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Exploiting the interparticle electron transfer process in the photocatalysed oxidation of phenol, 2-chlorophenol and pentachlorophenol: chemical evidence for electron and hole transfer between coupled semiconductors

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Abstract

The photocatalysed oxidation of phenol, 2-chlorophenol and pentachlorophenol was re-examined under conditions in which TiO_2 anatase was sensitized by CdS in air-equilibrated aqueous media; this was to assess whether or not the interparticle electron transfer pathway, first discovered a decade ago (N. Serpone, E. Borgarello and M. Gratzel, *J. Chem. Soc., Chem. Commun.*, (1984) 342) and subsequently applied to enhance reductive processes on titania, could also be applied to photo-oxidative processes. The results indicate that combinations such as CdS/TiO_2 lead to an enhanced rate of disappearance of the initial substrate by a factor greater than two, consistent with the notion that (irradiated) CdS electrons are vectorially displaced onto the non-illuminated TiO_2 particulates. Cadmium sulphide is a poorer photo-oxidation catalyst than titania. Other semiconductor materials have also been examined under a variety of conditions of pH and irradiation wavelength. The data also show that when both semiconductors in a coupled system are illuminated simultaneously and their valence and conduction bands are suitably disposed, both electron and hole transfer occur (as in the CdS/TiO_2, ZnO/TiO_2, TiO_2/Fe_2O_3 and ZnO/Fe_2O_3 couples), which will influence the efficiency of photo-oxidation. N_2O-saturated aqueous dispersions of TiO_2 have no effect on the photo-oxidation of phenol, although it was expected that nitrous oxide would scavenge the photogenerated electrons in a manner similar to chemisorbed molecular oxygen, and enhance the efficiency. It is suggested that the role of oxygen in photo- oxidations may be more than just a simple electron scavenger.

Keywords: Electron transfer; Photocatalyzed oxidation; Coupled semiconductors

1. Introduction

Semiconductor particulates have proven to be particularly attractive photocatalysts in heterogeneous photocatalysis and in advanced oxidation processes in general as they provide an interface with the aqueous medium. Redox species (conduction band electrons, e_{CB}^- and valence band holes, h_{VB}^+) are eventually poised at the interface (in the case of TiO_2 as Ti^{III} for the electrons and Ti^{IV}–$^{\cdot}OH$ for the holes) following irradiation of the dispersions with light energy appropriate to their band gaps (TiO_2 anatase, 3.2 eV; CdS, 2.4–2.6 eV). Much of the research on the photodegradation of organic substrates over irradiated anatase titania has been reviewed in detail in several recent articles [1–7]. In this paper, we examine the photocatalysed transformation of three selected substrates to determine whether or not the interparticle electron transfer (IPET) pathway can be applied, which was first reported in 1984 [8] and which demonstrated that the coupling of two semiconductors (e.g. CdS and TiO_2) leads to improved dihydrogen production from the photoreduction of water in the presence of hydrogen

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sulphide as sacrificial agent. We have also demonstrated the photocatalytic usefulness of coupled semiconductors in the dehydrogenation of alcohols [9] and have probed the IPET process by photoelectrochemical [10] and photoconductivity [11,12] experiments in solid systems. A limiting factor that controls the efficiency of photocatalysis is the rapid recombination of photogenerated electrons and holes in semiconductor particulates. A variety of methods have been employed to retard such recombination: the addition of surface dopants and electron or hole scavengers adsorbed on the surface. Recently, the application of the coupled systems WO_3/CdS and WO_3/Pt–CdS as photocatalysts has been shown to enhance the efficiency of hydrogen production [13].

The coupling of two semiconductors possessing different redox energy levels for their corresponding conduction and valence bands provides an attractive approach to achieve more efficient charge separation, increase the lifetime of the charge carriers and enhance the efficiency of the interfacial charge transfer to adsorbed substrates. In the case of CdS and TiO_2, a photoelectron generated on CdS can be injected into the (inactivated) TiO_2 conduction band while the photohole remains on CdS (Fig. 1(A) [14–18]). This IPET pathway therefore affords vectorial electron transfer which is irreversible under certain conditions. For a colloidal system of CdS and TiO_2 or ZnO, the rate constant for this vectorial electron transfer is 5×10^{10} s^{-1} or greater [19,20]. In alkaline aqueous dispersions, the conduction band of TiO_2 particulates is 100 mV more anodic than the corresponding band of CdS [10]. Our photoconductivity studies [11,12] have revealed that, in the solid phase, vectorial electron transfer occurs from TiO_2 to CdS, a reversal from the colloidal or dispersion phases owing to modifications of the surface properties of the TiO_2 particulates under the prevailing conditions used. An additional feature of Fig. 1(B) is that simultaneous activation of both semiconductors may lead to simultaneous electron transfer from CdS to TiO_2 and hole transfer from TiO_2 to CdS. Since our first report, several other coupled systems have been examined by a variety of photochemical and photophysical methods [14,19]. Although the photocatalysed oxidation of the substrates examined here has been investigated previously in oxygen-equilibrated aqueous suspensions of CdS [21–23] and TiO_2 and ZnO [1–7], the photocatalytic properties of coupled systems have hitherto remained largely unexplored.

