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Colloidal CdS-induced photocatalytic reaction of 2-methylindole—mechanistic analysis of oxidation of indoles

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ABSTRACT: 2-Methylindole (2-MI) is adsorbed on the surface of colloidal CdS particles with an adsorption intensity of 0.6×10^3 dm^3 mol^{-1}. A new emission band at 530 nm is produced by forming an exciplex between excited CdS and 2-MI and the red emission due to CdS is simultaneously quenched. The emission maxima of green bands for different indoles increase in the order indole < tryptophan < 2-MI < 3-MI and are observed at 508, 520, 530 and 540 nm, respectively. The shift in emission maxima is related to the oxidation potential of these substrates. The irradiation of an aerated reaction mixture containing CdS and 2-MI with visible light induces the oxidation of adsorbed 2-MI by photogenerated holes to produce 2-methyl-3-indolinone and 2-acetamidobenzaldehyde. The latter product is formed due to oxidative C—C bond cleavage of the pyrrole ring. The reactivity of trapped holes towards the adsorbed 2-MI is evidenced by a decrease in the lifetime of the red emission of CdS in the presence of 2-MI. In this reaction the possibility of the participation of singlet oxygen is ruled out. A general mechanism of CdS-induced oxidation of indoles is discussed. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: colloidal CdS-induced photochemical reactions; photocatalytic reactions; photoxidation; 2-methylindole

INTRODUCTION

Surface modification of nanoparticles of cadmium sulfide (CdS) has been widely investigated in efforts to control their size, elucidate their optoelectronic and emission properties and to study the dynamics of the photogenerated charge carriers.[1–9] As the surface of these quantum crystallites is very large, any interaction of additives with the surface defects of particles might consequently affect their optical and emission properties. For example, the doping of metal ions[2–5] and the binding of different substrates, e.g. thiophenol,[6] 3-mercaptopropane-1,2-diol,[7] aliphatic and aromatic amines,[8,9a] indole,[9b] methyl viologen[10] and thiazine dye,[11] are known to modify the optical and emission properties of colloidal CdS. In several of these investigations, adsorption of substrates on the surface of the particles was observed as a prerequisite to cause these changes. Both the yield of emission and products of photochemical reactions are controlled by the extent of adsorption. Surface capping of particles by thiophenol[6] and aniline[9a] also depict the phenomena of size quantization.

Aliphatic amines and indole enhance green emission whereas aniline, methyl viologen and thiazine dye reduce the yield of red emission. The enhancement of green emission has lately been explained by the formation of a charge-transfer complex between excited CdS and the substrate. The quenching of red emission is understood to involve the scavenging of the trapped charge carriers by the redox couple. Hence the analysis of the products of the reaction together with the change in luminescence behaviour of the photocatalyst in the presence of the redox couple might provide useful information for the elucidation of the overall reaction mechanism.

In the present work, we investigated the colloidal CdS-induced photochemical reaction of 2-methylindole (2-MI) and examined the luminescence behaviour of CdS in the absence and presence of 2-MI. The nature of the interaction between the substrate and the photocatalyst in the ground state was analysed. In the light of the present and earlier findings on similar systems, a general mechanism of CdS-sensitized reactions of indoles is discussed.

EXPERIMENTAL

Materials. Cadmium perchlorate (Alfa), sodium hexametaphosphate (Fluka), 2-methylindole (Aldrich) and all other chemicals were of analytical grade. All chemicals were used as received.

Equipment. The electronic spectra were recorded on a Shimadzu UV-2100/s spectrophotometer. The emission

