



Surface photovoltage measurements: A quick assessment of the photocatalytic activity?

S.W. Verbruggen^{a,b,*}, J.J.J. Dirckx^c, J.A. Martens^b, S. Lenaerts^a

^a Sustainable Energy and Air Purification, Department of Bioscience Engineering, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium

^b Center for Surface Science and Catalysis, Department of Microbial and Molecular Systems (M²S), Catholic University of Leuven, Kasteelpark Arenberg 23, 3001 Heverlee, Belgium

^c The Laboratory of BioMedical Physics (BIMEF), Department of Physics, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium

ARTICLE INFO

Article history:

Received 25 June 2012

Received in revised form 3 September 2012

Accepted 20 November 2012

Available online 16 January 2013

Keywords:

Surface photovoltage

Photocatalysis

Titanium dioxide

Silver

Methylene blue

Acetaldehyde

ABSTRACT

Surface photovoltage (SPV) measurements can contribute to a better understanding of electronic properties of photocatalysts under illumination. Direct linking of SPV data to the actual photocatalytic activity remains troublesome. This work aims to discuss SPV measurements from a photocatalytic point of view. By means of several application-based scenarios we illustrate that the trend between SPV and photocatalysis strongly depends on parameters such as the crystal structure, surface modifications, morphology and humidity. This makes the interpretation far from straightforward.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Surface photovoltage (SPV) measurement is a well-established contactless technique for the characterization of semiconductors, including photocatalysts, based on monitoring the changes in surface voltage before and during illumination. Several excellent review articles have been published on the physical and electrochemical fundamentals [1,2]. The electronic band structure of n-type semiconductors such as TiO₂ is characterized by upward band bending at the semiconductor–conductor interface, leading to a Schottky-type barrier. Surface-localized electronic states induce charge transfer between the bulk and the surface of the semiconductor in order to establish thermodynamic equilibrium. This charge transfer results in a non-neutral surface space charge region (SCR) near the surface [3]. This in turn results in a built-in electric field, V_s , commonly referred to as the surface potential barrier. When the photocatalyst is irradiated by light with a photon energy content greater than the bandgap, free charge carriers are generated by band-to-band transitions induced by the incident photons. Trap-to-band transitions are also possible, but since these are related to photons with a lower energy than the bandgap,

their effect becomes negligible and will therefore not be considered here [4]. The generated charge carriers will redistribute within the surface and/or the bulk as a result of the built-in electric field. Hence, the surface potential barrier will be altered after illumination. Exactly this difference between the surface potential barrier in dark (V_s) and the one under illumination (V_s'), is defined as the SPV signal (Fig. 1) and is used to characterize the photocatalyst. SPV spectroscopy could be further expanded to electric field induced SPV spectroscopy (EFISPS). In EFISPS an external electric field directly affects the response intensity of the SPV signal and the photovoltaic characteristics [5].

Using SPV measurements, information can be obtained concerning the (photo)electronic properties of semiconductors, such as the band bending, surface and bulk carrier recombination, type of defect states and magnitude of the bandgap [6–8]. One of the most interesting features of the SPV technique is that it is directly applicable to powders and therefore appears to be a valuable tool in mechanistic photocatalytic studies. It would indeed be wonderful to have a very fast, easy-to-use technique available that does not require tedious sample preparations and can be employed for assessing the photocatalytic potential of a great number of photocatalyst powders, without time-consuming catalytic experiments. Comparable information could also be acquired by means of electrochemical photocurrent measurements, in which the photocatalyst has to be attached to an electrode and is then immersed in an electrolyte solution [9,10]. However, by circumventing the necessity to fixate the catalyst to an electrode and excluding the

* Corresponding author at: Sustainable Energy and Air Purification, Department of Bioscience Engineering, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium. Tel.: +32 3 265 35 17; fax: +32 3 265 32 25.

E-mail address: Sammy.Verbruggen@ua.ac.be (S.W. Verbruggen).

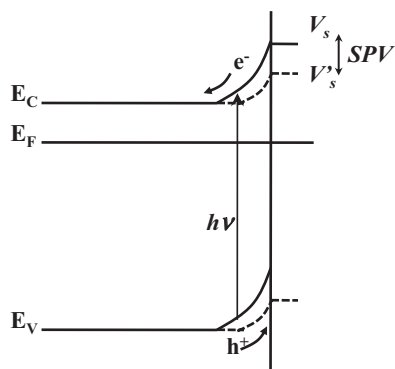


Fig. 1. Scheme on the origin of the SPV signal. The change in band bending is represented by dashed lines. The redistribution of generated charges is indicated with the arrows.

presence (and the influence) of the electrolyte, SPV measurements present a very attractive alternative.

The objective of this work is to discuss the concept of SPV measurements from a photocatalytic point of view. The thus far reported trends in literature indicate that directly relating SPV results to actual photocatalytic activity is not unambiguous [3,6,11–13]. Several situations where care should be taken when interpreting SPV measurements with regard to photocatalytic activity are discussed. It has to be stressed that in this work it was not the intention to use SPV for a detailed study of the (photo)electronic properties of photocatalysts, but rather to apply SPV as a simple, quick screening method for assessing photocatalytic performance. We show that photocatalytic activity is not merely predictable based on (photo)electronic properties as measured by SPV, but is also strongly influenced by the catalyst crystal phase composition, type of catalyst modification, morphology and general reaction conditions (type of fluid phase and the catalyst humidity).

