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Photophysics and photochemistry of colloidal CdS–TiO_2 coupled semiconductors — photocatalytic oxidation of indole

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Abstract

The photophysical changes taking place by coupling of $Cd(OH)_2$-coated Q-CdS with colloidal TiO_2 have been examined. The coupling of TiO_2 causes the quenching of the band gap emission of CdS and the red emission is not affected appreciably. For a typical 0.22×10^{-3} mol dm^{-3} of TiO_2 the average emission lifetime of $Cd(OH)_2$-coated CdS is reduced from 26.4 to 6.8 ns by trapping of the conduction band electron by TiO_2. $Cd(OH)_2$-coated Q-CdS does not sensitize the reaction of indole, however, the coupled CdS–TiO_2 catalyst photoinitiated this reaction efficiently. The photoactivity of the coupled semiconductor is suggested to increase due to chemical interaction between $Cd(OH)_2$-coated Q-CdS and TiO_2 which removes $Cd(OH)_2$ layer to form possibly [CdS–$TiO_2(OH)_2$]. The photogenerated hole in the coupled catalyst CdS(h^+) forms an emissive exciplex with indole. The exciplex is long lived and results in the decomposition of indole ($\phi = 0.18$) to yield indigo with a quantum efficiency of 0.08.The concentration of both TiO_2 and redox couple controls the extent of charge separation in the photocatalyst. The application of coupled semiconductors as catalysts for photosynthetic work is suggested. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Colloidal CdS–TiO_2; Photocatalytic oxidation of indole; Photophysics of Q-CdS–TiO_2

1. Introduction

Nanosized semiconductor systems have received considerable attention in recent years because of their photocatalytic activity in initiating redox reactions [1–7]. However, the quantum efficiency of the reactions studied at their interface have often been reported to be fairly poor, [3] the low yield has been attributed to the fast recombination of the photogenerated charge carriers which also causes the photodissolution of the catalyst. A number of strategies have been adopted in the past to improve their photocatalytic activity (for review see [1–7]). These comprise employing suitable redox couples, [8–13] sensitization and modification of large band gap semiconductors, [14–19] doping of transition metal ions into both large and small band gap semiconductors, [20–22] coupling of two semiconductors [23–29], etc. Increased separation of charge in the latter system makes them attractive particularly for photocatalytic work and development of photoelectrochemical devices. Such investigated photocatalysts are CdS–Ag_2S [21,22], CdS–TiO_2 [23–25], CdS–ZnO [23], Cd_3P_2–TiO_2 [26], AgI–Ag_2S [27], CdS–HgS [28], CdS–ZnS [29], ZnO–ZnS [30], ZnO–ZnSe [31], SnO_2–CdS [32], etc. With colloidal CdS–Ag_2S [22] system it was recently observed that the efficiency of oxidation of aniline is enhanced by about 40% in comparison to that of

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colloidal CdS alone. The catalytic action of Ag^+ was attributed to the efficient transfer of charge at $CdS–Ag_2S$ interface upon irradiation to the adsorbed redox species. The potential of mixed semiconductors to perform synthetic photocatalytic redox processes has not been fully explored so far [3,4]. The practical utilization of these catalysts requires to understand the nature of interaction between two components of semiconductors and analyze the interfacial interaction of the redox couple(s) with the coupled photocatalyst.

The present paper deals with the study of photophysical behavior of $Cd(OH)_2$-coated Q-CdS upon coupling with colloidal TiO_2 and an investigation of the reaction of indole–O_2 redox couple sensitized by the coupled $CdS–TiO_2$ catalyst in aqueous medium. $Cd(OH)_2$-coated CdS alone did not sensitize the reaction of indole–O_2 redox couple. However, combining these particles with TiO_2 photoinitiated their reaction efficiently by visible light radiations. Interestingly, the separated hole in the coupled catalyst $CdS(h^+)$ forms an emissive exciplex with indole. The exciplex is eventually decomposed by transference of electron from indole to the hole to produce indigo with a quantum efficiency of 0.08. Photophysics of indoles [33,34] and their photosensitized oxidation in the presence of oxygen [35] have interested both chemists and biologists for the understanding of their biological activity. Visible light induced oxidation of indoles may provide valuable information in this regard.