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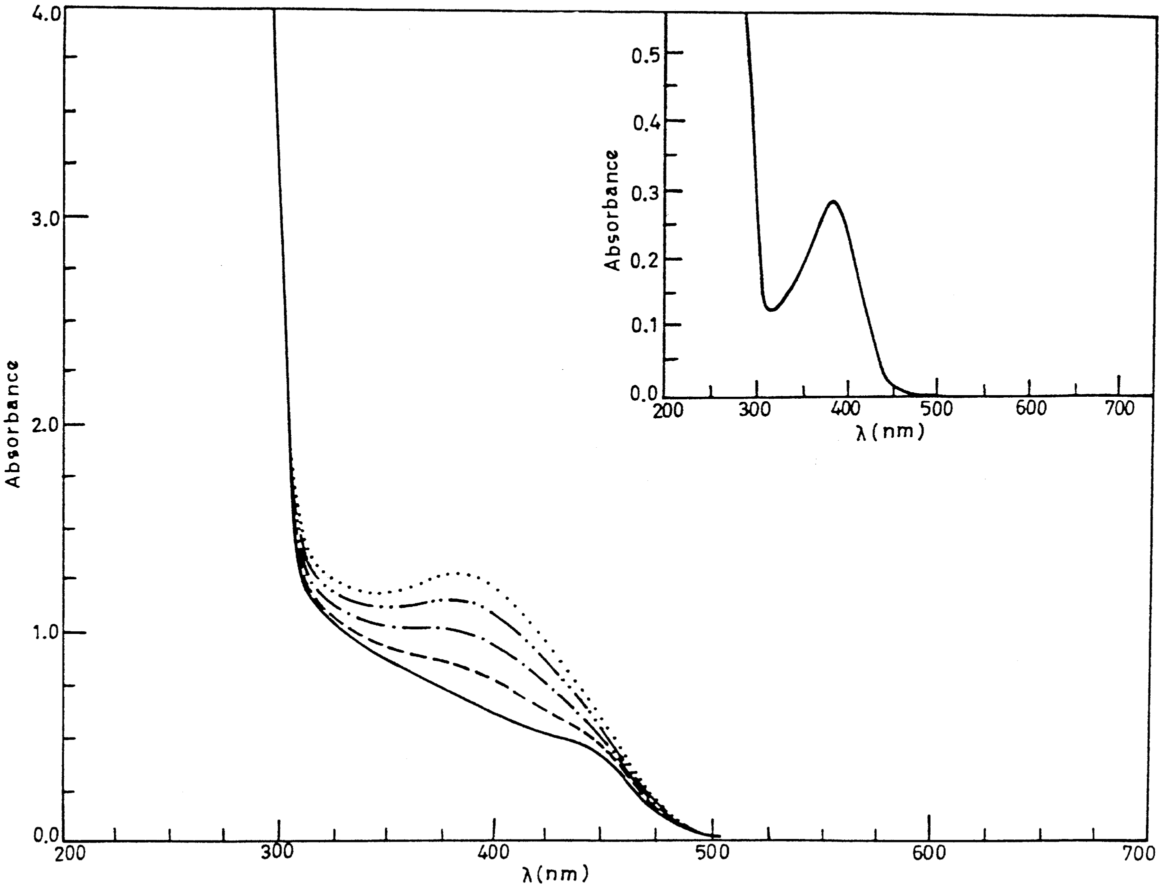


Figure 1. Electronic spectra of the reaction mixture containing 0.4 mM colloidal CdS and 4.0 mM 2-MI as a function of irradiation time: (—)0; (– – –)2; (– . –)5; (– .. –)10; (...)15 min. Inset: electronic spectrum of the chloroform extract of the product.

spectra were obtained on a Shimadzu RF-5000 spectrofluorimeter. Steady-state photolysis experiments were performed on an Oriel photolysis assembly equipped with a 200 W Hg (Xe) arc lamp. GC and GC–MS experiments were carried out on a Shimadzu QP-2000 instrument. GC separation was achieved on an HR-1 capillary column using temperature programming. The column temperature was kept constant at 50 °C for 6 min and then increased at 10 °C min^{-1}. GC–MS data were obtained at 70 eV and 250 °C, and were recorded after the elution of the solvent.

The electron micrographs of the particles were recorded on a Philips EM-400 transmission electron microscope.

The fluorescence lifetimes were measured with an IBH-5000 single photon counting spectrofluorimeter using a nanosecond discharge lamp for excitation. A Hamamatsu photomultiplier was used for the detection of fluorescence. Decay curves were analysed using a multiexponential fitting program from IBH.

Preparation of colloidal CdS solution. A yellow solution of colloidal CdS was prepared by the earlier reported method.[9,10] A stoichiometric amount of freshly prepared SH^- was added slowly to deaerated 0.8 mM cadmium perchlorate solution containing 0.4 mM sodium hexametaphosphate at pH 9.0 and stirred vigorously until completion of the reaction. This solution was subsequently purged with N_2 to remove any unreacted SH^-. The particles thus produced showed broad size distribution and had an average diameter of 4 nm.

