ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 134 (2000) 199–207

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Photophysical and photocatalytic behaviours of $Cd(OH)_2$-coated Q-CdS in the presence of tryptophan

Anil Kumar*, Devendra P.S. Negi

Department of Chemistry, University of Roorkee, Roorkee 247667, UP, India

Received 14 September 1999; received in revised form 29 February 2000; accepted 8 March 2000

Abstract

Coating of $Cd(OH)_2$ on Q-CdS particles enhances their photostability, luminescing efficiency and emission lifetime. The presence of tryptophan quenches the bandgap emission of CdS and reduces its emission lifetime. For a typical 2×10^{-4} mol dm^{-3} of tryptophan the average emission lifetime of CdS is reduced from 22.6 to 8.5 ns. For this process a quenching rate constant of about 4×10^{11} dm^3 mol^{-1} s^{-1} has been evaluated. The red emission is not influenced appreciably. $Cd(OH)_2$-coated Q-CdS sensitised photooxidation of tryptophan has been examined in the presence of oxygen by irradiating with visible light. The photogenerated hole on the particle is intercepted by the bulk substrate ($\phi_{-\text{tryp}}$=0.22) to produce 5-hydroxytryptophan ($\phi_{5\text{-OHtryp}}$=0.08) as one of the main products. Shallowly trapped hole has been assigned to participate in the oxidation via hydrogen bonding interaction involving the surface of the particle and the substrate. Emission experiments indicate a difference in nature of reactive hole photogenerated on stoichiometric and $Cd(OH)_2$-coated Q-CdS particles. A mechanism of this reaction has been proposed.

Keywords: Photophysics of Q-CdS; Photocatalytic behaviour of Q-CdS; $Cd(OH)_2$-coated Q-CdS; Photooxidation of tryptophan

1. Introduction

Photocatalytic reactions initiated by nanocrystallites of semiconductors are interesting from the viewpoint of utilisation of solar energy for performing synthetically useful chemical transformations [1–10]. Cadmium sulphide having a bandgap energy of 2.4 eV, can generate e^-–h^+ pair upon illumination by visible light radiations which enables it to act as a potential photocatalyst in the solar region. The surface of colloidal semiconductor particles is known to play an important role in the photocatalysis by providing binding sites to the redox couples [7–10]. Surface modification has also been found to alter the photophysics and photochemistry of these semiconductors [9–15]. In certain cases the extent of adsorption has been found to control the photochemical yield of the product(s). One of the major obstacles in the use of CdS as a photocatalyst is its anodic dissolution upon illumination. Surface capping of these particles by $Cd(OH)_2$ layer is known to minimise this drawback [16] by disallowing the hole to escape to the surface to react with free CdS. It in turn enhances the trapping of e^-–h^+ pair in various surface states and their radiative recombination. Lately, a number of reports have appeared on the study of surface interaction of biological molecules like polynucleotides, nucleic acids etc. with CdS [12,15,17]. In this context it would be important to examine the interaction of colloidal CdS with indole based molecules and investigate their visible light induced photochemical reactions.

In the present work, we have studied the photophysical and photocatalytic behaviour of $Cd(OH)_2$-coated Q-CdS in the presence of DL-tryptophan (tryp). Interestingly, tryp is neither adsorbed on the surface of these particles nor exhibited any chemical interaction. Photophysical changes, however, indicate some weak surface interaction between tryp and the used particles. The photogenerated hole intercepts the bulk substrate to cause its oxidation. Product analyses coupled with electronic and emission spectroscopic data have been used to probe the mechanism of the reaction. Photosensitised oxidation of tryp in the presence of O_2 has been considered to be of great biological importance [18,19].

2. Experimental details

2.1. Materials

Cadmium perchlorate (Alfa); DL-tryptophan, 5-hydroxytryptophan (Aldrich); kynurenine (Fluka); sodium hexam-

* Corresponding author. Tel.: +91-1332-72349; fax: +91-1332-73560.
E-mail address: anilkfcy@rurkiu.ernut.in (A. Kumar)

1010-6030/00/$ – see front matter
PII: S1010-6030(00)00263-X

etaphosphate (Qualigens); methanol (Merck) and all other chemicals used were of analytical grade. All chemicals were used as received.

2.2. Equipments

The electronic spectra were recorded on a Shimadzu UV-2100/s spectrophotometer. The emission spectra were obtained on a Jasco FP-777 and RF-5301 PC spectrofluorophotometers. The size of the CdS particles was determined by a Philips EM-400 transmission electron microscope. IR spectra were measured on a Perkin-Elmer 883 IR spectrophotometer in NaCl cell. Continuous photolysis experiments were performed on an Oriel photolysis assembly equipped with a 200 W Hg–Xe arc lamp and suitable solution and glass cut filters. The fluorescence lifetimes were measured on an IBH-5000 single photon counting fluorimeter using a nanosecond discharge lamp for excitation. Hamamatsu photomultiplier was employed for the detection of fluorescence. Decay curves were analysed by a multi-exponential iterative reconvolution technique provided by IBH. The goodness of fit was determined by evaluating χ^2 from a plot of weighted residuals and autocorrelation functions. HPLC separations were carried out on a Shimadzu LC-10 AD chromatograph using Shimadzu Shim-pack CLC-ODS (M) column (25 cm × 4.6 mm i.d.) and a UV–VIS detector.

2.3. Methodology

$Cd(OH)_2$-coated Q-CdS particles were synthesised by the method developed by Spanhel et al. [16]. Stoichiometric CdS was prepared by injecting SH^- to the deaerated solution of $Cd(ClO_4)_2$ containing sodium hexametaphosphate. This sol was activated by adding OH^- followed by excess Cd^{2+}. These solutions contained 3×10^{-4} mol dm^{-3} of Q-CdS and 6×10^{-4} mol dm^{-3} of excess Cd^{2+}.

