

On the behavior of modified TiO₂ nanotubes for a photoanode-driven photoelectrochemical reduction of CO₂

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ABSTRACT

Chemical reduction of CO₂ is thermodynamically feasible only in the presence of strong reducing agents. Photoelectrochemical (PEC) reduction represents one of the possible alternatives: this technique may be considered “green” when solar energy and water are used to drive the process, like in natural photosynthesis. Different system configurations and different experimental conditions are needed, depending on the use of photosensitive material as cathode, anode or both in the PEC cell. In the present paper we investigated the possibility to use a photoanode-driven PEC cell, in which a metal was used as cathode, while the anode material was a nanotubular structure of TiO₂. The photocatalytic performance of the anode was improved by deposition of tungsten oxide. Electrodeposition was performed both by potential step (PST) and pulse potential technique (PPT). Different morphology of the deposit was obtained and, in turn, different performance was measured in terms of photocurrent at the related samples.

Keywords: titania nanotubes, tungsten oxide electrodeposition, photoelectrocatalysis, pulse and step potential techniques.

1 INTRODUCTION

Carbon dioxide is one of the main greenhouse gases responsible for global warming. Due to the high costs of its disposal, many efforts have recently been addressed to its reuse: converting CO₂ to valuable compounds such as CO, methane and methanol, allows considering it as a feedstock, rather than a waste product [1, 2].

Actually, chemical reduction of carbon dioxide is thermodynamically feasible but only in the presence of strong reducing agents [2]. In alternative, electroreduction of CO₂ has been widely studied. The literature reports excellent overview of possible products obtained by electrochemical CO₂ reduction, at different electrode materials and experimental conditions [1-7]. However, research on this topic is still opened, being high energy efficiency achievable through a combination of high faradaic efficiency for the desired product, and low cell potential [4].

In this contest using a PEC cell, in which at least one electrode is a photosensitive material, could represent a valid solution to reduce the cell voltage.

In the present paper a photoanode-driven PEC cell is considered in which the lowering of the cell voltage is obtained from the photopotential generated at the nanotubular structure of TiO₂ n-type semiconductor, irradiated by a suitable light wavelength. This anode could be coupled with metals or metal composite oxides, which are indicated in the literature as effective cathodic materials to this aim [3]. Titania nanotubular anodes were already tested in our laboratory for the photoelectrolysis of water or oxidation of organics [8-11]. The basic properties of the original structure, such as regular architecture, straight path for photogenerated carriers, and high specific surface, confirmed the effectiveness of the samples in the UV range of light. In those cases a nominal 1 cm² of active surface was used.

In the present work a scale up of the system has been made to obtain electrodes of 15 cm². Moreover, to improve the final photocatalytic performance in the near visible range, surface modification by tungsten oxide was attempted. Electro-deposition was performed both by step potential (SPT) and pulse potential (PPT) techniques. Depending on the experimental technique, different morphologies of the deposit were obtained and in turn, different performances were measured in terms of photocurrent at the related samples.

2 EXPERIMENTAL

2.1 Preparation of nanotubular structures

Ti foils (0.25 mm thickness, 99.7 % metal basis, Aldrich) of 5 cm diameter were used as raw material to obtain the nanotubular structures by electrochemical oxidation (final samples are indicated as NT5 in the rest of the text). Figure 1 shows a schematic view of the electrochemical cell used to obtain NT5 samples. The teflon cell is composed by one cylindrical chamber (d=4.4 x h=5 cm) containing the electrolyte solution. The electrical contact with the Ti foil was realized by means of an aluminium disc (d=5 x h=0.5 cm) located at the bottom side of the cell. The electrode/electrolyte contact area was 15 cm². A platinum grid cathode was set at 1 cm distance, in front of the anode. Prior to the electrochemical oxidation,

Ti foils were degreased by sonication in acetone, then in isopropanol and finally in methanol; then, they were rinsed with deionized water and dried in a Nitrogen stream.

The oxidation process was performed in (10%) deionized water / (90%) glycerol organic solution with 0.14 M of NH_4F at room temperature. A potential ramp was imposed from open-circuit-voltage (OCV) at a fixed potential of 20 V with a scan rate of 100 mVs^{-1} . The applied potential was maintained at this fixed value for 4 h.

