The Electrophoresis of Semiconductor Particles

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1 Introduction

Since the early nineteen-sixties, colloid and surface science has undergone something of a metamorphosis. Driven by a growing appreciation of its wide applicability to a number of important industrial, environmental, medical, and academic problems, it has evolved from a collection of qualitative, macroscopic descriptions of some multi-phase systems into a quantitative subject supported by a sound theoretical framework. Accompanying, and to a certain extent leading, this expansion in theoretical descriptive power has been a concomitant growth in the number of experimental techniques available to the colloid/surface scientist. PCS, TEM, SEM, HDC, SAXS, SANS, STM, FTIR, FT-Raman, EXAFS, and XRD are just a few of the techniques capable of providing information relating to either particle size or surface topology/structure, many of which have only come on-line in the past two decades; the list is seemingly endless, with more techniques being added every year.

The progressing quantification of colloid and surface science has acted in a synergistic fashion to spur further interest in an expanding range of applications in such branches of science as protein chemistry, haematology (including the characterization of the behaviour of fluorocarbon-based blood substitutes), tribology, organic synthesis, cluster chemistry, pollution abatement studies, clay and zeolite chemistry, petroleum engineering, soil science, ceramic and new materials technology, photochemistry, electrochemistry, and semiconductor physics. It is the area of commonality of the last three topics with colloid science as concerned with photocatalytic particulate-based systems that will form the focus of this review.

Colloidal semiconductor particles have been used as photocatalysts in a number of reactions, such as the reduction of N_2 to NH_3 over TiO_2 particles doped with ferric ions[1] and the oxidation of NO_2^- to NO_3^- in the presence of O_2.[2] These reaction occur initially by the absorption of photons of energies greater than that corresponding to the semiconductor band gap to form conduction band electron–valence band hole pairs (e_{CB}^-, h_{VB}^+), as shown in Figure 1. These holes/electrons may subsequently recombine or diffuse to the particle surface where, subject to the process being thermodynamically allowed, they may either reduce/oxidize particle lattice sites or undergo interfacial electron transfer, reacting with a surface adsorbed substrate, a species in solution, the solvent or catalysts deposited on the surface of the particles. Such processes can be described by an electrochemical model[3], an approach which finds great utility in the design of photocatalytic particle systems.

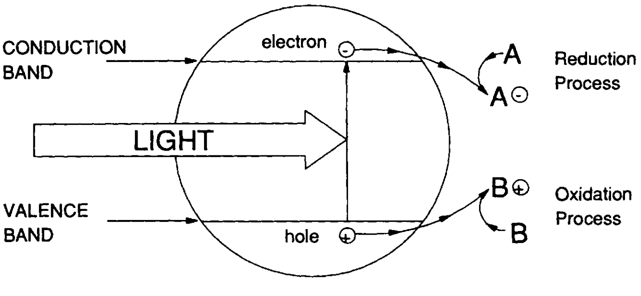

Figure 1 Semiconductor particle charge transfer processes induced by direct band gap excitation.

It is this latter phenomenon that has recently imparted additional momentum to the study of colloidal semiconductors. They can be used as models for redox species-mediated interfacial electron transfers in biological systems, or regarded as tiny electrochemical cells/engines capable of performing microheterogeneous photocatalysis within a dispersion phase that has the appearance of macro-homogeneity.[4] For example, materials such as SnO_2, TiO_2, and CdS have been used in laboratory-scale pollution abatement systems, reducing both organic (especially halogenocarbons[5] and benzene derivatives[6] and inorganic (*e.g.* cyanide, sulfite, sulfide, nitrites *etc.*[2,3,7]) impurities/toxins to chemically useful and/or biologically harmless compounds. Also, semiconductor photocatalysts find utility in environmentally important reactions; TiO_2 and CdS can act as both CO_2[8] and N_2 fixatives,[9] while airborne particulate oxide semiconductors photocatalytically contribute to acid rain generation.[2] The elucidation of the mechanistic details of such reactions has attracted a great deal of attention for the purposes of either trying to improve efficiency prior to engineering scale-up or, in the case of acid rain formation, deliberate inhibition. In all of the examples cited, reaction characterization by way of product analysis and rate determination measurements is relatively straightforward; however, very few techniques are available for *in situ* investigations of the mechanistic details and catalytic properties of colloidal semiconductors.

Electrophoresis is the movement of charged particles in a suspension resulting from the imposition of an electric field, a phenomenon which may be quantified by measurement of the electrophoretic mobility, u_E (units: $m^2\ V^{-1}\ s^{-1}$), the velocity v_E ($m\ s^{-1}$) of a particle per unit field strength E ($V\ s^{-1}$; $u_E = v_E/E$). Any difference in the reaction kinetics of valence band holes and conduction band electrons photogenerated on semiconductor particles will lead to a change in particle charge. For example, if photogenerated holes can react with a dissolved reductant but the electrons cannot, then a net negative charge will accumulate on the particles. This may be detected by electrophoretic means providing, in principle, a non-perturbative technique for following photoredox reactions by measurement of the net photoinduced change in surface charge – *photoelectrophoresis.*

The review will proceed as follows. After a discussion of some general semiconductor particle related concepts, some applied aspects of semiconductor colloid science and currently adopted methods of study will be presented. This will lead into a more specific description of the technique of electrophoresis and its

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utility in photochemical systems, photoelectrophoresis The review will conclude with a summary of some of the more recent advances in the field of semiconductor colloid chemistry

2 Semiconductor Particles

Calculations of photogenerated charge carrier intra-particle dynamics based on a random walk model have revealed that, for semiconductor particles of colloidal dimensions, the transit time of electrons/holes from the particle interior to the surface is, at most, a few tens of picoseconds [10] In the case of TiO_2, this is of the same order as the charge carrier recombination time By reducing the particle radius it is possible to obtain systems where transit from the particle interior to the surface occurs more rapidly than recombination, implying that quantum efficiencies for photoredox reactions of near unity are feasible However, the achieving of such high quantum efficiencies depends very much upon the rapid removal of one or both types of charge carrier upon their arrival at the semiconductor surface, underlining the importance of the interfacial charge-transfer kinetics

