Chemical Physics Letters 522 (2012) 62–66

Contents lists available at SciVerse ScienceDirect

Chemical Physics Letters

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

Photophysical and photocatalytic properties of histidine-stabilized CdS quantum dots in the presence of indole

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ARTICLE INFO

Article history:
Received 8 August 2011
In final form 28 November 2011
Available online 3 December 2011

ABSTRACT

The fluorescence band of the histidine-stabilized CdS quantum dots was found to be blue-shifted as well as enhanced in intensity in the presence of indole. Irradiation of the reaction mixture containing CdS and indole using visible light resulted in the formation of indigo and isatin as the products of the photocatalytic reaction. The presence of adenine was found to enhance the photocatalytic activity of the CdS quantum dots. Time-resolved fluorescence measurements indicated that adenine enhanced the lifetime of the photogenerated electron–hole pair thereby allowing more indole molecules to undergo reaction with the hole.

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1. Introduction

The photophysical and photocatalytic properties of colloidal semiconductors have been in the scientific focus since the early 80s. The adsorption of a substrate on the surface of semiconductors alters their emission behavior which has been utilized in sensing applications. Both quenching and enhancement of the fluorescence intensity of the semiconductors have been observed [1–7]. The quenching behavior has been usually explained by the interception of the photogenerated electron or hole by the substrate. The enhancement effect may be attributed to the blocking of surface sites responsible for radiationless recombination of electron–hole pair by the substrate.

The study of photocatalytic properties of semiconductors is useful from the point of view of converting solar energy into chemical or electrical energy since most semiconductors absorb either ultraviolet (UV) or visible light. However, the visible portion of the solar radiation is about 40% as compared to only 5% of UV [8]. Therefore CdS, whose band gap falls in the visible region, has been extensively studied for its photocatalytic properties. The interfacial transfer of photogenerated electron or hole to the adsorbed substrate leads to the formation of products of the photocatalytic reaction initiated on the semiconductor surface. It may be noted here that only molecules adsorbed on the semiconductor surface can react with the electron or hole. This is due to the fact that the electron–hole pair recombination rate is usually much faster than the diffusion of molecules from the bulk solution to the particle surface. Various approaches have been used to enhance the photocatalytic efficiency of the semiconductor-based systems. These include coupling with another semiconductor or using co-catalyst [9–12], platinization of the particle surface [13] and doping with metals and non-metals [14–16]. Zong et al. [10] reported that the rate of H_2 evolution on CdS was significantly enhanced by loading MoS_2 as co-catalyst under visible light irradiation. The activity of CdS was increased by up to 36 times when loaded with only 0.2 wt% of MoS_2.

Quantum dots are extremely small particles which show the phenomenon of size quantization effect. The optical, electronic and catalytic properties of such particles are drastically different from those of the corresponding macrocrystalline substance [17]. In the present Letter, we have investigated the fluorescence behavior and photocatalytic activity of histidine-stabilized CdS quantum dots in the presence of indole. The photocatalytic activity of the semiconductor particles has been improved by the incorporation of a biomolecule, adenine, to the system.

2. Materials and methods

2.1. Chemicals

Cadmium perchlorate, L-histidine (Aldrich), sodium sulfide (Acros), indole, indigo (Himedia) and chloroform (Rankem) were used without further purification. All other chemicals were of Analytical Reagent grade. Millipore water was used throughout for preparation of the solutions.

2.2. Instrumentation

UV–visible absorption and emission spectra were recorded using PerkinElmer Lambda 25 and Hitachi F-4500 fluorescence spectrophotometers, respectively. Fluorescence lifetimes were recorded on a time correlated single photon counter obtained from HORIBA scientific. The samples were excited using a Nano-LED

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doi:10.1016/j.cplett.2011.11.073

source (375 nm). For photocatalytic activity studies, the samples were irradiated using a 200 W Hg (Xe) arc lamp purchased from Oriel Instruments. Light of wavelength longer than 400 nm was selected using cut filter. Infrared spectra were recorded on a Perkin-Elmer BX FTIR system. HPLC separations were carried out on a Waters liquid chromatograph equipped with a UV–visible detector. A reverse-phase C18 coulmn was used as the stationary phase.

2.3. Synthesis of colloidal histidine-stabilized CdS quantum dots

The CdS quantum dots were synthesized using a method reported recently by us [6]. Two different CdS samples having histidine (stabilizer) concentrations of 4 and 20 mM were used in the studies.

