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Electronic and photocatalytic properties of purine(s)-capped CdS nanoparticles in the presence of tryptophol

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Abstract

Purine(s)-capped Q-CdS nanoparticles have been employed as photosensitizers to perform the reaction of tryptophol. Tryptophol replaces the purine in the outer shell of purine(s)-capped Q-CdS having core/shell structure. Its presence does not bring any noticeable change in its optical property but quenches the fluorescence and reduces the fluorescence lifetime significantly. The dynamics of the charge carries and their reactivity are related to the binding characteristics of purine to Cd^{2+} of CdS. The visible irradiation of the oxygenated system(s) in aqueous medium at room temperature results in the oxidation of tryptophol to form 3-hydroxyindoline and 1-(2-aminophenyl)-3-hydroxypropan-1-one as the products of the reaction. The participation of singlet O_2 in the reaction scheme is ruled out. The maximum photodecomposition of tryptophol and the formation of product(s) takes place in case of purine-capped Q-CdS system ($\phi_{-\text{tryp}} = 0.5$) and the minimum yield was observed in case of adenine-capped Q-CdS system ($\phi_{-\text{tryp}} = 0.1$). The difference between the reactivity of the two has been attributed to the difference in the nature of the capping agent.

Keywords: Purine(s)-capped Q-CdS; Electronic properties; Photophysics; Dynamics of charge carriers; Semiconductor nanoclusters

1. Introduction

In recent years, the size and shape controlled inorganic nanomaterials and their complex assemblies are being developed and investigated extensively in view of their vast applications in photonics, photophysics, photocatalysis and as electronic materials [1–4]. The passivation of the semiconductor's surface by organics produces the particles with improved physicochemical and photocatalytic properties [5–8]. Surface capping of CdS clusters by purine has been used recently to produce particles with varied electronic and photocatalytic behavior [8]. Purine-capped Q-CdS has been suggested to act as building block for replacing the purine present in the outer most shell by the bulk substrate.

Indoles are known to play important physiological role in different biological systems [9]. Tryptophol, a metabolite of l-tryptophan is one of the important derivatives of indole, which has been found both in plants and animals and controls their potent biological activity [10–16]. Its production in certain foodstuff influences their physicochemical properties [17]. The formation of tryptophol during alcohol fermentation causes the reduction in the sugar level and its presence in alcoholic beverages develops a bitter taste. In carbohydrate containing system, the secretion of vitamin B_6 becomes less in the presence of tryptophol. Its metabolite in higher and lower plants is known to undergo oxidation to yield indole-3-acetaldehyde and indole-3-carboxylic acid [18,19]. The study of photodynamic action of tryptophol in the presence of oxygen may provide important information about the metabolic activity occurring in plants and animals.

In view of the above, in the present work the oxidation of tryptophol induced by visible light has been examined using purine(s)-capped Q-CdS as photosensitizer.

2. Experimental section

2.1. Reagents

Cadmium perchlorate, adenine, 6-dimethylaminopurine (Aldrich); purine, tryptophol (indole-3-ethanol) (sigma);

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sodium hydroxide, perchloric acid (Merck); hydrochloric acid (Qualigens); N_2, O_2 (purity ≥ 99.9%) were of analytical grade and were used as received without further purification.

2.2. Equipment

Electronic spectra were recorded on a Shimadzu UV-2100S spectrophotometer. Steady state fluorescence spectra were measured on a Shimadzu RF-5301PC spectrofluorophotometer. Electron microscopy was performed by a Philips CM-10 transmission electron microscope equipped with a 35 mm camera by applying a small drop of colloidal CdS solution on a carbon coated copper G-200 grid (size 3.05 mm). Electron micrographs were obtained by scanning these grids at an accelerating voltage of 100 kV using different magnifications. Time-resolved fluorescence measurements were made on an IBH-5000 U single photon counter. A Tsunami Ti-sapphire mode locked picosecond laser was used as an excitation source. The emitted photons were detected by a Hamamatsu (R 3809 U) photomultiplier. The decay of fluorescence was recorded by using the excitation wavelength of 375 nm and emission wavelength of 550 nm at 293 K. Decay curves were analyzed by a multi-exponential iterative technique, the software of which was provided by IBH. The goodness of the fit was checked by evaluating χ^2 from a plot of weighed residuals and auto correlation function. Steady state photolysis was performed on an Oriel Photolysis assembly equipped with 200 W Hg (Xe) arc lamp. Samples were photolysed by light of wavelength >370 nm (370–430 nm) using suitable solution and glass cut filters. GC separation was carried out on a Hewlett Packard 5890 A gas chromatograph employing the flame ionization detector. GCMS experiments were performed on a Shimadzu QP-5000 GCMS apparatus. The product of the photochemical reaction was analyzed on a Shimadzu LC-10 AD liquid chromatograph using Shimadzu Shim-Pack CLC-ODS (M) reversed-phase columns.

2.3. Methodology

In the present work, Q-CdS was prepared by injecting 5×10^{-5} mol dm^{-3} of SH^- to 1×10^{-4} mol dm^{-3} of Cd^{2+} containing 5×10^{-3} mol dm^{-3} of each of the used purine using previously reported methods and were characterized by IR, NMR and XRD techniques [8]. Purine-capped CdS particles were found to have relatively broad size distribution with an average size of about 5 nm. 6-Dimethylaminopurine-capped Q-CdS had relatively narrow size distribution with an average size of about 2 nm. The reactant and the products were extracted in chloroform and their separation was obtained on a HP-1 capillary column under non-isothermal conditions. The column was temperature programmed from 50 to 250 °C at a heating rate of 10 °C/min. MS data was recorded at 70 eV after removing the solvent. Five microliters of aliquots were subjected to HPLC analysis under isocratic conditions using methanol-KH_2PO_4 mixture of varying compositions as eluents. The best separation was obtained with methanol:KH_2PO_4 mixture having a ratio of 35:65. The concentration of dissolved oxygen in different samples was determined by Winkler's method [20].

3. Results and discussion

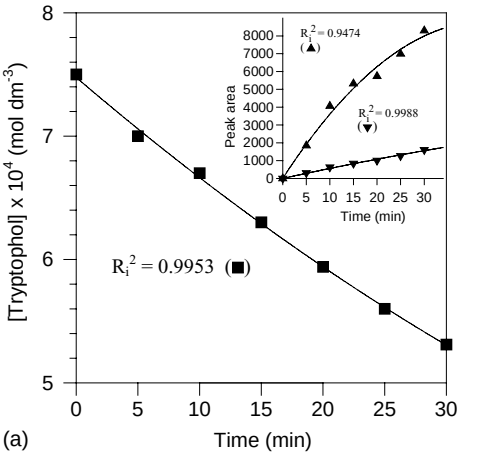
3.1. Purine-capped Q-CdS sensitized oxidation of tryptophol

The illumination of oxygenated reaction mixture containing purine(s)-capped Q-CdS (2.25×10^{-5} mol dm^{-3}) and tryptophol (2.5×10^{-3} mol dm^{-3}) at pH 11 was carried out by visible light of $\lambda > 370$ nm where tryptophol had no absorption. The electronic spectra of irradiated sample depicted an increase in the wavelength range of 200–420 nm. Similar changes in the absorbance of the illuminated reaction samples containing tryptophol were observed while using adenine and 6-dimethylaminopurine-capped Q-CdS as sensitizers. The illumination of purine-capped Q-CdS alone under the identical experimental conditions exhibited rather a decrease in the absorbance, which has been attributed to the dissociation of these clusters to yield smaller particles [8b].

