# Methyl Orange as a Probe of the Semiconductor–Electrolyte Interfaces in CdS Suspensions

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Cadmium sulphide (CdS) powder dispersions have been used to sensitise the photoreduction of methyl orange (D<sup>-</sup>) at pH < 7 in aqueous solution. A number of electron donors were added (PVA, TEOA, nitrate, tartrate, cysteine, citrate, acetate and EDTA), but at pH 4.4 only EDTA enhanced appreciably the rate of methyl orange photoreduction. A steady-state equation was developed which successfully described the observed variation in initial rate of methyl orange photoreduction as a function of the concentrations of methyl orange, photons, EDTA and O<sub>2</sub> (when present). From this work it was shown that the rate constant for hole  $(h^+)$  scavenging by EDTA was ca. 19000 times greater than that for the recombination reaction between  $h^+$  and a conductance band electron (e<sup>-</sup>). In addition, the rate constant for the reduction of  $O_2$  by a conductance band electron was ca. 40-50 times smaller than that for the reduction of methyl orange by  $e^{-}$ . Corrosion studies indicated that photoreduction of methyl orange to a hydrazine derivative (D<sup>3-</sup>) sensitised by CdS, was accompanied by anodic corrosion of the semiconductor even in the presence of EDTA. In this work the role of EDTA (at pH 4.4) appeared to be as a mediator of the reaction

$$2H^+ + D^- + CdS \xrightarrow{EDTA} DH_2^- + Cd_{aq}^{2+} + S_{\downarrow}$$

and not as an 'ideal' sacrificial electron donor. Reasons for this are discussed.

Few semiconductors have been employed as extensively over the past decade to photosensitise catalytic and synthetic reactions<sup>1</sup> as n-type CdS. Part of the interest in CdS arises from the size of its band gap (2.4 eV) since this enables CdS to absorb an appreciable fraction of the solar spectrum (*i.e.*  $\lambda \leq 516$  nm). This is in sharp contrast to many of the oxide semiconductors (such as TiO<sub>2</sub> and SrTiO<sub>3</sub>) which possess large band gaps  $(e.g. \ge 3.0 \text{ eV})$  and do not, therefore, absorb much of the solar spectrum (ca. < 6%).<sup>2</sup> In addition, part of the interest in CdS arises from the positions of the conduction band ( $E_c$ ) and valence bands ( $E_{vb}$ ) with respect to a reference point, such as the SCE, since these band positions are considered in general to be sufficiently negative (-0.9 V vs. SCE) and positive (1.5 V vs. SCE), respectively, so as to allow, in theory, the photocleavage of water into  $H_2$  and  $O_2$  to be sensitised by CdS. Indeed, several groups<sup>3-5</sup> have reported the successful photodissociation of water using CdS powder dispersions and colloids in the presence of Pt and RuO<sub>2</sub> as hydrogen and oxygen catalysts; however, other groups<sup>6, 7</sup> have not been so successful. The lack of success by these latter workers<sup>6, 7</sup> has invariably been attributed to the inability of the water oxidation reaction

$$4h^{+} + 2H_{2}O \longrightarrow 4H^{+} + O_{2} \tag{1}$$

to compete with the oxidation of the lattice by the photogenerated holes  $(h^+)$ 

$$2h^+ + CdS \longrightarrow Cd_{aq}^{2+} + S.$$
<sup>(2)</sup>

## Semiconductor–Electrolyte Interfaces

Several groups<sup>8-11</sup> have shown, however, that CdS can be protected to varying degrees from photoanodic decomposition by adding redox couples such as  $S^{2-}/S$ ,  $SO_3^{2-}/SO_4^{2-}$ , Fe(CN)<sub>6</sub><sup>4-/3-</sup> and I<sup>-</sup>/I<sub>2</sub> to the aqueous solution. The  $S^{2-}/S$  redox couple has proved exceptionally good at stabilising CdS and has enabled the development of durable and efficient CdS-based liquid-junction photovoltaic cells.<sup>10, 11</sup> Stabilisation of CdS can also be achieved using sacrificial electron donors (*e.g.* donors which, in theory, prevent back-reaction by decomposing rapidly and irreversibly upon oxidation) such as EDTA,<sup>12, 13</sup> TEOA<sup>14</sup> (triethanolamine), cysteine,<sup>15</sup> dextrose,<sup>14</sup> starch,<sup>14</sup> sulphite<sup>16, 17</sup> and disulphide,<sup>17, 18</sup> and this has led to a number of reports<sup>11-18</sup> on the photoreduction of water to H<sub>2</sub> sensitised by powder dispersions of CdS, CdS/Pt or CdS/RuO<sub>2</sub>.

Unlike single-crystal CdS electrodes, powder dispersions cannot be readily probed using many of the standard electrochemical techniques such as cyclic voltammetry, rotating ring-disc and capacitance measurements. In addition, unlike colloidal suspensions of CdS (which are optically transparent and show no tendency to settle out), powder dispersions cannot be easily studied using microsecond and nanosecond flash photolysis, luminescence and conductivity measurements. However, techniques such as electron spin resonance<sup>19, 20</sup> and photocoulometry<sup>1</sup> have been used successfully to study CdS powder dispersions. The latter technique, employed by White and Bard<sup>1</sup> to examine the photoreduction of methyl viologen ( $MV^{2+}$ ), appears particularly useful in providing estimates of net turnover number, suspension stabilities and the effectiveness of different surface treatments (metal deposits) and sacrificial donors in stabilising the CdS particles. In a recent paper<sup>21</sup> Darwent and Brown showed that methyl orange could be used to probe photo-oxidation reactions occurring at the semiconductor-electrolyte interfaces in colloidal suspensions of  $TiO_2$ . In this work we show how the same dye can be used to examine photoreduction reactions of powder suspensions of CdS and the effectiveness of EDTA as a sacrificial electron donor.

# **Experimental**

## Materials

The methyl orange and EDTA were supplied by BDH (AnalaR grade) and the CdS (99.999%) was purchased from Koch-Light Laboratories. From electron microscopy the average CdS particle diameter was estimated to be *ca*. 1.2  $\mu$ m. The water used was always deionised before being doubly distilled from quartz vessels.

