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PHOTOELECTROCHEMICAL CHARACTERIZATION OF ANATASE- RUTILE MIXED TiO₂ NANOSPONGES

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Abstract

This work studies the influence of using hydrodynamic conditions during anodization on the morphology and electrochemical properties of anatase/rutile mixed TiO₂ nanotubes (Reynolds number, $Re = 0$) and nanosponges ($Re > 0$). To this purpose different techniques were used, such as: microscopy techniques (Field-Emission Scanning Electron Microscope, FE-SEM, and Confocal Laser-Raman Spectroscopy), Electrochemical Impedance Spectroscopy (EIS), Mott Schottky (MS) analysis and photoelectrochemical water splitting tests. This investigation demonstrates that the morphology of TiO₂ nanostructures may be greatly affected due to the hydrodynamic conditions and it can be adjusted in order to increase the efficiency for energy and environmental applications.

Keywords: anatase/rutile mixed TiO₂, hydrodynamic conditions, water splitting, Electrochemical Impedance Spectroscopy, Mott-Schottky analysis.

1. Introduction

In recent years, growing consideration has been given to the design and fabrication of nanostructured metal oxides because of their unique and promising properties and applications [1-27]. In this way, nanostructures can be tailored to possess a characteristic nanosize, high surface area and porosity.

Titanium dioxide, TiO_2 , has many interesting properties that have turned it into the most studied compound for photochemical and photoelectrochemical purposes. TiO_2 nanostructures have a wide application in dye-sensitized solar cells and photocatalysis [1-6, 8, 9, 11, 14-18]. Moreover, TiO_2 nanostructures can be used to solve environmental problems, such as treatment and purification of polluted aqueous systems [7, 8, 12, 28].

In order to prepare TiO_2 nanostructures, various approaches have been reported, such as sol-gel techniques, hydrothermal methods, atomic-layer deposition, anodization, etc. [3]. Anodization allows fabricating highly ordered arrays of TiO_2 nanostructures in a controlled and reproducible way. Moreover, TiO_2 nanostructures formed by anodization grow directly on titanium, which is very useful, since it results in functional TiO_2 photoelectrodes that do not need to be compacted or sintered onto a back contact.

Recently, a new type of anodic nanosponges has been synthesized by means of electrochemical anodization of titanium under hydrodynamic conditions [15, 18]. This synthesis route provides photoelectrodes with high specific surface area and a direct connected path for electrons, properties that make nanosponges be suitable for their use

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6 in photoelectrochemical applications.
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10 In the present work, the influence of Reynolds number (Re) on the morphology and
11 electrochemical properties of anatase/rutile mixed TiO_2 nanotubes ($Re = 0$) and
12 nanosponges ($Re > 0$) has been studied by using different microscopy techniques (Field-
13 Emission Scanning Electron Microscope, FE-SEM, and Confocal Laser-Raman
14 Spectroscopy), Electrochemical Impedance Spectroscopy (EIS), Mott Schottky (MS)
15 analysis and photoelectrochemical water splitting tests. This investigation demonstrates
16 that the morphology of TiO_2 nanostructures may be greatly affected due to the
17 hydrodynamic conditions and it can be adjusted in order to increase the efficiency for
18 energy and environmental applications.
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31 **2. Experimental procedure**

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36 Titanium samples were cylinders 8 mm in diameter and with 99.3% purity. Prior to the
37 anodization process, the titanium rod surface was abraded with 500 to 4000 silicon
38 carbide (SiC) papers, in order to obtain a mirror finish. After this, the sample was
39 sonicated in ethanol for 2 min and dried in a N_2 stream. The polished Ti samples were
40 anodized in a glycerol/water (60:40 vol.%) electrolyte containing 0.27 M NH_4F , at
41 different Reynolds number (from $Re = 0$ to $Re = 500$) and at room temperature, by
42 increasing the potential from zero to 30 V at a rate of 200 mV s^{-1} , applying
43 subsequently the potential of 30 V for 3 hours. Anodization was performed in a
44 conventional two-electrode cell with a rotating electrode configuration and a platinum
45 mesh as counter electrode. The active anode area exposed to the electrolyte was 0.5
46 cm^2 . During the process, anodization current density was monitored with a computer.
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1 After anodization, the sample was washed with distilled water and ethanol and then
2 dried in a N₂ stream. Finally, the as-anodized samples were annealed at 650° C for 1
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4 hour in air atmosphere.
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9 After each test, a Field-Emission Scanning Electron Microscope (FE-SEM) was used
10 for morphological characterization of the obtained samples. The materials were also
11 examined by Raman spectroscopy (Witec Raman Confocal microscope) after the heat
12 treatment, in order to evaluate their crystalline structure. For these measurements the
13 samples were illuminated with a 632 nm neon laser using 420 μW.
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24 For the electrochemical and photoelectrochemical water splitting tests, a three-electrode
25 configuration was used. The area of the TiO₂ nanostructures (working electrode)
26 exposed to the test solution was 0.13 cm². A saturated Ag/AgCl (3 M KCl) electrode
27 was the reference electrode, and a platinum tip was the counter electrode. The
28 electrochemical measurements were conducted in a 0.1 Na₂SO₄ solution using an
29 Autolab PGSTAT302N potentiostat under dark conditions (without irradiation). EIS
30 experiments were conducted over a frequency range from 100 kHz to 10 mHz with a 10
31 mV (peak to peak) signal amplitude. MS plots were subsequently obtained by sweeping
32 the potential from the open circuit potential in the negative direction at 10 mV s⁻¹ with
33 an amplitude signal of 10 mV at a frequency value of 10 kHz.
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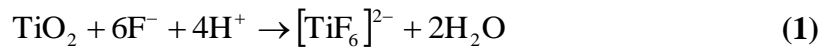
51 The photoelectrochemical experiments were carried out under simulated sunlight
52 condition AM 1.5 (100 mW cm²) in a 1M KOH solution. Photocurrent vs. potential
53 characteristics were recorded by scanning the potential from -0.8 V_{Ag/AgCl} to 0.5
54 V_{Ag/AgCl} with a scan rate of 2 mV s⁻¹. Photocurrent transients as a function of the
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1 applied potential were recorded by chopped light irradiation (60 s in the dark and 20 s in
2 the light). Samples were left at 0.5 V_{Ag/AgCl} in the light for one hour, in order to evaluate
3 their resistance to undergo photocorrosion attacks.
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9 **3. Results and discussion**

