Faradaic Efficiency of Photoelectrochemical Oxidation of Organic Compounds on n-type Oxide Semiconductor Electrodes
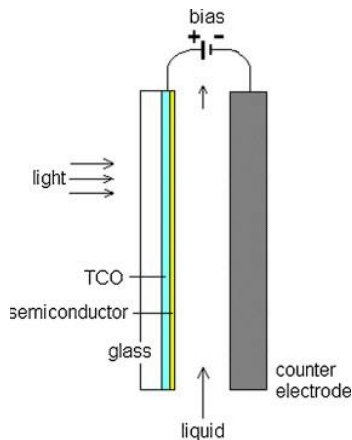
M. Neumann-Spallart, T. Imrich, M. Brada, J. Krýsa, Department of Inorganic Technology, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic.

The Faradaic efficiency of photoelectrochemical oxidation of aqueous solutions of organic compounds on various transition metal n-type semiconductor electrodes (WO_3, TiO_2, Fe_2O_3) as determined by coulometry at fixed potentials and chemical analysis is compared. The results show dependence mainly on semiconductor properties, in particular valence band energy positions of the tested semiconductors. Typically, values up to 13 % were obtained for 1 mM aqueous solutions.

Introduction

The degradation of organic pollutants stemming from industry, agriculture, households, sewage etc. is of great importance as it is directly linked to the quality of drinking water if mixing occurs. Following biological methods of purification, and electrocoagulation finally, advanced oxidation processes (AOP) can be envisaged for further purification towards drinking water purity. The basic idea is to run a purification process that does not produce byproducts and does not use chemicals at all. This is the case in electrochemical processes, such as electrooxidation on semiconductor electrodes, where the process is powered by (sun)light.

It turned out that in several cases, complete oxidation (mineralisation) of the organic impurities could be achieved, leading to the main end products CO_2 and water. An important consideration is that in the course of the process, next to the initially present compound(s) also intermediates which might be even more toxic than the initially present compounds are completely removed, i.e. to levels being specified by relevant controlling authorities.

The aim of the present comparison is to show how initial Faradaic degradation efficiencies originating from valence band charge carriers depend on the properties of several semiconductors often used in photoelectrocatalysis and photocatalysis.

Materials and Methods

In the studied cases (see references), photoelectrochemical measurements were carried out either in batch reactors and or in thin electrolyte film (1 mm) cells or at interdigitated printed electrodes. Potentiostatic control or fixed bias was used. Rapid stirring or recirculation was used for providing mass transport. The irradiation source is of no direct consequence for Faradaic efficiency measurements, as long as the irradiance is low enough to stay in control of the charge transfer process.

Results and Discussion

In semiconductor based photoelectrochemical reactions, the semiconductor absorbs light and produces positive and negative charge carriers:

$$semiconductor + h\nu \rightarrow e^- + h^+ \quad (1)$$
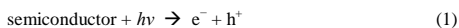
with e^- an electron in the conduction band and h^+ a hole in the valence band. Under electrical (reverse) bias, band bending occurs which precludes charge carrier recombination and withdraws electrons from the interface semiconductor / liquid electrolyte and directs them towards a counter electrode. Therefore, photoelectrochemical oxidation of solutes on n-type semiconductors occurs exclusively by valence band processes (originating from the action of holes). The efficiency of each of the electrochemical processes is the result of a competition between these reactions, namely oxidation of the solute (or of several solutes), and of the solvent itself (eq. 2) by photogenerated charge carriers (valence band holes, h^+) and/or their follow-up products (bound OH· radicals, hole traps).

$$2 h^+ + H_2O \rightarrow 2 H^+ + 1/2 O_2 \quad (2)$$
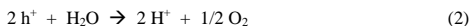
This reaction competes with the oxidative degradation of compound R (pollutant, eq. 3):

$$h^+ + R \rightarrow R^+ \quad (3)$$

As a measure of efficiency, the Faradaic efficiency, f, is representative of the rates of individual reactions to their sum by taking the ratio of partial electrical currents to the total current

$$f = F(dn/dt)/i \quad (4)$$

where F is the Faraday constant (96 485 C·mol^{-1}), n is the number of consumed or formed moles of the respective compound, and i is the photocurrent at time t in the course of the experiment. The individual rates (partial currents) depend on the concentration of the respective species.

