Improvement of photocatalytic activity of Zinc Oxide nanoparticles using Zinc Sulphide Shell

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Abstract: ***Core/shell nanoparticles having distinct attributes of both core and shell have, of late, become attractive candidates for applications involving surface engineering of nanoparticles. In this work, the synthesis of ZnO/ZnS core/shell nanoparticles by wet chemical method is reported, formation of which is confirmed by HRTEM analysis. Characterization of the core/shell nanoparticles was done using absorption spectroscopy and HRTEM. ZnO/ZnS core/shell nanoparticles exhibited higher photocatalytic activity than the already proved good photocatalyst ZnO. This was supported by photocatalytic degradation experiments carried out on an organic dye, methylene blue, under direct sunlight irradiation. The enhancement in the photocatalytic activity is attributed to the increase of the surface reactivity of the as synthesized material, which is confirmed through the blue shift in the UV Visible absorption spectra. This material can be a promising photocatalyst in the field of water purification.***

Keywords: *visible light, photocatalysis, ZnO, ZnO/ZnS Core/Shell, methelyne blue*

1. INTRODUCTION

The rapid pace of population growth has resulted in severe environmental contamination in air, water and soil. Attempts to deal with the issues related to population has adversely affected our ecosystem leading to health problems resulting from environmental pollution. With the rapid industrialization of the world, organic contaminants have become a major pollutant contributing to the degradation of the environment, and a considerable focus of research is oriented toward efficient removal or degradation processes of these contaminants.

Water is an essential requirement for life and its availability in pure form is important for different life sustaining activities like human consumption, agriculture, to name a few. Human activities have affected nature's very own water recycling and purification mechanism and have totally disturbed the balance between the consumption and natural purification processes resulting in a shortage of drinkable water. Almost all of the natural sources of drinking water have been found to be contaminated with a wide variety of toxic materials and pathogenic microorganisms [1].

The Report from the Workshop on Nanotechnologies for Environmental Remediation [2] entifies solar photocatalysis as the main technology breakthrough for water treatment and purification, particularly in developing regions. Photocatalytic systems may also complement existing techniques in the removal of trace contaminants. Such systems are commercially available e.g. for the disinfection of swimming pools. Heterogeneous photocatalysis shows promise as a water purification technique as compared to other conventional methods as this process does not generate harmful byproducts [1,3]. It can break up complex long chained organic molecules, which are mostly toxic, into benign fragments as well as immobilize microbial cells by fracturing the cell walls. Another interesting aspect of photocatalysis is the potential utilization of sunlight, which could allow energy efficient treatment in remote locations. The underlying mechanism of heterogeneous photocatalysis is schematically represented in Fig.1. It involves a wide band gap semiconductor photocatalyst, which upon irradiation with light of energy higher than the band gap energy of the material, electron-hole pairs (excitons) are created. Material like TiO_2, ZnO, CdS, Fe_2O_3 and ZnS, which are semiconductor shows good sensitivity for light induced redox processes due to the electronic structure of metal atom in chemical combination, which is characterized by a filled valence band, and an empty conduction band [4]. The photogenerated electron moves up to the conduction band while the hole drifts to the bottom of the valence band thus creating electron-hole pairs. Majority of these photogenerated charge carriers undergo wasteful recombination, while the remaining escapes recombination and initiate redox reactions in molecules adsorbed at the surface of the photocatalyst and thereby degrading them. The photogenerated electrons and holes have been found to degrade almost all types of organic, and microbial contaminants [5], owing to their high redox potentials. The

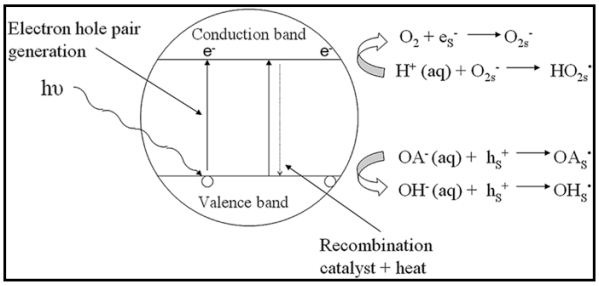


Figure 1: Schematic diagram explaining photocatalysis [1]

ZnO with a band gap of 3.37 eV is one of the most promising semiconducting material for photocatalysis [9]. Recently it has been discussed in many literature that coating the surface with different semiconductors can dramatically change the properties of ZnO nano-crystallites and can be synthesized in various ways. The hydrothermal method is a cheap and efficient way of doing it.