10 *3.1. Current density transients during anodization*

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19 The formation and growth of the TiO₂ nanostructures was monitored by recording the
20 current density-time behavior (**Figure 1**). Current density transients shown in **Figure 1**
21 were obtained once the final potential of 30 V was reached, after applying a potential
22 ramp of 200 mV s⁻¹ from a potential of zero to 30 V. During the first seconds of
23 anodization at 30 V (stage I in **Figure 1**), the current density decreased sharply,
24 indicating the growth of an anodic TiO₂ layer on the electrode surface. After this initial
25 stage, an increase in current density indicated the onset of TiO₂ dissolution due to the
26 presence of fluoride ions in the electrolyte (stage II), according to the following reaction
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49 In stage II, the TiO₂ dissolution by the F⁻ attack was highly localized, and irregular
50 nanoscale pits nucleated throughout the electrode surface. After that, the current density
51 reached a local maximum and started decreasing and increasing again, eventually taking
52 constant values (stage III), indicating the establishment of a steady state between the
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1 rate of TiO₂ formation and dissolution by the action of F⁻. It was in this third stage that
2 the formation of a regular nanotube or nanosponge layer took place.
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7 It can be observed from **Figure 1** that current densities increased, in general, with
8 increasing Re, in each of the three stages described above, indicating that hydrodynamic
9 conditions enhanced the electrochemical processes taking place during anodization,
10 especially the growth of a nanostructured layer at a steady state current density. The
11 increase in current density in the last stage is more marked when changing from Re = 0
12 to Re = 100 than at different Re > 0. Hence, the formation of nanosponges occurred at
13 high reaction rates than nanotubes. As it will be commented in the next section, these
14 high reaction rates are directly related to an increase in the active area of nanosponges
15 with respect to nanotubes.
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31 *3.2. Morphological characterization by means of Field Emission Scanning Electron* 32 *Microscopy (FE-SEM)* 33 34 35 36 37 38

39 The anodized nanostructures were morphologically characterized using a FE-SEM and
40 the obtained results are presented in **Figure 2**. Clearly, two different morphologies are
41 determined by the use of hydrodynamic conditions during anodization. First, under
42 static conditions, **Figure 2a** shows a nanotubular morphology typical of self ordered
43 nanotubes (**Figure 2b**) grown in glycerol-water electrolytes [30, 31], with irregular
44 open pores (140-230 nm), which does not present an initiation layer or nanograss. On
45 the other hand, under stirring conditions (Re > 0) the nanotubular morphology is
46 changed to anodic nanosponge, which is characterized by a connected and highly
47 porous TiO₂ structure with pore openings of approximately 50 nm (**Figures 2c-g** and
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1 **Figure 2h**, top and cross sectional views, respectively). According to **Figure 2**, the
2 porosity of the nanosponges seems to increase with Re.
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7 Additionally, the effect of hydrodynamic conditions is to increase the thickness of the
8 nanostructures from approximately 1.7 μm for the nanotubes ($\text{Re} = 0$) to roughly 4.4 μm
9 for the nanosponges synthesized at $\text{Re} = 500$ (**Figure 3**). However, the increase in the
10 thickness of the layers is more pronounced from $\text{Re} = 100$ to $\text{Re} = 200$ (2 to 3.9 mm,
11 respectively).
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22 *3.3. Characterization of the crystallinity of the nanostructures by means of Raman* 23 *Confocal Laser Microscopy* 24

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30 Raman Confocal Laser microscopy was used in order to determine the crystalline
31 phases of the nanostructures. The nanostructures before the heat treatment consisted of
32 amorphous TiO_2 , since no peaks were registered in the Raman measurements. **Figure 4**
33 shows, as an example, the Raman spectra of the amorphous nanotubes anodized at $\text{Re} =$
34 0. On the other hand, annealing the samples at 650 $^\circ\text{C}$ for 1 hour in air produces the
35 crystallinity of TiO_2 in both anatase and rutile phases. In this way, **Figure 4** shows, for
36 instance, the Raman spectra corresponding to the obtained nanotubes (anodized at $\text{Re} =$
37 0) and nanosponges (anodized at $\text{Re} = 500$), where the characteristic peaks of anatase
38 and rutile phases are presented; i.e. the five allowed modes of anatase: 143 cm^{-1} (E_g),
39 197 cm^{-1} (E_g), 395 cm^{-1} (B_{1g}), 517 cm^{-1} (A_{2g}) and 638 cm^{-1} (E_g) (indicated as A in
40 **Figure 4**) [32, 33] and the rutile peaks: 144 cm^{-1} (superimposed with the 143 cm^{-1} peak
41 of anatase phase) (B_{1g}), 235 cm^{-1} (two-phonon scattering), 445 cm^{-1} (E_g) and 612 cm^{-1}
42 (A_{1g}) (indicated as R in **Figure 4**) [33, 34].
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3.4. Electrochemical characterization

3.4.1. EIS measurements

EIS measurements were carried out in a 0.1M Na₂SO₄ solution at open circuit potential under dark conditions and at 25° C, in order to characterize the electrochemical properties of the nanotubes and nanosponges formed at different Re. **Figure 5** shows the experimental Nyquist (**Figure 5a**), Bode-phase (**Figure 5b**) and Bode-module (**Figure 5c**) plots for the nanostructures, together with a diagram of the equivalent circuit used to fit the EIS data (**Figure 5d**).

Regarding the information provided in the Nyquist plots, all the TiO₂ nanostructures possess one or two distorted small semicircles at high and intermediate frequencies followed by an unfinished semicircle at low frequencies, with higher amplitude. The amplitude of the small semicircle obtained at high frequencies is lower for the nanotubes anodized at Re = 0, and in general, the amplitude of the semicircle decreases with Re (see inset of **Figure 5a**). Additionally, the Bode-phase plots reveal the presence of three time constants. For the nanosponges anodized at Re = 500, only two peaks can be clearly observed in the Bode-phase plots (one at high-intermediate frequencies and another at low frequencies). This is due to the fact that the peak at intermediate frequencies involves the two time constant presented for the rest of nanostructures at high-intermediate frequencies.

In order to explain the obtained EIS data, an equivalent electrical circuit with three RC time constants was proposed (**Figure 5d**). Constant phase elements (*CPEs*) have been used instead of pure capacitors to account for frequency dispersion and non-ideality.

The elements proposed for the equivalent circuit are: the electrolyte resistance (R_s), the first time constant (R_1CPE_1), which is related to the TiO₂ nanoporous/nanotubular structure [11, 35-38], the second time constant (R_2CPE_2), associated with the rutile layer accumulated at the bottom of the nanostructures array and the third time constant (R_3CPE_3), related to the compact TiO₂ layer formed beneath the nanostructures arrays [6, 39]. The presence of rutile after annealing the samples at 650 °C during 1 h was confirmed using the Raman Confocal microscope. During the heat treatment, the walls of the TiO₂ nanostructures transform into anatase phase whereas a layer at the bottom transforms into rutile [1, 40, 41].