2.4. Preparation of samples for fluorescence and photocatalytic measurements

The reaction mixture containing CdS and indole was shaken on a water bath incubator shaker for half and hour and then allowed to equilibrate for a period of 2 h. For fluorescence measurements the samples were excited using 400 nm light to which indole is transparent. For the photocatalytic measurements, the samples (~3 ml) were taken in a 1 cm quartz cell and irradiated for various time intervals using light of wavelength longer than 400 nm. The light power was 190 W. The progress of the photocatalytic reaction was monitored by using UV–visible absorption spectroscopy. The CdS quantum dots are stable only above pH 9.5. Therefore the pH of the reaction mixtures was kept at a sufficiently high value (10.5). All the measurements were carried out at room temperature.

2.5. Computation of concentration of indole adsorbed on the surface of CdS

The amount of indole adsorbed on the surface of CdS was calculated by subtracting the absorbance of the reaction mixture (containing CdS and indole) from the sum of absorbances due to blank CdS and indole samples. The equilibrium concentration of indole was obtained by subtracting the concentration of indole adsorbed from the initial concentration of indole.

2.6. Analysis of fluorescence lifetime data

The average emission lifetime $\langle\tau\rangle$ of the CdS nanoparticles were calculated using the following relation [18] valid for emission from solid surfaces:

$$\langle\tau\rangle = \Sigma a_i \tau_i^2 / \Sigma a_i \tau_i$$

where a_i and τ_i denote the pre-exponential factor and the corresponding lifetime component respectively.

3. Results and discussion

3.1. Emission behavior of CdS in the presence of indole

The histidine-stabilized CdS quantum dots depicted a broad emission band centered at about 530 nm. The addition of mill-molar (mM) concentrations of indole resulted in an enhancement as well as blue-shift of the fluorescence band of the colloids. The fluorescence spectra of CdS stabilized by 4 mM histidine in the presence of various concentrations of indole (pH 10.5) have been displayed in Figure 1. The addition of 4 mM indole concentration resulted in the enhancement of the fluorescence intensity of CdS by a factor of 2. The fluorescence peak was also blue-shifted by

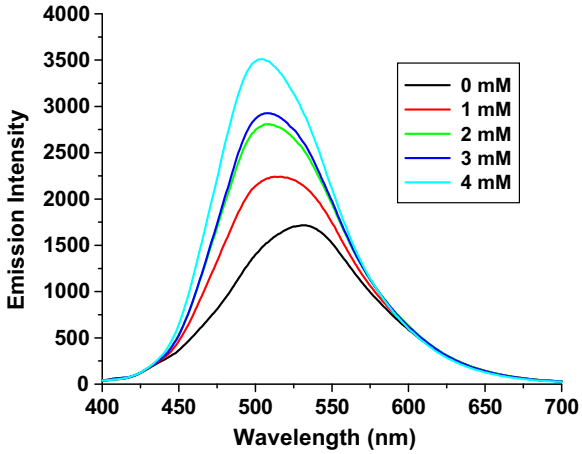

Figure 1. Fluorescence spectra of the CdS quantum dots in the presence of various concentrations of indole as indicated in the inset. Excitation wavelength: 380 nm.

27 nm. There was no further increase in the fluorescence intensity on increasing the concentration beyond 4 mM. Dannhauser et al. had also observed enhancement and blue-shift of the luminescence peak of Cd_2As_3 colloids on addition of triethylamine [19]. They suggested that triethylamine binds to lower energy trap sites which are directly involved in non-radiative decay. This binding raises the site energy, effectively removing these sites as efficient traps and increasing the emission quantum yield. We propose that a similar mechanism may be operating in the present case. These results are vastly different from those of similar studies carried out using CdS nanoparticles possessing bulk properties [20]. The earlier workers had observed a new band at 508 nm on the addition of indole to CdS, whereas the primary fluorescence band of CdS was centered at about 660 nm. Also, there was no progressive blue-shift on increasing the amount of indole. The different results in the two cases may be ascribed to the quantum dot nature of the CdS particles used in the present studies.

In order to determine the particle size dependency of the photophysical interaction of indole with the semiconductor, similar experiments were performed with CdS particles synthesized using 20 mM histidine as a stabilizing agent. Increasing the histidine concentration from 4 to 20 mM blue-shifted the absorption threshold of CdS from 465 to 452 nm [6]. A blue-shift in the absorption onset indicates a decrease in the particle size of the semiconductor. The fluorescence spectra of CdS stabilized by 20 mM histidine in the presence of various concentrations of indole have been displayed in Figure S1, Supplementary data. It may be seen that the extent of fluorescence enhancement and blue-shift is much reduced in this case. Presumably, a higher concentration of histidine leaves fewer sites on the surface of CdS for interaction with the substrate indole.

