QUANTSOL 2006 winter workshop. Rauris, Österreich, March 19-25, 2006

Photoelectrochemical measurements as a way to distinguish between direct and OH-mediated hole transfer from photoexcited semiconductor oxides and organic molecules in aqueous solution

T. Lana-Villarreal[1], D. Monllor-Satoca[1], R. Gómez[1], P. Salvador[1], G. Waldner[2],
M. Neumann-Spallart[3]

[1]Institut Universitari d'Electroquímica i Departament de Química Física, Universitat d'Alacant, Alacant, Spain.
[2]ARC-sr, Materials Research, Seibersdorf, A-2444 Austria
[3]Laboratoire de Physique des Solides et de Cristallogénèse, C.N.R.S., Meudon, France

Heterogeneous photocatalysis based on TiO_2 particles is one of the most promising advanced oxidation processes for environmental applications. However, there are still some fundamental aspects that are not fully clarified, as the reactant that initially attacks the dissolved pollutant molecules (hydroxyl radicals or holes). We present here a kinetic model for the analysis of photoelectrochemical results in order to distinguish between direct and indirect hole transfer from the semiconductor oxides to electron donors in solution.

The model is based on the idea that the photooxidation of the dissolved organics, RH_2, occurs in competition with the photooxidation of water[1]. The model assumes that surface recombination of photogenerated electron-hole pairs is inhibited; the quasi-steady state is considered to be achieved during photocurrent measurements, so that the surface concentration of the intermediate species is considered to be constant throughout the experiments. The model also considers the so-called "photocurrent multiplication" effect.

From the analysis of the dependence of the photocurrent intensity, j_{ph}, on the dissolved pollutant concentration, $\left[(RH_2)_{aq}\right]$ for different light intensities, Φ, we reach the conclusion that direct and indirect interfacial hole transfer mechanism can be distinguished. In fact, for direct hole transfer j_{ph} depends linearly on Φ, whereas for indirect hole transfer the linearity is lost. Moreover, for low enough values of $\left[(RH_2)_{aq}\right]$, $\frac{\partial j_{ph}}{\partial\left[(RH_2)_{aq}\right]}$ depends linearly on Φ for direct hole transfer and on $\Phi^{1/2}$ for indirect hole transfer.

The model has been applied to the photooxidation of methanol, formic and oxalic acid dissolved in water at acidic pH, using dense titanium dioxide (anatase) electrodes. Comparing the experimental results with the model, it can be deduced that the acids directly capture holes from the valence band while indirect hole transfer prevails in the case of methanol (Figure 1). Since the adsorption of RH_2 species seems to be a necessary condition for the direct hole transfer mechanism, it can be deduced that the interaction of formic and oxalic acid molecules with the TiO_2 surface is strong enough. By contrast, substances that interact weakly with the catalyst surface, as it is the case for methanol, are being mainly photooxidized indirectly, via surface-bound hydroxyl radicals. The different adsorbability of formic acid and methanol on anatase was evidenced by Raman measurements (Figure 2)[2].

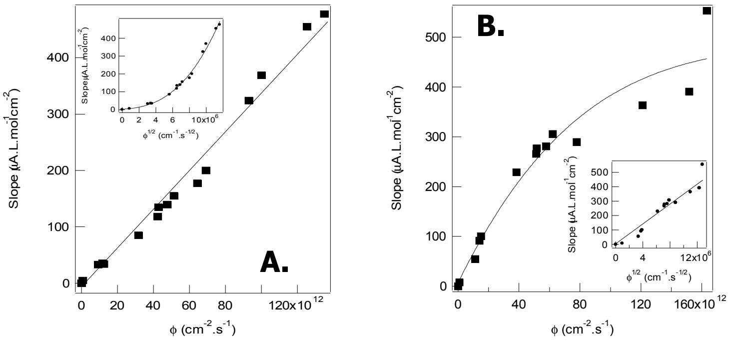

Figure 1. Plot of $(\partial j_{ph}/\partial[CH_3OH])$, for **A.** $[HCOOH]\rightarrow 0$, **B.** $[CH_3OH]\rightarrow 0$, as a function of Φ and $\Phi^{1/2}$. Data obtained under external polarization at 1.5 V (Ag/AgCl/KCl), for a polycrystalline TiO_2-anatase electrode in 0.5 M Na_2SO_4 at pH ≈ 3, as supporting electrolyte.

Finally, the model was applied to the photoxidation of formic acid on nanocrystalline WO_3 electrodes, yielding again a prevalent direct mechanism in keeping with anatase electrode results. The adsorption of formic acid at the surface of WO_3 was demonstrated by ATR-IR experiments[3].

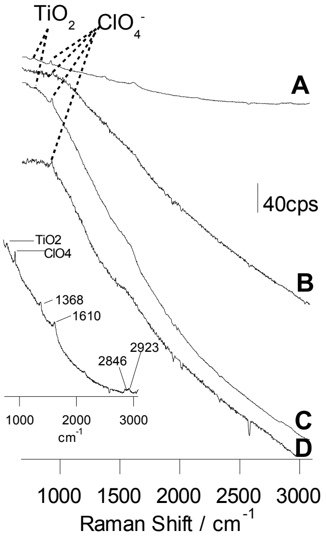

Figure 2. SERS spectra obtained at 0.6 V (SCE) for a gold electrode: **A.** covered with an anatase nanoparticle layer in presence of 1 mM HCOOH; **B.** in presence of 1 mM HCOOH; **C.** covered with an anatase nanoparticle layer in presence of 1.5 mM CH_3OH; **D.** in presence of 1.5 mM CH_3OH. The excitation line was provided by a 17 mW He-Ne laser with a 600 μm pinhole. Supporting electrolyte: $HClO_4$ 0.1 M. The inset shows curve A in a different scale.

The classification of the oxidation mechanisms at an illuminated semiconductor/ electrolyte junction into direct or indirect is useful in the evaluation of semiconductor oxide photocatalysts. In fact, the interfacial transfer of charge should be facilitated for the case of direct hole transfer mechanism, where specific adsorption is expected. Therefore, if a semiconductor surface featuring this behavior can be prepared, a high activity down to low enough pollutant concentrations can be expected, enabling photodegradation reactions to be pursued until concentrations are below maximal tolerable levels.

[1] T. Lana-Villarreal, R. Gómez, M. Neumann-Spallart, N. Alonso-Vante, P. Salvador, **J. Phys. Chem. B** 108, 2004, 15172.
[2] T. Lana-Villarreal, J.M. Pérez, R. Gómez, **C. R. Chimie**, in press.
[3] D. Monllor-Satoca, L. Borja, A. Rodes, R. Gómez, P. Salvador, under preparation.