Title: A Photo-(electro)-catalytic System Illustrating the Effect of Lithium Ions on Titania Surface Energetics and Charge Transfer.

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Manuscript Region of Origin: ITALY

Abstract: We describe the effect of Li+ on photoinduced charge transfer at TiO2 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 TiO2 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 -NO2 moiety while reduction of the aldehyde functional group is observed only at much more negative potentials than Efb 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 TiO2 in the presence of Li+.

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Ferrara, July 20th 2015

To the Editor of the Journal of
Electroanalytical Chemistry

Dear Prof. Feliu,

We are thereby submitting a revised version of the manuscript JELECHEM-D-15-00550 entitled "*A Photo-(electro)-catalytic System Illustrating the Effect of Lithium Ions on Titania Surface Energetics and Charge Transfer*" by Alessandra Molinari, Andrea Maldotti, Rossano Amadelli.
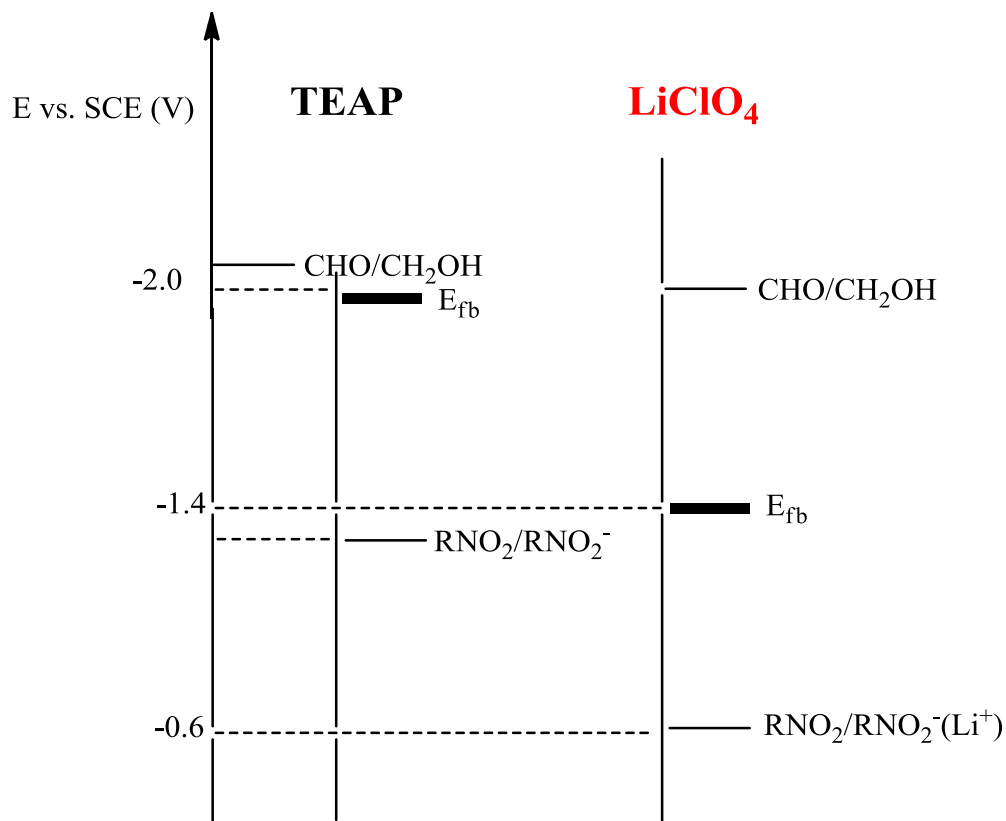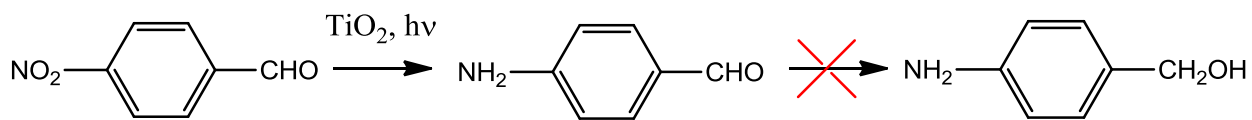
In the revised ms, we addressed the reviewers' constructive comments. Suggested changes have been made. The main are:

-   a new figure in the supplementary material (now Fig. 2 Supplementary)
-   we deleted old ref. [62]
-   we added two new refs. (53 and 66) in response to the reviewers' comments

Separately we report the original reviewers'comments in *italics* each point followed by our reply
All changes are yellow highlighted.

Best regards
Rossano Amadelli

Tuning the chemical role of electrons and holes controls surface and interface properties.

Adsorption of Li^+ in the dark causes a positive shift of the TiO_2 bands

Due to Li^+ adsorption/intercalation 4-nitrobenzaldehyde is selectively reduced

Li^+ causes changes in the photo-electro oxidation mechanism of 2-propanol

Main Changes

We addressed the reviewers' constructive comments. In this process, we added
- a new figure in the supplementary material (now Fig. 2 Supplementary)
- we deleted old ref. [62]
- we added two new refs. (53 and 66) in response to the reviewers' comments

Below, we report the original reviewers'comments in *italics* each point followed by our reply

Reviewer #1:

This is an interesting manuscript, describing the effect of lithium-containing electroyte on photocatalytic reactions at TiO2 nanocrystalline electrodes. As the authors point out, this might be the first report of the effect of lithium on photocatalytic reactions, although the effect of lithium on TiO2 electrochemistry has been extensively reported. I am not clear whether the authors are claiming that lithium is "redox-inert" or not. Based on the published electrochemical studies, it should not be much doubt that it is redox-active. The authors cite "DSSC" studies, but those studies mostly were about the intrinsic electrochemistry, and subsequently, it was realized that TiO2 could be useful in lithium-ion batteries, in which lithium is clearly not an innocent bystander.

Reply

We meant electrolyte cations that do not themselves undergo changes in their oxidation states. We have accordingly changed the text in order not to generate confusion.

Specific comments follow.

** *Page 2*
"...well established that the conduction band edge of TiO2 exhibits a positive shift as a function of electrolyte proton activity." This is a minor point, but this should be stated explicitly--is it increasing or decreasing proton activity?

Reply

we added as proton activity "increases"

** "...but also intercalated or, preferably, inserted into TiO2." What is the precise point of this distinction?

Reply

Semantics, we would say. Both intercalation and insertion are found in the literature. We have left only inserted as somebody points out that intercalation rigorously refers to the case when a 'layer structured' material is the host.

Page 3

✱✱ (a) *Are the authors implying or stating that Li is redox-inert? If that is the implication, what is the rationale? After all, as the authors point out, lithium batteries can be constructed with TiO2.   Quoting from Ref. 23 by Dylla et al., "Li+ insertion via pseudocapacitance is similar to a battery in that a redox reaction is required for charge storage but dissimilar in that the process is not diffusion limited." (b) Parenthetically, there is also a very recent paper by Patra et al. in Scientific Reports on lithium intercalation into anatase nanoparticles, which might be interesting in that it describes changes in crystal structure upon intercalation, although the degree of intercalation might be more extreme in their case.*

Reply

(a) The reviewer is right. In the above reply we explained that our tag is 'cations that do not change their oxidation state under our operative conditions'. **(b)** The mentioned work is indeed interesting and we think it is particularly relevant to the discussion on changes that are induced by light in the alcohol adsorption. We cite it in this connection, now ref [66] in the revised ms.

✱✱ *Pages 3-4 (Experimental)*

(a) Although it might be obvious, the authors should tie down certain details such as the "dark" measurements being carried out in complete darkness and the illumination being from the solution (front) side, which is finally mentioned on page 12.

