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A photo-(electro)-catalytic system illustrating the effect of lithium ions on titania surface energetics and charge transfer

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ABSTRACT

We describe the effect of Li^+ on photoinduced charge transfer at TiO_2 in acetonitrile solutions at open circuit (photocatalytic conditions) or under potential control. Using 2-propanol and 4-nitrobenzaldehyde as probe scavengers of holes and electrons, respectively, we aim to demonstrate the importance of tuning the chemical role of electrons and holes through control of surface and interface properties.

Adsorption of Li^+ in the dark causes a positive shift of the TiO_2 bands as revealed by cyclic voltammetry and Mott–Schottky analysis. Likewise, there is clear evidence that dark adsorption of 2-propanol brings about a redistribution of the bandgap states.

Electrochemical measurements show that, upon illumination, the charge of photo-accumulated electrons is compensated by Li^+ that can undergo insertion at the surface/subsurface region, which prevents a negative shift of the bands and has important consequences on the overall photo(electro) catalytic processes. Concerning the fate of electrons, 4-nitrobenzaldehyde is selectively reduced to 4-aminobenzaldehyde probing that electron transfer specifically involves the $\text{—}NO_2$ moiety while reduction of the aldehyde functional group is observed only at much more negative potentials than E_{fb} and is cation insensitive.

Regarding the fate of photogenerated holes, the effect of Li^+ is evident in the change of the mechanism of 2-propanol oxidation, as revealed by both electrochemical and EPR experiments. Adsorption as alcoholate occurs in the dark but it is strongly inhibited on pre-illuminated TiO_2 in the presence of Li^+.

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1. Introduction

Control of surface energetics is of paramount importance in semiconductor electrochemistry and this is presently a very significant research target [1]. It can provide, for example, alternative more selective synthetic pathways than conventional approaches. In this context, the results of a large number of studies focused on oxidation and reduction reactions have been reported [2–7]. The concern of a substantial number of these research publications can be also viewed as an effort to better understand what has been defined as the chemical role of electrons and holes in photocatalysis [8]. Results of photo-electrochemical studies often prove quite useful for the understanding of analogous photo-catalytic systems. As a matter of fact, photocatalysis is the same as photo-electrocatalysis at open circuit [9].

With regard to reductive chemical transformations, one of our recent publications has been devoted to the study of an electron photo-accumulation regime to drive the reduction of thermodynamically non reducible species [10]. In that work we examined the occurrence of photo-accumulation of electrons on TiO_2 and its effect on the partial or total reduction of 4-nitrobenzaldehyde ($O_2NC_6H_4CHO$) to 4-amino-benzaldehyde ($H_2NC_6H_4CHO$) or 4-amino-benzyl alcohol ($H_2NC_6H_4CH_2OH$). We found compelling evidence that the energy of electrons has a key role in the selective formation of reduction products. This paper is a continuation of our work on the importance of charge transfer dynamics in selective photo-catalytic transformations and is part of a broader study focusing on the influence on the effect of the nature of the electrolyte cations on surface energetics.

It is well known that electrostatic interaction of ions with the surface can influence electron transfer processes; specifically, it is well established that the conduction band edge of TiO_2 exhibits a positive shift as a function of an increase in proton activity [11]. In addition to protons, other small inorganic cations have also been found to induce analogous effects [11–13]. Our choice of lithium is dictated by the availability of a vast literature on its influence in photo-electrochemical reactions that can possibly increase our level of understanding of its effects in a photo-catalytic process. The influence of cations on semiconductor/electrolyte interfaces has been extensively investigated mainly due to its relevance to designing efficient photo-electrochemical as well as electrochemical energy storage devices such as TiO_2-based dye-sensitized photo-electrochemical solar cells (DSSC) [14–23],

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batteries [24–26]. Electrochromism [27–29], photochromism [30,31] and photo-rechargeable devices [32,33] are also important fields of interest. Specifically, an intensive research activity from both the experimental [34–38] as well as the theoretical side [39] has been devoted to the study of the control of surface energetics and charge transport by Li^+ which is well known ability to be not only adsorbed but also inserted into TiO_2. These studies largely concentrate on improvements brought about by high porosity and surface area and, in this respect, nanostructures play an important role due to an increased surface/volume ratio [40].