The values of the equivalent circuit parameters are shown in **Table 1**, where *CPEs* have been converted into pure capacitances, *C*, by using the following equation [42, 43]:

$$C = \frac{(Q \cdot R)^{1/\alpha}}{R} \quad (2)$$

where *Q* is the impedance of the *CPE* and *R* corresponds to R_2 and R_3 when determining capacitance values of the second and third time constants in **Figure 5d**. To determine C_1 from CPE_1 , *R* has been calculated as follows:

$$\frac{1}{R} = \frac{1}{R_s} + \frac{1}{R_1} \quad (3)$$

According to **Table 1**, the values of R_s for all the nanostructures are almost constant (around 43 Ω·cm²). The values corresponding to R_1 , R_2 and R_3 are of the order of kΩ·cm². The higher values of R_3 are consistent with the resistance of a compact TiO₂

1 layer. The values of the resistance of the rutile layer (R_2) are much lower than the
2 corresponding to a compact TiO_2 layer but higher than the resistance values of the
3 anatase nanostructures arrays (R_1). This is in agreement with the lower conductivity of
4 the rutile phase compared to the anatase one [3, 44, 45]. **Table 1** also shows that the
5 values of R_1 and R_2 (resistance corresponding to the array-bottom of the nanostructures)
6 decrease under hydrodynamic conditions, indicating that the nanosponges possess
7 higher electrical conductivity and surface area than the nanotubes formed under
8 stagnant conditions. No clear tendency of R_3 values is observed with Re , indicating that
9 the electrical properties of the compact TiO_2 underlayer are not dependant on the
10 hydrodynamic conditions.
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26 The values of α for each of the phase constants are not affected by the flowing
27 conditions and remain almost constant regardless of the Re . On the other hand, C_1
28 values are lower than those of C_2 , and the C_3 values are considerably higher than the C_2
29 ones, regardless of the value of Re . Additionally, all the capacitance values are higher
30 for the nanosponges in comparison to the nanotubes. This could be associated with a
31 decrease in the thickness of the particular layer or by an increase in the porosity of this
32 layer as a consequence of a transition to a more porous layer in the case of the
33 nanosponges [6, 39]. In this particular case, since the thickness of the nanosponges is
34 higher than the corresponding to the nanotubes (**Figure 3**), the increase in C_1 and C_2
35 with Re can be related to a higher porosity of the nanosponges.
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3.4.2. MS analysis

To study the influence of hydrodynamic conditions during the formation of TiO₂ nanostructures on their electronic properties, the electrochemical capacitance of the TiO₂ photoanode/electrolyte interfase was measured as a function of the applied potential. Mott-Schottky analysis was performed to obtain the donor density, N_D , as well as the flat-band potential, U_{FB} , of the anatase/rutile mixed TiO₂ nanotubes and nanosponges formed at different Re. The total capacitance has been calculated from the imaginary component of the impedance (Z'') using the relationship $C = -1/\omega Z''$, where ω is the angular frequency. MS plots have been obtained at a frequency of 10 kHz since at this high value the capacitance dependence on frequency is eliminated [18, 46, 47].

Figure 6 shows the MS plots at a frequency of 10 kHz of the different TiO₂ nanostructures. The positive slopes of the MS plots are characteristic of n-type semiconductors, with the dominant defects being oxygen vacancies [11, 16, 48-51]. The MS equation for n-type semiconductors:

$$\frac{1}{C^2} = \frac{2}{\varepsilon_r \varepsilon_0 e N_D} \left(U - U_{FB} - \frac{kT}{e} \right) \quad (4)$$

where ε_r represents the relative dielectric constant of the TiO₂ nanostructures (a value of 100 has been assumed [14, 16, 18]), ε_0 is the vacuum permittivity ($8.85 \cdot 10^{-14}$ F cm⁻¹), e is the electron charge ($1.60 \cdot 10^{-19}$ C), N_D is the donor density, U_{FB} is the flat-band potential, k is the Boltzmann constant ($1.38 \cdot 10^{-23}$ J K⁻¹) and T is the absolute temperature.

1 The values of N_D and U_{FB} are presented in **Table 2** for the anatase/rutile mixed TiO₂
 2 nanostructures synthesized at different Re. The results show that N_D values are of the
 3 order of 10^{17} cm^{-3} , which are two orders of magnitude lower than the values obtained
 4 for anatase TiO₂ nanotubes and nanosponges in a previous work [18], indicating that the
 5 anatase/rutile nanotubes and nanosponges have a lower degree of defectiveness than
 6 their anatase counterpart. It can also be observed that N_D decreases with increasing Re,
 7 that is, nanosponges formed under hydrodynamic conditions are less defective than
 8 nanotubes formed under static conditions. This decrease in the number of donor states
 9 did not negatively affect the conductivity of nanosponges, which has been observed to
 10 increase with Re (decrease in R_I , **Table 1**). Oxygen vacancies have been reported to act
 11 as recombination centers for electron and holes when they behave as deep donors,
 12 playing a critical role in the trapping process [17, 52, 53]. Hence, oxygen vacancies may
 13 favor the photoelectron activation or they may act as recombination centers, hindering
 14 the generation of photocurrent [17, 27].
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36 The flat-band potential, U_{FB} , is the potential that needs to be applied over the
 37 semiconductor/electrolyte interface to make the energy bands remain flat. This potential
 38 indicates the position of the semiconductor Fermi level with respect to the used
 39 reference electrode. In n -type semiconductors the Fermi level is close to the conduction
 40 band, so the value of the U_{FB} is an indication of the position of the conduction band
 41 lower edge. This potential is also related to the potential difference in the space charge
 42 region ($\Delta\phi_{SC}$) that develops inside the semiconductor when in contact with an
 43 electrolyte:
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$$\Delta\phi_{SC} = U_A - U_{FB} \quad (5)$$

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2 where U_A is the external potential applied to the system. It is clear that for a given value
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4 of U_A , the more negative the value of U_{FB} , the higher (more positive) the value of $\Delta\phi_{SC}$.
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6 This potential drop is directly related to the electric field strength within the space
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8 charge layer, which is the driving force to attain a proper separation of the
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10 photogenerated electron-hole pairs. Hence, the more negative the value of U_{FB} , the
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12 better the charge separation inside the semiconductor and the lower the electron-hole
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14 recombination probability [17, 18, 46].
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21 According to eq. (4), U_{FB} can be determined from the intercept of the straight line in the
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23 MS plots with the potential axis and its values for anatase/rutile mixed TiO₂ nanotubes
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25 and nanosponges are shown in **Table 2**. It can be observed that U_{FB} becomes more
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27 negative with increasing Re. Therefore, according to the previous explanations, the
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29 recombination probability decreases for nanosponges with respect to nanotubes. This is
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31 consistent with the lower values of N_D obtained for nanosponges, since oxygen
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33 vacancies may behave as recombination sites and, thus, a slight decrease in N_D can be
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35 beneficial.
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43 Furthermore, compared with the same TiO₂ nanostructures, but containing only anatase
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45 phase [18], the anatase/rutile mixed TiO₂ nanotubes and nanosponges possess more
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47 negative values of U_{FB} . These results also indicate that a mixture of anatase/rutile is
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49 better than only anatase in terms of reducing the recombination probability.
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3.5. Photoelectrochemical performance

Figure 7 shows the measured current density of the nanotubes and nanosponges arrays with respect to the applied potential, under dark and illumination (photocurrent) conditions. It can be observed that upon illumination, all the samples gave a photocurrent response. An increase in photocurrent can be observed with increasing R_e , indicating that the photoelectrochemical performance of nanosponges is better than that of nanotubes. This can be explained in terms of higher active areas in nanosponges. Besides, as commented above, the lower values of N_D and the more negative values of U_{FB} obtained for nanosponges also indicate that the recombination probability decreases with increasing R_e .

Comparing these values with those obtained for anatase TiO_2 nanotubes and nanosponges [18] (notice that in this previous work, the highest used R_e was 400, so values for $R_e = 500$ have not been taken into account in these comparison), it can be observed that for the same R_e , photocurrent densities are slightly higher in the present study (**Table 3**), indicating that the formation of a mixed anatase/rutile phase in the nanotubes and nanosponges somewhat enhanced the photoelectrochemical performance of the samples. This result is in accordance with the lower recombination probability of the anatase/rutile mixed nanostructures observed above.