3.2. Adsorption of indole on the surface of CdS

Taking into consideration the importance of the phenomena of adsorption in photocatalysis, we performed experiments to determine the nature of adsorption of indole on the surface of the CdS quantum dots. In these experiments the concentration of indole was varied from 1 to 8 mM. The plot of the concentration of indole adsorbed versus the equilibrium concentration of indole has been displayed in Figure 2. The curve resembles Type V adsorption isotherm which indicates multi-layer adsorption of indole on the surface of CdS.

Similar experiments were carried out with CdS colloids stabilized by 20 mM histidine. The extent of adsorption was found to

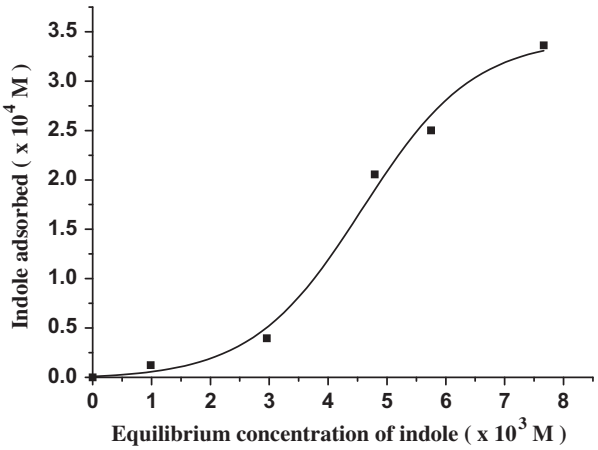

Figure 2. Adsorption isotherm for the adsorption of indole on the surface of CdS quantum dots.

be reduced although the pattern was still Type V (Figure S2, Supplementary data). These results support the assumption made in Section 3.1 that a higher concentration of histidine leaves fewer sites on the surface of CdS for interaction with indole.

3.3. Photocatalytic reaction of indole on the surface of CdS

For the photocatalytic studies, we used CdS colloids stabilized by 4 mM histidine since the extent of adsorption of indole was higher with these particles. Their average size was calculated to be 4.7 nm using the Brus model [21]. The reaction mixture containing 2.4×10^{-4} M CdS and 10 mM indole (pH 10.5) was irradiated with light of wavelength longer than 400 nm which is not absorbed by the substrate. The UV–visible absorption spectra of the reaction mixture as a function of irradiation time have been shown in Figure 3. From the figure it is seen that irradiation resulted in an increase in the absorbance of the reaction mixture in the entire visible region. It indicated the formation of product(s) of the photocatalytic reaction taking place on the surface of the semiconductor.

3.4. Characterization of the products of the photocatalytic reaction

Since indole contains a benzene ring, the products of the photocatalytic reaction between CdS and indole may be soluble in an organic solvent. Therefore, the irradiated reaction mixture containing the products was shaken with chloroform in a separatory funnel.

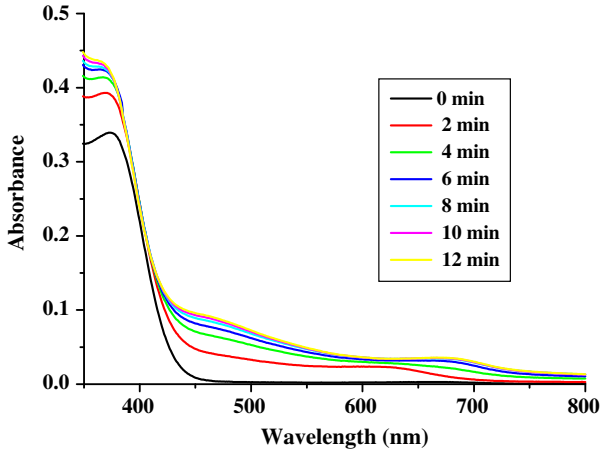

Figure 3. UV–visible absorption spectra of the reaction mixture containing CdS and indole as a function of irradiation time as indicated in the inset.