RESULTS AND DISCUSSION

CdS-induced oxidation of 2-MI

The photolysis of the aerated reaction mixture containing 0.4 mM colloidal CdS and 4.0 mM 2-MI at pH 10.6 by light of wavelength >400 nm results in an increase in its absorption in both the UV and visible regions. The change in absorption as a function of irradiation time is shown in Fig. 1. The product(s) of the reaction exhibits λ_{max} at 380 nm in the visible region. This suggests that the product(s) might contain a 2-substituted indoxyl type of chromophore, which is known to absorb around 400 nm in the visible range.[12] At low [2-MI] no such product was formed and instead dissolution of particles occurred efficiently. TLC and GC separation of the chloroform extract of the reaction mixture revealed the

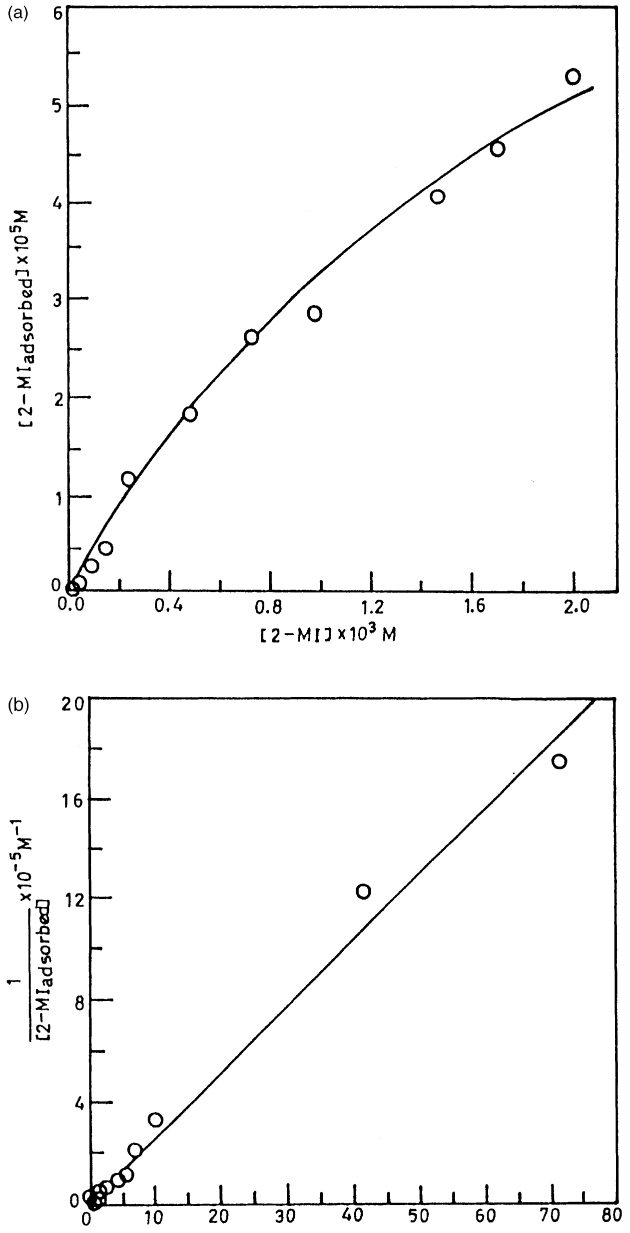


Figure 2. (a) Adsorption isotherm of 2-MI on colloidal CdS. (b) Plot of Langmuir adsorption isotherm of 2-MI.