(b) What would the possible effects be for the use of P25, which includes both anatase and rutile and contains comparatively large particles?

(c) As mentioned later, it should be mentioned how the light flux was estimated

Reply

(a) We now write that illumination is from the solution (front) side in the Experimental section. We have also added information on light/dark conditions in the captions of the figures;
(b) P25 is a kind of benchmark that offers the possibility to compare data obtained in different laboratories. Of course, there are interesting aspects about analysing anatase and rutile separately;

these are the focus on an ongoing investigation in our laboratories.
(c) now reported in the Experimental Section. Please see also below.

** *Page 6*

(a) "...Peaks in this potential region, lying below the conduction band edge, have been recently ascribed to the presence of band gap states located at grain boundaries [46]." Given the fact that the authors have already cited many papers that deal with this topic, they should make the statement more general and cite a few of those papers again.

(b) Later on this page, the authors discuss the interaction with the alcohol in reference to Fig.1. I suppose that this experiment was carried out in complete darkness? This is not mentioned explicitly in the Experimental Section.

Reply

(a) we added the references as suggested

(b) it's correct: experiments are in the dark. Dark/light conditions are now specified directly in all captions of the figures.

** *Page 10*
How was the light flux estimated?

Reply

Thank you for pointing out that this important information was missing. In the Experimental Section of the revised manuscript we describe illumination conditions in detail, including the estimation of the number of photons from the light flux.

** *Page 11*

"In the present instance, the data seem rather to suggest formation of trapped Ti3+- Li+ pairs at the surface or likely in subsurface region where they seem to be quite stable [59]."
What is the reasoning here?

Reply

Considerations are based on the data of Fig 3. Here we see that there is correspondence between experiments under illumination and electrochemical insertion in the dark at relatively low negative

potentials, below Efb. We state that significant insertion is usually achieved at more negative potentials. We changed the sentence into – significant <u>bulk</u> insertion -

✱✱ *Page 12*

"Interestingly though, Gregg et al. [62] found no effect of UV pre-illumination on photocurrents recorded for TiO2 electrodes in solutions containing Li+." What is the reason or this discrepancy?

Reply

Thanks for raising this aspect. On re-reading the text we concluded that our comparison was pointless. In fact, the experiments of Gregg et al. refer to DSSC conditions, in a medium that contains iodide. We removed this sentence as it can generate confusion and doubts rather of being of any help.

_____

Reviewer #2:

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Corresponding Author: Dr. Rossano Amadelli
All Authors: Alessandra Molinari; Andrea Maldotti; Rossano Amadelli, PhD
The manuscript describes the effect of Li+ ions present in the supporting electrolyte upon photo-accumulation of electrons in a TiO2 film and its photocatalytic activity towards reduction, respectively, oxidation of two model organic compounds. As indicated in the introduction, these photoreactions were investigated by the authors in a recently published (ref. 10) work, where, instead of a lithium salt, tetra-ethylammonium perchlorate (TEAP) was used as supporting electrolyte.
The paper is well written and carefully presented. Although my initial impression was that the manuscript is too long, after the 2nd reading it appeared that the length is quite generally justified. I suggest that after consideration by the authors below enumerated questions and remarks, the manuscript will be accepted for publication.

Specific questions:

✱✱ *Page 4:*

(a) Three different concentrations (10-4 - 10-3) of nitrobenzaldehyde used in various experiments are indicated in page 4; is this correct?

(b) Was the film absorbance (0.7 at 365 nm) measured within this work and which absorption coefficient has been used to calculate the film thickness?

Reply

(a) Correct. The lower concentrations were used for photocatalytic and EPR spectroscopy experiments.

(b) Yes, from reflectance data. The absorption coefficient was taken from ref [45]. We now wrote it in the revised ms.

    **   *Pages 4 and 5:*

    (a) *Given that determination of Mott-Schottky plots for porous SC films is of quite general interest to the electrochemist's community, it would be useful that authors indicate the range of CV scan rates and potentials over which capacitance was measured.*

    (b) *The large shift of the Efb associated with the presence in the solution of Li+ ions raises the question on what does determine the Efb in the TEAP electrolyte (surface OH groups?) and also on whether the Nernstian Efb dependence is observed in function of the Li+ concentration?*

Reply

(a) We added, in the Experimental Section, that voltammetry curves were recorded between -0.1 and + 1.0 V at scan rates in the range 50 to 100 mV/s

(b) It is a matter of Double Layer structure. TEA^+ cations interact electrostatically with the surface (adsorption at the outer Helmholtz layer). Li^+ is specifically adsorbed, i.e., chemically interacting with the surface, much like protons. We do not mention this difference here because it would have made the paper too long; it is discussed, for example, in refs. [16] and [39] of this work. The data reported herein refer a fixed Li^+ concentration in order not to further increase the complexity of the system.

    **   *Pages 6 to 8:*

    (a) *It is slightly confusing that currents shown in CVs (Figs 1 and 2) are, apparently, referred to the estimated "real surface" area of the TiO2 electrode that is, however, not the case of charges mentioned in page 6.*

    (b) *In this connection, how the authors explain the increase of the cathodic charge in 2-propanol solution; is it due to the reduction of surface bound protons (from Eq. 2)?*

Reply

(a) This was a slip. Charges reported were calculated from the original voltammetry where currents had not been normalized to the estimated real surface area. This has been corrected.

(b) The voltammetry curve actually moves cathodically. A significant amount of protons would shift in the other direction. Injection of negative charge from the coordinated alcohol seems a sensible explanation. In this context, we added a new ref. by Wang et al. [53].

** *Pages 7-8: (a) The presented description of Fig. 2 is rather confusing. The authors mention here extraction of the electrons photogenerated under the electrode illumination at open circuit; however neither open-circuit potential nor the starting point of the CVs is indicated. As presented, the CVs seem to begin from positive (ca 0 V) potential by the cathodic scan that, according to the description, is not the case.*

(b) The authors assign the cathodic currents in CV of Fig. 2 to filling of new surface states formed under film illumination. Since those cathodic features appear starting at ca -0.2 V these are the mid-bandgap states located 1.2 eV below the Efb. In this connection, how these CVs do compare with those obtained in a TEAP electrolyte?

Reply

(a) Unfortunately it is somewhat confusing since some details were missing. In the revised ms it is now written that, following illumination, the CV experiment is started at -1.0 V in the anodic direction to 0V and back to -1.0 V to complete the cycle.

(b) For a comparison of CVs in TEAP, we added a supplementary figure (new Fig. 2 Supplementary)

** *Page 10: The authors compare here the flux of photons absorbed by the film (how was it measured?) with the amount of extractable charge accumulated within the film. This comparison points at a very low quantum efficiency of electron accumulation, in the range of 10-5-10-4. Did the authors consider, besides regular charge recombination, the combined hole/electron mechanism of propanol oxidation where the reaction intermediates inject electrons to the conduction band of TiO2 : known in photoelectrochemistry as "the photocurrent doubling" phenomenon. Is this energetically plausible in the acetonitrile based electrolyte?.*

Reply

We added a comment on current doubling. In our previous work (ref 10) we ruled out this possibility on the basis of the redox potentials (T. Lund et al. J. Am.Chem. Soc., 123 (2001) 12590). The radicals oxidation potential are still too positive even in the presence of Li$^+$

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.

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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^+.