The kinetics of photogenerated electron/hole removal from a semiconductor particle by a suitable charge carrier acceptor in solution involves two steps The first step is the diffusion-controlled formation of an encounter complex between the electron/hole acceptor molecule and the particle The second step is the electrochemical interfacial charge-transfer, which may be characterized by a rate constant k_{ct} ($m\ s^{-1}$) Albery *et al* [11] and Gratzel *et al* [12] have independently arrived at the same result, relating the observed bimolecular rate constant for hole/electron acceptor oxidation/reduction, k_{obs} ($m^3\ s^{-1}$), to reactant diffusion and k_{ct}

$$\frac{1}{k_{obs}} = \frac{1}{4\pi R^2}\left(\frac{1}{k_{ct}} + \frac{R}{D}\right) \tag{1}$$

where R (m) and D ($m^2\ s^{-1}$) are the sums of the radii and diffusion coefficients respectively of the particle and the charge carrier acceptor Equation 1 has two limiting asymptotic forms The first case arises when interfacial charge-transfer is much slower than diffusion ($k_{ct} \ll D/R$) and therefore rate determining

$$k_{obs} = 4\pi R^2 k_{ct} \tag{2}$$

The second case arises when diffusion is much slower than charge transfer ($k_{ct} \gg D/R$) and therefore rate determining

$$k_{obs} = 4\pi RD \tag{3}$$

However, due to several complicating factors, these expressions are not as generally applicable to real systems as may first appear The first complicating factor to be considered is that of adsorption or chemical fixation of the charge carrier acceptor onto the particle surface Fortunately, under these circumstances, the net effect is that of simplification to equation 2 as diffusion effects may be eliminated and interfacial charge transfer kinetics take sole control [4] Then k_{ct} may be expressed as

$$k_{ct} = \frac{\delta}{\tau_{ct}} \tag{4}$$

where δ is the reaction layer thickness (m) and τ_{ct} is the average time(s) taken for a charge carrier to tunnel across the interface

The second complicating factor is that, unless steps are taken to prepare a monodisperse sample, colloidal dispersions frequently exhibit a distribution of particle sizes Equation 1 shows that k_{obs} is particle size dependent and that consequently particles with different radii should have different rate constants, the larger particles reacting faster than the smaller Such effects have indeed been observed and Albery *et al* [13] have proposed a general model based on a Gaussian distribution of the logarithm of the rate constant about some mean with the width of the distribution as an additional parameter, the dispersion in the rate constants being directly related to the dispersion in the particle radii Good agreement between the value of the radial dispersion found from dynamic light scattering and the value found from kinetic analysis has been demonstrated for semiconductor particle systems [13]

The third complication arises from the particle charge As will be described below, apart from under exceptional conditions, the surface of a solid immersed in a liquid will, by one or more of a variety of mechanisms, acquire a net charge The kinetic model of interfacial electron-transfer reactions described in equations 1—3 ignores Coulombic effects such as electrostatic migration and only considers the approach of the particle and acceptor in terms of diffusion Equations 1—3 would therefore only be valid under conditions where the particle is uncharged (exceptional and difficult to achieve, see below) or the acceptor is uncharged or the ionic strength is high Obviously, the latter is an undesirable condition to impose on any colloidal dispersions which derive their kinetic stability with respect to aggregation solely from inter-particle electrostatic repulsion Thus, in general, equations 1—3 must be corrected to account for electrostatic attraction/repulsion and, to facilitate this, the magnitude of the particle charge quantified The latter is properly the province of the next section The former has been investigated by Brown and Darwent[14] who demonstrated that the rate of reduction of methyl viologen, MV^{2+}, by the conduction band electrons of colloidal TiO_2 is significantly affected by the particle charge and the ionic strength of the sol Further, they semi-quantified this effect by empirically deriving an equation relating k_{ct} to pH and ionic strength from the control these two quantities are known to exercise over the particle surface charge/potential

The importance and utility of particle surface charge measurement is further highlighted by several other considerations relevant to particulate semiconductor systems The first of these is elucidation of the specifics of the reactions undergone by photogenerated charge carriers once they reach the particle surface Reactions of electrons/holes with lattice sites or adsorbed substrates at the semiconductor–solution interface will obviously lead to a surface charge change, however, surface charge changes will also be observed if the valence band hole/conduction band electron-driven oxidation/reduction of a solution phase species (solute or solvent) proceeds *via* a surface-adsorbed intermediate, or if the kinetics of the two photoredox processes differ, due for example to the catalytic properties of the particles, so allowing one type of charge carrier to accumulate on the particles with respect to the other Detection of the magnitude and time-dependent behaviour of this photogenerated charge change may impart valuable information concerning the mechanistics and kinetics of such systems

The second consideration highlighting the importance of particle surface charge is the need to better match the semiconductor band gap to the spectral profile of incident sunlight, calculations performed by Archer[15] indicate that the optimum band gap for threshold absorption-based solar energy conversion devices is 1 1 eV Materials such as TiO_2 and SnO_2 have band gaps (*ca* 3 2 and 3 5 eV respectively) that are prohibitively large for solar energy harvesting, however, the absorptive range and thus the photoresponse of such large band gap semiconductors may be extended by semiconductor surface modification In these systems a sensitizer molecule, usually a photoactive redox couple or dye with a high extinction coefficient in the visible *e g* eosin, cresyl violet, rhodamine B, phthalocyanines, or ferrocyanide and its analogues, is attached to the particle surface Illumination results in electron injection from a photoexcited state of the sensitizer into the conduction band of the semiconductor particle support, thus effecting charge separation with light of less energy than band gap The principle is illustrated in Figure 2 from which it is immediately obvious that such a process would result in a change in the particle surface charge Much relevant data has been accumulated over the past ten years on the behaviour of dye-sensitized semiconductor devices,[4] nevertheless, more precise information concerning the

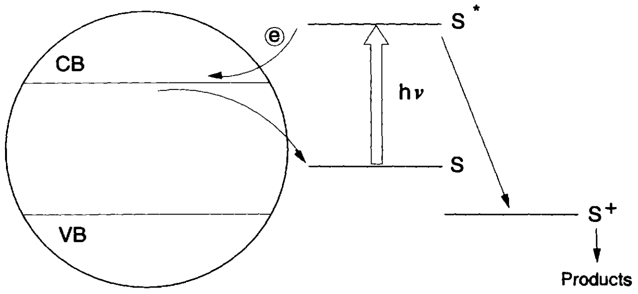

Figure 2 Charge transfer processes induced by charge injection from the excited state of an adsorbed molecule into the conduction band of a semiconductor particle

efficacy of sensitizer molecule surface attachment and the dynamics of the electron injection process are rapidly needed; indeed, one of the most important criteria for achieving efficient photosensitization is effective dye adsorption on the semiconductor surface *via* chemical or electrostatic interaction. Surface charge measurements on dye-sensitized semiconductor particles would afford some of that information.

The third consideration is the preference for non-perturbative interrogation methods with which to investigate the properties of colloidal semiconductor dispersions. Since aqueous dispersions of these particles are transparent (light scattering depending on particle size), optical methods may be used for reactant, reaction intermediate, and product analysis enabling reaction kinetics to be determined, mechanisms to be elucidated, and the probing of some catalyst properties *in situ*. Techniques such as flash photolysis, UV–visible spectrophotometry,[14] and the optical rotating disc electrode (ORDE)[16] have all found great applicability in the study of semiconductor colloids and it is expected that particle charge measurements by electrophoresis will be of similar utility.

3 Electrophoresis

3.1 The Origins of Surface Charge

Electrophoresis is the movement of suspended or dissolved material under the influence of an applied electric field. It is one of a family of phenomena that arise from the relative motion of the mobile and immobile components of the electrical double layer. These phenomena, of which there are four, are known as the *electrokinetic effects*.

