Effect of substrate surface treatment on electrochemically assisted photocatalytic activity of N-S co-doped TiO$_2$ films

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Abstract. To investigate whether different metal surface treatments, performed on meshes of stainless steel 304 and titanium, affect the photocatalytic activity (PCA) of supported modified anodic TiO$_2$ films, metallic substrates were coated with titanium isopropoxide sol-gel precursor modified with thiourea. Substrates were pretreated by some of the following techniques: a) sandblasting, b) pickling, c) hydroxylation and d) passivation. The as-prepared electrode materials were characterized by X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM), and voltammetry in the dark and under light UVA irradiation. PCA of modified N-S-TiO$_2$ electrodes was evaluated by electrochemically assisted photocatalytic degradation of methyl orange. The results of XPS revealed that N and S were incorporated into the lattice of TiO$_2$. FESEM showed that surface roughness and thickness of films varies depending on surface treatment. Voltammetric and XPS characterization of N-S co-doped TiO$_2$ films supported on stainless steel revealed that their surface contains alpha-Fe$_2$O$_3$/FeOOH. Accordingly, iron contamination of the films coming from stainless steel was detrimental to the degradation of methyl orange. Prior to sol-gel coating process, sandblasting followed by nitric acid passivation for stainless steel or hydrofluoric acid pickling process in the case of titanium improved the PCA of N-S co-doped TiO$_2$ films.

1. Introduction

In continuation of our previous studies on photoelectrocatalytic (PEC) performance of modified anodic TiO$_2$ films with non-metals elements for water decontamination [1], herein is determined the effect of substrate surface treatment on PCA of sol-gel modified TiO$_2$ films deposited on titanium and stainless steel (AISI 304) substrates. On one hand, it is known that titanium is covered by a native oxide film which is readily attacked by hydrofluoric acid [2], leading to a rough fresh surface after pickling [3]. Thus, this could be exploited to increase the surface area of sol-gel film and enhance the PCA of the photoanodes. On other hand, it is well known that TiO$_2$ thin films prepared on stainless steel by sol-gel are contaminated with significant amounts of iron and other metals, thereby decreasing its PCA [4-6]. In the field of photocatalysis, this problem has been solved by thickening of the TiO$_2$ film, avoiding the diffusion of metals from stainless steel to the TiO$_2$ film surface [6,7]. However, in photoelectrocatalysis, PEC activity diminishes with increase of film thickness [8,9], due to long and tortuous path of the electrons across the TiO$_2$ nanocrystal network where interface states can act as recombination centres, resulting in a decrease in the photocurrent and photocatalytic efficiency [9]. In the field of photoelectrocatalysis, very few efforts have been dedicated to enhance the PEC performance of above-mentioned type of photoanodes [1]. In an attempt to improve the PCA of
surface-modified anodic TiO\textsubscript{2} films, herein are evaluated various surface treatments on metallic substrates (stainless steel and titanium) before the sol-gel application.

2. Experimental

2.1. Preparation of S-TiO\textsubscript{2} coatings

AISI-SAE 304 stainless steel (mesh stem: 0.9mm; mesh open size: 6.6mm\times3.7mm–length of the diagonal diamond) and grade 2 ASTM B265 titanium (mesh stem: 0.9mm; mesh open size: 6mm\times3mm) plates were used as substrates. Mesh plates were cut into geometrical dimensions of 50\times45mm\textsuperscript{2}. Substrates were exposed to various pretreatment methods, as summarized in Table 1, to generate different modified surfaces prior to sol-gel application. The sandblasting was done with 60 grit aluminium oxide particles. Sandblasting was performed at an air pressure of 80 pounds, the distance between the nozzle and the stainless-steel mesh was 30cm.

| Substrate | Treatment | Description |
|-----------|-----------|-------------|
| SS\textsuperscript{a}, Ti | Chemical cleaning (CC) | Meshes were sonicated consecutively in ethanol (5 min) and ketone (5 min). After chemical cleaning, meshes were immersed in a standard piranha solution, H\textsubscript{2}SO\textsubscript{4}/H\textsubscript{2}O\textsubscript{2}, 70:30 (v/v), for 30 min. |
| SS\textsuperscript{a} | Hydroxylation (H) | After chemical cleaning, meshes were immersed in 30 % HNO\textsubscript{3}, for 1 h. |
| SS\textsuperscript{a} | Passivation (P) | After hydroxylation, meshes were immersed in 30 % HNO\textsubscript{3}, for 1 h. |
| SS\textsuperscript{a} | Hydroxylation-Passivation (H/P) | After chemical cleaning, meshes were immersed in 5% HF, for either 10 s [PC(10s)] or 20 s [PC(20s)]. |
| Ti | Pickling (PC) | After hydroxylation, meshes were immersed in 5% HF, for either 10 s [PC(10s)] or 20 s [PC(20s)]. |

\textsuperscript{a} Previous to treatment the substrates were sandblasted.