2. Experimental section

2.1. Materials

Cadmium perchlorate (Alfa); indole, indigo (Aldrich); sodium hexametaphosphate (Qualigens); silica gel G, chloroform, carbon tetrachloride, sodium hydroxide, perchloric acid (Merck) were used as received. Titanium tetrachloride (Reidel de Haen) was distilled under vacuum. The dialysis membrane was spectra/por with molecular weight cut off 6000–8000.

2.2. Equipment

Electronic spectra were recorded on Shimadzu UV-2100S and DU-6 Beckman spectrophotometers. Emission spectra were measured on a JASCO FP-777 and Shimadzu RF-5301-PC spectrofluorimeters. Steady-state photolysis was carried out on an Oriel photolysis assembly equipped with 200 W Hg (Xe) arc lamp, solution and glass cut filters. HPLC experiments were designed on a LC-10 AD Shimadzu chromatograph using UV detector. Electron microscopy was performed by a Philips EM-400 transmission electron microscope equipped with a 35 mm camera. The fluorescence lifetimes were measured on an IBH-5000 single photon counting fluorimeter using a flash lamp of 1.4 ns pulse width and a picosecond Ti-sapphire mode locked laser for excitation. Hamamatsu photomultiplier was used for detection of fluorescence. Decay curves were analyzed by iterative reconvolution technique. The multiexponential fitting program was provided from IBH. IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer by sandwiching the $CHCl_3$ extract of the chromatographically separated product between NaCl plates.

2.3. Methodology

Colloidal CdS [36] and colloidal TiO_2 [37] particles were synthesized by following the earlier methods except SH^- was injected to precipitate CdS. Cadmium hydroxide was coated on CdS particles by adding excess of NaOH followed by excess Cd^{2+} (6×10^{-4} mol dm^{-3}) to the stoichiometric 3×10^{-4} mol dm^{-3} CdS particles. Colloidal TiO_2 particles were synthesized by slow addition of $TiCl_4$ to water at 0°C. This solution was subsequently dialyzed at about 5°C till pH lay around 3. $CdS–TiO_2$ coupling was performed by quick injection of TiO_2 sol to the colloidal CdS solution under vigorous shaking.

Actinometry was performed using a ferrioxalate actinometer. For measurement of electron micrographs CdS was applied on a formvar coated copper G-200 grid (size 3.05 mm). The grid was scanned under the electron microscope with an accelerating voltage of 100 kV at different magnifications. The interaction between CdS and TiO_2 particles was monitored by recording the transmission electron micrographs of pure $Cd(OH)_2$-coated Q-CdS, colloidal TiO_2 particles and their mixture. The electron micrographs are shown in Fig. 1. Both CdS and TiO_2 particles are spherical in shape. The average size of colloidal CdS (6 nm) was a little smaller in compar-

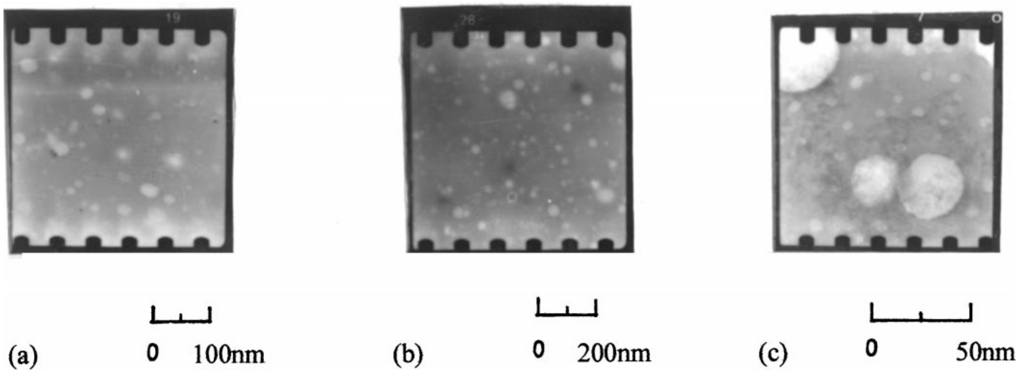


Fig. 1. Electron micrograph of (a) $Cd(OH)_2$-coated Q-CdS; (b) colloidal TiO_2; (c) coupled colloidal CdS–TiO_2.

ison to that of TiO_2 particles (8 nm). The electron micrograph of the coupled CdS–TiO_2 particles shows them to be associated with each other (Fig. 1c).

