# Semiconductor Photocatalysis:<sup>†</sup> Visible Light Induced Photoreduction of Aromatic Ketones and Electron-deficient Alkenes catalysed by Quantised Cadmium Sulfide

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Colloidal CdS suspensions (CdS-0) prepared at 0 °C from methanolic Cd(ClO<sub>4</sub>)<sub>2</sub> and Na<sub>2</sub>S solutions consist of quantised CdS microcrystallites (2–5 nm) and their loose aggregates, which catalyse the effective photoreduction of aromatic ketones and electron-deficient alkenes with triethylamine as electron donor. Under visible light induced photolysis, the methanolic CdS-0 suspension becomes brown owing to the reduction of lattice Cd<sup>2+</sup> to Cd<sup>0</sup>, leading to the effective formation of alcohols from ketones, and dihydro compounds from alkenes. With the reduction potential < -1.56 V vs. standard calomel electrode (SCE), ketones were partly photoreduced to pinacols in methanol. Compared with highly pure bulk CdS (CdS-Ald), CdS-0 is more effective for photoreduction because of the size quantisation effect. The presence of an excess of sulfide ion (S<sup>2–</sup>) in the CdS-0 system, however, suppresses the formation of lattice Cd<sup>0</sup>, inducing one-electron transfer photoreductions which result in the exclusive formation of pinacols and 1,2,3,4-tetra(methoxycarbonyl)butane from the respective ketones and dimethyl maleate. The relationship between the two-electron reductions and photogenerated lattice Cd<sup>0</sup> is discussed in terms of the regulation of semiconductor photocatalysis.

Photocatalytic reactions in semiconductor particulate systems are interesting from the viewpoint of utilisation of solar light energy, for example organic photosynthesis.<sup>1-5</sup> The construction of multi-electron-transfer photoreduction systems has been requested, and systems with quantised semiconductor particles deserve much attention from this point of view.<sup>6-11</sup> We recently reported that quantised ZnS microcrystallites and their aggregates catalyse quantitatively two-electron photoreduction of CO<sub>2</sub> and aliphatic ketones to formate and alcohols, respectively, and the size-quantisation effect contributes to the effective two-electron transfer reduction.<sup>12,13</sup>

Recently, much attention has been paid to the understanding of semiconductor photocatalysis at a molecular and atomic level. In fact, the heterogeneous transformation depends crucially on the formation of catalytic sites on irradiated semiconductor surfaces. Some studies in this vein have been reported recently involving the photoisomerisation and photohydrogenation of alkenes using semiconductors. For example, the photoformed O<sup>-</sup> and Ti<sup>3+</sup>-O<sup>-</sup> pairs were suggested to play significant roles as catalytic sites in the photoisomerisation of but-2-enes with  $TiO_2$ .<sup>14</sup> In addition, the photoformed  $e^{-}(Ti^{3+} \text{ or } H)-h^{+}(OH)$  pairs were reported to play a decisive role in the hydrogenation of alkenes and alkynes with TiO<sub>2</sub>.<sup>15</sup> In a series of our studies on ZnS photocatalysis, it was clarified that the disulfide ions  $(S_2^{2-})$  in the microcrystallite lattice, which must be incorporated during the preparation or the irradiation, should form catalytic sites for the cis-trans photoisomerisation of alkenes.<sup>16</sup>

Recently, we reported that freshly prepared colloidal CdS suspensions (CdS-0) catalyse sequential two-electron photoreduction of aromatic ketones and alkenes, producing, respectively, alcohols and dihydro compounds, and that commercially available CdS powder (Aldrich) (CdS-Ald) induces one-electron transfer to these substrates, giving the same products possibly through a disproportionation mechanism.<sup>17,18</sup> On the other hand, Gutiérrez and Henglein<sup>19</sup> previously reported the coloration of quantised CdS particles in water when irradiated with sulfite ion as electron donor. They ascribed it to the deposition of cadmium metal, discussing the catalytic action of the cadmium layer for the photoevolution of H<sub>2</sub>. Interestingly, we also observed a similar phenomenon in the photoreduction of organic substrates using CdS-0 as photocatalyst and triethylamine (TEA) as electron donor. The present report deals with the complex photoreduction of organic substrates catalysed by methanolic CdS-0 suspensions and dramatic regulation of products by photoformed Cd<sup>0</sup> on CdS-0 in the photocatalysis.

# Experimental

# Materials

Ketones were obtained from the following sources: benzophenone [guaranteed reagent (GR) grade] and acetophenone (GR grade) from Nacalai Tesque, 4,4'-dichlorobenzophenone (GR grade) from Wako Pure Chemical Industries, p-chlorobenzophenone (GR grade) from Tokyo Kasei, p-methoxybenzophenone (GR grade) and 4,4'-dimethoxybenzophenone (GR grade) from Aldrich. Dimethyl maleate, dimethyl fumarate and methyl cinnamate were GR grade of Tokyo Kasei. Bis(trimethylsilyl)sulfide was prepared from sulfur according to the literature.<sup>20</sup> p-Cyanocinnamonitrile was prepared and purified according to the literature.<sup>21</sup> Methyl viologen dichloride was GR grade of Nacalai Tesque. Amines were obtained from the following sources: TEA (GR grade), diethylamine (GR grade) and n-propylamine (GR grade) from Wako Pure Chemical Industries, 2-diethylaminoethanol (GR grade) and N,N-dimethylaniline (GR grade) from Nacalai Tesque, N-ethyldiethanolamine (GR grade) from Tokyo Kasei. Liquid amines were purified by fractional distillation before use. Sodium sulfide (GR grade of Nacalai Tesque) and cadmium perchlorate (GR grade of Mitsuwa) were used as delivered. Highly pure (99.999%) CdS powder was obtained from Aldrich (CdS-Ald) and Furuuchi (CdS-Furu). The crystal form of both CdS-Ald and CdS-Furu was hexagonal, and the average particle sizes of CdS-Ald and CdS-Furu were 1.5 µm and 2.5 µm, respectively.

<sup>&</sup>lt;sup>†</sup> Part 10: T. Shiragami, C. Pac and S. Yanagida, J. Phys. Chem., 1990, 94, 504.

#### Analysis

Analysis of alkenes and diethylamine was carried out by gas chromatography using a Shimadzu GC-12A apparatus equipped with a flame ionisation detector, and a Shimadzu capillary column (25 m  $\times$  0.2 mm) of OV-1 for alkenes and a 2 m  $\times$  3 mm column of ASC-L for diethylamine. As internal standard chemicals, methyl benzoate, methyl myristate and propan-2-ol were used. Analysis of ketones, alcohols and pinacols was carried out by liquid chromatography using a Cosmosil-ODS column and a UV detector (at 230 nm) (Tosoh; UV-8000). As eluent, a mixture of methanol and buffered aqueous solution (KH<sub>2</sub>PO<sub>4</sub>-NaOH; pH = 7) (6:4 mixture) was employed with an eluent rate of 0.5 cm<sup>3</sup> min<sup>-1</sup>. 1,2,3,4-Tetra(methoxycarbonyl)butane (**6a**) was identified with the authentic sample prepared from butane-1,2,3,4-tetracarboxylic acid.

High-resolution images were obtained with a Hitachi H-9000 transmission electron microscope (TEM) equipped with a tilting device  $(+10^{\circ})$  and operating at 300 kV (cs = 0.9 mm). Images were recorded under axial illumination at approximate Scherzer focus, with a point resolution better than 0.19 nm. The CdS-0 suspensions were deposited on carbon film on copper mesh.

Absorption spectra of CdS suspensions were obtained after diluting to a tenth of the suspension concentration.

# Preparation of the CdS-0 Photocatalyst

As reported in a previous paper,<sup>17</sup> CdS-0 suspensions were prepared *in situ* under an argon atmosphere by mixing equal quantities of methanolic solutions  $(2.5 \times 10^{-2} \text{ mol dm}^{-3})$  of Cd(ClO<sub>4</sub>)<sub>2</sub> and Na<sub>2</sub>S with magnetic stirring and cooling with ice and water.

