# Photocatalysis

# Probing the Role of Surface Energetics of Electrons and their Accumulation in Photoreduction Processes on TiO<sub>2</sub>

Alessandra Molinari,\*<sup>[a]</sup> Andrea Maldotti,<sup>[b]</sup> and Rossano Amadelli\*<sup>[c]</sup>

**Abstract:** We address the role of the energetics of photogenerated electrons in the reduction of 4-nitrobenzaldehyde on TiO<sub>2</sub>. This model molecule bears two functional groups featuring different reducibilities. Electrochemistry shows that reduction to 4-aminobenzyl alcohol occurs in entirely distinct potential ranges. Partial reduction of the  $-NO_2$  group, affording 4-aminobenzaldehyde, takes place through surface states at potentials positive of the flatband potential ( $E_{\rm fb}$ ). Dark currents caused by reduction of the aldehyde group

## Introduction

Heterogeneous photocatalysis with titanium dioxide is an important research field because of its attractive applications in environment remediation,<sup>[1]</sup> water splitting and hydrogen production,<sup>[2]</sup> solar energy conversion,<sup>[3]</sup> and the synthesis of chemical specialties.<sup>[4]</sup> Most investigations on TiO<sub>2</sub>-based photocatalysis adopt an application-driven perspective, and in this context, surface modification and doping represent important strategies.<sup>[5]</sup> The storage of photogenerated electrons in semiconductors modified with metal islands<sup>[6]</sup> or in hybrid photocatalysts<sup>[7]</sup> has also long been employed for catalyzing important processes.

A number of authors have approached the field by investigating the relationships between fundamental aspects of photon-initiated events and observed photocatalytic phenomena,<sup>[8]</sup> recognizing, for example, that the usefulness of photocatalysis depends critically on the energetic positions of the band edges relative to the solution species. Understanding and optimizing the semiconductor surface energetics may lead to significant improvements in power conversion efficiency in dye-sensitized cells and photocatalytic processes.

[a]	Dr. A. Molinari
	Dipartimento di Scienze Chimiche e Farmaceutiche
	Via Fossato di Mortara 17, 44121 Ferrara (Italy)
	Fax: (+ 39) 0532240709
	E-mail: alessandra.molinari@unife.it
[b]	Prof. A. Maldotti
	Dipartimento di Scienze Chimiche e Farmaceutiche
	Via Fossato di Mortara 17, 44121 Ferrara (Italy)
[c]	Dr. R. Amadelli
	ISOF CNR, UOS di Ferrara
	c/o Dipartimento di Scienze Chimiche e Farmaceutiche
	Via Fossato di Mortara 17, 44121 Ferrara (Italy)
	E-mail: rossano.amadelli@unife.it

are observed only at potentials more negative than  $E_{\rm fb}$ , and the process requires an electron accumulation regime. Photocatalysis with TiO<sub>2</sub> suspensions agrees with the electrochemical data. In particular, reduction of the nitro group is a relatively fast process (k=0.059 s<sup>-1</sup>), whereas that of the aldehyde group is slower (k=0.001 s<sup>-1</sup>) and requires electron photoaccumulation. Control of the photogenerated charge is a prospective means for achieving chemoselective reductions.

Electron accumulation represents a way of promoting control over band-edge positions (interface energetics). In this regard, dark electrochemistry in the accumulation regime has been the subject of several publications, focusing mainly on energy storage.<sup>[9]</sup> The phenomenon has been characterized by EPR spectroscopy,<sup>[7]</sup> and, in detail, by spectroelectrochemistry and luminescence.<sup>[10]</sup> Accumulation accompanied by the intercalation of protons or cations is referred to as "electrochemical doping".<sup>[11]</sup> In addition to energy storage, prospective additional developments of electrochemical doping<sup>[12]</sup> include a novel switching mechanism for sensor development.<sup>[13]</sup> It has been pointed out that reductive doping of TiO<sub>2</sub> is also achieved upon illumination, and is accordingly referred to as "photodoping".<sup>[14]</sup> Applications of anoxic photochemical electron accumulation are seemingly sparser<sup>[15]</sup> than for the analogous dark electrochemical doping. In particular, Kohtani et al. have very recently reported the photohydrogenation of acetophenone and its derivatives by illuminated TiO<sub>2</sub>, confirming that the role of electrons is an interesting research topic.[15c]

