

Photoelectrochemical photocurrent switching: from basic theory to semi-practical applications

Konrad Szacilowski and Wojciech Macyk

Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Kraków, Poland

e-mails: szacilow@chemia.uj.edu.pl, macyk@chemia.uj.edu.pl

Surface-modified nanocrystalline semiconductors have found numerous applications as (photo)catalysts,¹ chemosensors and biomimetic light-harvesting antennae.²⁻⁴ Recently systems containing molecular switches attached to the surface of titania were described.⁵ Up to date there are no detailed reports on photocurrent switching phenomena for cyanoferrate-modified titanium dioxide. The increasing interest in molecular electronics stimulated the research on switching properties of some semiconductor composite materials.

This presentation concerns the photoelectrochemical properties of multicomponent photoelectrodes based on nanocrystalline titanium dioxide modified with various penta- and hexacyanoferrate complexes. All the modifying complexes are redox-active and undergo reversible one-electron redox processes. They are easily bound to the surface of titanium dioxide via cyanide bridges. Chemisorption of cyanoferrates(II) on TiO₂ surface results in formation of new MMCT absorption bands extending in the visible range of the electromagnetic spectrum.

Irradiation of photoelectrodes comprising of surface-modified titania results in generation of photocurrent which direction depends in a complex way on electrode potential, incident light wavelength and presence of electron acceptors in solution. The mechanism of switching process is described in terms of surface states involving cyanoferrate moieties. It takes also into account electrostatic interactions of surface complexes with electrons inside the semiconductor crystal resulting in formation of accumulation, depletion and inversion layers depending on the oxidation state (and hence the charge) of the complex deposited on the surface.

This new effect called *PEPS* (*Photo**E**lectrochemical* *Photo**c**urrent* *Sw**i**ching*) opens a possibility for construction of new light-harvesting antennae, chemical switches, sensors, logic gates and other optoelectronic devices. Boolean logic analysis and a tentative mechanism of the device are presented.

Not only the direction, but also the kinetic features of photocurrent generated upon pulsed irradiation strongly depend on photoelectrode potential and incident light wavelength.

In order to understand this behaviour the ITO-TiO₂-electrolyte junction was modelled using a circuit of three RC loops and a resistor connected in series. These loops correspond to the ITO-TiO₂ junction, TiO₂ particle and particle-electrolyte junction, respectively. The resistors marked R_e and R_e' stand for the resistance of the electrolyte solution: R_e is the resistance of the bulk electrolyte, while R_e' is the resistance of the electrolyte permeating the porous electrode. R_{ITO} is the resistance of ITO electrode.

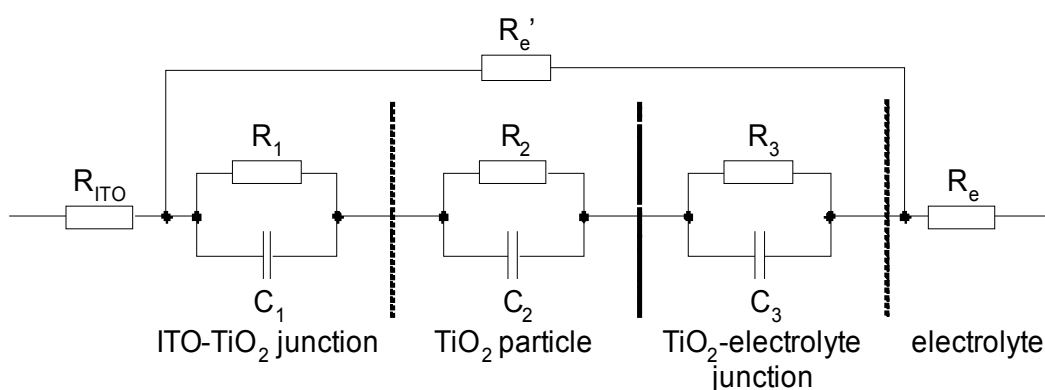


Fig. 1. Simple model for ITO-TiO₂-electrolyte junction.

This simple model (Fig. 1) can easily mimic all the kinetic features of recorded photocurrent when the RC constant of one loop is varied with respect to other loops.

The effect presented here may serve as a platform for construction of switches and various logic devices. Complex photoelectrochemical response to optical and electrical stimulation can be easily described in terms of Boolean logic. The cathodic and anodic photocurrents may represent opposite logic values of TRUE (1) and FALSE (0).^{6,7} Photocurrent switching upon stimulation results in an answer being a Boolean function of input parameters. Facile redox tuning of the semiconductor surface makes the system very flexible with respect to the range of applied potentials and photon energies, which can be also applied in various chemosensors.

References

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