Keywords: lithium ions, titanium dioxide, surface energetics, photo-(electro)-chemical measurements, EPR spin trapping

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], 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 photo-catalytic 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$_2$NC$_6$H$_4$CHO as electrons acceptor and of 2-propanol as holes scavenger. O$_2$NC$_6$H$_4$CHO 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$_2$NC$_6$H$_4$CHO (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 x 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 $C = i/v$, where v 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 x 10^{-4} cm^3. Then the volume effectively occupied by TiO_2 is $V = V_{tot} (1-p)$, i.e., 2 x 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 x 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 electrodes 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],

$$Absorbance = 0.434 \alpha d (1-p) \qquad (1)$$

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 x 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 x 10^{-2} M) as spin trap and $O_2NC_6H_4CHO$ (1 x 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 gL^{-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 $x10^{-5}$ 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 and, in this context, electrochemical methods can provide valuable information.

In a previous work we carried out cyclic voltammetry (CV) and capacitance measurements with Ti/TiO_2 electrodes in 2-propanol/CH_3CN (1:4 v/v) containing tetra-ethylammonium perchlorate (TEAP) [10]. The flat band potential (E_{fb}), obtained from Mott-Schottky plots, was found to be ~ -2.0 V *vs* SCE. This value is in good agreement with that previously obtained by a spectroscopic technique for a polycrystalline TiO_2 electrode in neat anhydrous CH_3CN containing the same supporting electrolyte [12].

In keeping with the aim of the present investigation, we have carried out analogous electrochemical measurements with a Ti/TiO_2 electrode using $LiClO_4$ as supporting electrolyte. In this case, the flat band potential E_{fb} obtained from Mott-Schottky plots (Fig. 1 Supplementary) is -1.4 V vs SCE, i.e., about 0.6 V more positive than with TEAP. This is the expected behavior since Li^+ ions, like protons, are potential determining cations and are able to shift E_{fb} to more positive values, in accordance with a vast literature [12-21]. A decrease of the slope after illumination has often been observed as we discussed it in our previous work [10].

3.2 Effect of Propanol on electrodes in the dark

Curve 1 in Fig. 1 shows the CV of TiO_2 in CH_3CN containing Li^+ in the dark. The integrated charge is about 5-fold higher than that measured in a solution with TEAP. Moreover, the addition of 2-propanol (curve 2) causes quite conspicuous changes in the CV profile. In the cathodic scan direction one notices that peak (a) at $\sim$ -0.65 V is shifted to lower potentials by $\sim$ 0.13 V and becomes somewhat sharper (b) and more intense (Fig. 1 inset). For a quantitative comparison, the integrated charge from zero current to the peak maximum is 32.8 $\mu C/cm^2$ and 9.5 $\mu C/cm^2$ in the presence and in the absence of 2-propanol, respectively. Peaks in this potential region, lying below the conduction band edge, have been ascribed to the presence of band gap states located at grain boundaries [10,17,19,46]. However, the behavior described above suggests a strong interaction of 2-propanol with surface sites. From a general point of view, bandgap states are identified with surface or subsurface defects among which oxygen vacancies and interstitial Ti^{IV} or Ti^{III} are considered dominant [47]. It is noteworthy that surface defects are susceptible to interaction with adsorbed species, and reported interactions of defects with Li^+ [48] and alcohols [49-51] may occur also in the system described here. It is well known that alcohols are preferentially adsorbed at oxygen vacancies and, according to the current understanding, an alcohol molecule is dissociatively adsorbed to unsaturated Ti^{IV} producing charged species such as alkoxy (RO^-) and a proton bound to a nearby O^{2-} surface anion (Eq. 2).

$$(CH_3)_2CHOH \rightarrow (CH_3)_2CHO^-_{(ads)} + H^+_{(ads)} \qquad\qquad (2)$$

This can lead to formation of a charge transfer complex with a consequent shift of band gap energy levels toward the conduction band, in a similar way as described for catechol bound to TiO_2 [52]. Examination of the anodic scan of Figure 1 confirms that alcohol adsorption causes remarkable

changes in the shape of the CV curves (cfr. curves 1 and 2), reflecting an alteration of the processes corresponding to re-oxidation of reduced surface species (Eq. 3).

$$\text{-O-Ti}^{III}\text{–O -} \xrightarrow{\text{Li}^+} \text{-O- Ti}^{IV}\text{-O-} + \text{Li}^+ + \text{e}^- \tag{3}$$

Although the integrated anodic charge for curves (1) and (2) is the same within experimental error, the charge extraction curve recorded in 2-propanol/CH$_3$CN appears to be sharper, and the peak is shifted to more negative potentials by ~ 0.2 V. This behavior is reminiscent of effects due to charge accumulation in traps [53] and seemingly confirms an alcohol effect on the distribution of surface states possibly due coordination as alcoholate and negative charge injection. The photo-oxidation of 2-propanol to radical species in the presence of Li$^+$ will be discussed in more detail later.
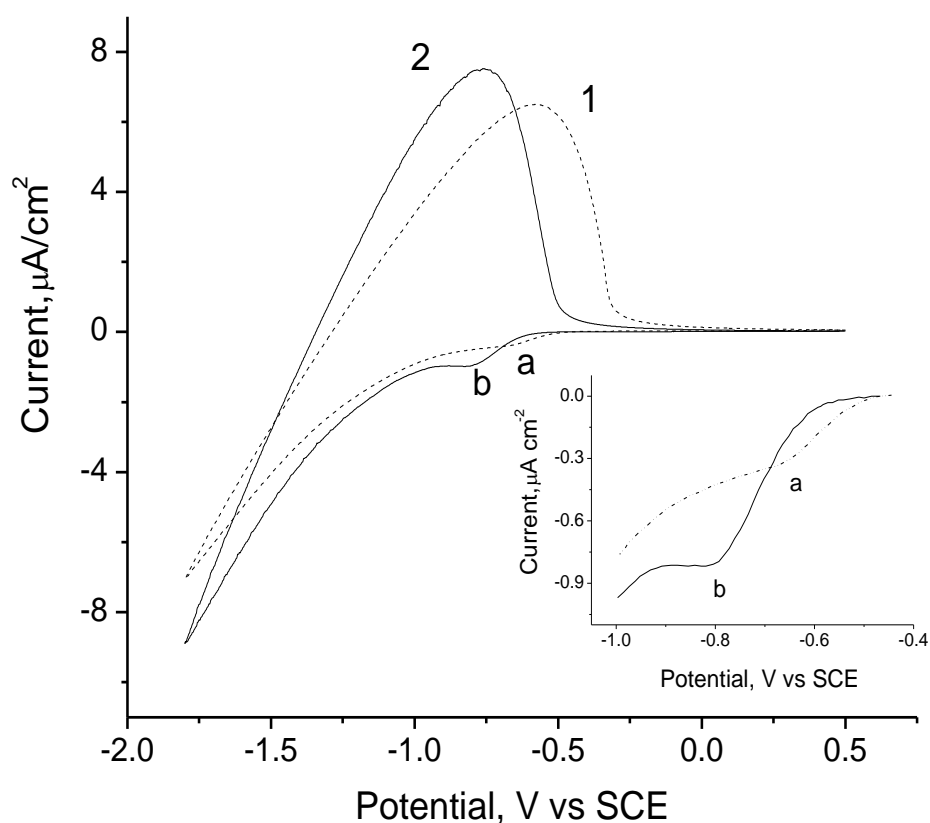
Figure 1

3.3 Effect of Light on electrodes

In Fig. 2 are displayed CV curves recorded in the dark from E_i = -1.0 V to E_f = 0.0 V and back to -1.0 V, after different periods of electrode illumination at open circuit (see scheme in the inset of Fig. 2). Earlier [10] we used CV experiments to calculate electron accumulation caused by illumination. The re-oxidation charge was obtained by integration of the anodic CV curves from different initial potentials E_i to a final potential E_f that was positive enough to, in principle, warrant full oxidation of accumulated Ti^{III} back to Ti^{IV}.