## **Methods and Apparatus**

All steady-state irradiations were carried out with an I-REM 250 W Xe arc lamp (Applied Photophysics) with a 320 nm cut-off filter (unless stated otherwise). Solutions (30 cm<sup>3</sup>) were irradiated in a thermostatted  $(25\pm0.1 \text{ °C})$  cylindrical quartz reaction cell with taps which enabled N<sub>2</sub>, O<sub>2</sub> or N<sub>2</sub>–O<sub>2</sub> mixtures to be passed continuously through the suspension. The cell is identical in almost all respects of design to one used previously in conjunction with a hydrogen and oxygen membrane polarographic detector.<sup>22</sup> During the course of an irradiation the light beam was interrupted at periodic intervals so as to allow samples (*ca.* 3 cm<sup>3</sup>) of the CdS/methyl orange suspension to be analysed spectrophotometrically. A gas-tight syringe with a 0.2  $\mu$ m membrane filter (supplied by Schleicher and Schüell), fitted between the needle and syringe barrel, was used to take the samples. Incorporation of this filter allowed the u.v.–visible absorption spectrum of the methyl orange solution alone (*i.e.* free from CdS particles) to be recorded (in a 1 cm quartz cell, using a Perkin-Elmer Lambda 3 spectrophotometer) before being returned to the reaction vessel for subsequent irradiation. The extinction coefficient for unprotonated methyl orange was taken as 2.68 × 10<sup>4</sup> dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> at  $\lambda_{max} = 463$  nm.<sup>23</sup>

The CdS-methyl orange solutions contained in the reaction vessel were purged for at least 15 min before and during any irradiation. The purging gases used were usually  $N_2$ ,  $O_2$  or (as in one set of experiments) mixtures of  $N_2$ - $O_2$ . These  $N_2$ - $O_2$  mixtures were generated using the tangential gas mixer described in a previous paper<sup>22</sup> and their percentage  $O_2$  compositions were determined by gas chromatography using a Perkin-Elmer F33 thermistor gas chromatograph, incorporating a 2 m stainless-steel column (0.3 cm i.d.) packed with activated 5A molecular sieve and using Ar as the carrier gas.

In the study of the corrosion of the CdS powder dispersions, the filtered (CdS-free) samples (see above) were analysed by atomic absorption spectroscopy (AAS) using a Perkin-Elmer Alpha 2 instrument which had been previously calibrated using  $Cd^{2+}$  solution standards prepared from Spectrosol  $Cd(NO_3)_2$  (BDH).

## **Results and Discussion**

#### **Initial Studies**

In a typical experiment an N<sub>2</sub>-purged solution (30 cm<sup>3</sup>) containing only methyl orange ( $3.9 \times 10^{-5}$  mol dm<sup>-3</sup>), CdS (2 mg cm<sup>-3</sup>) at pH 4.4 was irradiated and the u.v.-visible absorption spectrum of the methyl orange was monitored as a function of irradiation time (see fig. 1). The disappearance of the absorption band at 463 nm (*i.e.*  $\lambda_{max}$  of the unprotonated form of methyl orange) and the concomitant appearance of an absorption maximum at 247 nm as the irradiation progressed indicated that the CdS powder dispersion was able to sensitise the photoreduction of unprotonated methyl orange (I) (p $K_a = 3.5$ )<sup>24</sup> to a hydrazine derivative (II), *i.e.* 

$$(CH_3)_2NC_6H_4N = NC_6H_4SO_3^- + 2H^+ + 2e^- \xrightarrow{Cus} (CH_3)_2NC_6H_4NHNHC_6H_4SO_3^-.$$
(3)  
(I) (II)

0.40

The source of the electrons appeared to be the CdS itself since the alternative, water oxidation, is in general considered extremely unlikely, especially when no platinum-group  $O_2$ -catalysts (such as  $RuO_2$  and  $Rh_2O_3$ ) are employed, as is the case here.<sup>7, 10, 11</sup> The overall reaction may be better expressed as

$$2h^{+} + (\mathbf{I}) + CdS \xrightarrow{h_{\nu \geq 2.4 \text{ eV}}} (\mathbf{II}) + Cd_{aq}^{2+} + S\downarrow.$$
(4)

In a previous paper<sup>25</sup> Darwent and Brown showed that PVA-supported colloids of TiO<sub>2</sub> were also able to bring about the photoreduction of methyl orange to its hydrazine derivative (II) and the spectral changes and  $\lambda_{max}$  at 247 nm for (II) recorded by these workers agree very well with our observations. In the absence of CdS, no bleaching of the methyl orange is observed upon illumination and this is attributed to its well documented short excited-state lifetime owing to a rapid *trans-cis* photoisomerisation process.<sup>26</sup> In addition, only ultra-band-gap radiation ( $\lambda \leq 516$  nm) appeared to be able to bring about the photobleaching of methyl orange was observed, even though the absorption spectrum of methyl orange extended up to *ca*. 580 nm (see fig. 1). In addition, the rate of photobleaching of methyl orange in the presence of CdS powder was only fractionally reduced (by *ca*.  $\frac{1}{2}$ ) when a methyl orange filter solution (absorbance > 2 at  $\lambda_{max} = 463$  nm) was introduced between the irradiation source/390 nm filter and the photolysis cell. These observations support the argument that the CdS particles were responsible for photosensitising reaction (3).

The rate of reduction of methyl orange in anaerobic solution was noticeably altered upon addition of different electron donors (ED). Fig. 2 illustrates the absorbance  $(\lambda_{\max} = 463 \text{ nm}) vs.$  time profiles observed for a selection of the electron donors tried and table 1 lists the relative initial rates ( $R_i$ ) of reduction of (I) determined for these and Semiconductor-Electrolyte Interfaces



Fig. 1. U.v.-visible absorption spectra (recorded using a 1 cm cell) showing the photobleaching of methyl orange  $(3.9 \times 10^{-5} \text{ mol dm}^{-3})$  when irradiated in the presence of CdS (2 mg cm<sup>-3</sup>, pH 4.4,  $\lambda > 320$  nm, N<sub>2</sub>-purged solution). The irradiation times after which the spectra were recorded were: (a) 0, (b) 5 min, (c) 11 min, (d) 18 min, (e) 30 min, (f) 50 min.