When brought into contact with a polar medium, most materials acquire a net surface electric charge due to one or more of four possible charging mechanisms:

(i) Surface dissociation – metal oxides and hydroxides acquire their charge mainly through the ionization of surface hydroxy groups:

$$\mathrm{M{-}OH(s) \rightarrow M{-}O^-(s) + H^+(aq)} \qquad (5a)$$

$$\mathrm{M{-}OH(s) + H^+(aq) \rightarrow M{-}OH_2^+(s)} \qquad (5b)$$

The ionization of these groups, and so the net surface charge, can be seen to depend on the pH of the solution. At low pH the surface will be positively charged and at high pH it will be negatively charged. The pH of a solution free of ions capable of surface adsorption (such as Na^+ or Cl^-) at which the net charge due to surface ionization is zero is called the iso-ionic point or *point of zero charge* (p.z.c.). The pH at which the electrophoretic mobility is zero is called the *iso-electric point* (i.e.p.) or point of zero zeta potential (p.z.z.p.). The concept of the zeta potential will be discussed below.

(ii) Ion adsorption – net surface charge may be acquired by the adsorption of charged ions. It is this adsorption that may be the cause of an observed non-coincidence of the i.e.p. and the p.z.c. For example, a surface which is already charged due to surface ionization may show a tendency to adsorb counter ions. Such adsorption, in the extreme case, may lead to a reversal of surface charge and a concomitant separation of the i.e.p. from the p.z.c.

(iii) Surface dissolution – a net surface charge can arise on ionic materials due to unequal dissolution of the oppositely charged ions from which they are composed.

(iv) Crystal lattice defects – crystal lattice defects are responsible for the large charge densities observed on some clay mineral systems. In those cases the defect is usually the isomorphous replacement of one ionic species with another of lower charge.

Once acquired, the surface charge will influence the distribution of ions in the polar medium; ions of opposite charge (counter ions) are attracted towards the surface and ions of like charge are repelled away. This, in tandem with the mixing effect of thermal motion, leads to the formation of the *electric double layer*.

3.2 The Structure of the Electric Double Layer

To enable quantitative interpretation of electrokinetic phenomena and their relevance to colloid and surface science, an understanding of the structure of the electric double layer is necessary. The history of the model of the electric double layer is complicated and too long to describe within the bounds of this review; thus, discussion will be restricted to the currently accepted model due to Grahame,[17] illustrated in Figure 3, with the interested reader being referred to any of the many excellent texts that already exist about the subject.

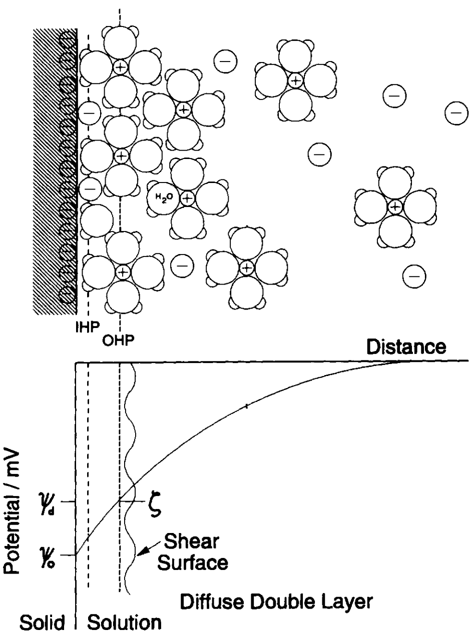

Figure 3 Schematic model of the electric double layer as described by Grahame.[17] The ion (top) and potential (bottom) distributions are in a direction perpendicular to the plane of the solid phase IHP is the inner Helmholtz plane, OHP is the outer Helmholtz plane

Figure 3 shows that potential decreases exponentially with distance from the solid material phase surface, eventually reaching zero in the solution bulk, as counter ions in solution shield and neutralize the potential at the outer Helmholtz plane (OHP). The OHP is recognized as the plane of closest approach of non-specifically adsorbed, fully solvated ions. Figure 3 also shows that some ions are rigidly attached to the solid material surface, some are loosely bound, while others in bulk solution are not attached at all. If the solid material phase is a moving particle, then the boundary of that particle and its associated solvent and counter ions with the surrounding solution constitutes a slipping/shear plane. Direct measurement of the potential at the solid material surface or the OHP is virtually impossible. However, measurement of the potential at the plane of shear between the charged particle–solvent–counter ion assembly and the electrolyte solution is simple, quick, and accurate; it is then a matter of employing a suitable model of the double layer to estimate the other potentials.

The potential at the slipping plane is known as the electrokinetic or zeta potential (ζ: V) and, for particles, is most conveniently measured by electrophoresis, the measurement of particle velocity under the influence of an applied electric field. A long, thin cylindrical capillary cell is used to produce a uniform electric field and the particle velocity along the capillary measured by either direct optical microscope observation or by use of laser Doppler light scattering techniques (Figure 4). The electrophoretic mobility, the constant of proportionality relating the particle velocity to the applied field strength, may then be evaluated by dividing the former quantity by the latter.

3.3 The Relationship between Electrophoretic Mobility, Zeta Potential, and Particle Surface Charge

The Henry equation, the relationship between u_E and ζ-potential most usually employed in particle charge measurement by electrophoresis, is obtained by the incorporation of an extra electrical body force term into the equations of Stokes and their analytical solution, assuming that the charge density on the particles is unaffected by the applied field. The Henry equation is usually written as

$$u_E = \frac{2\epsilon_0\epsilon_r\zeta}{3\eta}f(\kappa a) \qquad (6)$$

where ϵ_0 is the vacuum permittivity (8.854×10^{-12} F m^{-1}), ϵ_r is the relative permittivity of the dispersion medium, η is the viscosity of the dispersion medium (N m^{-2} s), a is the particle radius (m) and κ is the reciprocal Debye length (m^{-1}), given by

$$\kappa = \left(\frac{2Le^2I}{\epsilon_0\epsilon_r k_B T}\right)^{\frac{1}{2}} \qquad (7)$$

where e is the electronic charge (1.602×10^{-19} C), L is Avogadro's number (6.02205×10^{23} mol^{-1}), k_B is the Boltzmann constant (1.38×10^{-23} J K^{-1}), T is the absolute temperature (K), and I is the ionic strength (mol m^{-3}), given by

$$I = 0.5\sum_i c_i z_i^2 \qquad (8)$$

where c_i and z_i are respectively the concentration (mol m^{-3}) of, and number of elementary charges on, ionic species i.

