

Morphological and photoelectrochemical properties of porous, superimposed Au/TiO₂ layers

O. ENEA, B. ZAYTOUNI

Laboratoire de Chimie 4, URA CNRS 350, Université de Poitiers, 40, avenue du Recteur Pineau, 86022, Poitiers, France

J. MOSER

Institut de Chimie Physique, EPFL, CH-1015, Lausanne, Switzerland

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Porous semiconducting ceramics deposited on a porous metallic film acting both as catalyst and electronic collector gave large photocurrents and considerably enhanced electrooxidation currents when irradiated in the presence of small amounts of alcohol vapours. The morphological properties of these layered materials, was studied by electron (SEM, ESEM) and atomic force (AFM) microscopy in order to observe the modification in shape and size of the precursor particles because such knowledge is helpful to the preparation of suitable anodes for photo-assisted processes in the gas-phase.

Keywords: *titanium dioxide, ceramic, porous, metallized, photoanode, electrooxidation*

1. Introduction

Aqueous suspensions of TiO₂ powders have been found very efficient in the photooxidation of various alcohols [1, 2], polyols [3, 4] and sugars [5, 6]. More recently, transparent ceramics prepared from different TiO₂ precursors [7, 8], were studied in relation to light energy conversion and their morphological features were characterized by scanning force microscopy [9]. The photoelectrochemical properties of such ceramics have so far been examined in electrolytic solutions, but not in gas-phase processes. On the other hand, metallic films deposited on Nafion[®] membranes [10, 11], zeolite discs [12], and alumina ceramics [13], have been found to be very efficient in the electrooxidation of various organic vapours.

In the present work various thin ceramic membranes prepared from TiO₂ precursors were deposited onto a thin, porous gold film evaporated on a commercial glass frit of fine porosity. Such composite layers, used under light irradiation to carry out electrochemical processes in the gas phase, possess a number of technical advantages and possibilities: (i) each semiconductor grain does not need to be metallized and thus the planar structure is easier to fabricate; (ii) since the size, distribution and optimum loading of metal deposits on TiO₂ particles are no longer factors, the characterization of the catalyst is simplified; (iii) the metallization of the planar structure is macroscopic and, therefore, external circuitry can be attached and electrical current drawn or driven through the layer. This indicates possible photovoltaic cell application and waste water treat-

ment; (iv) the semiconducting layer is adaptable to the fabrication of more complex PEC structures involving an array of PEC cells formed from different semiconducting layers deposited on a metallic pattern.

The morphologies of several TiO₂ ceramics prepared in different ways have been examined by scanning electron microscopy (SEM), environmental scanning electron microscopy (ESEM) and atomic force microscopy (AFM). Their photoelectrochemical properties have been tested for methanol oxidation, chosen because of its interest as a fuel, and because of the relatively limited number of oxidation products compared to other alcohols.

2. Experimental details

2.1. Anode preparation

A thin layer (320 nm thick) of gold was evaporated on one side of a glass frit (GF) disc (40 mm in diameter), having a fine (4) porosity. Several types of TiO₂ ceramic were prepared on the metallized side of the glass frit (GF/Au): (i) from a commercial powder (Degussa P 25), transformed first into a paste by grinding the powder with a very small amount of acetyl acetone in a mortar, and next suspended in an aqueous solution of glycerol [14, 17]. The application of this viscous suspension onto the porous gold film was followed by drying several hours at room temperature and firing at 450 °C, a temperature approached gradually; and (ii) from an aqueous sol containing 10 g dm⁻³ of TiO₂ particles of mean radius

5 nm [18]. In a first procedure termed 'spray pyrolysis', a small amount of sol was sprayed onto the supported gold film heated at 400 °C. In a second procedure termed 'spin coating', the surface of the porous GF/Au was covered with a thin layer of sol and the disc was spun (10 min at 500 rpm) and progressively heated up to 450 °C, a sequence of operations repeated up to six times, as previously described [15].