Fig. 2. Absorbance vs. time plots (recorded using a 1 cm cell,  $\lambda_{max} = 463$  nm) showing the photobleaching of methyl orange  $(3.9 \times 10^{-5} \text{ mol dm}^{-3})$  by CdS (2 mg cm<sup>-3</sup>, pH 4.4,  $\lambda > 320$  nm, N<sub>2</sub>-purged solution) in the presence of various electron donors: (a) PVA solution (0.1% w/v), (b) KNO<sub>3</sub> (0.1 mol dm<sup>-3</sup>), (c) none (water), (d) acetate buffer (10<sup>-2</sup> mol dm<sup>-3</sup>), (e) EDTA (10<sup>-2</sup> mol dm<sup>-3</sup>).

 Table 1. Relative initial rates of photoreduction

 of methyl orange in the presence of various

 electron donors

electron donor <sup>a</sup>	R <sub>i</sub>	
EDTA	100 <sup>b</sup>	
acetate	50	
none (water)	37	
citrate	37	
cysteine	31	
tartrate	29	
nitrate <sup>c</sup>	29	
TEOA	16	
$\mathrm{PVA}^d$	2	

<sup>*a*</sup> All electron donors at  $10^{-2}$  mol dm<sup>-3</sup> and pH 4.4, unless stated otherwise. <sup>*b*</sup> An initial relative rate of 100 corresponds to an actual rate of  $7.28 \times 10^{-8}$  mol dm<sup>-3</sup> s<sup>-1</sup>. <sup>*c*</sup> 0.1 mol dm<sup>-3</sup> KNO<sub>3</sub> solution was used. <sup>*d*</sup> 0.1% (w/v) solution was used.

other electron donors. A 'good' electron donor is one which reacts with the strongly oxidising photogenerated hole  $(h^+)$  before it is able to oxidise the lattice, *i.e.* 

$$h^+ + ED \longrightarrow ED^+.$$
 (5)

The oxidised donor,  $ED^+$ , must then rapidly desorb from the surface of the CdS before the photogenerated electron can 'neutralise' it. If the donor is 'sacrificial', then  $ED^+$ will, before and/or after desorption, undergo a facile, irreversible decomposition reaction, *i.e.* 

$$ED^+ \longrightarrow products.$$
 (6)

Of the well established sacrificial electron donors [such as EDTA, cysteine and triethanolamine (TEOA)], only EDTA appeared to be effective (see table 1) at this [H<sup>+</sup>] (pH 4.4) in promoting the photoreduction of methyl orange by the hole-scavenging reaction (5). However, it should be noted that these sacrificial donors are more commonly used at higher pH, *i.e.* pH  $\ge$  pK<sub>a</sub> of the electron donors for amine deprotonation [pK<sub>a</sub>: 6.26 (EDTA), 8.36 (cysteine) and 7.9 TEOA)],<sup>27</sup> since it is their deprotonated amine forms which appear to be most easily and irreversibly oxidised. In the cases of citrate, cysteine, tartrate and TEOA, the initial rates of photoreduction of methyl orange (table 1) were lower than when no electron donor (just water) was present. This most likely reflects their inability to act as irreversible sacrificial electron donors at this pH (pH 4.4) and, in addition, indicates their involvement as mediators in an indirect e<sup>-h+</sup> recombination reaction *via* their initial oxidation by a valence-band hole (h<sup>+</sup>), reaction(s), followed by reduction reaction

$$e^- + ED^+ \longrightarrow ED.$$
 (7)

The overall process [reactions (5) and (7)], represents the catalysis by the electron donor of an indirect  $e^{-h^+}$  recombination reaction which does not produce luminescence. Evidence for this process is provided by the results of Henglein,<sup>28</sup> which demonstrate that the fluorescence (owing to a direct  $e^{-h^+}$  recombination process) exhibited by colloidal CdS is quenched by a variety of anions including SO<sub>4</sub><sup>2-</sup>, SCN<sup>-</sup>, Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>, which are unable to act as 'good' sacrificial electron donors.

When PVA was used as an electron donor, the rate of photobleaching was extremely slow (see fig. 2). This is somewhat surprising since Darwent and Brown<sup>25</sup> were able to

## Semiconductor–Electrolyte Interfaces

use PVA at the same concentrations reported here as a sacrificial electron donor in the photoreduction of methyl orange using colloidal TiO<sub>2</sub>. However, the CdS particles are much bigger [particle diameter (CdS) =  $1.1 \mu m$ , whereas  $d(TiO_2) = 66 nm$ ] and the valence-band holes less oxidising  $[E_{VB} (CdS) = 1.5 V \text{ and } E_{VB} (TiO_2) \approx 2.6 V vs. SCE]$  than those of the TiO<sub>2</sub> colloid. Thus, the surface of the CdS particles may have a greater covering of PVA (lessening access/adsorption by the methyl orange to the semiconductor surface) and also may be unable to oxidise the PVA [encouraging photocorrosion of the CdS particles *via* reaction (4)]. Evidence for this last effect has been provided by Bard and White<sup>1</sup> in an electrochemical investigation of CdS suspensions in the presence of methyl viologen and a variety of electron donors, including PVA.

The high initial rate of methyl orange photoreduction obtained with acetate ions is an interesting result since, although capable of scavenging holes from the surface of  $TiO_2$ , Bard and his group<sup>1</sup> have found it to be poor at stabilising CdS against anodic corrosion [reaction (2)]. Its role in the photoreduction of methyl orange appears likely therefore to be one of mediating the photocorrosion reaction (4) and, as we shall see later, surprisingly, this also appears to be the role of EDTA.