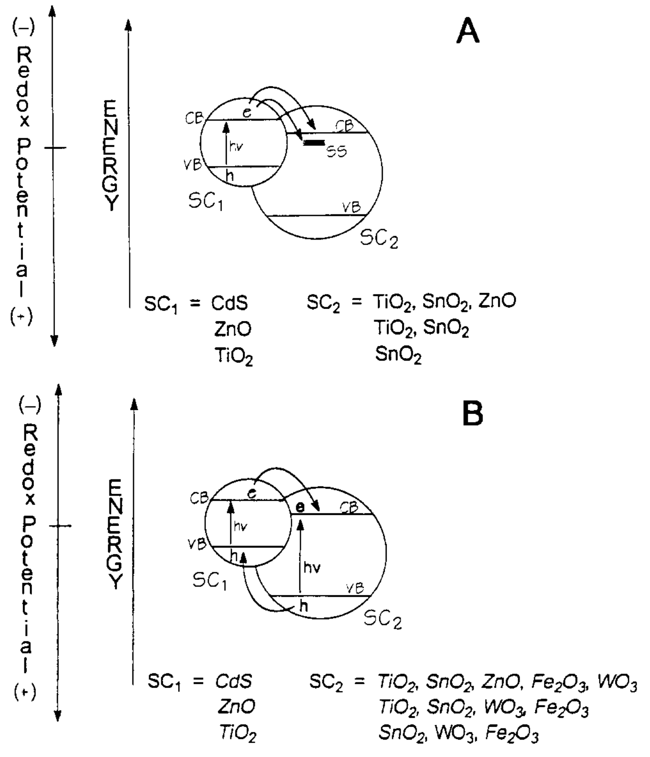

Fig. 1. (A) Energy diagram illustrating the coupling of various semiconductors (SCs) in which vectorial electron transfer occurs from the light-activated SC to the non-activated SC. (B) Diagram depicting the coupling of various SCs in which vectorial displacement of electrons and holes is possible.

Photocatalytically, in the past the coupling of semiconductors has been examined only from the photoreductive side. In this report, we explore the potential applications of the IPET process for the oxidative decomposition of selected polluting organic substances. We have chosen phenol, 2-chlorophenol and pentachlorophenol as test substrates. We show the usefulness of using a semiconductor (CdS) to sensitize a larger band gap semiconductor such as TiO_2; other coupled systems have also been explored. We also infer that both electron transfer from illuminated CdS to light-activated TiO_2 and hole transfer from illuminated TiO_2 to activated CdS occur in the CdS/TiO_2 coupled system. This double charge transfer has not hitherto been reported for coupled or sandwiched semiconductor systems; however, hole transfer from light-activated ZnO particulates sandwiched by a layer of ZnSe or ZnS has been observed [24–26].

2. Experimental section

2.1. Materials

Phenol, 2-chlorophenol and pentachlorophenol were purchased from Aldrich and were of the best grade available; they were subjected to no further treatment. The semiconductor powders, CdS, ZnO and SnO_2 (Fluka), WO_3 (Johnson Matthey), WS_2 (Alfa), TiO_2 (Degussa P-25) and Fe_2O_3 (prepared by Dr. M. Castellano of ENI, Milan), were used as received. In a few cases, SnO_2 was further ground mechanically to a finer powder. The water used throughout was deionized and doubly distilled.

2.2. Procedures

The irradiation source was a 1000 W Hg/Xe arc lamp (Oriel Corporation) operated at 900 W. Suitable cut-off filters (355 and 406 nm) were used to eliminate undesirable UV radiation; a water jacket was employed to eliminate IR radiation. The reactor consisted of a 60 ml capacity glass vessel. The photocatalyst materials (80 mg of each) and 50 ml of an aqueous solution of the substrate (about 200 μM unless stated otherwise) were stirred magnetically. In other cases, the irradiation source was a Solar Box (1500 W Xe lamp; CO.FO.MEGRA, Milan, Italy) which delivered air mass (AM) 1 simulated solar light (about 80–100 mW cm^{-2}).

The apparent kinetics of disappearance of the original substrate (or formation and decay of the intermediate species) were followed by determining the concentration of the substance at various time intervals by high performance liquid chromatography (HPLC). The HPLC assembly consisted of a Waters 151 HPLC pump, a Millipore μ Bondapak reverse phase C-18 column, a Millipore Waters 441 absorbance detector and a Hewlett Packard HP 3396A integrator. The detection wavelengths were 254 and 280 nm. A 3 ml aliquot of the reaction mixture was sampled periodically and filtered with a 0.2 μm membrane filter before acidification to pH 1–2 prior to analysis. Analyses of the pentachlorophenol system were carried out at the experimental value of pH ≈ 12. The mobile phase consisted of a 40 : 60 methanol–water mixture, except for pentachlorophenol where the phase was a 50 : 50 mixture of methanol and water.

3. Results and discussion

3.1. Phenol oxidation

The photocatalysed disappearance of phenol in air-equilibrated aqueous CdS, TiO_2 and CdS/TiO_2 systems (pH 12), irradiated in the UV–visible region at wavelengths greater than 320 nm (Pyrex reactor used) or greater than 406 nm (cut-off filter used), is illustrated in Figs. 2(A) and 2(B) respectively. The rates for TiO_2 and the CdS/TiO_2 system are identical (2.05 ± 0.06 μM min^{-1} and 2.0 ± 0.2 μM min^{-1}, Table 1; irradiation wavelength, greater than 320 nm); that for CdS alone is twofold slower (1.09 ± 0.04 μM min^{-1}). By contrast, when only visible radiation is used to illuminate the photocatalytic materials, there is no reaction with the TiO_2 dispersions (bandgap, 3.2 eV; 380 nm). For the CdS system, the rate is 0.56 ± 0.08 μM min^{-1}, while it is twofold faster for the coupled CdS/TiO_2 system (Table 1). In both cases, the rates are slower by a factor of two when visible radiation is used.