Reaction mixture containing the photocatalyst and tryp was prepared by mixing them on a shaker for about 20 min and then equilibrating it for about an hour. All solutions were made afresh just before conducting the experiments. For electron microscopy, a drop of $Cd(OH)_2$-coated Q-CdS was applied on a copper grid with formvar (polyvinyl formal) supported film. Formvar provides an embedding medium for the sample. The grids were scanned with an acceleration voltage of 100 kV at different magnifications. The average size of these particles was determined to be 6 nm with a size distribution from 3 to 8 nm. HPLC separation was obtained under isocratic conditions using methanol–water (20:80) mixture as mobile phase. The flow rate of the mobile phase was kept at 0.5 ml min^{-1}. The intensity of light source was determined by using ferrioxalate actinometer. Quantum efficiency measurements were reproducible within the error limit of ±5%.

3. Results and discussion

The electronic and emission spectra of $Cd(OH)_2$-coated Q-CdS are shown in Fig. 1. The electronic spectrum of these particles is similar to that of stoichiometric CdS but their fluorescence spectrum is fairly different having a prominent bandgap emission and a broad weak red emission band. At the first instance, one may consider the bandgap emission to be the excitonic emission which might have been contributed by the recombination of free e^- and h^+. It was examined by following the decay of emission at 475 nm kinetically (Fig. 2a). This decay curve was found to be the best fit in a three exponential process which indicated that possibly different excited electronic states or particles of various sizes having traps of different energies for electrons and holes are involved in contributing to the decay of the emission. It gave an average emission lifetime ($\langle\tau\rangle$) of 22.6 ns. The average emission lifetime was calculated by using the expression given by James et al. [20]. Apparently, there is a distribution of traps of different energy for the electrons and holes in the particle. The bandgap emission results due to recombination of shallowly trapped e^- and h^+ and the red emission observed in 550–700 nm range arises by the recombination of deeply trapped charge carriers. The long emission lifetime of 475 nm emission suggests that it is contributed by shallowly trapped charge carriers. Had it been due to the recombination of free e^- and h^+, the decay of emission should have followed the second-order rate law and this process should have been over somewhere on femtosecond time scale which is contrary to our observations. These particles were relatively more photostable and underwent photodissolution with a quantum efficiency of 0.002. To exploit this characteristic, $Cd(OH)_2$-coated Q-CdS was tried as a photosensitiser to initiate the photochemical reaction of tryp by using visible light radiations.

3.1. Interaction of tryptophan with CdS

Cd^{2+} is known to form a complex with tryp [21] which is likely to take place in the present case since the activation of the photocatalyst requires the addition of excess Cd^{2+}. This possibility was examined by recording the absorption spectrum of the reaction mixture containing Cd^{2+} (6×10^{-4} mol dm^{-3}) and tryp (2×10^{-4} to 6×10^{-4} mol dm^{-3}) in the presence of stabiliser, hexametaphosphate (3×10^{-4} mol dm^{-3}). The resultant absorption at various wavelengths was simply the additive absorption due to the reactants. It thus suggests the absence of complexation between Cd^{2+} and tryp in the presence of hexametaphosphate. A careful examination of the electronic spectrum of CdS in the absence and presence of varying [tryp] (1×10^{-4} to 6×10^{-4} mol dm^{-3}) revealed that the presence of tryp did neither modify it nor gets adsorbed at its surface. The later finding was confirmed by recording absorption due to individual reactants and of reaction mixture at various wavelengths (200–300 nm) where tryp possesses absorp-