Using an initial 10<sup>-2</sup> mol dm<sup>-3</sup> solution of sodium acetate and adjusting the acid concentration with concentrated (0.1 mol  $dm^{-3}$ ) solutions of NaOH and H<sub>2</sub>SO<sub>4</sub> a study was carried out of the initial rate of photoreduction of methyl orange  $(R_i)$  vs. pH (fig. 3). Above pH 7 no photobleaching of methyl orange was observed and this was attributed to the inability of the photogenerated electrons to reduce the deprotonated form of the semi-reduced dye ( $D^{2-}$ ) to the hydrazine derivative (II), since the pK<sub>a</sub> for this species is expected to be ca. 7.1.<sup>25</sup> As the pH was decreased from 7 the value of  $R_i$ was found to increase. It appeared that the conductance-band electrons of CdS were readily capable of reducing the unprotonated form of methyl orange (D<sup>-</sup>;  $pK_a = 3.5$ ) via the protonated form of the semi-reduced radical (DH<sup>-</sup>). This is hardly surprising since the conduction band potential of CdS (-0.88 V vs. SCE) is far more negative than that of methyl orange  $[E^{\circ}(D^{-}/DH_{2}^{-})] = -(0.058 \text{ pH}) vs. \text{ SCE}]^{29}$  Although there are conflicting reports in the literature<sup>30-32</sup> concerning the dependence of the conductance-band potential ( $E_{CB}$ ) of CdS upon pH, for all the reported values of  $E_{CB}$  (CdS), for pH < 7,  $E_{\rm CB}$  (CdS) < E (D<sup>-</sup>/DH<sup>-</sup>) and thus reduction of D<sup>-</sup> by a CdS conduction-band electron should be a spontaneous process. At acid concentrations below pH 3.5, the dye is in its protonated form (DH) which is more readily reduced than D<sup>-</sup>;<sup>25</sup> however, at and below pH 3.5 the protonated form of methyl orange starts to be adsorbed in a dark reaction onto the CdS particles. In addition, around this  $pH H_2S$ , from the acid corrosion reaction (8), is evolved<sup>27</sup>

$$\operatorname{CdS} + 2\mathrm{H}^{+} \underbrace{\Longrightarrow}_{\mathrm{p}K - -5.96} \operatorname{Cd}_{\mathrm{aq}}^{2+} + \mathrm{H}_{2}\mathrm{S}_{\mathrm{aq}}.$$
(8)

## The CdS/EDTA System

Several groups have used EDTA as a sacrificial electron donor in the photoreduction of water sensitised (poorly) by aqueous dispersions of CdS<sup>12, 33</sup> and [much more efficiently (ca. 20–50 times)] by plantinised CdS dispersions.<sup>12–15, 33</sup> From the work of Darwent *et al.*<sup>12, 15</sup> it would appear that even at pH 6.2 [at which a large fraction (> ca. 50%) of the EDTA molecules will have a deprotonated amine group] the EDTA is noticeably less than 100% efficient at preventing the photocorrosion of the CdS particles, *i.e.* reaction (2).

In our work we used methyl orange to probe the semiconductor-electrolyte interfacial reactions which occur upon illumination with ultra-band-gap irradiation of CdS powders dispersed in an aqueous solution containing EDTA at pH 4.4 and, in some cases,  $O_2$ . The role of the  $O_2$  was envisaged as that of a competitive inhibitor of the photoreduction



Fig. 3. Initial rate  $(R_1/10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1})$  for the photoreduction of methyl orange  $(3.5 \times 10^{-5} \text{ mol dm}^{-3})$  by CdS (2 mg cm<sup>-3</sup>,  $\lambda > 320 \text{ nm}$ ) as a function of pH. The photoreduction was carried out (under continuous nitrogen purging) in  $10^{-2}$  mol dm<sup>-3</sup> acetate buffer.

of methyl orange sensitised by the CdS particles. The overall reaction mechanism may be summarised as:  $h > F_{1}$  (a.t.  $h > F_{2}$ 

excitation: CdS 
$$\xrightarrow{h_{V \ge L_g}(2.4 \text{ eV})} h^+ + e^-; I_a$$
 (9)

recombination: 
$$h^+ + e^- \longrightarrow heat; k_R[h^+]$$
 (10)

oxygen reduction: 
$$e^- + O_2 \xrightarrow{} O_2^-; k_0[O_2][e^-]$$
 (11)

dye reduction: 
$$H^+ + e^- + D^- \longrightarrow DH^-$$
;  $k_d[D^-][e^-]$  (12)

hole scavenging: 
$$h^+ + EDTA \longrightarrow EDTA^+$$
;  $k_s[EDTA][h^+]$  (13)

lattice oxidation: 
$$2h^+ + CdS \longrightarrow Cd_{aq}^{2+} + S\downarrow; k_L[h^+].$$
 (14)

In the above scheme  $I_a$  (mol dm<sup>-3</sup> s<sup>-1</sup>) is the rate of photoabsorption by the CdS particles (2 mg cm<sup>-3</sup>) dispersed in 30 cm<sup>3</sup> solution contained in the thermostatted cylindrical quartz reaction cell (see the Experimental section). Although the CdS used was not intentionally doped and the concentration of carriers was probably low, it is still likely that in this n-type semiconducting material the number of majority carriers (e<sup>-</sup>) (the thermal electrons) would far outnumber the minority carriers (h<sup>+</sup>) and so electron-hole pair recombination would be expected to exhibit pseudo-first-order kinetics.

From time-resolved luminescence studies of colloidal CdS the lifetime of the photogenerated electron-hole pairs in the absence of any scavengers has been determined as  $0.3 \pm 0.2$  ns.<sup>34</sup> In order for the interfacial electron-transfer reactions [reactions (11)–(13)] to occur before recombination reaction (10), the reactants (X = O<sub>2</sub>, D<sup>-</sup> and EDTA) must be adsorbed onto the surface of the CdS. Despite continuing effort, the determination of the adsorption isotherms of these reactants on the surface of CdS has proved very difficult. As a result we have, like many others<sup>1, 21, 25</sup> using semiconductor powder or colloidal dispersions, made the assumption that for the reactants (X), referred to in reactions (11)–(13), the bulk and surface concentrations are related directly, *i.e.* 

$$[X]_{bulk} = K_{x}[X_{surface}]$$
(15)

as is the case for any Langmuir-type adsorption where the fraction of surface coverage

## Semiconductor–Electrolyte Interfaces

( $\theta$ ) is small (*i.e.*  $\theta < 0.1$ ). Thus in each of the rate equations for reactions (11)–(13) the reactant concentration term [X], (where  $X = O_2$ ,  $D^-$  and EDTA, respectively) refers to the bulk rather than to the surface concentrations. This assumption proves extremely useful when the steady-state equations are derived later on in this paper and the assumption appears to be borne out by the excellent fit of the experimental results with those predicted from the steady-state equations.

