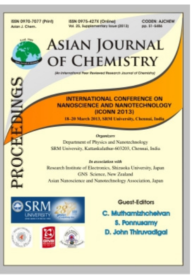
Asian Journal of Chemistry; Vol. 25, Supplementary Issue (2013), S1-S4

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Photocatalytic Degradation of Rhodamine B Dye Using Histidine-Stabilized CdS Quantum Dots†

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AJC-12777

CdS quantum dots were prepared using the amino acid histidine as a stabilizing agent. Using a concentration of 4×10^{-4} M for the precursor Cd^{2+} and S^{2-} ions and taking the concentration of histidine as 20 mM, the average size of the CdS nanoclusters was determined to be 4.2 nm. The absorption onset of these particles was 452 nm which is considerably blue shifted compared to those of the bulk CdS. Such particles are known as quantum dots. The photocatalytic efficiency of the CdS quantum dots was evaluated by studying the degradation of rhodamine B dye. About 21 % of the dye was degraded in 30 min of irradiation using light of wavelength longer than 400 nm. The degradation of the dye was found to follow first order reaction kinetics. The addition of adenine was found to enhance the photocatalytic activity of the CdS quantum dots.

Key Words: Photocatalytic, Quantum dots, Degradation, Adenine, Rhodamine B.

INTRODUCTION

The organic pollutants that are emitted from various sources cause severe ecological problems because the biodegradation of these pollutants is often very slow and conventional treatments are either ineffective or environmentally incompatible. The dye contaminated wastewater is unattractive and harmful for aquatic life[1,2]. Therefore the decolourization and degradation of organic dyes before release to the environment are important. Rhodamine B is one of the most important xanthene dyes and is used in a variety of applications such as paper industry[3]. It has become a common organic pollutant. Various techniques have been used to remove the dyes from wastewater such as chemical coagulation, ozonization, electrolysis, oxidation and biodegradation[4-8]. However, these methods are unable to reduce the concentration of the contaminants to the desired levels[9]. Therefore, there is a need for more effective and economic techniques. Photocatalysis is a technique which can be used for the destruction of pollutants in a simple and efficient manner[10]. Photocatalytic reactions take place when a semiconductor absorbs a photon of light more energetic than its band gap energy. Thus upon photoexcitation, an electron is transferred from the valence band to the conduction band leaving a hole in the valence band. The electron-hole pair thus formed initiates the reduction and oxidation processes respectively of the adsorbed substrates. The photocatalytic activity of semiconductor nanoparticles such as TiO_2 has been extensively studied for the degradation of the dyes[11-13]. In this paper, we report the photocatalytic degradation of rhodamine B dye using histidine-stabilized CdS quantum dots. The photocatalytic efficiency of the semiconductor has also been analyzed in the presence of the biomolecule adenine.

EXPERIMENTAL

Cadmium perchlorate, histidine and adenine (Sigma Aldrich), sodium sulphide (Acros) and rhodamine B (Himedia) were used without any further purification. All other chemicals were of analytical reagent grade. The water used for preparing the solutions was purified through a Millipore system. A water bath cum incubator shaker was used for shaking the samples.

The CdS quantum dots stabilized by histidine were synthesized using a method reported earlier[14]. Briefly, a 150 mL solution containing cadmium perchlorate (4×10^{-4} M) and 4 mM histidine at a pH of 10 was bubbled with nitrogen gas for 15 min in a three neck flask. This was followed by the addition of 4×10^{-4} M sodium sulphide under vigorous stirring. The formation of CdS particles was indicated by the appearance of faint yellow colour.

The reaction mixture containing CdS and rhodamine B was shaken in a water bath cum incubator shaker for 0.5 h. The solution was then allowed to stand in the dark for 2 h for equilibration to be achieved. The reaction mixture was then

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†International Conference on Nanoscience & Nanotechnology, (ICONN 2013), 18-20 March 2013, SRM University, Kattankulathur, Chennai, India

irradiated using a Hg(Xe) arc lamp. Light of wavelength longer than 400 nm was selected using a glass cut filter.

The degradation of rhodamine B was monitored using a Perkin Elmer Lambda 25 UV-visible spectrophotometer. The absorbance of the dye (at 554 nm) was recorded at various irradiation times in order to calculate the concentration of the dye degraded.