$$Q = \int_{Ei}^{Ef} \frac{i}{v} dE \tag{4}$$

It is seen in Fig. 2 that illumination causes an increase in the anodic charge Q_a (cfr. curves 1 and 2). However, it turns out that for prolonged pre-illumination the extracted charge actually decreases and then remains constant. For example, Q_a for 5 min light exposure is ∼ 15% lower than for 2 min (curves 2 and 3). This phenomenon persists even at a low scan rate of 2 mV/s, testifying that re-oxidation of photo-accumulated charge is a slow process in the presence of a LiClO$_4$ electrolyte.
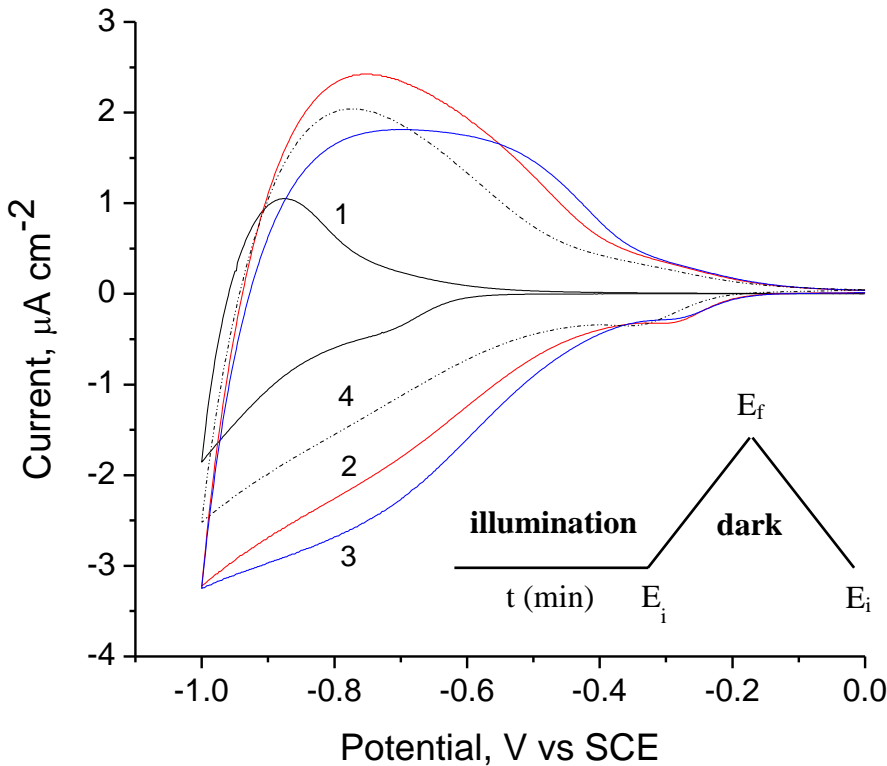
Figure 2

The reverse cathodic scan from 0.0 V to -1.0 V, completing a CV cycle, shows that the onset of the cathodic current appears to be significantly shifted to positive potentials after illumination. It is also interesting to note that the integrated cathodic charge Q_c becomes higher than Q_a at potentials positive to E_{fb}, depending on the pre-illumination time. This phenomenon was not observed in a TEAP electrolyte and then cannot be assigned to protons reduction (Fig. 2 Supplementary)

It is tempting to ascribe this behavior to the filling of new surface states created by light and, indeed, previous studies by Gregg [16] and Wang et al. [54] have shown that open circuit illumination (light soaking) brings about a redistribution of localized bandgap states below the conduction band edge and/or formation of new bandgap states, both in the absence and in presence of Li^+ which are very effective in favoring trapping [55]. All in all, on the basis of current understanding, attempts to elicit a full explanation would likely give an answer which is too approximate in the fact that the origin can be multifold.

We observed that upon continuous cycling in the dark, the overall charge decreases again until $Q_a \approx Q_c$ (Fig. 2, curve 4). The CV curve approaches its original shape (curve1) only after prolonged electrode polarization at a positive potential. This eventual recovery of the initial CV profile that can take place after hours is an evidence of changes [46] that persist for a relatively long time, depending on the length of pre-illumination. Photo-generated electrons are accumulated and screened by adsorbed or inserted Li^+ at the interface or inside the oxide, respectively, and dark re-oxidation of Ti^{III} to Ti^{IV} (Eq. 3) is accompanied by Li^+ release into the electrolyte, but slow or even incomplete lithium de-insertion (*vide infra*) can cause a modification of the oxide. Adding that, one should not overlook that photo-desorption of 2-propanol can cause quite substantial changes of surface equilibria, as discussed in the following.

3.4 Extraction of accumulated charge

We observed that the cathodic and anodic charges in CV experiments of Fig. 2 decreased as the potential scan rate was increased, which is not out of keeping with literature on oxides electrodes [56]. This is due to a slow response of the inner regions of the porous film to a relatively fast change of potential. We then used potential step experiments to evaluate the photo-accumulated charge at conditions better approaching quasi-steady state.

Immediately after illumination was switched off, a positive constant potential was applied (0.5 V) and the oxidation current recorded as a function of time. The approach is similar to that

reported by Lindström et al. for the case of electrochemically driven electron accumulation [57]. The plots of log i vs log t from potential steps (Fig. 3 Supplementary) are similar to those reported by Lindström et al. for the case of thick films. For relatively short pre-illumination times ($\leq$ 2 min), the plots show a linear region at log t < 1 with a slope of 0.5, which conforms to a diffusion controlled process where the current is proportional to $t^{1/2}$ according to the Cottrell equation. The integrated charge during the first 10s has been reported to correspond roughly to the amount of Li^+ ions in the cavities of the porous film [57].

At longer times the current decline is faster, and for pre-illumination times > 2 min a region with a slope of 0.5 is not observed, due to kinetic control/restricted diffusion. To corroborate these results, we constructed plots of $it^{1/2}$ vs. log t (Fig. 4 Supplementary), which are ideally characterized by a horizontal line reflecting the Cottrell behavior; i.e. the semi-infinite diffusion. In practice these plots are bell-shaped with a maximum that is more or less flat depending on the degree of diffusion control [58]. A flat maximum is seen only for the short pre-illumination (Fig. 4 Supplementary, curve 1) confirming the results of Fig.3 (Supplementary). Additionally, this maximum shifts toward longer time for increasing pre-illumination time; the shift is modest but apparently indicates the occurrence of some Li^+ insertion [58]. Also noteworthy is that oxidation current (Fig.3 Supplementary) and the corresponding charge reported in Fig. 3 (curve 1) increase slowly for illumination t > 2 min, likely because extraction of photo-inserted lithium is kinetically controlled and incomplete even on a time scale of 1 h, as sometimes reported in the literature.
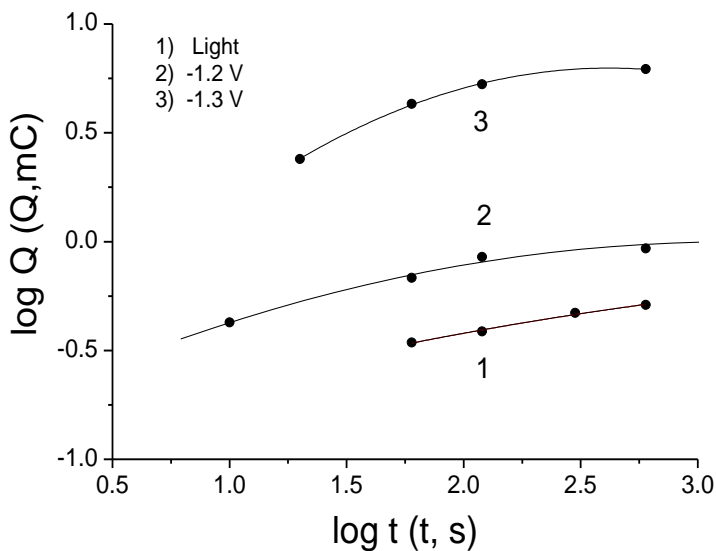

