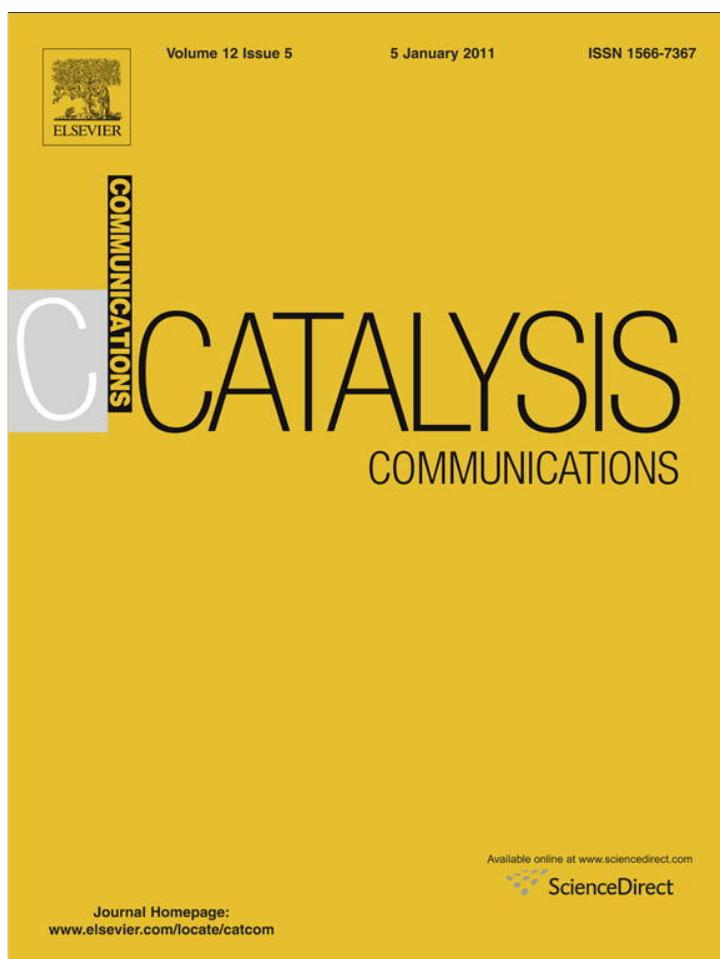


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Short Communication

Platinum-coated nanostructured oxides for active catalytic electrodes

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ABSTRACT

In this work we propose the use of platinum-coated nanostructured oxides for improving the redox rate of active electrodes for applications in catalysts for water splitting, fuel cells, organic depollution, etc. In order to test this concept, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanorods were grown by magnetron sputtering over $\text{Si}/\text{SiO}_2/\text{Ti}/\text{Pt}$ substrates and coated with a platinum layer using the same technique. The performance of this active electrode was studied by cyclic voltammetry and electrochemical impedance spectroscopy. Other Pt films (both dense and porous) deposited on oxidized silicon, and platinum-coated FTO-glass, when tested under the same conditions, were less efficient. The charge transfer resistance and the capacitance of one dimensional platinum-coated nanostructured electrodes were at least one order of magnitude better than those measured for platinum-coated FTO-glass.

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1. Introduction

The increasing need for the replacement of conventional energy sources in favor of carbon-neutral technologies has boosted the research on new materials and devices for clean energy, environmental depollution and to improve catalytic reactions. For instance, solar cells are able to directly convert sunlight into electricity so that a great research effort is currently devoted to developing these devices [1,2]. Dye-Sensitized Solar Cells (DSCs) based on mesoporous titania are low cost photovoltaic devices that have achieved efficiencies up to 11% at one full sun [2–4]. These cells have also reached remarkable stability even when ionic liquids are used [2].