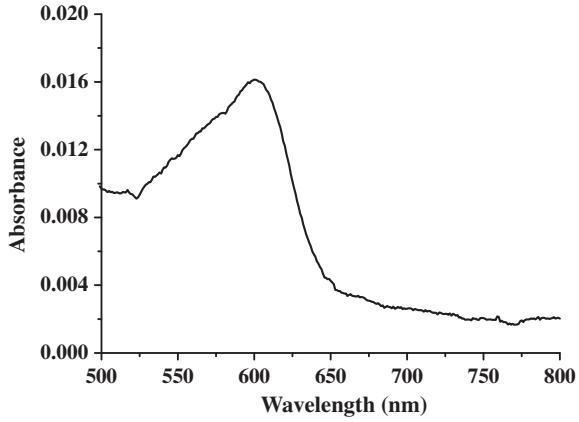

Figure 4. UV–visible absorption spectrum of the chloroform extract of the irradiated reaction mixture containing CdS and indole.

The UV–visible absorption spectrum of the chloroform extract has been displayed in Figure 4. The extracted product showed a λ_{max} at 601 nm. This value is close to the λ_{max} of 602 nm for an authentic indigo sample in chloroform. In order to confirm the identity of the product, we recorded the FTIR spectra of the extracted product and an authentic indigo sample (Figure S3, Supplementary data). The infrared spectra of the extracted product and indigo were almost identical. Thus it may be concluded that the photocatalytic reaction of indole on the surface of the CdS quantum dots leads to the formation of indigo as one of the products. Earlier workers had also reported indigo as the product of the photocatalytic reaction between indole and CdS particles possessing bulk properties [20]. However they reported indigo as the sole product of the photocatalytic reaction. The quantum dot nature of the CdS particles used may be responsible for the formation of multiple products in the present study. It may also be noted that the product(s) absorbing in the 420–580 nm region could not be extracted in the chloroform layer. This may be due to the presence of more polar groups in the product(s).

In order to characterize the other products we carried out the HPLC separation of the irradiated reaction mixture containing CdS and indole. The separation was carried out under isocratic conditions using water: methanol (50:50) as the eluent. The flow rate was maintained at 1.0 ml/min while the absorbance was monitored at 300 nm. As displayed in Figure 5, the HPLC chromatogram was found to contain several peaks indicating the formation of multiple products. The peaks having retention times of 11.8 and 18.4 min matched with authentic indole and indigo samples respectively. To identify the other products, the irradiated reaction mixture was subjected to mass spectral analysis. The mass spectrum (MS) (Figure S4, Supplementary data) showed an intense peak corresponding to an m/z value of 147 indicating the presence of isatin. Isatin has been known to be a product of the enzyme catalyzed oxidation of indole [22]. The other major peaks in the MS could not be assigned to any oxidation product of indole reported in the literature. We do not rule out the possibility of formation of other products in the present case. However, the concentration of those products may be too low to be detected. Therefore, we propose that indigo and isatin are the two main products of the photocatalytic reaction of indole with the histidine-stabilized CdS quantum dots.

3.5. Enhancement of the photocatalytic activity of CdS in the presence of adenine

Recently, we reported that the addition of adenine to histidine-stabilized CdS quantum dots enhanced the fluorescence intensity

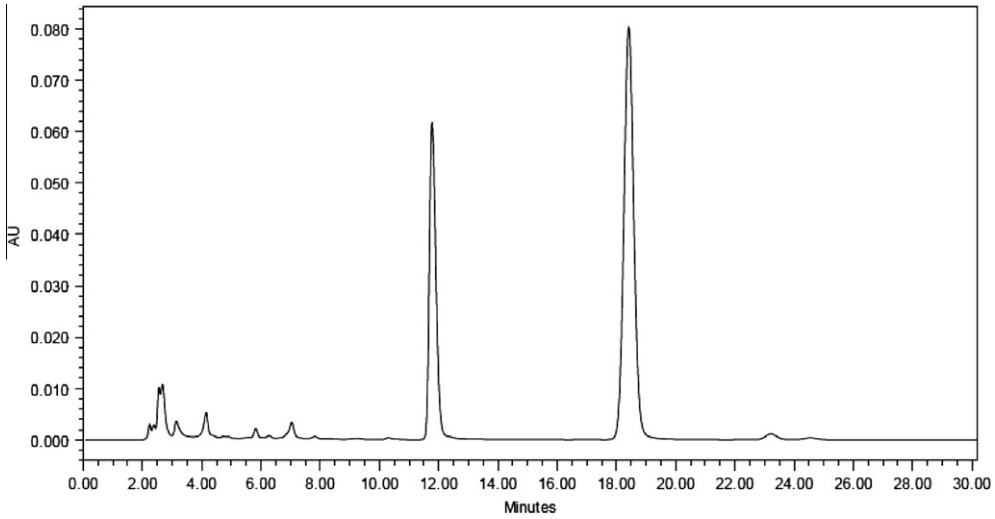

Figure 5. HPLC chromatogram of the irradiated reaction mixture containing CdS and indole.

