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Using photoelectrochemical measurements for distinguishing between direct and indirect hole transfer processes on anatase: Case of oxalic acid

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Abstract

Photocurrents collected from an interface between polycrystalline anatase and an aqueous solution of oxalic acid were measured as a function of oxalic acid concentration and photon flux at 365 nm. According to a kinetic model previously developed, such data can be used as a diagnostic tool for distinguishing between direct oxidation involving valence band holes and an indirect process, involving (surface bound) OH radicals. In the case of oxalic acid studied here, from the linear relation between initial slopes of photocurrent versus concentration and photon flux, a direct process is indicated.

Keywords: Titanium dioxide; Oxalic acid; Pollutant degradation; Reaction mechanism; Photocatalysis

1. Introduction

Heterogeneous photocatalysis has emerged as a viable technology for the degradation of pollutants in air and water. This process uses an n-type semiconducting oxide on which, under illumination, pollutants in solution are oxidized by photogenerated charge carriers. In spite of the attention devoted to this process, there are many fundamental aspects that are not fully clarified and require further studies. A detailed knowledge of the reaction mechanism of oxidation of different compounds is necessary for both designing photocatalysts and maximizing the efficiency of the process. One of the points still to be settled refers to the actual reactant that initially attacks the organic compound being oxidized. Most authors assume that the photogenerated holes are either captured by adsorbed hydroxyl ions/water, generating adsorbed OH radicals, or react with interfacial water generating free OH radicals [1–6]. However, there is concurrent experimental evidence supporting that the initial attack is done by direct reaction of the adsorbed organic substrate with mobile holes [5,7]. It is noteworthy that, lately, several reports supporting the direct oxidation mechanism have been published for different alcohols [8], trichloroethylene [9], oxalic and acetic acid [10], acetate [11], thiocyanate [12] and sulfite [13]. Recent kinetic studies for TiO_2-photoassisted oxidations take into account the existence of parallel direct and indirect hole transfer paths [11,12–20]. In summary, although this subject has been repeatedly considered, the nature of the interfacial hole transfer mechanism is still, in most cases, object of controversy, mainly due to the lack of experimental techniques able to give an unambiguous response.

On the other hand, the combination of photocatalytic and electrochemical techniques has proven to be useful not only from a practical viewpoint but also on fundamental grounds. On the practical side, immobilized photocatalysts have the advantage of avoiding the separation step after the purification process. In addition, when the photocatalysts are supported on an electrically conducting substrate, reverse bias can be applied (i.e. electrode potentials at which strong band bending prevails), as a way of reducing recombination of photogenerated charge carriers, thereby increasing the efficiency of electrode processes. In fact, several papers have recently appeared on electrochemically driven photocatalysis [21–26]. It is significant that in such an experimental variant the presence of an oxidant (commonly O_2)

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at the semiconductor surface is no longer required, as photogenerated conduction band electrons are driven away from the interface into the semiconductor electrode bulk. Different photoelectrochemical measurements may help to elucidate mechanistic details of the photocatalytic process. Photocurrent density (j_{ph}) versus potential (E) [27–35], j_{ph} versus time (t) [28,29,31,34,35], j_{ph} versus substrate concentration [29–31,33–35] and incident-photon-to-current efficiency (IPCE) versus photon flux (light intensity) measurements [29,33] have been used in order to acquire a better understanding of the photocatalytic behavior of TiO_2.

Recently, it was developed a model able to discriminate between direct and indirect interfacial hole transfer in the photooxidation of dissolved pollutants on the basis of photoelectrochemical measurements on dense TiO_2 electrodes for molecules leading to the so-called current doubling phenomenon [36]. The model is based on the fact that photooxidation of dissolved pollutants competes with that of the solvent (water molecules). The notion of competitive oxidation has already appeared in previous reports on photoelectrochemistry [37–39].

Yet this idea has not been taken into account in most of the kinetic studies concerning heterogeneous photocatalytic systems, with a few remarkable exceptions [20,40,41]. The model was, in a first report, applied to formic acid and methanol as candidates for direct and indirect hole transfer. In fact, the expected behavior was confirmed. The different photooxidation mechanism was attributed to the different interaction of the molecule with the semiconductor surface. It was suggested that the specific adsorption of the molecule to be oxidized would promote its direct photooxidation whereas for a weak interaction between the molecule and the semiconductor surface the indirect photooxidation would prevail. Very recently, by means of Raman spectroscopy, the specific adsorption of formic acid as an anion at the surface of TiO_2 was evidenced, whereas methanol did not seem to adsorb at the oxide surface [42]. This observation adds independent credit to the validity of the model.

