

TiO₂:Au thin film electrodes for electrochemical solar cells

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TiO₂ nanocermetts are obtained by RF reactive co-sputtering from mosaic targets of Au:Ti or by sequential deposition from metallic Ti and Au targets. The influence of noble metal content on the microstructure of thin film nanocermetts has been studied by means of optical, structural, and electrochemical measurements. Increased photocurrent responses have been observed over the visible range of the light spectrum. TiO₂ samples with a discontinuous Au film give significantly better photoresponses than those with Au in the bulk.

Key words: *photoelectrolysis; titanium dioxide; nanocermet*

1. Introduction

The photoelectrolysis of water, i.e. water decomposition into hydrogen and oxygen as a result of the absorption of sunlight is considered to be the most important unconventional future energy source. This process is conducted in a photoelectrochemical cell (PEC) composed of an aqueous electrolyte and two electrodes [1]. At least one electrode, typically the anode, should be formed from a semiconducting material. Titanium dioxide, TiO₂, is one of the most suitable candidates for the photoanode material in the photoelectrochemical solar cell (PEC) due to its high resistance to corrosion, stability and a negative flat band potential. The band gap of TiO₂ is of the order of 3 eV, too high for the efficient absorption of the sunlight. Several methods providing higher sunlight conversion efficiency and improving the photo-response of TiO₂ have been proposed. These methods include: a) doping with aliovalent ions in order to produce an additional band within the band gap of TiO₂ [2], b) band gap self-regulation in solid solutions and photoelectrode sensitisation [3], c) incorporation of

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noble metals [4–7], and d) coating with organic dyes [8]. All these methods rely on modifying the spectral dependence of the absorption coefficient of TiO₂ with the goal of matching the solar spectrum.

One of the most promising methods is the incorporation of noble metal nanoparticles (Au) into the TiO₂ dielectric matrix. Thus obtained nanocermets show an additional absorption feature due to the surface plasmon resonance (SPR) occurring over the visible range of the light spectrum. This phenomenon results from the excitation of collective oscillations of conduction electrons in the noble metal inclusions under the influence of electromagnetic radiation.

The purpose of this work was to study the performance of thin films of TiO₂:Au in photoelectrochemical systems.

2. Experimental

Sample preparation and characterization. Thin films of TiO₂:Au were deposited by RF reactive co-sputtering from Ti:Au mosaic targets and by the sputtering of Au onto the surface of TiO₂ (sequential deposition). NaCl, carbon foil, titanium foil and amorphous silica were used as the substrates. The film thickness varied from 20 to 200 nm. The sputtering conditions have been described in detail elsewhere [4–6].

The microstructure of the thin-film nanocermets was characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), and X-ray diffraction at grazing incidence (GID). X-ray photoelectron spectroscopy (XPS) was used with a multi-technique system of VSW Science Instruments. The binding energy shifts due to surface charging were corrected assuming the C 1s XPS peak is located at 285.0 eV.

Optical studies were carried out with the Perkin Elmer double beam spectrophotometer Lambda 19 over a wavelength range of 220–2500 nm.

Electrochemical measurements. Electrochemical measurements were performed in an experimental cell consisting of a photoanode, a working electrode, and a reference electrode (SCE) with a TRIAX 180 Jobin Yvon monochromator and a 450W Xe lamp as the light source. The electrodes were immersed in a buffer solution with pH = 8. The photocurrent was recorded with a Keithley 6517A electrometer. Bias voltages were supplied by a Hewlett-Packard 34401A power supply.

3. Results and discussion

According to the experimental evidence provided by GID and TEM, TiO₂ dielectric matrix is amorphous when nanocermets are obtained by co-sputtering. Crystallized gold nanoparticles are distributed within the bulk of TiO₂ [6, 7]. On the contrary, thin-film nanocermets prepared by sequential deposition consist of 200–300 nm thick TiO₂ covered by a thin overlayer of noble metal (Au, or Ti with Au) with the thick-

ness depending on the deposition time. AFM micrographs for TiO₂ covered with Au reveal that the overlayer is discontinuous. The morphology of a titanium dioxide film 200–300 nm thick depends on the substrate temperature [5, 9]. Films crystallized at an elevated temperature of 350 °C give a significantly better photoresponse than those deposited at room temperature [5].

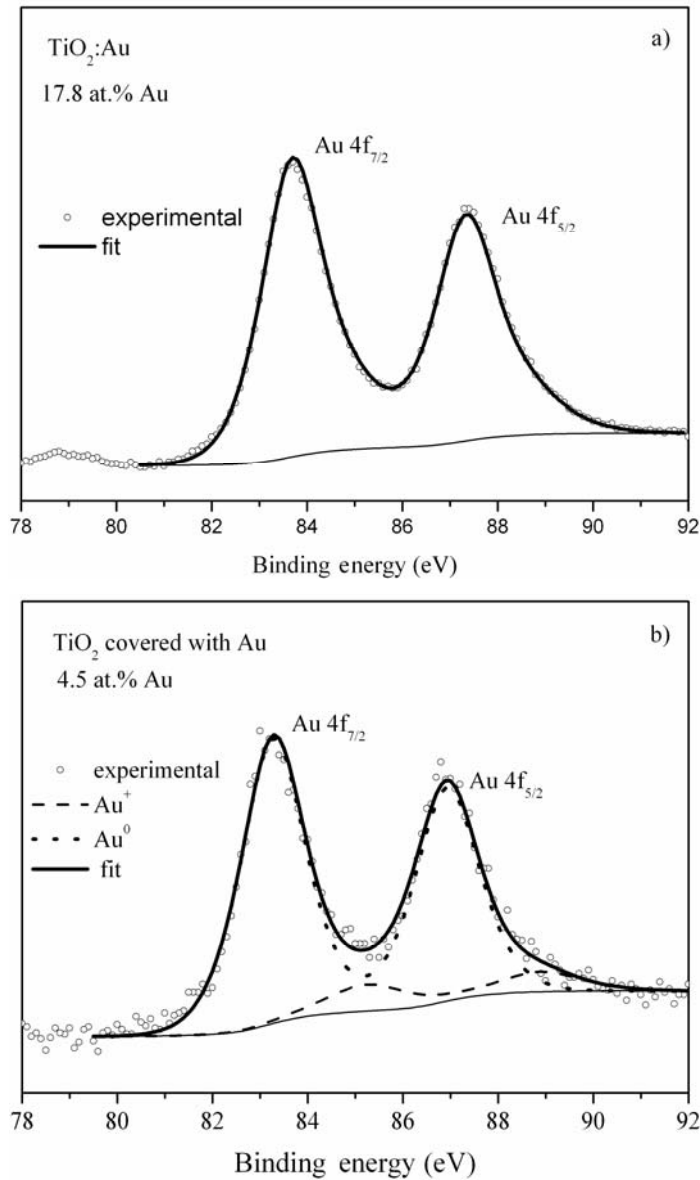


Fig. 1. XPS spectra of TiO₂ thin films with Au:
a) TiO₂:Au nanocermet; b) TiO₂ covered with a thin, discontinuous Au layer

X-ray photoelectron spectroscopy (XPS) has been used to study the oxidation states of Ti and Au. This is very important, especially in view of the fact that $\text{TiO}_2\text{:Au}$ thin films are grown in the presence of oxygen. Figure 1 illustrates the XPS spectra for thin films of TiO_2 with Au. The incorporation of Au into TiO_2 (Fig. 1a) gives one double peak, attributed to $\text{Au } 4f_{7/2}$ (83.5 eV) and $\text{Au } 4f_{5/2}$ (87.4) at binding energies corresponding to Au^0 [10]. This indicates that metallic gold is present as an inclusion. Figure 1b shows a Au 4f doublet measured in thin films of TiO_2 covered with gold. The Au 4f XPS peak could be resolved into two contributions. The highest energy components (85.2 eV) have been assigned to Au^+ [10].

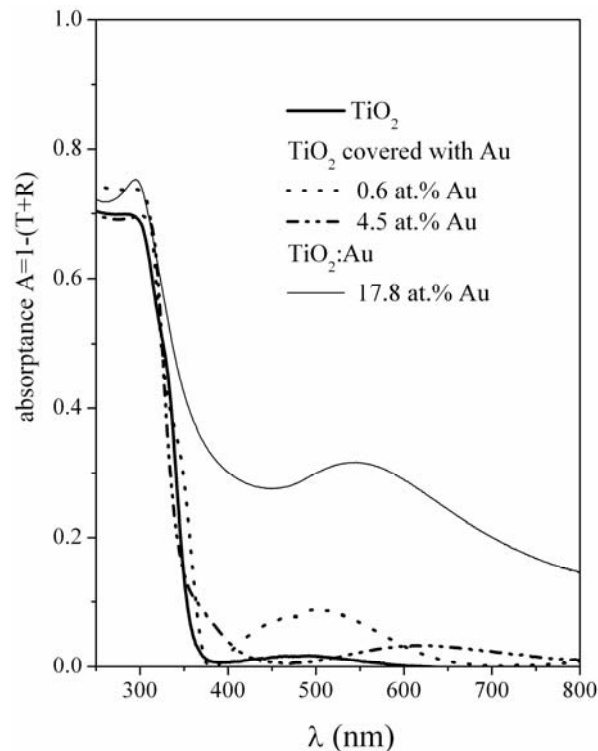


Fig. 2. Optical absorbance spectra for $\text{TiO}_2\text{:Au}$ nanocermet and TiO_2 thin film covered with a discontinuous gold film