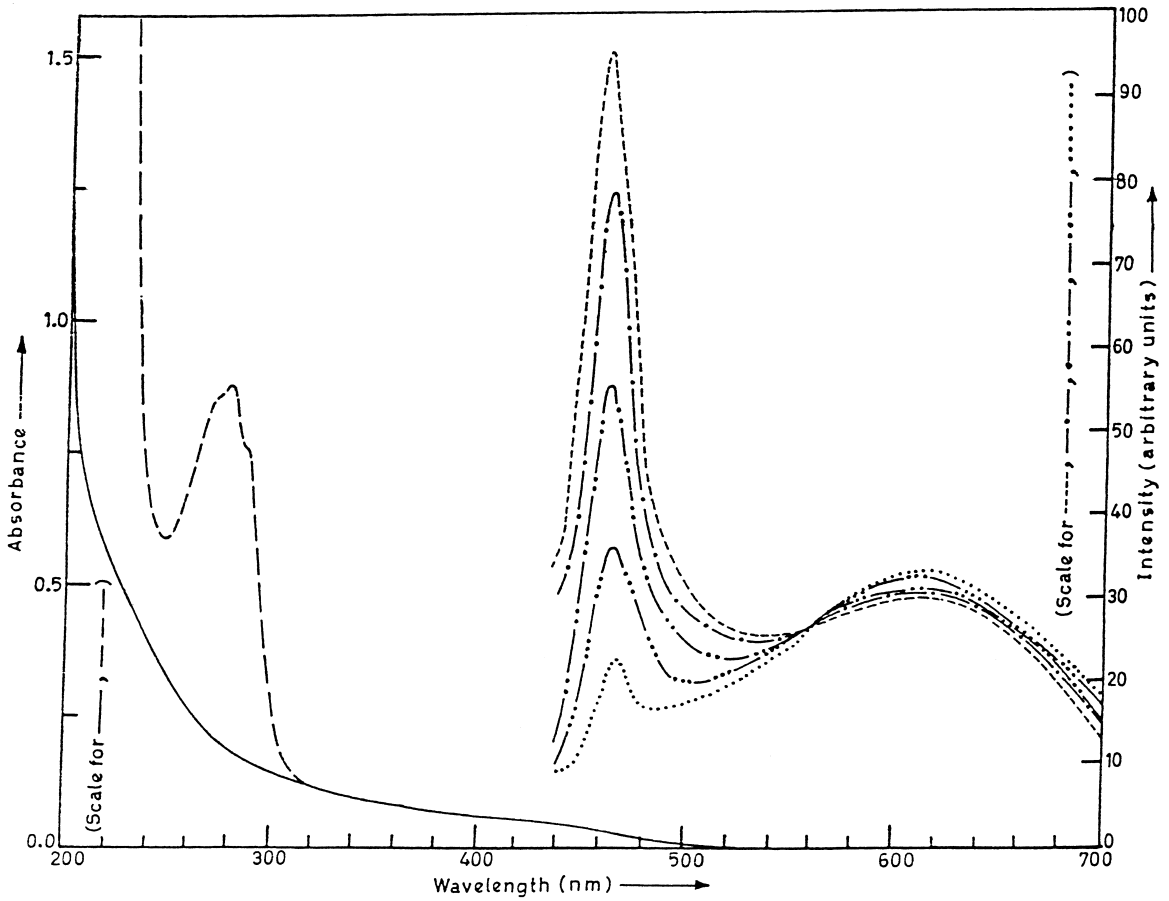


Fig. 1. Absorption spectra of $Cd(OH)_2$-coated Q-CdS (2.8×10^{-4} mol dm^{-3}) in the absence (——) and presence (– – –) of 6×10^{-4} mol dm^{-3} tryptophan. Luminescence spectra of Q-CdS in the absence (- - -) and presence of varying concentrations of tryptophan ($\times10^{-3}$ mol dm^{-3}): 0.05 (- · -); 0.1 (- · · -); 0.2 (- · · · -); 0.5 (· · · ·); λ_{ex}=400 nm.

tion. The additive absorption due to reactants matched with that of the reaction mixture. This indicates the absence of physiosorption of tryp on the surface of CdS.

The addition of tryp to $Cd(OH)_2$-coated Q-CdS, however, affected its emission spectrum drastically (Fig. 1). An increase in [tryp] quenched the bandgap emission increasingly but its red emission is slightly improved. These changes demonstrate an isoemissive point at 560 nm. This observation is in contrast to that noted with stoichiometric CdS–tryp system [13] where a new green band was developed upon addition of tryp and the red emission was quenched simultaneously. Besides this, the quenching of 470 nm emission follows Stern–Volmer relationship and takes place with a rate constant of 3.8×10^{11} dm^3 mol^{-1} s^{-1} (Fig. 3a). This suggests that the nature of quenching may be dynamic in the present case.

The emission behaviour of $Cd(OH)_2$-coated CdS was also examined in the presence of indole and 3-substituted indoles viz. 3-methylindole (3-MI), indole-3-acetic acid (IAA) and *N*-acetyl tryp. The quenching was negligibly small in the presence of indole and 3-MI whereas IAA and *N*-acetyl tryp caused the quenching appreciably. In the presence of both IAA and *N*-acetyl tryp, the quenching of emission followed Stern–Volmer relationship (Fig. 3a) from which the quenching rate constants were determined to be 3.6×10^9 and 8.4×10^9 dm^3 mol^{-1} s^{-1}, respectively. These rate constants are about two orders of magnitude smaller as compared to tryp. The order of decreasing quenching efficiency for different substrates was tryp>*N*-acetyl tryp>IAA>3-MI>indole. Obviously, the presence of $-NH_2$ group at C-3 in the tryp induces the process of quenching.

To further analyse the possibility of complexation between Cd^{2+} and tryp, some experiments were designed in which tryp was added to Cd^{2+} solution (3×10^{-4} mol dm^{-3}) in the presence of sodium hexametaphosphate (3×10^{-4} mol dm^{-3}) prior to precipitation of CdS. The preparation of CdS particles and their activation was then carried out using similar procedure as described under methodology. The electronic and emission spectra of the CdS samples containing different concentrations of tryp are shown in Fig. 4. An increase in [tryp] caused a blue shift in the onset of absorption in the electronic spectra and bandgap emission maxima in the emission spectra without appreciably affecting the red emission band. A

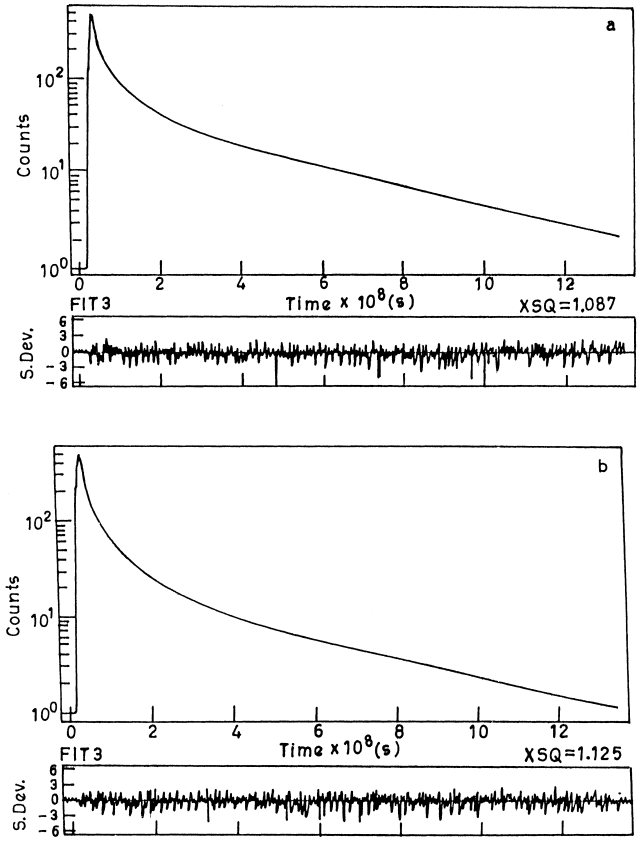


Fig. 2. (a) Decay profile of $Cd(OH)_2$-coated Q-CdS in the absence of tryptophan and (b) decay profile in the presence of 1×10^{-4} mol dm^{-3} of tryptophan.