# CdS-catalysed Photoreduction of Ketones and Alkenes

A stirred methanol suspension containing CdS powder (70  $\mu$ mol) or CdS-0 (13  $\mu$ mol), a ketone (2 mmol dm<sup>-3</sup>) or an alkene (10 mmol dm<sup>-3</sup>) and TEA (1 mol dm<sup>-3</sup>) was flushed with argon gas and cooled using an ice bath. The container was then closed with a rubber stopper and irradiated with a 300 W tungsten-halogen lamp through an aqueous sodium nitrite solution filter (>400 nm).

#### Preparation and Photoreactions of CdS-0-Cd

CdS-0 suspensions were prepared in a Pyrex tube and irradiated in the presence of TEA for 1 h as mentioned above. To the coloured suspension in the tube was added a prescribed quantity of ketones or alkenes and the mixture was irradiated in the same way as described above.

#### **Deuterium Incorporation Experiments**

Deuterium incorporation experiments were performed during photoreduction of dimethyl maleate in MeOD as mentioned above. When 40% of the substrate disappeared, the irradiation was stopped and the deuterium isotopic distribution for the substrate and the products was determined by GC-mass spectrometry.

# Determination of the Amount of Cd<sup>0</sup>

The formation of  $Cd^0$  was determined by the method of Gutiérrez and Henglein<sup>19</sup> as follows; the irradiated suspension (50 mm<sup>3</sup>) was added to a 1 mmol dm<sup>-3</sup> methanolic solution of methyl viologen under an argon atmosphere. The blue colour of the methyl viologen radical cation (MV<sup>++</sup>) was

immediately analysed by spectrophotometry at 606 nm ( $\varepsilon$  of MV<sup>++</sup> is 13 700 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>).<sup>22</sup>

# **Results and Discussion**

# CdS-catalysed Photoreduction of Aromatic Ketones and Electron-deficient Alkenes by TEA under Visible Light Irradiation

As reported in the previous paper,<sup>17</sup> freshly prepared colloidal CdS suspensions (CdS-0) and commercially available bulk CdS (CdS-Ald) catalyse the photoreduction of some aromatic ketones and alkenes in the presence of TEA as electron donor under visible light irradiation in methanol as shown in Scheme 1 and Table 1.

Compared with commercially available bulk CdS (CdS-Ald), CdS-0 is more effective and selective for the formation of alcohols (2a-2e) and dihydro compounds (5a-5d). Note that the production of pinacols (3) tends to increase with the negative shift of the reduction potentials of the ketones. The CdS-0 suspension is very effective for the photoreduction of 1a-1g whose reduction potentials range from -1.17 to -2.00 V vs. SCE in methanol. However, acetophenone (1g) with a reduction potential of -2.00 V vs. SCE was converted exclusively to the pinacol (3g), while no reduction was observed in the bulk CdS-Ald system. These results may be rationalised as due to the negative shift of the conduction band potential of CdS-0 particles arising from the size-quantisation effect.

# Effect of Electron Donors on Photocatalysis of Quantised CdS-0

In Table 2 are summarised the results for the CdS-0-catalysed photoreduction of benzophenone (1d) and dimethyl fumarate (4b) using various amines as electron donor in methanol. TEA was the best sacrificial electron donor for the CdS-catalysed reductions. Ethanolamine derivatives, whose structures are similar to that of TEA, also work fairly well as electron donor and the coloration of CdS-0 was also recognised (see following sections). However, other amines did not work as electron donors. This also held true for photolysis with bulk hexagonal CdS-Ald. Recently, Meissner *et al.*<sup>23</sup> reported that the flat band potential of the bulk hexagonal CdS is -1.80 V vs. SCE. This value agrees closely with the threshold value for the reduction potential of the substrates, which are reducible with the photoexcited CdS-Ald as shown in Table 1; the ketones and alkenes whose reduction potential