In this paper, we examine the influence of surface energetics, paying particular attention to the effect of photochemical electron accumulation, in the multistep photoreduction of 4-nitrobenzaldehyde ( $O_2NC_6H_4CHO$ ) on TiO<sub>2</sub>. This compound has been chosen as a model molecule containing two functionalities with different reducibilities. Several literature studies have been devoted to the photoreduction of either nitroaromatics<sup>[16]</sup> or aromatic aldehydes<sup>[16e, 17]</sup> on TiO<sub>2</sub>, but seemingly none examine specifically the factors governing the photocatalytic reduction of the two functional groups present simultaneously in the same molecule. From a general point of view, we think this is an interesting issue of direct concern in studies on the selectivity of photocatalytic processes. Furthermore, selective reduction of this type of substrate by thermal catalysis is difficult and not always successful, as often demonstrated.<sup>[18]</sup>

Chem. Eur. J. 2014, 20, 7759 - 7765

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From results of electrochemical measurements we confirm that "accumulation" is a broad term that refers generally to the increase in the concentration of conduction-band electrons following the saturation of intra-bandgap trap states. In this context, their degree of filling with electrons has a close relationship with the main topic of this paper: until there are free states, photoreactions are channeled toward the chemoselective reduction of  $O_2NC_6H_4CHO$  to  $H_2NC_6H_4CHO$ ; then, their complete filling will cause the accumulation of electrons in the conduction band, eventually leading to complete reduction to  $H_2NC_6H_4CH_2OH$ . On the basis of the results presented and discussed, we underline the prospective developments in the field of photocatalysis.

### **Results and Discussion**

In the following, we examine the behavior of TiO<sub>2</sub> electrodes and suspensions. In all cases, the working medium is a mixture of acetonitrile and 2-propanol containing  $O_2NC_6H_4CHO$ . We first present the results of electrochemical measurements in the dark, with and without prior illumination on the electrode at an open circuit. Then, we discuss the photocatalytic behavior in both the absence and presence of  $O_2$ . More specifically, we evaluate the possibility of channeling the interface photoreactions toward the chemoselective reduction of  $O_2NC_6H_4CHO$ . Moreover, ESR measurements provide information on the nature of the radical intermediates, which is important for the formulation of the reaction mechanism.

#### **Electrochemical characterization**

Electrochemistry is an important tool for studying physical and chemical phenomena occurring at interfaces.<sup>[19]</sup> Moreover, this technique can be conveniently employed for investigating separately the reduction and oxidation processes that occur simultaneously during photocatalytic experiments as a consequence of primary charge separation.<sup>[20]</sup>

Among several parameters, the flat band potential is a very important one for the characterization of a semiconductor/ electrolyte interface as it correlates the band edges to the redox potential in the electrolyte. The value of the flatband potential ( $E_{\rm fb}$ ), from Mott–Schottky plots obtained from capacitance measurements in CH<sub>3</sub>CN/TEAP, was in the range -2.0 to -2.1 V versus SCE, in good agreement with that obtained previously through spectroscopic techniques for a polycrystalline TiO<sub>2</sub> electrode in neat CH<sub>3</sub>CN containing the same supporting electrolyte.<sup>[21]</sup> In the mixed solvent, it decreased slightly to a value between -2.0 and -1.95 V (Figure 1). It is seen in the figure that illumination does not change  $E_{\rm fb}$ , whereas the slope decreases significantly. This has frequently been observed in the literature, and is attributed to an increase in the number of donors or, more probably, to the intercalation of protons, which compensates charge accumulation and leads to changes in the surface characteristics, as shown in Equation (1), in which (H<sup>+</sup>)<sub>i</sub> refers to intercalated protons.<sup>[14,22]</sup>