The resistance of the formed TiO_2 nanostructures to photocorrosion was studied by recording the photocurrent at an applied constant potential of $0.5 V_{Ag/AgCl}$ for 1 hour.

Figure 8 shows that photocurrents barely changed with irradiation time, indicating that

1 anatase/rutile mixed TiO₂ nanotubes and nanosponges were resistant to degradation and
2 photocorrosion in the studied electrolyte (1M KOH).
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7 **4. Conclusions**

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11 Two different morphologies were determined by the use of hydrodynamic conditions
12 during anodization in glycerol-water-ammonium fluoride electrolytes. FE-SEM
13 revealed that under static conditions, self ordered nanotubes were grown whereas under
14 flowing the nanotubular morphology is changed to nanosponge. The thickness and the
15 porosity of the nanostructures increase with Re, which is in accordance with the higher
16 current densities obtained during anodization with increasing Re.
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29 Raman Confocal Laser microscopy shows that annealing the samples at 650 °C for 1
30 hour in air produces the crystallization of TiO₂ in both anatase and rutile phases.
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36 According to the values of the resistances obtained by EIS, the values of resistances
37 corresponding to the array-bottom of the nanostructures decrease under hydrodynamic
38 conditions, indicating that the nanosponges possess higher electrical conductivity and
39 surface area than the nanotubes formed under stagnant conditions. Additionally, all the
40 capacitance values increase with Re, this fact can be related, in this case, to a higher
41 porosity of the nanosponges.
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53 The density of donor species, N_D (mainly oxygen vacancies), was found to decrease
54 with increasing Re, that is, nanosponges formed under hydrodynamic conditions were
55 less defective than nanotubes formed under static conditions. Besides, N_D decreased
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with respect to the values obtained for anatase TiO₂ nanostructures. On the other hand, U_{FB} became more negative with increasing R_e , indicating that the recombination probability decreased for nanosponges with respect to nanotubes. Moreover, the anatase/rutile mixed TiO₂ nanostructures possessed more negative values of U_{FB} than anatase TiO₂ nanostructures, which also indicates that a mixture of anatase/rutile is better than only anatase in terms of reducing the recombination probability.

An increase in photocurrent was observed with increasing R_e , indicating that the photoelectrochemical performance of nanosponges was better than that of nanotubes, because of the higher active areas of nanosponges and their lower recombination probability. On the other hand, photocurrent values for anatase/rutile mixed TiO₂ nanostructures were slightly higher than that for anatase TiO₂ nanostructures, meaning that the former system presents better photoelectrochemical performance than the latter one.

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12 **Tables captions**

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16 **Table 1.** Equivalent circuit parameters for TiO_2 nanostructures (nanotubes and
17 nanosponges) at different values of Re.
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23 **Table 2.** Values of N_D and U_{FB} for the different anatase/rutile mixed TiO_2
24 nanostructures anodized under static (Re = 0) and hydrodynamic (Re > 0) conditions.
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31 **Table 3.** Comparison between the photocurrents measured at $0.5 V_{\text{Ag/AgCl}}$ for the
32 systems anatase TiO_2 nanostructures and anatase/rutile mixed TiO_2 nanostructures, at
33 different Re.
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38 **Figures captions**

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43 **Figure 1.** Current density transients obtained during the potentiostatic anodization of Ti
44 at 30 V at different Re.
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54 **Figure 2.** FE-SEM images of the top-view of the TiO_2 nanotubes (Re = 0, image a) and
55 nanosponges (Re from 100 to 500, images b to f) anodized at 30V, for 3 h, and cross
56 sectional views of the nanotubes and nanosponges (at Re = 500).
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1 **Figure 3.** Thickness of the nanotubes ($Re = 0$) and nanosponges ($Re > 0$) vs Re .
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4 **Figure 4.** Raman confocal laser spectra of the amorphous nanotubes and annealed (650
5 °C-1 h) TiO_2 nanotubes ($Re = 0$) and nanosponges ($Re = 500$) anodized at 30 V, for 3 h.
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7 The letter A indicates anatase and the letter R indicates rutile.
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13 **Figure 5.** Experimental Nyquist (a), Bode-phase (b) and Bode-module (c) plots for the
14 samples anodized from $Re = 0$ to $Re = 500$; (d) electrical equivalent circuit used to
15 simulate experimental EIS data.
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24 **Figure 6.** Mott-Schottky plots of the different anatase/rutile mixed TiO_2 nanostructures
25 anodized under static ($Re = 0$) and hydrodynamic ($Re > 0$) conditions.
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31 **Figure 7.** Current density vs. applied potential curves under dark and illumination
32 conditions for the different anatase/rutile mixed TiO_2 nanostructures anodized under
33 static ($Re = 0$) and hydrodynamic ($Re > 0$) conditions.
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41 **Figure 8.** Photostability of the different anatase/rutile mixed TiO_2 nanostructures
42 anodized under static ($Re = 0$) and hydrodynamic ($Re > 0$) conditions.
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Figure 1