f(κa) is a monotonically varying function which increases from 1 at $\kappa a = 0$ to 1.5 at $\kappa a = \infty$. Asymptotically, when $\kappa a \ll 1$ (Debye length > particle radius), f(κa) = 1 and the Henry equation reduces to the Huckle equation

$$u_E = \frac{2\epsilon_0\epsilon_r\zeta}{3\eta} \qquad (9)$$

More commonly, the thickness of the particle double layer is found to be small compared with the particle radius. Under this condition ($\kappa a \gg 1$), f(κa) asymptotically approaches 1.5 and the Henry equation reduces to the Smoluchowski equation

$$u_E = \frac{\epsilon_0\epsilon_r\zeta}{\eta} \qquad (10)$$

However, the assumption of non-perturbation of the particle surface charge density distribution by the applied field is not always valid. Consequently, exact numerical solutions of the coupled differential equations that govern flow around colloidal particles and the ion densities around a sphere have been obtained by O'Brien and White,[18] from whom user friendly software facilitating simple application of their findings may be obtained.*

Although it is impossible to provide an analytical solution for the complete Poisson–Boltzmann equation in the spherical case and thereby relate particle charge to the zeta potential directly, a number of analytical approximations are available, the most useful of which is the semi-empirical relationship of Loeb *et al.*, which for a monovalent electrolyte is

$$Q = \frac{8\pi\epsilon_0\epsilon_r k_B T\kappa a^2}{e}\left[\sinh\left(\frac{e\zeta}{2k_BT}\right) + \frac{2}{\kappa a}\tanh\left(\frac{\epsilon\zeta}{4k_BT}\right)\right] \qquad (11)$$

where Q is the total charge on the particle (C). Finding application over a wide range of values of κa and ζ, the Loeb equation can be seen to reduce to either the approximate Debye–Hückel expression at low values of ζ, or the expression for flat plates at large κa.[19]

Calculations show that under the conditions employed in most of the work reviewed in the next section, for $\zeta < 0.040$ V the particle charge is directly proportional to the electrophoretic mobility. Thus, if an ongoing chemical reaction at the particle surface can be related to a change in the surface charge of the

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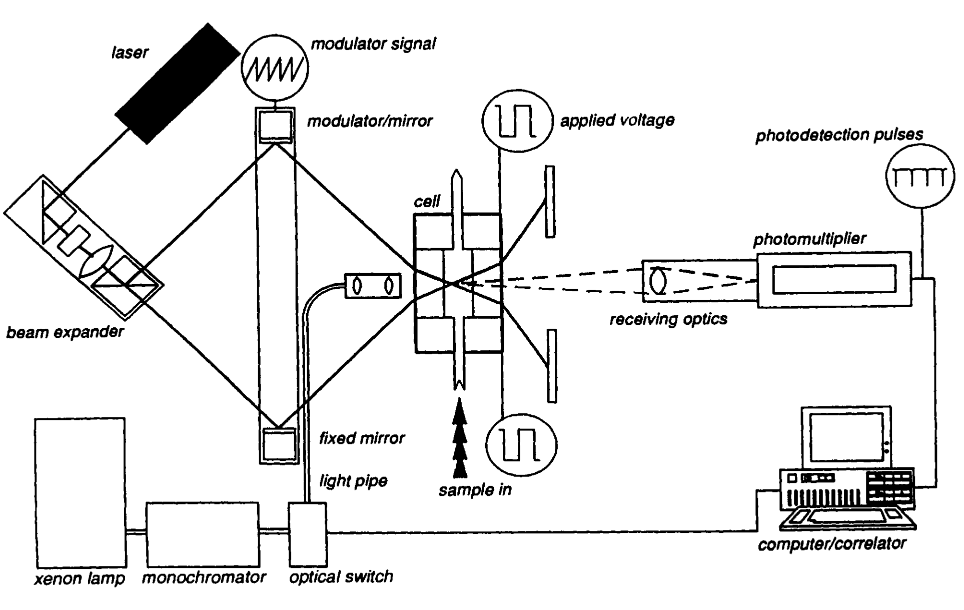
Figure 4 The photoelectrophoresis apparatus.



particle, electrophoresis will provide an excellent, non-perturbative method by which the reaction may be followed

4 Photoelectrophoresis

As described in the introduction, any difference in the kinetics of the oxidation reaction associated with photogenerated valence band holes and the reduction reaction associated with photogenerated conduction band electrons on semiconductor particles will lead to a change in the particle net surface charge This phenomenon was first observed in 1967 by use of microscope electrophoresis, presumably with particles of sizes $\geqslant 10^{-6}$ m

Oppenheim *et al* [20] studied the effect of 365 nm UV radiation on the microelectrophoresis of aqueous ZnO suspensions, on which dissolved oxygen was reduced to hydrogen peroxide The surface charge became more positive in the presence of UV light and O_2, but the effect decreased with increasing pH, no effect was observed in deoxygenated solutions It was proposed that oxygen captured conduction band electrons from ZnO, forming O_2^- ions which desorbed leaving the surface more positively charged, presumably due to hole accumulation

$$O_2(aq) + e_{CB} \rightarrow O_2^-(ads) \rightarrow O_2^-(aq) \qquad (12)$$

The pH effect was ascribed to either surface ionization by proton loss from the Zn–OH groups, or adsorption of OH^- or hydrolysed Zn^{II} species, both effects leading to an increasingly negative surface charge with increasing pH, which was supposed to inhibit electron transfer to the oxygen molecule A further possibility considered is that the effect could have arisen from photocorrosion of the ZnO, producing hydrolysed Zn^{II} species, which then re-adsorbed from solution, causing the observed change in electrophoretic mobility

$$2ZnO(s) + 2H_2O(l) + 4h^+_{VB} \rightarrow O_2(aq) + 2ZnOH^+(ads) + 2H^+(aq) \qquad (13)$$

Monohydroxy complexes such as $ZnOH^+$ ions are well known to adsorb on metal oxide surfaces by both coulombic interaction and hydrogen bonding

The work of Hauffe and Volz[21] involved n-type TiO_2, ZnO, and CdS particles dispersed in toluene with calcium diisopropylsalicylate or decanate to stabilize the dispersion The observed change in the particle zeta potentials with UV irradiation was attributed to the oxidation of isopropanol added to the toluene in the case of CdS, and to oxidation of toluene in the case of TiO_2 and ZnO In the presence of an electron scavenger, such as dissolved oxygen, it was proposed that reversal of the charge in both the space-charge zone and the surface, led to a reversal of the direction of the electrophoretic motion for all three materials when illuminated

The experiments of Dunn *et al* [22] involved determination of the electrophoretic mobility of aqueous dispersions of TiO_2 particles in the 'dark' and under illumination, as a function of pH The results showed that irradiation with light from a xenon arc lamp directed at the electrophoresis cell with fibre optics, caused an increase in the negative charge on the particle surfaces in the absence of easily reducible species in solution This was attributed to the hole-driven oxidation of water coupled to a slower electron reduction of protons, so that electrons accumulated on the particles

$$2H_2O(l) + 4h^+_{VB} \rightarrow O_2(aq) + 4H^+(aq) \qquad (14)$$

When the TiO_2 particles were coated with platinum, illumination had no effect on the electrophoretic mobility, as the Pt catalysed the dissipation of the net photocharge by proton reduction

$$2H^+(aq) + 2e^-_{CB} \rightarrow H_2(aq) \qquad (15)$$

Assuming the measured change in electrophoretic mobility on illumination was due to electronic charge (h^+_{VB} or e^-_{CB}), the latter quantity was estimated using established methods at 150 C m^{-2} [18,19]