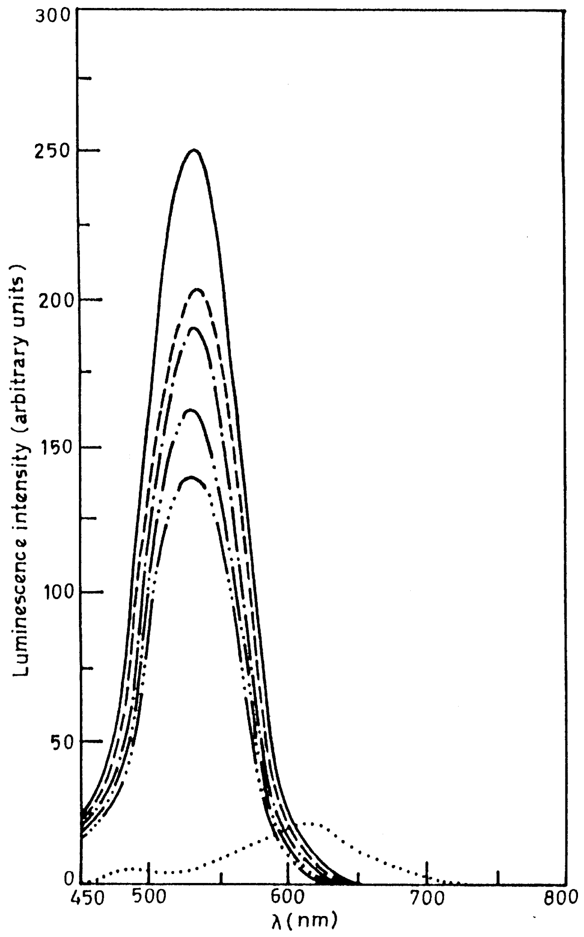


Figure 3. Luminescence spectra of 0.24 mM colloidal CdS in the absence (...) and presence of various concentrations of 2-MI: (-...-)0.5; (-..-)1.0; (-.-)1.5; (——)2.0; (—)2.5 mM.

presence of three components. In GC these components had retention times of 23.55, 24.50 and 25.35 min and were identified by GC–MS as unreacted 2-MI **(1)**, *m/z* 131 (70)P, 130(B) 103(13), 77(20), 65(16), 51(15), 2-methyl-3-indolinone **(2)**, *m/z* 147(33), 146(16), 145(88), 144(B), 130(64), 118(22), 117(20), 104(21), 77(40), 44(54), and 2-acetamidobenzaldehyde **(3)**, *m/z* 163(33)P, 148(12), 135(47), 120(B), 92(48), 65(46), 43(48), respectively.

The formation of **2** and **3** indicates the difference in reactivity of photogenerated holes towards 2-MI in comparison with indole. CdS - sensitized oxidation of indole under identical experimental conditions leads to indigo. The formation of **3** suggests the occurrence of C—C bond cleavage of the pyrrole ring of 2-MI. This observation is in agreement with the earlier findings on the oxidation of 2-MI and its derivatives by other oxidizing agents, viz. chromic acid and $KMnO_4$.[13] The increased electron density at the nitrogen of the pyrrole ring due to the methyl group at the C-2 position and the difference in the reactivities of the intermediates formed may have contributed to the C—C bond cleavage in the case of 2-MI.

Nature of surface interaction and luminescence behaviour

From the above results, it is not clear whether the products are formed by reaction of photogenerated holes with the bulk or surface-bound substrate. In addition, the organic substrate added to the colloidal CdS solution may also interact with CdS chemically. These different possibilities were examined by recording the electronic spectra of CdS in the absence and presence of 2-MI. The presence of 2-MI neither affected the optical absorption of CdS in the visible region nor caused the development of any new peak. It eliminated the possibility of any chemical interaction between the two. However, the scanning of the absorption in the UV region showed a decrease in absorbance where 2-MI had absorption. This suggested that 2-MI is physisorbed on the surface of the particles. From the Langmuir plot of the adsorption data, its binding constant was found to be 0.6×10^3 dm^3 mol^{-1} (Fig. 2). For other indoles, namely indole, 3-MI[14], 2,3-dimethylindole[15] and tryptophan, also no chemical interaction between the substrate and CdS has been reported and their intensities of adsorption were found to be 2.0×10^3, 2.1×10^3, 3.3×10^3 and 0.6×10^3 dm^3 mol^{-1}, respectively. These values are of similar order of magnitude to that of 2-MI. These investigations reveal that the photogenerated holes possibly intercept the surface-bound substrate.