A final annealing treatment was required in order to transform the amorphous structure into crystalline one. Thermal treatment was performed in air atmosphere at 400°C for 1 h.

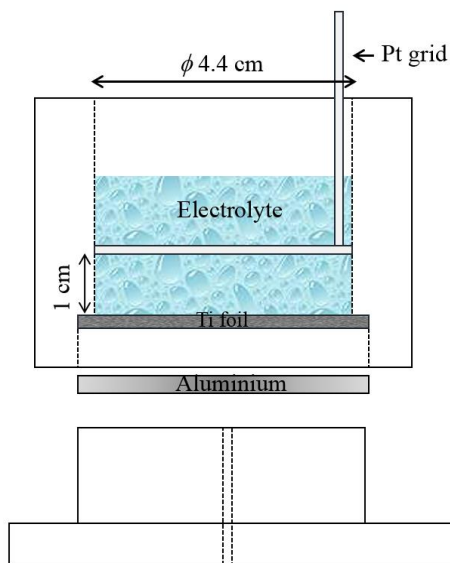


Figure 1: Electrochemical cell for NT5 preparation.

2.2 Electrodeposition of tungsten oxide

The electrodeposition of tungsten oxide was performed at room temperature in a classical three-electrode cell in which a saturated calomel electrode (SCE) was the reference, a platinum grid was the counter electrode, while titania was used as working electrodes. To this aim samples of 3.75 cm^2 nominal area, were derived by cutting an NT5 sample, previously obtained (final samples at which deposit of tungsten oxide was obtained are indicated as NTW x in the rest of the text, x indicating the deposition time). The electrodes were connected to a potentiostat-galvanostat (Amel 7050), controlled by Junior Assist software. A receipt suggested by the literature was adopted to deposit tungsten oxide [12]. Typically, 25 mL of electrolytic solution, composed by 25 mM Na_2WO_4 , 30 mM of concentrated H_2O_2 , was used. pH of the solution was adjusted to 1.4 by adding nitric acid.

Preliminary voltammetric study was performed (results not showed) which allowed to individuate the main reductive wave at -0.3 V vs. SCE. This potential value was adopted in the deposition process of tungsten oxide by

potentiostatic runs. To this aim both step (SPT) and pulse (PPT) techniques were used in order to obtain the oxide deposits over the nanotubular structures. During SPT, the electrodeposition of tungsten oxide was performed at different times, fixing the potential value at -0.3 V for 8 and 12 min, respectively. During PPT the potential was alternately swiftly between opened circuit potential (OCV = 0.4 V) and -0.3 V . A serie of pulses of equal amplitude but different width was performed. Each pulse consisted of an ON-time of 10 s during which -0.3 V was applied, and an OFF-time of 1 s during which the electrode was maintained at OCV. The number of pulses required to reach the same deposition times adopted for the deposition step technique, was calculated according to the ON-time duration. The current density was recorded during all the deposition experiments. The obtained NTW x samples were annealed in air atmosphere at 400°C for 1h.

2.3 Characterization of the samples

The uniformity of the NT5 structure and its photoactivity was tested in the three-electrode cell: cyclic voltammeteries and photo-currents were measured at 9 points of the NT5 sample (see figure 2). Specific runs were performed in which a teflon holed mask allowed one section a time to be exposed to the solution and to the irradiation of a Xenon lamp (nominal power: 300W). The photocurrents were recorded at different wave lengths; also measurements were done in which the lamp was used without filter, in order to simulate the solar radiation. SEM analysis was performed to investigate on the morphology of the structures. Elemental maps were also collected for NTW x samples to assess the presence of W.