RESULTS AND DISCUSSION

CdS particles were synthesized in the aqueous medium using the amino acid histidine as a stabilizing agent by reported method[14]. The Cd^{2+} and S^{2-} precursor concentration was kept at 4×10^{-4} M and the histidine concentration was varied between 4 mM and 20 mM. It may be mentioned here that the colloidal solution was stable only above a pH of 9.5. The pk_a of the amino group in histidine is 9.2. Above a pH of 9.5, the amino group is predominantly in deprotonated state. When the histidine concentration was 4 mM, the onset of absorption of CdS was 475 nm which is considerably blue shifted to that for bulk CdS (515 nm)[14]. It indicates that the particles are formed in the quantum confined size regime. Such particles are often referred to as quantum dots. When the stabilizer concentration was increased to 20 mM the onset of absorption shifted to 452 nm indicating the formation of even smaller particles. Using the theoretical model proposed by Brus[15], the size of CdS quantum dots was calculated to be 4.2 nm.

In order to determine the photocatalytic activity of the as-prepared CdS quantum dots, we carried out the photocatalytic degradation of rhodamine B dye. The reaction mixture containing CdS stabilized by 4 mM histidine and rhodamine B (5 μM) was irradiated using light of wavelength longer than 400 nm. The pH of the reaction mixture was kept at 10.5. The reaction mixture was irradiated for various intervals of time. The degradation of the dye was monitored using UV-visible absorption spectroscopy. The absorption spectra of the reaction mixture as a function of irradiation time have been displayed in Fig. 1. The absorption peak due to rhodamine B at 554 nm was found to decrease with increase in the irradiation time. It indicates that the dye was degraded in the presence of the CdS quantum dots. The degradation efficiency may be calculated using the following relation

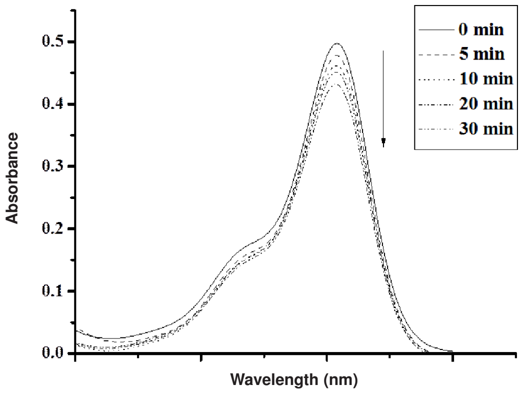

Fig. 1. Photocatalytic degradation of rhodamine B (5×10^{-6} M) using CdS quantum dots stabilized by 4 mM histidine at various irradiation times as indicated in the inset

$$\text{Efficiency (\%)} = (1 - C/C_0) \times 100$$

where C_0 is the initial concentrations of the dye and C denotes the concentration of the dye after t minutes of irradiation. After 0.5 h of irradiation, 21 % of rhodamine B was degraded. It may be mentioned here that in the absence of the CdS quantum dots there was negligible degradation of the dye. It indicates that the CdS quantum dots were effective as a photocatalyst for the degradation of the dye.

In order to determine the effect of histidine concentration on the degradation efficiency of the CdS quantum dots, we carried out similar experiments using CdS stabilized with 20 mM histidine. Using higher concentration of the stabilizer results in the formation of smaller particles of CdS[14]. For the same concentration of the semiconductor, production of smaller particles results in increase in the effective surface area. Larger surface area may lead to an increase in the adsorption capacity of the CdS quantum dots. Therefore, it is expected that the photocatalytic activity of the semiconductor quantum dots should increase. However, only 6 % of rhodamine B was degraded during 0.5 h of irradiation using the CdS quantum dots. Our earlier work suggests that a higher concentration of histidine leaves fewer sites available on the surface of the CdS quantum dots[14]. Thus fewer molecules of the dye will be adsorbed on the surface of the semiconductor particles. Since the photogenerated electron-hole pair recombination is extremely fast, only the dye molecules adsorbed on the surface of the CdS particles would interact with the charge carriers. Hence the photocatalytic activity of the CdS quantum dots decreases on increasing the concentration of the stabilizer.

The kinetics of degradation of the dye may be described by the first order rate equation.

$$\ln(C_0/C) = kt$$

where C_0 denotes the initial concentration of the dye, C denotes the concentration of the dye at any time t after irradiation and k denotes the first order rate constant. The plot of $\ln(C_0/C)$ *versus* irradiation time for the degradation of rhodamine B using CdS quantum dots stabilized by 4 mM histidine has been displayed in Fig. 2. The linearity of the plot indicates that the degradation of the dye on the surface of the CdS quantum dots obeys first order kinetics. From this plot, the rate constant for the degradation of the dye was calculated to be 0.007 min^{-1}.

