Employment of photosensitized TiO_2 in photoelectrochemical energetic sources

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Abstract: *The combination of photoactivity and semiconductivity of TiO_2-solids is an important factor to find application in entire new generations of light-induced electrochemical devices, able to produce electricity or/and "green" combustibles, such as hydrogen. The present paper is an attempt to describe the possibilities to apply TiO_2 films or particles in Dye Sensitized Solar Cells and in Water Spitting Electrolysers.*

Key words: *TiO_2, Solar Cells, Water Splitting Electrolysers*

INTRODUCTION

Titanium oxide is widely used as a photocatalyst, because of its ability to raise the energetic content of the respective substrates, when illuminated by UV-light. In other words, this substance converts the light energy into activation energy (E_a) for creation of intermediated complexes with the substrates, thus catalysing the overall chemical process [1]. Except for a photocatalyst, titanium oxide encounters application in the photo-disinfection process, as described in ref. [2]. In addition, its photocatalytic activity could be further enhanced via modification by involvement of transition metal ions [3 - 7], noble metals [8, 9] or by other doping agents [10 - 12]. The band of TiO_2 photo-activity could be extended to the visible range by impregnation of various dyes [13 - 15]. The combination of photo-activity with semiconductive properties appears to be the most interesting feature of titanium oxide. This feature enables us to apply TiO_2 in the production of photoelectrodes [16 - 20]. Namely, this conjunction of properties, showed by titanate composed solids, is the reason to employ them in light induced electrochemical elements, intended for energy generation.

The aim of the present paper is to present a brief description of the basic photoelectrochemical devices with TiO_2 layers: Dye Sensitized Solar Cells (DSSC) and Water Splitting Electrolysers (WSE).

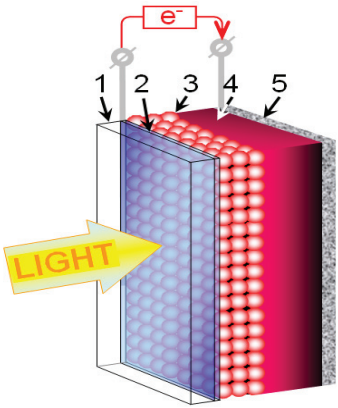

Figure. 1. Schematic view of DSSC
1- Frontal glass; 2 – Transparent conductive layer; 3 – Photosensitized TiO_2 layer; 4 – Electrochemically active substance; 5 – Pt–counter electrode

DYE SENSITIZED SOLAR CELLS

DSSC represent entire class of light induced electrochemical elements, able to generate electrical energy, due to photoelectrochemical reactions. As all electrochemical cells, they include electrochemical reduction/oxidation processes on the electrode surfaces, coupled by charge transfer of ions, as charge carriers between the electrodes, (i.e. in bulk of the electrolyte). The photoelectrochemical devices require excitation by photons, in order to convert the chemical energy to electrical current or vice-versa. Fig.1 shows a schematic view of typical DSSC. The principle of work of DSSC is described by Grätzel [21, 22] and will be not object of discussion in the present paper. However, it should be mentioned that the role of the dye-sensitized TiO_2 is to expulse electrons from the valence to the conduction band in the transparent semiconductor layer. This expulsion is possible only after absorption of photons (i.e. light energy). Thus, the DSSC elements could produce electric power, only when they are illuminated and because of their abilities to be used as sensors or detectors in UV/Vis spectrophotometers and other analytical equipment. Nevertheless, taking in account that in numerous articles [23 - 25] the

photocatalytic ability of TiO_2 is evaluated, namely by the rate of dye decomposition, it could be assumed that not every dye is appropriate to be used in DSSC. The respective dyes should be robust and durable in order to resist the presence of TiO_2 in their surrounding. As mentioned above, their function in the DSSC is to act as *photosensitizers*. According to Stacow et.al. [26], this group of compounds could be considered as substances, generally with organic origin, able to transmit the light energy, absorbed by them, to the neighbouring molecules. Thus, in DSSC, the photosensitized TiO_2 layers serve to activate the transparent semiconductor, in order to absorb the light energy. Usually transparent inorganic semiconductive films are: cadmium oxide [27], copper-indium-gallium-selenium (CIGS) [28] and others [29, 30].

