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Photocatalytic Oxidative C–C Bond Cleavage of the Pyrrole Ring in 3-Methylindole induced by Colloidal CdS Particles†

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Binding of 3-methylindole (3-MI) to the surface of colloidal CdS particles modifies their luminescence behaviour so that the trapped electron and hole generated upon photoirradiation are scavenged by adsorbed O_2 and 3-MI to yield 2-acetylformanilide and 2-aminoacetophenone.

Recently, intense interest has been aroused in the investigation of the photochemical and photophysical behaviour of colloidal semiconductors in regard to understanding their photocatalytic properties.[1] Many of these investigations have focused on colloidal CdS particles because of their stability in various homogeneous and heterogeneous media and their absorption which extends to the visible region.[1] The high specific surface of these particles has been exploited in order to modify their photophysics by binding different additives[2–6] and to enhance the reactivity of the photogenerated charge carriers for performing useful synthetic transformations.[6–12] Moreover, unlike bulk semiconductors, nanosized particles can be utilized to carry out simultaneous oxidation and reduction. In the present investigation, colloidal CdS-sensitized oxidation of 3-MI was examined in the presence of air. Interestingly, the reaction occurred through cleavage of the pyrrole ring C–C bond.

The electronic spectrum of the reaction mixture containing colloidal CdS and 3-MI neither depicted any new peak in the entire recorded wavelength region (200–600 nm) nor caused any change in the absorption of CdS in the visible region. This suggested the absence of any chemical interaction between CdS and 3-MI. 3-MI is, however, adsorbed onto the surface of the CdS clusters. The amount of adsorbed 3-MI was computed by subtracting the absorbance of the reaction mixture from the sum of the absorbances due to blank CdS and 3-MI at various wavelengths at which 3-MI depicted absorption. The observed adsorption isotherm is shown in Fig. 1. At low [3-MI], the adsorption data followed the Langmuir isotherm (inset Fig. 1) from which the intensity of its adsorption was calculated to be 2.1×10^3 dm^3 mol^{-1}.

Photolysis of the aerated reaction mixture containing 0.4 mM CdS and 4 mM 3-MI by visible light in the wavelength range 410–440 nm resulted in growth of its absorption in the blue-green region. A chloroform extract of the product showed λ_{max} at 325 nm. In TLC and GC experiments this extract was found to contain three components, the retention times of which in the GC chromatogram were 4.29, 5.37 and 6.78 min, respectively. In GC-MS experiments, the fragmentation pattern of component I [*m*/*z* 135 (64%, M$^+$), 120 (100), 92 (69), 65 (60) and 44 (27)] was identical with that of an authentic sample of 2-aminoacetophenone **6**, while that of component III [*m*/*z* 163 (22%, M$^+$), 148 (9), 135 (55), 120 (100), 92 (50), 65 (53) and 43 (53)] matched the earlier reported fragmentation pattern of 2-acetylformanilide **5**.[13] Component II was identified as being the unreacted 3-MI. The amount of **6** was quantified by GC (using an authentic sample for calibration purposes) and was found to form with a quantum efficiency of 0.07 after 5 min of irradiation. Thus CdS-induced oxidation of 3-MI results in the formation of products due to cleavage of its pyrrole ring. At low [3-MI] (<2 mM), the amount of product formed was much less and anodic dissolution of the particles occurred efficiently. No product formation was detected in the absence of photocatalyst.

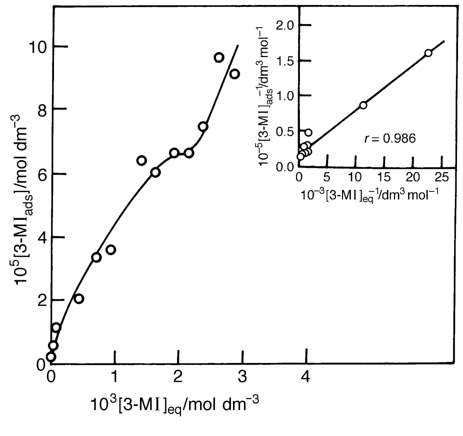

Fig. 1 Adsorption isotherm of 3-MI on 0.32 mM colloidal CdS. Inset: Plot of Langmuir adsorption isotherm of 3-MI

To illustrate the mechanism of this reaction, the luminescence behaviour of colloidal CdS in the absence and presence of 3-MI was monitored (Fig. 2). In the presence of 3-MI, the luminescence spectrum of CdS showed a new band in the green region at 540 nm along with a simultaneous small quenching of red emission. The band at 540 nm is different to the fluorescence maxima of 3-MI.[14] Any contribution to this emission due to 3-MI can also be excluded because of the excitation wavelength used (400 nm) since 3-MI does not absorb in the visible region. It may be noted that the 540 nm band is red-shifted from the band-gap emission due to CdS itself, and that the luminescence intensity increases with an increase in [3-MI] together with a further small red shift in emission maxima at higher [3-MI]. These emission changes did not exhibit any isoemissive point. An increase in emission intensity and a shift in the emission maxima with increasing [3-MI] without depicting any isoemissive point indicate the formation of luminescing exciplexes of varying stoichiometry between the excited-state CdS and 3-MI. The low extent of quenching of red emission (Fig. 2) is understood by the fact that the colloidal CdS and its complex in the excited state with 3-MI might have similar emission characteristics in this wavelength region.