**Figure 1.** Mott–Schottky plots for a TiO<sub>2</sub> (P-25) film electrode both in the dark and under illumination ( $\lambda > 360$  nm, 100 mW cm<sup>-2</sup>). Electrolyte: CH<sub>3</sub>CN/ 2-propanol (4:1, v/v) containing tetraethylammonium perchlorate (TEAP, 0.2 M).

$$Ti^{3+}O_2(H^+)_i \to Ti^{4+}O_2 + e^- + (H^+)_{ads}$$
(1)

In the present case, protons released from the oxidation of 2propanol are first adsorbed and then intercalated as the negative field caused by electron accumulation increases. In any case, as expected, no capacity change is observed in the presence of  $O_2NC_6H_4$ CHO, because its reduction consumes both electrons and protons.

Generally, the role played by surface states (ss) is an important feature of photo(electro)catalytic processes. We sought insights into this aspect and on the effects of illumination by using a variant of the potentiostatic method described by Wang et al.<sup>[23]</sup> We recorded anodic linear sweep voltammetry (LSV) curves in the dark from a potential slightly more positive than  $E_{\rm fb}$  to 0.0 V, immediately (2 s) after illumination for different lengths of time at an open circuit. Curves of charge versus potential are then obtained by integrating the LSV curves. These are recorded as a function of potential, and can be converted to a timescale knowing the scan rate (100 mV  $s^{-1}$ ). In the absence of electron acceptors, the re-oxidation charge is equivalent to the total accumulated charge<sup>[24]</sup> in the form of Ti<sup>3+</sup>. Illumination causes a conspicuous accumulation of charge (Figure 2), which is rather persistent after the light is switched off. Typically, after 10 min illumination, the cyclic voltammetry profile returns to its original value after cycling the electrode in the dark from -1.85 to 0.5 V for 140 s.

Plots of charge versus potential (Figure 2) are expected to provide information on the presence and distribution of ss across the bandgap.<sup>[23]</sup> The potential variation of the charge associated with ss shows that they are widely distributed energetically. Their filling reaches saturation (curve c) under continued illumination, that is, at E < -1.6 V, and the bands tend to become flat, whereas at potentials above -0.7 V there are no trapped electrons. For prolonged illumination, a shoulder appears (not shown) in the plots of Q versus E in the range -1 to -0.8 V, which can be attributed to the filling of deeper ss.<sup>[12]</sup> At intermediate potentials, the charge changes rapidly, and the derivatives of the curves (dQ/dE) show a peak (bottom of Figure 2) corresponding to a maximum density of ss.<sup>[23]</sup> The

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**Figure 2.** Top: Plots of the charge accumulated during illumination of a TiO<sub>2</sub> electrode at open circuit ( $\lambda > 360$  nm, 100 mW cm<sup>-2</sup>). The charge was obtained by integration of linear sweep voltammetry curves recorded from -1.85 to 0.0 V versus SCE following illumination: a) dark, b) 4 min irradiation, and c) 10 min irradiation. Bottom: dQ/dE versus potential. Electrolyte: CH<sub>3</sub>CN/2-propanol (4:1, v/v) containing TEAP (0.2 m).

maximum is located at -1.6 V in the dark and shifts to -1.5 V under illumination, probably on account of protons formed during the photo-oxidation of 2-propanol. Indeed, there is no positive shift of the maximum if potential is used to accumulate electrons in the dark.