Recently, improvement of charge transfer characteristics has been obtained by using materials such as CdSe or Cu_2S in DSC counter-electrodes [5,6]. One-dimensional (1-D) nanostructures synthesized by chemical or physical methods were proposed as an attractive alternative for reducing the electron-hole recombination processes, consequently increasing efficiency [4,7–9]. These nanostructured electrodes allow the direct connection between the charge-generating sites and the transparent conducting oxide (TCO) layer while maintaining the high surface area typical of the classical films based on nanoparticles [2]. Results for 1-D nanostructure-based DSCs have already been reported [8–11], indicating that electron transfer and electronic transport have a key role on cell efficiency [3,4]. The design of nanostructured anodes has been largely based on nanoparticle thick

films and 1-D nanostructures [3,4,7–9,11,12]. The control of composition and structure of catalytic materials over length scales from 1 nm to 1 μm can provide catalytic materials that accurately and efficiently control reaction pathways, but there are only a few studies concerning the use of nanostructured counter-electrodes for DSCs [12].

In the last few years, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) ceramics have attracted a great deal of research, mainly due to their unusual dielectric properties [13–15]. The fabrication of polycrystalline CCTO nanorods at low substrate temperatures by RF sputtering has recently been reported [16]. These nanostructures grow perpendicular to the substrate, being regular both in length and morphology, with about 50% substrate coverage, allowing a uniform platinum coating to be deposited on their surface. Moreover, this geometry increases the effective electrode surface area and, at the same time, yields a sufficiently open structure for electrolyte permeation. A 2 nm thick layer of Pt is enough for the catalytic action [17]. Thicker layers do not improve charge transfer rate and electrode efficiency.

In this work, we compare the performance of platinum-coated CCTO nanorods with several other Pt-based active electrodes from the point of view of charge transfer resistance and capacitance of redox sites involved in catalytic reactions. We observed that hole regeneration at the electrode/liquid electrolyte interface was improved in the case of iodide/triiodide (I^-/I_3^-) redox couple in acetonitrile. This example is very important in the context of DSC devices, since I^-/I_3^- is the most widely used redox couple for this application. However, the concept of using Pt-coated nanostructured oxides could be extended for any kind of catalytic electrode for applications in environmental and clean energy devices, for instance.

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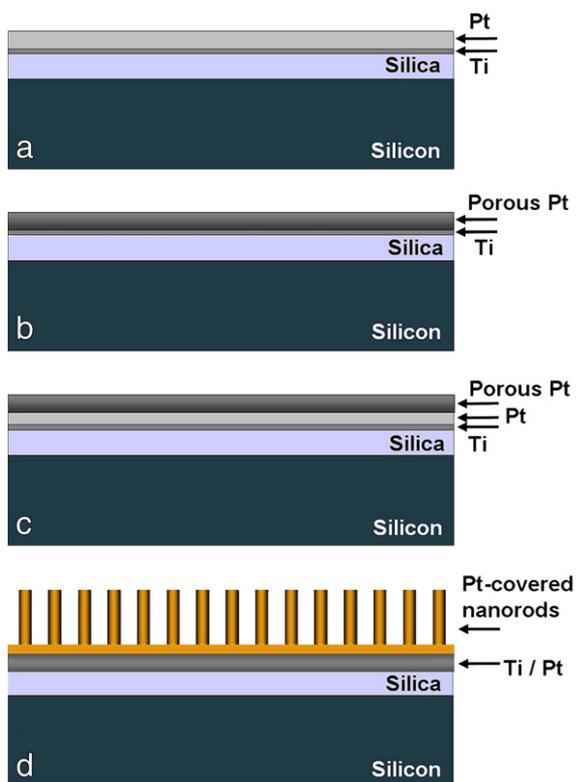


Fig. 1. Schematic drawing showing the layers composing the sputtered counter-electrodes used in this study: a) dense Pt; b) porous Pt; c) dense/porous Pt bi-layer and d) dense Pt/CCTO nanorods/dense Pt coating.

2. Experimental

The samples fabricated for this study are schematically represented in Fig. 1. Platinum-coated CCTO nanostructures as well as