The morphological features of the TiO₂ ceramics deposited either onto porous GF/Au or plane supports (silicon, glass or conducting glass) were examined by scanning electron microscopy (SEM), by environmental scanning electron microscopy (ESEM) or by atomic force microscopy (AFM). Three different instruments, JEOL 35CF (Jeol Co.), Environmental SEM (Electroscan) and Nanoscope III (Digital Instruments), were used for SEM, ESEM and AFM observations, respectively.

2.2. Photoelectrochemical cell

All the photoelectrochemical experiments were performed in a two-compartment cell having a reference compartment filled with supporting electrolyte, 0.5 M H₂SO₄ or 1 M KOH, carefully deoxygenated, and a reaction compartment in which alcohol vapours were introduced (Fig. 1(a)). A large area carbon cloth immersed in the supporting electrolyte was used as counter electrode (CE), while the reference electrode (RE) was connected through a Luggin capillary in close proximity to the nonmetallized edge of the glass frit. The working electrode (WE) was a

gold film covered by the TiO₂ ceramic facing the reaction compartment, and the whole GF/Au/TiO₂ disc also played the role of separator between the two compartments (Fig. 1(b)). The electrical contact with the gold deposit was ensured through a carbon ring pressed onto the metal surface. The reaction chamber was equipped with an optical port and an appropriate filter so that u.v. photons (from a 150 W Xenon lamp) could irradiate the structure homogeneously at $\lambda > 350$ nm.

3. Results and discussion

3.1. Morphology

The morphological features (grain size, porosity) of the ceramic (TiO₂) layer deposited on gold, examined by scanning force microscopy (AFM), clearly show a small increase in the size of the precursor particles due to the firing process. Environmental and scanning electron microscopy was used to observe the general shape of the samples on a larger scale (up to 50 μ m), and to measure the thickness of the metallic (Au) or semiconducting (TiO₂) layers on micrographs showing images of areas only a few micrometres wide.

The micrographs shown in Fig. 2 are typical of the images obtained by SEM or ESEM for the GF/Au/TiO₂ samples: crevices (Fig. 2(a) and (b)) on the surface of thick TiO₂ ceramics made from suspensions of P 25 Degussa, conglomerates of TiO₂ particles deposited by 'spray pyrolysis', or thin ceramics deposited onto GF/Au by 'spin coating' (Fig. 2(c)

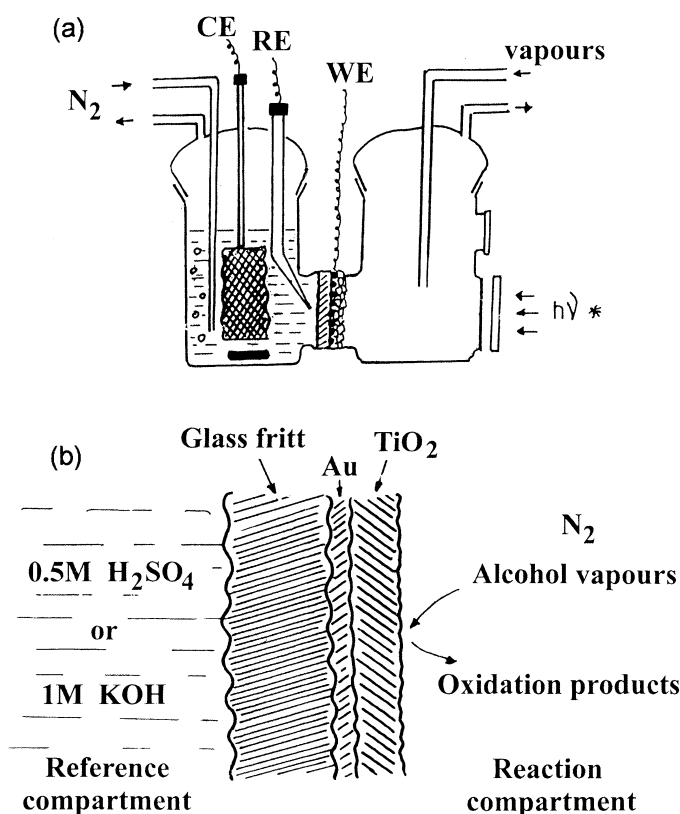


Fig. 1. Schemes of the two-compartment cell (a) and of the enlarged view of the porous diaphragm (b).