3. Results and discussion

3.1. Photophysical and photochemical behavior of coupled CdS–TiO_2

Cadmium hydroxide-coated Q-CdS has an absorption spectrum very similar to that of stoichiometric colloidal CdS particles. Its emission spectrum is, however, very different which exhibits an excitonic band centered at 475 nm and a broad weak red band at around 620 nm (Fig. 2). $Cd(OH)_2$-coated colloidal CdS synthesized by injection of H_2S [36] also depicted similar spectral features except that it did not contain the weak red emission. In contrast to stoichiometric CdS, $Cd(OH)_2$-coated colloidal CdS was relatively more photostable and underwent photodissolution with a quantum efficiency of ∼0.002 in the presence of oxygen [38]. The electronic spectrum of the coupled catalyst obtained by the addition of colloidal TiO_2 to $Cd(OH)_2$-coated CdS is shown in Fig. 2 (—·—). This spectrum is different to the sum spectra of the two individual components — colloidal $Cd(OH)_2$-coated CdS and TiO_2. The illumination of the coupled catalyst by light of $\lambda > 400$ nm where, TiO_2 does not have any absorption, results in the enhanced photodecomposition of CdS component. About 1.28×10^{-3} mol dm^{-3} of TiO_2 caused the decomposition of CdS particle with a quantum efficiency of 0.09. It also affected the photophysics of CdS particles significantly. The emission due to CdS at 475 nm is quenched, but the red emission is slightly improved Fig. 2.

The lifetime of emission of colloidal CdS was also monitored both in the absence and presence of different concentrations of colloidal TiO_2. A few representative traces of the decay profiles of emission are shown in Fig. 3. The emission due to colloidal CdS as well as CdS–TiO_2 coupled particles consisted of multiexponential decay and were found to be best fitted in three exponential decay curve. The average lifetime ($\langle\tau\rangle$) was calculated by using the expression given by James et al. [39]. The average lifetime of CdS in the absence and various compositions of TiO_2 are summarized in Table 1. For $Cd(OH)_2$-coated colloidal CdS, $\langle\tau\rangle$ is observed to be 26.4 ns which is about three times higher to that of stoichiometric colloidal CdS [13]. Obviously, the 475 nm emission does not arise from the radiative recombination of free e^- and h^+ which would have occurred much faster somewhere on picosecond time scale and might be contributed from the e^- and h^+ trapped in shallow traps. From the data of Table 1 it is seen that $\langle\tau\rangle$ of CdS is decreased as [TiO_2] increases. For a typical 0.73×10^{-3} mol dm^{-3} of TiO_2 this value decreases from 26.4 to 0.83 ns. An increase in quenching of emission and a decrease in emission lifetime of CdS by increasing the [TiO_2] clearly indicates it to be a consequence of increasing contact between CdS and TiO_2 in the mixture. An intimate contact between them was also evidenced by their TEM