Upon complete filling of the ss, electrons accumulate in the conduction band. From Figure 2*c*, saturation of the ss corresponds to a charge of 7.7 mC, and using a roughness factor of 690,<sup>[25]</sup> we calculate a trap density ( $N_t = Q/eA$ ) of  $8.7 \times 10^{13}$  cm<sup>-2</sup>, in agreement with the values reported by Wang et al.<sup>[23]</sup> and Kay et al.<sup>[26]</sup> In principle, this density of states may cause a potential drop in the Helmholtz layer ( $\Delta V_H = eN_t/C_H$ ) and unpinning of the band edges.<sup>[10,24]</sup>

The steady-state reduction of  $O_2NC_6H_4CHO$  in the dark is shown in Figure 3 (curve 1). Reduction starts at E < -1.1 V and leads to  $H_2NC_6H_4CHO$ , as established by chemical analysis. For comparison purposes, we also examined the reduction of  $O_2NC_6H_4CHO$  on a gold electrode (not shown), and observed two reduction peaks at about a -1.0 and -1.3 V, which are attributed to consecutive reductions of the  $-NO_2$  group. The first reduction process is reversible, whereas the second is irreversible, indicating that the  $NO_2^{2-}$  species can be protonated by the alcohol, as reported previously by Bard.<sup>[27]</sup> Both redox processes are reversible in neat  $CH_3CN$  under otherwise identical conditions. There is no evidence of any further process involv-



**Figure 3.** Top: Steady-state current versus potential curves for the reduction of 1.1 mmol  $O_2NC_6H_4CHO$  (curve 1) and 1.1 mmol  $H_2NC_6H_4CHO$  (curve 2) on TiO<sub>2</sub> in the dark. Curve 3 shows the reduction of 1.1 mmol  $H_2NC_6H_4CHO$  on a gold electrode. Electrolyte: CH<sub>3</sub>CN/2-propanol (4:1, v/v) containing TEAP (0.2 m). Bottom: Partial currents for the photo-oxidation of 2-propanol and for the dark reduction of  $O_2NC_6H_4CHO$  (see text).

ing the reduction of the aldehyde functional group at potentials more positive than -2.0 V.

Considering, then, that  $H_2NC_6H_4CHO$  is a possible stable reduction intermediate, we studied its electrochemical reduction on both Au and TiO<sub>2</sub> electrodes. The results reported in Figure 3 (curves 2, 3) show that the process starts at E < -2.0 V on both electrodes, that is, in a potential range in which TiO<sub>2</sub> behaves as a metal. In other words, electron accumulation is seemingly necessary for the reduction of -CHO to  $-CH_2OH$ .

From a comparison of the data of Figures 2 and 3, it appears that ss can mediate the reduction of the  $-NO_2$  group. In this case, ss continue to trap electrons until complete reduction of  $-NO_2$  to  $NH_2$  has occurred, as proposed, for example, by Redmond et al.<sup>[9a]</sup> for H<sup>+</sup> reduction through surface states. Subsequently, electron accumulation takes place as shown by the experimental data of Figure 4. In this figure, in the presence of added  $O_2NC_6H_4CHO$  (curve 1), the open-circuit photopotential first decreases to a negative value (a), and then increases. After reaching a constant value (b), it becomes more negative again (c) owing to electron accumulation. The results suggest that the nitro group should be reduced completely before -CHO can, in turn, be reduced. No such positive drift of the photopotential is seen for the same concentration of added  $H_2NC_6H_4CHO$  and on the same timescale (curve 2).





**Figure 4.** Open-circuit potential versus time for a TiO<sub>2</sub> electrode in CH<sub>3</sub>CN/2propanol (4:1, v/v) containing TEAP (0.2 M). Curve 1: with added  $O_2NC_6H_4CHO$  (0.4 mmol). Curve 2: in the presence of  $H_2NC_6H_4CHO$ (0.4 mmol). Illumination at  $\lambda > 360$  nm, 100 mW cm<sup>-2</sup>.

Figure 3 (bottom) shows that photo-oxidation of 2-propanol is also likely to be influenced by ss. Their signature is evident in the slow increase in photocurrent in the potential range -1.5 to -0.8 V, in the region where accumulated charge varies significantly with potential (Figure 2). The stability of electrons trapped in the surface states is probably responsible for the slow photocurrent response in this potential interval. At more positive potentials at which electron traps are empty, the current increases markedly. More results on the photo-oxidation of 2-propanol will be discussed in the next section.