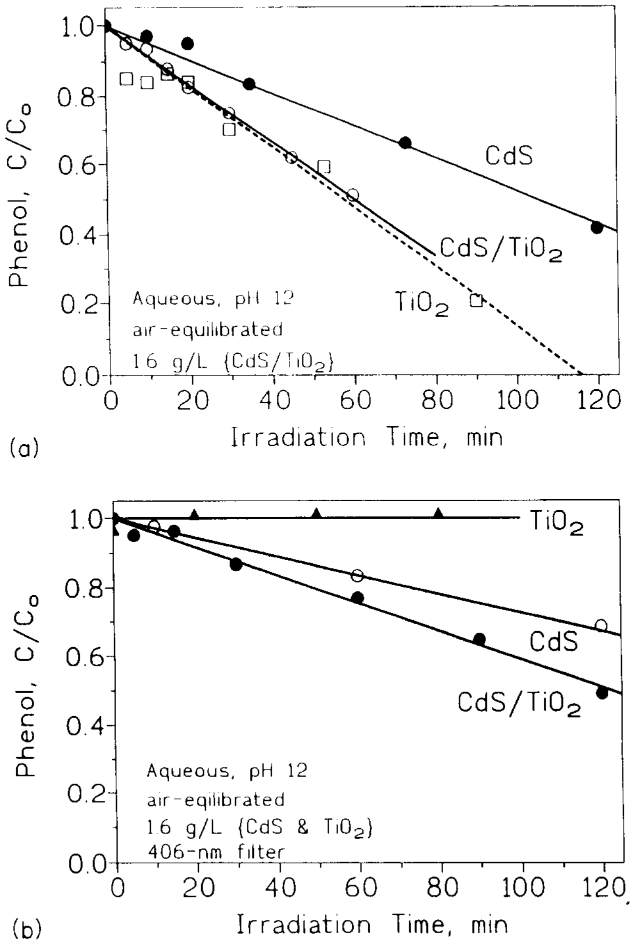

Fig. 2. Plots showing the photocatalysed transformation of phenol as a function of irradiation time under various conditions (concentration of phenol, 230–250 μM): (A) Pyrex reactor used (wavelengths above 320 nm); (B) 406 nm cut-off filter used.

In argon- or nitrous-oxide-purged aqueous TiO_2 suspensions (pH ≈ 5.7–6), there is no effect on the photo-oxidation of phenol (Fig. 3) in contrast with air-equilibrated systems where molecular oxygen has a significant impact. The result for the nitrous-oxide-purged systems was somewhat unexpected. When a colloidal aqueous ZnO suspension is saturated with N_2O, which reacts with solvated electrons in the pulse radiolysis of aqueous systems, the trapped electrons on the ZnO surface decay faster than in N_2O-free suspensions [24], suggesting that the trapped electrons are scavenged from the ZnO surface by nitrous oxide in a manner which parallels the behaviour of oxygen-saturated ZnO suspensions. Evidently, nitrous-oxide-saturated TiO_2 particulates behave differently, as N_2O has no apparent effect on the photo-oxidative decomposition of phenol. We speculate that the surface trapped e$^-$ on ZnO, $(Zn^{II}\text{-}e^-)_{aq}$ where the interaction between the metal ion and the electron is relatively small, resembles e_{aq}^- more so than does the corresponding $(Ti^{IV}\text{-}e^-)_{aq}$ where the interaction is significantly greater and the trapped electron is considered to be Ti^{III}. Alternatively, the

Table 1
Rates of disappearance of phenol, 2-chlorophenol and pentachlorophenol for CdS, TiO_2 and CdS/TiO_2 combinations

System[a]	Rate (μM min^{-1})	
	No filter[b]	With 406 nm filter
Phenol[c]		
CdS	1.09 ± 0.04	0.56 ± 0.08
TiO_2	2.05 ± 0.06	NR
CdS/TiO_2	2.0 ± 0.2	0.95 ± 0.05
2-Chlorophenol[d]		
CdS	0.3 ± 0.1	NR
TiO_2	5.1 ± 0.1	NR
CdS/TiO_2	4.1 ± 0.5	2.2 ± 0.1
Pentachlorophenol[e]		
CdS	0.76 ± 0.11	0.39 ± 0.05
TiO_2	3.61 ± 0.06	0.33 ± 0.01
CdS/TiO_2	4.9 ± 0.2	1.6 ± 0.2

[a] pH ≈ 12 in all cases; $[CdS] = [TiO_2] = 80$ mg per 50 ml of aqueous phenolic solution; lamp Hg/Xe, 900 W.
[b] Pyrex reactor used allowing wavelengths greater than 320 nm.
[c] Concentration, $(2.3–2.5) \times 10^{-4}$ M.
[d] Concentration, $(2.0–2.3) \times 10^{-4}$ M.
[e] Concentration, $(1.2–1.5) \times 10^{-4}$ M.
NR, no reaction.

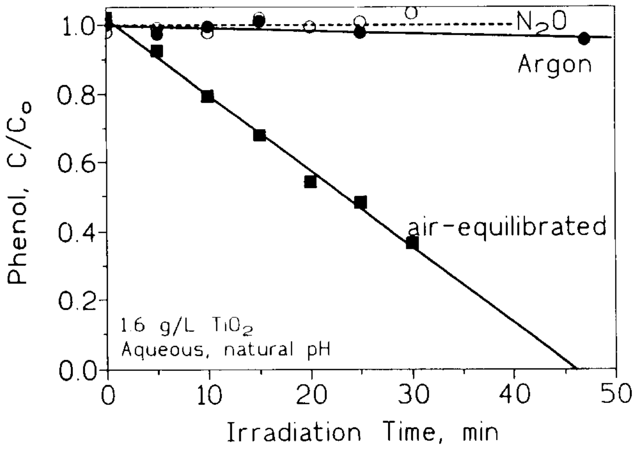

Fig. 3. Effect of added gases on the photocatalysed conversion of phenol (Pyrex reactor used). Other conditions as in Fig. 2(A); pH ≈ 5.8.

N_2O may act simply (as argon) to deprive the suspension of much needed oxygen. However, if nitrous oxide does scavenge electrons, the role of molecular oxygen in O_2-saturated (or air-equilibrated) aqueous TiO_2 dispersions may be more than just a simple electron scavenger [27a]. In this regard, we note that N_2O has no effect on the electrical photoconductivity of a solid TiO_2 P-25 specimen in the "dry state" [27b], so that nitrous oxide is not an electron scavenger under these conditions.

Fig. 4 depicts the AM1 simulated sunlight irradiation (wavelengths greater than 310 nm) of three alkaline, air-equilibrated phenolic dispersions of CdS, TiO_2 and CdS/TiO_2. The photo-oxidative transformation of phenol follows first-order kinetics. Cadmium sulphide is a poorer photocatalyst than TiO_2 (k values are $(3.8 \pm 0.5) \times 10^{-3}$ min^{-1} and $(19 \pm 5) \times 10^{-3}$ min^{-1} respectively; Table 2); the coupled CdS/TiO_2 system also photocatalyses the oxidative conversion of phenol, but at a twofold slower rate than TiO_2, even though this system absorbs more light than TiO_2 alone (see below).

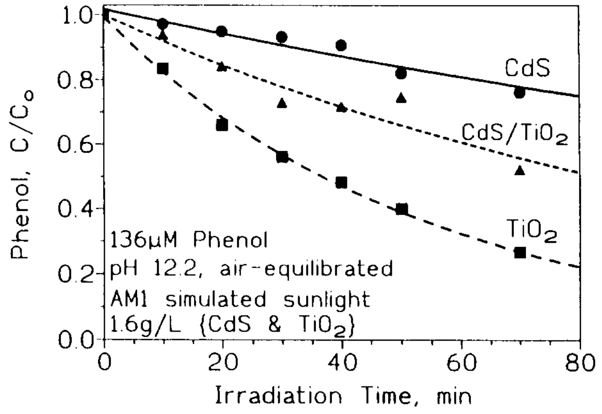

Fig. 4. Photocatalysed transformation of phenol in alkaline media with various semiconductor dispersions irradiated with AM1 simulated sunlight from a Solar Box.

Table 2
Apparent first-order kinetics for the disappearance of phenol in air-equilibrated aqueous media using AM1 simulated solar light for irradiation

Semiconductor 1[a]	Semiconductor 2[a]	k (10^{-3} min^{-1})	Intermediates
Conditions: pH ≈ 12.2; [Phenol] ≈ 136 μM			
CdS	–	3.8 ± 0.5	–
–	TiO_2	19 ± 5	–
CdS	TiO_2	8 ± 1	(CC)[b]
Conditions: pH ≈ 8.2; [Phenol] ≈ 150–170 μM			
ZnO	–	52 ± 3	HQ, CC
CdS	–	0.8 ± 0.2	HQ, (CC)
–	SnO_2	NR	–
CdS	SnO_2	2.7 ± 0.4	HQ, (CC)

[a] Concentration, 80 mg in 50 ml aqueous phenolic solution.
[b] Trace quantities of catechol formed under these conditions.
CC, catechol; HQ, hydroquinone; NR, no reaction.

3.2. 2-Chlorophenol oxidation

The photo-oxidative disappearance of 2-chlorophenol in the presence of CdS, TiO_2 and CdS/TiO_2 in aqueous alkaline media (pH 12) is depicted in Figs. 5(A) and 5(B) for UV–visible (Pyrex reactor) and visible (406 nm cut-off filter) illumination respectively. The corresponding rates are 0.3 ± 0.1 μM min^{-1}, 5.1 ± 0.1 μM min^{-1} and 4.1 ± 0.5 μM min^{-1} for irradiation wavelengths above 320 nm. For the CdS system, the apparent photo-oxidation in the UV-illuminated system is probably due to direct photolysis and not to a photocatalysed

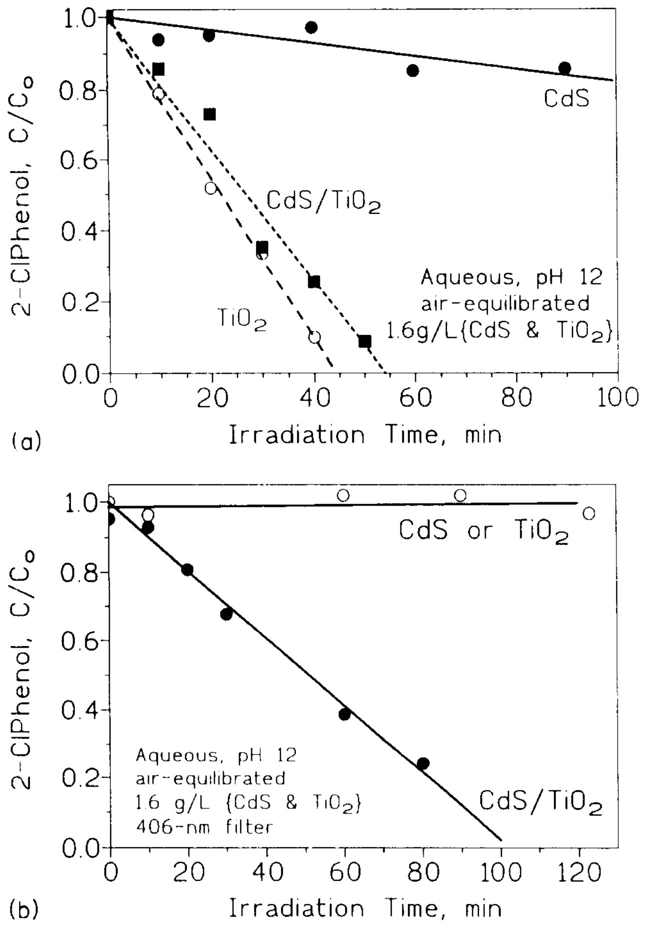

Fig. 5. Photocatalysed conversion of 2-chlorophenol in alkaline media (concentration of 2-ClPhOH, 200–230 μM): (A) Pyrex reactor used; (B) 406 nm cut-off filter used.

process, since visible radiation which activates CdS has no effect (Fig. 5(B) and Table 1). By contrast, when the coupled CdS/TiO_2 system is illuminated with visible radiation only, the photo- oxidative disappearance of 2-chlorophenol is effective (rate, 2.2±0.1 μM min^{-1}).

3.3. Pentachlorophenol oxidation

The photo-oxidation of pentachlorophenol by UV–visible and visible illumination of the three photocatalytic systems in aqueous alkaline media (pH 12) is examined in Figs. 6(A) and 6(B) respectively. With visible illumination only, the rates for CdS and TiO_2 are nearly identical; for the coupled semiconductor system the rate is fourfold faster (Table 1). When UV–visible radiation is used, the photo-oxidative processes are accelerated both for direct photolysis in the presence of CdS (0.76±0.11 μM min^{-1}) and for the photocatalysed oxidation with TiO_2 and CdS/TiO_2; the respective rates are 3.61±0.06 μM min^{-1} and 4.9±0.2 μM min^{-1}.