The function of the shell is like a barrier between the core and the environment and can alter the charge, functionality, and reactivity of the surface. Furthermore, improvement in the electrical, catalytic, optical, or magnetic properties of the core material can be seen by covering with another material. In general, the synthesis of core–shell structured material leads to a new composite material having properties between the core and shell materials. Zinc Sulphide (ZnS) with wide band gap (3.72 eV) is one of the suitable material to create shell around the core as ZnO.

ZnO@ZnS core–shell nanoparticles (CSNPs) shows improved physical and chemical properties for different applications.. Various ZnO@ZnS core–shell nanostructures have been synthesized, most of them at elevated temperature. The size for these CSNPs reported in literature are of the order of 200 nm which are quite large compared to core-shell structures reported in this work [7].

Nanotechnology is a disruptive technology that can make an impact in the area of water purification as nanostructures offer large surface to volume ratios ideal for surface reactions [6]. Replacement of other forms of energy with renewable energy like solar energy can present a cleaner and more efficient way of water purification, even in isolated rural sites.

2. EXPERIMENTAL

Colloidal solutions of ZnO and ZnO/ZnS were synthesized using the solvents ethanol and deionized water. The prepared samples were used to test the photocatalytic degradation of organic dye.

2.1 Material used

The following materials were used: Zinc acetate 138ehydrate [$(CH_3COO)_2Zn.2H_2O$], Sodium hydroxide(NaOH), ethanol(C_2H_5OH), Sodium sulphide(Na_2S).

2.2 Synthesis

Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized in ethanol. A 4mM zinc acetate solution was prepared in ethanol under rigorous stirring at 50^0C. The solution was further diluted and cooled to room temperature. To the cooled solution 4mM sodium hydroxide solution was mixed under mild stirring. This mixed colloidal solution was then kept in a hot water bath for 2 hours.

Synthesis of ZnO/ZnS nanoparticles

A shell of ZnS is grown over the as synthesized ZnO nanoparticles. A 250 mM zinc acetate solution was prepared in deionized water. This solution was mixed with adequate amount of as prepared colloidal solution of ZnO nanoparticles and stirred at 100^0C. To this mixed solution 250 mM sodium sulphide solution was mixed under mild stirring. The reaction was quenched by keeping the colloidal solution in an ice bath.

2.3 Characterization

Transmission electron microscopy (TEM) was performed using a JEOL JEM 2010 operating at 120 kV. Samples for TEM were prepared by dropping diluted colloids on carbon-coated TEM grids, followed by controlled drying. Optical absorption measurements were made using UV–visible spectroscopy (ELICO SL-159).

