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Short Communication

Photoelectrochemical properties of sol–gel synthesized titanium dioxide nano-particles using different acids: X-ray photoelectron spectroscopy reveals the induced effect of hydrolysis precursor

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ABSTRACT

Properties such as crystalline structure (X-ray diffraction – XRD), surface chemistry–electronic states (X-ray photoelectron spectroscopy – XPS), morphology and particle size-distribution (Transmission Electron Microscopy – TEM), electronic structure-band-gap (UV–vis spectroscopy) and surface area (BET-nitrogen physisorption) were analyzed for titanium dioxide (TiO_2)-semiconductor-surfaces synthesized by sol–gel route using nitric, acetic and phosphoric acids as hydrolysis precursors. According to XRD analysis, it was established that anatase phase has been obtained with a particle size linked to the acid of hydrolysis employed (i.e. dissociation constant), as also demonstrated by TEM and area BET. On the other hand, using XPS, a shift toward lower binding energies was observed from TiO_2 obtained using HNO_3 promoting some structural modification and the reduction in the band-gap, inducing a better faradic current-performance by decreasing charge-transfer resistance during polarization and at induced-generated photocurrent using UV-light.

1. Introduction

The study at intermediate-size regime in TiO_2 based structures gives information about the collective behavior of materials bulk, which emerges from the discrete nature of molecular properties. An exponential growth of research activities has been seen in nano-sciences and nanotechnology in the past years. New physical and chemical properties emerge when the size of the materials becomes smaller [1–3]. Then, the synthesis route with controlled pore structure, morphology and porosity is of great importance to prove the potential applications in catalysts [4], hydrogen production [1,5], hydrogen storage [6] and in other based-electrochemical applications such as sensors [7]. In this sense, the modification of TiO_2-physicochemical properties

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is required to increase the activity in different model reactions through different synthesis routes such as sol–gel [8], colloidal [9], or sonochemistry [10]. In this context, this work is presented and discussed the role of the hydrolysis catalyst (i.e. HNO_3, CH_3COOH and H_3PO_4) in the preparation of titanium dioxide by using the sol–gel route. For such an approach structural, morphological, physicochemical and (photo)-electrochemical technique were employed.

2. Experimental section

2.1. Materials synthesis

TiO_2 nanoparticles were prepared by sol–gel method using titanium butoxide (97%, Sigma-Aldrich) as titanium precursor and HNO_3 (71% Realyt's), H_3PO_4 (89.4% Alyt) or CH_3COOH (99.7% R. Quim. Meyer) as hydrolysis-acid precursors. The molar ratio of reagents was 1:0.14:43:5 (alkoxide:acid:water:ethanol). Briefly, 21.93 mL of titanium butoxide was mixed with 18.77 mL of ethanol and 49.9 mL of water into a volumetric flask, then magnetic stirring was applied followed by annealing at 80 °C. When the desired temperature was reached, acid was added to obtain controlled hydrolysis reaction. The reaction was kept under these conditions for 2 h and then the formed gels were cooled at ambient temperature and stirring was stopped. The resulting titanium precursors were dried at 110 °C in an oven for 24 h and finally they were annealed at 400 °C during 4 h [11].

2.2. Electrode preparation

An emulsion of 0.3 g of TiO_2 sample, 6 mg of poly (methyl methacrylate) and 1.2 ml of methyl methacrylate was prepared by ultrasound during 20 min. Then, an aliquot of 12 μl from the prepared mixture was taken and deposited onto an ITO surface, and dried during 15 min.

2.3. Physicochemical characterization

The materials prepared in this work were characterized by X-ray diffraction using a Rigaku MiniFelx II type equipment diffractometer with Cu Kα (30 kV, 15 mA) radiation and scan rate of 2θ (degree). Morphology of synthesized particles was observed by Transmission Electron Microscopy (JEOL, JEM-2010F). The samples bandwidth was calculated from diffuse reflectance spectra in the interval ranging from 200 to 900 nm, using a Nicolet 380 UV–vis spectrophotometer equipment coupled with an integration sphere. The nitrogen physisorption test was performed in NOVA 200 Quantachrome equipment. Finally, Intercovamex XPS 1100 apparatus was used to perform the X-ray photoelectron spectroscopy (XPS) analyses.

2.4. Electrochemical characterization

The electrochemical experiments were performed in a three-electrode photo-electrochemical cell using saturated calomel electrode (SCE) and a graphite plate as reference and auxiliary electrode, respectively. The potential was controlled using a potentiostat–galvanostat EG&G 263A. A solution of 0.1 M KCl was used as supporting electrolyte for all experiments described therein. The scan rate was fixed at 5 mV/s for cyclic voltammetry. On the other hand, for experiments during illumination an UV lamp (UVP at 254 nm) was employed, recording the transients current (i) versus time (t). Whereas, for electrochemical impedance spectroscopy (EIS) the frequency was varied from 10 to 1 KHz with an amplitude of 10 mV/SCE. For all cases, argon gas was used to eliminate dissolved oxygen from the electrolyte.

3. Results and discussion

3.1. Physicochemical characterization

3.1.1. X-ray diffraction (XRD)

Fig. 1 shows the results obtained by X-Ray diffraction for the different samples of TiO_2 prepared by sol–gel method and annealed at 400 °C during 4 h. According to this, in the interval of $2\theta = 20–70°$ the three samples prepared with different hydrolysis catalyst are polycrystalline materials since they have reflection characteristic of TiO_2 in anatase phase, according to card JCPDS no. 070-6826. In addition, the reflection intensity is very similar and only in the case of TiO_2 prepared with H_3PO_4 there is evidence of rutile phase at ca. $2\theta = 27.5°$. In order to obtain an average particle size, the Sherrer's equation was applied using the most intense reflection peak (at $2\theta = 26°$). Table 1 lists the

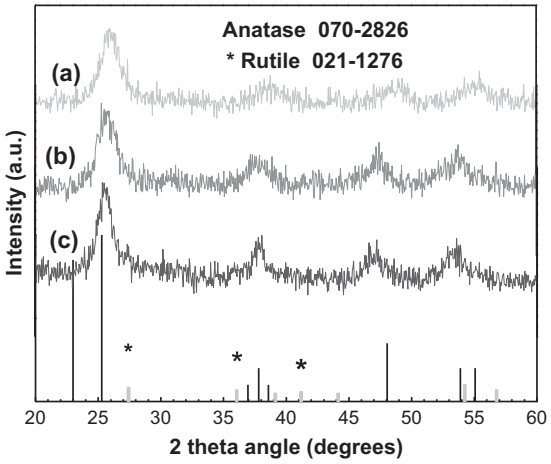

Fig. 1. XRD patterns of various TiO_2 powders synthesized with different hydrolysis catalysts and annealed at 400 °C, (a) TiO_2 (using HNO_3), (b) TiO_2 (using CH_3COOH), and (c) TiO_2 (using H_3PO_4).

Table 1
Main physicochemical properties of TiO_2 prepared by sol–gel route using different hydrolysis catalysts.

Sample	Hydrolysis catalysts	Particle size (nm)	Band gap (eV)	K_a	Surface area ($m^2\,g^{-1}$)
TiO_2	HNO_3	14	3.1	10×10^2	94
	CH_3COOH	10	3.2	6.3×10^{-3}	120
	H_3PO_4	6	3.3	1.8×10^{-5}	251