In contrast to a vast literature on TiO_2 modification with transition metals, studies on the effect of metal ions that do not undergo changes in their oxidation state, under common photo-catalytic conditions, are rather exiguous and have been recently reviewed [41]. Upon adsorption on TiO_2 metal cations, such as Zn(II) or Al(III), can form surface complexes with OH groups thus altering the pathway of photocatalytic processes. Recent investigations on the specific effect of Li^+ on photocatalytic processes include the photo-electrochemical oxidation of water [42] and that of phenol [43] both on TiO_2 nanotube electrodes in alkaline solutions.

In this paper, the main focus is the effect of Li^+ ions on photoinduced charge transfer at TiO_2 in the presence of $O_2NC_6H_4CHO$ as electrons acceptor and of 2-propanol as holes scavenger. $O_2NC_6H_4CHO$ is again the case in point since it is a good model that is representative of molecules containing two functionalities with different reducibility. Although several literature studies deals with the photocatalytic reduction of either nitro- or aldehyde groups [5], only few efforts have been devoted to examine the factors that govern the photocatalytic reduction of the two functionalities simultaneously present in the same molecule [10]. Selective reduction of this type of substrates by thermal catalysis is difficult and not always successful, as often underlined [44]. Additionally, for a more comprehensive assessment of interface reactions, parallel photo-oxidation of 2-propanol to radical species has been studied by EPR spin trapping spectroscopy since we were aware of a possible influence of Li^+ ions on this process too. From a general point of view, the photo (electro)oxidation of alcohols also represents a model catalytic reaction that is often used to investigate effects of surface modification and to identify catalytically active sites. On this basis, to our knowledge, this is the first report of the effect of lithium ions on photocatalytic reactions on TiO_2.

2. Material and methods

Commercial TiO_2 (Evonik, formerly Degussa P25) was used as photocatalyst. Solvents and reagents were commercial from Sigma-Aldrich. Anhydrous acetonitrile (<0.001% water) was used as received while 2-propanol was first refluxed for 1 h in the presence of Mg and a catalytic amount of I_2 and then distilled. $O_2NC_6H_4CHO$ (Fluka) and $LiClO_4$ (Sigma) were employed as purchased.

All the irradiations were performed with a Helios Q400 Italquartz medium-pressure Hg lamp using a cut off filter ($\lambda > 360$ nm).

Electrochemical experiments were performed with an EG&G potentiostat using EG&G software. Glassy carbon and Ag wire electrodes served as the counter and reference electrodes, respectively. The potential of the latter was found to be 0.025 V versus SCE through comparison of cyclic voltammograms of ferrocene as an internal standard. All potentials are given versus SCE. Measurements were done in de-aerated CH_3CN or 2-propanol/ CH_3CN (1:4 v/v) mixture both in the absence and in the presence of $O_2NC_6H_4CHO$ (1×10^{-3} M). $LiClO_4$ (0.1 M) or tetra-ethylammonium perchlorate (TEAP, 01 M) were employed as supporting electrolytes. Mott-Schottky plots were obtained from cyclic voltammetry curves recorded in the range from -0.1 to $+1.0$ V using the relationship $C = i/\nu$, where ν is the scan rate (50 and 100 mV/s).

Titanium dioxide electrodes were prepared by spreading, on a titanium foil, a paste obtained mixing TiO_2 (Degussa P-25, 3 g), bi-distilled water (6 mL), acetylacetone (0.2 mL) and Triton X-100 (0.2 mL) with subsequent calcination at 450 °C for 30 min. The area covered by TiO_2 is 0.95 cm^2 and from the film weight and a density of 3.9 g/cm^3 we calculated a total volume of 5.4×10^{-4} cm^3. Then the volume effectively occupied by TiO_2 is $V = V_{tot}(1 - p)$, i.e., 2×10^{-4} cm^3 assuming a porosity (p) ~ 60% [13]. Using this value and a total active area of TiO_2 P25 films of 1.5×10^6 cm^2/cm^3 [13], we estimate that the area of the film in contact with the electrolyte is ~300 cm^2.

Experiments with illumination were carried out using a medium pressure mercury lamp (Hanau model Q 400) equipped with filters. Light intensity was measured by a Newport Power Meter model 1918 C, equipped with a model 818 P detector. The lamp has an intense emission line at 365 nm which was isolated, using bandpass filters (Edmund Optics), when calculation of the incident photon flux was needed. In this case, the measured radiant power density in mW/cm^2 (at 365 nm), was then converted to photons/s. Electrodes were illuminated from the surface/electrolyte contact. Under conditions of electrode illumination at open circuit, the photo-potential reached a value of ~− 1.1 V.

In the experiments under illumination, we must consider that incident UV light penetrates only a fraction of the total film thickness, which can be calculated from the relationship written in Eq. (1) [45],

$$\text{Absorbance} = 0.434\alpha d(1-p) \tag{1}$$

where α is the adsorption coefficient at 365 nm, d is the thickness, p is the porosity (60%). From a measured absorbance of 0.7 at 365 nm (this work) and an absorption coefficient of 5×10^4 [45], it is possible to calculate a light penetration depth of 0.8 μm compared to a total film thickness of 5.7 μm.

EPR spin trapping experiments were carried out with a Bruker ER 200 MRD spectrometer equipped with a TE 201 resonator, at a microwave frequency of 9.4 GHz. In a typical experiment, TiO_2-P25 (20 mg) was suspended in the de-aerated medium consisting of 2-propanol/ CH_3CN (1:4 v/v) solution (1 mL) containing $LiClO_4$ (0.1 M when required), α-phenyl N-*tert*-butyl nitrone (pbn, 5×10^{-2} M) as spin trap and $O_2NC_6H_4CHO$ (1×10^{-4} M) as the electron acceptor. The samples were put into a flat quartz cell and irradiated directly in the EPR cavity. De-aeration has been carried out fluxing N_2 and transferring the samples into the cell under a N_2 saturated atmosphere. No signals were obtained in the dark and during irradiation of the solution in the absence of TiO_2.

In a typical photocatalytic experiment, TiO_2-P25 (3.5 g L^{-1}) was suspended in a mixture of 2-propanol/CH_3CN (1:4, v/v) containing $LiClO_4$ (0.1 M) and $O_2NC_6H_4CHO$ (7.8×10^{-5} M). Then, the suspension was purged with N_2 for 20 min and subsequently irradiated. The reaction course was followed by recording UV spectra of the irradiated solutions and comparing them with UV spectra of pure substances. The disappearance of $O_2NC_6H_4CHO$ was evaluated on the basis of the absorbance decrease at 264 nm, and the formation of $H_2NC_6H_4CHO$ was calculated from the absorbance increase at 312 nm.

3. Results and discussion

In the following we describe the effect of Li^+ on the photo-reactivity of TiO_2 in acetonitrile using 2-propanol and $O_2NC_6H_4CHO$ as electron donor and acceptor, respectively. We first examine the effect on surface energetics in the dark both before and after pre-illumination. Then, we discuss the results of photo-electrochemical and EPR measurements on the oxidation of 2-propanol in the absence and in the presence of Li^+. We finally show that the Li^+ ions can interact not only with TiO_2 but also with the electron acceptor itself causing its partial, selective reduction to $H_2NC_6H_4CHO$.

3.1. Surface energetics of TiO_2-P25/Li^+

From a general point of view, heterogeneous charge transfer requires a detailed knowledge of the surface and interfacial chemistry

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