of the latter [6]. The time-resolved fluorescence data of CdS in the absence and presence of adenine has been summarized in Table 1 and the corresponding decay curves have been displayed in Figure S5 of Supplementary data. On analyzing the data in Table 1, it was observed that a 2×10^{-4} M concentration of adenine enhanced the average fluorescence lifetime of CdS from 17.3 to 18.2 ns. The emission lifetime of a semiconductor indicates the period of separation of the photogenerated electron–hole pair prior to their recombination. A longer lifetime implies that the charge carriers are available for a longer time to react with the adsorbed substrate. Therefore, the photocatalytic activity of CdS is expected to increase by the incorporation of adenine. To verify this hypothesis, we carried out photocatalytic studies by the incorporation of adenine in the system. Indeed, the yield of the products was increased in this case. The absorbance of isatin (monitored at 470 nm) as a function of the irradiation time in the absence and presence of two different concentrations of adenine has been displayed in Figure 6. The yield of isatin was enhanced by 18.9% and 40.0% in the presence of 2×10^{-4} and 5×10^{-4} M adenine, respectively. The yield of the other product, indigo was also found to increase when the photocatalytic reaction was carried out in the presence of adenine (Figure S6, Supplementary data).

3.6. Mechanistic aspects of the CdS-sensitized photocatalytic reaction

Figure 6 depicts the formation of isatin as a function of the time of irradiation. Initially, the product formation is fast and gradually it slows down and reaches a plateau after 12–14 min of irradiation. In order to understand this behavior, one has to take into account the nature of adsorption of indole on the surface of CdS. As discussed in Section 3.2, indole is adsorbed on the surface of CdS in a multi-layer fashion. After the formation of the primary layer, fewer molecules of indole are adsorbed on the secondary and subsequent layers due to weakening of the attractive forces between the adsorbent and the adsorbate. The initial fast rate of the product formation may be attributed to the reaction of indole molecules adsorbed on the primary layer. Since, fewer molecules are available in the subsequent layers, the rate of the product formation slows down. After about 14 min absence of any further product formation indicates that all indole molecules adsorbed on the surface of CdS may have reacted.

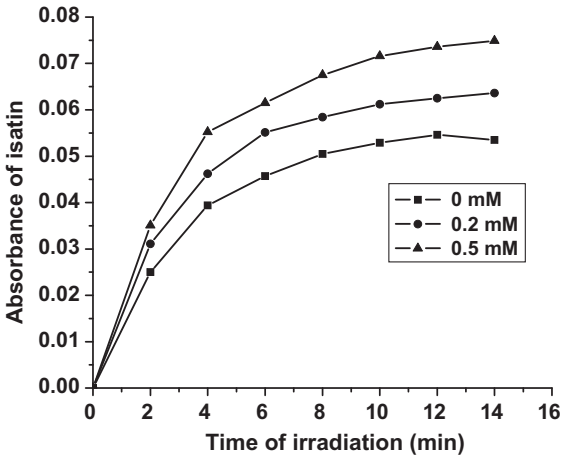

Figure 6. Plot of the absorbance of isatin at various irradiation times in the absence and presence of adenine concentrations as indicated in the inset.

A. Kumar and S. Kumar had studied the photocatalaytic behavior of sodium hexametaphosphate stabilized CdS nanoparticles in the presence of indole [20]. They suggested that indole reacted with the photogenerated hole leading to the formation of indigo as the product. Since indigo is also formed as one of the products in the present work, it may be concluded that the hole is the photogenerated species which is responsible for initiating the photocatalytic reaction in the present studies. The formation of isatin should also occur from one of the intermediates formed after the reaction of the hole with indole. On this basis we propose the following reaction mechanism of the CdS-sensitized photocatalytic reaction of indole (Figure 7). The mechanism is a minor modification of the one proposed by earlier workers for the formation of indigo from indole [20]. The absorption of light by CdS results in the formation of the electron–hole pair. The photogenerated hole reacts with indole adsorbed on the CdS surface to form a radical

Table 1
Fluorescence lifetime data of CdS in the absence and presence of adenine.