Deionized water and analytical reagents were used in all experiments. To prepare the N-S co-doped TiO\textsubscript{2} sol, a mixture of 5mL of titanium(IV) isopropoxide and 5mL of isopropyl alcohol was added dropwise to 31mL of 0.3M HNO\textsubscript{3} containing 1mL of acetyl acetone. The mixture was stirred for 12h, afterwards 0.033g thiourea was added and the sol was again stirred for an additional 12h. In order to improve the adherence of sol-gel layer on substrates, the sol was aged in the dark for 21 days. Each metallic substrate was dipped into the aged sol, holded for 2min and withdrawn out of the sol at 3cm min\textsuperscript{-1}. After withdrawal, the coated substrates were dried at room temperature and later at 110°C for 1 h. After drying, samples were calcined at 400°C for 1h at a heating rate of 3deg· min\textsuperscript{-1}.

2.2. Characterization of surface modified TiO\textsubscript{2} films and photoelectrocatalytic degradation

XPS data were obtained on a SPECS PHOIBOS 150 spectrometer with a hemispheric analyser using the K\alpha radiation of an Al anode (1486.6eV). Deconvolution was performed by fitting after Shirley background subtraction using the Casa XPS software package. Surface morphologies of the films were observed by using a FEI QUANTA FEG 650 field emission scanning electron microscope, the analyses were performed at an accelerating voltage of 20kV. Diffuse reflectance spectra (DRS) were obtained with a Shimadzu double beam UV-2401 PC UV/Vis spectrophotometer. Band gaps of the films were determined from the DRS using the Kubelka-Munk function [1]. (Photo)electrochemical measurements were made in a conventional three-electrode cell, using each one of modified TiO\textsubscript{2} films as working electrode. The geometric area of each electrode plate in contact with the electrolyte was 44mm\times33mm (22.5 diamonds) for SS and 41mm\times34 mm (27 diamonds) for Ti. The counter electrode was a high purity graphite rod, and an Ag/AgCl, KCl (3.0M) electrode (+0.207V vs NHE)
supported by a home-made Luggin capillary filled with 3.0M KCl was used as reference electrode. Dissolved oxygen was removed from the solutions prior to the measurements by bubbling nitrogen for 20min. All (photo)electrochemical measurements were performed on an Autolab PGSTAT302N potentiostat. Oxides and hydroxides of iron were determined by voltammetry by reductive dissolution of TiO$_2$/SS films. A HPL-N 250W UVA-visible lamp (Phillips) was used for the illumination. PEC degradation was performed by holding the potential at 0.65V vs Ag/AgCl. Discoloration of 4.5ppm solution of methyl orange at pH 3.2 (adjusted with H$_2$SO$_4$) in 0.1M Na$_2$SO$_4$ was followed by measuring the decrease in absorption at 501nm.

3. Results and discussion

3.1. Characterization of TiO$_2$ films

![Figure 1](image)

**Figure 1.** Typical XPS spectra of (a) N 1s and (a') S 2p for a TiO$_2$ film photoanode. FESEM images of N-S co-doped TiO$_2$ films supported on titanium pretreated by chemical cleaning (b), (b') and pickling for 10s (c), (c') and 20s (d), (d'). Magnifications: 800X (b)-(d) and 3000X (b')-(d').

XPS measurements were performed in order to investigate the chemical modification by thiourea on the crystal structure of the as-prepared and aged sol-gel TiO$_2$ films. Figure 1(a), (a') shows representative XPS spectra in the N 1s and S 2p regions. The results of XPS analysis for TiO$_2$ films supported on stainless steel are given in Table 2. Titanium dioxide films shows peaks in the range of 398.9–402.0eV (N1s) indicating the presence of N–Ti–O, N–O–Ti, and O–N–Ti–O bonds in the bulk of films, ascribed to interstitial and substitutional nitrogen doping [10]. Additional N 1s peaks on TiO$_2$ film supported on hydroxylated SS surface have been attributed to nitrogen adsorbed compounds [10]. XPS peaks in the range of 167.1–170.2eV have been attributed to the presence of S(IV) and S(VI) species. According to literature, peaks around 167.4eV can be attributed to sulphur doping, while peaks close to 170.1 has been associated to adsorbed surface sulphate species [11]. These results indicate that N and S atoms are co-doped into the bulk phase of TiO$_2$. The decrease in the band gap energy of modified TiO$_2$ confirms the doping (see Table 2). The surface morphology of TiO$_2$ films supported on SS and Ti was investigated by FESEM. Figure 1 shows the surface of the films deposited on the pickled titanium support for 20s was more cracked than that deposited for 10s. It is well-known that formation of cracks in sol-gel films depends on layer thickness [12,13]. Thus, thickness of N-S co-doped TiO$_2$ films increases with the cracking of the layer in the following order: CC<PC(10s)<PC(20s). As a result of the sandblasting required to improve the adherence of N-S co-doped TiO$_2$ films on SS, Figure 2 shows that these coatings exhibit a strong non-uniformity, thereby
making it difficult to determine the thickness of the films. However, it is clearly observed that surface roughness of films on passivated stainless steel substrates is greater than in the other pretreated surfaces. Passivated surface was rouglier than that hydroxylated/passivated. Thus, roughness increases in the following order: CC < H < H/P < P.