	R <sup>1</sup>	R <sup>2</sup>		R <sup>3</sup>	R⁴
1a	p-CNC <sub>6</sub> H <sub>4</sub>	С,Н,	<b>4</b> a	CO <sub>2</sub> CH <sub>3</sub>	CO <sub>2</sub> CH <sub>3</sub> (cis)
1b	p-ClC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H,	<b>4b</b>	CO <sub>2</sub> CH <sub>3</sub>	CO2CH3(trans)
1c	p-ClC <sub>6</sub> H <sub>4</sub>	p-ClC <sub>6</sub> H <sub>4</sub>	4c	p-CNC <sub>6</sub> H <sub>4</sub>	CN(cis)
1 d	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	4d	p-CNC <sub>6</sub> H <sub>4</sub>	CN(trans)
le	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	$C_6H_5$	4e	p-CNC <sub>6</sub> H,	$CO_2CH_3(cis)$
lf 🗌	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	4f	p-CNC <sub>6</sub> H,	$CO_2CH_3(trans)$
lg	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	4g	C <sub>6</sub> H <sub>5</sub>	$CO_2CH_3(trans)$

Scheme 1

				yield (%) <sup>c</sup>						
	$-E^{\rm red}_{1/2}/{ m V}^b$	conversion (%)		2		3		5		
substrate		CdS-0	CdS-Ald	CdS-0	CdS-Ald	CdS-0	CdS-Ald	CdS-0	CdS-Ald	
lad	1.17	100	100	95	90	0	0			
1b	1.32	98	95	70	15	12	75			
1c	1.35	98	98	90	4	4	90			
1d	1.55	100	100	95	5	5	90			
le	1.56	97	98	33	3	56	66			
1f	1.56	52	10	15	0	40	trace			
1g	2.00	10	0	trace	0	80	0			
4a <sup>d</sup>	1.56	100	100					70	20	
<b>4b</b> <sup>d</sup>	1.60	100	100					60	10	
4c	1.75	70	98					47	42	
<b>4d</b>	1.73	68	95					41	26	
<b>4</b> e	1.75	100	100					76	53	
4f	1.75	100	100					92	57	
4g	1.98	10	0					trace	0	

 Table 1
 CdS-catalysed photoreduction of ketones and alkenes with TEA in MeOH<sup>a</sup>

<sup>a</sup> Irradiated in MeOH at >400 nm for 3 h. <sup>b</sup> Polarographic half-wave reduction potentials vs. SCE in MeOH. <sup>c</sup> Yields are based on the substrate converted. Unknown products were detected. <sup>d</sup> Irradiated at 400 nm for 2 h.

tials are less negative than -1.75 V vs. SCE were photoreducible. The valence-band potential of bulk CdS was estimated to be 0.65 V vs. SCE on the basis of the band gap of bulk CdS,  $E_g = 2.45$  eV.<sup>24</sup> This value is almost equal to the oxidation potential of TEA but less than those of diethylamine and dipropylamine. Taking into account the effective band gap of CdS-0, 3.0 eV, the valence-band potential should become more favourable for the oxidation of TEA but still not for oxidations of diethylamine and dipropylamine (see Table 2). The generally accepted energetics of CdS ( $E_{fb} = -1.0$  V vs. SCE and  $E_g = 2.45$  eV) cannot rationalise the effect observed for the electron donors.

Note, however, that N,N-dimethylaniline (DMA), whose oxidation potential is more negative than that of TEA, could not be a sacrificial electron donor at all. This result may be explained as due to the rapid back electron transfer of the conduction-band electron to the stable radical cation once formed from DMA. Thus, it seems conceivable that the formation of the radical cation, which may undergo rapid further oxidation to  $[(Et)_2N=CHCH_3]^+$  through deprotonation, should be an important factor in determining effective electron donors.

Analysis of the oxidation products from TEA revealed that only diethylamine (DEA) was detected during the photocatalysis. As reported, the formation of DEA can be explained by hydrolysis of the iminium intermediate  $[(Et)_2N=CHCH_3]^{+,17,25}$  In the CdS-0-catalysed photolysis of benzophenone, however, the quantity of DEA formed was

