Photocatalytic reduction of methyl yellow by CdS nanoparticles mediated in reverse micelles: microheterogeneous electron transfer across a water–oil boundary

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A microheterogeneous photocatalytic reduction system mediated in AOT–isooctane reverse micelles is reported, using CdS nanoparticles prepared in the aqueous phase as the catalyst and methyl yellow solubilized in the organic phase as a probe for the photoreduction.

The utilization of semiconductor particles as photocatalysts to initiate interfacial redox reactions has evoked great interest in recent years.[1–3] Band-gap excitation of semiconductor particles produces electron–hole pairs, which move towards the surface where they are trapped. In the absence of oxygen, the photogenerated electrons lead directly to the reduction of reducible species at the particle surface, and this has been applied to water splitting and nitrogen fixation. This provides a promising route for conversion and storage of solar energy. However, in homogeneous solutions the semiconductor mediated system suffers from several limitations, such as the back reaction, in which the electrons captured by the adsorbates can transfer back to the particle and recombine with the positive holes in the valence band and the net photoconversion efficiency is thus decreased. Organized surfactant assemblies such as vesicles and reverse micelles have been shown to be effective in compartmentalizing semiconductor particles and reactants, thus aiding charge separation.[4] We report here, for the first time, a photocatalytic reduction system mediated in AOT–isooctane micelles, using CdS nanoparticles prepared in the aqueous phase as the catalyst and an azo dye solubilized in the organic phase as a probe for the photoreduction (Fig. 1). Willner *et al.*[5] showed that methyl yellow (4-dimethylaminoazobenzene) could be used to effectively probe photoinduced electron transfer across a phase boundary mediated by reverse micelles. In this work the same dye is employed to examine whether the conduction band electrons can transfer from CdS particles to an acceptor present in the bulk organic phase.

The synthesis of colloidal CdS was performed by mixing under stirring two 0.1 mol dm^{-3} AOT–isooctane micellar solutions with aqueous solutions of Na_2S and $Cd(NO_3)_2$ ($[H_2O]/[AOT] = 5$).[6] The materials were of the purest available quality and were used as received and doubly distilled water was used throughout. Three types of CdS particles prepared from different ratios of $Cd^{2+}:S^{2-}$ ($X = [Cd^{2+}]/[S^{2-}]$) were synthesized (Table 1). The absorption onset of the particles was in the range 440–460 nm for each of the three samples. From the relation between the absorption onset and size of CdS particles,[7] the average radius (R) can be deduced for a given value of X, and is found to be *ca.* 1.2 nm in each case. Owing to the stabilization imparted by the reverse micelles, no aggregation of CdS particles was observed.

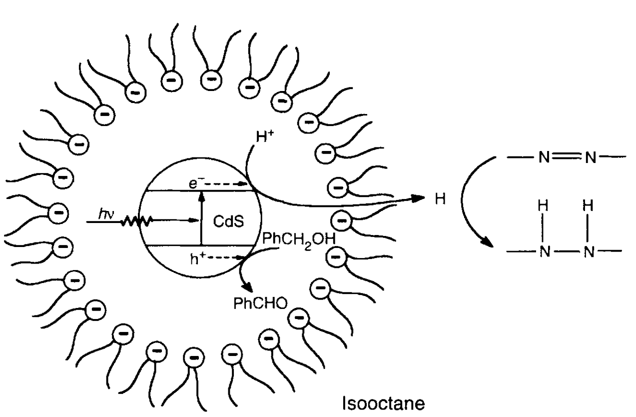

Fig. 1 Schematic diagram illustrating the microheterogeneous electron transfer from the conduction band of CdS particles to methyl yellow molecules present in the organic phase

Irradiation experiments were carried out using a stoppered 1 cm quartz cell so preventing contact with air. In a typical experiment, 2 ml of a CdS micellar solution containing 2×10^{-5} mol dm^{-3} methyl yellow was used. To improve the photocatalytic efficiency and protect the CdS particle against photoanodic corrosion, *ca.* 4 µl benzyl alcohol was added to act as a hole scavenger. The reaction solution was deaerated by bubbling with nitrogen gas for 10 min prior to illumination, and was stirred while being illuminated ($\lambda > 330$ nm) by a 300 W medium pressure mercury lamp. During each run, the reaction solution was subjected to absorption measurements at given time intervals.

Upon irradiation, electrons are excited into the conduction band and are captured by protons to produce high-energy hydrogen atoms or molecules, while the holes left in the valence band are scavenged by benzyl alcohol to generate benzaldehyde. The hydrogen atoms produced in the aqueous phase can easily migrate into the bulk organic solution and hydrogenate methyl yellow molecules [eqn. (1)].

$$PhN{=}NC_6H_4NMe_2 + 2H^+ + 2e^- \xrightarrow[CdS]{h\nu} PhNHNHC_6H_4NMe_2 \qquad (1)$$

From the absorption spectrum of the reaction solution, it can be seen that as the irradiation progresses, the absorption band at 402 nm (λ_{max} of methyl yellow in isooctane) disappears steadily, indicating photoreduction of methyl yellow.[5] Control experiments show that the presence of both CdS and light is necessary for reduction of methyl yellow. Fig. 2 illustrates the photoreduction of methyl yellow (2×10^{-5} mol dm^{-3}), catalysed by each of the three types of CdS particles as a function of irradiation time. The relative concentration of methyl yellow (c/c_0) decreases steadily with irradiation time.

Table 1 Ion contents and average radii of CdS particles

X	$10^4[Cd^{2+}]$/ mol dm^{-3}	$10^4[S^{2-}]$/ mol dm^{-3}	R/nm
0.7	6.6	9.4	1.3
1.0	6.6	6.6	1.2
1.5	9.9	6.6	1.2

It is found that an increase in X value is conducive to the enhancement of photoreduction. This can be explained by the fact that increasing the concentration of H^+ ions or electrons at the particle surface is favourable for promoting the reaction of eqn. (1). At the lower X value of 0.7, the aqueous phase contains much more S^{2-} ions than Cd^{2+}, and hence is strongly basic and cannot provide sufficient H^+ ions. For $X > 1$, the higher concentration of Cd^{2+} ions makes the aqueous phase acidic leading to an increase in the concentration of H^+ ions. On the other hand, the increase of Cd^{2+} concentration also causes the CdS particle surface to be positively charged, and as reported in previous papers,[8] this favours the transfer of the photogenerated electron from the bulk of particle to the surface.

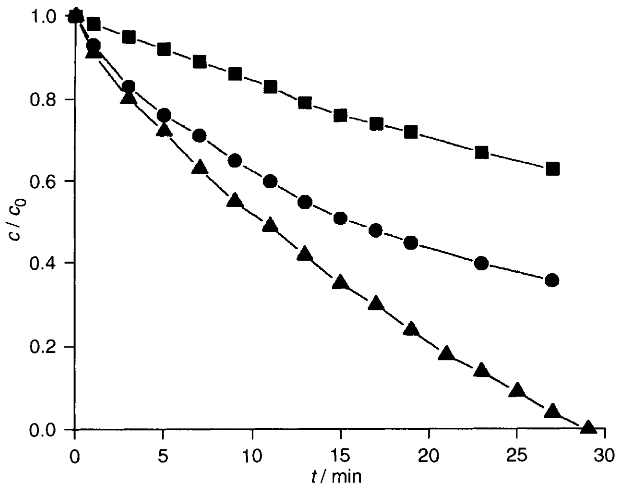

Fig. 2 c/c_0 *vs.* time plots showing the photoreduction of methyl yellow catalysed by CdS particles; X = 0.7(■), 1.0(●) or 1.5(▲)

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