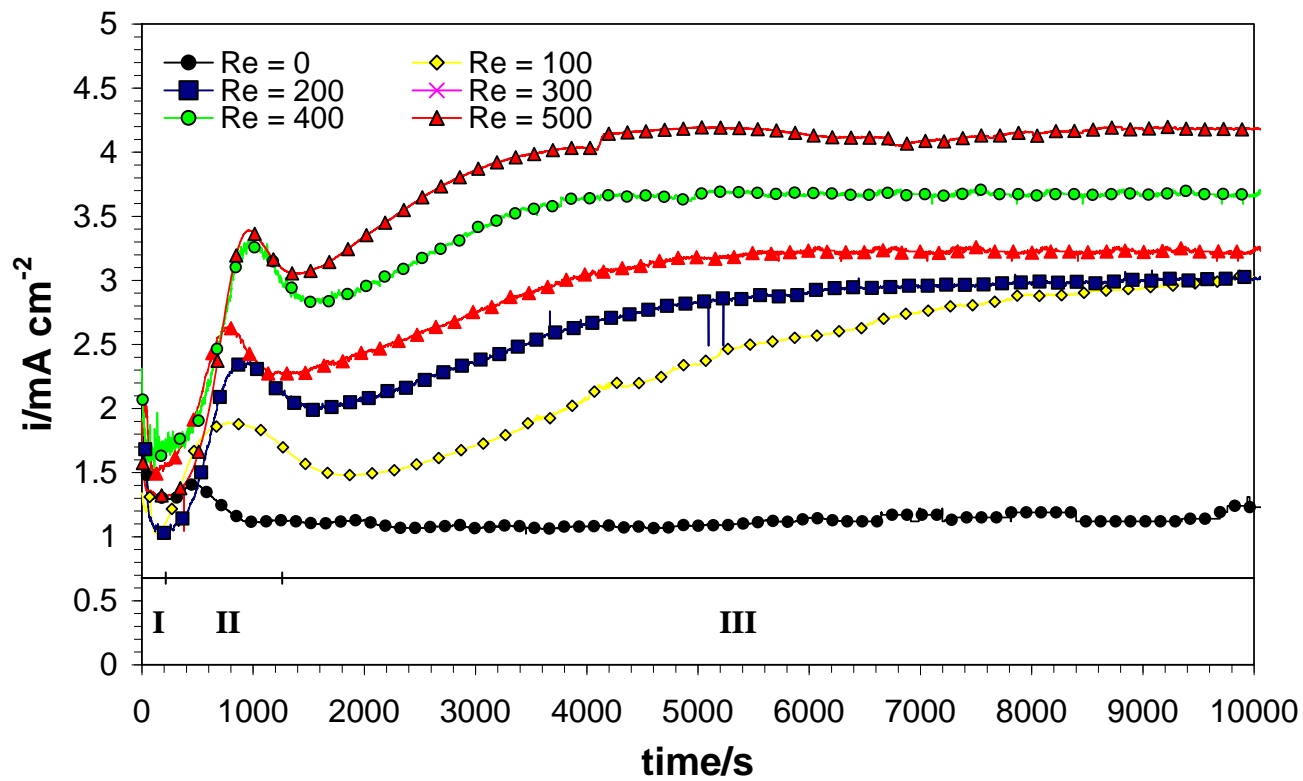


Figure 2

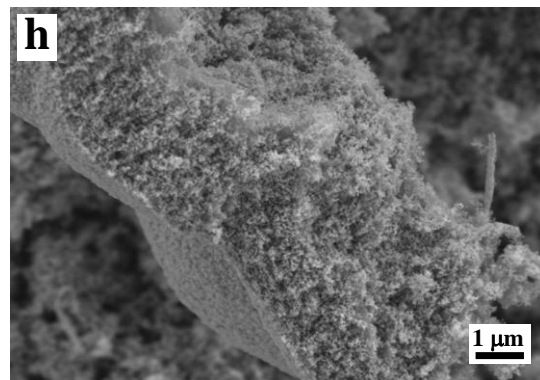
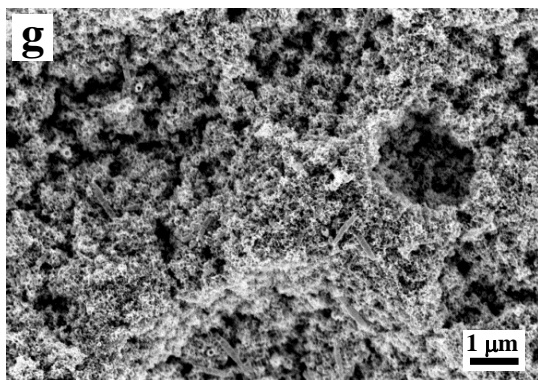
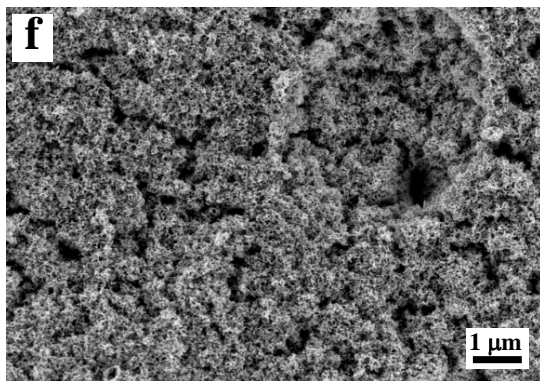
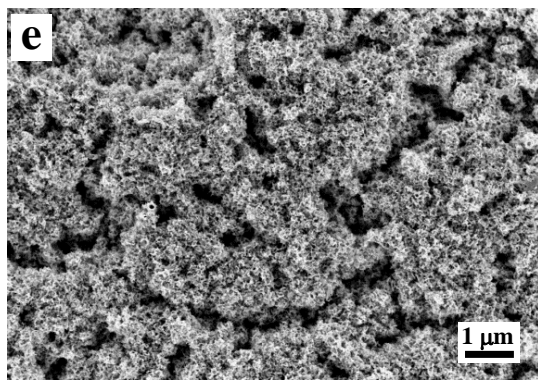
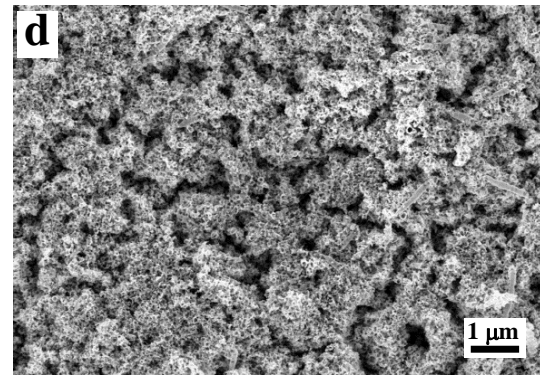
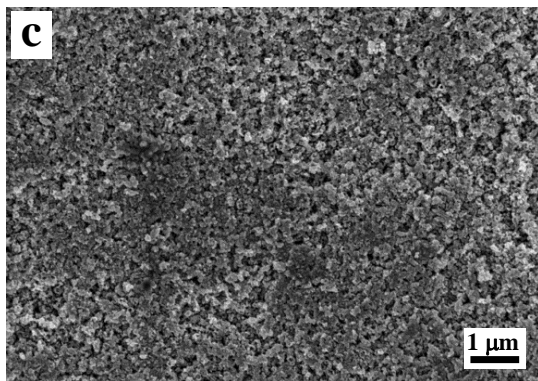
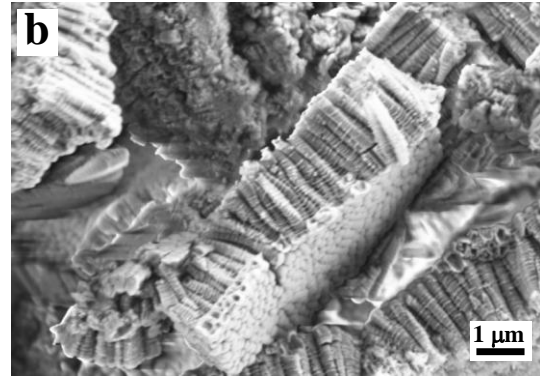
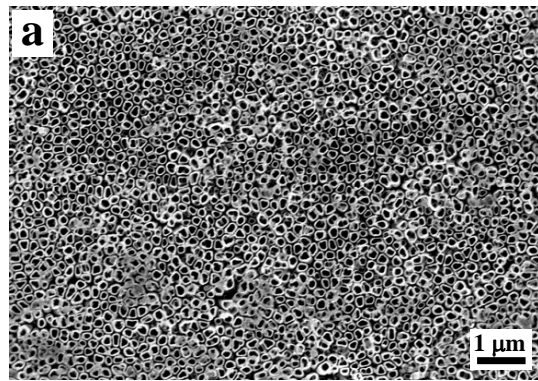