Figure 3

The present photocatalytic system and DSSC have some common aspects concerning the role of Li^+ and the papers by Gregg [16], Wahl and Augustynski [14] and Highfield and Grätzel [31], for example, provide important background information. There are, however, significant differences, and we think it will be useful to comment briefly on factors that condition the open-circuit photo-charging in the presence of Li^+ described in this work. In particular, we calculated that light penetration depth is 0.8 μm compared to a total film thickness of 5.7 μm and then only 1/7 of the total volume and surface area are involved in photochemical generation of charges (see experimental section). Analogous experiments with a film having of thickness of 1 μm did not give different results, confirming that light penetration depth is < 1 μm. Considering that the incident light flux (see experimental section) is 2×10^{17} photons/s, in the light absorbing portion of the film a maximum amount of 2×10^{17} electrons/s are in principle photo-generated. On the other hand, the charge extracted (Eq. 3) after 600s pre-illumination is 0.51 mC (Fig. 3, curve 1) corresponding to 3.2×10^{15} electrons instead of 1.2×10^{20}. This can be due to i) charge recombination, ii) incomplete or slow re-oxidation of Ti^{3+}-Li^+ pairs, some of which may have diffused from illuminated to inner dark regions of the film where they may be confined at trap sites. We remark that when photo-accumulation of electrons was carried out at open circuit, surface charge recombination in the illuminated areas [14] cannot be *a priori* excluded although it can be limited by efficient scavenging of holes by 2-propanol. In fact, previous reports have clearly demonstrated the low efficiency of photocatalytic systems compared, for example, with analogous photo-electrochemical ones where an applied potential can further reduce recombination phenomena [9, 59].

In order to increase our level of understanding of reactions induced by UV illumination, we thought it would be informative to compare the results with those obtained in tests in which the oxide is charged electrochemically in the dark. In Fig. 3 (curves 2 and 3) are displayed results of chronocoulometry measurements in which the anodic charge is measured following a potential step at some negative potential for different lengths of time. Substantial differences between the photo-charging and electrochemical charging experiments are seen when the negative potential approaches E_{fb} (curve 3). The re-oxidation charge becomes comparable for charging at constant potentials 200-250 mV below E_{fb} (Fig. 3, curve2). In this potential range exploitation of the electrochemically active surface area is limited and it seems possible to infer that pre-polarization at these negative potentials or pre-illumination under open circuit leads to occupancy of bandgap traps, followed by the slower build-up of Ti^{3+} that are screened by Li^+ [57]. Usually, significant Li^+ bulk insertion is achieved at more negative potentials than those used in these experiments. In the present instance, the data seem rather to suggest formation of trapped Ti^{3+}- Li^+ pairs at the surface or likely in subsurface region where they seem to be quite stable [60].

The electrochemical experiment allows a direct measurement of the amount of charge involved in the constant potential reduction and re-oxidation. We observed that upon holding the potential at -1.2 V for 1 and 2 min the extracted charge after 15 min anodic polarization (0.5 V) decreases respectively from 40% to 8 % of the insertion charge. Although several publications report reversible insertion-de-insertion of Li^+ in TiO_2, irreversibility has also been often observed [61,62] and discrepancies are likely due to different film morphology as well as to light intensity [55] in the photo-charging experiments. In these cases [23, 29], Eq. 3 has been actually written as Eq.5:

$$Li_x\,TiO_2 \rightleftharpoons Li_{x-y}\,TiO_2 + yLi^+ + ye^- \qquad (5)$$
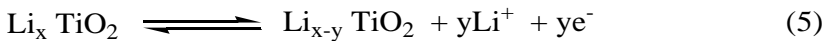
3.5 Reactivity of holes: 2-propanol oxidation

The picture that in part emerges from the results reported above is that photo-insertion, albeit shallow, and slow de-insertion of Li^+ cause surface modifications (*vide supra*) that may dramatically change the adsorption of the hole scavenger and increase recombination. We showed that 2-propanol strongly interacts with TiO_2 surface sites in the dark (Fig. 1) and additional information can be collected by measuring photocurrents on anodically polarized films. The current vs. time transients (Fig. 5 Supplementary, curve 1) show that, as illumination is switched on, the photocurrent rises sharply and reaches a limiting value within few seconds. By comparison, for an electrode that is pre-illuminated for several minutes at open circuit under otherwise identical conditions (Fig. 5 Supplementary, curve 2), one notes that the photocurrent increases rather slowly as a function of the time and finally reaches a limiting value, which is significantly lower than that in the absence of the UV treatment. Illumination was carried from the oxide/electrolyte side and electrons generated in this area will have to be transported to the metal support through the dark part of the film (*vide supra*). If low photocurrents are due to electron transport limitations across the film, it must be assumed that pre-illumination will cause modifications in the whole film, for example by ambipolar diffusion of electrons and Li^+ to dark areas where they may form trapped Ti^{3+}- Li^+ pairs at the surface and/or subsurface as mentioned above.

Alternatively, we think that the results observed in our system can be explained in terms of an alteration of adsorption of 2-propanol due to photo-induced lithium insertion in near surface regions. In this particular case, recombination would increase due to decreased re-adsorption of the hole scavenger on the pre-illuminated electrode. While it is well known that photo-oxidation of 2-propanol on TiO_2 exhibits near 100% selectivity toward acetone [63], this reaction involves the formation of radical intermediates, and the possibility to distinguish between iso-propoxy and

hydroxy-isopropyl radicals provides invaluable details about the reaction mechanism [64]. In this context, spin-trapping EPR spectroscopy is a powerful tool for this kind of studies [65]. In a typical EPR-spin trapping experiment, TiO_2 is suspended in CH_3CN/2-propanol containing Li^+ and the spin trap pbn: as soon as light is switched on, one notes the appearance of a triplet of doublets with hyperfine splitting constants $a_N = 14.1$ G and $a_H = 2.3$ G, which is ascribed to the trapping of iso-propoxy radicals $(CH_3)_2CHO\bullet$ (**I**) by pbn (Fig. 4a) [65]. Formation of (**I**) is observed both in the presence and in the absence of Li^+, which indicates that adsorption of 2-propanol is strong and qualitatively not hindered by the cations. In agreement with previous work [65], dissociative adsorption of the alcohol with formation of surface alcoholate $(C_3H_7O^-)$ (Eq. 2) is facilitated by adsorption of H^+ at nearby surface oxygen sites. As a consequence, upon illumination, capture of photo-generated holes by $C_3H_7O^-_{(ads)}$ leads to the alkoxy radical, which is subsequently trapped by pbn and revealed by its characteristic EPR spectrum.