The data of Figs. 2(A), 4, 5(A) and Table 1 show that CdS is a poorer photocatalyst in the oxidative degradation of phenol, 2-chlorophenol and pentachlorophenol than TiO_2 by a factor of 2–17, even though the former material absorbs a greater quantity of light (UV and visible wavelengths to 520 nm). As expected, no degradation of phenol or 2-chlorophenol occurs when TiO_2 is irradiated with visible light only (wavelengths above 406 nm; Table 1), but pentachlorophenol shows a small but measurable rate of oxidation. Since TiO_2 is not activated by visible radiation, photo-oxidation must proceed via direct photolysis of the pentachlorophenolate anion, probably adsorbed to some extent on TiO_2 under the prevailing conditions. Substrates adsorbed onto metal chalcogenide supports may have their absorption spectra red shifted by several tens of nanometres. Direct photolysis is also probable for the CdS system even though this photocatalyst material is activated by light.

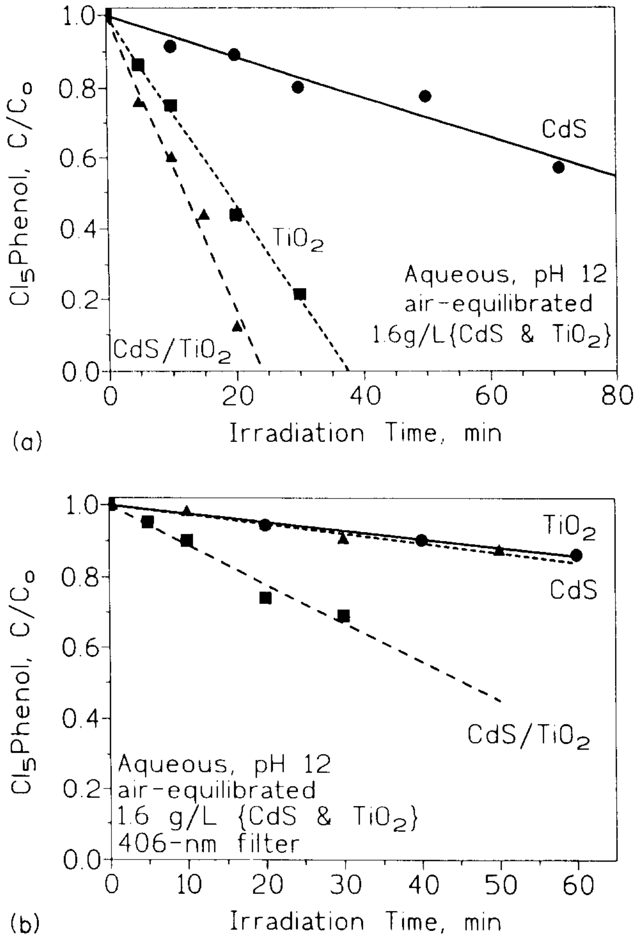

Fig. 6. Photocatalysed conversion of pentachlorophenol (PCP) in alkaline media (concentration of PCP, 120–150 μM): (A) Pyrex reactor used; (B) 406 nm cut-off filter used.

It is noteworthy that CdS quenches the degradation of phenol on TiO_2 at pH 12 when the coupled system is irradiated with simulated sunlight (Table 2 and Fig. 4). This observation is consistent with the notion that electron and/or hole transfer between the activated CdS and activated TiO_2 particulates inhibits the photocatalytic activity of the latter, thereby decreasing the concentration of the active oxygen species that lead to oxidation (namely the surface bound ·OH radicals [28]). At near-neutral conditions, ZnO is a very efficient photocatalyst for phenol degradation, unlike CdS for which degradation is some 65 times slower and unlike SnO_2 which shows no photocatalytic activity (Table 2). By contrast, when CdS is coupled with SnO_2, phenol oxidation is threefold faster, reflecting the charge transfer between CdS and the conduction band of SnO_2 or one of its surface states, thereby increasing the concentration of active oxidative entities in the former material (see below). The major intermediate product(s) is hydroquinone, with trace quantities of catechol, except for the ZnO dispersion where catechol and hydroquinone are both produced in nearly equal amounts.

3.4. Various semiconductor combinations

Table 3 summarizes the kinetic results from the photo-oxidation of phenol for a variety of semiconductors used either alone or in binary combinations under a variety of conditions, but all in air-equilibrated aqueous media; it also summarizes the various intermediates detected by liquid chromatography. At the more acidic pH values, both hydroquinone and catechol are readily formed; in more alkaline media, catechol is not an important intermediate, unlike hydroquinone and benzoquinone. Several features of the results in Table 3 are worth noting.

At pH 12.2, on exposure to visible irradiation ($\lambda > 406$ nm), both TiO_2 and WS_2 are inactive (Table 3) towards phenol oxidation; however, when these two materials are coupled with CdS, a twofold improvement in the photo- oxidative conversion is witnessed. The Fe_2O_3 specimen used in this study shows activity similar to CdS and to the coupled systems CdS/TiO_2, CdS/Fe_2O_3, CdS/WS_2, CdS/SnO_2 and CdS/WO_3. Hydroquinone and benzoquinone together with trace amounts of catechol are formed under alkaline conditions for CdS and CdS/TiO_2; no intermediates are detected for Fe_2O_3 and for the coupled systems under otherwise identical conditions. Decreasing the pH value to pH$\approx$8 (Table 3), SnO_2, WS_2 and ZnO are inactive as is the CdS/WS_2 combination. Tin oxide, iron oxide and zinc oxide appear to quench the CdS oxidation of phenol. Only hydroquinone is formed in observable quantities under the prevailing conditions.