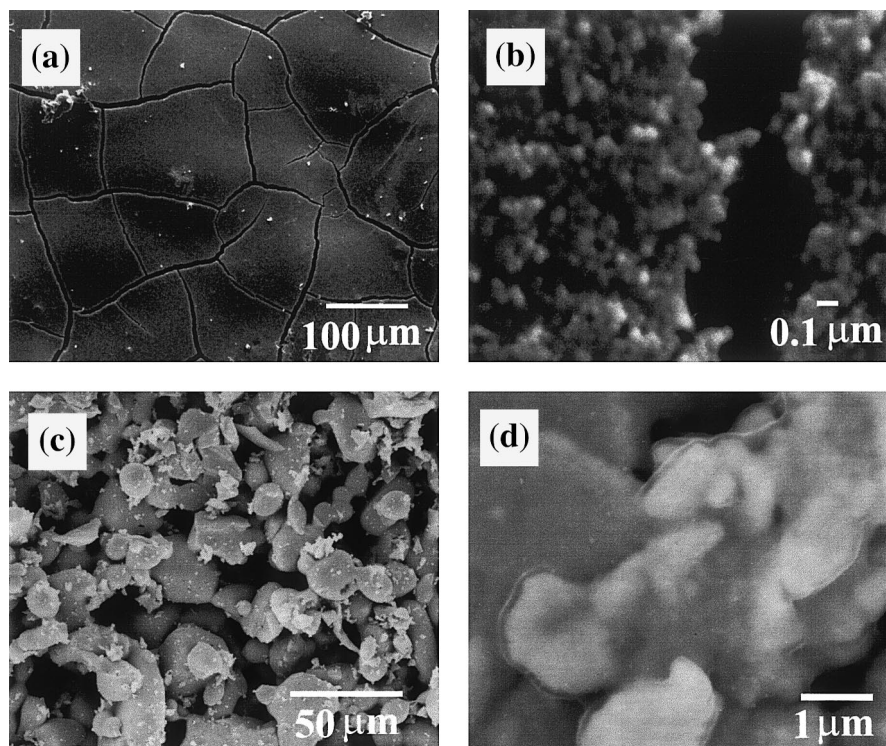


Fig. 2. Electron microscopy of TiO_2 ceramics prepared by coating with a suspension of Degussa P 25 powder (a, b) and 'spin coating' of Au/GF with a TiO_2 sol (c, d).

and (d)). Therefore, it is clear that, depending on the preparation methods, the access of gaseous reactive species to the gold sites may be completely different: that is, (i) a direct access in the case of samples prepared by 'spray pyrolysis'; (ii) passing through the porosity of thin TiO_2 ceramics prepared by 'spin coating', or (iii) both direct and indirect access, through crevices and thick (Degussa P 25) ceramic, respectively.

However, from the point of view of the formation of (e^-, h^+) pairs, of their transfer, and especially of their subsequent consumption or collection, the thickness of TiO_2 ceramic must be thin, below a tenth of a μm [16], in order to allow a significant fraction of the (e^-, h^+) pairs to reach the metal/semiconductor interface before recombination occurs.

3.2. Photoelectrochemical measurements

The real surface of gold deposits was calculated by using the area of the characteristic peaks on I/E profiles recorded before deposition of TiO_2 ceramic (Fig. 3), and was found to be 4.5 times higher than the geometric area, which was always 6.15 cm^2 . The shape of the I/E profiles recorded for Au/GF under nitrogen atmosphere is similar to that of a gold electrode immersed in the same supporting electrolyte. Presumably, a thin layer of electrolyte covers the surface of gold deposit and thus makes the adsorption of oxygen species on the metallic sites possible, as well as their desorption when the potential is scanned in the cathodic direction. Moreover, after depositing TiO_2 the behaviour of GF/Au/ TiO_2 material used as a working electrode facing pure

nitrogen was, in the absence of light, similar to that already observed in the same conditions for Au/GF, Au/Nafion[®] [10, 11], Au/zeolite [12], or Au/ Al_2O_3 [13] metallized membranes.