Among the most durable and reliable photosensitisers the tetrapyrole derivatives, such as: porphyrines, chlorines, phatlocyanines and naphtalocyanines are known. Furthermore, these compounds enable formation of metal complexes, where the metallic moiety could predetermine the optical properties of the respective metal-organic complex [31]. Consequently, the properties of the respective metal-organic photosensitizer could be rather easily modified by involvement of ions of different metals. Another advantage of these classes of substances is their tremendous thermal and chemical durability, resulting in their compatibility with the TiO_2-composed solids, (i.e. nano-particles, films, etc.). Additionally, in the same book, these compounds are described as generally non-toxic and environmentally friendly substances. Indeed, the most famous presenters of these classes of compounds are the chlorophyll in the algae and plants and the haemoglobin in the human and animal's blood [32]. Generally, the tetrapyrrole-based dyes have various applications, for instance: photodynamic therapy of cancer diseases, bleaching of textile and paper, purification of air, or water disinfection, as is mentioned elsewhere [33].

At last, the efficiency of photosensitized TiO_2 electrodes could be significantly enhanced via immobilisation of a photosensitizer, preliminary impregnated by various metal ions. The posterior immobilization could be performed either by direct adsorption into a porous TiO_2 structure, or by covalent binding to other ingredients of a composite photosensitized TiO_2 containing photoelectrode. In this context, chitosan membranes, photosensitized by Zn-phtalocyanine for volatile organic contaminants decomposition, are proposed by Kozhukharov at.el. [34]. Similar photosensitized membranes are proposed [35, 36] for water disinfection, as well. Various aspects of extraction, purification and application of chitosan are described in the works of Zvezdova at.el. [37 – 39].

Finally, could be concluded that there are large possibilities for elaboration of entire technologies for efficient, durable and environmentally friendly photoelectrodes. Alternative approach of the employment of dye sensitised photoelectrodes is their application in water splitting electrolysers, as discussed below.

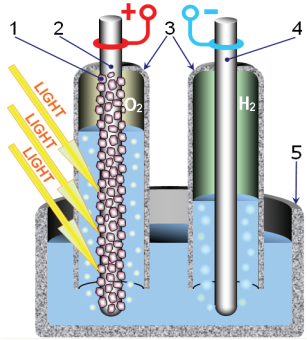

Figure. 2. Schematic view of WSE
1- Photosensitized TiO_2 particles;
2 – Photoanode; 3 –Gasholders;
4 – Pt. Cathode 5 – Water

WATER SPLITTING ELECTROLYSERS

These devices render another opportunity for application of photosensitized TiO_2 electrodes. Contrary to the DSSC elements, the water splitting electrolysers (WSE) using photoelectrode in a cell to produce hydrogen and oxygen. The first water electrolysers were invented during the XIX century [40]. However, the classical electrolysers were not reliable for practical applications, due to the remarkable expense of electrical energy. Recently, this inconvenience was overcome, by use of photoelectrodes, allowing decrease of electric energy expense, by substituting it by photoenergy. This approach has led to a significant improvement of the usability of the electrolysers, making them suitable for industrial and house-hold applications. Fig. 2 illustrates a possible

construction of a WSE- electrolyser. As in a typical photoelectrochemical device, the entire process of water splitting is composed by: a *reduction* process of the water molecules to H_2 on the cathode side; photoactivated *oxidation* process of water to O_2, on the anode side, and *ion-transfer* between the electrodes (in the water container). Although the electrode for production of H_2 is not photosensitised, the entire electrochemical process should pass with reduced expenditure of electric power, because the H_2O- oxidation is favoured by light energy. The efficiency of hydrogen and oxygen generation by water splitting process using photovoltaic electrolyses is well described in ref. [41].

Finally, we should underline the use of titanium dioxide based solids, are applicable for other kinds of alternative electrochemical energy sources, e.g. SOFC application [42] or in other photoelectrochemical devices [43], and has RTD potential for the future.

CONCLUSIONS

The literature review extracted for the present paper reveals the great potentials for application of photosensitized TiO_2–based solids for the elaboration of highly efficient, durable, and environmentally friendly photoelectrodes.

Among the dyes available, the tetrapyrroles are the most appropriate for photoapplication, because of their extremal strength and durability. These features prevent the undesirable dye-photodecomposition, promoted by the presence of TiO_2 – solids.

The optimisation of TiO_2-simultaneous presence of several metal-tetrapyrrolic complexes or/and by enlarging of active surface porosity of TiO_2 supports enables to extend drastically the efficiency of the respective photo-electrochemical devices.

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