The results of Darwent and Brown<sup>25</sup> on the photoreduction of methyl orange by colloidal TiO<sub>2</sub> particles suggest that at pH 4.4, the rate-determining step for reduction of the unprotonated form of methyl orange  $(D^-)$  is the formation of the semi-reduced radical  $(DH^-)$  [*i.e.* reaction (12)] and, therefore, that the subsequent reactions which lead to hydrazine formation such as

$$DH^{-} + e^{-} + H^{+} \longrightarrow DH_{2}^{-}$$
(16)

$$2DH^{-} \longrightarrow DH_{2}^{-} + D^{-}$$
(17)

Continuous illumination of a suspension of CdS powder particles in an aqueous solution containing methyl orange,  $O_2$  and EDTA will lead to steady-state concentrations of holes (h<sup>+</sup>) and electrons (e<sup>-</sup>) where

$$[h^+]_{ss} = I_a / (k_R + k_s [EDTA] + k_L)$$
(18)

and

$$[e^{-}]_{ss} = (I_{a} - k_{R}[h^{+}])/(k_{0}[O_{2}] + k_{d}[D^{-}]).$$
(19)

The initial rate of photobleaching of methyl orange  $(R_i)$  will be given by

$$R_{\rm i} = k_{\rm d} [\rm D^-] [\rm e^-]_{\rm ss} \tag{20}$$

which, using eqn (18) and (19), can be reformulated as:

$$R_{\rm i} = \frac{k_{\rm d}[{\rm D}^-] I_{\rm a} k_{\rm s}[{\rm EDTA}]}{(k_{\rm 0}[{\rm O}_2] + k_{\rm d}[{\rm D}^-])(k_{\rm R} + k_{\rm s}[{\rm EDTA}] + k_{\rm L})}.$$
(21)

The above equation can be simplified further if the not too unreasonable assumption is made that h = h = 0 (22)

$$k_{\rm s}[{\rm EDTA}] \gg k_{\rm L}$$
 (22)

*i.e.* direct lattice oxidation by the photogenerated holes [reaction (14)] is suppressed by EDTA in the range of concentrations  $(5 \times 10^{-5} - 10^{-2} \text{ mol dm}^{-3})$  employed in this study. If the above condition holds then the reciprocal of the initial rate can be expressed as

$$\frac{1}{R_{\rm i}} = \frac{k_{\rm R} k_0 [O_2]}{I_{\rm a} k_{\rm d} [D^-] k_{\rm s} [{\rm EDTA}]} + \frac{k_{\rm R}}{I_{\rm a} k_{\rm s} [{\rm EDTA}]} + \frac{k_0 [O_2]}{I_{\rm a} k_{\rm d} [D^-]} + \frac{1}{I_{\rm a}}.$$
(23)

The above equation was tested extensively in a series of steady-state irradiations under conditions of different  $I_a$ ,  $[O_2]$ ,  $[D^-]$  and [EDTA]. The results of this work are as follows.

# (A) Anaerobic Conditions (i.e. $O_2$ -free)

(i)  $1/R_i$  vs. 1/[EDTA]. In a series of experiments, aqueous powder dispersions of CdS (2 mg cm<sup>-3</sup>; 30 cm<sup>3</sup> solution) containing: methyl orange  $(3.9 \times 10^{-5} \text{ mol dm}^{-3})$  and different concentrations of EDTA ( $5 \times 10^{-5}$  to  $5 \times 10^{-3}$  mol dm<sup>-3</sup>) at pH 4.4 were irradiated under anaerobic conditions and the initial rates of photobleaching of methyl orange ( $R_i$ ) were determined. Since the concentration of oxygen in solution is negligibly small, eqn (23) becomes

$$\frac{1}{R_{\rm i}} = \frac{k_{\rm R}}{I_{\rm a}k_{\rm s}[{\rm EDTA}]} + \frac{1}{I_{\rm a}}.$$
(24)

Fig. 4 illustrates that, as predicted from eqn (24), a plot of  $1/R_i vs. 1/[EDTA]$  yields a straight line of gradient m = 830 s and intercept  $c = 1.6 \times 10^7 \text{ dm}^3 \text{ mol}^{-1}$  s (correlation coefficient = 0.9997). The ratio of gradient and intercept is, according to eqn (24),

$$\frac{m}{c} = \frac{k_{\rm R}}{k_{\rm s}} \tag{25}$$

and from our experimentally determined values of m and c, this ratio is  $5.2 \times 10^{-5}$  mol dm<sup>-3</sup>. Thus the rate constant for hole scavenging by EDTA ( $k_s$ ) appears to be ca. 19000 times larger than that for the recombination reaction. In addition, since the actual quantum yield,  $\phi$ , of photobleaching of methyl orange by the CdS particles is by definition

$$\phi = \frac{R_{\rm i}}{I_{\rm a}} \tag{26}$$

it would appear that when concentrations of EDTA  $\geq ca$ .  $10^{-2}$  mol dm<sup>-3</sup> are employed then  $\phi \approx 1$ . Using monochromatic light ( $\lambda = 400 \pm 10$  nm), a formal quantum yield ( $= R_i/I_0$ ;  $I_0$  = incident, light intensity) of 0.003 was measured under the same experimental conditions. This formal quantum yield provided a lower limit of the actual quantum yield ( $\phi$ ), since in its calculation the assumption is made that all the photons reaching the sample are absorbed and no allowance is made for the considerable (>99% in this case) amount of light reflected and scattered by the particles as well as being absorbed by the methyl orange present. [In the measurement of the formal quantum yield, the methyl orange solution ( $3.9 \times 10^{-5}$  mol dm<sup>-3</sup>) had an absorbance (per cm) of *ca*. 0.5 at 400 nm and thus it will have absorbed (see fig. 1) an appreciable fraction (up to *ca*. 70%) of the incident ultra-band-gap radiation.]

(*ii*)  $R_i$  vs.  $[D^-]$ . The steady-state expression (23) implies that  $R_i$  should be independent of the methyl orange concentration  $[D^-]$  when no oxygen is present in the reaction mixture. This predicted invariance in  $R_i$  with respect to  $[D^-]$  arises from the limited number of reaction routes [reactions (10), (11) and (12)] in the proposed reaction scheme, eqn (9)-(14). Although it is possible for CdS particles to reduce water in the absence of a Pt catalyst (but in the presence of EDTA),<sup>15, 32</sup> *i.e.* 

$$2e^{-} + 2H^{+} \longrightarrow H_{2}$$
<sup>(27)</sup>

this reaction is extremely inefficient (formal quantum yield  $< 10^{-3}$ ) and some<sup>13</sup> have failed to observe it. As a result, we have omitted reaction (27) from the reaction scheme and the steady-state equations derived therefrom, thus making the assumption that any photogenerated electrons must react *via* pathways (10)–(12).