Figure 3

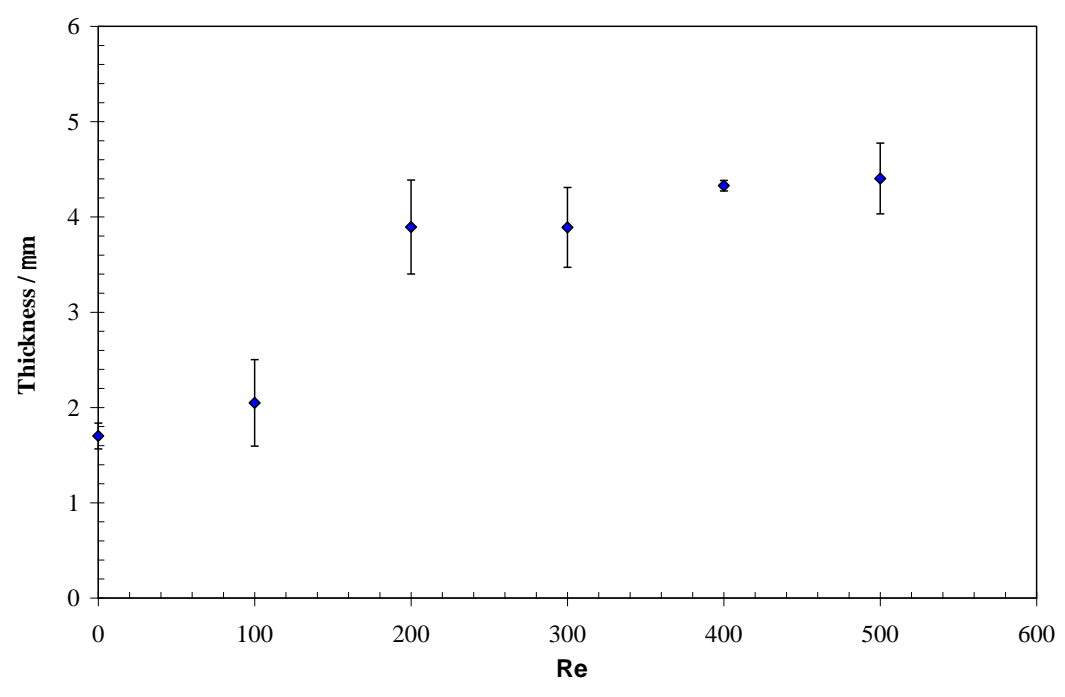


Figure 4

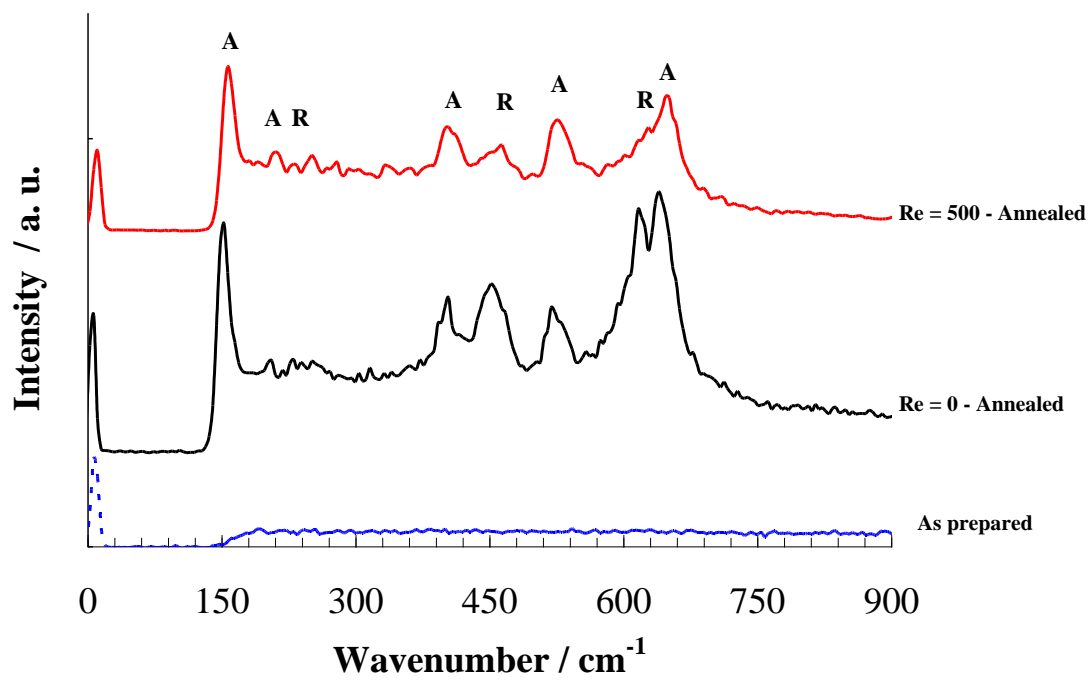


Figure 5

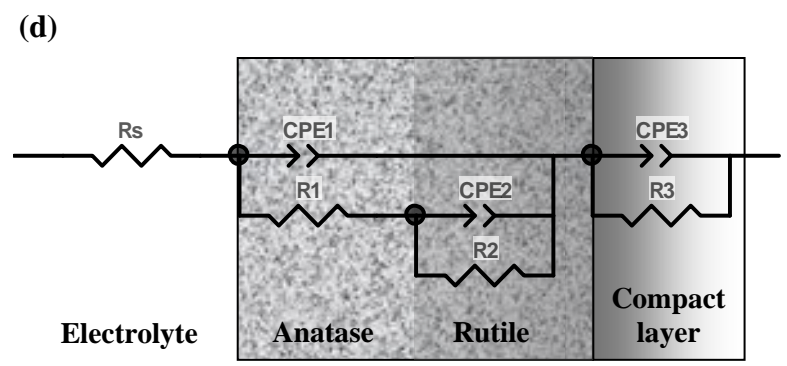
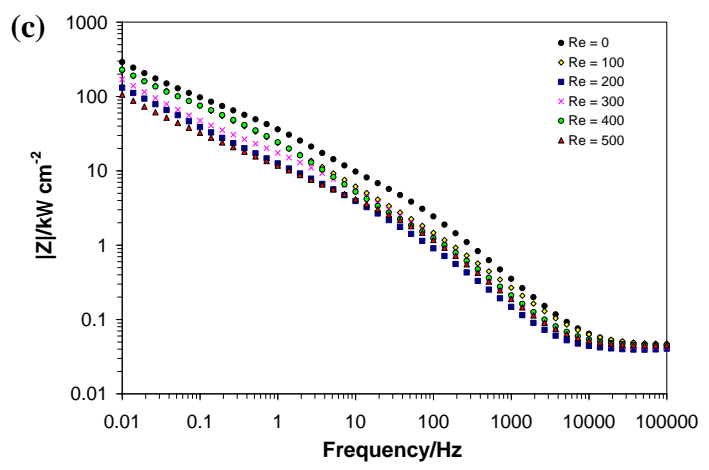
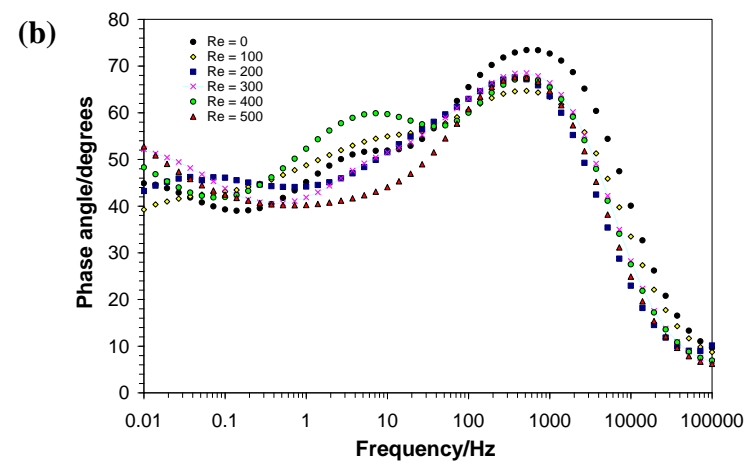
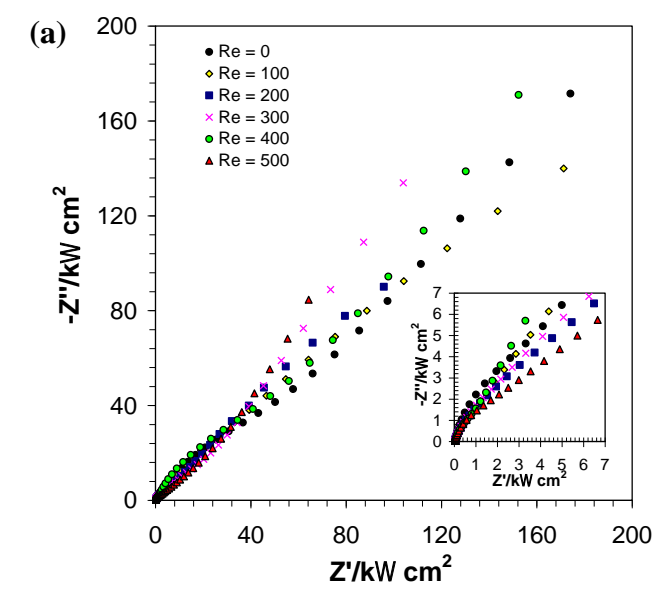