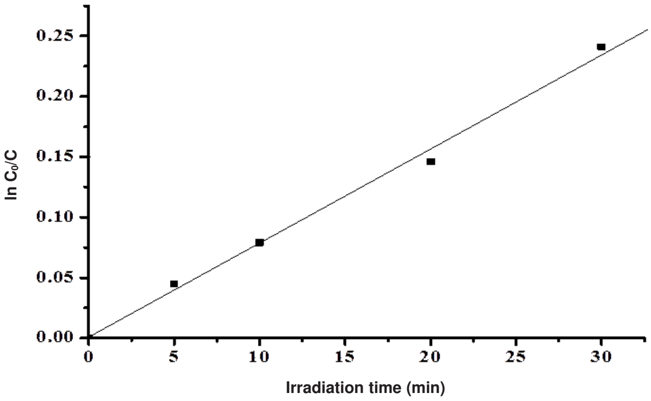

Fig. 2. Plot of $\ln(C_0/C)$ *versus* irradiation time for the degradation of rhodamine B using CdS quantum dots stabilized by 4 mM histidine

In our earlier studies with the histidine-stabilized CdS quantum dots, we had shown that the addition of adenine results in the enhancement of the fluorescence intensity of the semiconductor[14]. The addition of 2×10^{-4} M adenine enhanced the average emission lifetime of CdS quantum dots stabilized by 4 mM histidine from 17.3 to 18.2 ns[16]. The emission lifetime of a semiconductor indicates the period of separation of the electron-hole pair prior to their recombination. A longer lifetime implies that the charge carriers are available for a longer time to interact with the adsorbed substrate. Therefore the photocatalytic degradation of rhodamine B is expected to be enhanced by the addition of adenine. We performed experiments wherein the CdS catalyzed photodegradation of the dye was performed in the presence of adenine. First adenine was added to the solution containing the CdS quantum dots and then the dye was added. The reaction mixture was shaken for 0.5 h. The absorption spectra of the reaction mixture containing rhodamine B and CdS quantum dots (stabilized by 4 mM histidine) in the presence of 2×10^{-4} M adenine have been displayed in Fig. 3. After 0.5 h of irradiation about 26 % of the dye was degraded. Thus the addition of adenine enhances the photocatalytic activity of the CdS quantum dots by increasing their fluorescence lifetime. We carried out similar experiments in the presence of higher concentrations of adenine. The absorption spectra of the reaction mixture containing the CdS quantum dots and the dye in the presence of 5×10^{-4} M adenine have been displayed in Fig. 4. Under those conditions, 38 % of rhodamine B was degraded in 0.5 h of irradiation. These observations confirm the assumption that increase in the fluorescence lifetime of the CdS quantum dots results in enhancement of the photocatalytic activity of the semiconductor. The plots of $\ln(C_0/C)$ *versus* irradiation time for the degradation of the dye in the presence of the two concentrations of adenine were also found to be linear (Figs. 5 and 6). From these plots, the first order rate constants for the degradation of rhodamine B in the presence of 2×10^{-4} M and 5×10^{-4} M adenine were determined to be 0.010 and 0.016 min^{-1} respectively. The rate constants for the degradation of the dye in the absence and presence of two different concentrations of adenine have been summarized in Table-1.

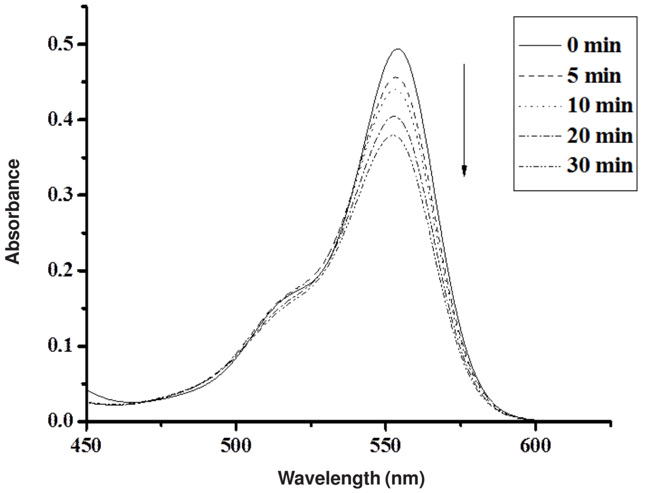

Fig. 3. Photocatalytic degradation of rhodamine B (5×10^{-6} M) using CdS quantum dots stabilized by 4 mM histidine in the presence of 2×10^{-4} M adenine at various irradiation times as indicated in the inset