3 RESULTS AND DISCUSSION

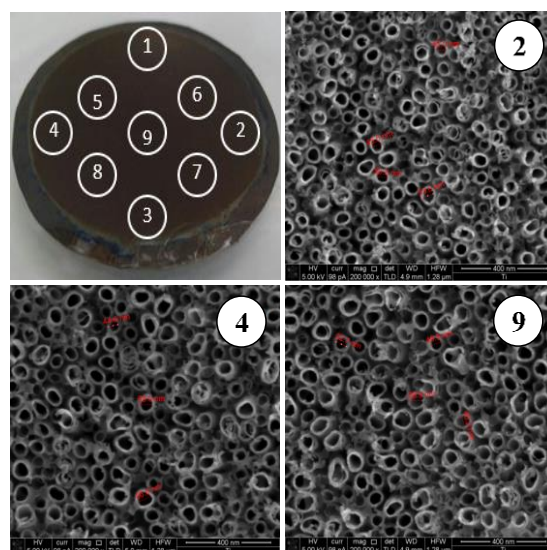


Figure 2: SEM micrographs of NT5 sample at 3 investigated points.

The adopted procedure, described in the experimental section, allowed us to obtain NT5 with an active surface of 15 cm².

Figure 2 shows some examples of the results of the SEM analyses performed at different section points in order to verify the uniformity of the NTs.

If we exclude the border line effects (about 5mm corresponding to the thickness of the wall of the cylindrical cell), a almost regular structure of the NTs was observed with a mean tube diameter between 40 and 50 nm measured in different points of the sample.

Also border effects are visible from the results obtained from photocurrent measurements. Figure 3 resumes the values of photocurrent measured at the different points of the active surface. Also in this case we may observe a quite regular trend, most in the central part of the surface, while peripheral points 1,2,3,4 exhibit lower values. However, in this case, the effect could result not only from border effects, but also from a higher concentration of the light irradiation in the central part of the spot emitted by the Xenon lamp.

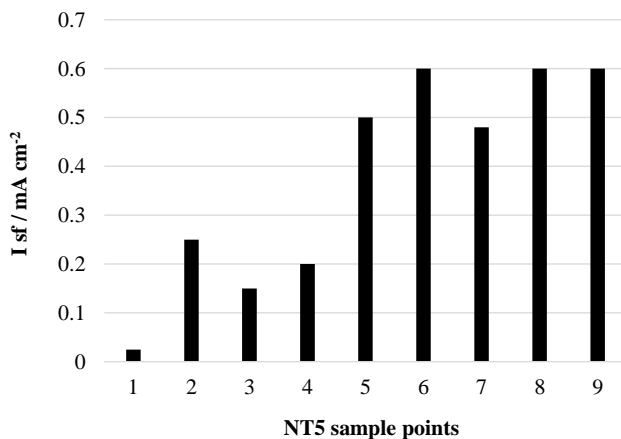


Figure 3: Photocurrents density distribution at NT5 sample obtained by irradiating with the Xenon lamp without filter.

Slight morphological differences observed in different points of the sample also resulted in a slight shift of the peak current densities in the CV, as shown in Figure 4, while no variation of the peak potential position was observed.

Similar results were obtained at the different samples prepared under the same conditions, confirming a good uniformity and, overall, a good reproducibility of the synthesis.

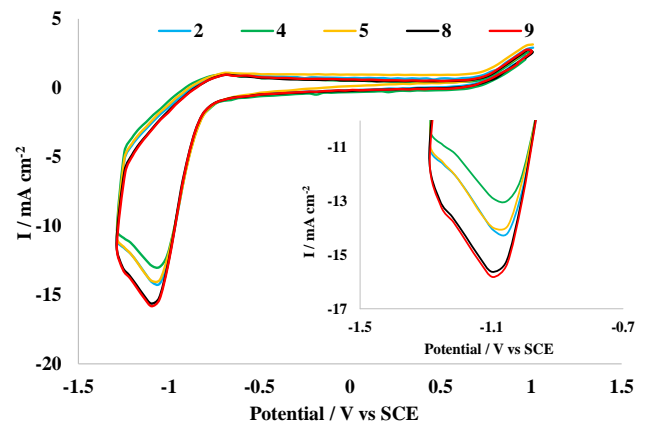


Figure 4: Cyclic voltammeteries of NT5 sample recorded in different points of the surface.

Figure 5 shows the results of photoactivity of the NTW_x samples, in terms of photocurrents obtained by irradiating the samples with light of 380 and 400 nm wavelength.

In particular, data obtained with PPT and SPT are compared with those obtained at original NT (no tungsten deposit).