A second consecutive irradiation run has been carried out on the sample already illuminated, after an interval of about ten minutes in the dark. During this time, equilibrium conditions very similar to the initial ones are restored. In fact, in the absence of Li^+ ions, illumination causes again the formation and detection of alkoxy-radicals (**I**). On the contrary, in the sample pre-illuminated with Li^+ a new spectrum is recorded (Fig. 4B), consisting of a triplet of doublets with different hyperfine coupling constants ($a'_N = 15.2$ G and $a'_H = 3.5$ G). This signal is assigned to the paramagnetic adduct between pbn and hydroxyalkyl radicals of 2-propanol $(CH_3)_2C^{\bullet}OH$ (**II**) [65]. Formation of these radicals is an evidence that adsorption 2-propanol is decreased and holes react instead with surface OH groups to give OH• radicals [65]. These, in turn, extract a hydrogen atom from the α C-H bond of 2-propanol forming (**II**).
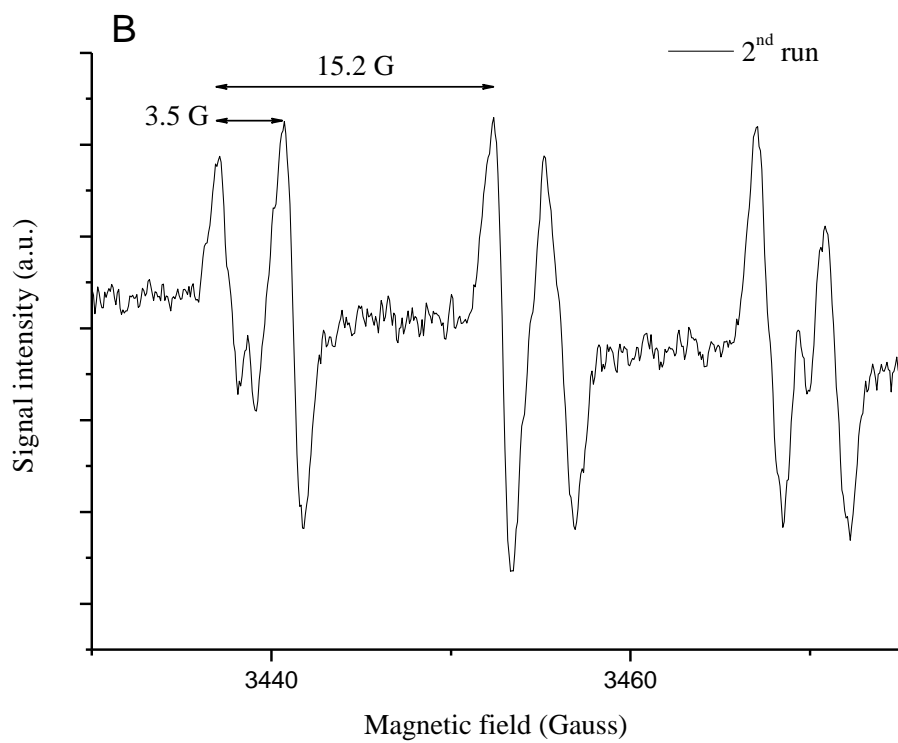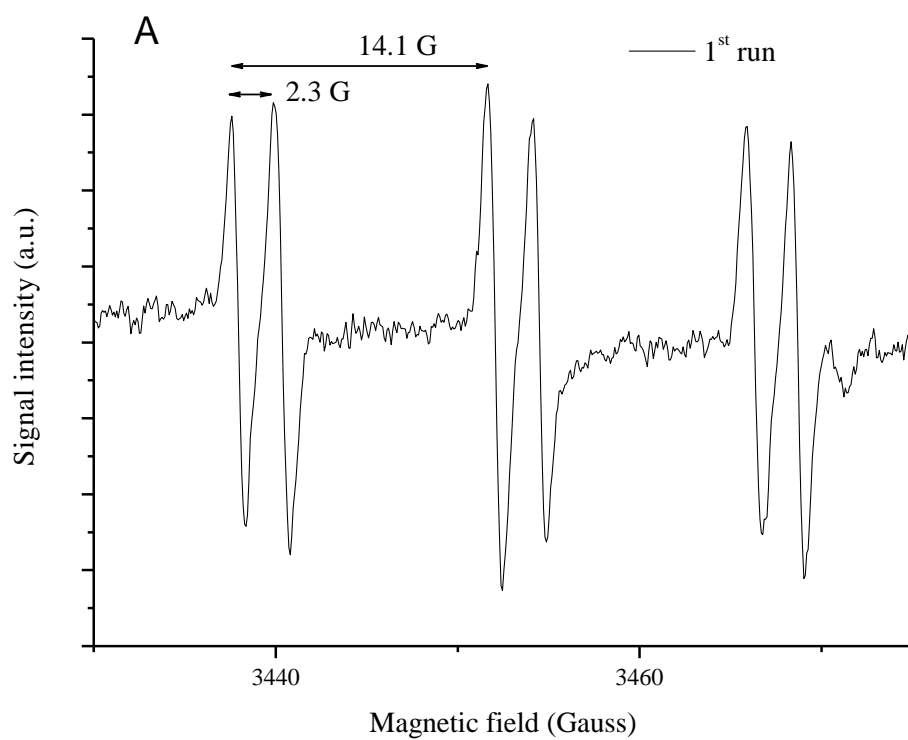
Figure 4.

The results point out that some important interfacial changes, occurring during the first irradiation run in the presence of Li^+, become evident during the second irradiation. Adsorption of 2-propanol as an alcoholate is strongly inhibited on the pre-illuminated powder and indeed the initial interfacial environment is not completely recovered even after hours in the dark, in agreement with the decrease of the photocurrent after pre-illumination (Fig. 5 Supplementary). Additionally, we remark that the reduction power of the alcohol radicals (E = - 0.61 vs SCE) [10] is not enough to give current doubling phenomena despite the positive shift of E_{fb} induced by Li^+.

To sum up, EPR spin trapping results reinforce the statement that light-induced surface modifications [66] by Li^+ occur and that this brings about a change in the initial 2-propanol photo-oxidation mechanism. As discussed above, it is conceivable that, under illumination, charge that is initially stored in the double layer can migrate to subsurface lattice sites where, maybe in the form of trapped Li^+-Ti^{3+} pairs [14, 55] possibly evolving to Li_xTiO_2, can significantly influence surface properties [47,60,67]. Based on the discussion of the data of Fig. 3, Li^+-Ti^{3+} pairs are likely photo-accumulated and stabilized at the surface/interface region, which is characterized by high densities of dangling bonds, surface defects and vacancies that can trap lithium ions; interestingly, these Li^+-Ti^{3+} pairs have been reported to concentrate near the surface [47,68].

Reactivity of electrons

A large amount of studies in DSSC research report on effects of Li^+- induced modification of TiO_2 but attention has also been drawn to interactions of Li^+ with the dye molecules [69]. This turned out to be a particular important aspect in the present photo(electro)catalytic study where $O_2NC_6H_4CHO$ was chosen as the probe reducible species.