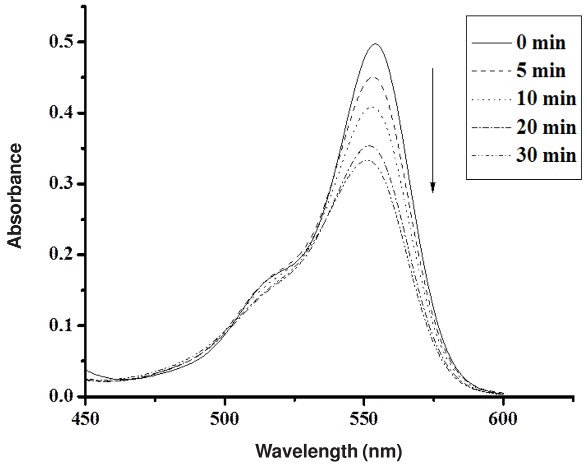

Fig. 4. Photocatalytic degradation of rhodamine B (5×10^{-6} M) using CdS quantum dots stabilized by 4 mM histidine in the presence of 5×10^{-4} M adenine at various irradiation times as indicated in the inset

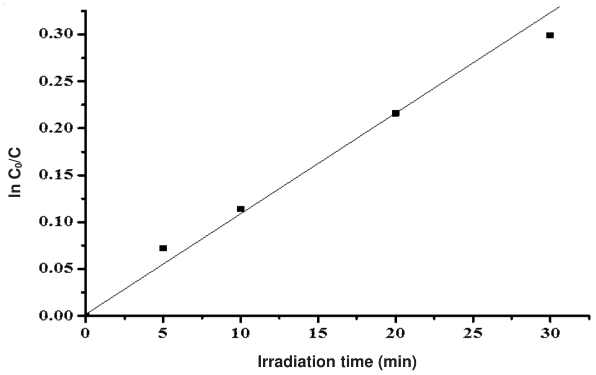

Fig. 5. Plot of $\ln(C_0/C)$ *versus* irradiation time for the degradation of rhodamine B using CdS quantum dots stabilized by 4 mM histidine in the presence of 2×10^{-4} M adenine

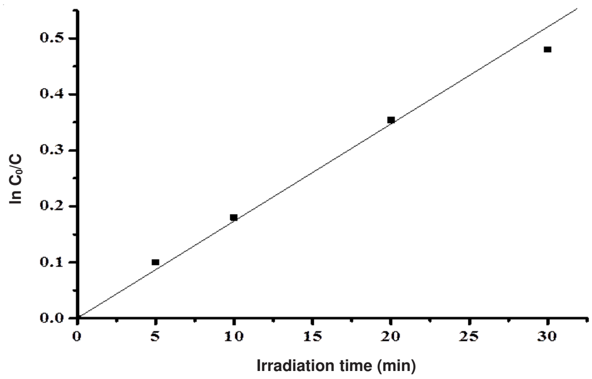

Fig. 6. Plot of $\ln(C_0/C)$ *versus* irradiation time for the degradation of rhodamine B using CdS quantum dots stabilized by 4 mM histidine in the presence of 5×10^{-4} M adenine

TABLE-1
RATE CONSTANTS FOR THE DEGRADATION OF RHODAMINE B USING CdS QUANTUM DOTS IN THE ABSENCE AND PRESENCE OF ADENINE

Photocatalyst	Rate constant (min^{-1})
CdS	0.007
CdS + 2×10^{-4} M adenine	0.010
CdS + 5×10^{-4} M adenine	0.016

Conclusion

Histidine-stabilized cadmium sulfide quantum dots show good photocatalytic activity for the degradation of rhodamine B dye using light of wavelength longer than 400 nm. The degradation of the dye on the surface of CdS followed first order rate law. Increasing the concentration of the stabilizer resulted in decrease in the catalytic activity of the CdS quantum dots. The presence of adenine enhanced the photocatalytic activity of the semiconductor quantum dots by increasing the fluorescence lifetime of the semiconductor. The water soluble histidine-stabilized CdS quantum dots may be tried as a photocatalyst for the treatment of organic dyes present in industrial wastewater under visible light irradiation.

ACKNOWLEDGEMENTS

This work was financially supported by DST and UGC, New Delhi, India. The author thank his former research student Ms. T. I. Chanu for carrying out the experimental work.

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