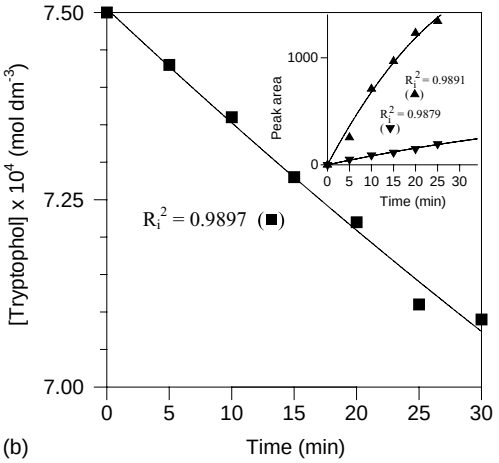
The reactant and product from the irradiated sample could be extracted in chloroform. The photocatalyst remaining in the aqueous medium could be reused to initiate the photochemical reaction with a similar efficiency. TLC and GC separation of the chloroform extract depicted the presence of three components. In GC, these components had retention times of 11.76, 12.14, and 13.66 min, respectively. GCMS analysis indicated these components to be 3-hydroxyindoline [*m/z* 177 (100, M^+), 159 (4.8), 148 (1.8), 146 (52.4), 130 (40.5)], 1-(2-aminophenyl)3-hydroxypropan-1-one [*m/z* 165 (28.6), 146 (33.3), 135 (9.5), 120 (100), 92 (85.7)] and the unreacted tryptophol [*m/z* 161 (23.8), 143 (2.4), 130 (100), 103 (9.5), 77 (14.3)], respectively. It is worth pointing out that the first component corresponding to *m/z* 177 could also be interpreted as 5-hydroxytryptophol. The retention time and electronic spectrum of this component, however, differed significantly to that of the authentic sample of 5-hydroxytryptophol recorded under identical conditions of experiments. The observed GCMS fragmentation of this component matched very well to that of 3-hydroxyindoline [21].

Both the reactant as well as the products of the photochemical reaction were also followed as a function of time (Fig. 1). For the used purine(s) as capping agents for Q-CdS, the quantum efficiency of decomposition of tryptophol followed the order: purine > 6-dimethylaminopurine > adenine (Table 1). Data in Fig. 1 reveal that the maximum decomposition of tryptophol and the formation of the products take place with purine-capped Q-CdS as photosensitizer. In this

case, tryptophol decomposes with a quantum efficiency of 0.5. The quantum yields of the product(s) could not be estimated because of the non-availability of their respective authentic samples. In the aerated environment the yield of product is observed to reduce by about a factor of 15, and in N_2 atmosphere no product formation is noted. This observation suggests the participation of oxygen in the reaction scheme.



(a)



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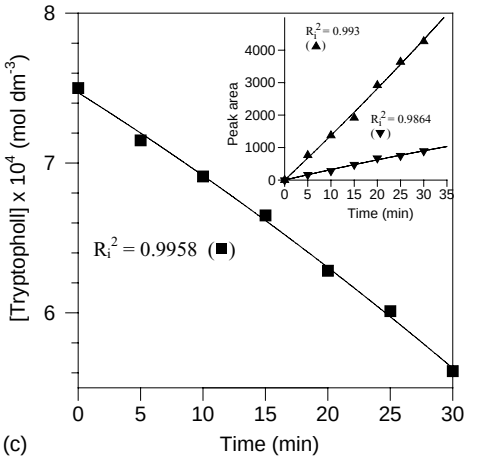


(c)

Table 1
Quenching rate constants in the presence of tryptophol and quantum efficiencies for the decomposition of tryptophol using Q-CdS capped by different purines as sensitizer

Q-CdS capped by	Quenching rate constant ($\times 10^9$ dm^3 mol^{-1} s^{-1}) measured using technique		$\Phi_{-\text{tryptophol}}$
	Steady state	Time-resolved	
Purine	7.3	5.7	0.5
Adenine	8.2	8.1	0.1
6-Dimethylaminopurine	12.6	10.4	0.4

3.2. Optical properties

The electronic spectrum of the reaction mixture containing purine(s)-capped Q-CdS and tryptophol did not show any chemical interaction between the two as the absorbance spectrum of the mixture was simply the additive spectrum of the two reactants in each case. It also suggested the absence of physical adsorption of tryptophol at the interface of these particles.