Results displayed in Fig. 5 illustrate the CV for TiO_2 in CH_3CN/2-propanol/$LiClO_4$ in the absence (curve 1) and in the presence of $O_2NC_6H_4CHO$ (curve 2). Dark reduction of the organic species starts at $\sim$ -0.6 V, in correspondence to the small peak (a) which is observed only in the base electrolyte and is attributed to surface states as discussed earlier in this paper (Fig. 1). Its disappearance indicates that reduction of the organic species prevents filling of surface states [10]. Moreover, in keeping with a reaction involving Ti^{3+} as the reductant, on reversing the scan direction one notes that the anodic charge decreases (curve 2) to an extent that depends on the experimental conditions which, in the CV experiment, includes the cathodic limit, the sweep rate and the concentration of $O_2NC_6H_4CHO$. Even under the non steady-state experimental conditions of Fig. 5, the re-oxidation charge is negligible for cathodic potential limits more positive than E_{fb}.
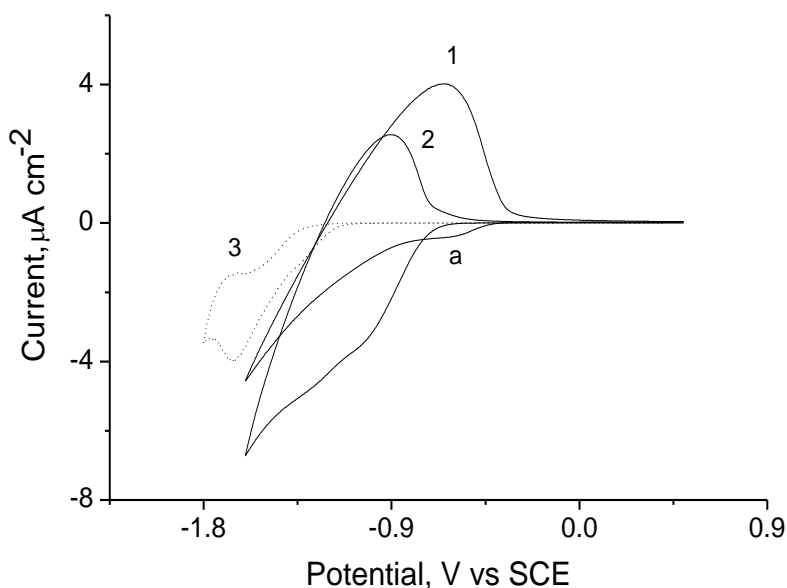
Figure 5.

For the sake of comparison, Fig. 5 also reports the CV of $O_2NC_6H_4CHO$ in CH_3CN/2-propanol/TEAP (curve 3). It is apparent, in this case, that dark reduction onset is ~ 0.6 V more negative than in $LiClO_4$. The relative positions of energy levels are illustrated in Scheme 1. According to this summary diagram, reduction of $O_2NC_6H_4CHO$ can still occur even if the energy bands alone shifted positive; however, the simultaneous positive shift of the onset of dark reduction generates a higher driving force for electron transfer. The scenario brings out an effect of Li^+ that is not limited to a change in the surface energetics but must involve the whole interface. In other words, the positive shift of the conduction band alone, caused by Li^+ adsorption/intercalation, does not explain the positive onset of $O_2NC_6H_4CHO$ reduction. The reason must be an interaction of Li^+ with the electron acceptor itself or with its reduced intermediates.
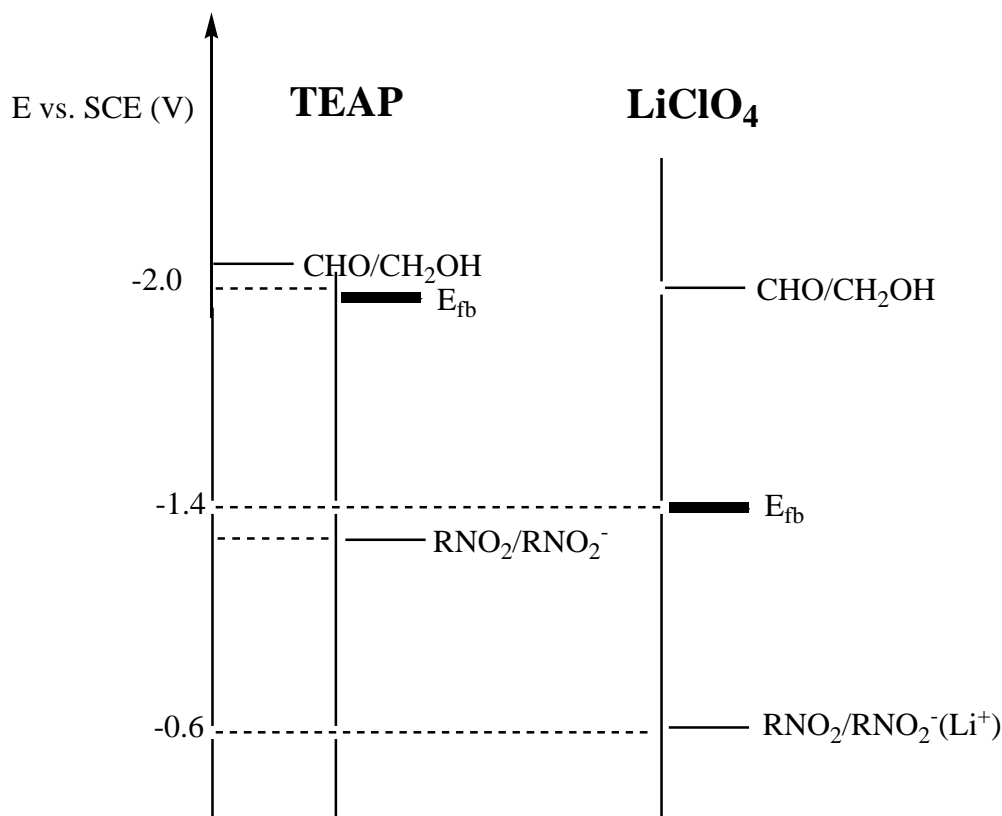
Scheme 1.

We have previously reported [10] that interaction of $O_2NC_6H_4CHO$ with the surface occurs preferentially through the $-NO_2$ group and in fact reduction has been found to occur firstly through this moiety (*vide infra*). Interestingly also, MO calculations reported in early literature [70] have demonstrated that most of the total charge density tends to be localized on $-NO_2$ group despite the high conjugation with the CHO group. The $R-NO_2^-$ and $R-NO_2^{2-}$ anion intermediates can experience repulsion if excess electrons are trapped at the surface, and this is expected to slow down the multi-electron process. In this regard, Li^+ can favor the reduction process in at least two ways, i.e., by i) screening the surface charge thereby decreasing electrostatic repulsion and ii) forming ion pairs with the aromatic anions in spite of the high polarity of the solvent [70]. In particular, interaction with Li^+ can shift the LUMO level downwards by Coulomb stabilization [69].

To complete our electrochemical analysis, we have examined the CV behavior of $O_2NC_6H_4CHO$ on a gold electrode in CH_3CN/2-propanol/$LiClO_4$. Results (Fig. 6 Supplementary, curve 1) show an irreversible reduction at -0.8 V and a reversible process at -0.45 V, which are ascribed to $-NO_2$ reduction on the basis of $H_2NC_6H_4CHO$ formation. The processes appear to be shifted anodically by ~ 0.5 V compared with analogous results in CH_3CN/2-propanol/TEAP (Fig. 6

Supplementary, curve 2). Seen in the context of the behavior outlined for TiO_2, the data unequivocally prove the importance of double layer effects on the positive shift of $O_2NC_6H_4CHO$ reduction i.e., formation of cation bridges between Li^+ and anion intermediates.

So far our attention has gone to the reduction of the $-NO_2$ functional group but the chosen electron acceptor is an interesting probe in the fact that it has two reducible groups and since we aimed at a comprehensive analysis, we obviously could not dispense with considering the fate of the $-CHO$ moiety, all the more so as this group will determine the reduction selectivity of this important compound. The stepwise reduction of $O_2NC_6H_4CHO$ leads to intermediate $H_2NC_6H_4CHO$ formation and eventually to $H_2NC_6H_4CH_2OH$ as the final product. Formation of the latter depends on the occurrence of electron accumulation that leads to a shift of the conduction band to more negative potentials [10]. This phenomenon does not take place in the present instance since the accumulated charge is screened by Li^+. Indeed open circuit illumination of TiO_2 films or suspensions in CH_3CN/2-propanol/$LiClO_4$/$O_2NC_6H_4CHO$ yielded $H_2NC_6H_4CHO$ with a 100% selectivity. Prolonged illumination did not yield the complete reduced $H_2NC_6H_4CH_2OH$, in contrast with the case of a TEAP containing medium [10].