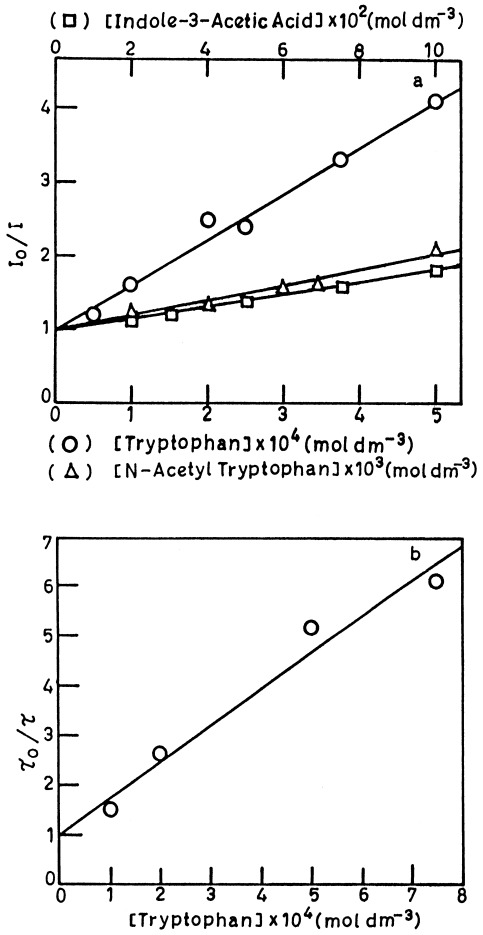


Fig. 3. (a) Stern–Volmer plots for the quenching of emission due to $Cd(OH)_2$-coated Q-CdS in the presence of different substrates and (b) a plot between τ_0/τ vs. [tryptophan].

typical 1×10^{-3} mol dm^{-3} of tryp moved the absorption and emission peaks to higher energies by 0.045 and 0.046 eV, respectively. These changes exhibit the phenomenon of size quantisation effect which suggests that the presence of tryp induces the production of smaller particles as has been observed earlier in case of aliphatic [22] and aromatic amines [10]. However, the extent of quenching of CdS emission in this case (Fig. 4) is strikingly similar to that of when tryp was added after the preparation of CdS sol (Fig. 1). An amount of 1.5×10^{-4} mol dm^{-3} of tryp caused a quenching of more than 50% of emission. This analogy in the two cases indicates that the observed quenching of emission is not caused due to complexation of free Cd^{2+} with tryp, instead it involves some weak interaction of tryp with $Cd(OH)_2$-coated CdS.

3.2. Emission lifetime measurement

The effect of addition of tryp on emission behaviour of CdS was further investigated by monitoring the emission lifetime in its absence and presence. For a typical 1×10^{-4} mol dm^{-3} of tryp, the emission lifetime decay curve is shown in Fig. 2b. This decay curve was also found to be the best fit in a three exponential decay programme just like to that of in the absence of tryp (Fig. 2a). The average lifetimes as a function of [tryp] are summarised in Table 1. These results reveal a decrease in emission lifetime of CdS with an increase in [tryp]. A plot of τ_0/τ versus [tryp] gives a linear curve from which the value of quenching rate constant was evaluated to be 4×10^{11} dm^3 mol^{-1} s^{-1} (Fig. 3b). This value is of the same magnitude as was computed from the steady state emission data. On the basis of this experiment the quenching of emission by the used substrates is concluded to be dynamic. Obviously, holes are scavenged by tryp almost at a diffusion controlled rate.

3.3. CdS-sensitised reaction of tryptophan

The photolysis of the oxygenated reaction mixture containing 2.8×10^{-4} mol dm^{-3} of CdS and 6×10^{-3} mol dm^{-3} of tryp at pH 10.8 was carried out by light of wavelength $\geq$400 nm. Tryp does not possess any absorption in this wavelength region. Irradiation of the reaction mixture results in an increase in its absorption in both UV and visible