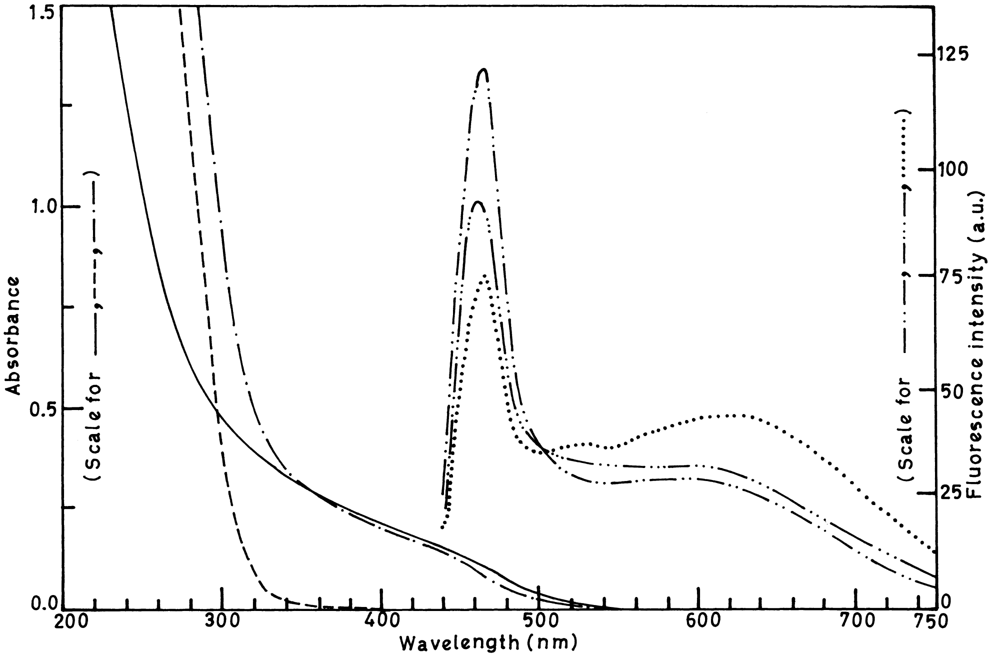


Fig. 2. Absorption spectrum of $Cd(OH)_2$-coated Q-CdS (—), [CdS] = 1.35×10^{-4} mol dm^{-3}; TiO_2 (- - -), [TiO_2] = 1.28×10^{-3} mol dm^{-3}; and coupled CdS–TiO_2 Particles (—·—), [CdS] = 1.35×10^{-4} mol dm^{-3}, [TiO_2] = 1.28×10^{-3} mol dm^{-3}. Emission spectra of $Cd(OH)_2$-coated Q-CdS containing various [TiO_2] (mol dm^{-3}) at pH 11.0:0 (—·—); 3.7×10^{-5} (—··—); 1.1×10^{-4} (···).

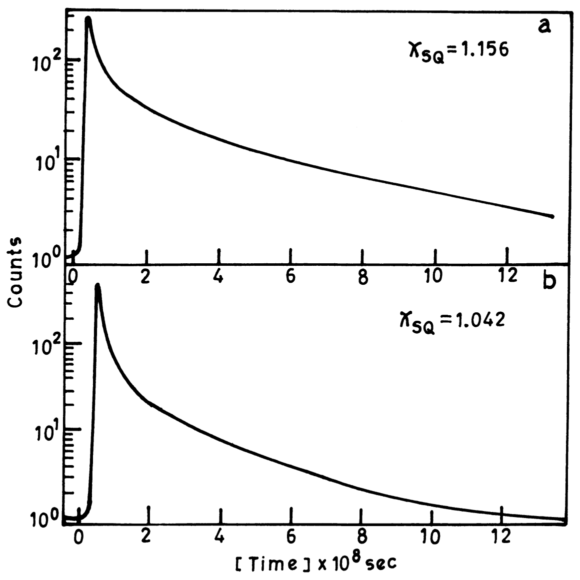


Fig. 3. Fluorescence decay curves for $Cd(OH)_2$-coated Q-CdS in the absence (a) and in the presence of TiO_2 (b) [TiO_2] = 1.1×10^{-4} mol dm^{-3}.

micrograph (Fig. 1c). In view of the coupling of CdS and TiO_2 particles, a decrease in emission lifetime and the quenching of emission of CdS are understood in terms of the transport of electron from the conduction band of excited CdS to the conduction band of TiO_2. This process will also be favourable thermodynamically since the conduction band energy level of CdS is more negative by about 1 eV in comparison to that of TiO_2. For colloidal CdS–TiO_2 system in acetonitrile, Gopidas et al. [24] have estimated a rate constant of $>5\times10^{10}$ s^{-1} for the injection of charge from excited CdS into TiO_2 using laser flash photolysis. Although these particles had relatively much larger emission lifetime than observed in aqueous medium. Grätzel et al. [40] have reported earlier that each increasing unit of pH lowers the flat band potential of TiO_2 as per equation $E_{\mathrm{fb}} = 0.13 - 0.059$ (pH) V (versus NHE). Thus, the flat band potential of TiO_2 in the aqueous basic medium would be significantly lowered compared to that of in acetonitrile medium. Therefore, the electron transfer would be more facile in composite CdS–TiO_2 system in aqueous basic medium. It is possibly this reason that CdS emission lifetime in

Table 1
Fluorescence lifetimes of CdS in the absence and presence of TiO_2[a]