We then examined the electrochemical behavior of $H_2NC_6H_4CHO$, which is the stable product of partial reduction. Importantly, the potential step experiments of Figure 6 show that an appreciable current, ascribable to $-CHO$ reduction, is recorded only at E < -1.9 V (curves b, c), i.e., quite more negative than E_{fb}; while at E > E_{fb} the current decays slowly to zero (curve a) revealing mainly the filling of surface states. It seems possible to conclude that despite interaction of Li^+ with both the surface and the electron scavenger, the first plays a crucial role in determining reduction selectivity.
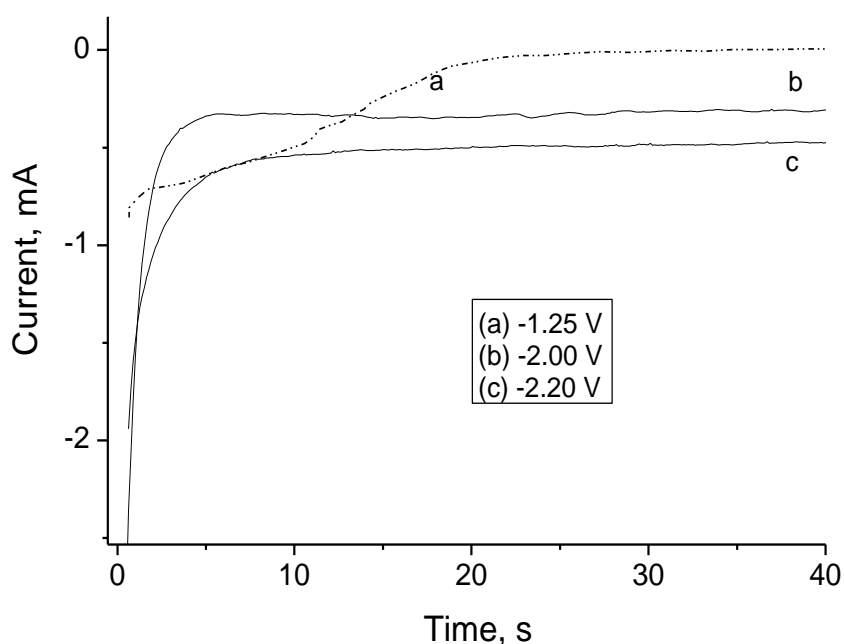
Figure 6.

4. Conclusions

Lithium ions control surface energetics of TiO_2 in acetonitrile. The dynamics of holes and electrons transfer are investigated using 2-propanol and $O_2NC_6H_4CHO$ as charge scavengers. We demonstrate the possibility of channeling interface reactions in a pathway that allows us to control both the reduction and the oxidation mechanisms.

Results of photo-electrochemical measurements show that adsorption of Li^+ in the dark causes a significant positive shift of the TiO_2 conduction band edge. Moreover, there is clear evidence that 2-propanol is strongly adsorbed bringing about a redistribution of the bandgap states. Upon illumination, the charge due to photo-generated electrons is screened by Li^+ that undergoes adsorption/insertion at the surface/subsurface region. This causes alteration of the interface properties that is evidenced, in particular, in the mechanism of 2-propanol photo-oxidation, as revealed by EPR spin trapping experiments. This study reveals that conditions can be found whereby different photooxidation intermediates are formed, which is potentially interesting for the regioselective oxidation of polyalcohols, i.e. primary versus secondary OH functional groups.

Interesting effects are seeing in the reduction of $O_2NC_6H_4CHO$. In addition to the positive shift of the TiO_2 conduction band edge, Li^+ also affects the dark reduction of $O_2NC_6H_4CHO$ through ion pairs formation between Li^+ and the $R\text{-}NO_2^{n-}$ anions intermediates. Conversely, reduction of the –CHO functional group is possible only at much more negative potentials than E_{fb} and appears to be insensitive to the presence of lithium ions. Thus, these play a crucial role in determining reduction selectivity opening up new approaches for reduction pathways.

Although Li^+ show a peculiar interaction with reduction intermediates of the electron scavenger, its dominant effect is on the surface and interface properties of the semiconducting oxide. This is of great importance in heterogeneous photocatalysis, which requires a detailed knowledge of reaction mechanisms in order to tune and control oxidation and reduction processes occurring simultaneously on the same illuminated TiO_2 particle.

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Captions to the Figures

Figure 1. Cyclic voltammetry curves in the dark for a TiO_2 electrode in de-aerated solutions of CH_3CN (curve 1) and of CH_3CN/2-propanol (4:1 v/v) (curve 2). Supporting electrolyte is $LiClO_4$ (0.1 M). Inset: expanded view of peaks marked (a) and (b) in the main graph. Scan rate: 25 mV/s.

Figure 2. Cyclic voltammetry curves in the dark for a TiO_2 electrode in de-aerated solutions of CH_3CN/2-propanol (4:1 v/v) containing $LiClO_4$ (0.1 M). Before (curve 1) and after pre-illumination ($\lambda > 360$ nm) at open circuit for 2 min (curve 2) and 5 min (curve 3). Curve (4) was recorded after electrode cycling for 10 min in the dark following 5 min pre-illumination. Scan rate: 25 mV/s.

Figure 3. Logarithmic plots of the integrated charge from anodic potential steps in the dark (-0.2 to 0.5 V) after electrode illumination (350-370 nm) at open circuit (curve 1) or after holding the potential at -1.2 V (curve 2) and -1.3 V (curve 3) for different times in the dark. TiO_2 electrode in de-aerated solutions of CH_3CN/2-propanol (4:1 v/v) with $LiClO_4$ (0.1 M).

Figure 4. A) EPR spin trapping spectrum of [pbn-$(CH_3)_2$CHO]· obtained after irradiation (90 s) of TiO_2 suspended in a deaerated CH_3CN/2-propanol (4:1 v/v) solution containing $LiClO_4$ (0.1 M), pbn (5 x 10^{-2} M) and $O_2NC_6H_4CHO$ (1 x 10^{-3} M). **B)** sample A left 10 min in the dark and then irradiated for a second time (90 s). the spectrum is relative to the [pbn-C(OH)$(CH_3)_2$]· adduct.

Figure 5. Cyclic voltammetry curves in the dark for a TiO_2 electrode in de-aerated solutions of CH_3CN/2-propanol (4:1) and $LiClO_4$ (0.1 M) in the absence (curve 1) and in the presence of $O_2NC_6H_4CHO$ (1 x 10^{-3} M) (curve 2). Curve (3) was recorded using tetra-ethyl-ammonium perchlorate (TEAP, 0.1 M) instead of $LiClO_4$ as the electrolyte. Scan rate: 20 mV/s.

Figure 6. Current-time transients in the darkness for a TiO_2 electrode in de-aerated solutions of CH_3CN/2-propanol (4:1 v/v) containing $LiClO_4$ (0.1 M) in the presence of $O_2NC_6H_4CHO$ (1 x 10^{-3} M)**.**

Scheme 1. Schematic energy diagrams illustrating positions of E_{fb} and reduction of $-NO_2$ and CHO groups of $O_2NC_6H_4CHO$ in the presence of TEAP or $LiClO_4$.

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