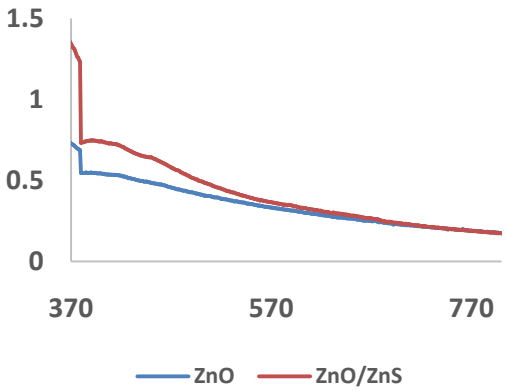


Figure 2: UV-Vis absorbtion spectra of ZnO and ZnO/ZnS nanoparticles

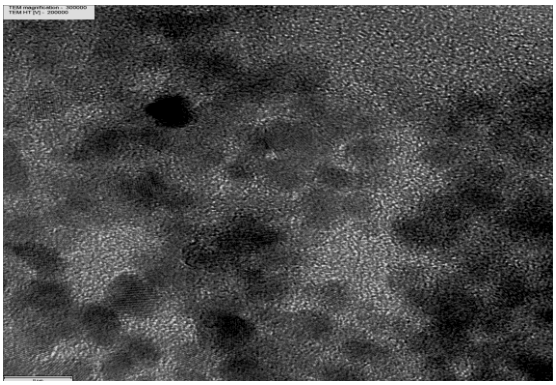


Figure 3: HRTEM image of ZnO nanoparticles

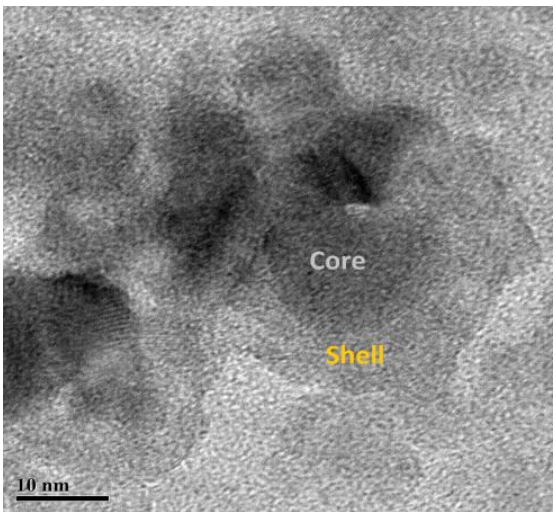
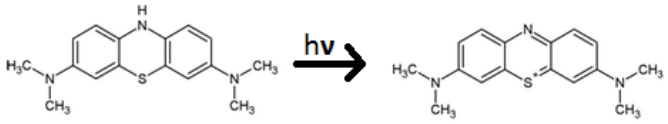


Figure 4: HRTEM image of ZnO/ZnS Core/Shell nanoparticles

2.4 Photocatalysis tests

The photocatalysis tests were done by taking methylene blue (MB) as a representative of biological contaminants. The application of this work is to see a comparison of removing the biological contaminants from water using ZnO and ZnO/ZnS core/shell nanoparticles so the tests were carried out in aqueous solution in which nanoparticles particles of ZnO and ZnO/ZnS core/shell were mixed with methylene blue. A sample was prepared in which 2 ml of ZnO nanoparticle solution was added with 2 ml 10μM (prepared in deionized water) of methylene blue. Similarly another sample was prepared using ZnO/ZnS core/shell nanoparticles. Both the samples were put in different corvettes and were placed under the sun. The intensity of light from sun at sample position was noted to be 50Klux. Optical absorption spectra were taken after different time durations to check the degradation of the organic dyes.

Organic dye (methylene blue) which resembles the organic pollutants are long chain molecules which break into smaller fragments through photocatalysis. The process is shown below.



Methylene Blue (Blue) Leucomethylene Blue (Transparent)

Figure 5: Degradation of the methylene blue dye

3. RESULTS AND DISCUSSION

The main objective of the work is to compare the efficacy of two different structures of semiconducting nanomaterials for degradation of organic contaminants through visible light photocatalysis. The performance of a photocatalyst depends primarily on its capacity to absorb electromagnetic waves for generating electron–hole pairs, which contribute to photocatalysis through redox reactions [7]. ZnO and ZnO/ZnS core/shell nanoparticles were synthesized in ethanol and deionized water solvents and their optical absorptions studied to determine how the nanoparticles absorb maximum visible light in the optical band ranging between 400nm and 800 nm.

TEM micrographs of the nanoparticles are shown in figure 3 and figure 4.

Photocatalysis tests were carried out using MB ($C_{16}H_{18}N_3CIS$) as a test contaminant. MB has an optical absorption peak at around 660 nm and its degradation can be observed visually. 10 μM MB in deionized water was used along with the ZnO and ZnO/ZnS core/shell nanoparticles and exposed to visible light, as described in the experimental section. Figures 6 and 7 show the degradation of MB through photocatalysis using the conventionally synthesized ZnO nanoparticles and ZnO/ZnS core/shell nanoparticles.

It was observed that the ZnO/ZnS core/shell nanoparticles exhibited better photocatalytic activity than the ZnO nanoparticles, which is shown in a comparative graph taken at interval of 20min, in figure 8.

This improvement in the photocatalytic activity of the ZnO using a shell of ZnS is due to the enhancement of the surface activity. The possible cause in the shown improvement can be due to covering the ZnO nanoparticles with ZnS leads to form a type II system. From the figure 9 as shown below, the effective band gap of the core–shell system is smaller than both the core and the shell material. Low amount of energy is required to form electron-hole pairs if the band gap is small