porous and dense platinum thin films were deposited by RF and DC sputtering onto oxidized silicon substrates in a pure argon atmosphere using a target-substrate distance of 15 cm. In order to provide a better adhesion between the electrodes and the substrate, 30 nm thick Ti layers were previously deposited at 2×10^{-2} mbar, 150 W RF power and 200 °C substrate temperature. Dense (Fig. 1a) and porous (Fig. 1b) Pt thin films, as well as a combination of these two morphologies (Fig. 1c), were deposited at a temperature of 200 °C, using DC powers between 36 and 130 W and argon pressures in the range from 2×10^{-2} to 4×10^{-1} mbar. For the fabrication of CCTO nanorods on Si/SiO₂/Ti/Pt substrates, depositions were carried out by sputtering a CCTO target at a pressure of 2×10^{-2} mbar with an RF power of 200 W (Fig. 1d). Over these nanostructures a sputtered platinum coating layer with a thickness of 100 nm (measured *in situ* with a film thickness monitor) was deposited at room temperature (Fig. 1d). Due to the morphology of the sample, the material arriving at the surface meets the nanorods head-on. As a consequence, the tips of the nanorods should have a Pt layer nearly 100 nm thick, but the bodies of the rods receive a much thinner layer, since a “glancing angle” deposition will occur on these surfaces. The relatively large thickness of the Pt layer was chosen in order to guarantee the full coating of these high aspect ratio nanostructures.

The morphology of the samples was observed by means of field-emission scanning electron microscopy (FE-SEM, Zeiss Supra 35). The set of electrodes schematically represented in Fig. 1 was tested regarding their electrical behavior and their response was compared with counter-electrodes based on Pt-coated FTO-glass. The electrical measurements were carried out in a three electrode cell configuration, with the samples performing as the working electrode. The counter-electrode was a Pt plate and the reference electrode was Ag/AgCl in saturated KCl solution (3 M). The charge transfer resistance and the capacitance were measured by Electrochemical Impedance Spectroscopy (EIS) in a liquid electrolyte composed of 0.1 M LiI, 0.05 M I₂, 0.8 M tetrabutylammonium iodide, 0.5 M 4-tertbutylpyridine in acetonitrile and 3-methoxypropionitrile (50:50 volume ratio). This electrolyte is commonly used in DSCs. Cyclic voltammetry

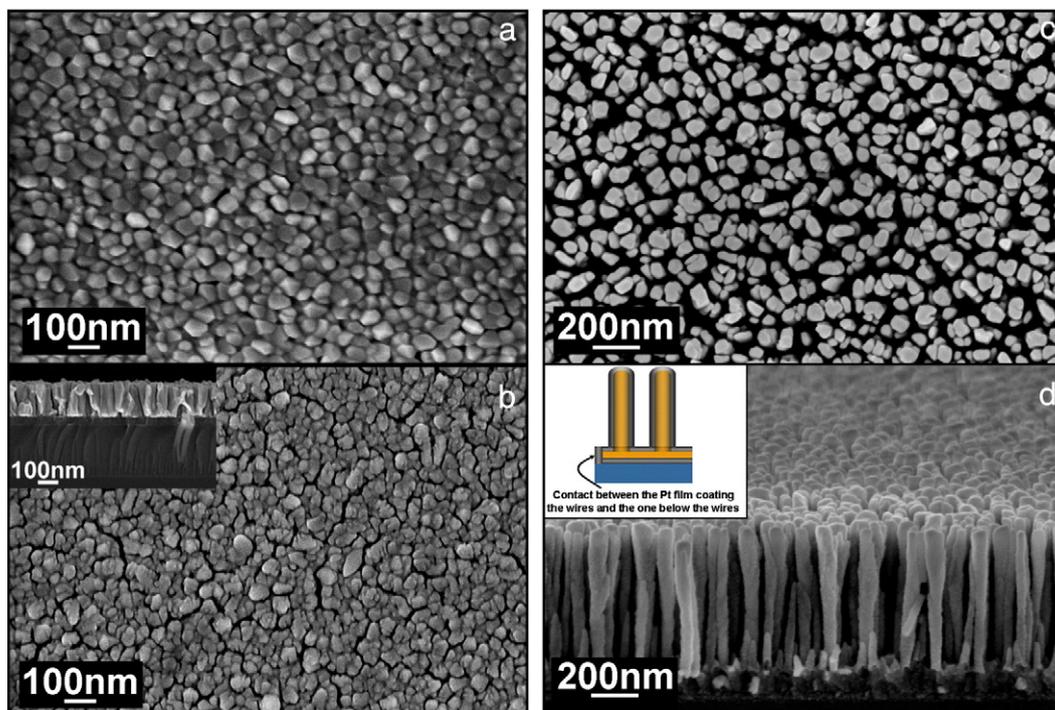


Fig. 2. FE-SEM images for the dense (a) and porous (b) platinum counter-electrodes. The inset shows the columnar structure of a porous Pt film in cross-section. FE-SEM micrographs with surface (c) and the cross-sectional (d) views of the CCTO nanostructured sample. The inset shows a schematic view of the Pt-covered nanorods. Both Pt layers (under and over the rods) are joined at the edge of the substrate.