3.3. Steady state emission

In the presence of tryptophol the fluorescence of purine(s)-capped Q-CdS is simply quenched without producing any new band. The representative quenching behavior observed with purine-capped Q-CdS-tryptophol system is presented in Fig. 2. The emission due to other purines-capped Q-CdS also demonstrated a similar quenching behavior. The addition of 1×10^{-2} mol dm^{-3} of tryptophol reduced the fluorescence intensity to about half of its emission intensity. This process follows the dynamic quenching and obeys Stern–Volmer relationship (Fig. 3). The rate constants for the quenching process for different purine(s)-capped Q-CdS have been summarized in Table 1. A comparison of the quenching rate constant of purine-capped Q-CdS-tryptophol system with that of purine-capped Q-CdS-3-methylindole system examined under identical conditions [7d] reveals the later to be higher by a factor of about 3.5. Similar experiments were designed with purine-capped Q-CdS-tryptophan system. It also resulted simply in the dynamic quenching of emission due

Fig. 1. (a) Amounts of unreacted tryptophol (■) as a function of illumination time using purine-capped Q-CdS as sensitizer containing tryptophol-O_2 at pH 11. *Inset*: Peak areas of 3-hydroxyindoline (▲); 1-(2-aminophenyl) 3-hydroxypropan-1-one (▼) produced as a function of illumination time. (b) Amounts of unreacted tryptophol (■) as a function of illumination time using adenine-capped Q-CdS as sensitizer containing tryptophol-O_2 at pH 11. *Inset*: Peak areas of 3-hydroxyindoline (▲); 1-(2-aminophenyl) 3-hydroxypropan-1-one (▼) produced as a function of illumination time. (c) Amounts of unreacted tryptophol (■) as a function of illumination time using 6-dimethylaminopurine-capped Q-CdS as sensitizer containing tryptophol-O_2 at pH 11. *Inset*: Peak areas of 3-hydroxyindoline (▲); 1-(2-aminophenyl) 3-hydroxypropan-1-one (▼) produced as a function of illumination time.

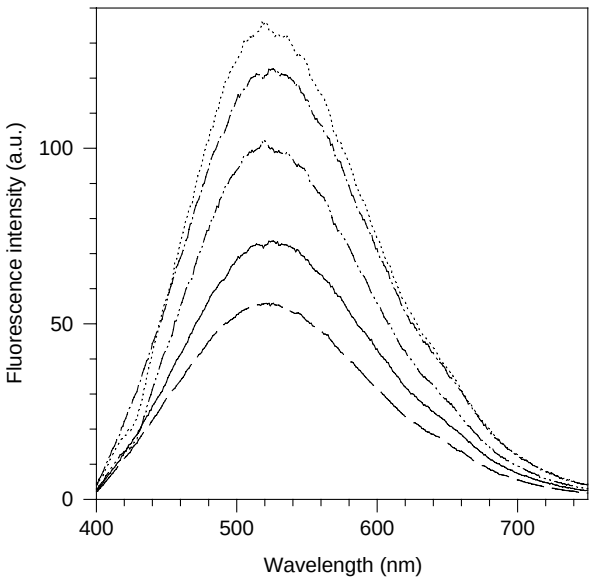


Fig. 2. Fluorescence of purine-capped Q-CdS in the absence (···) and presence of varying [tryptophol] ($\times 10^{-3}$ mol dm^{-3}); 2.0 (- · -); 6.0 (- · · -); 10.0 (—); 20.0 (– –) at pH 11.0. $\lambda_{ex} = 375$ nm.

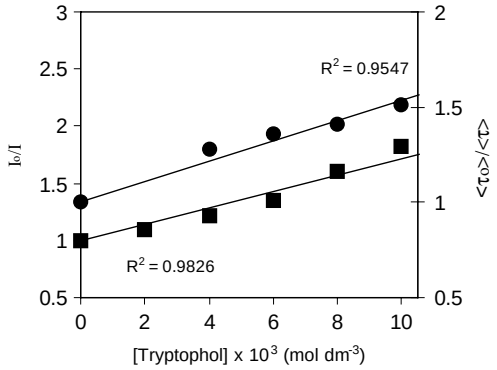


Fig. 3. Plots for $\langle\tau_0\rangle / \langle\tau\rangle$ (●); I_o/I (■) as a function of [tryptophol] observed using purine-capped Q-CdS as sensitizer.

to Q-CdS following Stern–Volmer relationship. From the Stern–Volmer plot the quenching rate constant of 1.7×10^{10} dm^3 mol^{-1} s^{-1} was observed. The quenching by these solutes followed the order 3-methylindole > tryptophan > tryptophol. A lower value of quenching rate constant in the present case might be attributed to the relatively higher oxidation potential of tryptophol[1] as compared to that of tryptophan and 3-methylindole.