2. Materials and methods

2.1. Sample preparation

For all tests in this work, TiO₂ P90 (Evonik) was selected as the reference material. It consists predominantly of crystalline anatase particles and a small fraction of rutile (~10%). Therefore, it has proven to be an excellent starting material for further modifications such as the introduction of higher rutile content or the deposition of silver particles on the surface. P90 also offered a good basis for comparative experiments with other (commercial) photocatalysts with different material characteristics. The other commercial photocatalysts used in this work were P25 (Evonik) and PC500 (Cristal Global). Both were used as received.

2.1.1. TiO₂ with variable rutile content

In order to obtain TiO₂ samples with different anatase/rutile ratios, commercial P90 (Evonik) was used as such or calcined at 450 °C, 525 °C, 600 °C, 675 °C, 750 °C or 900 °C for 3 h. The precise rutile content was calculated based on the XRD crystal spectra of the resulting powders. The weight fraction of rutile was calculated using the formula originally introduced by Spurr and Myers [14]:

$$W_{\text{rutile}}\% = \frac{1}{1 + 0.8 \times (I_{\text{anatase}}/I_{\text{rutile}})}$$

with I_{anatase} and I_{rutile} the peak intensities of the strongest anatase and strongest rutile reflection peak respectively.

The change in crystallite size due to the heat treatment was calculated using the Scherrer equation:

$$D = 0.9 \frac{\lambda}{\beta \times \cos \theta}$$

with D , crystallite size [nm]; λ , X-ray wavelength [nm] (CuK α X-rays: 0.1542 nm); β , full width at half maximum (FWHM) [radians]; θ , Bragg angle [radians].

2.1.2. TiO₂ modified with silver nanoparticles

Silver was deposited on the TiO₂ P90 (Evonik) surface by the photodeposition method using an adapted protocol based on Iliev et al. [15,16]. For 0.5 g of TiO₂ P90, AgNO₃ (Sigma–Aldrich, >99.0% purity) was used as the silver precursor and dissolved in 50 mL of bidistilled water, so that samples with 0.1, 0.3, 0.6 and 1 at% of silver (TiO₂ basis) were obtained. Methanol (Merck, >99.5% purity) was used a sacrificial hole scavenger and added to the solution in a molar ratio methanol:AgNO₃ of 500:1. The P90 powder was added to the solution and brought to pH 2 with nitric acid (Merck, 65%). The mixture was stirred for 30 min at 750 rpm in the dark and consecutively illuminated with UV light (Philips Cleo, 25 W, 205 $\mu\text{W cm}^{-2}$ at 365 nm) for 30 min while stirring. The resulting colored suspension was centrifuged and washed 2 times with bidistilled water. The cake was further dried overnight at 110 °C and grinded in an agate mortar.

2.1.3. TiO₂ with different intrinsic properties or water content

Three commercial photocatalysts were selected for this study. P90 (Evonik), P25 (Evonik) and PC500 (Cristal global), were used to determine the SPV response and the photocatalytic activity in the aqueous as well as in the gas phase.

In order to study the qualitative effect of the humidity of the catalyst powder, P90 was dried overnight at 300 °C. While handling this dried P90, it was continuously kept at 110 °C to avoid unwanted rehydration of the catalyst. Controlled rehydration of the catalyst was achieved by the deposition of 2.5 or 5.0 $\mu\text{L H}_2\text{O}$ onto 4 mg dried P90 powder on the ITO glass slide of the SPV setup.

2.2. SPV measurements

This work aims to study the possible use of SPV for quickly assessing the photocatalytic performance, rather than carrying out a detailed study of the (photo)electronic properties. Therefore, no classical SPV ‘sweep’ spectra were recorded, but a single SPV signal was measured after illumination with a low-intensity UVA lamp (Philips Cleo, 25 W, 205 $\mu\text{W cm}^{-2}$ at 365 nm). This was the same light source as used in all photocatalytic tests, and therefore best suited for a realistic study of the relation between SPV and photocatalysis.

The set-up itself was a custom-made apparatus, in which the catalyst powder was sandwiched between two ITO electrodes (Sigma–Aldrich, $d = 1.2$ mm, resistivity: 8–12 $\Omega \text{ cm}^{-2}$), connected to a photo-amplifier (1×10^6 voltage amplification). No external bias was applied. A schematic representation of the SPV set-up is depicted in Fig. 2. In order to perform highly reproducible measurements, only a controlled square section of 5 mm \times 5 mm was illuminated. A constant amount of catalyst was spread out on this marked area and sandwiched. For all tests on TiO₂ based samples, the ideal amount of catalyst that covered this area and resulted in a good contacting layer between both ITOs was determined to be 4.0 ± 0.1 mg. Since the Ag-P90 samples were considerably coarser due to the photodeposition treatment, 11.0 ± 0.1 mg was used for these specific tests. For the exact determination of the SPV value, the difference was taken between the steady voltage readout after 1.5 min of UVA illumination and the steady voltage readout in dark.

Download English Version:

<https://daneshyari.com/en/article/55051>

Download Persian Version:

<https://daneshyari.com/article/55051>

[Daneshyari.com](https://daneshyari.com)