In order to test this assumption and eqn (23), a series of irradiations was carried out in N<sub>2</sub>-purged solutions (30 cm<sup>3</sup>) containing: CdS (2 mg cm<sup>-3</sup>), EDTA (10<sup>-2</sup> mol dm<sup>-3</sup>) and different concentrations of methyl orange [(1-6) × 10<sup>-5</sup> mol dm<sup>-3</sup>]. A filter solution of methyl orange [absorbance ( $\lambda = 463$  nm) > 2.0] was used in these experiments to ensure that the light intensity absorbed by the CdS particles was the same for all concentrations of methyl orange. Fig. 5 illustrates the variation of  $R_i$  with [D<sup>-</sup>], which is slight over the concentration range studied and suggests that the prediction made from eqn (23), and described above is correct.

(*iii*)  $R_i$  vs.  $I_a$ . Using the same experimental conditions as described in section [A(i)] with an EDTA concentration of  $10^{-2}$  mol dm<sup>-3</sup>, aqueous suspensions of CdS containing methyl orange were irradiated with light ( $\lambda > 400$  nm) of different intensity. A u.v. cut-off filter was used to remove light < 400 nm and variation of the incident light intensity ( $I_0$ ) was achieved using a series of neutral density filters (supplied by Balzers). It was assumed

## Semiconductor-Electrolyte Interfaces



Fig. 4. Reciprocal of the initial rate  $[(1/R_i)/10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}]$  for the photoreduction of methyl orange  $(3.9 \times 10^{-5} \text{ mol dm}^{-3})$  by CdS (2 mg cm<sup>-3</sup>),  $\lambda > 320 \text{ nm pH 4.4}$ , N<sub>2</sub>-purged solution) as a function of the reciprocal of the EDTA concentration  $[(1/[EDTA])/10^3 \text{ mol}^{-1} \text{ dm}^3]$ .



Fig. 5. Initial rate  $(R_1/10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1})$  for the photoreduction of methyl orange by CdS  $(2 \text{ mg cm}^{-3}, \lambda > 320 \text{ nm} \text{ as a function of dye concentration } ([D^-]/10^{-5} \text{ mol dm}^{-3})$  in EDTA  $(10^{-2} \text{ mol dm}^{-3})$  solution under N<sub>2</sub> purge. In this case a methyl orange filter [absorbance  $(\lambda = 463 \text{ nm}) > 2$ ] was incorporated into the steady-state irradiation system.

that the intensity of radiation absorbed by the CdS particles  $(I_a)$  and, therefore  $R_i$ , would be directly related to  $I_0$ . Thus a plot of  $R_i$  vs. relative light intensity [where  $I_0$  (*i.e.* no neutral density filter present) is arbitrarily set at 100%] should produce a straight line with a zero intercept. The experimental results did yield a very good straight line (8 points, correlation coefficient = 0.9996) with a gradient of  $6.8 \times 10^{-10}$  dm<sup>3</sup> mol<sup>-1</sup>, but with an extrapolated intercept of  $1.5 \times 10^{-8}$  mol dm<sup>-3</sup> s<sup>-1</sup>. Although stray light and/or a dark thermal reaction (*e.g.* dye adsorption onto the CdS particles) would provide a simple explanation for this non-zero intercept, blank experiments carried out in the dark did not fully confirm this interpretation.

(iv)  $R_i$  vs. [CdS]. Using the same conditions as described above (with the exception of a neutral density filter) aqueous suspensions of CdS of different concentration (0-6 mg cm<sup>-3</sup>) containing methyl orange and EDTA were irradiated with light  $\lambda > 400$  nm and the results are shown in fig. 6. The shape of the profile is very typical of many other profiles to be found in the literature<sup>13, 35</sup> illustrating the rate of a photochemical reaction vs. the semiconductor sensitiser concentration. From fig. 6 it is possible to estimate approximately the initial rate of photoreduction of methyl orange at infinite [CdS], *i.e.*  $R_{i\infty} = 1.37 \times 10^{-7}$  mol dm<sup>-3</sup> s<sup>-1</sup>. Interestingly, a plot of  $\log[R_{i\infty}/(R_{i\infty} - R_i)]$  vs. [CdS] (in mg cm<sup>-3</sup>) yields a gradient of 0.16±0.01 and an intercept of 0.04±0.04. This result suggests that the intensity of light absorbed by the CdS particles ( $I_a$ ) (which we have shown above to be directly related to  $R_i$ ) varies with [CdS] in a manner similar to that expressed by Beer's law, *i.e.* 

$$\log[I_0/(I_0 - I_a)] = Kc$$
(28)

where c is the concentration of the absorbing substance, assumed to be uniformly and finely dispersed. Other experiments, using a calibrated thermopile placed behind the quartz reaction vessel containing the CdS suspension showed that  $\log(I_0/I_T)$  was not directly proportional to [CdS], although using neutral density filters,  $I_T$  was found to be proportional to  $I_0$  for fixed [CdS].

# (B) Oxygen-saturated Conditions

(i)  $1/R_i$  vs.  $1/[D^-]$ . In a series of experiments, identical to those described in section [A(ii)] with the exception that in this work the solutions were oxygen-saturated, the initial rate of photoreduction  $(R_i)$  of methyl orange  $(D^-)$  by the CdS particles was determined as a function of its concentration. A plot of  $1/R_i$  vs.  $1/[D^-]$  is illustrated in fig. 7 from which a gradient  $m = 7.1 \times 10^2$  s, an intercept  $c = 2.2 \times 10^7$  dm<sup>3</sup> mol<sup>-1</sup> s, and a correlation coefficient of 0.9987 were determined. From (23), the ratio (m/c) should be

$$\frac{m}{c} = \frac{k_0[O_2]}{k_d}.$$
(29)

Thus from our experimental results

$$\frac{k_{\rm ol}O_2}{k_{\rm d}} = 3.2 \times 10^{-5} \,\mathrm{mol}\,\mathrm{dm}^{-3} \tag{30}$$

and since  $[O_2] = 1.3 \times 10^{-3}$  mol dm<sup>-3</sup>, the ratio  $k_0/k_d$  would appear to be  $2.5 \times 10^{-2}$ , *i.e.* the rate constant for  $O_2$  reduction is *ca*. 40 times smaller than that for methyl orange reduction. Eqn (23) also predicts that  $c (2.2 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s})$  should be the same value as found at high  $[D^-]$  in section [A(ii)]. From fig. 5 we can estimate c to be *ca*.  $2.4 \times 10^7 \text{ dm}^3 \text{ mol}^{-1}$  s the inverse of the initial rate  $(1/R_i)$  and this value is in close agreement with that reported above.