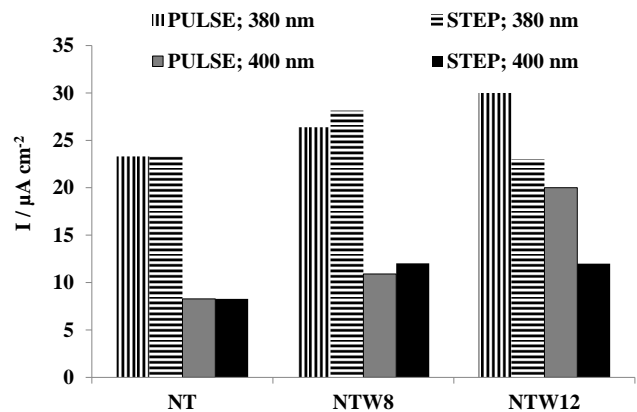


Figure 5: Effect of electrodeposition method on the photocurrents density response at different wave lengths.

A slight increase of the performance is generally observed at samples where tungsten oxide was deposited. Moreover, as we expected, at the highest wave length lower values of photocurrent are obtained (full bars). If the data related to samples obtained by PPT are considered, at both 380 nm (vertical lines bars) and 400 nm (gray bars), an increasing trend is observed while passing from NT to NTW8 and NTW12. The trend is different when we consider the results related to samples obtained by SPT: actually, a sort of saturation point may be observed at 400 nm (black bars) at which the performance at NTW12 is almost the same as at NTW8, and especially at 380 nm

(horizontal lines bars) where the performance of NTW12 is even lowered with respect to that measured at NTW8.

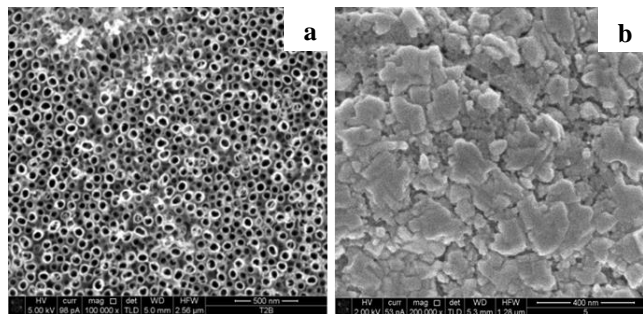


Figure 6: SEM micrographs of electrodeposited tungsten oxide obtained by SPT at a) 8 min; and b) 15 min.

In order to justify these results also the morphology of the tungsten oxide deposit has been considered. Elemental map analysis of the surface (data not shown) indicated a regular distribution of W all over the surface: according to the pH (1.4) and V (-0.3 V), at which the deposit is obtained, WO_3 could be the termodinamically stable form of W [13]. Figure 6 shows as an example, the sample surface after a step potential of 8 minute (left) and 15 minutes (right) was applied. As we can observe, the high deposition time provoks an eccess of deposit which plugs all the NTs so that the performance is strongly affected.

4 CONCLUSIONS

This paper reported the results of an experimental work in which an attempt is made to scale up the process of oxidation of Ti foils, obtaining titania NTs of 15 cm^2 nominal surface to be used in a photoanode-driven PEC cell. The results confirm the quite regular structure of the samples, in terms of morphology and photoactivity.

Samples were also used to derive the substrates to test the tungsten oxide deposition, performed with SPT and PPT. Even if the exact composition of the oxide is not identified, the results obtained up to now indicate the presence of W on the nanotubular structure of the electrodes as well as its positive effect on the photoactivity. Deposition with the PPT seems to give better results. In particular the performance obtained at NTW12 at 400 nm is very similar to that measured at the sample obtained by SPT at 380 nm.

However, it must be observed that the data reported in this paper are not optimised: in particular, an optimum in the times selected for the deposits has to be identified. Further research will be addressed to study this effect both for PPT (in order to evaluate the effect of different times of

the ON-OFF states), and especially for samples obtained by SPT, because high deposition times may originate deposits which may shield the nanotubular structure, which in turn loss the good properties, so decreasing the performances of the whole electrode. Moreover, a comparison based on the electrical charge involved in the two techiques will be performed.

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