3.4. Emission lifetime

The reactivity of charge carriers, generated upon illumination of aerated purine(s)-capped Q-CdS, with tryptophol was examined kinetically by measuring the fluorescence lifetime in its absence and presence. Some representative traces observed with these systems are given in Fig. 4A. The fluorescence of CdS particles decays following three-exponential kinetics. The three lifetime components lie in sub-nanosecond, nanosecond and tens of nanosecond time scale. In the presence of tryptophol, the first two components did not show appreciable variation, the third component with long time constant, however, decreases appreciably. The lifetime data for purine-capped Q-CdS in the absence and presence of tryptophol are presented in Table 2. The fluorescence quenching data obtained by lifetime measurements for all the systems obey Stern–Volmer relationship (Fig. 4B). These quenching rate constants are of the same order as observed above in steady state experiments (Table 1).

3.5. Role of O_2 on the dynamics of the charge carriers

The presence of O_2 quenched the fluorescence of all the purine(s)-capped Q-CdS. The quenching follows the dynamic behavior and takes place with a bimolecular rate constant of $(3 \pm 0.5) \times 10^9$ dm^3 mol^{-1} s^{-1} irrespective of the structure of purine used as capping agent. On the contrary, tryptophol quenches the emission of aerated Q-CdS capped by different purine(s) at varied rates and follows the order purine > adenine > 6-dimethylaminopurine (Table 1). It may be added that very similar values for the quenching of emission by tryptophol were obtained when the oxygenated purine(s)-capped Q-CdS were employed as sensitizer(s). Had the oxidation of tryptophol involved the formation of $^1O_2$ as shown in Eq. (1), one would

$$CdS^* + O_2 \not\rightarrow CdS + {}^1O_2 \quad (1)$$

anticipate the rates of this process to be the same for all the purine(s)-capped Q-CdS and the rates would have been much higher for the oxygenated photocatalyst compared with that of the aerated system. The absence of the same thus rules out the possibility of the participation of the singlet O_2 in the process.

Moreover, the quantum efficiency of the decomposition of tryptophol and the amounts of products formed differ significantly for different purine(s)-capped Q-CdS particles. It is the highest in case of purine-capped Q-CdS (0.5) and the lowest with adenine-capped system (0.1). A comparison of the rate constant(s) for the quenching of emission of different purine(s) stabilized Q-CdS by tryptophol to the quantum efficiencies of its decomposition in Table 1 reveals that the two do not follow the same trend. This difference can obviously be attributed to the nature of the capping agent.

The O_2 molecule, which is required to affect this process, possibly acts as an efficient electron acceptor. This process is expected to be fairly fast due to the low effective mass [22] and high mobility of the conduction band electron [23].

[1] Oxidation potentials of tryptophol and 3-methylindole were measured by cyclic voltammetry under the used experimental conditions and were observed to be 1.06 and 1.046 V, respectively