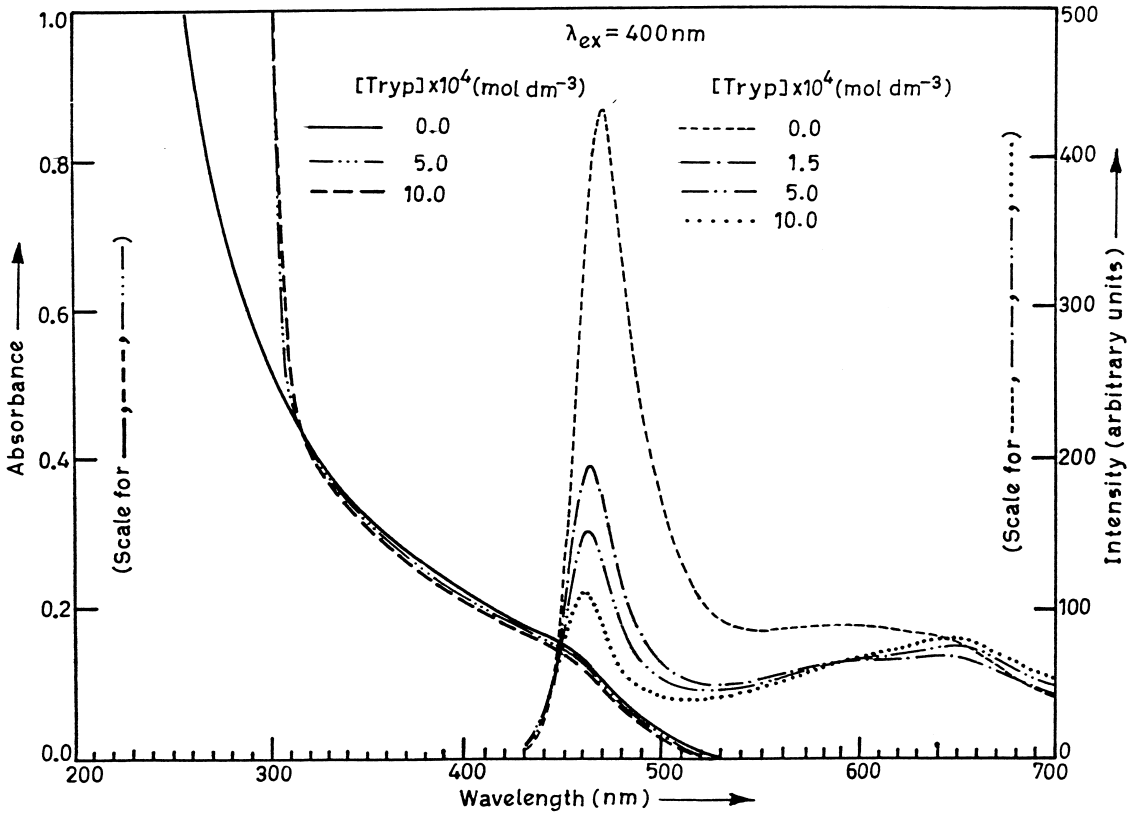


Fig. 4. Electronic and emission spectra of $Cd(OH)_2$-coated Q-CdS in the presence of different [tryptophan] (indicated in figures) added prior to the preparation of sol by injecting SH^-.

regions. Changes in the absorption spectra as a function of illumination time are shown in Fig. 5. The product(s) of the reaction depict λ_{max} around 280 and 300 nm. Neither reactant nor product(s) of oxidation could be separated by extraction in non-aqueous solvents. For this reason their separation was tried by HPLC. HPLC chromatogram of the irradiated reaction mixture is shown in Fig. 6a. It contains five components. Components 2 and 5 were found to contain the characteristic ir peaks (cm^{-1}) due to authentic tryp (1638, 1468,1412, 1016 and 604). Components 2, 3 and 5 were identified as 5-hydroxytryptophan, kynurenine and the unreacted tryp by matching their retention times and electronic spectra with their respective authentic samples. Components 1 and 4 could not be identified as such due to the non-availability of their authentic samples. The amount of different components were followed as a function of irradiation time and were found to vary linearly for about 30 min. From these data quantum efficiencies for the formation of 5-hydroxytryptophan and consumption of tryp were found to be 0.06 and 0.22, respectively. Interestingly, upon keeping the irradiated sample overnight, the absorption due to components 1 and 4 is reduced along with an enhancement in the absorption due to components 2 and 3 (Fig. 6b). In this sample 5-hydroxytryptophan and kynurenine

Table 1
Fluorescence lifetimes of $Cd(OH)_2$-coated Q-CdS in the presence of tryptophan[a]

[Tryptophan] ($\times 10^4$ mol dm^{-3})	Lifetime (ns)				χ^2
	τ_1	τ_2	τ_3	$\langle\tau\rangle$	
0.0	0.580 (0.2628)	7.052 (2.4796×10^{-2})	40.396 (8.4653×10^{-3})	22.6	1.087
1.0	0.697 (0.2399)	7.338 (2.3052×10^{-2})	37.559 (4.4255×10^{-3})	15.1	1.125
2.0	0.422 (0.3779)	5.045 (2.5027×10^{-2})	23.804 (4.8128×10^{-3})	8.5	1.014
5.0	0.327 (0.4994)	3.861 (2.0431×10^{-2})	12.345 (7.0882×10^{-3})	4.4	1.048
10.0	0.116 (2.046)	2.689 (3.2128×10^{-2})	10.635 (1.2713×10^{-2})	3.7	1.088

[a] Value(s) given in bracket denote the pre-exponential factors corresponding to the respective τ.