More recently, results have been reported that were obtained by use of a commercially available laser Doppler electrophoresis system, the Malvern Zetasizer IIc, that had been customized as shown in Figure 4 to accommodate a fibre optic light source from a 900 W xenon arc lamp and monochromator, to enable semiconductor particle (photo-) electrophoretic mobilities to be determined as a function of wavelength of exciting radiation [23] An optical switch, under software control, was incorporated into the apparatus to facilitate determination of time-dependent photoelectrophoresis behaviour

Figure 5 shows the electrophoretic mobility distributions obtained for TiO_2 particles under acid conditions in the dark and when exposed to monochromatic light of wavelength 310 nm Irradiation of the particles with the xenon lamp caused a distinct change in the mobility corresponding to the formation of net positive charge on the surface

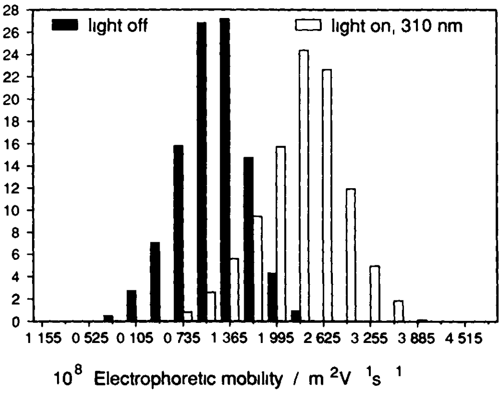


Figure 5 Effect of 310 nm illumination on TiO_2 sample at pH 2 8 Average dark mobility, 1 18 × 10^{-8} m^2 V^{-1} s^{-1}, average light mobility, 2 34 × 10^{-8} m^2 V^{-1} s^{-1}, photogenerated mobility change, 1 16 × 10^{-8} m^2 V^{-1} s^{-1}, mean particle diameter, 5 85 × 10^{-7} m
(Reproduced by permission from *J Chem Soc Faraday Trans* , 1991, **87**, 3537)

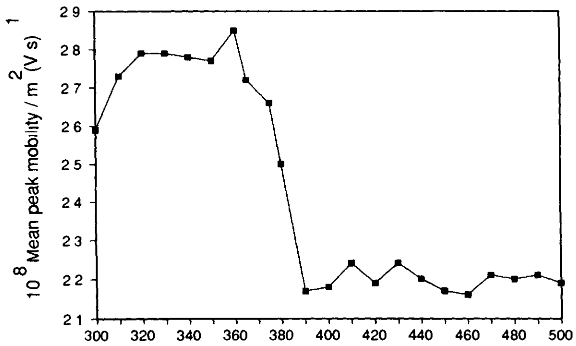


Figure 6 TiO_2 particle electrophoretic mobility distribution median as a function of illumination wavelength pH 2 8, mean particle diameter, 7 5 × 10^{-7} m, band gap, 390 nm(3 2 eV)
(Reproduced by permission from *J Chem Soc , Faraday Trans* , 1991, **87**, 3537)

Figure 6 shows the photo-induced electrophoretic mobility change under acid conditions as a function of the irradiation wavelength At photon energies less than the band gap, no change from the dark mobility was detected, at photon energies greater than the band gap, the observed mean mobility changed in such a fashion as to be congruent with an increase in the net surface positive charge, demonstrating that this was attributable directly to photogenerated charge Conversely, when the particles were irradiated at basic pHs, the photo-induced change in

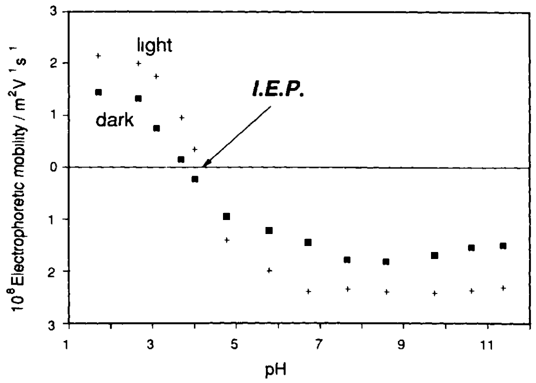


Figure 7 TiO_2 particle electrophoretic mobility–pH isotherm (■), in the dark, (+), under 310 nm illumination Ionic strength, 7 5 mol m $^{-3}$
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mobility corresponded to the accumulation of negative charge on the surface, as shown in Figure 7 This may be explained by considering the two types of surface oxygen that exist on TiO_2 those having monodentate attachment to the surface Ti (terminal –Ti–O in base) and those having a bidentate linkage (bridged –Ti–O–Ti–) Photogenerated holes oxidize the former whilst photogenerated electrons reduce the latter Under acid conditions, the bidentate oxygen sites may then be 'protonated' to produce a net increase in surface positive charge, under basic conditions, the oxidized monodentate sites may react with solution hydroxide to produce surface $(\text{–Ti–O–O–H})^-$ sites and a consequent net increase in surface negative charge The photonically induced surface processes of TiO_2 are summarized in Figure 8

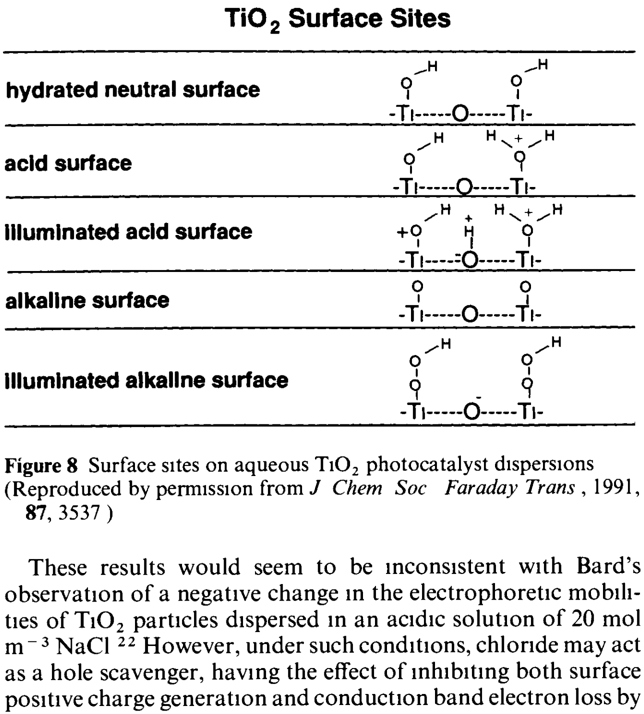

Figure 8 Surface sites on aqueous TiO_2 photocatalyst dispersions (Reproduced by permission from *J Chem Soc Faraday Trans*, 1991, **87**, 3537)

These results would seem to be inconsistent with Bard's observation of a negative change in the electrophoretic mobilities of TiO_2 particles dispersed in an acidic solution of 20 mol m^{-3} NaCl [22] However, under such conditions, chloride may act as a hole scavenger, having the effect of inhibiting both surface positive charge generation and conduction band electron loss by intra-particle recombination, resulting in a negative change in the charge on the particle surface The results presented in Figures 5—7 were obtained in the absence of any such deliberately introduced solution phase charge scavenger

Photoinduced changes in electrophoretic mobility have also been observed for suspensions of SnO_2 [24] and CeO_2 Encouraging results have been obtained from photoelectrophoretic measurements on Ti_4O_7, a hydrogen-reduced phase of TiO_2, and $Fe(CN)_6^{4-}$ photo-sensitized TiO_2 particles in an effort to better match the absorption profile of the particles with the spectral profile of incident sunlight [23] photoinduced mobility changes have been observed in such systems at illumination wavelengths corresponding to photon energies less than the band gap of TiO_2 No such shifts have been observed for CdS or FeS_2 particles in the absence of any excess lattice ions, probably due to decomposition of the particles to generate a surface layer of photo-inactive sulfur [23]

A second-order kinetic model for the time dependence of photo-generated changes in electrophoretic mobilities of aqueous dispersions of semiconductor particles in the absence of hole and electron scavengers has recently been reported and used to derive rate parameter values [25] In the case of TiO_2, the second-order rate constant for intra-particle electron hole recombination, k_r, was determined as $> 10^6$ times greater than either of the pseudo-first-order rate constants for charged surface site generation from electrons and holes, indicating that recombination is a dominant process in determining the efficiency of surface charge generation in the absence of any charge carrier scavengers The rate constants for positive and negative surface charge removal by electrons and holes (essentially surface recombination) have been determined as being ~ 1 to 100 m^3 mol^{-1} s^{-1}, and compare very closely with the value of k_r, indicating that these processes compete with direct electron–hole recombination The quantum efficiencies for hole/electron capture by oxidizable/reducible sites on the particle surface were determined and found to be very low, in the range $5\ 2 \times 10^{-6}$ to $7\ 9 \times 10^{-6}$, indicating the lack of applicability of such particles as solar energy conversion systems whilst in the absence of charge carrier scavengers

The photoelectrophoretic properties of colloidal haematite have recently been described [26] As iron oxides are ubiquitous in nature, the possibility of their adventitious precipitation on and modification of surface properties of colloidal photocatalysts in water/effluent treatment processes presents itself The photocatalytic behaviour of iron oxides is of interest in that the band gap of haematite ($\approx 2\ 2$ eV) is well matched to the solar spectrum and that iron–titanium mixed oxide systems have been shown to act as N_2 fixatives [1] The surface chemistry of aqueous dispersions of colloidal haematite, magnetite (Fe_3O_4), and iron oxyhydroxide surface-modified haematite has been studied using photoelectrophoresis and Fourier transform infra-red spectroscopy (FTIR) As in the cases of TiO_2 and SnO_2, absorption of ultra-band gap energy photons results in the generation of hole pairs, which may then recombine or react with lattice sites, solvent, or solution species

Changing the pH of α-Fe_2O_3 particle preparation from 2 to 1 4 was found to alter the resultant surface from one comprised mostly of α-Fe_2O_3, α-FeOOH and γ-FeOOH with an i e p of 7 4, to one whose behaviour was dominated by the presence of δ-FeOOH with an i e p of 1 5 α-Fe_2O_3 particles whose surfaces are found to be mostly '$Fe(OH)_3$'/Fe_2O_3 $n H_2O$ in character exhibit a continuum of i e p s due to the non-crystalline nature of that phase Large changes in the electrophoretic mobility of colloidal α-Fe_2O_3 at pH $< \approx 7$—8 were observed upon irradiation with photons of ultra-band gap energies, indicative of the formation of net surface positive charge, due to the hole-driven photo-oxidation of surface >Fe—OH sites to form $(\text{>Fe—OH})^+$ sites Photogenerated conduction band electrons were removed from the particles *via* either the reductive dissolution of the α-Fe_2O_3 surface or, possibly, the formation of hydrogen from the reduction of H^+ ions The photoelectrophoretic mobility – illumination wavelength spectrum of colloidal α-Fe_2O_3 (Figure 9) exhibited two distinct mobility change onsets, one at 2 2 eV, the other at 3 eV, reflecting the presence of an 'upper' and 'lower' valence band on haematite The oxidation of surface >Fe—OH groups responsible for the change in net surface positive charge was found to proceed ten times more slowly than the corresponding reaction on colloidal TiO_2

The photoelectrophoretic behaviour of semiconductor colloids in the presence of deliberately added solution-phase electron or hole scavengers has also been investigated [26] Colloi-

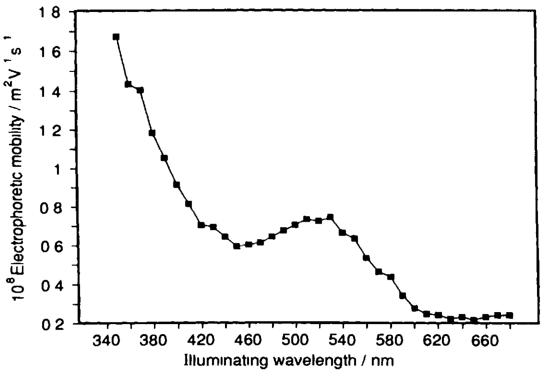

Figure 9 α-Fe_2O_3 particle electrophoretic mobility distribution median as a function of illumination wavelength pH 2 5, mean particle diameter, 6 5 × 10^{-7} m, ionic strength, 3 2 mol m^{-3}, band gap, 590 nm (2 2 eV)

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dal α-Fe_2O_3 was found to exhibit a greater change in electrophoretic mobility corresponding to the formation of net surface positive charge in the presence of O_2 than in its absence (Figure 10) This may be attributed to the scavenging of conduction band electrons by oxygen, so reducing the extent of electron/hole recombination, allowing an increased number of photogenerated holes to reach the particle–solution interface and consequently enhance the rate of surface positive charge generation This technique was applied to charge scavengers relevant to pollution abatement studies, such as CN^-, SO_3^{2-}, and HS^- ions, however, interpretation of the results is not straightforward

