

Photo-electrochemical characterization of TiO₂ nanoparticles synthesized by the sol-gel route

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ABSTRACT

Titanium dioxide nanoparticles were synthesized by the sol-gel method using titanium butoxide, HNO₃ or CH₃COOH as hydrolysis precursors, ethanol and water. The reaction was carried out at 80°C during 2h. The obtained materials were dried and calcined at 400°C. The as-prepared materials were deposited on an ITO substrate and electrochemical techniques as cyclic voltammetry (CV) and open circuit potential (OCP) were performed. It was found that, during illumination with UV light, the OCP is highly modified compared with P25 from commercial source. Therefore, the generation of electron-hole pairs leads to changes in the flat band potential and a decrease to more negative values at lower electron transfer, which are closely related with the pKa of the hydrolysis precursor (pKa_{HNO₃}= -2.0 and pKa_{CH₃COOH}=4.8). Then, it is possible that the slow dissociation of the precursor (i.e. CH₃COOH) during the synthesis process modifies the structural and morphological characteristics (e.g. particle size, surface area) inducing a more efficient generation of electron-hole pairs and a more reversibility toward the OCP. Supposition also verified by CV. In these profiles the peak-to-peak potential gradients (ΔE) are 0.28 mV, 0.24mV and 0.18 mV for P25, HNO₃ and CH₃COOH respectively, indicating that in this last the electrochemical redox reaction linked to the couple Fe³⁺/Fe²⁺ is more efficient.

Keywords: Semiconductors, photo-electrochemistry, titanium dioxide, sol-gel, hydrolysis precursor.

Introduction

Titanium dioxide (TiO₂) is the most used semiconductor for photo-catalytic and photo-electrochemical reactions including degradation of organic compounds and redox mechanistic studies [1], and as a carrier material for nanocomposites [2]. Moreover, the use of titanium dioxide as gas sensor has been growing recently due to its high intrinsic resistance compared to conventional materials such as SnO₂ and ZnO [4]. In this context, it is important to study its electronic and structural-morphological properties in order to major understand the overall process during charge transfer at the semiconductor-electrolyte interface under dark and illumination. For example, during illumination-induced reactions, there is a local charge density that strongly differs from the bulk solution, producing an electric field, which acts as a driving force in the charge transfer process. Therefore, the photo-electrochemical activity may vary depending on the electrolyte pH, because it modifies the transfer phenomena of the interfacial region, causing a charge separation and then, modifying the anodic and cathodic current evolution [9,10]. Other critical factors involving the charge transfer includes the band gap energy, crystallite size and particle shape that can be controlled by the synthesis route employed and several conditions during the process of synthesis, including the pH [3]. The use of soft chemistry routes (e.g. sol-gel method) is an interesting alternative. This pathway involves a hydrolysis step, which can be controlled by several factors such as the alkoxide used as precursor, molar ratios of the precursor for hydrolysis, among others [5]. Other methods for improving the crystallinity and obtain different properties to control the morphology have been also employed [7,8]. In this work, the TiO₂ photo-electrochemical evaluation, synthesized by the sol-gel method using HNO₃ and CH₃COOH as hydrolysis precursors, was conducted. These evaluations include electrochemical techniques such as cyclic voltammetry and open-circuit potential transients.

Experimental section

Materials and Methods

Titanium dioxide nanoparticles were synthesized by the sol-gel method at pH=7. Briefly, titanium butoxide 97% (Sigma Aldrich), ethanol and deionized water were mixed under constant stirring in a glass reactor with a refrigeration system in order to avoid evaporation. Then, the hydrolysis precursor (HNO₃ or CH₃COOH) was added dropwise at 25°C. Thereafter, the reaction was carried out at 80°C during 2h. The molar ratios used were 1: 0.14: 43: 8 for alkoxide, acid, deionized water and ethanol, respectively. The obtained materials were dried and calcined at 400°C [10, 11]. The electrode preparation was carried out as follow: 0.3 g of TiO₂ as-prepared, 6 mg of polymethyl methacrylate and 1.2 ml of methyl methacrylate were subject to ultrasound for 15min. Then, 12 µl of this suspension were deposited on a SnO₂ glass substrate and then dried for 15min in an argon atmosphere. The electrochemical measurements were performed potentiostatically (EG & E Model 263) in a three-electrode standard electrochemical cell. A carbon and Calomel were used as counter and reference electrodes, respectively. For cyclic voltammetry (CV) experiments, a solution of 0.1 M KCl + 6x10⁻³ M K₃Fe [CN]₆ was used as supporting electrolyte in a potential