We therefore compare here the efficiency of this competition for the initial oxidation step, involving only the parent compound – the initial Faradaic efficiency which gives information about the first step (charge transfer) in oxidizing a compound. Typical transition metal n-type semiconductor electrodes are used in the

comparison, known for their "oxidative power", i.e. the ability to deliver species of high redox potential under illumination, like WO_3 and TiO_2 (used a lot in photocatalysis), and Fe_2O_3 which is of interest due to its ability to absorb greater parts of the solar spectrum. The organic compounds selected in this comparison are typical aromatic compounds, used as model substances, or compounds that are often encountered in the environment like bisphenol A (precursor for plastics), ethylparaben (growth inhibitor), terephthalic acid (chemical synthesis), monuron (a herbicide), the azo-dye acid orange 7 (AO7), coumarin (precursor for pharmaceuticals).

The comparison shows that the efficiency mainly depends on semiconductor properties, in particular the energy of their valence bands (redox potential). Typically, values up to 13 % were obtained for 1 mM aqueous solutions. WO_3 and TiO_2 reach comparable values for most tested substances, whereas on Fe_2O_3 with a much less positive valence band, benzoic acid and 4-CP are showing much lower values than on WO_3 and TiO_2. An untypical case is AO7. It can very easily be oxidized on TiO_2, probably due to the ease of attacking the azo bond and due to the specific adsorption of the protonated dye [2]. As the initial Faradaic efficiency depends on concentration, the result for 0.1 mM is about a factor of 10 lower than for the other cases. Another exception of this case study is the monitoring of an oxidation product (hydroxycoumarin) which seems to be the product initially formed by the addition of OH. The same is thought to happen in the oxidation of benzoic acid and salicylic acid. In the case of oxidation of benzoic on WO_3, salicylic acid has indeed been found by HPLC [4] and in the case of photoelectrochemical oxidation of benzoic acid, hydroxybenzoic was identified by fluorescence [6].

Table 1. Initial Faradaic efficiency (*f*, in percent) of photoelectrochemical oxidation (removal of organic compounds, 1 mM aqueous solutions) on different transition metal n-type semiconductor electrodes.

	pH	WO_3	TiO_2	Fe_2O_3	ref.
benzoic acid	1	13.1			4
	1.7		6.7	0.1	2,3
	4	12.2			4
salicylic acid	1.7		6.1	6.2	2,3
phthalic acid	1.7	1.4		2	
ethylparaben	1.7		9.7		2
bisphenol A	1.7	1.3		2	
4-CP	1.7		5.9	0.7	2,3
monuron	1	7.2			4
	4	7.5			4
AO7	1.7	32.6	30.0	7.5	2,2,3
	7.2			1.7	3
	13			1.7	3
coumarin 0.1 mM*	1.7		0.6		5

*f calculated from the product generation rate of hydroxycoumarin through fluorescence

Conclusions

Initial Faradaic efficiencies of photoelectrochemical oxidation of aqueous solutions (1 mM) of organic compounds on various n-type oxide semiconductor electrodes are compared. The processes were run under applied electrical bias, such that only valence band processes were measured. The results show dependence mainly on semiconductor properties, in particular valence band energy positions of the tested semiconductors. Typically, values up to 13 % were obtained.

References

[1] S.B. Sadale and M. Neumann-Spallart, *Mater. Res. Bull.,* 43 (2008) 1472.

[2] M. Neumann-Spallart, S.S. Shinde, M. Mahadik, C.H. Bhosale, *Electrochim. Acta*, 111 (2013) 830.

[3] T. Imrich, M. Neumann-Spallart, J. Krýsa, *Photochem. Photobiol. Sci.*, 22 (2023) 419.

[4] M. Brada, J. Rusek, T. Imrich, M. Neumann-Spallart, J. Krýsa, *J. Photochem. and Photobiol. A: Chemistry*, in press.

[5] P. Dzik, M. Veselý, M. Pachovská, M. Neumann-Spallart, *Environ. Sci. Pollut. Res.*, 24 (2017) 12547.

[6] P. Dzik, M. Veselý, M. Blašková M. Králová, M. Neumann-Spallart, *J. Appl. Electrochem.*, 45 (2015) 1265.