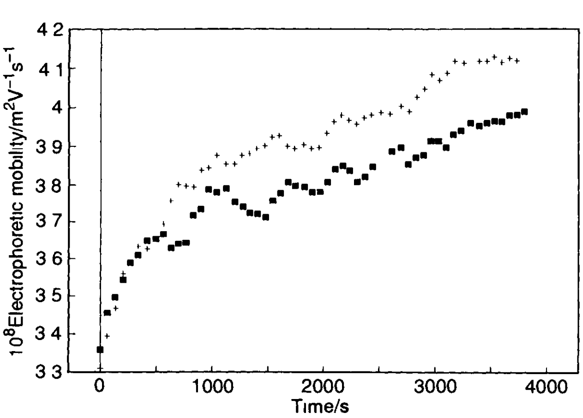

Figure 10 Electrophoretic mobility distribution median as a function of illumination time at 350 nm for α-Fe_2O_3 (pH 2 09, mean particle diameter, 3 5 × 10^{-7} m) ■, O_2-free (nitrogen purge), +, O_2-saturated (oxygen purge) Initial mobility in the dark is 3 3 × 10^{-8} m^2 V^{-1} s^{-1}, final mobility in the light for O_2-free sample is 3 95 × 10^{-8} m^2 V^{-1} s^{-1}, final mobility in light for O_2-saturated sample is 4 15 × 10^{-8} m^2 V^{-1} s^{-1}

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At pH = 11, addition of CN^-, SO_3^{2-}, or HS^- ions, species known to scavenge charge from semiconductor particles under other conditions, to the solution phase of colloidal TiO_2 and SnO_2 dispersions made no difference to the observed photoelectrophoretic behaviour [27] At that pH, both TiO_2 and SnO_2 surfaces are above their respective i e p s and are consequently negatively charged Therefore, the lack of any change in the photoelectrophoretic behaviour generated in the presence of anionic scavengers may be attributed to the Coulombic repulsion that would be expected between the scavengers and the particles

Experiments have been performed on SnO_2 sols in the absence (Figure 11a) and presence of HSO_3^- ions (Figure 11b) and H_2S at pHs low enough to render the particles positively charged [27] Figure 11a shows behaviour typical of SnO_2 at low pH, *i e* a photogenerated mobility change consistent with the formation of a net positive surface charge On addition of HSO_3^- ions, the behaviour of the electrophoretic mobility distribution median of colloidal SnO_2 as a function of ultra-band gap illumination time changed radically, as shown in Figure 11b There are several points to note First, the electrophoretic mobility observed in the dark decreased from 0 9 × 10^{-8} m^2 V^{-1} s^{-1} to 0 × 10^{-8} m^2 V^{-1} s^{-1} upon addition of sulfite, due to the strong adsorption of HSO_3^- anions on positively charged SnO_2 particles Secondly, the photogenerated electrophoretic mobility change observed was initially consistent with the formation of negative surface charge This may be attributed to the HSO_3^- ions being oxidized by photogenerated holes and their subsequent dissolution, so allowing the accumulation of negative charge However, at times > ≈ 150 s, the accumulated negative charge was diminished by an additional process, similar to that observed in the absence of charge scavengers A fuller understanding of the processes occurring in this system will require a range of analytical techniques providing complementary information to that obtainable from photoelectrophoresis

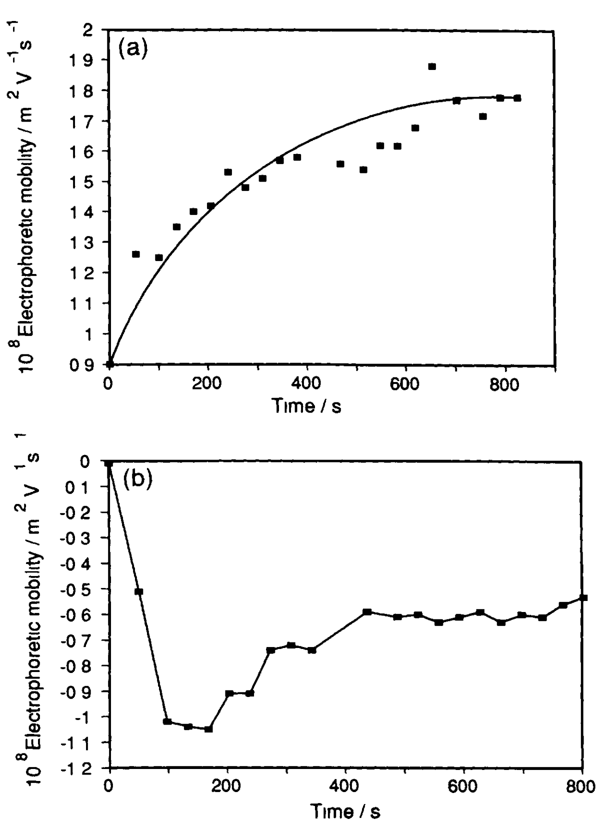

Figure 11 (a) Electrophoretic mobility distribution median as a function of illumination time at 310 nm for SnO_2 pH 3 5, initial mobility in the dark is 0 9 × 10^{-8} m^2 V^{-1} s^{-1}, final mobility in the light is 1 74 × 10^{-8} m^2 V^{-1} s^{-1} (b) Electrophoretic mobility distribution median as a function of illumination time at 310 nm for SnO_2 in the presence of 10 mol SO_3^{2-} m^{-3} pH 3 5, initial mobility in the dark is 0 m^2 V^{-1} s^{-1}, mobility in the light after 150 s is − 1 05 × 10^{-8} m^2 V^{-1} s^{-1}, final mobility in the light is − 0 55 × 10^{-8} m^2 V^{-1} s^{-1}

5 Future Trends

As stated above, materials such as TiO_2 only absorb a small portion of the solar spectrum in the near UV (band gap ≈ 3 2 eV), it is therefore desirable to shift the absorption of large band gap semiconductors to the red region of spectrum or find materials with better solar absorption characteristics Of equal importance is the identification of materials that exhibit greater charge separation and better interfacial electron transfer kinetics Many strategies have been adopted to achieve these ends and experiments have already been conducted on dye-sensitized materials, hydrogen-reduced metal oxides, metal-doped materials, surface catalyst loaded materials, binary particle systems *etc* However, it is prudent to characterize the exact mechanism of the reaction of interest on the parent semiconductor material before considering modification, *e g* is OH˙ H_2O_2, or h^+_{VB} the reaction primary in the oxidation of some specified pollutant or biocide generation over particulate TiO_2?

The examination of the mechanism and efficiency of such systems is necessarily model-dependent For example, one model for the process of photodegradation of organic compounds by colloidal semiconductors assumes that surface adsorption of the pollutant may be necessary for efficient remediation Consequently, a Langmuir–Hinshelwood or multi-layer adsorption BET kinetic model modified to accommodate reactions occurring at the solid–liquid interface would find great utility in the study of such systems [28] Unfortunately, difficulties can arise because of the widely established coexistence of acid and base sites on MO_x surfaces, the extent of the adsorption of pollutants with acid and base character may vary with pH, further, the Langmuir–Hinshelwood model suffers from some ambiguity in that its analytical formulation is identical with that obtained even for reactions occurring entirely within a homogeneous phase Photoelectrophoresis, with its information relating to charge change on adsorption (which may be investigated as a function of solute concentration and pH) and surface charge change as a function of illuminaton time, may go some way to answering the questions associated with such a kinetic analysis