On exposure to UV–visible irradiation (greater than 355 nm), iron oxide quenches the photocatalytic activity of TiO_2 by a factor of 3–4, while it has little effect on the photocatalytic activity of ZnO (Table 3); hydroquinone is formed with the TiO_2 systems and both hydroquinone and catechol are formed with the ZnO dispersions. On acidification to about pH 6.7 (Table 3), the rate of photo-oxidation of phenol by ZnO and TiO_2 decreases by about 30%; the photo-oxidation of phenol by irradiated WO_3 is quenched by SnO_2 by a factor of approximately four, while it slightly enhances the efficiency of ZnO-photocatalysed oxidation. In more acidic aqueous media, pH 3, and with UV–visible irradiation (Table 3), the TiO_2 photo-oxidation of phenol is not affected by the simultaneous presence of either SnO_2 or WO_3; the latter semiconductor material is also photo-oxidatively active.

3.5. Mechanistic considerations

Hydrous CdS contains two types of surface functional site [29]: (a) Brönsted sites where hydrogen ions and hydroxide ions determine the surface potential; (b) Lewis sites where cadmium and sulphide ions determine the potential ($pK_a = 6.10$ and 9.02; point of zero charge (pzc), 7.5). The dissociative interaction of water with the non-polar face of CdS therefore gives Cd–OH and S–H groups; molecular water is weakly chemisorbed on the polar face of the CdS particle [30]. Organic substrates, such as phenol and chlorophenols, are adsorbed on the CdS particle surface, with the adsorption increasing with the number of chloro substituents on the phenol group [21,23].

Irradiation of aqueous CdS dispersions with UV–visible or visible light (wavelengths below 520 nm) generates conduction band electrons and valence band holes which migrate to the surface and subsequently become trapped as S^- and Cd^+ (or Cd^0) species [31] (Eq. (1)). In oxygen-equilibrated media, the trapped electrons are scavenged by molecular oxygen to yield the superoxide radical anion and then the peroxide ion (Eq. (2)) [32,33].

$$\mathrm{CdS} + h\nu \longrightarrow \mathrm{CdS}(e_{CB}^- + h_{VB}^+) \longrightarrow \mathrm{CdS}(e_{tr}^- + h_{tr}^+) \quad (1)$$

$$e_{tr}^- + O_2 \longrightarrow O_2^- \xrightarrow{e_{tr}^-} O_2^{2-} \quad (2)$$

$$n h_{tr}^+ + \mathrm{CdS}(nS^-) \longrightarrow n\mathrm{S(CdS)} + \mathrm{Cd}^{2+}(aq) \quad (3)$$

If the photogenerated holes are not consumed rapidly by the Cd–OH groups (or chemisorbed water) and/or the adsorbed phenolic substrate, photoanodic corrosion rapidly ensues, leading to the release of Cd^{2+} ions in solution [32] (in rather large quantities; about 1 mM [23]) and the formation of a layer of elemental sulphur on the CdS particulate surface (Eq. (3)); this may affect significantly the subsequent efficiency of the photo-oxidation of organic substrates. Illuminated aqueous CdS dispersions oxidatively decompose adsorbed substrates such as the phenols examined here (see above and Refs. [21–23]).

The photocatalytic expectations from coupled systems can best be predicted and described from a knowledge of the flat band potentials of the system components.

Table 3
Apparent first-order kinetics for the disappearance of phenol in air-equilibrated aqueous media[a]

Semiconductor 1[b]	Semiconductor 2[b]	k (10^{-3} min^{-1})	Intermediates detected
Conditions: pH 12.2 and 406 nm filter; [Phenol] ≈ 215 M			
CdS	–	3.1 ± 0.3	BQ, HQ, others[c]
–	TiO_2	NR	–
CdS	TiO_2	5.3 ± 0.4	BQ, HQ, (CC), others
–	WS_2	NR	–
–	Fe_2O_3	4.6 ± 0.8	[d]
CdS	Fe_2O_3	4.0 ± 0.6	[d]
CdS	WS_2	5.9 ± 0.3	[d]
CdS	SnO_2	3.1 ± 0.4	[d]
CdS	WO_3	7.4 ± 0.7	[d]
Conditions: pH ≈ 8 and 406 nm filter; [Phenol] ≈ 210–220 μM			
CdS	–	4.3 ± 0.5	HQ, (CC)
–	SnO_2	NR	–
–	WS_2	NR	–
–	Fe_2O_3	2.5 ± 0.4	[d]
–	ZnO	NR	–
CdS	WS_2	(≈ 0.07)	–
CdS	SnO_2	0.9 ± 0.2	HQ
CdS	Fe_2O_3	0.9 ± 0.3	[d]
CdS	ZnO	2.0 ± 0.8	HQ
Conditions: pH ≈ 8.1 and 355 nm filter; [Phenol] ≈ 181 μM			
TiO_2	–	27 ± 2	HQ
–	Fe_2O_3	1.6 ± 0.6	[d]
TiO_2	Fe_2O_3	6.7 ± 0.8	HQ
ZnO	–	90 ± 5	HQ, CC
ZnO	Fe_2O_3	76 ± 2	HQ, CC
Conditions: pH ≈ 6.7 and 355 nm filter; [Phenol] ≈ 200 μM			
ZnO	–	61 ± 4	HQ, CC
–	SnO_2	NR	–
–	WO_3	3.3 ± 0.4	HQ, CC
–	TiO_2	19 ± 1	HQ
ZnO	SnO_2	84 ± 5	HQ, CC
ZnO	WO_3	50 ± 7	HQ, CC
ZnO	TiO_2	71 ± 2	HQ
WO_3	SnO_2	0.8 ± 0.2	HQ, CC
Conditions: pH ≈ 3 and 355 nm filter; [Phenol] ≈ 204 μM			
TiO_2	–	14 ± 1	HQ, CC
–	WO_3	3.8 ± 0.4	HQ, CC
–	SnO_2	NR	–
TiO_2	SnO_2	12 ± 1	HQ, CC
TiO_2	SnO_2	15 ± 2	HQ, CC
TiO_2	WO_3	11 ± 1	HQ, CC

[a] Abbreviations used: BQ, benzoquinone; HQ, hydroquinone; CC, catechol; NR, no reaction.
[b] Concentration, 80 mg in 50 ml aqueous phenolic solution.
[c] Other HPLC peaks were not identified.
[d] No HPLC peaks other than those of the initial substrate and the mobile phase were noted (note that there may have been species that eluted with the mobile phase or may have remained adsorbed on the particulates).