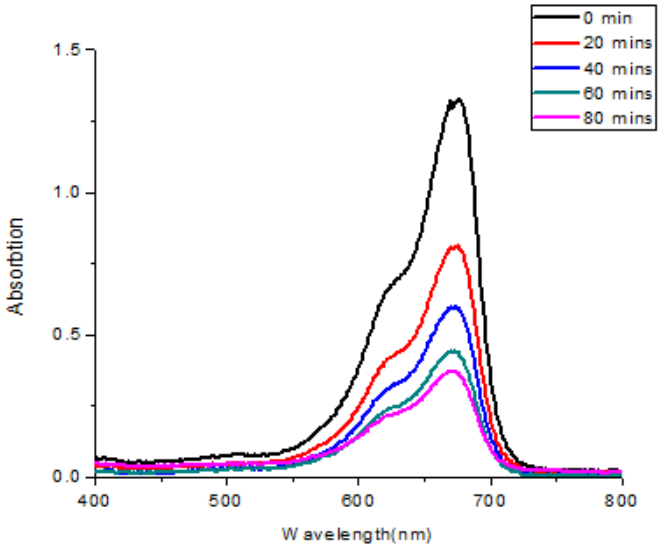


Figure 6: Photocatalytic degradation of MB dye using ZnO nanoparticles

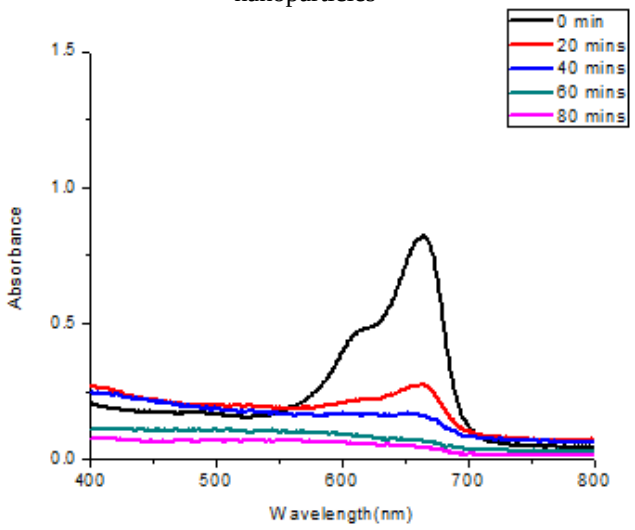


Figure 7: Photocatalytic degradation of MB dye using ZnO/ZnS nanoparticles

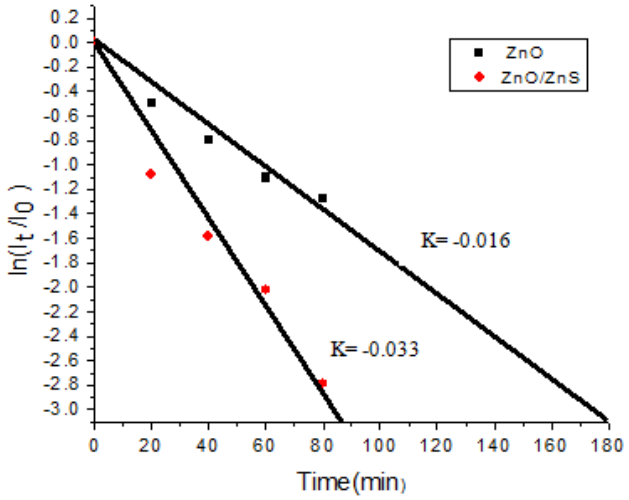


Figure 8: Linear fitted Time Vs $\ln(I_t/I_0)$ curve of ZnO and ZnO/ZnS nanoparticles. (K= gegradation ratio co-efficient.)

which also leads to a more effective transfer of electrons between the core and the shell in addition to a relatively long lifetime of the photogenerated electron–hole pairs [10]. These conditions can make us conclude that ZnO/ZnS CSNPs can show better photocatalytic activity than only

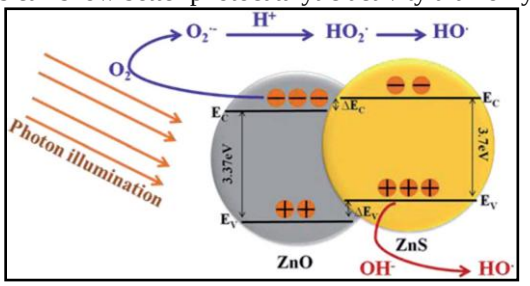


Figure 9: Schematic illustration of dye degradation over ZnO/ZnSCSNPs. [7]

ZnO nanoparticles, but in some cases electron–hole recombination occurs at the interface between the core and the shell material and this can reduce the photocatalytic activity of core–shell nanostructures.

4. CONCLUSION

From the available literature we already know that ZnO is a wide and direct band gap semiconductor used for photocatalytic activities. In this work we have shown the enhancement of photocatalytic activities of zinc oxide nanoparticles by covering it with a shell of ZnS nanoparticles. The development of such photocatalysts may be considered a breakthrough in large-scale utilization of heterogeneous photocatalysis via visible light to address water contamination and environmental pollution.

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