Surface interaction of the substrate could also be probed by exploiting the luminescence from colloidal CdS. If indeed the surface of the particles is modified by adsorption of 2-MI, the luminescence of colloidal CdS should change in its presence. The luminescence spectra of CdS in the absence and presence of 2-MI are shown in Fig. 3. It can be seen that the addition of 2-MI produced a new emission band at 530 nm and the red emission due to CdS was simultaneously quenched. The 530 nm band is different to the band gap emission of CdS, which lies around 490 nm, and corresponded to a quantum efficiency of 5×10^{-3}. The green emission of used CdS particles is weak and has been assigned earlier to the recombination of free charge carriers.[9,10b,16] At higher [2-MI], the 530 nm band shifts slightly to the red. Any contribution to the observed emission on account of 2-MI can be neglected as 400 nm light was used for excitation; 2-MI does not have any absorption at this wavelength. Since the absorption spectrum of CdS remains unchanged in the presence of 2-MI, it shows the absence of any complexation in the ground state between the two. The surface of colloidal CdS particles is known to have many defects and traps. Binding of 2-MI to these sites may, thereby, occur through physical adsorption. Hence the appearance of the 530 nm band can be attributed to the emission from the exciplex formed between the excited CdS and the adsorbed 2-MI. In contrast to indole, no isoemissive point is observed with 2-MI and a bathochromic shift of the green band is noted at high [2-MI]. This is possibly due to the formation of intermediate complexes of varied stoichiometry at various [2-MI] which may have different emission characteristics.

Similar green emission bands at different wavelengths have also been noted for other substituted indoles. The wavelengths of the green band in comparison with that of indole follow the trend indole < tryptophan < 2-MI < 3-MI and are observed at 508, 520, 530 and 540 nm, respectively. A change in the wavelength of the green band for different indoles evidently rules out the possiblity of it being the band gap emission due to CdS. This behaviour is understood in terms of the varied oxidation potential of these substrates which affects the extent of charge transfer in the exciplex formed between excited CdS and the respective indole. The order of decreasing oxidation potential[17] of the indoles studied is indole < tryptophan < 2-MI < 3-MI, which is the same as the order in which the bathochromic shift of the wavelength of the green emission band changes. The enhancement of the luminescence of colloidal CdS and Cd_3As_2 particles by binding of tertiary amines and aliphatic thiols[8] can also be argued along similar lines.

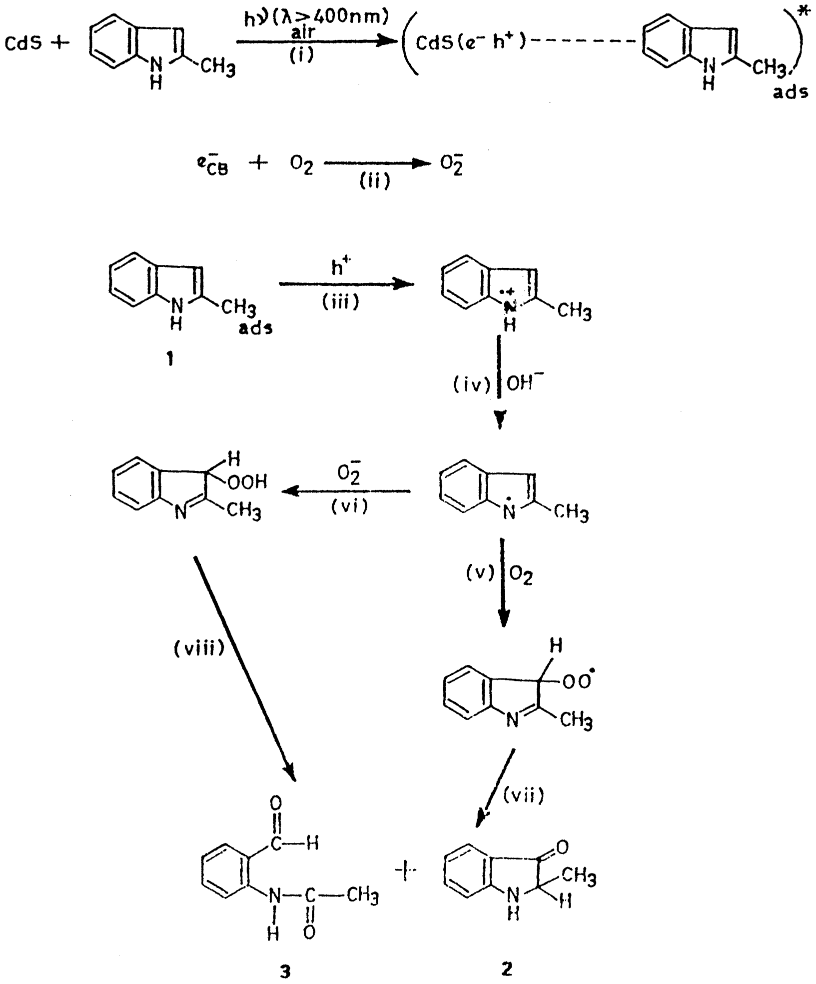
The reactivity of photogenerated trapped holes towards 2-MI was checked by measuring the emission lifetime of CdS in the absence and presence of 2-MI. In these experiments CdS particles were excited by 400 nm light, where 2-MI does not show any absorption. The emission was followed at 600 nm. The decay curve of CdS emission could be fitted in a three exponential decay program. In the presence of 2 mM of 2-MI the average lifetime of CdS emission decreased from 8.0 to 1.2 ns. The decrease in the lifetime confirms the interception of holes by 2-MI following dynamic quenching.