$[TiO_2] \times 10^4$ (mol dm^{-3})	Lifetime (ns)				χ^2
	τ_1	τ_2	τ_3	$\langle\tau\rangle$	
0.0	0.8390 ($B_1 = 0.2090$)	7.9639 ($B_2 = 2.5309 \times 10^{-2}$)	43.379 ($B_3 = 1.1309 \times 10^{-2}$)	26.4	1.156
1.1	0.17691 ($B_1 = 1.090$)	3.4451 ($B_2 = 2.4571 \times 10^{-2}$)	23.242 ($B_3 = 6.2806 \times 10^{-3}$)	16.0	1.043
2.2	0.2105 ($B_1 = 0.9322$)	3.1282 ($B_2 = 2.1745 \times 10^{-2}$)	20.231 ($B_3 = 6.4039 \times 10^{-3}$)	6.8	1.023
7.3	0.2413 ($B_1 = -192.8$)	2.4240 ($B_2 = 192.5$)	3.4053 ($B_3 = 3.8048 \times 10^{-3}$)	0.8	1.071

[a] Values given in bracket denote the preexponential factors corresponding to the respective τ.

the presently used CdS–TiO_2 system is comparatively much shorter to that of in acetonitrile medium.

The charge separation thus achieved makes the electron and hole to be more reactive which results in increased dissolution of CdS. Obviously, electrons are scavenged by O_2 and holes corrode the particles in anodic reaction. In order to check the reactivity of the photogenerated charge carriers in the above coupled photocatalysts, oxygen and indole were used as a redox couple in the present work.

3.2. Cd(OH)$_2$-coated Q-CdS sensitized reaction of indole–O_2 couple

Cd(OH)$_2$-coated Q-CdS alone did neither exhibit any physical nor any chemical interaction with indole in the ground state as was evident by the absence of any change in the absorption spectra of reaction mixture containing CdS and indole to that with the addition spectrum of individual CdS and indole by electronic spectroscopy. The presence of indole did not affect the emission behavior of Cd(OH)$_2$-coated Q-CdS either. Irradiation of Cd(OH)$_2$-coated Q-CdS in the presence of indole–O_2 redox couple by light of $\lambda_{ex} > 400$ nm having 1×10^{-2} mol dm^{-3} of indole did cause the negligible decomposition of indole ($\phi < 0.003$). The observed photophysical and photocatalytic behaviors are entirely different to those observed with stoichiometric CdS where CdS sensitized the reaction of indole–O_2 redox couple [12]. All above experiments demonstrate that the e^-–h^+ pair generated by illumination of Cd(OH)$_2$-coated CdS are not scavenged by the dissolved redox couple efficiently. There may be two reasons for this observation. Firstly, the indole is not adsorbed on Cd(OH)$_2$-coated CdS particles. Secondly, e^-–h^+ pair cannot escape to the surface of particle because of coating by Cd(OH)$_2$ layer. Thus, the coating of CdS by Cd(OH)$_2$ though made it relatively more photostable towards anodic photocorrosion, but such particle becomes ineffective to photoinitiate the redox reaction at their interface.

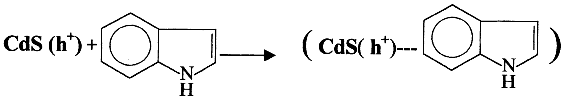
3.3. Coupled Cd(OH)$_2$-coated Q-CdS–TiO_2 sensitized reaction of indole–O_2

The oxygenated reaction mixture containing nanoclusters of coupled CdS–TiO_2 semiconductor and indole also did not show any physical or chemical interaction between the catalyst and the substrate. In the absence of indole the band gap emission of Cd(OH)$_2$-coated Q-CdS is fully quenched by the addition of TiO_2 (1.3×10^{-3} mol dm^{-3}) but, in the presence of indole a new band develops at about 495 nm without quenching the red emission. The intensity of 495 nm band was found to vary with [indole] (Fig. 4). The illumination of photocatalyst by light of $\lambda_{ex} > 400$ nm generates an e^-–h^+ pair in the particle. The electron from excited CdS is injected into the conduction band of TiO_2 which are then scavenged by acceptor O_2.

$$(\mathrm{CdS{-}TiO_2}) \xrightarrow{h\nu} [\mathrm{CdS(h^+){-}TiO_2(e^-)}] \quad (1)$$

$$[\mathrm{CdS(h^+){-}TiO_2(e^-)}] \xrightarrow{O_2} \mathrm{O_2}^- + \mathrm{CdS(h^+)} + \mathrm{TiO_2} \quad (2)$$

The absence of complexation between the photocatalyst and indole by absorption spectroscopy in the ground state suggests the 495 band to be due to the formation of an emissive exciplex between the acceptor CdS(h^+) and the donor indole.