In relation to the results displayed in Figure 3 (bottom), we note further that the photocurrent and dark reduction of  $O_2NC_6H_4CHO$  are superimposable and become equal at approximately -1.25 V. We can then infer that, according to the flux matching theory,<sup>[28]</sup> the reduction of  $-NO_2$  can take place on electrodes at an open circuit and in TiO<sub>2</sub> suspensions in the same medium. In contrast, the reduction of the -CHO functional group is not predicted under normal photocatalytic conditions.

#### Surface energetics and photocatalysis

Irradiation of deaerated suspensions of TiO<sub>2</sub>-P25 in the same mixture of CH<sub>3</sub>CN/2-propanol containing O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO brings about significant UV/Vis spectral changes, as illustrated by the photoreduction course reported in Figure 5. This shows qualitatively that photoexcitation causes a rapid conversion of O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO ( $\lambda_{max}$ =264 nm) to H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO, as indicated by the growth of a spectrum with two absorption maxima at 232 and 312 nm. These results are in agreement with the electrochemical data of Figures 3 and 4, from which we saw that reduction of the nitro group takes place at potentials more positive than *E*<sub>fb</sub>, and as anticipated (vide supra), occurs under normal photocatalytic conditions. On the other hand, it also appears that reduction of the CHO group to give H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OH ( $\lambda_{max}$ =243 nm) does take place, and is a comparatively much slower process.

Figure 6 (top) shows the formation of  $H_2NC_6H_4CHO$  from  $O_2NC_6H_4CHO$  quantitatively as a function of time. Under our



**Figure 5.** Spectral changes obtained upon irradiation ( $\lambda > 350$  nm, 25  $\pm$  1 °C) of deaerated suspensions of TiO<sub>2</sub>-P25 (3.5 gL<sup>-1</sup>) in a 2-propanol/acetonitrile mixture (1:4, v/v) containing O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO (7.8 × 10<sup>-5</sup> M).



**Figure 6.** Time courses of the amounts of  $O_2NC_6H_4CHO$  ( $\bullet$ ),  $H_2NC_6H_4CHO$  ( $\bullet$ ), and  $H_2NC_6H_4CH_2OH$  ( $\bullet$ ) during irradiation ( $\lambda > 350$  nm,  $25 \pm 1$  °C) of TiO\_2-P25 (3.5 g L<sup>-1</sup>) suspended in a 2-propanol/acetonitrile mixture (1:4, v/v). Initial concentration of  $O_2NC_6H_4CHO$ :  $7.8 \times 10^{-5}$  m. Top: first 90 s; Bottom: up to 3000 s.

experimental conditions, the nitro compound is consumed almost completely after photoexcitation for 50 s. The decay curve of  $O_2NC_6H_4CHO$  is characteristic of first-order kinetics, and the corresponding apparent rate constant is 0.059 s<sup>-1</sup>. At the same time, the only photoreduction product is accumulated in the liquid phase in more than 90% yield.

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These relatively high kinetics seem to imply an interaction of the substrate with the surface. FTIR measurements confirm that  $O_2NC_6H_4CHO$  interacts with the surface through the  $NO_2$  group, as evidenced from the shift of the asymmetric vibration frequency of the N–O bond from 1541 to 1529 cm<sup>-1</sup>, in accordance with previous data on nitrobenzene adsorption on TiO<sub>2</sub>.<sup>[29]</sup>

The plot shown in Figure 6 (bottom) indicates that the amount of  $H_2NC_6H_4CHO$  reaches a maximum value corresponding to 90% conversion of the starting compound; it is then reduced slowly to produce  $H_2NC_6H_4CH_2OH$ . The apparent first-order rate constant for the disappearance of  $H_2NC_6H_4CHO$  is 0.001 s<sup>-1</sup>, and the conversion yield to the alcohol is higher than 80% with respect to the starting nitro compound after 50 min photoexcitation.

