



# Photocatalytic and antibacterial activity of cadmium sulphide/zinc oxide nanocomposite with varied morphology



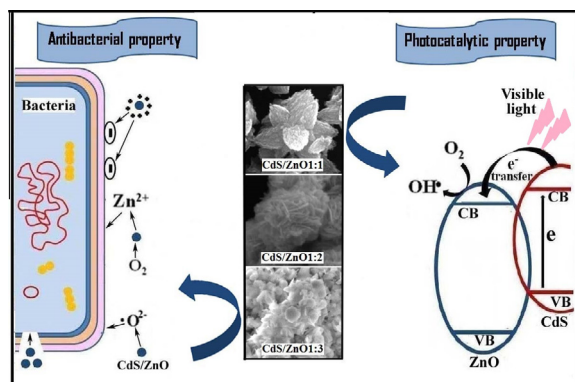
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## GRAPHICAL ABSTRACT



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## ABSTRACT

Nanocomposites with multifunctional application prospects have already dragged accelerating interests of materials scientists. Here we present CdS/ZnO nanocomposites with different morphology engineering the precursor molar ratio in a facile wet chemical synthesis route. The materials were structurally and morphologically characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray analysis (EDX) and high-resolution transmission electron microscopy (HRTEM). The growth mechanism of the composite structure with varying molar ratio is delineated with oriented attachment self assemble techniques. Photocatalytic activity of CdS/ZnO nanocomposites with varying morphology were explored for the degradation of rhodamine B (RhB) dye in presence of visible light irradiation and the results reveal that the best catalytic performance arises in CdS/ZnO composite with 1:1 ratio. The antibacterial efficiency of all nanocomposites were investigated on *Escherichia coli*, *Staphylococcus aureus* and *Klebsiella pneumonia* without light irradiation. Antibacterial activity of CdS/ZnO nanocomposites were studied using the bacteriological test-well diffusion agar method and results showed significant antibacterial activity in CdS/ZnO composite with 1:3 ratio. Overall, CdS/ZnO nanocomposites excel in different potential applications, such as visible light photocatalysis and antimicrobial activity with their tuneable structure.

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## 1. Introduction

The demand for efficient and smart nanostructured composite materials is increasing and has attracted a comprehensive attention because of their synergic novel physical, chemical, and biological properties and potential applications in areas such as optoelectronics, catalysis, and biology [1–5]. Unprecedented opportunities in material designing have fuelled the rapid development in the synthesis of semiconductor/semiconductor nanocomposites, combining the advantages of both the constituents. One such well-investigated component, zinc oxide (ZnO) has been extensively reported with many other associate such as ZnO/CdS, ZnO/ZnS, SnO<sub>2</sub>/ZnO, Co<sub>3</sub>O<sub>4</sub>/ZnO, ZnO/TiO<sub>2</sub>, CuO/ZnO and ZnO/ZnSe [6–13] for exhibiting outstanding applications. CdS is one visible sensitizer with a narrow band gap of 2.42 eV and the conduction band edge of CdS (−4.1 eV) is slightly higher than that of ZnO (−4.3 eV). Therefore, CdS is an excellent choice of coupling with ZnO and the coupled CdS/ZnO system has attracted a comprehensive attention because of their novel properties and potential use in many applications in the area of optics, electronics, photocatalysis and antibacterial activity [1,6,14–18]. Heterostructured visible light photocatalyst like CdS/ZnO is effective because charge injection from one semiconductor to another leads to an efficient charge separation due to a reduction in the exciton recombination [19,20]. In addition, morphology and surface alteration have a strong influence on the photocatalytic effect as the photocatalytic reaction takes place on the surface of the semiconductors [21].

On the other hand, antibiotic resistance is a serious and growing phenomenon in public health. Especially antibiotic resistant bacterial strains, fungi and parasites have become a serious problem for health care and food technology sectors. Therefore, antibiotics having a different mechanism of action are urgently needed for modifications in the traditional antimicrobial compounds. Owing to their large specific surface area and high bioactivity the developments of nanoparticles with antimicrobial activity have been emerging as a new class of biomedical materials having improved or distinct antibacterial activity against multidrug-resistant human pathogenic microbes to fulfil the increasing demands for hygiene in daily life [22]. With regard to nanomaterials, metal-oxide nanocomposites with distinct morphologies have drawn attention as they combine the properties of the constituent elements to exert a more pronounced and synergistic effect [23,24].