Extending this research to other organic acids, we present here the case of oxalic acid at anatase electrodes. The oxidation of oxalic acid also occurs in a two-electron process, involving injection of a second electron into the conduction band of the semiconductor. The final product is CO_2, which can be conveniently measured [26]. Our interest in oxalic acid derives from the fact that it has been studied by a number of authors because it can be considered to be a model molecule for adsorption [43–45] and photocatalytic studies [46–48]. In addition, its facile photooxidation has prompted its use as a sacrificial hole scavenger in several photoelectrochemical processes [45,49–52]. In some of these studies, direct hole transfer is either assumed or suggested [44,45,47,48], while in others, direct and indirect pathways are considered to be simultaneous [51], or an OH radical mediated process is assumed to prevail [46].

2. Model

The model [36] for distinguishing between the two types of initial attack is based, as mentioned before, on photoelectrochemical measurements. Reverse bias is applied to the semiconductor electrode leading to a high band bending. This allows us to neglect the surface concentration of electrons and therefore, all the recombination reactions that can occur via surface trapped electrons.

In the case of oxalic acid photooxidation, the following reactions are considered to occur at the illuminated electrode:

$$\mathrm{TiO_2} \xrightarrow{h\nu} \mathrm{h_s^+} + \mathrm{e_s^-}, \quad v_0 = \eta\phi \tag{1}$$

$$\mathrm{OH_s^-} + \mathrm{h_s^+} \xrightarrow{v_1} \mathrm{OH_s}^{\bullet}, \quad v_1 = k_1[\mathrm{h_s^+}][\mathrm{OH_s^-}] \tag{2}$$

$$\mathrm{OH_s}^{\bullet} + \mathrm{OH_s}^{\bullet} \xrightarrow{v_2} (\mathrm{H_2O_2})_\mathrm{s}, \quad v_2 = k_2[\mathrm{OH_s}^{\bullet}]^2 \tag{3}$$

$$(\mathrm{H_2O_2})_\mathrm{s} + \mathrm{h_s^+} \xrightarrow{v_3} (\mathrm{HO_2}^{\bullet})_\mathrm{s} + \mathrm{H_{aq}^+}, \quad v_3 = k_3[\mathrm{h_s^+}][(\mathrm{H_2O_2})_\mathrm{s}] \tag{4}$$

$$(\mathrm{HO_2}^{\bullet})_\mathrm{s} + \mathrm{h_s^+} \xrightarrow{v_4} \mathrm{O_2} + \mathrm{H_{aq}^+}, \quad v_4 = k_4[\mathrm{h_s^+}][(\mathrm{HO_2}^{\bullet})_\mathrm{s}] \tag{5}$$

$$\mathrm{OH_s}^{\bullet} + \mathrm{HOx^-} \xrightarrow{v_5} \mathrm{CO_2} + \mathrm{CO_2}^{\bullet -} + \mathrm{H_2O}, \quad v_5 = k_5[\mathrm{OH_s}^{\bullet}][\mathrm{HOx^-}] \tag{6}$$

$$\mathrm{h_s^+} + \mathrm{Ox_s^{2-}} \xrightarrow{v_6} \mathrm{CO_2} + \mathrm{CO_2}^{\bullet -}, \quad v_6 = k_6[\mathrm{h_s^+}][\mathrm{Ox_s^{2-}}] \tag{7}$$

$$\mathrm{CO_2}^{\bullet -} \xrightarrow{v_7} \mathrm{CO_2} + \mathrm{e_s^-}, \quad v_7 = k_7[\mathrm{CO_2}^{\bullet -}] \tag{8}$$

In these equations, η and ϕ stand for the quantum yield of free carrier generation and the photon flux absorbed by the electrode, respectively. The quantum yield of charge separation is given by $(j/F)/(\eta\Phi)$, with j being the photocurrent that is actually measured. IPCE is proportional to this quantum yield. The subindex s denotes surface bound species and v_0–v_7 are the rates for the different reactions. HOx^- denotes HOOC–COO$^-$ and Ox^{2-} denotes $^-$OOC–COO$^-$.

The first reaction (Eq. (1)) describes the rate of charge carrier generation in the semiconductor, due to illumination. The holes, h_s^+, can either form surface bound OH radicals (Eq. (2)) (part of which are lost in a combination process (Eq. (3)) and the remaining part reacts with the solute (Eq. (6)) or react directly with adsorbed oxalic acid (Eq. (7)). In the latter case, we can speak of a direct oxidation process, and if the OH radicals are the oxidizing species we have an indirect process. Both processes may occur in parallel, but the experimental data (see below) shows that often one or the other process prevails. The reaction product of Eqs. (6) and (7) is a radical with low enough redox potential to afford electron injection into the conduction band of the semiconductor, thereby leading to additional current flow. Assuming a photostationary state (the concentration of all intermediates is considered to be constant), we can derive an explicit equation for the photocurrent in the plateau potential region: