Oxide/Electrolyte interface: Electron transfer phenomena

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Electron transfer on a titanium dioxide/electrolyte solution interface has been studied. As observed by other researchers on similar interfaces (TiO₂- and ZnO- electrolyte solution), slow consumption of OH⁻ ions was found.

A theoretical model has been developed for calculating the change in Fermi energy levels of both electrolyte solution and semiconductor, showing that ion consumption from the solution is favoured by a decreased difference in their Fermi energies. A kinetic constant (ν) is found to characterise the consumption process, its value increasing with electrolyte and semiconductor mass concentrations. Furthermore, this process may be used to estimate the point of zero charge of a titanium dioxide colloidal dispersion.

Keywords: Titanium dioxide, Fermi level, point of zero charge, electrophoretic mobility.

Interfase Óxido/Electrolito: Fenómeno de transferencia de electrones.

En este trabajo se ha estudiado un proceso de transferencia de electrones en la interfase dióxido de titanio/electrolito acuoso. Tal y como han observado otros investigadores en interfases similares (TiO₂- y ZnO- electrolito), se ha detectado un consumo lento de iones OH⁻. Para dar explicación a este proceso, se ha desarrollado un modelo teórico basado en el cálculo de las energías de Fermi en el semiconductor y en el electrolito. De este modo, se demuestra que dicho consumo de iones está favorecido por una disminución de la diferencia entre ambos niveles de Fermi. Para caracterizar el proceso de consumo lento de OH⁻ se define una constante cinética (ν), cuyo valor aumenta a medida que crece la concentración másica de semiconductor y de electrolito en la suspensión. Adicionalmente, este fenómeno proporciona una herramienta para determinar experimentalmente el punto de carga nula de la suspensión de dióxido de titanio en el medio acuoso.

Palabras clave: Dióxido de titanio, nivel de Fermi, punto de carga nula, movilidad electroforética.

1. INTRODUCTION

The TiO₂/electrolyte solution interfaces have been shown to be of great importance in industrial photocatalytic water treatment (1-6), in which the photocatalytic activity of titanium dioxide particles plays an important role. Under incident solar-UV light, reactions take place close to or on the surface of these particles, which yield the destruction of non-biodegradable organic compounds that might be present in the waste water (9,10-13).

Process efficiency is related to TiO₂-suspension management. The particles must be removed from the water after the photocatalytic treatment. Therefore, studies on the colloidal semiconductor/electrolyte solution interface, which increase knowledge about them, will help improve photocatalytic process efficiency.

Study of the macrodispersion of semiconductor powders in these systems is restricted by their intense turbidity, making it impossible to study transient species by fast kinetics spectroscopy (14, 15). A study of the kinetics of electron transfer through the colloidal semiconductor/electrolyte solution interface is reported. The consequent reaction of chemical species in solution with conduction-band electrons was monitored by analyzing the drop in pH in the suspensions using the electrophoretic mobility technique.

In this study, the experimental method enabled the Point of

Zero Charge (PZC) to be measured in the presence of a negligible concentration of ions by making use of the semiconductor properties of the catalyst (TiO₂) (16). It was also found that the hydroxyl ions in the water are consumed by the colloidal semiconductor surface. As reported elsewhere, slow consumption of OH⁻ in the electrolyte by the semiconductor yielding spontaneous decrease in the pH of the suspension (16-18) was also observed here.

A model of electron transfer through the TiO₂/electrolyte interface is proposed. Electrons from the electrolyte have a tendency to move to the free conduction-band state of the semiconductor. This tendency is aided by the strong difference in electron Fermi-energy between the states of the electrolyte and semiconductor. The use of this model explains the consumption of OH⁻ ions showing that it is favoured by a decrease in this difference. Equilibrium in the semiconductor/electrolyte junction is reached when no transfer occurs.