experiments were performed in the range from -0.5 to 0.5 V at the scan rate of 50 mV.s^{-1} . The EIS measurements were carried out with an AUTOLAB PGSTAT 30 potentiostat with a frequency analysis module. The impedance spectra were measured at different bias potentials (in the range between 0.5 and -0.4 V). The amplitude of the AC signal used was 10 mV and the frequency was varied between 0.01 Hz and 100 kHz . The data were fitted using a classical Randles equivalent circuit model. The target elements during the fitting procedure were the charge transfer resistance and the capacitance of the electrodes.

3. Results and discussion

Fig. 2 shows the FE-SEM images for the dense (Fig. 2a) and porous (Fig. 2b) platinum sputtered active electrodes. As one can notice, the dense Pt sample is characterized by high film uniformity and density, being composed of grains in the range from 20 to 50 nm (Fig. 2a). In contrast, the porous Pt sample exhibits higher porosity and smaller grains (Fig. 2b). Moreover, as presented in the inset of Fig. 2b, this film, with a thickness of 200 nm , has a columnar morphology. Fig. 2 also presents surface (Fig. 2c) and cross-section (Fig. 2d) FE-SEM micrographs of the sputtered CCTO nanorods. The sample is composed of an array of aligned 600 nm long nanorods growing perpendicular to the substrate and exhibiting diameters between 50 and 100 nm . The inset in Fig. 2d shows a schematic drawing of the counter-electrode developed based on the CCTO nanorods coated with a dense Pt film. The coating layer was sputtered immediately after the nanostructural growth, without breaking the vacuum, thus avoiding surface contamination. The same procedure was adopted for the deposition of combined porous/dense Pt layers.

Fig. 3a presents the voltammetric response for the counter-electrodes studied. The redox process related to the injection of electrons in the electrolyte due to the reduction of I_3^- ionic species into I^- can be observed for voltage values from 0.1 to -0.5 . It can be noticed that for Pt-coated FTO-glass and Pt-coated CCTO nanorods, the peak related to this process is well defined when compared to the other counter-electrodes. The reduction process for Pt-coated CCTO nanostructures occurs at higher potential (more positive) and the width of the peak is narrower. These facts indicate a better electrochemical and catalytic performance for this kind of electrode.

On the other hand, dense, porous and dense/porous Pt films obtained by sputtering present a typical capacitive voltammetric response with undefined peak potentials. Similar response is obtained even with the Pt plate, albeit the current peak is higher and similar in shape to that of porous and dense/porous Pt electrodes prepared by sputtering. The dense Pt presented the worst response, most likely due to its low surface area and/or surface passivation.

Fig. 3b,c shows the graphs for charge transfer resistance (R_{ct}) and capacitance (C) obtained through EIS analysis. The R_{ct} provides a direct indication of the catalytic properties of the electrode in the redox couple regeneration process. In DSCs, the R_{ct} directly affects the fill factor: when this value decreases, the fill factor increases, having a positive effect on the efficiency of the cell [18].

For the potentials higher than 0.2 V vs Ag/AgCl , which is the normal operating condition of counter-electrodes in the DSCs, the R_{ct} of Pt-coated CCTO nanorods and Pt-coated FTO glass present the lowest values (Fig. 3b). This result is in good agreement with the data shown in Fig. 3a. For the Pt-coated CCTO nanorods, the R_{ct} presents the best values, decreasing by nearly one order of magnitude when compared to the other sputtered electrodes in this potential range. It is important to mention that R_{ct} performance in Pt-coated FTO-glass, a widely used counter-electrode in DSC devices, is surpassed only by the Pt-coated CCTO nanorods.