 Table 2
 CdS-0-catalysed
 photoreduction
 of
 benzophenone
 and

 dimethyl fumarate in the presence of various amines<sup>a</sup>
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		conversi	on (%)	yield (%) <sup>c</sup>		
amine	$E_{p}^{\mathrm{ox}}/\mathrm{V}^{b}$	1d	4b	2d	5b	
Et <sub>3</sub> N	0.69	100	100	95	70	
Et,NCH,CH,OH		50	60	80	24	
EtN(CH,CH,OH),		38	67	90	26	
Et <sub>2</sub> NH	0.90	0	0	0	0	
n-Pr,NH	0.90	0	0	0	0	
Ph <sub>3</sub> N	0.87 <sup>d</sup>	0	0	0	0	
DĂĂ	0.54	0	0	0	0	

<sup>*a*</sup> Irradiated in MeOH containing amine (0.5 mol dm<sup>-3</sup>) at >400 nm for 6 h. <sup>*b*</sup> Voltammetric oxidation peak potentials vs. SCE in H<sub>2</sub>O. <sup>*c*</sup> See ref. 2. <sup>*d*</sup> In MeCN. <sup>*e*</sup> N,N-dimethylaniline.

greater than that of the reduction product 2d, while the CdS-Ald-catalysed photolysis of benzophenone gave stoichiometric DEA formation. The reason for the discrepancy in the electron balance in the CdS-0 system is not clear at present.<sup>†</sup>

### Physical and Spectral Properties of CdS-0

Analysis with a high-resolution transmission electron microscope (Fig. 1) revealed that methanolic CdS-0 suspensions consist of very small crystallites whose sizes range from 2 to 5 nm in diameter. In addition, each crystallite was shown to have a cubic structure based on analysis of the lattice fringe.

Fig. 2 shows UV-VIS absorption spectra of some CdS-0 suspensions. They were measured after diluting the suspensions prepared for photolysis to a tenth of their original concentration. The absorption spectrum of fresh CdS-0 shows a



Fig. 1 Transmission electron micrograph of CdS-0; Magnification 4 500 000  $\times$ 

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<sup>&</sup>lt;sup>†</sup> Neither H<sub>2</sub> due to the reduction of water nor ethanol due to the reduction of the photoformed acetaldehyde<sup>25c</sup> were detected. Ethene, which may be formed by the decomposition of the intermediary iminium salt, and its reduction product, ethane, were not detected during the photolysis. The electrons consumed for the formation of Cd<sup>0</sup> in the lattice were almost negligible in quantity (0.3 µmol).



Fig. 2 Absorption spectra of CdS-0 suspensions; (——) before irradiation, (-–-) after irradiation in the presence of TEA, (·—·—) after the irradiation and the addition of  $MV^{2+}$ , (·-·--) after bubbling of oxygen

sharp onset at a shorter wavelength than that observed for bulk CdS (the onset wavelength is around 550 nm),<sup>18</sup> which is quite comparable with the reported value for the quantised CdS whose particle size is 5.4 nm.<sup>26</sup>

These observations suggest that size-quantisation effects should be operative in CdS-0 photocatalysis as well as in ZnS-0 photocatalysis.<sup>13</sup>

# Photochemical Properties of CdS-0

Upon visible light irradiation, the CdS-0 suspension became increasingly brown in the presence of TEA. Because of the brown coloration, the absorption increased at longer wavelengths as shown in Fig. 2. However, the original yellow colour was restored when  $O_2$  was introduced to the brown CdS-0 suspension. The fact that the onset of its absorption spectrum shifts only to slightly longer wavelengths than that of the starting one suggests that no remarkable change in the size of CdS-0 particles is caused by irradiation in the presence of TEA and by the coloration and decoloration.

When methyl viologen  $(MV^{2^+})$  was added to the irradiated CdS-0 under an argon atmosphere, the solution became blue. The spectrum of this blue solution shown in Fig. 2 is identical to that of the methyl viologen radical cation  $(MV^{*+})$ . With these observations, we have confirmed that the coloured CdS-0 suspensions (CdS-0-Cd) are very similar to those obtained by irradiation of quantised CdS in the presence of sulfite ions in water.<sup>19</sup> Henglein and his group explained this as due to the Cd metal photodeposited on quantised CdS.