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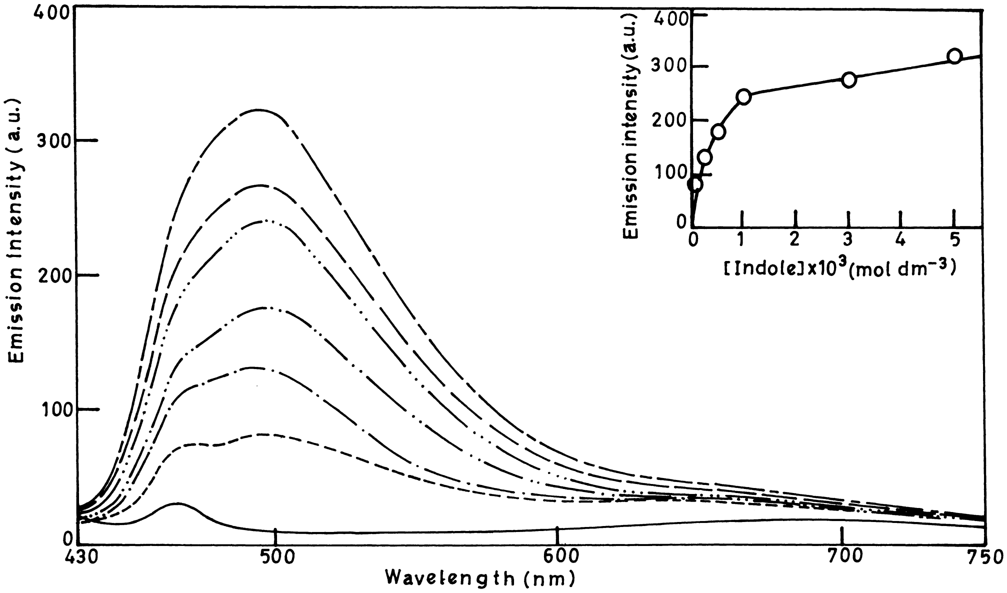


Fig. 4. Emission spectra of Cd(OH)$_2$-coated CdS (1.35×10^{-4} mol dm^{-3}) coupled with TiO$_2$ (1.28×10^{-3} mol dm^{-3}) in the absence (—) and presence of various concentrations of indole ($\times 10^{-3}$ mol dm^{-3}) — 0.05(- - -); 0.2(—·—); 0.75(—··—); 1.0(—···—); 3.0 (——); 5.0(— - —). Excitation at 400 nm. Inset: variation of emission intensity as a function of [indole].

The lifetime of the emissive exciplex was measured by monitoring 495 nm emission in the absence and presence of indole. These traces are shown in Fig. 5. The average lifetime of the coupled CdS–TiO$_2$ containing 3.7×10^{-4} mol dm^{-3} of TiO$_2$ was 1.35 ns ($\tau_1 = 1.8533 \times 10^{-11}$ s ($B_1 = 1.514$); $\tau_2 = 4.732 \times 10^{-10}$ s ($B_2 = 3.5179 \times 10^{-2}$); $\tau_3 = 3.6976 \times 10^{-9}$ s ($B_3 = 6.0027 \times 10^{-3}$)) which in-