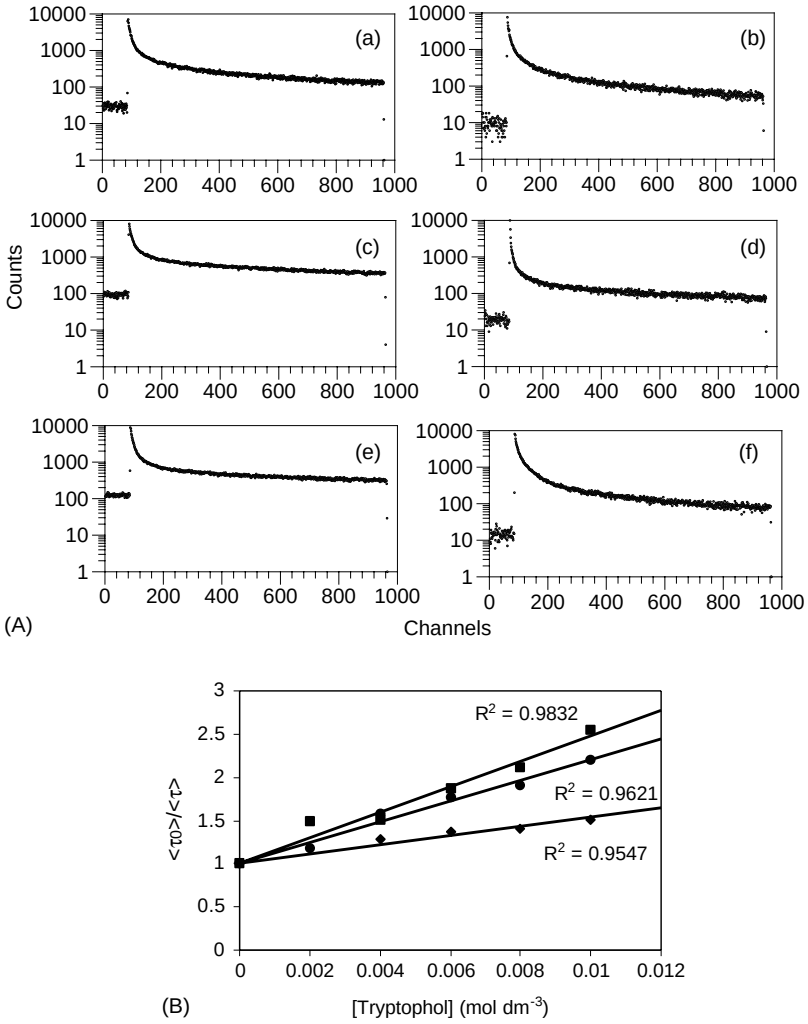


Fig. 4. (A) Decay profile of Q-CdS at pH 11.0 in the absence of tryptophol capped by (a) purine; (c) adenine; (e) 6-dimethylaminopurine. Decay profile of Q-CdS at pH 11.0 in the presence of tryptophol capped by (b) purine; (d) adenine; (f) 6-dimethylaminopurine. $\lambda_{ex} = 375$ nm, $\lambda_{em} = 550$ nm. (B) Plots for $\langle\tau_0\rangle / \langle\tau\rangle$ as a function of [tryptophol] observed using purine-capped (◆); adenine-capped (●) and 6-dimethylaminopurine-capped (■) Q-CdS as sensitizer.

This argument is also supported by the observation that the quenching of emission of Q-CdS

