



Photocatalytic Hydrogen generation by oxide based nanostructures

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Abstract—Oxide based nanostructures were grown by aerosol assisted chemical vapor deposition onto borosilicate glass substrates. Experimental setup and general synthesis conditions were reported elsewhere. Nanostructures were coatings of: Ti oxide, composites of Ti-Fe and Cu-Fe oxides and multilayers of TiO_x-FeO_x and CuFeO_x-SnO_x. All nanostructures were covered with a layer of Pt nanoparticles. Microstructure of the samples was analyzed by electron microscopy and x-ray diffraction. Optical properties were also determined in the UV-visible-near IR interval. Photocatalytic generation of Hydrogen was evaluated in a batch reactor under visible light irradiation, using a filtered low vapor pressure Hg lamp of 250 W. Hydrogen evolution was tested every hour by gas chromatography.

Keywords—direct water splitting, Hydrogen generation, metal oxide heterostructures

I. INTRODUCTION

Solar water splitting represents a promising alternative for energy generation [1-5]. This, since the resulting molecular H₂ can be used as a sustainable and clean power source [1-3]. However, physical limitations related to the efficient energy conversion have been found [2]. From existing methods, direct water splitting [1] and photo-electrochemical processes [4, 5] using semiconductors, are being extensively studied and in some cases, efficiently applied [1]. Thus, in search for effective and stable materials, this work focus on the development of composite and hetero-structured metal oxide layers with Pt nanoparticles for direct oxidation of water.

II. EXPERIMENTAL

Samples comprising metal oxide based materials were synthesized onto borosilicate glass substrates (BGS) using the aerosol assisted chemical vapor deposition (AACVD) technique as in [6]. The layers' structure of the samples appears summarized in Table 1. The microstructure, including elemental composition of the synthesized coatings, was analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM), involving energy dispersive x-ray spectroscopy (EDXS). The total transmittance and reflectance spectra of the samples were measured in the UV-visible- near

IR interval. Moreover, the generation of H₂ was evaluated using each sample inside a customized radiation chamber. A solution of distilled water and 2% of methanol was used for the generation of H₂. All samples were irradiated with a filtered low vapor pressure Hg lamp of 250 W. The evolution of the generated H₂ was monitored every hour, up to 24 h, using gas chromatography (GC).

TABLE I. CONFIGURATION OF THE METAL OXIDES USED FOR THE GENERATION OF H₂

Oxide layers	Sample				
	A	B	C	D	E
First layer	TiO ₂	TiO ₂	TiO ₂	TiO ₂	TiO ₂
Second layer	nano Pt	FeO _x	TiO ₂ /FeO _x	CuFeO ₂	CuFeO ₂
Third layer		nano Pt	nano Pt	nano Pt	SnO _x
Fourth layer					nano Pt

III. RESULTS AND DISCUSSION

A. Morphology, chemical composition, crystalline structure and optical properties

Secondary electron micrographs revealing the surface morphology of representative samples are shown in Fig. 1. All micrographs show well distributed grains covering the surface. No cracks or defects were evident. Micrograph for sample A, obtained using backscattered electrons at high magnification (Fig. 1 a), shows the existence of a layer formed of irregular nanoparticles of around 20 - 30 nm. According to synthesis configuration, this layer corresponded to the formation of Pt nanoparticles. Fig. 1 e) shows the elemental composition determined by EDXS of samples C, D and E. Results prove the existence of the different metals oxides in the nanostructures.