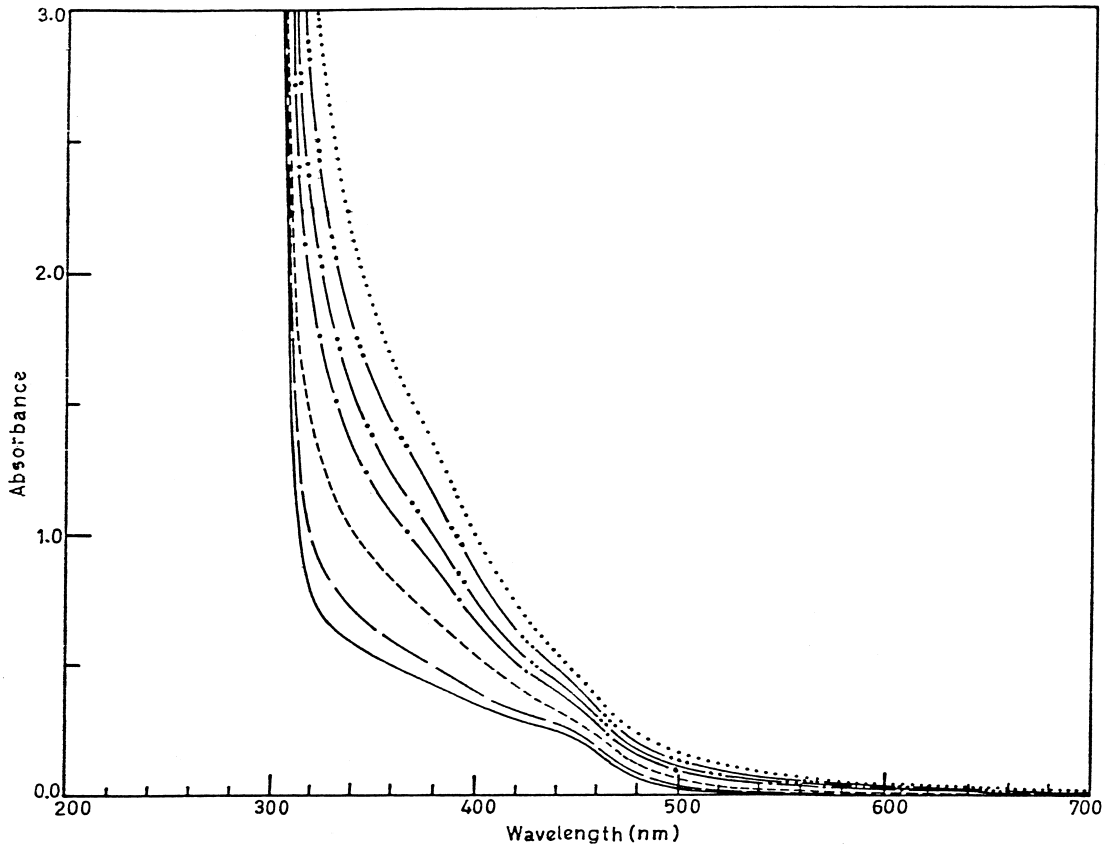
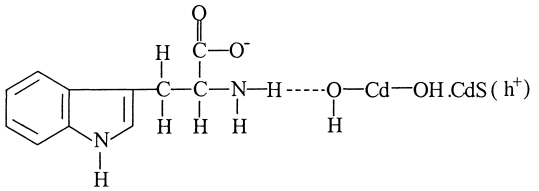


Fig. 5. Electronic spectra of the reaction mixture containing 2.8×10^{-4} mol dm^{-3} $Cd(OH)_2$-coated Q-CdS and 6×10^{-3} mol dm^{-3} tryptophan at different irradiation times (min): 0 (—); 5(– – –); 10(- - -); 15(- · -); 20 (- · · -); 25(- · · · -) and 30(····).

were estimated to form with a quantum efficiency of 0.08 and 0.002, respectively. The amount and nature of products were found to vary with the content of oxygen. In aerated reaction mixture the quantum yield for the photodecomposition of tryp and formation of 5-hydroxytryptophan were reduced to 0.15 and 0.015, respectively, and the formation of kynurenine was not detected.

The fact that tryp does neither depict physical nor chemical interaction with CdS but affects its emission behaviour and is oxidised at its interface, it is, therefore, arrived at that tryp present in the bulk perturbs in some way the hole trapping site. The interaction might possibly be taking place through hydrogen bonding between –OH of $Cd(OH)_2$ and either –NH of the pyrrole ring or any of the $–NH_2$ and –COOH of the side chain of tryp. Indole as such did not affect the emission behaviour of $Cd(OH)_2$-coated CdS and in a separate experiment it was observed that $Cd(OH)_2$-coated CdS sensitises the photochemical reaction of indole poorly (ϕ=0.002). It thus eliminates the possibility of participation of –NH of the pyrrole ring in hydrogen bonding. Further, the quenching efficiency of IAA was relatively poor as compared to tryp (vide supra), it is, therefore, concluded that hydrogen bonding prominently takes place through $–NH_2$. This argument is further supported by emission data on *N*-acetyl tryp. In this substrate one H of $–NH_2$ is replaced by acetyl group which causes a decrease in the electron density at N and should reduce the extent of hydrogen bonding through it. It indeed reduced the quenching efficiency by more than an order of magnitude to that of tryp (Fig. 3a). The high value of quenching rate constant observed with tryp ($\sim10^{11}$ dm^3 mol^{-1} s^{-1}) can, therefore, be attributed to its H-bonding interaction with the particle. Thus the hole intercepts the tryp molecule immediately after its photogeneration.



These experiments reveal the distribution of charge carriers on the surface of $Cd(OH)_2$-coated particles in different defect states. The long radiative lifetime of bandgap emission indicates the presence of shallowly trapped e^-–h^+ pair. Since the bandgap emission is quenched by tryp and the red emission remains almost unaffected, it suggests that shallowly trapped hole participates in this interaction and the