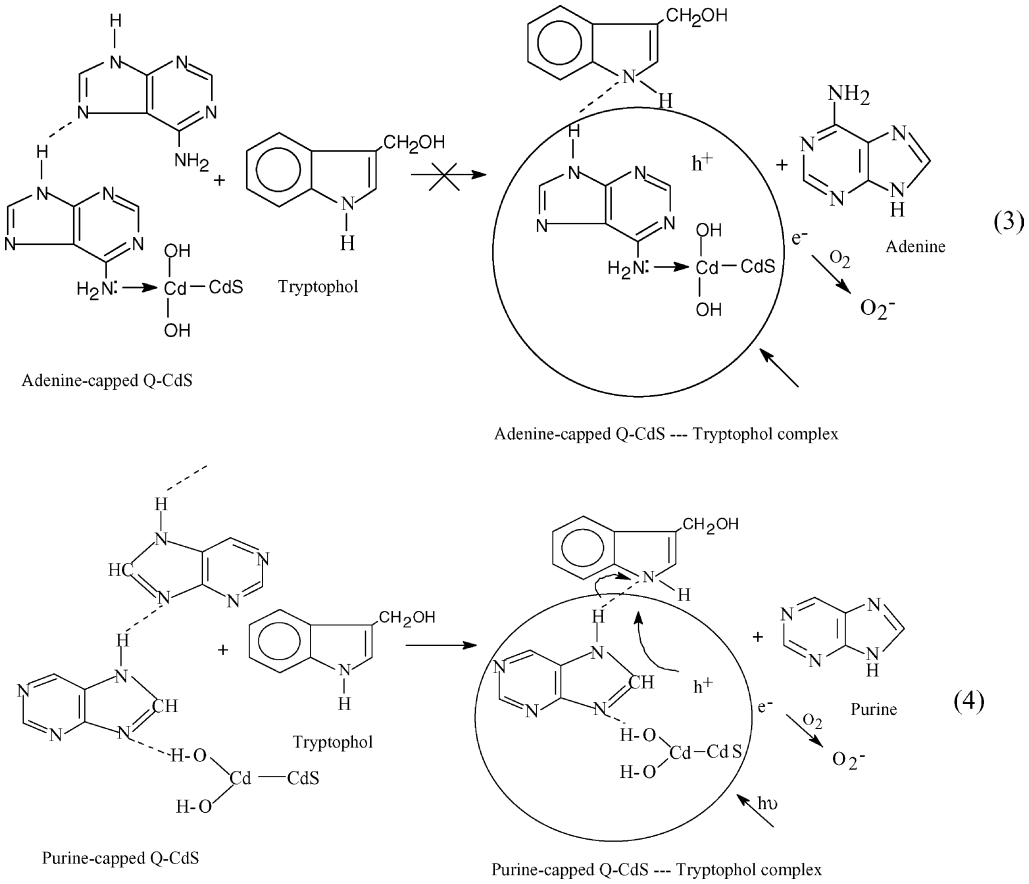
$$CdS(e_{CB}^{-}) + O_2 \rightarrow CdS + O_2^{-} \quad (2)$$

capped with different purine(s) by O_2 molecule takes place almost at the diffusion controlled rate. This characteristic of these particles is quite different to CdS nanoparticles stabilized by polyphosphate [24–26], the fluorescence of which is not quenched by the dissolved oxygen. In the present case, relatively deep among shallow trapped charge carriers are involved in the quenching of emission as is evident by the decrease in the value of long time constant component in

Table 2
Effect of [tryptophol] on the emission lifetime of purine-capped CdS at 550 nm

[Tryptophol]× 10^3 (mol dm^{-3})	Lifetime (ns)							χ^2
	Component 1		Component 2		Component 3		$\langle\tau\rangle$	
	τ_1	Emission (%)	τ_2	Emission (%)	τ_3	Emission (%)		
0	0.41 (13.39)	12.62	2.16 (4.46)	22.04	14.14 (2.02)	65.34	9.77	1.04
4	0.37 (24.17)	15.78	1.93 (7.70)	25.96	12.13 (2.75)	58.26	7.63	1.05
6	0.36 (27.56)	14.50	1.90 (11.34)	31.57	12.08 (3.04)	53.93	7.16	1.01
8	0.36 (23.12)	15.32	1.76 (8.33)	26.65	11.01 (2.90)	58.02	6.91	1.12
10	0.32 (26.97)	15.76	1.73 (9.29)	29.56	10.80 (2.75)	54.68	6.47	1.22

Values given in the brackets denote the pre-exponential factors corresponding to the respective τ.