2. THEORETICAL ASPECTS

The semiconductor/electrolyte solution interface system (16-18) was studied in order to explain the phenomenon of electron transfer between semiconductor and electrolyte

(16,17,20). The semiconductor/electrolyte solution interface has been studied by comparing the P-N junction (18-19) because of the phenomenological similarities found between semiconductor/electrolyte and P-N junctions (16,19,20,23). On each of the faces, a concentration of free charge-carriers can move through the interface, so that, in both cases, the charge currents are charge-transfer phenomena. Moreover, on the P/N junction, charge transfer is pure, without chemical transformation of any system component. But, on the semiconductor/electrolyte interface, charge transfer supposedly occurs due to a chemical process in the semiconductor or in the electrolyte or in both. Consequently, the nature of the semiconductor electrolyte interface could change over the time (23). In this study, these points are accounted for so that the energy in the same reference system can be calculated.

The free energy of a redox electrolyte is given by the redox potential of the electrolyte (E_{elec}). The electron energy in a semiconductor material is given by the Fermi energy (F) of the semiconductor. When semiconductor and electrolyte solution remain in contact, the system reaches equilibrium and free energy is constant in the entire region (19-20), the same way as on a P-N junction (21). This means that when the P-N contact starts, the mutual diffusion of the majority charge carriers begin; the electrons will flow to the P-type region and the holes in the reverse sense. This charge flow induces a charge separation in the interface, positive charge in the N-type region and negative in the p-type one, such charge distribution generates an electric field, which produces the movement of holes to the N-type side and electrons to the P-type. These charge carriers exchange will continue until both currents are equal and in reverse ways, since an equilibrium state begins, under which the total current through the interface is zero. The equilibrium state is characterised by the same Fermi energy value over the entire system; therefore the energy levels become bent in the interface. In this situation, it is assumed that the system reaches this equilibrium by a process under which the electrons tend to have less energy, as occurs on P-N junctions.

The electrolyte redox ions can play a role in electron transfer reactions. Their free energy can be defined by means of their redox potential in standard conditions of pressure and temperature (μ_0). The electrochemical potential of the electrolyte (μ) obeys a Nernst-type behaviour (25). The Fermi energy of this electrolyte can be given by:

$$E_{\text{elec}} = -e \cdot \mu \quad [1]$$

Where “-e” is the electric charge of the electron.

Since TiO_2 is an N-type semiconductor, it is of interest to study an N-type system. TiO_2 conductivity is intrinsic due to the presence of a certain ionised impurity concentration at room temperatures. The band theory provides a solution for the Fermi energy in this case. This expression can be approximated to equation 2 by taking into account that at working temperatures the energy of ionisation becomes thermal energy (24).

$$F = E_c + kT \ln \left(\frac{N_c}{N_D} \right) \quad [2]$$

Where the edge of the conduction-band energy is E_c , the absolute temperature is T , the effective density of states in the conduction band is N_c and concentration of donor ionised impurity is N_D .

In the semiconductor/electrolyte solution interface, as on other oxide/electrolyte interfaces, the ions that determine the

potential difference are called potential-determining ions (p.d.i.). In this case, the p.d.i. are the OH^- and H^+ given by the water in the solution (26-27). Since the oxide surface consists of amphoteric places that may be either positively or negatively charged (23,27), TiO_2 electrode flat-band measurements show a Nernst equation for the conduction-band energy at the edge. Grätzel et al. and Dounghong et al. [19-20] have found the same experimental behaviour for the flat-band potential of colloidal TiO_2 particles, which was observed to be

$$EC = -(0.12 \pm 0.02) - 0.059 \text{ pH} \quad [3]$$

(eV, referred to zero H_2/H^+ ; 25 °C)

2.1 Electron transfer model for TiO_2 /electrolyte interface

The semiconductor electronic surface state and the electrolyte hydroxyl ions on the interface studied in this work are able to accept electrons. Due to the drop of pH in the presence of colloidal semiconductors in the experiments, it is thought that the electrolyte is able to release electrons by means of a chemical redox reaction, the tendency of this redox reaction depending on the value of the redox potential (μ). Furthermore, when the electron is liberated, it tends to have less free energy. We say that electrons produced by redox reactions “jump” to the state of less energy on the semiconductor surface (See Figure 1). Since the flow continues until the Fermi energies are the same, Equilibrium is reached at that moment.

The chemical equation, characterized by a standard redox potential μ_0 , that governs electron transfer is given as

Figure 1. Scheme of electron transfer model proposed.

The electron donors to the TiO_2 surface are hydroxyl ions and the acceptors are the surface states of the semiconducting particle. Electrolyte (Eq. 1) and semiconductor (Eq. 2 and Eq. 3) Fermi energy (free energy) on the interface is expressed as a function of the hydroxyl concentration and electron density in the conduction band. If the increase in the number of electrons in the conduction band of the semiconductor is equal to minus the decrease in OH^- at any instant, the following relationships between Fermi energies and concentration of donors or acceptors can be obtained.

$$\frac{1}{C_e(\text{CB})} \frac{dC_e(\text{CB})}{dt} = - \frac{1}{kT} \frac{dF}{dt} \quad [5]$$

Combining equations 5 and 6 we obtain

$$-\frac{1}{kT} \frac{dE_{\text{elec}}}{dt} = \frac{1}{[\text{OH}^-]} \frac{d[\text{OH}^-]}{dt} - \frac{1}{C_e(\text{CB})} \frac{dC_e(\text{CB})}{dt} \quad [6]$$

$$\frac{1}{kT} \frac{d(F - E_{\text{elec}})}{dt} = -\frac{1}{[\text{OH}^-]} \frac{d[\text{OH}^-]}{dt} \quad [7]$$

which shows that a minimum in the difference in Fermi energies corresponds to completion of OH^- disappearance, as is to be expected from a previous report.

3. EXPERIMENTAL PROCEDURE

3.1 Materials

Titanium dioxide P25 from Degussa was used as supplied. Its specific surface area, measured by gas adsorption isotherms (BET method), has been found to be $50\text{--}55 \text{ m}^2\text{g}^{-1}$, in irregularly shaped particles of between 20 and 40 nm as shown by TEM (Transmission Electron Microscopy) measurements. In agreement with the above, PCS (Photoncorrelation Spectroscopy) measurements show also irregularly shaped clusters of TiO_2 in colloidal suspension with high polydispersity. Ultrapure water with conductivity of less than $1 \mu\text{S cm}^{-1}$ was employed as the liquid medium for preparing colloidal suspensions and analytical grade NaOH and NaCl were used.

3.2 Methods

The colloidal TiO_2 suspensions were prepared with the given quantity of TiO_2 powder (200 and 300 mg) dispersed in 1L of ultrapure water or in a solution with the desirable concentration of electrolyte (0 and $5 \cdot 10^{-3} \text{ M}$). The initial pH of the suspension of around 9 was adjusted by adding NaOH. During experiments in the slow consumption of OH^- , the samples were stored and measured at predetermined times.

The suspensions were dispersed by 10 minutes of sonication in order to obtain small stable particle suspensions. This protocol, used by other authors (16,28), ensures colloidal stability and reproducibility of results. Each experiment involves pH and electrophoretic mobility measurement over time. The initial pH was always around 9 and at the end was around 6.8. As the effect of CO_2 is superimposed to the slow down consumption of OH^- , all the experiments were carried out in pairs, one sample with TiO_2 and another one without it.

25 mL were pipetted out of the suspension during the experiments with OH^- consumption by TiO_2 as a function of time. The pH and electrophoretic mobility of samples were measured immediately. Electrophoresis was measured with a Zetamaster-S (Malvern Instruments).

4. RESULTS AND DISCUSSION

The spontaneous drop in pH of colloidal suspensions was measured under four experimental conditions: two NaCl concentrations of 0 and $5 \cdot 10^{-3} \text{ M}$, and two semiconductor concentrations ($[\text{TiO}_2] = 200$ and 300 mg/L). Figure 2 shows a spontaneous decrease in pH in the presence of TiO_2 and in the absence of TiO_2 . The concentration of OH^- consumed due to TiO_2 particles was calculated and noted as $[\text{OH}^-]_{\text{TiO}_2}$. This OH^-

concentration is also depicted in Figure 2. After an initial pH of 9, the suspension becomes stationary at pH 6.8. The effect of the Oxygen on the solution pH has been taken into account by making experiments in pairs: one without TiO_2 and other with it.

Figure 2. Left axe: temporary evolution of pH the suspension ($200 \text{ mg-TiO}_2/\text{L}$) in presence of NaCl, $5 \cdot 10^{-3} \text{ M}$ () and pH evolution of the NaCl electrolyte solution, $5 \cdot 10^{-3} \text{ M}$ (). Right axe: concentration of consumed OH^- as a function of time (x).

The reason for this drop in pH seems to be the presence of a P-type semiconductor surface region (presented on the TiO_2 interface due to the charge inversion on the normally N-type semiconductor), which, as proposed by Trimbos and Stein (18), offers free holes in the neighbourhood of the hydroxyl groups. Furthermore, other possibilities such as the OH^- adsorption at the TiO_2 surface was discarded due to the negative electrical charge of the particle surface at those pH values (Figure 4).

4.1 Process velocity

The consumption of the OH^- ($[\text{OH}^-]_{\text{TiO}_2}$) concentration as a function of time has an asymptotic tendency (Fig. 2). Under all experimental conditions, this "slow" consumption can be described by

$$[\text{OH}^-]_{\text{TiO}_2} = I(1 - e^{-vt}) \quad [8]$$

Where t is the time and I and v are adjustable parameters. Both are obtained by a statistical fitting of experimental data. " I " is expressed in terms of molar concentration and can be considered the total slow consumption of OH^- ions in a 1-L sample up to time. The parameter v is considered as a kinetic constant that characterises the rate of each process, the reciprocal, v^{-1} , being time constant. In order to make this parameter more comprehensible, the following parameter is defined, $\tau_{90\%} = 2.3v^{-1}$, indicating the time necessary for 90% consumption of the total OH^- consumed to be observed. This provides a tool for comparing results obtained from several experiments under different conditions.

TABLE I. ν AND $\tau_{90\%}$ VALUES OBTAINED FROM MATHEMATICAL FITTING OF THE OH^- CONSUMPTION RESULTS IN FOUR DIFFERENT EXPERIMENTAL CONDITIONS.

$[\text{TiO}_2]$, mg L ⁻¹	$[\text{NaCl}]$, M	$\nu \cdot 10^4$, min ⁻¹	$\tau_{90\%}$, min
200	0	9.5 ± 0.8	2400 ± 200
200	$5 \cdot 10^{-3}$	37 ± 3	620 ± 50
300	0	47 ± 3	490 ± 30
300	$5 \cdot 10^{-3}$	180 ± 11	128 ± 8

The values obtained for ν and $\tau_{90\%}$ are presented in Table I. The good fit of experimental data to Equation 8 was tested by the Chi-square statistical criteria and in all cases was lower than $3 \cdot 10^{-12}$. The results and their mathematical fit (Equation 8) presented in Figure 3 correspond to a pH-drop experiment carried out with 200 mg-TiO₂/L and no electrolyte. The temporary adjustment proposed by other researchers (16,18) ($[\text{OH}^-]_{\text{TiO}_2} = a \cdot t^{1/2}$) is also presented in that figure.

Figure 3. Statistical fitting of the OH^- consumption experimental results (■) at 200 mg-TiO₂/L; $[\text{NaCl}] = 0$ mM. Comparison between two models: $[\text{OH}^-]_{\text{TiO}_2} = a \cdot t^{1/2}$ (ref. 17,28) and $[\text{OH}^-]_{\text{TiO}_2} = I(1 - e^{-\nu t})$.