Capacitance data in Fig. 3c show that the improvement in R_{ct} is associated to an increase in the active surface. In the negative region of potentials it is possible to ensure that all the Pt films studied are fully

saturated with electrons. Therefore, the observed capacitance is the Helmholtz capacitance of the film surface. The Pt plate, dense Pt, porous Pt and combined (dense/porous) Pt electrodes present similar values of capacitance in this region; consequently, their charge transfer resistance is very similar. In the case of Pt-coated FTO glass and Pt-coated CCTO the increased capacitance indicates the larger active surface responsible for the decrease in R_{ct} . In the case of Pt-coated nanorods the pronounced increase in capacitance observed is derived from the nanostructured surface. Data in Fig. 3 indicate that for the porous Pt and the combined dense/porous Pt electrodes, the expected increase in surface area and activity is not obtained. Other effects, such as surface passivation may be responsible for the reduction in the performance of these electrodes [7].

The prominent effect obtained for the Pt-coated CCTO electrode confirms the observation that 1-D nanostructures may amplify the

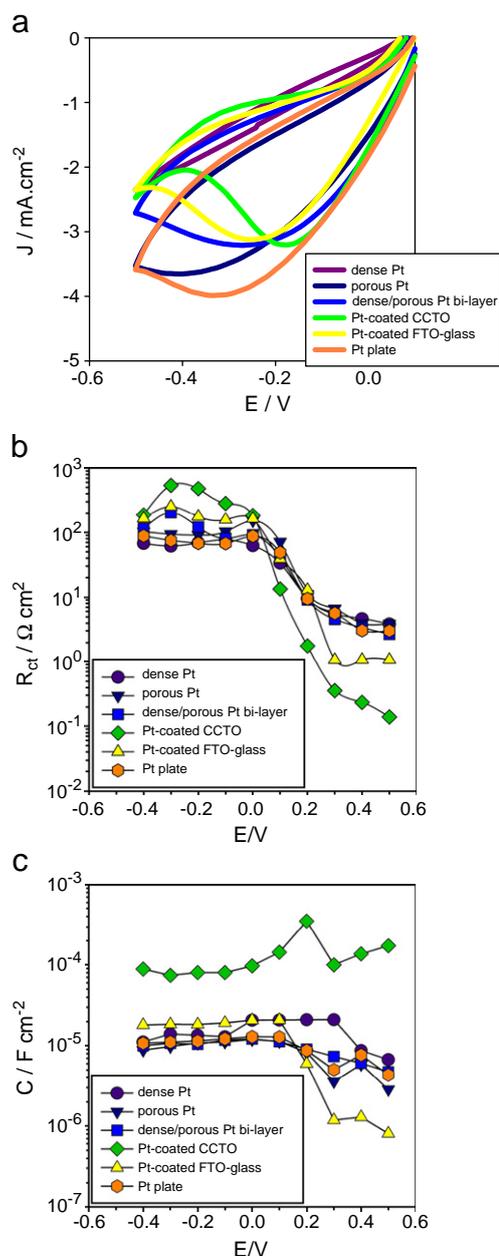


Fig. 3. (a) Voltammetric cyclic response and (b) charge transfer resistance and (c) capacitance derived from the EIS measurements of the sputtered counter-electrodes based on dense Pt, porous Pt, porous/dense Pt thin films and Pt-coated CCTO nanorods in comparison with Pt-coated FTO-glass electrodes.

number of active sites for the electrolyte reduction and hole regeneration processes that occur at the electrode/electrolyte interface.

4. Conclusion

In conclusion, we demonstrate the possibility of developing high-performance solar cell counter-electrodes based on nanostructured platinum-coated oxides with suitable 1-D morphologies. Some of the advantages of using oxide nanostructures covered with platinum instead of platinum nanostructures are the smaller amount of platinum needed for obtaining the same surface area, the freedom to use different sizes and morphologies for the nanostructures (for the oxides, the variety of possible sizes and shapes for the nanostructures is remarkable) and the possibility to use a large number of chemical and physical methods for fabrication. The concept proposed here could be extended to a variety of electrochemical and photocatalytic applications.

Specifically, the electrodes studied herein improved the kinetics of both redox and hole regeneration processes in an electrocatalytic surface that could be useful for DSC applications.

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