In the light of the above results, the reaction scheme for the formation of **2** and **3** in the CdS-mediated oxidation of 2-MI can be outlined as shown in Scheme 1.

O_2^- formed in the cathodic reaction (ii) may eventually produce H_2O_2.[18] The photochemical and thermal reaction of H_2O_2 with 2-MI under similar experimental conditions did not produce any of the above - identified products. These experiments support the participation of O_2^- depicted in step (vi). Indolyl radical is known to couple with O_2^- to yield hydroperoxide.[19] Hence the initial step in CdS-sensitized reaction of 2-MI may consist of its oxidation to produce 2-methylindolyl radical cation. The pK_a of this radical cation is 5.7 ± 0.1,[20] and at pH 10.5 it will be converted largely into 2-methylindolyl radical.

In contrast to the CdS-sensitized reaction of indole,[9b] O_2 and O_2^- react with 2-methylindolyl radical to produce the corresponding peroxy radical and hydroperoxide in steps (v) and (vi). These intermediates subsequently disproportionate and decompose to yield **2** and **3** in steps (vii) and (viii), respectively. The higher reactivity of 2-methylindolyl radical with molecular oxygen in comparison with that of indole radical can be explained by the difference in their reduction potentials.[17,19] In case of indole the initially produced radical cation mainly forms an adduct with OH^- at the electron-deficient C-2 position,[9b] in contrast to 2-MI, in which the C-2 position is blocked by a methyl group. The OH adduct is then oxidized by the photogenerated hole to give 3-hydroxyindole, which is known to autooxidize readily to indigo in the presence of oxygen.[21]

Hence in CdS-sensitized reactions of indole and 2-MI, the difference in reactivity of radical intermediates formed with O_2/O_2^- is responsible for the formation of different products of oxidation in these reactions.



Scheme 1

In flash photolysis experiments, the primary event upon illumination of CdS is the formation of an electron–hole pair.[22] The trapped conduction band electron caused the bleaching of CdS absorption to produce $(CdS)_x^-$.[22e,23] In the presence of O_2 the bleaching of CdS is recovered by the reaction shown in step (ii) (Scheme 1) and this process takes place with a second-order rate constant of 2.2×10^5 dm^3 mol^{-1} s^{-1}.[22e] Apparently, the molecular oxygen does not quench the excited CdS but instead reacts with the trapped electron in the secondary step. In addition, the emission due to CdS and the CdS – 2-MI reaction mixture is not quenched in the presence of air. This observation also eliminates the possibility of the formation of singlet oxygen by energy tranfer from the excited CdS to molecular oxygen. Therefore, the involvement of $^1O_2$ in the studied reaction can be neglected.

CONCLUSIONS

This work has illustrated an important mechanism in the surface interaction of redox couples with colloidal CdS particles. Indoles did not exhibit any chemical interaction with colloidal CdS. Binding of indoles to different defect sites through adsorption modifies the surface of colloidal CdS particles. The adsorbed substrates form a green luminescing exciplex with excited CdS. This green emission is different to the CdS band gap emission. Interestingly, the emission maxima are related to the oxidation potential of the substrate. The electron–hole' pairs generated upon photoirradiation of CdS are scavenged by the adsorbed redox couple to yield the products of reaction. At high concentrations of indoles the anodic photodissolution of CdS particles does not occur.

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