Colloidal CdS emission is known to consist of a range of lifetimes.[9,15] The emission decay curve recorded with the used CdS colloids at 600 nm could be fitted into three exponential decay programmes having $\tau_1 = 0.054$ ns ($B_1 = 0.5341$), $\tau_2 = 1.03$ ns ($B_2 = 1.2193 \times 10^{-3}$) and $\tau_3 = 19.82$ ns ($B_3 = 1.2496 \times 10^{-3}$) with $<\tau>$ of about 8 ns. In the presence of 2.25 mM 3-MI, this emission decayed within the lamp pulse which suggests that the quenching of the red emission which occurs is due to interception of the photogenerated hole by the adsorbed 3-MI. This eventually results in the formation of **5** and **6** as products. The mechanism of this reaction may be depicted as in Scheme 1.

In basic medium, the indolyl cation **2**, having p$K_a = 5$,[16] is converted into the indolyl radical **3**. This may couple with O_2^- to yield the corresponding hydroperoxide[17] **4** which decomposes to produce 2-acetylformanilide **5** [eqn. (4)].

The relative amounts of **5** and **6** as a function of irradiation time were also followed by GC. The yield of **5** increased proportionately whereas the amount of **6** attained a limiting value after 10 min of irradiation. This suggests that **6** is not

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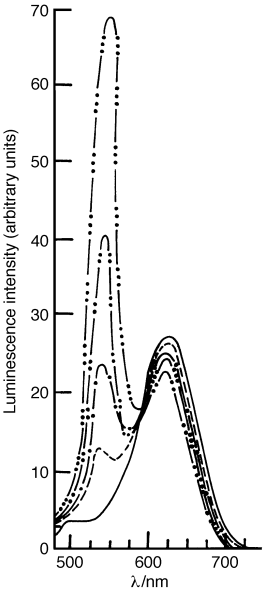
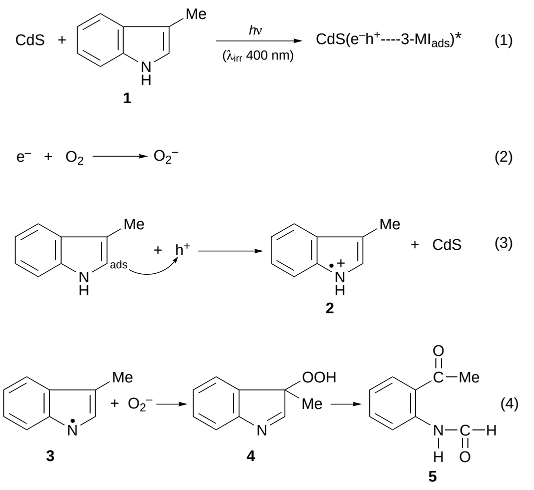


Fig. 2 Luminescence spectra of 0.24 mm colloidal CdS in the absence (———) and presence of varying concentrations of 3-MI (mm): 0.5 (---); 1.0 (-··-); 2.0 (-···-); 2.5 (–····–); excitation wavelength 400 nm



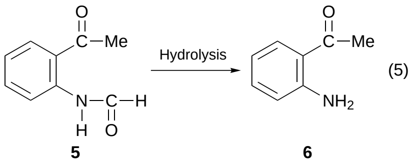
Scheme 1

produced photochemically but possibly by hydrolysis of **5** [eqn. (5)].[18]

Thus 3-MI at its low concentration binds to the shallow traps on the surface of the colloidal CdS, modifying its luminescence behaviour by forming green luminescing exciplexes of varying stoichiometry between the excited CdS and 3-MI. The quenching of the red emission which occurs is due to transfer of the deep trapped holes[1,10,12] from the irradiated semiconductor to the secondary layers of adsorbed 3-MI which eventually results in the formation of **5** and **6**.

This work elucidates the mechanism of an interesting system in which products are formed *via* C—C bond cleavage of the pyrrole ring. Photophysical and photochemical studies of 3-MI are also important since this molecule is considered as a model for tryptophan in proteins. The photocorrosion of CdS particles could be prevented under the experimental conditions used. Investigations on related heterocycles are under way to arrive at a general mechanism. Efforts are being made to bring about increased charge separation in these systems upon photoirradiation.

Experimental



Absorption data were recorded on a Shimadzu UV-2100/s spectrophotometer. Emission measurements were made on a Shimadzu RF-5000 spectrofluorophotometer. Fluorescence lifetimes were determined on an IBH-5000 single photon counting fluorimeter using a nanosecond discharge lamp for excitation. Decay curves were analysed by using a multiexponential fitting program from IBH. Steady-state photolysis experiments were designed on an Oriel photolysis assembly equipped with 200 W Hg(Xe) lamp and cut filters.

Colloidal CdS was prepared by injecting a stoichiometric amount of SH^- to the deaerated $Cd(ClO_4)_2$ solution containing sodium hexametaphosphate as stabilizer following an earlier reported method[6,10] and was characterized by its electronic and emission spectra. The particles had an average size of 4 nm (determined by a Philips EM-400 transmission electron microscope).

GC separation of products was achieved on an HP-1 capillary column under non-isothermal conditions. The column was temperature-programmed from 50 to 230 °C at a heating rate of 10 °C min^{-1}. GC-MS data were obtained on a Shimadzu QP-2000 instrument at 70 eV after elution of the solvent.

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