On the basis of the electrochemical data of the previous section, the reduction of the aldehyde group occurs only if electrons can accumulate. This accumulation can take place after the complete transformation of the nitro group (cf. Figure 4), that is,  $H_2NC_6H_4CH_2OH$  formation is observed only after  $O_2NC_6H_4CHO$  has been converted completely to  $H_2NC_6H_4CHO$ .

It has been reported previously that photocatalytic reduction of nitrobenzenes at TiO<sub>2</sub> occurs even under aerobic conditions.<sup>[16f]</sup> On this basis, and in line with the above statements, O<sub>2</sub> can possibly be used as a competitive electron scavenger to prevent charge accumulation on the semiconductor surface, and consequently, to control the selectivity of the photocatalytic process. Indeed, if the photocatalytic experiment is carried out under aerobic conditions, O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO reduction does not proceed beyond H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO, which can be accumulated in the liquid phase in more than 90% yield (Figure 7). The apparent rate constant of O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO reduction decreases to 0.027 s<sup>-1</sup> because of the electron-scavenging ability of O<sub>2</sub>.

In the overall photocatalytic process, 2-propanol can work as a hole scavenger that can limit charge recombination, free a large number of reductive equivalents, and act as a source of



**Figure 7.** Time courses of the amounts of  $O_2NC_6H_4CHO$  (•) and  $H_2NC_6H_4CHO$ (•) during irradiation ( $\lambda > 350$  nm, 25 ± 1 °C) of aerated suspensions of TiO<sub>2</sub>-P25 (3.5 g L<sup>-1</sup>) in a 2-propanol/acetonitrile mixture (1:4, v/v). Initial concentration of  $O_2NC_6H_4CHO$ : 7.8 × 10<sup>-5</sup> M.

protons. Pathways involving holes generally entail the formation of radicals that may, in turn, play an important role as reducing species in the overall photocatalytic process. Reasoning that the nature of radical intermediates is also important for the formulation of a reaction mechanism, we performed EPR measurements using the spin-trapping technique, which is a particularly potent tool for the detection of short-lived radical species.<sup>[30]</sup>

Irradiation of powder dispersions of TiO<sub>2</sub>-P25 suspended in a deaerated 2-propanol/CH<sub>3</sub>CN mixture containing O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO and the spin trap  $\alpha$ -phenyl *N*-tert-butyl nitrone (PBN) leads to the detection of a triplet of doublets with hyperfine splitting constants  $a_N = 13.9$  G and  $a_H = 2.2$  G, which can be attributed to the paramagnetic adduct [PBN-(CH<sub>3</sub>)<sub>2</sub>CHO]<sup>•</sup> (Figure 8).<sup>[31]</sup> Then, the signal is derived from the



**Figure 8.** EPR spin-trapping spectra obtained upon irradiation (10 s,  $\lambda > 350$  nm) of TiO<sub>2</sub>-P25 suspended in deaerated 2-propanol/CH<sub>3</sub>CN (1:4, v/v) solutions containing PBN (5×10<sup>-2</sup> M) and O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO (1×10<sup>-4</sup> M).

trapping of isopropoxy radicals ( $CH_3$ )<sub>2</sub>CHO<sup>•</sup>, formed by the reaction of adsorbed 2-propanol with photogenerated holes as shown by Eqs. (2) and (3).

$$(CH_3)_2 CHOH_{ads} + h^+ \rightarrow (CH_3)_2 CH - O^{\bullet} + H^+$$
(2)

$$\begin{array}{c} \begin{array}{c} \begin{array}{c} H & O^{\bullet} \\ -C = \stackrel{\bullet}{N} - C(CH_3)_3 \end{array} + (CH_3)_2 CHO^{\bullet} & \longrightarrow & \begin{array}{c} H & O^{\bullet} \\ -C = \stackrel{\bullet}{N} - C(CH_3)_3 \end{array} \end{array}$$
(3)