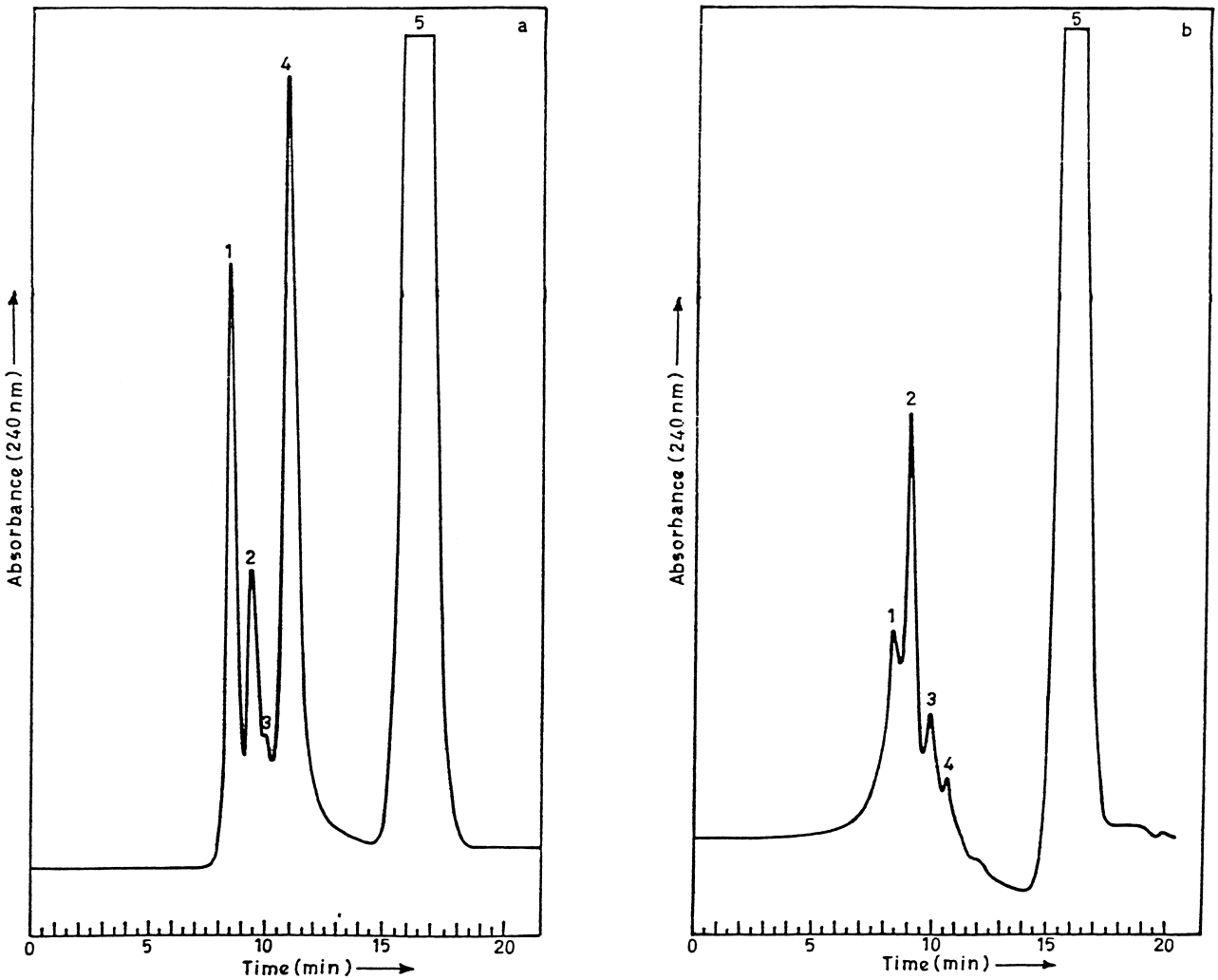


Fig. 6. (a) HPLC chromatogram of the irradiated reaction mixture containing $Cd(OH)_2$-coated Q-CdS (2.8×10^{-4} mol dm^{-3}) and tryptophan (6×10^{-3} mol dm^{-3}) and (b) HPLC chromatogram of the irradiated reaction mixture shown in (a) after keeping it overnight.

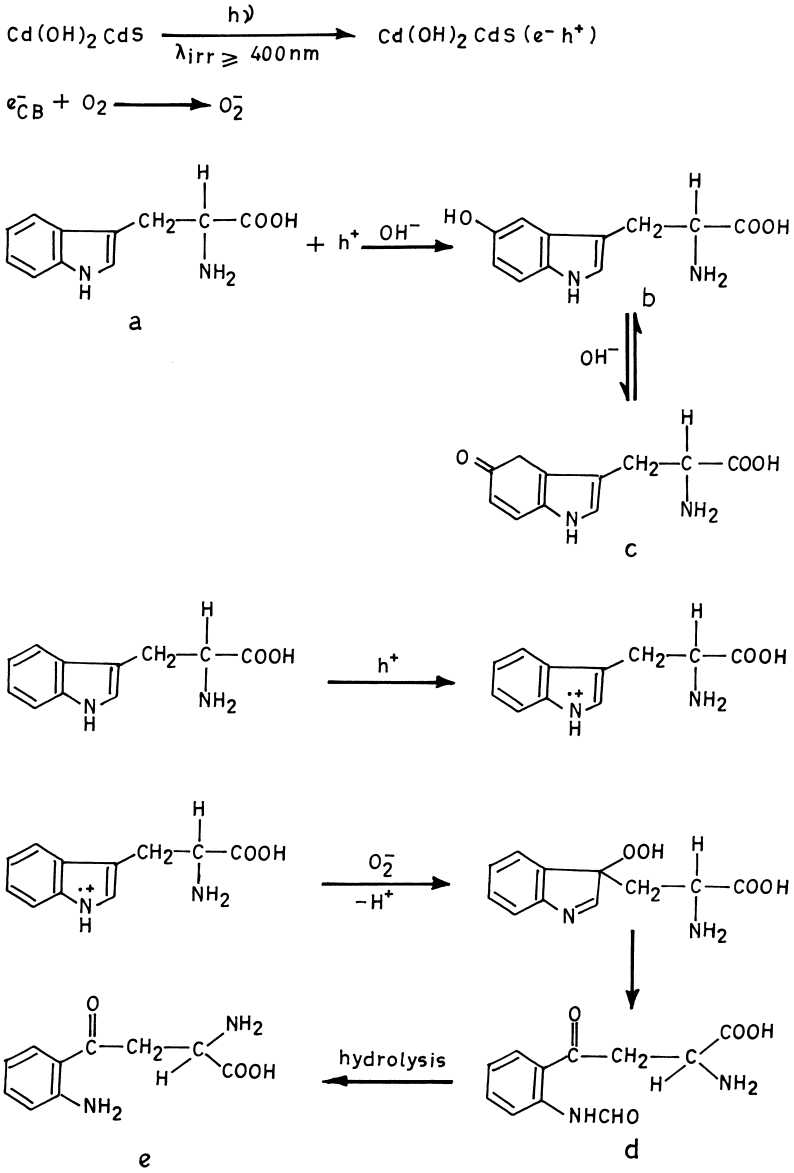
deeply trapped hole remains inaccessible to tryp. However, interaction of tryp with particles assists in creating more deep traps involved in radiative recombination and thereby causes a slight increase in red emission. Hasselbarth et al. [23] have earlier shown the presence of shallowly trapped electrons on the surface of Q-CdS using electron acceptors.

