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Biomolecule capped semiconductor quantum dots for the photocatalytic activity

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Abstract

Photocatalysis is one of the most powerful tools for the degradation of dyes and textile waste water. Heterogeneous photocatalyst like TiO₂, ZnO, CdS, and CdSe are mostly used semiconductor Quantum dots (QD's). Biocompatible ZnSe QD's with the direct band gap 2.7eV were synthesised by hydrothermal route. The as-synthesised biomolecule capped ZnSe QDs were characterized by UV-visible, FT-IR, PL, XRD and SEM. The photocatalytic degradation of Methyl Red (MR) in aqueous solution was monitored at 456nm. Hence this study paves a way to use this biocompatible photocatalyst for the treatment of textile dye industry wastewater under solar light irradiation.

Keywords: Quantum Dots, photocatalyst, solar light, kinetics

1. Introduction

Semiconductor nanocrystals (also named as QDs) are attracted due to their controlled size, composition electrical, magnetic, optical, chemical and mechanical properties are currently used in medical field for diagnosis and drug delivery ^[1] or in the fields of catalysis, water treatment and solar energy conversion ^[2]. Nanomaterials synthesis is usually done by various physical and chemical methods, such as laser ablation, pyrolysis; vapour deposition, sol gel and electro deposition which require the use of toxic solvents ^[3]. Recently great efforts are made to use environmentally friendly methods for the synthesis of metal nanoparticles. Among the various metal nanoparticles, Zn is one of the most eco-friendly and environmentally available material for the synthesis of Semiconductor QDs.

ZnSe is an II- VI semiconductor material with a large band gap (2.7ev) at room temperature. It is chemically inert, non-hygroscopic and is a promising material for optothermal devices, LED's. Infrared devices, photovoltaic solar cells and photocatalysis ^[4].

ZnSe nanostructures are prepared by various routes. Among this hydrothermal method is an easy way to prepare the nanostructured materials because of their high crystalline, pure products, narrow size distribution and low aggregation. In developing these materials there is a possibility of agglomeration and it affects the size and surface of the materials. To overcome this challenge biomolecules can be used stabilizers or capping agents. Most of the researchers used thiols, polymers, amines, carboxylic acids, amino acids as stabilizing agents. In this work, L-cysteine is chosen for capping purpose owing to their coordination between amino acids and metal ions for the thiols (-SH-) linkage of this material.

However, hitherto there are limited articles for the L-cysteine capped ZnSe nanomaterials. It mainly focuses due to their solar absorption and it is a good choice for the degradation of dyes and organic pollutants. In predominant, the photocatalytic activity using solar energy provides an alternative way of water purification and it is a highly useful method to preserve the environment ^[5]. Heterogeneous photocatalysis has been proven to be one of the most significant methods for waste water treatment. It is a low cost method with ambient temperature and pressure under sunlight or other light sources. This approach can decompose a wide range of organic pollutants into biodegradable compounds or less toxic molecules even mineralize them without leaving secondary pollutants. This work, mainly deals with the degradation of azo dyes into aromatic amines that are potentially hazardous.

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2. Experimental Methods

2.1 Materials

Zinc acetate, NaBH₄, Se Powder, L-cysteine and Ethanol were purchased from Merck chemicals Ltd, India and used without further any purification. NaOH, HCl were purchased from LOBA chemicals Ltd and used for the pH measurements. Double Distilled H₂O was used throughout the reaction.

2.2 Synthesis of L-cysteine capped ZnSe QD's

Heavy metals free L-cysteine capped ZnSe QDs were synthesized according to the literature [6]. Typically the synthesis of ZnSe precursor was as follows: Zn(Ac)₂ and L-cysteine were dissolved in 100 ml of double distilled water and the pH value was adjusted to 10.5 by the drop wise addition of 1M NaOH solution with stirring. A solution containing Se²⁻ was prepared by mixing Se powder with NaBH₄ in 50ml double distilled water. Then this solution was stirred and heated at 55 C. Then fresh NaHSe solution was added through a syringe into the ZnSe precursor solution at room temperature. The resultant solution was heated to 90 C in an oil bath with an air condenser. After the reaction, the product was washed with double distilled water and ethanol several times and dried at 60 -70 °C for an hour to obtain pure L-cysteine capped ZnSe QDs.

2.3 Photocatalytic decolourization of Methyl Red (MR) under sunlight irradiation

The photocatalytic efficiency of the as-synthesized photocatalyst namely Cys/ZnSe was analysed through photodegradation of MR dye solution under natural sunlight irradiation. All photocatalytic reactions were carried out in 50ml borosilicate petridishes. A certain amount of the as-synthesised photocatalyst was added to 50ml MR dye aqueous solution (1X10⁻⁵M) in all the experiments. At specific intervals 3ml of the suspension was collected. The percent decolourisation of the dye was calculated according to the following equation,

Percentage decolourisation (%) = $\frac{A_0 - A_t}{A_0} \times 100$ -----Eq. (1)
where A₀ is the initial concentration of the dye and A_t is the concentration of MR at a particular reaction time 't' in minutes.

3. Results and Discussion

3.1 Characterization of the as-synthesised material

The optical properties of biocompatible Cys/ZnSe were characterized by UV-visible absorption and photoluminescence (PL) analysis, and the results are shown in Fig. 1A. In the UV-vis absorption spectrum of Cys/ZnSe there is a strong absorption peak obtained at 370 nm, these results suggest that the optical properties of ZnSe are quite sensitive to the detailed reaction conditions. Obviously, synthetic

conditions, crystal size, and shape strongly influence the optical quality of ZnSe semiconductor nanocrystals [7].

The PL measurements were carried out at 35 °C using He-Cd laser with 370nm as excitation wavelength. The room temperature PL spectra of the as-synthesized Cys/ZnSe using an excitation wavelength of 375 nm, shows a sharp emission peak at 420 nm is shown in Fig1A. The emission peak at 420nm is usually attributed to NBE emission of ZnSe that is the recombination of free excitons. According to Yan Zhang ZnSe prepared under Zn-rich condition had a strong NBE emission, while a strong (deep defect) DD emission is observed under Se-rich condition. During the preparation of cysteine capped ZnSe QDs, there are excessive ZnO₂²⁻ ions in the reaction system and therefore Cys/ZnSe was grown under Zn-rich condition and are of high optical activity [4].

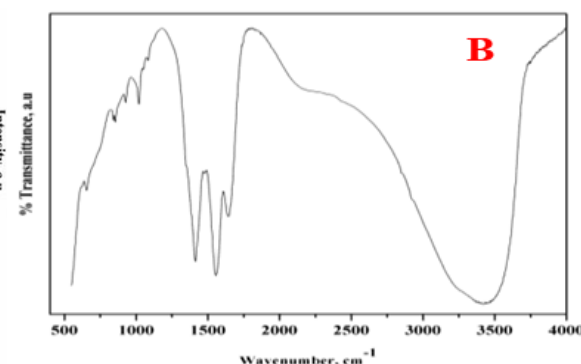
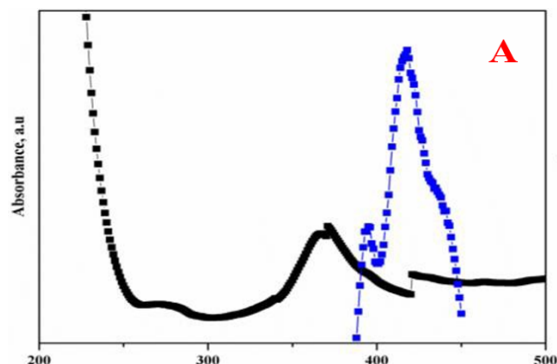
Further characterization using Fourier Transform Infrared Spectroscopy (FT-IR) measurements was conducted in order to ascertain the role of L-cysteine on the crystallization of ZnSe QDs and also to detect the changes of chemical environment of the functional groups are shown in Fig. 1B. We can observe clearly the presence of -OH stretching vibration at 3423 cm⁻¹, N-H bending vibration and C=O stretching vibration at 1643 cm⁻¹, and the overlap of C-O bending vibration and C-N stretching vibration at 1413cm⁻¹ in the spectrum of L-cysteine capped ZnSe QDs, implying both carboxyl and amine functional groups exists on the surface of the prepared QDs. Disappearance of the characteristic S-H stretching vibration at 2600cm⁻¹ proves that L-cysteine binds on the surface of QDs through thiol groups [8].