(*ii*)  $1/R_i$  vs. percentage  $O_2$ . Using the same experimental conditions as described above (with  $[D^-] = 3.9 \times 10^{-5}$  mol dm<sup>-3</sup>), a series of dispersions of CdS in aqueous solution containing methyl orange, EDTA and different concentrations of oxygen (0-100%, where  $100\% = 1.3 \times 10^{-3}$  mol dm<sup>-3</sup>), were irradiated. A plot of  $1/R_i$  vs. percentage  $O_2$  yielded a very good straight line (5 points, r = 0.9991) with a slope of  $9.1 \times 10^4$  dm<sup>3</sup> mol<sup>-1</sup> s (%  $O_2$ )<sup>-1</sup> and an intercept of  $1.3 \times 10^7$  dm<sup>3</sup> mol<sup>-1</sup> s. According to eqn (23) from the ratio of these values for the gradient and intercept a second estimate {see section [B(i)]} of the ratio  $k_0/k_d$  can be obtained. Calculations show this to be  $2.1 \times 10^{-2}$ , which compares favourably with the value of  $2.5 \times 10^{-2}$  calculated in the previous section. The implication that electron transfer to methyl orange is much greater than that to  $O_2$  is not surprising, especially in the light of the recent work of Darwent and his group<sup>25</sup> involving a timeresolved study of the photoreduction of  $O_2$  and methyl orange by TiO<sub>2</sub> colloids. These



Fig. 6. Initial rate  $(R_i/10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1})$  for the photoreduction of methyl orange  $(3.9 \times 10^{-5} \text{ mol dm}^{-3})$  by CdS as a function of semiconductor concentration ([CdS]/mg cm<sup>-3</sup>). The reaction was carried out in  $10^{-2}$  mol dm<sup>-3</sup> EDTA, pH 4.4, N<sub>2</sub>-purged solution and with visible light,  $\lambda > 400$  nm.



Fig. 7. Reciprocal of the initial rate  $[(1/R_i)/10^7 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}]$  for the photoreduction of methyl orange by CdS (2 mg cm<sup>-3</sup>, pH 4.4,  $\lambda > 320 \text{ nm}$ ), as a function of the reciprocal of the dye concentration  $[(1/[D^-])/10^4 \text{ dm}^3 \text{ mol}^{-1}]$  in O<sub>2</sub>-saturated solution with [EDTA] =  $10^{-2} \text{ mol} \text{ dm}^{-3}$ . In this case a methyl orange filter [absorbance ( $\lambda = 463 \text{ nm}$ ) > 2] was incorporated into the steady-state irradiation system.

workers determined, via microsecond flash photolysis, the bimolecular rate constants for electron transfer from the TiO<sub>2</sub> particles to HD (*i.e.* the protonated form of methyl orange) and O<sub>2</sub> to be  $8.3 \times 10^7 [\text{H}^+]^{-0.38}$  (dm<sup>3</sup> mol<sup>-1</sup>)<sup>-0.38</sup> s<sup>-1</sup> and  $5.5 \times 10^3 [\text{H}^+]^{-0.42}$  (dm<sup>3</sup> mol<sup>-1</sup>)<sup>-0.42</sup> s<sup>-1</sup>, respectively. At pH 4.4 the ratio  $k_d/k_0$  (for TiO<sub>2</sub> colloids) is  $ca. 9 \times 10^3$  (mol dm<sup>-3</sup>)<sup>0.05</sup>, *i.e.* reduction of the protonated form of methyl orange is much faster than O<sub>2</sub> reduction. Interestingly, at this pH,  $E_{CB}(TiO_2) \approx -0.380$  V vs. SCE, which is much less reducing than that for CdS [ $E_{CB}(CdS) = -0.9$  V vs. SCE] and yet the ratio of  $k_d/k_0$  is much smaller (ca. 40–50 times) for the latter. However, since  $E_{CB}(CdS)$  is so much more reducing than  $E_{CB}(TiO_2)$  it is quite likely that at the [H<sup>+</sup>] of our experiments,

*i.e.* pH 4.4, the rate-determining step for photobleaching of methyl orange is electron transfer to its deprotonated form [as indicated in reaction (12)] and not to its protonated form as found for  $TiO_2$ .<sup>21</sup> Under these circumstances it might be expected that the two ratios for  $k_d/k_0$  might differ considerably.

# (C) Corrosion Studies

Irradiation of an N<sub>2</sub>-purged aqueous powder dispersion of CdS (2 mg cm<sup>-3</sup>) containing methyl orange  $(3.9 \times 10^{-5} \text{ mol dm}^{-3})$  and without EDTA led to a release of Cd<sup>2+</sup><sub>aq</sub> ions into solutions at two markedly different rates (fig. 8). In the absence of ultra-band-gap irradiation, the Cd<sup>2+</sup><sub>aq</sub> levels in solution (as determined by atomic absorption spectroscopy) remained constant. The observation of low levels of Cd<sup>2+</sup><sub>aq</sub> ions (*ca.* 1.2 ppm, *i.e. ca.*  $1.1 \times 10^{-5}$  mol dm<sup>-3</sup>) in solution at this pH (4.4) cannot be attributed solely to acidic corrosion [reaction (8)] since this would produce Cd<sup>2+</sup><sub>aq</sub> levels of *ca.*  $4.2 \times 10^{-8}$  mol dm<sup>-3</sup> (assuming [Cd<sup>2+</sup><sub>aq</sub>]  $\approx$  [H<sub>2</sub>S<sub>aq</sub>]). Instead it appears to be more likely that the Cd<sup>2+</sup><sub>aq</sub> levels detected are due to CdS particles < 0.2  $\mu$ m passing through the membrane filter employed to remove all the CdS particles when sampling the irradiated solution (see Experimental section).