As well as the remediation of inorganic pollutants such as CN , SO_3^2 , HS , colloidal semiconductors may also be employed in the destruction of organic materials such as benzene, phenol, chlorobenzenes, chlorophenols, naphthol, fluorinated aromatics *etc* [10] However, the poor aqueous solubility of some organic pollutants of interest, such as the carcinogenic polycyclic aromatic hydrocarbons (PAHs), results in low particle–pollutant contacting Thus, attention is turning towards the photoelectrochemical properties of semiconductor particles dispersed in organic solvents because of the higher solubilities exhibited therein by many classes of organic contaminant, further, the use of non-aqueous solvents prevents the corrosion (and photocorrosion) that is a major cause of the degradation of semiconductor particles in aqueous dispersions

While it has been shown by many workers that TiO_2 and other metal oxides may oxidize organic pollutant species in non-aqueous solvents [reference 10 and the references therein], much is still unknown about the metal oxide/non-aqueous solvent interface Therefore, a need exists to characterize particle surfaces in organic solvents and to interrogate the efficiency of organic pollutant destruction in such systems using, amongst other techniques, electrophoresis

Gerisher and Heller have performed a theoretical analysis of the efficiency of photocatalytic oxidation of organic molecules at particulate TiO_2 in aqueous solution [29] If the holes are assumed to react faster than the electrons at the solid/liquid interface, the particles must necessarily contain, in the steady state, an excess of electrons under illumination Gerisher and Heller found that the rate of depolarization of the particles by molecular oxygen will not be limited by O_2 diffusion but by the rate of electron transfer to adsorbed oxygen molecules Consequently, smaller particles (< 0 1 μm) may be expected to exhibit higher quantum efficiencies for organic solute destruction than larger particles (> 1 μm) owing to their lower rates of hole loss *via* recombination The quantum efficiencies of larger particles may be enhanced by the introduction of shallow (≈ 0 1—0 3 eV) surface and near surface electron traps although such traps, while decreasing the rate of hole loss *via* electron–hole recombination, may have the effect of decreasing the overall rate of electron loss from the particles because of slower oxygen reduction kinetics Photoelectrophoresis could be used to investigate the efficiency of particle surface charge generation as a function of particle radius, surface pretreatment, and oxygen and/or organic solute concentration as an indication of the applicability of this model to real systems

However, problems relating to the subsequent solid/liquid separation and recovery of the particle photocatalyst present themselves when considering the scale-up of colloidal semiconductor-based processes to pilot photoelectrochemical reactor scale One approach is to immobilize the photocatalytic particles upon carrier beads Heller *et al* [30] have employed this method in their work on the use of Pd-activated TiO_2 in solar-assisted oxidative dissolution of oil slicks on sea water The metal-loaded semiconductor particles are attached to hollow alumino-silicate beads of 100 μm average diameter which float on oil or water Upon illumination, the photogenerated conduction band electrons reduce O_2 to peroxide which, in tandem with the concomitantly generated valence band holes, may oxidize the organics in the oil rendering them more susceptible to microbial breakdown Heller estimates that 1 tonne of such beads could disperse a 35 tonne slick in 1 week

Such assemblies will prove effective in the relatively mechanically benign environment of the ocean surface Their applicability will be somewhat limited however in the more frictionally abrasive conditions of a fluidized bed reactor wherein particle cleavage from the carrier bead can be easily envisaged Thus, other avenues of particle/carrier attachment must be explored, one is semiconductor incorporation into clay particles This is another system that lends itself to direct study by photoelectrophoresis, the information available being an indication of the effectiveness of semiconductor incorporation into the clay lattice and how the photocatalytic behaviour of such systems as a function of pH and illumination differs with that observed from the semiconductor and clay particles in isolation from each other

Binary particle systems are also of interest for another reason As stated above, materials such as TiO_2 can only absorb a small portion of the solar spectrum in the near UV and it is therefore desirable to find materials with better solar absorption characteristics One route by which this may be accomplished is by coupling a large band gap semiconductor colloid such as TiO_2 with a short band gap colloid, extending the photoresponse into the visible The feasibility of this approach has been demonstrated with CdS–TiO_2 and several other semiconductor systems [4] Such systems not only extend the photoresponse into the visible but also improve efficiency of charge separation For example, an enhancement in the quantum efficiency of methyl viologen reduction has been observed upon increasing the TiO_2 content of a colloidal TiO_2–CdS system Photoelectrophoresis would find utility as a screening technique by which to gauge quality of spectral match to the solar profile and the efficiency of charge separation/transfer as a function of pH, by examination of the mobility–pH isotherms of the binary particle components both separately and together in differing concentration ratios

The role of semiconductor particles in photonically driven nitrogen fixation has been alluded to several times in this article Fe^{III}-doped 'dry' samples of TiO_2 show a nitrogen fixation ability that expires after extended periods of illumination due, it is posited, to the exhaustive consumption of surface OH groups that facilitate the regeneration of Fe^{III} electron trap sites involved in the initial adsorption of nitrogen on the particle surface [1] Other materials demonstrate nitrogen fixation in the gas–solid regime, such as substoichiometric tungsten oxides and chromium-doped TiO_2 Aqueous dispersions of particulate metal oxides also exhibit this ability, V^{III}-substituted ferric oxide, Pt-and Pd-loaded TiO_2, and partially reduced Fe_2O_3 for instance However, in all cases the mechanism of photolytic fixation and the role of the metal dopant atom or oxygen vacancy is not thoroughly understood Surface charge measurements during the photosynthetic reduction of N_2 to NH_3 will provide information relating to changes in particle surface composition and hydroxide group availability Detailed studies on the photoelectrophoretic behaviour of the iron oxides have already been carried out to this end [26]

6 Concluding Remarks

This review has sought to highlight the important role that surface chemistry, and specifically surface charge, plays in microheterogeneous photocatalysis As in any conventional photoelectrochemical process, ideas and concepts such as site specific adsorption, surface states, electrostatic effects, interfacial charge transfer, charge carrier recombination, substrate corrosion and reaction intermediate adsorption find great utility – the presence and effects of which may be readily probed by the simple device of surface charge measurement Whilst providing no molecular level information about surface structure/chemistry in the sense that a technique such as SECM can, photoelectrophoresis has the advantage of being able to provide information directly related to the kinetics of surface and interfacial charge transfer processes and the electronic structure of the solid substrate and the solution phase reactant of interest It may act as a screening technique for determining the photoelectrochemical activity of a new or modified semiconductor material and may provide information relating to the quantum efficiency of photogenerated charge generation/utilization

Surface photochemistry has come of age Surface electrochemistry is in renaissance The possibilities for the use of semiconductor particles to carry out very specific redox processes with high efficiency makes them attractive candidates for solar energy conversion/storage and photolytically driven pollution abatement Developments are already taking place in the study of particle size effects upon process efficiency and the study of particle surface modification for the purposes of better spectral matching between the particle absorption spectrum and the solar profile, enhanced charge separation, and improved interfacial charge transfer kinetics It is expected that new devices for signal transduction through photoinduced redox reactions will employ particulate semiconductor-based components The technique of electrophoresis is uniquely placed to provide information on all of these research fronts

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