Fig. 7 depicts the flat band potentials [14–18] of the valence and conduction bands at pH 7 (vs. the normal hydrogen electrode (NHE)) for various semiconductor materials together with their band gap energies. It should be noted that suitable redox levels are only one factor affecting IPET and thus photocatalysis. No doubt, the geometry of the particles, surface texture and particle size also play a significant role.

In the presence of TiO_2 in a coupled CdS/TiO_2 system, where this metal oxide semiconductor is not light activated, it can be sensitized by IPET from the irradiated (greater than 406 nm) CdS particulate to the conduction band (or surface states, see Fig. 1(A)) of TiO_2, thereby leaving an excess of surface trapped holes on CdS (Eq. (4)). This vectorial transfer of charge should therefore enhance the photo-oxidation of the

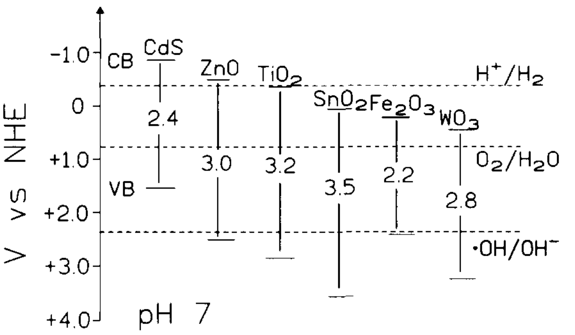

Fig. 7. Diagram depicting the redox potentials of the valence and conduction bands and the band gap energies for various semiconductor particulates estimated at pH 7. Adapted from data and analogous diagrams at other pH values from Refs. [14–18]. Also illustrated are the redox potential positions of the water couples at pH 7 together with the potential of the $^{\cdot}OH/OH^-$ couple estimated at pH 7. Note that the redox potentials for the water couples and the $^{\cdot}OH$ radical pertain to a homogeneous aqueous phase not the heterogeneous phase [34].

sorbed organic substrate; this is shown in Tables 1, 2 (for CdS/TiO_2 and CdS/SnO_2) and 3 (for the various combinations indicated) and in Figs. 2(B), 5(B) and 6(B) (Eq. (5)).

$$CdS(e^- + h^+) + TiO_2 \longrightarrow CdS(h^+) + TiO_2(e^-) \qquad (4)$$

$$CdS(h^+ \text{ or OH radical}) + \text{phenol}_{(ads)} \longrightarrow \text{intermediates} \longrightarrow \text{products} \qquad (5)$$

Where both components of the coupled systems are simultaneously activated by the UV–visible irradiation conditions used, Fig. 1(B) suggests that, where the flat band potentials are suitably disposed for the components and combinations indicated, electron transfer may occur from the more cathodic band of one semiconductor (e.g. CdS) to the more anodic band of the other component (e.g. TiO_2), while hole transfer may occur from the more anodic valence band of TiO_2 to the valence band of CdS, in competition with electron–hole recombination in the respective semiconductors. Thus

$$CdS(e^- + h^+) + TiO_2(\underline{e}^- + \underline{h}^+) \longrightarrow CdS(h^+ + \underline{h}^+) + TiO_2(\underline{e}^- + e^-) \qquad (6)$$

The excess holes on CdS ultimately oxidize the organic substrate (see Table 2 and Fig. 4) and may also anodically autocorrode the CdS particulates [21–23]; the excess electrons on TiO_2 are scavenged by chemisorbed molecular oxygen to produce the superoxide radical anion, the rate of which may be the decisive factor on the overall rate of oxidation by the active oxygen species [35]. It is clear from the earlier discussion that CdS is a poorer photocatalyst than TiO_2, such that a slower rate of oxidation is observed for the CdS/TiO_2 couple (Fig. 4). Along these lines, in a recent study on the photo-oxidation of 2-propanol with irradiated CdS/Al_2O_3, Green and Rudham [30] noted that TiO_2-based catalysts are about 20 times more active than CdS-based catalysts; interestingly, activation energies predicted an activity ratio for TiO_2 to CdS of about 5×10^5 which was offset by the greater entropic factor on CdS.

A similar situation is encountered in the ZnO/TiO_2 combination (see Table 3), where electron transfer occurs from light-activated ZnO to the conduction band of light-activated TiO_2 and, conversely, hole transfer can take place from the valence band of TiO_2 to the corresponding band of ZnO. The kinetic evidence reported in Table 3 demonstrates that ZnO is a more efficient photocatalyst than TiO_2 under the present conditions (90×10^{-3} min^{-1} vs. 27×10^{-3} min^{-1}). Thus the slight increase (Table 3) in k from $(61 \pm 4) \times 10^{-3}$ min^{-1} for ZnO suspensions alone to $(71 \pm 2) \times 10^{-3}$ min^{-1} for the ZnO/TiO_2 couple is in keeping with the above expectation.

Of the various combinations examined in Table 3 with phenol as the test substrate, the TiO_2/Fe_2O_3 system is rather unique in that both the valence and conduction bands of Fe_2O_3 are sandwiched between the corresponding bands of TiO_2 (Fig. 7). Thus simultaneous excitation of both components can lead to a one-way vectorial transfer of both electrons and holes from TiO_2 particulates to Fe_2O_3; the latter is a less efficient photocatalyst than its counterpart (k values are 27×10^{-3} min^{-1} and 1.6×10^{-3} min^{-1} respectively; Table 3) under otherwise identical conditions. A parallel situation is evident in Table 3 on comparing ZnO and Fe_2O_3 performances alone and in the ZnO/Fe_2O_3 combination; electron and hole transfer from ZnO to Fe_2O_3 diminishes the efficacy of ZnO.