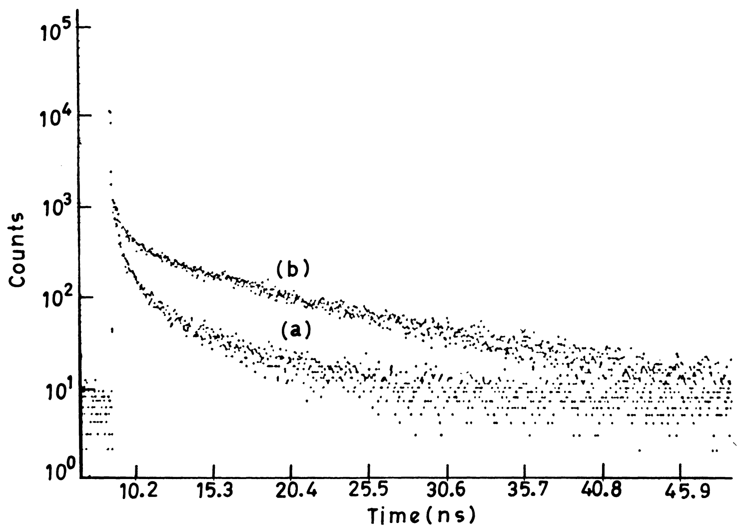


Fig. 5. Fluorescence decay curve for Cd(OH)$_2$-coated Q-CdS in the presence of (a) [TiO$_2$] = 3.7×10^{-4} mol dm^{-3}; (b) [TiO$_2$] = 3.7×10^{-4} mol dm^{-3}; and [indole] = 3×10^{-3} mol dm^{-3} at pH 11.0.

creased to 5.89 ns ($\tau_1 = 1.8867 \times 10^{-11}$ s ($B_1 = 1.727$); $\tau_2 = 5.6962 \times 10^{-10}$ s ($B_2 = 3.7085 \times 10^{-2}$); $\tau_3 = 8.3106 \times 10^{-9}$ s ($B_3 = 1.5096 \times 10^{-2}$)) in the presence of 3×10^{-3} mol dm^{-3} of indole.

The illumination of the reaction sample containing CdS–TiO_2–indole in the presence of O_2 by visible light of $\lambda_{ex} > 400$ nm, where, indole does not depict any absorption, produced color product. TLC analysis of the chloroform extract of the product showed the formation of a single product and it was identified to be indigo by its R_f value and characteristic electronic and infrared spectra using authentic sample of indigo. The reaction conditions were optimized by following the amount of product as a function of [indole] and [TiO_2] (Fig. 6a and b). At low [indole] ($\leq 1 \times 10^{-3}$ mol dm^{-3}), a small amount of product is formed and CdS is partially decomposed by positive hole. An increase in [indole] enhanced the yield of product almost linearly upto 5×10^{-3} mol dm^{-3} and attained a limiting value at around 1×10^{-2} mol dm^{-3}. An increase in [TiO_2] (1.8×10^{-4}–1.3×10^{-3} mol dm^{-3}) increased the yield of indigo proportionately upto about 0.9×10^{-3} mol dm^{-3} of TiO_2, thereafter, the yield of indigo approached the limiting value. The concentration of TiO_2 could not be increased beyond 1.28×10^{-3} mol dm^{-3} since it coagulated the colloidal CdS within few hours.

The time illumination of the oxygenated reaction mixture containing Q-CdS solution (1.35×10^{-4} mol dm^{-3}) and the above optimized concentrations of indole (1×10^{-2} mol dm^{-3}) and TiO_2 (1.28×10^{-3} mol dm^{-3}) shows initially a proportionate increase in the yield of product upto about 10 min (Inset, Fig. 6a). At longer irradiation time(s) (>30 min), the reaction sample turned turbid because of poor solubility of indigo in water. Although, after removing the product the solution of photocatalyst became transparent again and could be reused. The quantum efficiencies for the formation of indigo and the decomposition of indole upto about 10 min of reaction were found to be 0.08 and 0.18, respectively.

The fact that $Cd(OH)_2$-coated Q-CdS does not undergo appreciable photodissolution upon irradation, but its anodic reactivity is drastically increased upon coupling with TiO_2 can be understood by chemical interaction between TiO_2 and $Cd(OH)_2$ layer of CdS. This is also manifested by a change observed in the electronic spectrum of CdS upon coupling with TiO_2 (Fig. 2, curve (—·—). TiO_2 possibly undergoes hydroxylation to form $[TiO_2(OH)_2]^{2-}$ and thus removes $Cd(OH)_2$ layer surrounding CdS which did not allow e^-–h^+ to escape the particle. The two catalysts might be attached through [CdS–O–$TiO(OH)_2$] linkage which assists in the separation of charge upon illumination of CdS component. Now e^- from excited CdS can be injected efficiently into the conduction band of TiO_2 and the hole on the particles may react with donor. In the presence of indole h^+ forms an emissive exciplex (Eq. (3)). An increase in the [indole] enhances the intensity of exciplex which suggests