However, the adsorption of oxygen species on the surface of gold, as well as their subsequent desorption, is noticeably slowed down by the presence, at

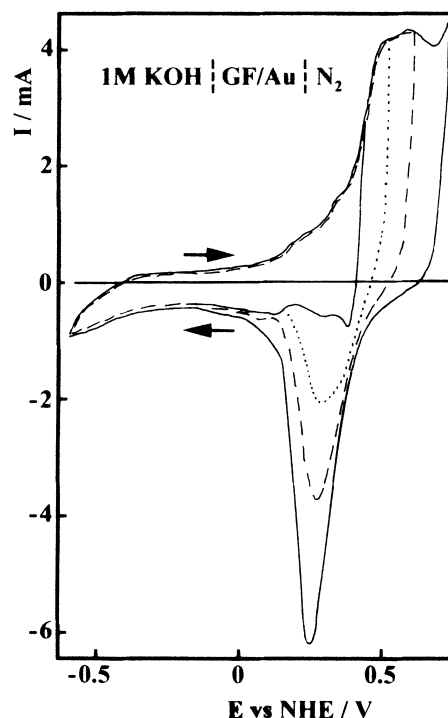


Fig. 3. Cyclic voltammograms recorded between various anodic limits at a sweep rate of 50 mV s^{-1} for a gold film evaporated onto a glass frit. The real surface of the gold is 28 cm^2 .

the gold surface, of a TiO₂ ceramic, the pores of which are filled with the supporting electrolyte. As a consequence, most of the *I/E* profiles recorded for GF/Au/TiO₂ materials give noticeably smaller peaks (Fig. 4(a)) for the desorption of oxygen species from the surface than those seen for Au/GF (Fig. 3), when no TiO₂ was deposited.

In the case of a TiO₂ ceramic prepared by 'spray pyrolysis', irradiation under nitrogen flow produces a small photocurrent, as shown in Fig. 4(a). The intensity of the photocurrent, as well as that of the electrooxidation current, is significantly increased when alcohol vapours are introduced to the gas compartment (Fig. 4(b)). The oxidation peak in the anodic potential scan is located at 0.45 V vs NHE, and a second oxidation peak, located at 0.35 V vs NHE can be seen when the potential is scanned in the cathodic direction. These potential values are close to that of the peak due to the desorption of oxygen species from gold sites (Fig. 4(a)). Therefore, the significant photocurrents and oxidation peaks seen in Fig. 4(b) are due to the reaction between methanol molecules and the active oxygen species on the surface of the gold layer. For this kind of preparation ('spray pyrolysis'), a photocurrent was detected even at -1.2 V vs NHE and the highest photocurrent values, measured on the photocurrent-time curves, reached 1 mA.

Figure 5 gives a typical *I/E* curve obtained under chopped light for a GF/Au/TiO₂ ceramic prepared