4. Conclusions

The vectorial transfer of electrons and holes between semiconductor particulates is a significant process in the photo- oxidative degradation of aromatic polluting substances, e.g. phenol and chlorophenols. The aim of this study was to select reactions that allowed the occurrence of such charge transfer to be shown. To our knowledge, this is the first report of hole transfer between coupled semiconductor particulates, together with a vectorial one-way displacement of both electrons and holes from one semiconductor to another. Work is under way to establish simultaneous charge transfer by picosecond laser spectroscopy on the appropriate colloidal materials. It must be pointed out that the photocatalytic activity of a semiconductor material depends, to a large extent, on its preparation (source), its nature (where more than one polymorph is available) and the pre-treatment the material receives prior to utilization. Thus the conclusions reached here pertain to those materials examined. Moreover, from a practical viewpoint, utilization of CdS alone or in coupled systems is not desirable owing to the significant quantities of toxic cadmium that are released into aqueous media from the photoanodic corrosion of the CdS-based system.

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References

[1] N. Serpone and E. Pelizzetti (eds.), *Photocatalysis—Fundamentals and Applications*, Wiley-Interscience, New York, 1989.

[2] D.F. Ollis, E. Pelizzetti and N. Serpone, *Environ. Sci. Technol., 25* (1991) 1529.

[3] R.W. Matthews, in E. Pelizzetti and M. Schiavello (eds.), *Photochemical Conversion and Storage of Solar Energy*, Kluwer Academic Publishers, Dordrecht, 1991, pp. 427–449.

[4] M.A. Fox and M.T. Dulay, *Chem. Rev., 93* (1993) 341.

[5] E. Pelizzetti and C. Minero, *Electrochim. Acta, 38* (1993) 47.

[6] D. Bahnemann, J. Cunningham, M.A. Fox, E. Pelizzetti, P. Pichat and N. Serpone, in G.R. Helz, R.G. Zepp and D.G. Crosby (eds.), *Aquatic and Surface Photochemistry*, Lewis Publishers, Boca Raton, FL, 1994, Chapter 21, pp. 261–316.

[7] N. Serpone, in T.L. Rose, O. Murphy, E. Rudd and B.E. Conway (eds.), *Water Purification by Photocatalytic, Photoelectrochemical Processes,* The Electrochemical Society Inc., Pennington, NJ, volume 94-19, pp. 236–254.

[8] N. Serpone, E. Borgarello and M. Gratzel, *J. Chem. Soc., Chem. Commun.*, (1984) 342.

[9] N. Serpone, E. Borgarello, E. Pelizzetti and M. Barbeni, *Chim. Ind. (Milano), 67* (1985) 318.

[10] N. Serpone, E. Borgarello and E. Pelizzetti, *J. Electrochem. Soc., 135* (1988) 2760.

[11] P. Pichat, E. Borgarello, J. Disdier, J.-M. Herrmann, E. Pelizzetti and N. Serpone, *J. Chem. Soc., Faraday Trans. 1, 84* (1988) 261.

[12] N. Serpone, P. Pichat, J.-M. Herrmann and E. Pelizzetti, in V. Balzani (ed.), *Supramolecular Photochemistry*, Vol. 214, Reidel, Dordrecht, 1987, pp. 415–434.

[13] M. Ashokumar and P. Maruthamuthu, *Int. J. Hydrogen Energy, 16* (1991) 591.

[14] P.V. Kamat and N.M. Dimitrijevic, *Sol. Energy, 44* (1990) 83.

[15] M. Fujii, T. Kawai and S. Kawai, *Chem. Phys. Lett., 106* (1984) 517.

[16] G. Redmond, A. O'Keefe, C. Burgess, C. MacHale and D. Fitzmaurice, *J. Phys. Chem., 97* (1993) 11 081.

[17] M.F. Finlayson, B.L. Wheeler, N. Nakuta, K.-H. Park, A.J. Bard, A. Campion, M.A. Fox, S.E. Webber and J.M. White, *J. Phys. Chem., 89* (1985) 5676.

[18] J.R. White and A.J. Bard, *J. Phys. Chem., 89* (1985) 1947.

[19] P.V. Kamat, *Chem. Rev., 93* (1993) 267.

[20] S. Hotchandani and P.V. Kamat, *J. Phys. Chem., 96* (1992) 6834.

[21] A.P. Davis and C.P. Huang, *Water. Sci. Technol., 24* (1989) 455.

[22] A.P. Davis and C.P. Huang, in Y.C. Wu (ed.), *Proceedings of the International Conference on Physicochemical and Biological Detoxification of Hazardous Wastes*, Technomic Publ., 1989, pp. 337–352.

[23] A.P. Davis and C.P. Huang, *Water Res., 24* (1990) 543.

[24] P.V. Kamat and B. Patrick, *J. Phys. Chem., 96* (1992) 6829.

[25] J. Rabani, *J. Phys. Chem., 93* (1989) 7707.

[26] P.V. Kamat, *Langmuir, 1* (1985) 608.

[27] (a) K. Vinodgopal, U. Stafford, K.A. Gray and P.V. Kamat, *J. Phys. Chem.*, in press. (b) P. Pichat, J.-M. Herrmann, H. Courbon, J. Disdier and M.N. Mozzanega, *Can. J. Chem. Eng., 63* (1982) 27.

[28] N. Serpone, E. Pelizzetti and H. Hidaka, in D.F. Ollis and H. Al-Ekabi (eds.), *Photocatalytic Purification and Treatment of Water and Air*, Elsevier Science, Amsterdam, 1993, pp. 225–250.

[29] S.W. Park and C.P. Huang, *J. Colloid Interface Sci., 117* (1987) 431.

[30] K.J. Green and R. Rudham, *J. Chem. Soc., Faraday Trans. 1, 88* (1992) 3599.

[31] T. Rajh, O.I. Micic, D. Lawless and N. Serpone, *J. Phys. Chem., 96* (1992) 4633.

[32] A. Henglein, A. Fojtik and H. Weller, *Ber. Bunsenges. Phys. Chem., 91* (1987) 441.

[33] J.R. Harbor and M.L. Hair, *J. Phys. Chem., 82* (1978) 1397.

[34] N. Serpone et al., work in progress.

[35] (a) H. Gerischer, *Electrochim. Acta, 38* (1993) 3. (b) L. Almaric, C. Guillard and P. Pichat, *Res. Chem. Intermed., 20* (1994) 579.