On the basis of the above experiments, the mechanism of $Cd(OH)_2$-coated Q-CdS sensitised reaction of tryp can be outlined in the following steps (Scheme 1).

The photogenerated hole attacks electrophilically at C-5 which is followed by nucleophilic attack of OH^- to form 5-hydroxytryptophan. This interaction of hole differs mechanistically with that observed earlier with indole in which electrophilic attack takes place at C-3. In indole like substrate, C-3 contains the highest π electron density [24]. Since C-3 position is blocked in tryp by the substitutent, it is possibly for this reason that oxidation predominantly takes place at the location which contains the next higher electron density, i.e. C–5. The hydroxylation of tryp at the 5-position has been observed earlier in a number of biological systems [24,25]. In another pathway, hole may abstract one non-bonding electron from the N of the pyrrole ring. The radical cation thus formed couples with O_2^- to give corresponding hydroperoxide. This intermediate eventually decomposes to yield **d** which hydrolyses to give **e**.

4. Conclusions

In summary $Cd(OH)_2$-coated Q-CdS induces the oxidation of tryp by visible light to produce 5-hydroxytryptophan as one of the main products. There is a distribution of the trapped charge carriers to various depths on the surface of these particles. Shallowly trapped hole affects the oxidation by intercepting the bulk substrate possibly via hydrogen bonding interaction involving $–NH_2$ of tryp and –OH



Scheme 1.

of $Cd(OH)_2$. Deeply trapped hole remains inaccessible for the substrate to accomplish its oxidation.

Acknowledgements

The generous financial support of DST, New Delhi, to undertake this work is gratefully acknowledged. DPSN is thankful to UGC, New Delhi, for the award of SRF. We also thank Dr. A. Samanta, University of Hyderabad, for providing the facilities for fluorimetric measurements.

References

[1] A. Henglein, Chem. Rev. 89 (1989) 1861.
[2] M.A. Fox, M.T. Dulay, Chem. Rev. 93 (1993) 341.
[3] H. Weller, Angew. Chem., Int. Ed. Engl. 32 (1993) 41.
[4] P.V. Kamat, Chem. Rev. 93 (1993) 267.
[5] A. Hagfeldt, M. Grätzel, Chem. Rev. 95 (1995) 49.
[6] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[7] P.V. Kamat, N.M. Dimitrijevic, R.W. Fessenden, J. Phys. Chem. 91 (1987) 396.
[8] P.V. Kamat, M. Gevaert, K. Vinodgopal, J. Phys. Chem. B 101 (1997) 4422.
[9] Y. Wang, A. Suna, J. McHugh, E. Hilinski, P.A. Lucas, R.D. Johnson, J. Chem. Phys. 92 (1990) 6927.
[10] A. Kumar, S. Kumar, J. Photochem. Photobiol. A: Chem. 69 (1992) 91.
[11] J. Kuczynski, J.K. Thomas, J. Phys. Chem. 87 (1983) 5498.
[12] S.R. Bigham, J.L. Coffer, J. Phys. Chem. 96 (1992) 10581.
[13] A. Kumar, S. Kumar, J. Photochem. Photobiol. A: Chem. 83 (1994) 251.
[14] A. Kumar, S. Kumar, J. Phys. Org. Chem. 11 (1998) 277.

[15] J.L. Coffer, S.R. Bigham, R.F. Punizzotto, H. Yang, Nanotechnology 3 (1992) 69.
[16] L. Spanhel, M. Haase, H. Weller, A. Henglein, J. Am. Chem. Soc. 109 (1987) 5649.
[17] S.R. Bigham, J.L. Coffer, Colloids and surfaces, A: Physicochem. Eng. Aspects 95 (1995) 211.
[18] C.S. Foote, Science 162 (1968) 963.
[19] W.E. Savige, Aust. J. Chem. 24 (1971) 1285.
[20] D.R. James, Y.S. Liu, P. Mayo, W.R. Ware, Chem. Phys. Lett. 120 (1985) 460.
[21] R.D. Gillard, J.A. McCleverty, Comprehensive Coordination Chemistry, Vol. 5, Pergamon Press, Oxford, 1987, p. 939.
[22] T. Dannhauser, M. O'Neil, K. Johansson, D. Whitten, G. McLendon, J. Phys. Chem. 90 (1986) 1674.
[23] A. Hasselbarth, A. Eychmuller, R. Eichberger, M. Giersig, A. Mews, H. Weller, J. Phys. Chem. 97 (1993) 333.
[24] R.J. Sundberg, The Chemistry of Indoles, Academic Press, London, 1970, p. 2 and 308 and references therein.
[25] O. Hayaishi, M. Nozaki, Science 164 (1969) 389.