts is an integral matter of concern for the environmental remediation issues because of production of large scale organic pollutants from the textile and food industries. Varieties of dye are produced in enormous quantities all over the world to meet the requirements of textile industry. The Alizarin red S (ARS) is an anionic dye which is widely used in woven fabrics, wool and cotton textiles [1,2]. When untreated wastewater containing these types of dyes is thrown into the environment, lots of health problems are being faced by living organisms. Therefore, it becomes one of the challenging tasks to treat the wastewater containing dyes.

Heterogeneous photocatalysis has been emerged as a promising technology which can treat wastewater effectively. Till now, numerous oxides and sulfides semiconductor nanomaterials have been synthesized, researched and utilized as photocatalysts in this process [3–10]. In particular, zinc sulfide (ZnS) is flourishing nowadays as of being its high photocatalytic activity, cost effectiveness and unique band structure. Due to generation of electron and hole pairs upon photoexcitation and

---

* Corresponding author.
E-mail addresses: sushilkk1@yahoo.co.in, sushilkk1@pu.ac.in (S.K. Kansal).

http://dx.doi.org/10.1016/j.spmi.2016.08.011

highly negative reduction potential of electrons makes ZnS a good photocatalytic material [11,12]. However, a rapid recombination of photogenerated charge carriers and the confined absorption band of the ZnS photocatalyst are the major limitations that restrict its applicability to the photocatalysis. Thus, a plenty of endeavors have been made to improve the photocatalytic behavior of ZnS. In order to overcome these issues, an appropriate modification is imperative for developing advanced varieties of ZnS nanostructures [13,14].

Carbon quantum dots (CQDs) have emerged as a novel issue and gained significant attention due to its numerous attributes and outstanding photophysical properties [15]. Particularly, its size and excitation wavelength-dependent photoluminescence (PL) behavior would improve the photocatalytic properties of the CQDs-based composites [16]. It was reported that the electron-transfer and accepting properties of CQDs present a favorable approach to obstruct the recombination of photogenerated electrons and holes; accordingly, enhanced photocatalytic performance can be accomplished by the fabrication of semiconductor/CQDs composites [17]. Lately, the construction of complex photocatalysts (CQDs/BiOI, WO_3/CQDs, N–ZnO/CQDs) has exhibited considerable proficiency towards photocatalytic degradation of organic contaminants [18–20]. Martins et al. demonstrated the photocatalytic activity of nitrogen doped CQDs/TiO_2 composite for photo-oxidation of NO under UV and visible light irradiation [21]. Qian et al. reported the synthesis of CQDSBi_2WO_6 for removing gaseous volatile organic compounds photocatalytically under UV and visible light irradiation [22]. In view of remarkable characteristic properties of CQDs and the drawbacks of ZnS photocatalytic system, the consolidation of CQDs and ZnS can be accounted as an exemplary strategy to design exceptionally efficient photocatalytic system.

In this work, we report a facile methodology for synthesizing ZnS, CQDs, and ZnS/CQDs nanocomposite. The results interpreted that the CQDs were successfully combined with the ZnS nanoparticles and the introduction of CQDs could effectively enhance the amount and the transfer ratio of the photogenerated charge carrier, which was the key factor for the enhanced photocatalytic activity for the degradation of ARS dye under visible light irradiation.

2. Experimental section

2.1. Materials and methods

All the chemicals are commercially available and brought into use as received. Zinc acetate dihydrate ($Zn(OAc)_2 \cdot 2H_2O$), sodium dodecyl sulfate ($CH_3(CH_2)_{11}SO_4Na$), sodium azide (NaN_3), potassium iodide (KI), formic acid (HCOOH) and sodium chloride (NaCl) were bought from Merck, India. ARS (C. I. No. 58005)($C_{14}H_6Na_2O_7S$),a hydrophilic anthraquinone dye was purchased from SD fine Chemicals, India. Sodiumsulfide hydrate ($Na_2S \cdot H_2O$) and L-ascorbic acid were procured from Himedia, India. All the stock solutions were prepared in distilled water.

2.2. Synthesis of ZnS

A facile co-precipitation method was adopted for the synthesis of ZnS. In a typical reaction process, 25 mL of 0.5 M of $Zn(OAc)_2\ 2H_2O$ was added into 25 mL of 0.5 M Na_2S dropwise with vigorous stirring. 0.5 M SDS solution (25 mL) was added into above resultant solution under stirring. White precipitates tend to form; these were filtered and washed with ethanol and water several times. Then precipitates were dried in an oven at 60 °C for overnight.

2.3. Synthesis of Zns/CQDs

For the synthesis of CQDs, 0.25 g of ascorbic acid was immersed in 50 mL of ethanol and 20 mL of water. The resultant solution was kept under stirring for 10 min. Then it was transferred to Teflon lined stainless steel autoclave and kept in oven for 3 h at 160 °C. Finally the brown alcoholic suspension of CQDs was obtained. 50 μL of alcoholic suspension of CQDs was again diluted with 50 mL of ethanol and 0.1 g of above ZnS was added into it. It was kept under stirring for an hour. The resultant precipitates were then washed with distilled water and filtered off and dried in an oven.

2.4. Characterization

The structure and crystal phase of the as-prepared catalyst were analyzed withX-ray diffraction (XRD) using Proto Analytical X-ray Diffraction System (AXRD) fitted with a Cu Kα radiation source. The XRD patterns of all the samples were recorded in 10°–80° region with a 0.04 step size (Dwell time = 1 s). X-ray photoelectron spectroscopy (XPS) data were obtained with AMICUS, Kratos Analytical (Shimadzu), spectroscope. The binding energy in XPS analysis was corrected by the C (1s) adventitious peak. The general morphology of the synthesized nanoparticles was analyzed by transmission electron microscopy (TEM), using a TEM; JEOL-JEM-2100Fand Field emission transmission electron microscopy (FESEM), using HITACHI, SU8010equipped with energy dispersive spectroscope (EDS) at an accelerating voltage of 10 kV. The UV–vis absorption studies of the photocatalysts were conducted on UV–vis diffuse reflectance spectrophotometer (Shimadzu UV-2450) using $BaSO_4$as a reference. Fourier transform infrared (FTIR) spectroscopy was performed by using a Thermoscientific (Nicolet iS50) FTIR spectrometer, equipped with a diamond ATR at room temperature in the range of 400–4000 cm^{-1}. The room temperature photoluminescence (PL) spectra were measured on a Hitachi F-7000 Fluorescence spectrophotometer (5J1-004 model)using quartz cuvette 1 cm path length at an excitation wavelength of 315 nm.