On the other hand, we have found that irradiation of the methanolic CdS-0-TEA solution did not cause any such coloration in the presence of excess  $S^{2-}$  (2.5 × 10<sup>-3</sup> mol dm<sup>-3</sup>). As expected,  $MV^{2+}$  was not reduced to  $MV^{+}$  by the resulting solution.

### Photocatalysis of Coloured CdS-0 Suspensions

Coloured CdS-0 suspensions (CdS-0–Cd) are easily prepared by pre-irradiation of CdS-0 suspensions for 1 h in the presence of TEA. The abbreviation CdS-0–Cd means that  $Cd^0$ metal has already been deposited on CdS-0 suspensions before the photocatalytic reactions with organic substrates are carried out. Fig. 3 shows time-conversion plots for the photolyses of benzophenone (1d) catalysed by CdS-0 and



Fig. 3 Time-conversion plots for photoreduction of benzophenone catalysed (a) by CdS-0, (b) by CdS-0-Cd: ( $\bigcirc$ ) benzophenone (1d), ( $\bigcirc$ ) benzhydrol (2d)

CdS-0-Cd. In the CdS-0 system, the induction period was recognised from the increasing formation of the alcohol 2d, whereas in the CdS-0-Cd system, 2d was formed efficiently without such an induction period. Similarly, the CdS-0-Cd-catalysed photoreduction of dimethyl maleate (4a) also led to the linear formation of dimethyl succinate (5a), accompanying the slow photoisomerisation to methyl fumarate when compared with the CdS-0-catalysed photoreduction [Fig. 4(b)]. Under dark conditions, the reduction products were not detected in the presence of CdS-0-Cd.

Since the presence of an excess of  $S^{2-}$  inhibits the coloration under irradiation, the photoreduction was conducted in the presence of excess of  $S^{2-}$ . Fig. 5(*a*) and (*b*) show timeconversion plots for the CdS-0-catalysed photolyses of **1d** and **4a**, respectively, in the presence of excess of  $S^{2-}$  (2.5 × 10<sup>-3</sup> mol dm<sup>-3</sup>). The ketone, **1d**, was quantitatively photoreduced



Fig. 4 Time-conversion plots for photoreduction of dimethyl maleate (4a) catalysed (a) by CdS-0, (b) by CdS-0–Cd: ( $\bigcirc$ ) dimethyl maleate (4a), ( $\bigcirc$ ) dimethyl fumarate, ( $\triangle$ ) dimethyl succinate (5a)



**Fig. 5** Time-conversion plots for CdS-0-catalysed photolyses in the presence of  $S^{2-}$ . (a) Photolysis of benzophenone, **1d**: ( $\bigoplus$ ) benzophenone (**1d**), ( $\triangle$ ) benzpinacol (**3d**), ( $\bigcirc$ ) benzhydrol (**2d**). (b) Photolysis of dimethyl maleate, **4a**: ( $\bigoplus$ ) dimethyl maleate (**4a**), ( $\bigcirc$ ) dimethyl fumarate, ( $\triangle$ ) dimethyl succinate (**5a**), ( $\square$ ) the dimer **6a** 



Fig. 6 Plausible mechanism for the formation of Cd<sup>0</sup> on the lattice under irradiation of CdS-0 suspensions in the presence of TEA

to either benzpinacol, 3d, or benzhydrol, 2d. This was also true for the photolysis of 4a in the presence of S<sup>2-</sup>. Note that one-electron reduction products, *i.e.* benzpinacol (3d) and 1,2,3,4-tetra(methoxycarbonyl)butane (6a) were formed much more than 2d and 5a at the beginning of the photolyses.



Fig. 7 Relationship between reduction to dimethyl succinate (5a) and the formation of  $Cd^0$  in the CdS-0-catalysed photolysis. ( $\triangle$ ) Dimethyl succinate (5a), ( $\square$ )  $Cd^0$  on lattice estimated by the formation of  $MV^{++}$ 