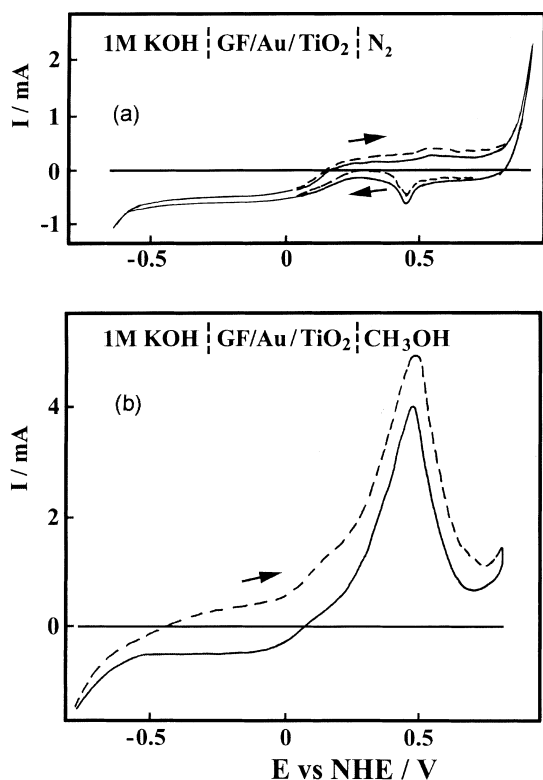


Fig. 4. Photocurrents recorded in dark (full curves) or under illumination (dotted curves) for a GF/Au/TiO₂ anode prepared by 'spray pyrolysis' (a) under N₂ flow, (b) in the presence of alcohol vapours at a partial pressure of 91 torr. Potential scan rate 1 mV s⁻¹.

from a suspension of Degussa P 25 powder, which is covered with crevices such as those seen in Fig. 2(a) and (b). The photocurrent onset is at -0.5 V vs NHE and reaches a maximum value of 3.5 mA, even when the supporting electrolyte is acidic. For the same partial pressure of alcohol vapour (91 torr), but in the presence of an alkaline medium, the photocurrent increases up to 5 mA and, the peak due to the electrooxidation current also becomes visible (Fig. 6). This behaviour can be explained by the fact that the gas-phase electrooxidation process on the Au sites becomes photoassisted by the semiconducting ceramic under illumination, which provides the gold surface with an additional amount of hydroxyl radicals.

In the case of a ceramic having crevices, such as those observed (Fig. 2(a) and (b)) for the preparations made from viscous suspensions of Degussa P 25 powder, the access of reactive species to the catalytic layer can occur directly through crevices or indirectly through the porosity of the ceramic.

In the case of a crack-free ceramic (Fig. 2(c) and (d)) its thickness, estimated from the SEM micrographs to be around 100 nm, plays a crucial role, not only for the transfer of (e⁻, h⁺) pairs to the catalyst layer, where they can be collected or consumed, but also for the oxidizable species such as alcohol molecules or oxidation intermediates like aldehydes, acids or ketones. If the ceramic layer is 1 mm thick, no photocurrent or photoassisted electrooxidation process is observed [16].

In Fig. 7 we show the *I/E* profiles obtained for a GF/Au/TiO₂ anode in dark (full curve) or under illumination (dotted curve). The photocurrent onset is at -0.5 V vs NHE in the case when the supporting electrolyte is acidic, and the maximum value is 0.7 mA. In contrast with the results observed for Au/Nafion[®] anodes, in the case of GF/Au/TiO₂ anodes the partial pressure of methanol vapour does not influence the magnitude of the electrooxidation currents, presumably due to the slow accumulation of the oxidizable species in the pores of the ceramic layer.

In all cases, the photocurrent values measured under chopped light on *I/E* profiles, were confirmed

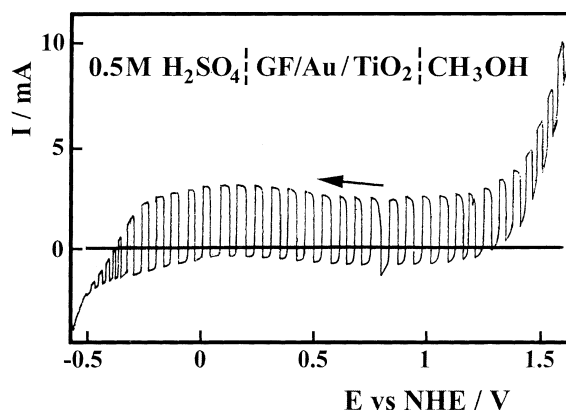


Fig. 5. Photocurrents measured under chopped illumination of GF/Au/TiO₂ (P25) ceramic in the presence of methanol vapours (91 torr). Potential scan rate 1 mV s⁻¹.