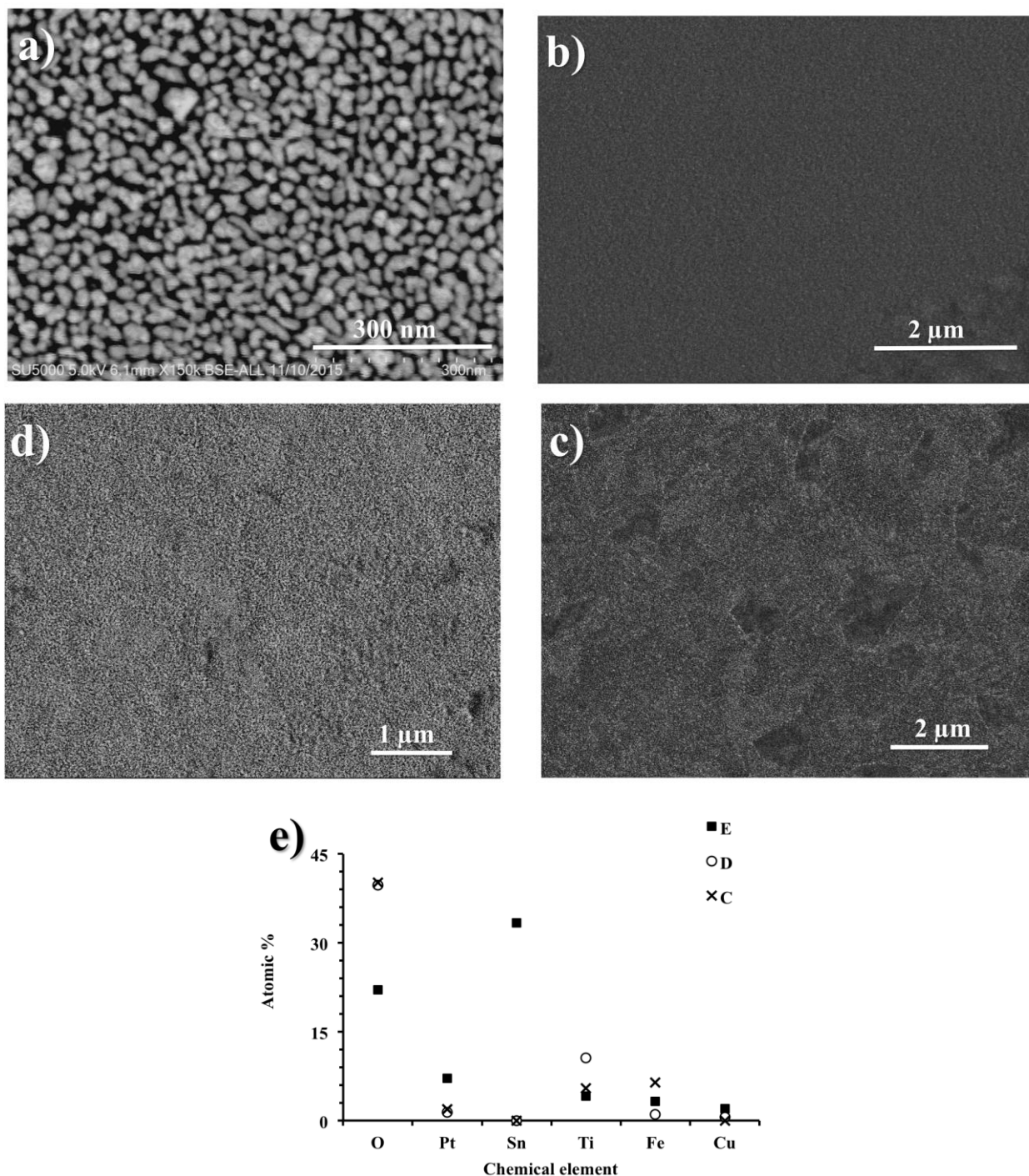


Fig. 1 a) Backscattered SEM micrograph of sample A showing the uniform distribution of Pt nanoparticles. b), c) and d) Secondary SEM micrographs of samples C, D and E, respectively. e) Elemental composition of samples C, D and E proving the existence of different metal oxide layers. All images reveal the surface topography of the developed materials. Most of the images exhibit smooth and uniform coatings.

The crystalline structure and optical absorbance of selected samples appear in Fig. 2. Diffractograms in Fig. 2 a) evidenced the existence of amorphous and crystalline phases on the developed materials. Interestingly, the presence of crystalline TiO_2 as anatase was identified in all cases using the peak at around 25.2° (PDF 021-1272). For sample C, mostly

amorphous components were detected. For samples D and E, the formation of crystalline Pt nanoparticles accompanying the layer of TiO_2 (peaks at around 39.7° and 46.2° , PDF 01-071-6560), was observed.