Values for the parameters indicate that as semiconductor mass concentration increases the OH^- consumption rate increases. Consequently, as observed by other researchers, slow consumption of ions was found to be due to the presence of the semiconductor surface (16,18).

Moreover, the electrolyte concentration diminishes the disappearance rate. Two cases have been studied with a fixed concentration of semiconductor particles (200 or 300 mg/L): 0 and $5 \cdot 10^{-3}$ M NaCl concentration. The presence of electrolyte ions in the vicinity of the particle accelerates the consumption process. This result can be explained due to the screening effect of the electrolyte ions on the electric double layer potential of the colloidal semiconductor particles (28-30). This potential becomes lower when the electrolyte concentration is not negligible and, thus, the drop in potential across the semiconductor particle/electrolyte interface becomes lower. Consequently, interface equilibrium is reached sooner in the presence of the electrolyte than without it.

All phenomena observed can be accounted for with the following mechanism. At $\text{pH} > \text{PZC}$ ($\text{pH} \sim 7$), the interface semi-

conductor electrolyte behaves as a P-N junction. The electrolyte is the N-type system donating electrons (by means of OH^- ions) and the semiconductor surface is a P-type acceptor (Figure 1.)

4.2 Fermi levels

Before the pH starts to fall, the situation on the semiconductor/electrolyte interface is characterised by higher Fermi energy in the electrolyte than in the semiconductor. Therefore, although it is an N-type semiconductor, it behaves like a P-type one under the P-N junction equivalence (18,19,20), which must accept negative charge carriers (from the other medium in the interface) to increase its Fermi energy, as shown in scheme of Figure 1. Similarly, the electrolyte can donate electrons, decreasing its Fermi energy. This characteristic phenomenon found on all semiconductor interfaces is called inversion of charge on the semiconductor surface (20). The Fermi energy on both faces is calculated by using the equations in theoretical section. The Fermi energies calculated for both semiconductor surface and electrolyte, in two limit situations, initial and equilibrium states, are given in Table II, where the difference in Fermi energy across the semiconductor/electrolyte interface in the initial states is observed to be 565 meV, going down to 329 meV in equilibrium. This reduction in Fermi electron energy of around 236 meV justifies the tendency to OH^- consumption. As Equation 7 predicts, the charge-carrier flow ends when the two Fermi energies reach similar values in equilibrium. This mechanism justifies the drop observed in the pH.

TABLE II. FERMI ENERGY VALUES CALCULATED IN THE INITIAL AND EQUILIBRIUM STATES FOR ELECTROLYTE SOLUTION AND TITANIUM DIOXIDE.

TiO ₂ /electrolyte interface	Initial state (pH9, 25°C)	Final state (pH7, 25°C)
E_{elec} , eV	-0.114	-0.232
F , eV	-0.679	-0.561

4.3 Determination of the Point of Zero Charge

In Figure 4, electrophoretic mobility measurements are shown as a function of pH. Mobility was measured for the TiO₂ suspension in the presence of a negligible concentration

Figure 4. Electrophoretic mobility of the TiO₂ suspension (200 mg-TiO₂/L; $[\text{NaCl}] = 0$ mM) versus pH.

of ions at different times, allowing the pH at which particles have a total electrokinetic charge of zero to be determined. The point of zero charge of the suspensions has thus been found experimentally to be around pH7.

5. CONCLUSIONS

The theoretical kinetics model proposed here has been proven suitable for describing the slow consumption of OH⁻ on the Titanium Dioxide/electrolyte interface. The parameter describes the process kinetics, ν , depends on semiconductor mass and electrolyte concentration. It has been established that ion consumption is favoured by the diminishing difference in Fermi energies across this interface. Before slow consumption, the difference is 565 meV and afterwards is 329 meV. Finally, the Point of Zero Charge of a TiO₂ suspension has been estimated as pH 7

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