The oxidation potential is a measure of the reducing power of radicals. In the case of 2-propanol, to the best of our knowledge, the oxidation potential of alkoxy radicals has not been reported. That of hydroxyalkyl radicals  $(CH_3)_2C^{\circ}OH$  in  $CH_3CN/2$ propanol falls in the range -0.61 to -1.0 V versus SCE.<sup>[32]</sup> Even assuming that the oxidation potential of  $(CH_3)_2CHO^{\circ}$  radicals is more negative, it is very unlikely that the difference is as much as 1 V. From this reasoning, we infer that detected  $(CH_3)_2CHO^{\circ}$ radicals may only be able to inject electrons into deeper intrabandgap surface states, and not directly into the conduction band. The photoreduction of the nitro group to an amino

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Figure 9. Schematic energy diagrams illustrating the reduction of  $O_2NC_6H_4CHO$  through surface states (– $NO_2$  group) or through accumulated electrons (–CHO group).

group is not a limiting factor, because trapped electrons are able to reduce  $O_2NC_6H_4CHO$ , as discussed earlier. Figure 9 is an illustrative scheme that summarizes the findings in an energy scale before and after electron accumulation.

For prospective applications in synthetic photocatalysis, it is noteworthy that the photocatalyst is completely recyclable after washing, drying in an oven, and calcination at 400 °C for 6 h. The absence of oxygen probably prevents the formation of carboxylates that are able to poison the surface of the semiconductor in aerated conditions.<sup>[33]</sup> In addition, we have experimental evidence that for initial concentrations of  $O_2NC_6H_4CHO$ as high as  $10^{-2}$  M, the process proceeds as described above, first accumulating  $H_2NC_6H_4CHO$ , and then yielding  $H_2NC_6H_4CH_2OH$  as the final reduction product. From a quantitative point of view, after a long irradiation time (about 20 h) the photocatalytic yield of  $H_2NC_6H_4CH_2OH$  is over 80%. This result is encouraging, and opens up new synthetic routes to be verified with the use of other substrates.

## Conclusion

We have examined the effect of the photoaccumulation of electrons on TiO<sub>2</sub> and its role within the context of the partial and total reduction of  $O_2NC_6H_4CHO$ , which was chosen as a model organic compound bearing two reducible functional groups. We have reported parallel investigations on TiO<sub>2</sub> electrodes and suspensions; the results are in agreement, and show that partial reduction to  $H_2NC_6H_4CHO$  is probably mediated by intra-bandgap states, and must be nearly complete before the reduction of the aldehyde group occurs, affording  $H_2NC_6H_4CH_2OH$ . The latter process occurs at potentials more negative than the flatband potential, and then requires an electron accumulation regime.

We have demonstrated that control of the photogenerated charge is a suitable means for selective reduction of a model organic molecule, and we think that this is an interesting issue of direct concern for studies on the selectivity of photocatalytic processes. It is well known that selective reduction through the use of chemical species is quite difficult to achieve. On the other hand, experimental conditions that favor electron accumulation allow operation on molecules that are difficult to reduce, which is also an important aspect. Future work will consider the reduction of various structurally different multifunctional organic species.

## **Experimental Section**

 $TiO_2$  Degussa P25 ( $TiO_2$ -P25) was used throughout this work, because this commercial photocatalyst is well characterized and has become a benchmark for comparative photocatalytic studies. Solvents and reagents were purchased from Sigma and used without further purification.

Titanium dioxide electrodes were prepared by spreading, on a titanium foil, a paste obtained by mixing TiO<sub>2</sub> (Degussa P-25, 3 g), bidistilled water (6 mL), acetylacetone (0.2 mL), and Triton X-100 (0.2 mL), with subsequent calcination at 450 °C for 30 min. The electrodes had a geometric area of 1.3 cm<sup>2</sup>.

Cyclic voltammetry curves were obtained with an EG&G potentiostat using EG&G software. All measurements were made in deaerated CH<sub>3</sub>CN or 2-propanol/CH<sub>3</sub>CN (1:4 v/v) using *tetra*-ethylammonium perchlorate (TEAP, 0.2 M) as supporting electrolyte. A conventional three-compartment glass cell was employed, in which the working electrode was a Ti/TiO<sub>2</sub> electrode (or Au sheet in some experiments). O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO or H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO were added as necessary for the experiments. 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 cycling voltammograms of ferrocene as an internal standard. All potentials are given versus SCE.