The development of effective material having both photocatalytic and antimicrobial properties is of great significance. CdS/ZnO nanocomposites shows great prospects as a photocatalyst in decomposing organic pollutants in the environment and also as an antimicrobial material [20,18]. ZnO/CdS system has been reported as antibacterial material for a complete inactivation of bacteria under visible light irradiation [18]. There has been growing demand in the use of antibacterial materials being active and sustainable under dark condition [25]. However, to the best of our knowledge, there is no such report on application of CdS/ZnO system as antibacterial material without light irradiation. In the present study, synthesis and self assemble heterostructures of CdS/ZnO composite with varied morphology have been addressed. Different structures of CdS/ZnO nanocomposites were evaluated for their photocatalytic degradation ability of rhodamine B dye in aqueous solution under visible light irradiation. The CdS/ZnO heteronanostructures were further investigated for antibacterial activity against *Escherichia coli*, *Staphylococcus aureus* and *Klebsiella pneumoniae* bacteria culture in dark condition.

## 2. Experimental section

### 2.1. Synthesis and characterization

All the chemicals are Merck made of analytical grade and used without further purification.

The synthesis procedure of CdS/ZnO nanocomposites, as described earlier [20] is modified here for developing different composite structures. First CdS seeds were prepared taking CdCl<sub>2</sub> and Na<sub>2</sub>S as the precursors with molar ratio 1:1. Precipitates of CdS nanoparticle were prepared by adding Na<sub>2</sub>S solution drop wise with continuous stirring in CdCl<sub>2</sub> solution in an ice-bath. The obtained precipitate was centrifuged, washed with distilled water for several times and was allowed to dry in a vacuum furnace at 100 °C for 2 h to get CdS nanoseeds.

In the second step, CdS/ZnO nanocomposites in a molar ratio of 1:1 (CZ1:1), 1:2 (CZ1:2) and 1:3 (CZ1:3) were synthesized. For the preparation of CZ1:1, CZ1:2 and CZ1:3 the precursor of ZnO (Zn(NO<sub>3</sub>)<sub>2</sub> and NaOH in 1:1 M ratio) was taken in 1:1, 1:2 and 1:3 ratio with CdS in wt%. Measured amount of CdS nanoparticles were well dispersed in 25 ml distilled water. Appropriate amount of Zinc nitrate solution and NaOH solution were also prepared separately and added in the first solution very slowly under stirring condition. The obtained precipitate for three different samples were centrifuged and washed with distilled water for several times until the pH becomes 7. The final product were collected after drying in a vacuum furnace at 100 °C for 2 h. To prepare the bare ZnO sample the second part of the synthesis has been carried out exactly in the same way without the CdS seed nanoparticles.

Structural analysis of all the powdered samples was carried out by Rigaku Mini-Flex X-ray diffractometer using Cu K $\alpha$  radiation ( $k = 1.54178 \text{ \AA}$ ) source. Morphological analysis was done by both JEM 2100 Transmission Electron Microscope at an accelerating voltage of 200 keV and FEI, Inspect F Scanning Electron Microscopy. EDX was carried out in S-4200, Hitachi. Optical absorption spectra of the powdered samples were recorded in an UV–vis 1700 Shimadzu Spectrophotometer and to get these spectra the powdered samples were dispersed in ethyl alcohol and mounted in the sample chamber while pure ethyl alcohol was taken in the reference beam position. In case of photocatalysis study the organic dye RhB was taken in distilled water and the sample was dispersed in that solution.

### 2.2. Photocatalytic evaluation

The photocatalytic activity of the as prepared samples for the degradation of RhB in aqueous solution was evaluated by measuring the absorbance of the visible light irradiated solution. Prior to irradiation, 10  $\mu\text{M}$  solution of RhB in DI water was taken and sample was added to it to maintain a catalyst concentration of  $1 \text{ gm L}^{-1}$ . Afterward, the organic dye with a catalyst solution was magnetically stirred in dark for 1 h to assure the adsorption/desorption equilibrium between CdS/ZnO catalyst and RhB. The photocatalytic process was performed by exposing the solution to 1000 W halogen lamp radiation and the solution was kept in a cold water bath containing  $1 \text{ mol L}^{-1}$  NaNO<sub>2</sub> which is used for removing light wavelength shorter than 400 nm [26]. The beaker containing the solution was kept in cold water bath to maintain the reaction temperature at 290 K. The radiation from the halogen lamp in the NIR region was balanced by keeping the solution always in the room temperature and ensuring that the degradation was only the result of photocatalysis without having any thermal effect. Analytical samples for absorption measurement were taken out from the reaction suspension at different time intervals. Optical absorption

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