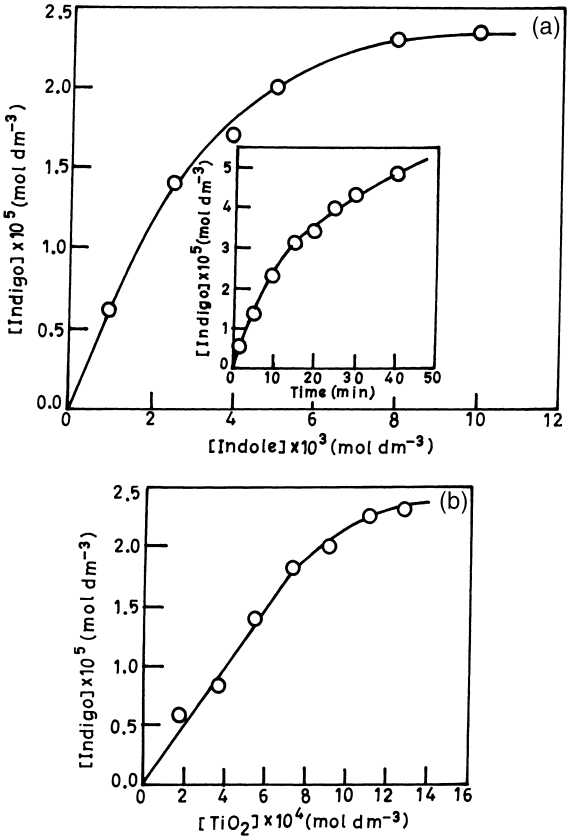
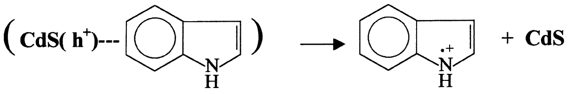


Fig. 6. (a) Amount of indigo formed as function of indole for oxygenated reaction sample containing $Cd(OH)_2$-coated Q-CdS (1.35×10^{-4} mol dm^{-3}) and TiO_2 (1.28×10^{-3} mol dm^{-3}). Inset: amount of indigo formed vs. illumination time. (b) Amount of indigo formed as a function of [TiO_2] after 10 min of illumination of oxygenated reaction sample containing $Cd(OH)_2$-coated Q-CdS (1.35×10^{-4} mol dm^{-3}) and indole (1.0×10^{-2} mol dm^{-3}) at pH = 11.0.

that the extent of charge transfer in the exciplex is increased at higher [indole]. Thus, the employed redox couple assists further in the separation of charge. It is also revealed by the increased quantum efficiencies of decomposition of indole ($\phi = 0.18$).



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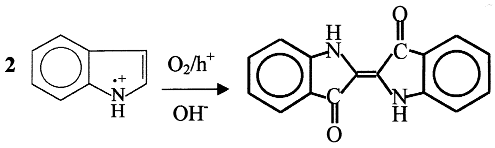

(5)

Indigo formation is significantly reduced in N_2/degassed environment. It is very likely that initially separated e^-–h^+ pair upon illumination eventually recombines in N_2 environment since O_2 is not available to pick up the electrons from TiO_2 particles. The presence of O_2 component in the redox couple thus provides a drive for the separation of charge. A very similar photocatalytic effects for the oxidation of several organics, viz. aromatic amines, substituted indoles and purine bases have been observed by coupling of colloidal TiO_2 with $Cd(OH)_2$-coated Q-CdS and will be published elsewhere.

In summary $Cd(OH)_2$-coated Q-CdS is fairly photostable and sensitizes the reaction of indole–O_2 redox couple poorly. Coupling of $Cd(OH)_2$-coated Q-CdS with TiO_2 causes relatively efficient separation of charges through chemical interaction of the two components. The separated $CdS(h^+)$ forms an emissive exciplex with indole which is eventually decomposed to produce indigo. Thus, CdS–TiO_2 coupled semiconductors provide an efficient photocatalytic system for performing synthetic photochemistry. The sensitization of large band gap semiconductors has great potential in developing the efficient photocatalytic and photoelectrochemical solar conversion systems.

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