Mott–Schottky analysis was performed by cyclic voltammetry using the relationship  $C = i/\nu$ , in which  $\nu$  is the scan rate (100 mV s<sup>-1</sup>). Experiments were performed in the potential range 0.0 to 1.0 V, in which pure capacitive behavior is observed.

Infrared spectra were obtained with a Nicolet 510P FTIR instrument in KBr, fitted with a Spectra-Tech collector diffuse reflectance accessory (range 4000 to 200 cm<sup>-1</sup>). The sample was prepared using an aliquot of TiO<sub>2</sub>-P25, which was put in contact with a CH<sub>3</sub>CN solution of O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO (1×10<sup>-4</sup> M). The suspension was stirred at room temperature until the evaporation of the solvent was complete. Then the powder impregnated with 4-nitrobenzaldehyde was dried overnight in an oven.

In a typical photocatalytic experiment, TiO<sub>2</sub>-P25 (3.5 gL<sup>-1</sup>) was suspended in a mixture of 2-propanol and acetonitrile (1:4, v/v) containing  $O_2NC_6H_4CHO$  (7.8×10<sup>-5</sup> м). Then, the suspension was purged with nitrogen for 20 min and subsequently irradiated at wavelengths above 350 nm (25±1°C, 15 mW cm<sup>-2</sup>). 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  $H_2NC_6H_4CHO$  and  $H_2NC_6H_4CH_2OH$  was calculated from the absorbance increases at 312 and 243 nm, respectively.

We also verified that direct light absorption by  $O_2NC_6H_4CHO$  was negligible under the experimental conditions employed ( $\lambda > 350$  nm) and that no reaction occurred when photoexcitation was carried out in the absence of the semiconductor. Other control experiments indicated that no reduction products were formed when the solution of  $O_2NC_6H_4CHO$  was kept in contact with the semiconductor in the dark. The optimal amount of TiO\_2-P25 (3.5 gL<sup>-1</sup>) used throughout this work was chosen on the basis of

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measurements performed with a radiometer, which indicated that this amount of semiconductor was able to absorb more than 90% of the impinging radiation.

For recycling experiments, TiO<sub>2</sub>-P25 used in a first photocatalytic experiment was washed twice with aliquots of  $CH_3CN$  and then with  $CH_2CI_2$ . The photocatalyst was dried overnight in the oven, and then calcined for 6 h at 400 °C. After this treatment, it was reused in a second photocatalytic experiment, performed as described above.

EPR spin-trapping experiments were performed with a Bruker ER 200 MRD spectrometer equipped with a TE 201 resonator, at a microwave frequency of 9.4 GHz. The samples were constituted by deaerated suspensions of TiO<sub>2</sub>-P25 (20 mg) in 2-propanol/CH<sub>3</sub>CN (1:4, v/v) solution (1 mL) containing  $\alpha$ -phenyl N-*tert*-butyl nitrone (PBN,  $5 \times 10^{-2}$  M) as the spin trap and O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO ( $1 \times 10^{-4}$  M). The obtained samples were put into a flat quartz cell and irradiated ( $\lambda > 350$  nm) directly in the EPR cavity. Deaeration was carried out by fluxing N<sub>2</sub> and transferring the samples into the cell under a nitrogen-saturated atmosphere. Irradiations were performed with a Helios Q400 Italquartz medium-pressure Hg lamp using a cutoff filter ( $\lambda > 350$  nm). No signals were obtained in the dark or during irradiation of the solution in the absence of TiO<sub>2</sub>.

**Keywords:** electrochemistry · electron energetics photocatalysis · reduction · titanium dioxide

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Received: February 5, 2014 Revised: March 14, 2014 Published online on May 14, 2014