Absorption spectra, calculated from the measured transmittance $T(\lambda)$ and reflectance $R(\lambda)$ coefficients, are presented in Fig. 2. TiO_2 thin film nanocermet shows, besides the fundamental absorption edge below 350 nm due to the band-to-band transition, an additional peak located in the visible range of the spectrum. This additional absorption feature results from surface plasmon resonance (SPR) and has been found to be correlated with the type, size, and distribution of noble metal inclusions [6, 7]. The SPR is located at $\lambda = 500\text{--}600$ nm for $\text{TiO}_2\text{:Au}$ thin films obtained by co-sputtering. As shown in Figure 2, the SPR is shifted to a shorter wavelength $\lambda = 500$ nm when the

noble metal is deposited at the TiO₂ film surface, i.e. by the sequential sputtering of TiO₂ and Au (1 sec). A longer deposition time of TiO₂:Au (8 sec) results in some red shift of the absorption peak. This behaviour is similar to that observed for nanocermet with a bulk distribution of noble metal [5].

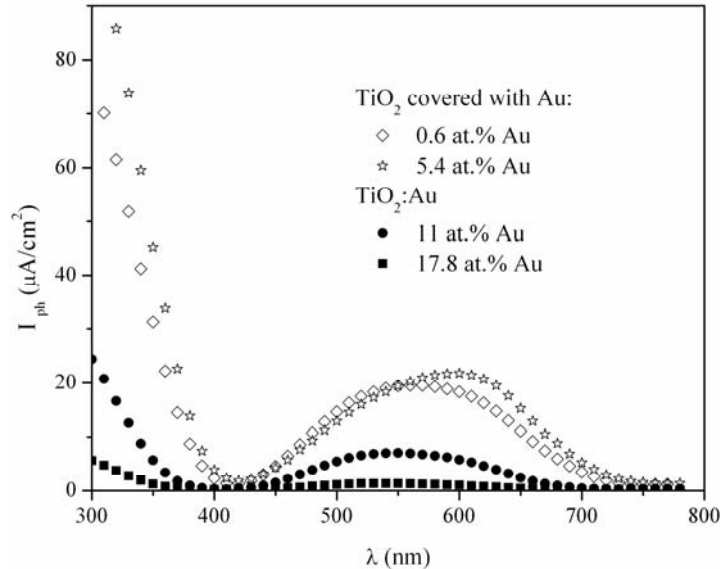


Fig. 3. Photocurrent densities for TiO₂:Au thin film nanocermet and TiO₂ covered with a discontinuous Au film

The effect of gold nanoparticles in the bulk of TiO₂ thin films and that of a discontinuous gold film covering the TiO₂ film surface on the spectral dependence of the photocurrent density in the PEC is presented in Figure 3. The photoresponse is high over the UV region due to the fundamental absorption edge of TiO₂. An additional, local maximum in the photocurrent appears over the visible range of the light spectrum, between 500 nm and 600 nm in the case of discontinuous thin films of gold on TiO₂. For nanocermet, a local maximum in the photocurrent appears at about 540 nm. This effect is related to the spectral dependence of optical absorption (Fig. 2). Samples covered with a discontinuous Au film, however, give a significantly better photoresponse than those with Au in the bulk. A correlation exists between the microstructure, optical properties, and photoresponse of the photoanodes based on TiO₂. As expected, gold distributed in the bulk of TiO₂ nanocermet modifies the spectral dependence of absorption in the vicinity of the fundamental absorption edge and at longer wavelengths. This means that the incorporation of gold into the TiO₂ lattice affects the electronic structure of TiO₂ and extends the fundamental absorption edge to longer wavelengths. As demonstrated in our previous work [2, 11], an enhanced recombination process of photoelectrons and holes may be correlated with the formation of this absorption “tail” in the band gap of TiO₂.

On the contrary, for TiO₂ covered with a thin layer of Au, the absorption spectra are strongly modified only over the spectral range 500–600 nm. The electronic structure of TiO₂ is apparently not affected by the deposition of a thin layer of gold on top of TiO₂.

4. Conclusions

The effects of gold nanoparticles in the bulk of TiO₂ thin films and of a discontinuous gold overlayer on the optical and photoelectrochemical properties of TiO₂ thin film photoanodes have been investigated. Thin film nanocermet based on TiO₂ with noble metal inclusions seem to be promising candidates for photoanodes in photoelectrochemical systems. The presence of Au in TiO₂ increases optical absorption over the visible range of the light spectrum, thus improving the photoresponse of the system under illumination. Increased optical absorption in nanocermet results from Surface Plasmon Resonance (SPR) and affects the spectral dependence of the photocurrent density. Photoanodes of TiO₂ with a discontinuous Au film give a significantly better photoresponse than those with Au in the bulk. A careful characterization of the material microstructure is necessary for the successful application of such systems in photoelectrochemical applications.

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