Figure 6

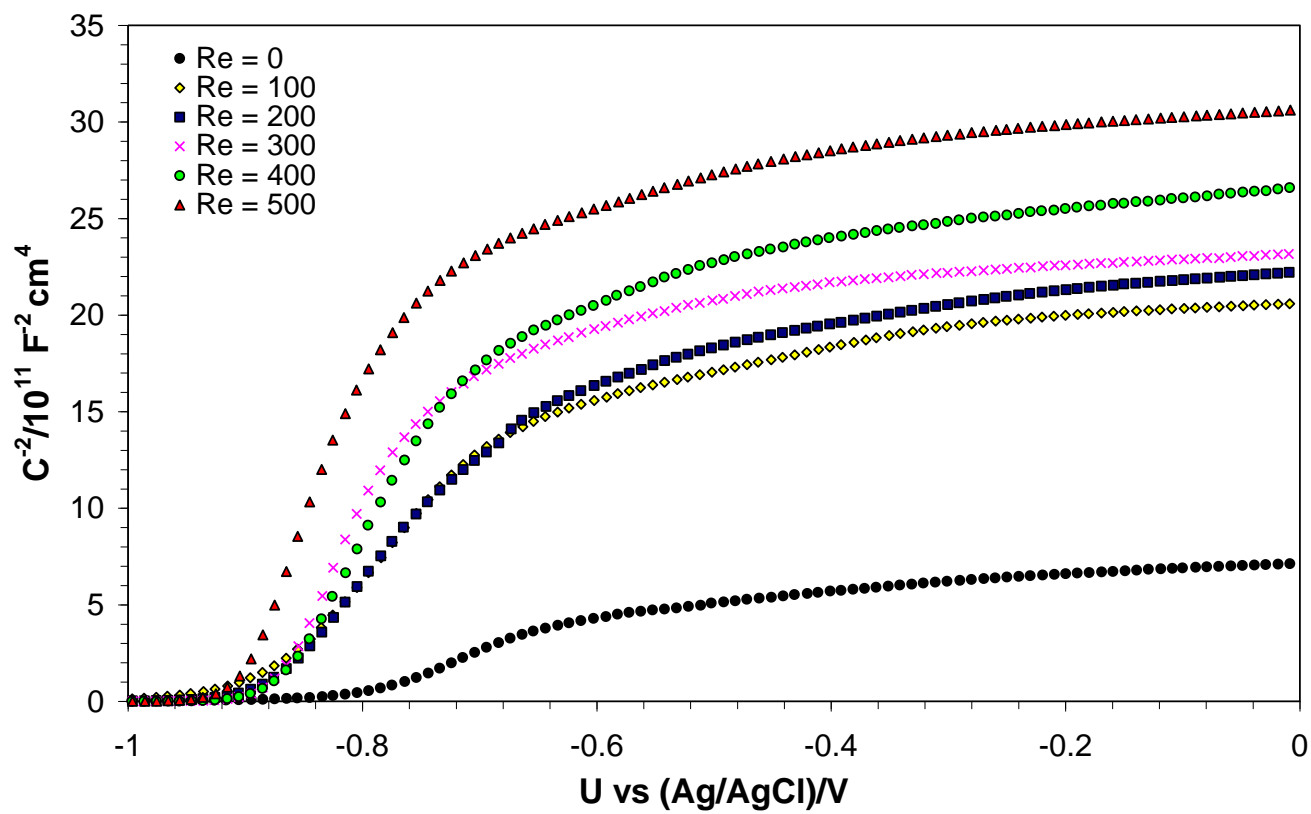


Figure 7

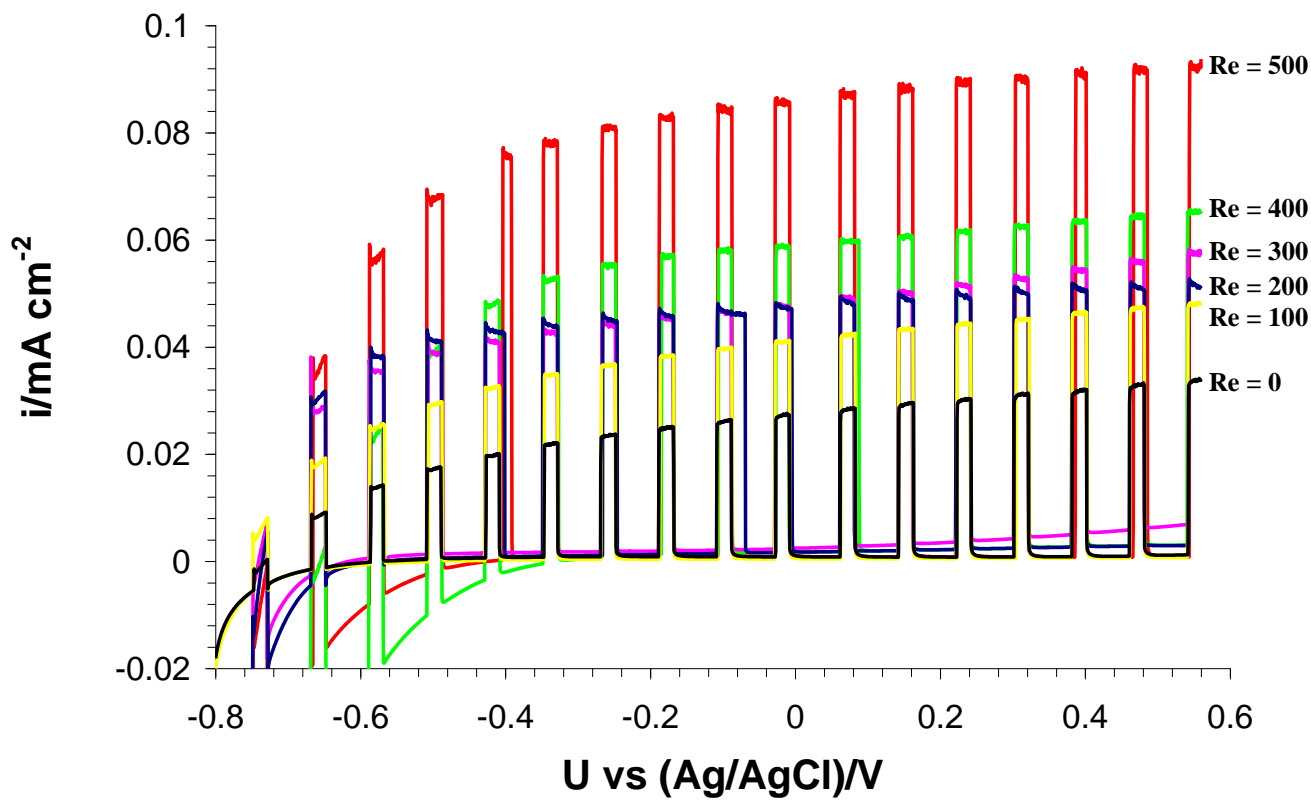


Figure 8

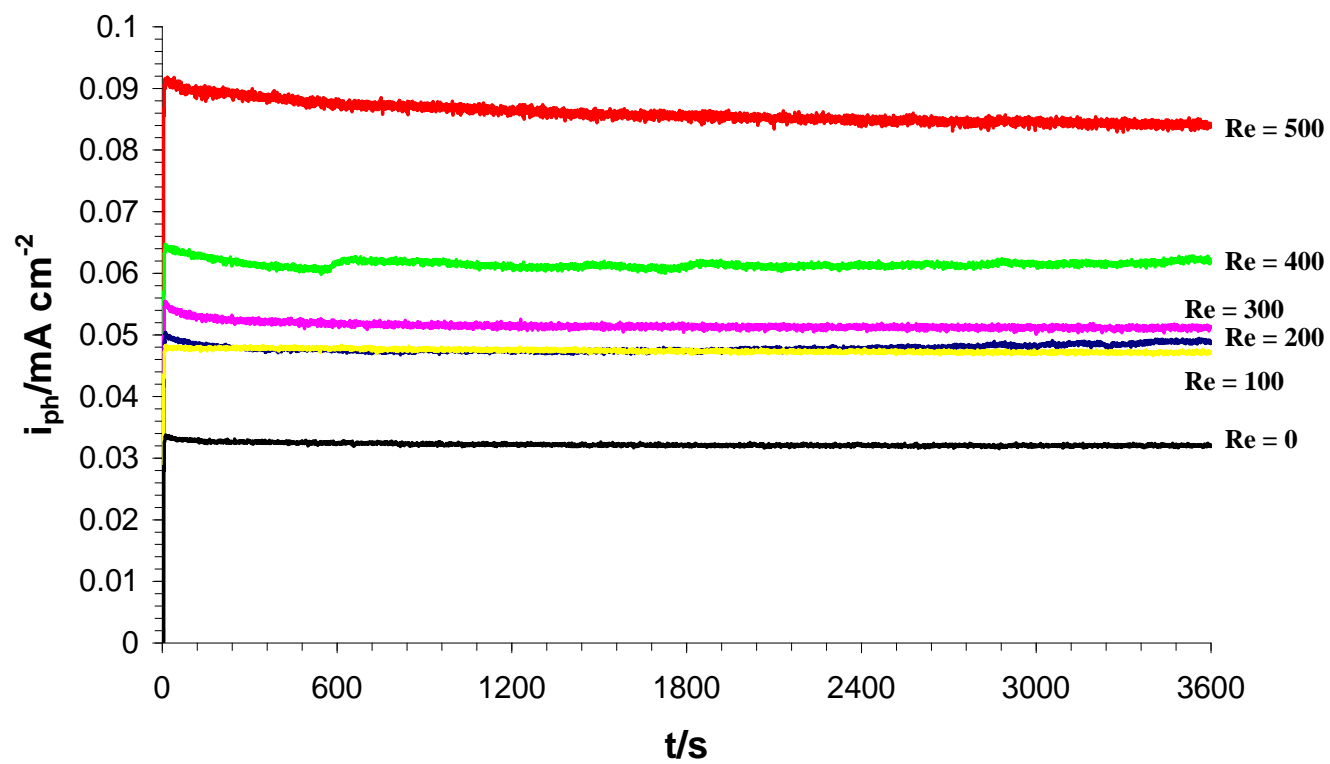


Table 1

<i>Re</i>	$R_S/\Omega \text{ cm}^2$	$C_1/\mu\text{F cm}^{-2}$	α_1	$R_1/\text{k}\Omega \text{ cm}^2$	$C_2/\mu\text{F cm}^{-2}$	α_2	$R_2/\text{k}\Omega \text{ cm}^2$	$C_3/\mu\text{F cm}^{-2}$	α_3	$R_3/\text{k}\Omega \text{ cm}^2$	$\chi^2 (\times 10^{-4})$
0	43 ± 3	0.5 ± 0.9	0.96 ± 0.02	4.6 ± 2.1	6 ± 2	0.65 ± 0.07	64 ± 14	97 ± 43	0.73 ± 0.02	1140 ± 102	3
100	44 ± 5	0.7 ± 0.0	0.93 ± 0.03	1.2 ± 0.1	18 ± 1	0.57 ± 0.06	58 ± 10	115 ± 50	0.70 ± 0.02	609 ± 45	2
200	43 ± 8	0.6 ± 0.2	0.91 ± 0.06	1.2 ± 0.8	39 ± 10	0.46 ± 0.01	32 ± 9	286 ± 68	0.87 ± 0.01	421 ± 35	3
300	40 ± 1	1.2 ± 0.1	0.94 ± 0.03	1.1 ± 0.1	18 ± 4	0.49 ± 0.08	24 ± 7	324 ± 65	0.71 ± 0.09	813 ± 94	1
400	43 ± 3	1.1 ± 0.1	0.99 ± 0.03	1.1 ± 0.6	10 ± 2	0.71 ± 0.05	48 ± 15	165 ± 70	0.71 ± 0.01	1437 ± 210	3
500	43 ± 3	1.0 ± 0.1	0.97 ± 0.04	1.1 ± 0.4	50 ± 11	0.46 ± 0.09	26 ± 4	669 ± 91	0.69 ± 0.02	1950 ± 182	2