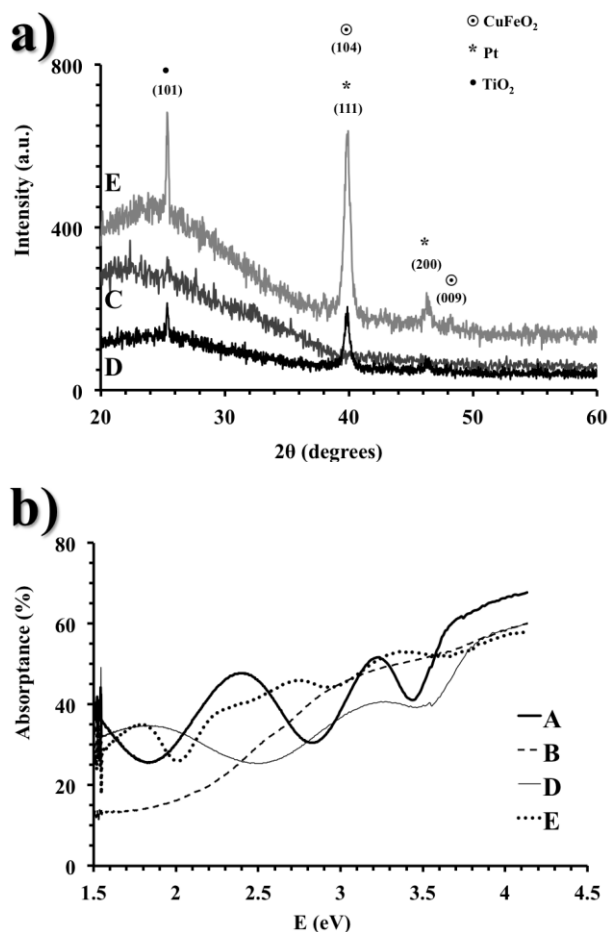


Fig. 2. a) diffractograms of samples C, D and E exhibiting the crystalline structure of the samples. b) absorbance spectra of selected samples.

Also, a barely detected peak at around 47.6° suggests the existence of delafossite phase of CuFeO_2 (PDF 01-075-2146). No crystalline Sn or Fe oxides were identified. Absorbance spectra in Fig. 2 b) was calculated from the total transmittance and reflectance measurements. Outcomes reveal that all materials are able to absorb photons in the UV-Vis region. For most of the cases, absorption in the Vis region was more than 30% and up to 65% in the UV interval (above 3.1 eV). The modulations observed in the absorbance spectra are associated with smooth interfaces and uniform layers' thickness.

B. H₂ generation

The photoassisted generation of H₂ was monitored in a batch reactor under visible light irradiation, using a customized reaction chamber. Outcomes summarized in Fig. 3 a) show that, after 24 h of continuous irradiation with the multiple wavelengths emitted by the lamp (Fig. 3 b), significant generation of H₂ was achieved with most of the samples. Individual layers of TiO₂ and FeO_x in samples A and B,

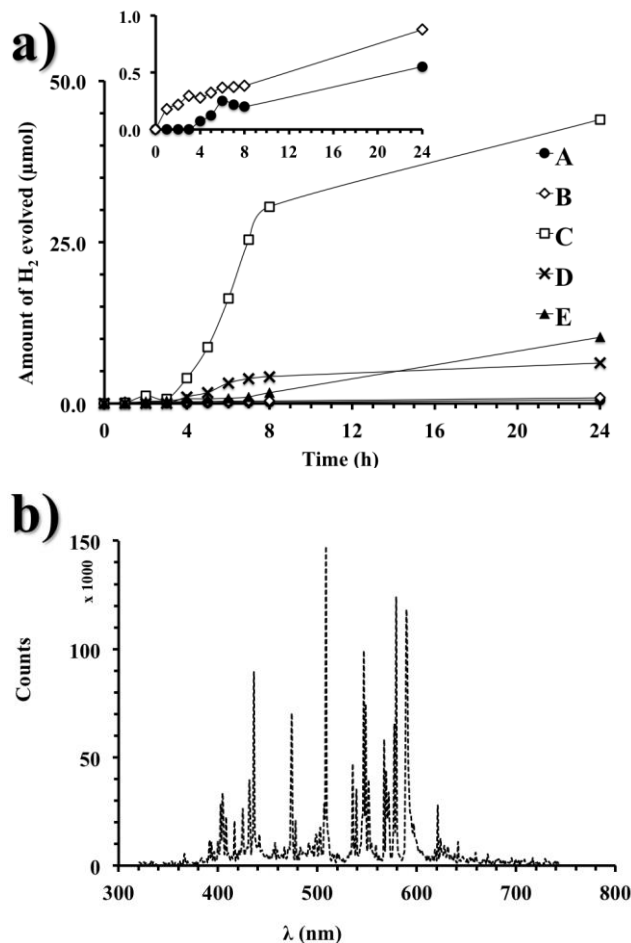


Fig. 3. a) Photoassisted generation of H₂ as a function of time, obtained inside the irradiation chamber. b) Qualitative emission spectrum of the filtered lamp used as excitation source (Hg lamp of 250 W).

presented the less satisfactory outcomes (0.55 and 0.9 μmol, respectively). However, a marked increase resulted within the incorporation of a composite material (CuFeO_2), as in samples D and E. In fact, within the incorporation of an additional amorphous layer of SnO_x (sample E), it was noted that the H₂ generation augmented from 6.26 (sample D) to 10.25 μmol, after 24 h. Moreover, a noteworthy increases of the amount of H₂ (44 μmol) was observed using sample C, which incorporated a composite amorphous layer of Ti and Fe oxides. Since no clear differences among the samples was established, further tests to determine the influence of other parameters, such as the thickness of the layers, stoichiometry of the components, mobility of the carriers, etc., have to be studied in detail.

IV. CONCLUSIONS

Outcomes show that hetero-structures comprising metal oxide based materials can be used effectively for H₂ generation.



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