When EDTA ( $10^{-2}$  mol dm<sup>-3</sup>) was present the background Cd<sup>2+</sup><sub>aq</sub> levels (as measured by AAS) appeared to increase almost twofold. Once again some of this (*ca.* 1.2 ppm) was probably due to < 0.2  $\mu$ m CdS particles passing through the membrane filter and the rest due to a combination of reaction (8) and the following complexation reaction

$$\operatorname{Cd}_{\operatorname{aq}}^{2+} + \operatorname{EDTA}^{4-} \xleftarrow{K} [\operatorname{Cd}(\operatorname{EDTA})^{2-}]$$
 (31)

where  $K \approx 9.9 \times 10^8$  at pH 4.4.

In the absence of EDTA the initial rate of photocorrosion  $[R_i(Cd_{aq}^{2+})]$  was found to be  $3.1 \times 10^{-8}$  mol dm<sup>-3</sup>  $(Cd_{aq}^{2+})$  s<sup>-1</sup> and the initial rate of photobleaching of methyl orange  $(R_i)$  was determined as  $2.7 \times 10^{-8}$  mol dm<sup>-3</sup> s<sup>-1</sup> (see table 1), thus the ratio of these two  $[R_i(Cd_{aq}^{2+})/R_i] = 1.2$ . In the presence of EDTA  $(10^{-2} \text{ mol dm}^{-3})$ ,  $R_i(Cd_{aq}^{2+}) = 6.8 \times 10^{-8}$  mol dm<sup>-3</sup>  $(Cd_{aq}^{2+})$  s<sup>-1</sup> and  $R_i = 7 \times 10^{-8}$  mol dm<sup>-3</sup> s<sup>-1</sup>, thus the ratio is 0.97. It would appear, therefore, that for every methyl orange molecule reduced (which requires 2e<sup>-</sup>) a CdS molecule is oxidised to Cd\_{aq}^{2+} and an S species (which requires 2 h<sup>+</sup>). This would imply that EDTA, although a good hole-scavenger [reaction (13)], once oxidised reacts subsequently with the CdS, *i.e.* 

$$2EDTA^{+} + CdS \longrightarrow 2EDTA + Cd_{ad}^{2+} + S\downarrow$$
(32)

rather than undergoing irreversible decomposition [reaction (6)] to glyoxylic acid and ethylenediamine-N,N'-diacetic acid.<sup>36</sup>

The above result is not surprising in the light of work by Bard and Wrighton,<sup>37</sup> pointing out that the standard potential for anodic dissolution  $(E_D^{\circ})$  for CdS [reaction (14)] is 0.08 V vs. SCE and that an electron donor (ED) can quench the photoanodic dissolution of CdS by competitive hole capture if its redox potential [E(ED<sup>+</sup>/ED)] lies at a potential more negative than  $E_{VB}$ (CdS) (=1.5 V vs. SCE). However, for an ideal electron donor, the oxidation product (ED<sup>+</sup>) must be incapable of oxidising the semiconductor, *i.e.*  $E(ED^+/ED)$  must be more negative than  $E_D^{\circ}$ (CdS). When we look at the standard redox potential for EDTA [McLendon and Miller report<sup>38</sup> it to be pH dependent, varying from -0.12 V at pH 9 to 0.21 V at pH 2 (vs. SCE)], which we estimate, using the above data, to be ca. 0.16 V vs. SCE at pH 4.4, it would appear that EDTA is not a 'good' sacrificial electron donor at this pH since its oxidised form (ED<sup>+</sup>) would be capable of subsequently oxidising CdS; however, this may not be the case at higher pH. At pH 4.4, the oxidation of CdS by EDTA<sup>+</sup>[*i.e.* eqn (32)] is thermodynamically feasible and from our experimental

2659



**Fig. 8.** A plot of the concentration of  $Cd^{2+}$  ions liberated into solution {[ $Cd^{2+}$ ](ppm)} as a function of irradiation time. [The time range is that for almost complete photoreduction of the dye when EDTA ( $10^{-2}$  mol dm<sup>-3</sup>) is present.] The reaction conditions were as follows: [CdS] = 2 mg cm<sup>-3</sup>, pH 4.4, [methyl orange] =  $3.9 \times 10^{-5}$  mol dm<sup>-3</sup>, N<sub>2</sub>-purged solution,  $\lambda > 400$  nm. (a) Shows the corrosion of CdS in EDTA ( $10^{-2}$  mol dm<sup>-3</sup>) solution, while (b) shows the subsequent corrosion of CdS in water.

results it would appear that this reaction is the preferred route for EDTA<sup>+</sup> removal and not irreversible decomposition [reaction (6)]. Interestingly, earlier work by Harbour and Hair,<sup>13</sup> using aqueous suspensions of platinised CdS powder particles in the presence of EDTA to photoreduce water, investigated the variation of the rate of hydrogen production as a function of pH. At pH 4–5 these workers found a definite minimum in the rate of H<sub>2</sub> production with respect to other pH. Darwent and Porter<sup>12</sup> have also carried out work on this system and they report (at pH 6.2) that a turnover number of 3 for CdS could be obtained. However, they also observed that the rate of hydrogen production had diminished appreciably, although only < 12% of the EDTA (mainly in its amine deprotonated form) had been consumed. Both these pieces of work help to support our findings which indicate that EDTA does not, as is usually envisaged, act as an 'ideal' sacrificial electron donor in the presence of CdS, but rather mediates the anodic corrosion of CdS, particularly at pH  $\ll$  6.

#### Conclusions

In this paper, we have shown that CdS suspensions can be used to sensitise the photoreduction of methyl orange (D<sup>-</sup>) at pH < 7 in the presence and absence of a variety of electron donors including EDTA. By making the assumption that steady-state concentrations of conductance-band electrons (e<sup>-</sup>) and valence-band holes (h<sup>+</sup>) would be set up within the CdS particles upon illumination it proved possible to develop a kinetic equation which described very successfully the observed behaviour of the initial rate of photoreduction of methyl orange as a function of the concentrations of methyl orange, photons, EDTA and O<sub>2</sub> (when present). Further work is now in progress to ascertain if the steady-state approach to a semiconductor powder and colloid sensitised photoreaction has a greater, more general application.

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