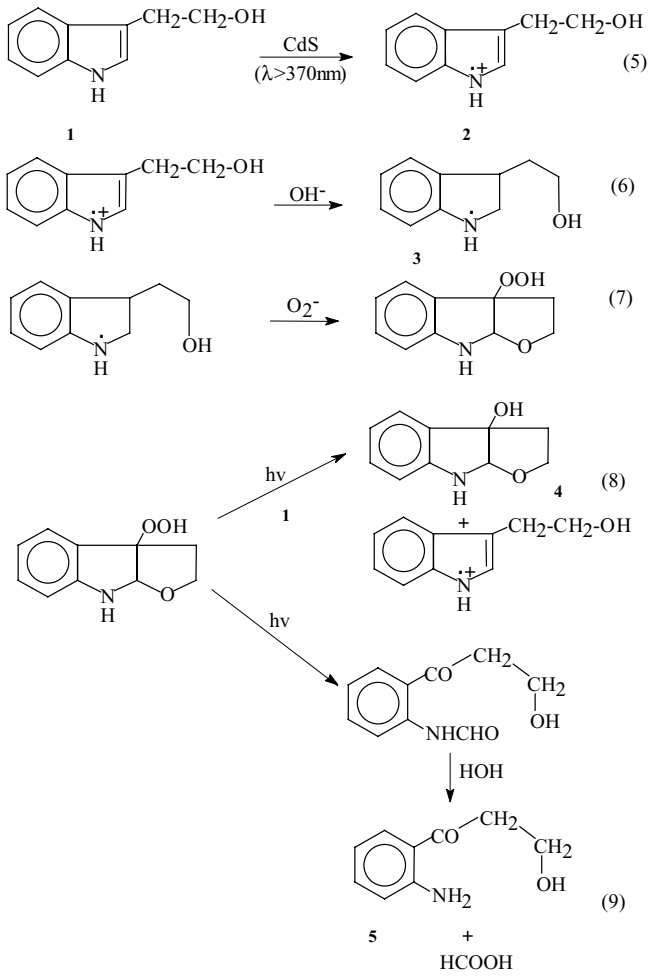
Scheme 1.

lifetime data (Table 2), whereas in the polyphosphate stabilized particles the deeply trapped charge carriers have been suggested to participate in the quenching as well as oxidation processes in the presence of donors [24,25,27].

It is likely that upon addition of tryptophol to purine(s)-capped Q-CdS, tryptophol removes the loosely bound purine from the outer shell in the ground state. Upon illumination of these systems by visible light, adenine being bound strongly and having relatively high oxidation potential does not allow the hole/oxidized species to become available in plenty on the surface of the CdS particle for reaction with the dissolved additive. On the other hand, the loosely bound purine channelises the hole efficiently to the dissolved additive (Scheme 1). In case of 6-dimethylaminopurine having slightly lower oxidation potential than adenine, the hole is transferred possibly through the oxidized 6-dimethylaminopurine to the tryptophol present in solution more efficiently. It thus explains the observed variation in the quantum efficiency of decomposition of tryptophol (Table 1).

It is interesting to note that visible light could initiate photochemical reaction of tryptophol (**1**) to yield 3-hydroxyindoline (**4**) and 1-(2-aminophenyl) 3-hydroxypropan-1-one (**5**). The Rosebengal-sensitized photooxygenation of tryptophol is known in literature to produce 3-hydroxyindoline and 2-acetylformanilide [21]; this study was carried out in dry methanol at −70 °C and has been suggested to involve the participation of singlet oxygen in the reaction scheme. Unlike this system in the present case, CdS-sensitized reaction is carried out in the aqueous medium at room temperature and does not involve the participation of singlet oxygen in the reaction mechanism. Instead O_2^- formed in the cathodic process (Eq. (2)) possibly adds to the tryptopholyl radical to produce corresponding hydroperoxide in Eq. (7), which upon photodecomposition produces **4** and **5** as shown in Scheme 2. Moreover, in contrast to the Rosebengal-sensitized photooxygenation reaction, under the present experimental conditions 2-acetylformanilide is not formed. It is likely to undergo fast hydrolysis to yield 1-(2-aminophenyl) 3-hydroxypropan-1-one (**5**) (Eq. (9)).

In conclusions, the surface-capped nanoparticles of semiconductors present a novel composite system, in which the electronic and photocatalytic properties of the semiconductor could be manipulated by changing the capping agent. In the purine(s)-capped Q-CdS particles having core/shell structure, the added biomolecule/bulk additive replaces the purine molecule present in the outer shell. The dynamics of the charge carriers in the illuminated composite CdS could be controlled by suitably selecting the capping agent and the donor-acceptor couples. The redox reactions of these



Scheme 2.

moieties could be accomplished by illuminating the photocatalyst selectively using visible light, which is not directly absorbed by the species attached in the outer shell.

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