Recently, bis(trimethylsilyl)sulfide  $[S(TMS)_2]$  was found to be a good source of  $S^{2-}$  in the preparation of CdS.<sup>27</sup> When  $S(TMS)_2$  was employed instead of Na<sub>2</sub>S, the exclusive formation of pinacols **3c**, **3d** was also confirmed. In Table 3 are summarised the results of the effect of  $S^{2-}$  on the distribution of photoproducts from ketones **1c-1d** and dimethyl maleate (**4a**). The concentration,  $2.5 \times 10^{-3}$  mol dm<sup>-3</sup>, of  $S^{2-}$  was enough for the suppression of Cd<sup>0</sup> formation. Note that the dimer **6a** was not detected in the CdS-0-Cd-catalysed photoreduction of **4a**. These observations suggest that dramatic regulation of the CdS-0-catalysed photoreduction can be achieved by controlling the formation of Cd<sup>0</sup> on quantised CdS-0 particles.

## Structure of CdS-0-Cd and Mechanism of Coloration

We demonstrated in the photocatalysis of quantised ZnS that an excess of  $S^{2-}$  should eliminate sulfur vacancies by combination with excess  $SO_3^{2-}$ , serving to maintain the effective photocatalysis of defect-free quantised ZnS.<sup>13</sup> The brown coloration (a kind of photochromism) was observed only for quantised CdS, and was completely suppressed by the presence of an excess of  $S^{2-}$ . Such coloration was not observed for bulk CdS-Ald even in the presence of the Cd<sup>2+</sup> ion.

Table 3Effect of  $S^{2-}$  addition on product distribution by photo-<br/>catalysis of CdS-0<sup>a</sup>

	$S^{2}$ /mmol dm <sup>-3</sup>			yield (%) <sup>b</sup>				
substrate	Na <sub>2</sub> S	S(TEM) <sub>2</sub> <sup>c</sup>	conversion (%)	2	3	5	6	
1b	0		98	70	12			
	2.5		100	15	82			
	5.0		100	3	70			
1c	0		88	76	0			
	2.5		100	9	87			
	5.0 <sup>d</sup>		68	3	56			
		5.0	100	5	87			
1d	0		100	95	5			
	2.5		99	5	87			
	5.0		90	0	80			
		5.0	100	5	87			
<b>4</b> a	0		100			78	0	
	2.5		100			17	70	

<sup>a</sup> Irradiated in MeOH at >400 nm for 2 h. <sup>b</sup> Yields are based on the substrate converted. <sup>c</sup>  $S(TMS)_2$  is  $Me_3Si-S-SiMe_3$ , bis(trimethysilyl) sulfide. <sup>d</sup> Irradiated for 4 h.



Fig. 8 Regulation of the CdS-0-catalysed photoreduction of benzophenone with TEA in the presence of Na<sub>2</sub>S. Initial concentration of Na<sub>2</sub>S, 2.5 mmol dm<sup>-3</sup>; after 30 min photolysis, methanolic Cd(ClO<sub>4</sub>)<sub>2</sub> solution equivalent to S<sup>2-</sup> was added. ( $\bigcirc$ ) Benzophenone (1d), ( $\triangle$ ) benzpinacol (3d), ( $\bigcirc$ ) benzhydrol (2d), ( $\square$ ) Cd<sup>0</sup>

Further, the brown colour is readily bleached by  $O_2$  oxidation. These facts suggest that the photochromism (the coloration) should be due to reduced Cd atoms (Cd<sup>0</sup>) formed in the vicinity of surface sulfur vacancies of CdS-0. Sulfur vacancies once formed should trap electrons, leading to the feasible reduction of lattice Cd<sup>2+</sup> by electrons trapped at sulfur vacancies as depicted in Fig. 6. Energetically speaking, valence-band and conduction-band edges of CdS-0 are further separated owing to the effective band gap, *ca.* 3.0 eV, and then photoinduced holes are rapidly taken up by the electron donors so that excess electrons may remain on the particle, making the conduction-band edge cathodic enough to reduce the lattice Cd<sup>2+</sup> at sulfur vacancies.

The quantity of  $Cd^0$  on the lattice was estimated by the formation of  $MV^{*+}$  from  $MV^{2+}$  as reported.<sup>20</sup> Their forma-

tion was monitored by following the production of the succinate 5a in the photolysis of the maleate 4a, as shown in Fig. 7. Interestingly, the formation of Cd<sup>0</sup> levels off at an early stage of the irradiation and compensates for the induction period for the formation of the succinate 5a. On careful examination, the coloration was accompanied by all of the CdS-0-catalysed photoreductions and the induction period was found to correspond to the coloration time, *i.e.* the time for the formation of lattice Cd<sup>0</sup>.