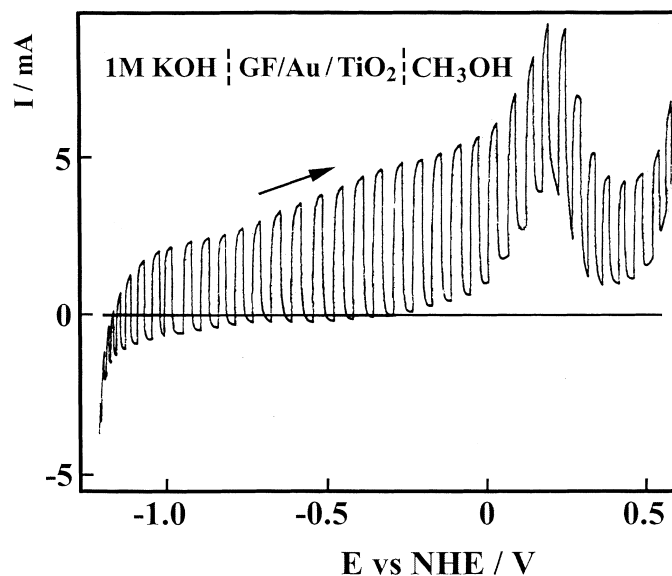


Fig. 6. Photocurrents obtained under chopped illumination of GF/Au/TiO₂ (P 25) ceramic in the presence of methanol vapours (91 torr). Potential scan rate 1 mV s⁻¹.

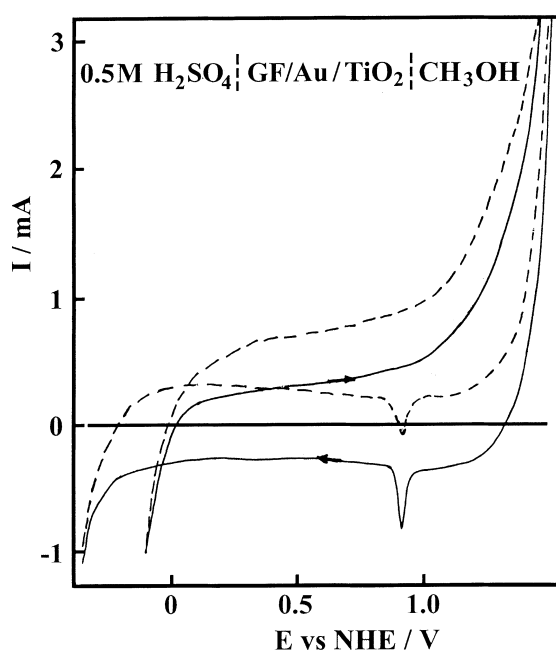


Fig. 7. Photocurrents (dotted lines) measured for a GF/Au/TiO₂ anode prepared by 'spin coating' repeated six times, in the presence of 29 torr of methanol. Potential scan rate 1 mV s⁻¹.

by the photocurrent transients recorded under the same experimental conditions (partial pressure of alcohol vapour, concentration and nature of the supporting electrolyte in the reference compartment, thickness and type of TiO₂ ceramic, etc.)

These experimental results clearly show that a photoassisted electro-oxidation process occurs even in acidic media at the interface of TiO₂ ceramics with the catalytic film and this may be of great interest in the conversion of light energy and in the degradation of organic pollutants. However, the understanding of the processes occurring at the interface between the porous layered materials and a gaseous (hydrophobic or hydrophilic) reactant which must cross the surface

electrolyte layer, is not simple from the fundamental point of view. The same is also true for other materials, made of powder layers [19], or from a silica-wool disc containing phosphoric acid [20], which have been demonstrated to have practical interest for gas-sensors [19] and gas-phase electrosynthesis [20], despite the complex interfaces involved.

Several parameters, such as the thickness of the ceramic, the preparation method and the type of catalytic layer are currently under study in order to obtain a better insight into the photoelectrochemical properties of the layered catalyst/semiconductor materials.

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