interval from -0.2 to 0.6 mV. Whereas, the open-circuit potential transients were performed in a 0.1 M KCl solution during 1500s, using a UV lamp (PS-01 UVP) as a light source toward the surface of the as-prepared electrode. Argon gas was used to remove dissolved O₂.

Results and Discussion

Figure 1 shows the profiles E versus t for the synthesized samples. Notice that the open-circuit potential is strongly affected during illumination after 250s. This potential variation indicates a transfer of charge carriers. Moreover, this variation is most important with respect to P25 from commercial source (curve a). Therefore, the generation of electron-hole pairs leads to changes in the flat band potential and a decrease in the open-circuit potential to more negative values at lower electron transfer [12], which are closely related with the pK_a of the hydrolysis precursor (pK_aHNO₃=-2.0 and pK_aCH₃COOH =4.8) curves (b) and (c), respectively. According to this, it is possible that the slow dissociation of the precursor (i.e. CH₃COOH) during the synthesis process modify the structural and morphological characteristics (e.g. particle size, surface area, Figure not shown) inducing a more efficient generation of electron-hole pairs and a more reversibility toward the OCP. This assumption was also verified by CV in a 0.1 M KCl + 6x10⁻³ M K₃Fe [CN]₆ at 20mV/s (see inset in Figure 1). In these profiles the peak-to-peak potential gradients (ΔE) are 0.28 mV, 0.24mV and 0.18 mV for P25, HNO₃ and CH₃COOH, indicating that in this last the electrochemical redox reaction linked to the couple Fe³⁺/Fe²⁺ is more effective.

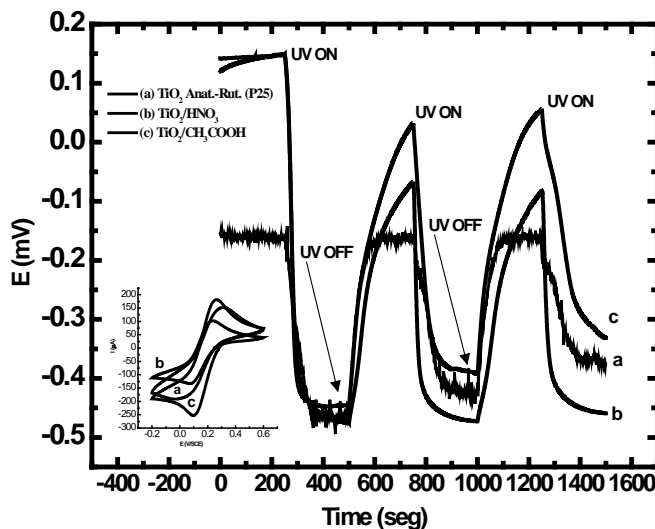


Figure 1. Open circuit potential transients during UV illumination. Inset: *i* vs *E* obtained by CV for the semiconductors evaluated.

Significance

This study focuses in the evaluation of the photo-electrocatalytic activity of TiO₂ synthesized by sol-gel method. The intrinsic properties obtained can be of high impact in view of the degradation of organic compounds (e.g. dyes, as a reducing agent) using TiO₂ as a photo-anode in a galvanic cell, producing electricity, and hydrogen in the cathode.

Conclusions

The exchange of species at the electrode-electrolyte interface is strongly linked to the acid of hydrolysis employed during the synthesis of TiO₂, affecting the electrochemical activity given by the ΔE during cyclic voltammetry experiments. In this context, the variation in the open circuit potential transients during UV illumination promotes the generation of electron-hole pairs more efficiently in the material synthesized with acetic acid, phenomena also linked to its dissociation constant.

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