Fig. 1(C) shows the XRD patterns of the sample. The peaks are assigned to the diffractions from (111), (220), (311) and (400) planes of the cubic zinc blende phase of ZnSe [9], which are in complete agreement with the PDF card (F43m, JCPDS file #00-002-0479). Moreover, no diffraction peaks from Zn or other impurities are observed within the detection limit. The grain size of the crystallites (mean crystallite diameter, d) of as-obtained product was calculated using Scherrer's formula

$$d = 0.9\lambda / \beta \cos \theta$$

Where λ is the wavelength of X-ray used (0.15418nm Cu α radiation), β is the full width in radiation at half- maximum of the peak and θ is the Bragg angle of the X-ray diffraction peak. Calculation made on these peaks gave a value of 9.7nm, 12nm and 11.5nm for the average crystallite diameter of the as-prepared ZnSe nanoparticles is 11nm.

The morphology of the as-synthesised materials was evaluated using SEM analysis. SEM image of the material is shown in Fig. 1D. From the SEM, the ZnSe QDs are uniformly anchored with amino acid group.



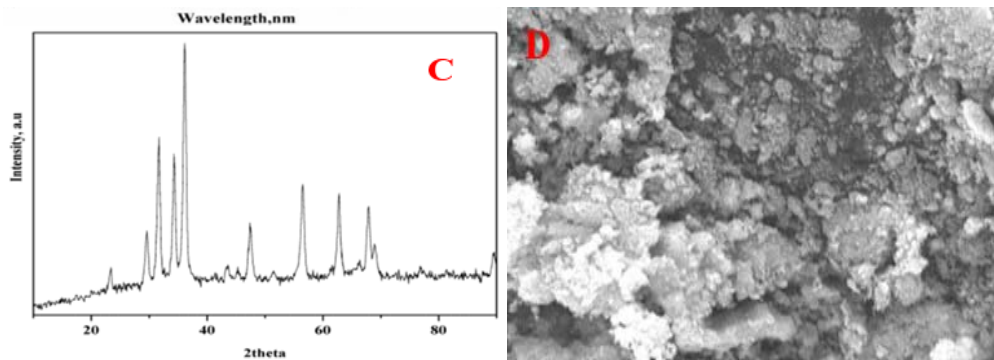


Fig 1: Characterization of the as-synthesised Cys/ZnSe QD: A) UV-v is and fluorescence overlap spectra, B) FT-IR spectrum, C) XRD pattern, D) SEM image

3.2 Photocatalytic Experiment

The photo activity of the as-synthesized material for the decolourisation of MR dye was performed under sunlight irradiation. MR was chosen as a model dye pollutant as it is highly sensitive to sunlight irradiation. In the absence of the photocatalyst, the MR dye solution was not degraded successfully and only 12.3% colour removal was achieved after 120min of sunlight irradiation. Meanwhile neat ZnSe showed 23.4% decolourisation and the percent decolourisation reached 82.6% with cysteine doped ZnSe after 120min of irradiation are shown in Fig: 2a. The photodegradation kinetics of the MR dye was determined by monitoring the absorbance of MR solution at 456nm. A plot of $\ln C_0/C$ vs time shows a linear relationship for the photocatalyst prepared, indicating that the photodegradation of MR catalyzed by neat ZnSe, Cys/ZnSe fits well into the pseudo first order reaction shown in Fig.2b. $\ln (C_0/C) = kt$, where k is the apparent rate constant of the degradation

process. The rate constant and regression values shown in Table 1.

The evolution of the absorption peak of MR at 456nm is assigned to the azo structure of the dye. The time dependent absorption spectra during sunlight irradiation of MR solution containing as- synthesized material are shown in Figs.2c respectively for 120 min. The intensity of the peaks diminished by 82.4% in the presence of Cys/ZnSe QD. As the irradiation time increased, both absorption bands gradually decreased (almost flat) and finally disappeared which indicated the decomposition of the chromophoric groups present in MR. As no new peak was observed, it is understood that the MR has been mineralized. These results reveal that the azo bonds and the aromatic rings of MR were broken under sunlight irradiation in the presence of biocompatible ZnSe QDs material. The schematic representation of the MR dye degradation under sunlight irradiation using the Cys/ZnSe QDs is depicted in Fig.1d

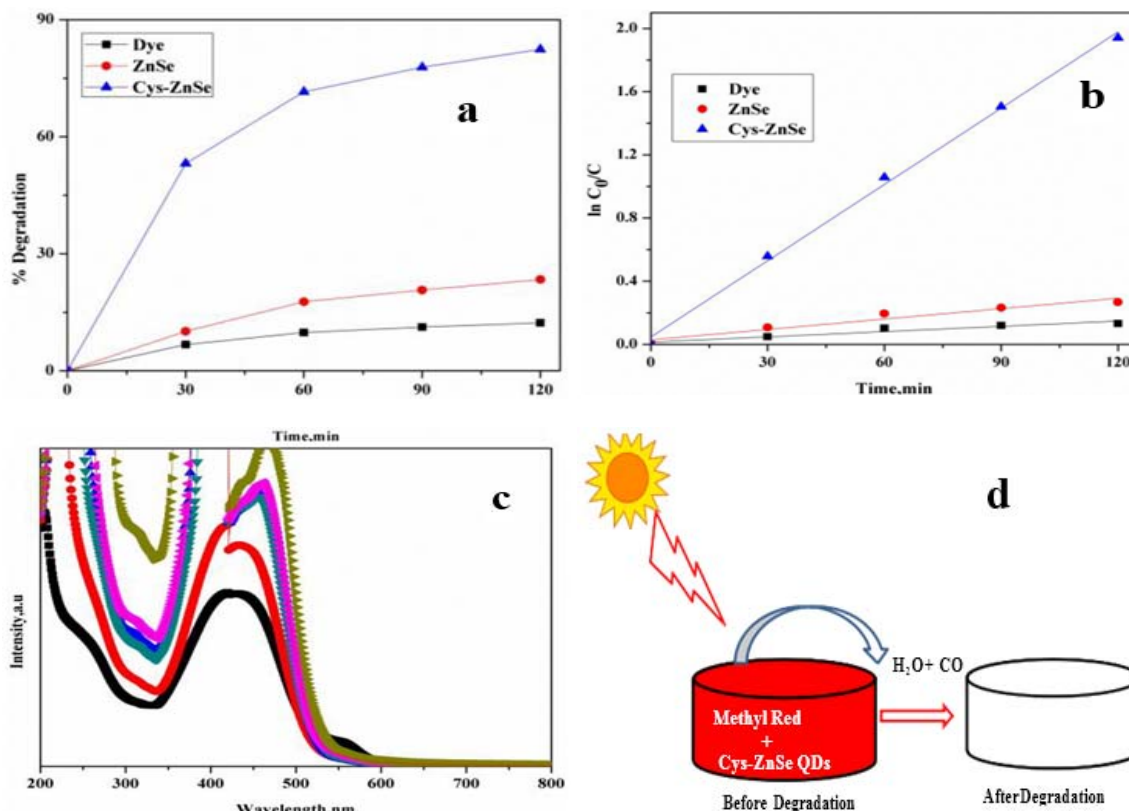


Fig 2: a) Photocatalytic activity of the as-synthesised materials b) kinetic plot c) UV-visible spectral changes for the degradation of MR dye solution under sunlight irradiation and d) schematic representation of MR dye solution degradation using the biocompatible material.

Table 1: Rate Constants and half-life period of the as-synthesised ZnSe QDs

Photocatalyst	Kapp (min ⁻¹)	R2	t1/2
Neat ZnSe	0.0022	0.9178	5.25
Cys- ZnSe	0.0166	0.9962	41.74

4. Conclusion

In summary, the biocompatible ZnSe QDs capped with L-cysteine amino acid sizes from 9.7 to 12 nm were successfully synthesized by a hydrothermal method. The as-prepared ZnSe QDs exhibited zinc-blende structure which was confirmed by the XRD pattern. The room-temperature PL results showed that the NBE emission peak could be attributed to bound excitons. The ZnSe QDs with smaller particle size demonstrated higher photocatalytic activity compared to the NPs with larger particle size. The photodegradation of Methyl Red catalyzed by the Cys/ZnSe QDs follows a pseudo-first-order reaction. Our results provide a novel biocompatible and promising ZnSe QDs for the treatment of textile dye industry wastewater containing organic compounds.

5. References

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