Adenine	Lifetime (ns)			
	τ_1	τ_2	τ_3	$<\tau>$
–	0.36 (3.18)	3.77 (0.3071)	30.41 (0.1230)	17.3
2×10^{-4} M	0.31(0.8619)	2.93 (0.1067)	26.36 (0.0438)	18.2

The values in parentheses denote the pre-exponential factors corresponding to the respective τ.

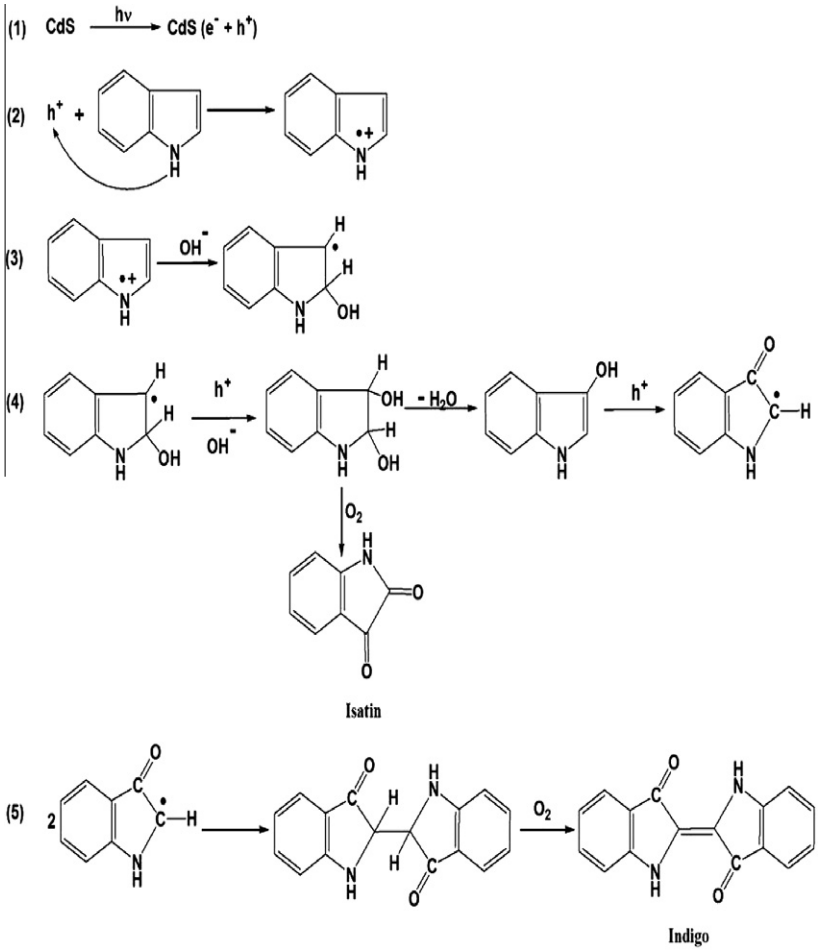

Figure 7. Schematic representation of the mechanism of the formation indigo and isatin from indole.

cation. The radical cation then reacts with the OH^- to produce another radical. This radical after a series of steps leads to the formation of isatin and indigo as the reaction products.

4. Conclusions

The fluorescence behavior of the CdS quantum dots in the presence of indole showed particle size dependence. The photocatalytic reaction of CdS with indole resulted in the formation of indigo and isatin as the products. Both the photophysical and photocatalytic properties of the CdS quantum dots in the presence of indole were found to be different as compared to those of CdS particles possessing bulk properties. These results support the theoretical prediction that the optical and photocatalytic properties of quantum dots are different from those of the corresponding bulk material. The presence of adenine enhanced the photocatalytic activity of CdS by increasing the lifetime of the photogenerated electron–hole pair.

Acknowledgments

This research was financially supported by the Department of Science and Technology, Government of India, through Grant No. SR/FTP/CS-57/2005. One of the authors (T.I. Chanu) thanks UGC and CSIR, New Delhi, for research fellowships. We are indebted to Professor P. Ramamurthy, Director, National Centre for Ultrafast Processes, Chennai, for the fluorescence lifetime measurements. We thank the Sophisticated Analytical Instrumentation Facility (SAIF) of our university for the mass spectral analysis.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2011.11.073.

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