#### **Regulation of Electron Transfer on Quantised CdS**

It has now been clarified that CdS-0 induces effective oneelectron transfer reductions in the presence of an excess of  $S^{2-}$  and the Cd<sup>0</sup> deposited quantised CdS (CdS-0-Cd) is effective for sequential two-electron transfer reductions. With these findings in mind, photocatalysis was attempted by controlling the concentration of free  $S^{2-}$  and/or Cd<sup>2+</sup>. Fig. 8 shows time-conversion plots for the photoreduction of benzophenone (1d) in the presence of an excess of  $S^{2-}$ . The selective formation of the pinacol 3d was observed. After 30 min irradiation, Cd<sup>2+</sup> equivalent to  $S^{2-}$  was added to the reaction system to eliminate the excess  $S^{2-}$  as CdS. Then, the alcohol 2d was mainly produced with gradual formation of Cd<sup>0</sup>, and the formation of the pinacol 3d levelled off.

Deuterium incorporation experiments for the CdS-0catalysed photoreduction of **4a** in MeOD reveal that dideuterated and monodeuterated **5a** were formed in a ratio of 74:20, which is almost identical with that of the CdS-0catalysed photoreduction,<sup>17</sup> supporting the sequential twoelectron transfer (ECE process) reduction mechanism. These results strongly suggest that Cd<sup>0</sup> photoformed on the lattice should act as a catalytic site for the two-electron reduction of organic substrates on quantised CdS particles.

As for how  $Cd^0$  mechanistically affects the two-electron reduction of ketones and alkenes, there seem to be two possibilities: (1) Electron transfer assisted by a strong interaction between  $Cd^0$  and an electron-deficient carbonyl or carboncarbon double bond as shown in Scheme 3 [see eqn. (1)]. Such complexation should decrease the overpotential for the electron transfer through  $Cd^0$ , leading to sequential electron transfer. (2) The adsorption of a hydrogen atom on  $Cd^0$  possibly through the Volmer reaction shown in Scheme 3 [see eqn. (2)]. Hydrogen-atom transfer from  $Cd^0-H$  should result



Fig. 9 Schematic diagram of CdS-0-catalysed photoreduction of benzophenone with TEA as electron donor. V.B., valence band. C.B., conduction band

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in the formation of two-electron reduction products as exemplified for the reduction of benzophenone in Scheme 3 [see eqn. (3)].

$$H^{+} + Cd^{0} + e^{-} - Cd^{0} - H$$
 (2)

$$\begin{array}{ccc} O & OH & OH \\ H - C - Ph & \frac{CdS(e), H^{+}, or Cd^{0} - H}{H} & Ph - C - Ph & \frac{Cd^{0} - H}{H} & Ph - C - Ph & (3) \\ H \end{array}$$

#### Scheme 3

#### Conclusion

As shown in Fig. 9, it has been clarified that photoformed electrons on quantised CdS microcrystallites can induce sequential electron transfer through spontaneously formed Cd<sup>0</sup> on CdS-0 or the adsorption of a hydrogen atom on Cd<sup>0</sup>, leading to much more selective two-electron photoreductions than those on the bulk CdS crystallites which never form Cd<sup>0</sup> metal on the surface by irradiation. The excess of S<sup>2-</sup> presumably fills surface sulfur vacancies on CdS-0, giving defect-free quantised CdS-0. As for such defect-free CdS-0, the reduction of Cd<sup>2+</sup> to Cd<sup>0</sup> should be inhibited and the oneelectron transfer prevails, giving exclusively dimeric products of intermediary radicals from benzophenone and dimethyl maleate. To our knowledge, this reaction is the first example of visible light induced reductive carbon–carbon bond formation reactions on semiconductor particles.

Chemoselectivity in semiconductor photocatalysis is important from the viewpoint of organic synthesis and is now under extensive investigation by our group.

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