| Label | Element | Binding energy (eV) | Atomic ratio N/S | Band gap (eV) |
|-------|---------|---------------------|------------------|--------------|
| CC    | N 1s    | 399.82, 401.44      | 1.45             | 3.13         |
|       | S 2p    | 167.19, 170.15      |                  |              |
| H     | N 1s    | 399.22, 400.11, 400.96, 402.03 | 1.90 | 2.89 |
|       | S 2p    | 167.42, 170.09      |                  |              |
| H/P   | N 1s    | 399.35, 401.67      | 1.10             | 2.90         |
|       | S 2p    | 167.70, 169.51      |                  |              |
| P     | N 1s    | 398.89, 400.99      | 1.47             | 2.97         |
|       | S 2p    | 167.08, 170.12      |                  |              |

**Table 2.** Sample labels of substrate surface treatment, XPS binding energies of the doping elements, their stoichiometric ratio, and band gap energies of TiO$_2$ films supported on stainless steel.

**Figure 2.** FESEM images of N-S co-doped TiO$_2$ films supported on stainless steel pretreated by chemical cleaning (a), (a’), hydroxylated (b), (b’), hydroxylated/passivated (c), (c’) and passivated (d), (d’). Magnifications: 800X (a)-(d) and 3000X (a’)-(d’).

3.2. *Characterization of the Fe(III) contamination on N,S-TiO$_2$/stainless steel*

Formation of iron oxide in sol-gel TiO$_2$ films deposited on stainless steel has been reported in the literature [4-7]. Voltammetry is a suitable technique for identification of iron oxides and oxyhydroxides in acid media [14,15]. Figure 3 shows the electrochemical behaviour of SS before and after being coated with N-S co-doped TiO$_2$ film. Voltammogram of bare stainless steel does not present any current before hydrogen evolution reaction (Figure 3(a)). Two voltammetric peaks are observed around -0.2 and -0.4V (vs Ag/AgCl) for films deposited on hydroxylated and hydroxylated followed by passivated (Figure 3(b), (c)) substrates. According to literature report [14], peaks C$_1$ and C$_2$ are assigned to the reductive dissolution of α-FeOOH and α-Fe$_2$O$_3$, respectively. In such wise, chemically cleaned and passivated substrates coated with N-S co-doped TiO$_2$ films were only poisoned by α-Fe$_2$O$_3$. Analysis of these results indicates that hydroxylation favours the formation of α-FeOOH in the film, and passivation decreases the contamination of film surface. It is noteworthy that the response in current for passivated substrate is lower than that of stainless steel substrates treated (see Figure 3). These results are in good agreement with XPS analysis (results not shown).
3.3. Photocurrent measurements and dye discoloration

The photocurrent response depends on type of substrate and on received surface treatment. The photocurrent transient behaviour in Figure 4(i) show that the charge involved in discoloration process (area under the curve), for each of the four surface treatments on SS substrates, increases in the following order (see labels in Table 1): H<H/P<CC<P, according to the following values of charge in mC: 0.033<0.084<0.132<0.182, respectively. The higher photoresponse is obtained for passivated process, which is ascribed to lower iron contamination of the modified TiO₂ films supported on SS. Likewise, the lower photoresponse showed for electrodes that were hydroxylated is associated to high content of iron by the presence of both α-Fe₂O₃ and α-FeOOH in the film. It is noteworthy that photocurrent responses coming from SS are noisy, unstable (photocurrent increases vary over time), and have a lower magnitude than those from Ti substrates; thereby, films supported on Ti show high and stable photocurrents. This can be explained because α-FeOOH or α-Fe₂O₃ can modify the electronic states of TiO₂ acting as electron-hole recombination sites [4,16]. These results are consistent with those of PEC degradation of methyl orange, since the rate of dye discoloration (Figure 4(ii)) increases as photocurrent increases. The increase in photocurrent over time was most likely due to iron dissolution; however, more evidence is needed to confirm this hypothesis. On other hand, dye discoloration on modified TiO₂ films supported on Ti substrates enhances in the following order: PC(10s)<CC<PC(20s). Thus, titanium after 20s of pickling in HF improves both the PCA and PEC discoloration rate with respect to the other electrode materials; it is associated to an increase in surface area of the film (Figure 1).

4. Conclusions

Metallic meshes were coated by N-S co-doped TiO₂ through sol-gel dip-coating technique. It was found that certain surface treatments, depending on the substrate, are required to improve the photocatalytic activity of N- and S-modified TiO₂ films. Hence, surface preparation of substrate is a critical factor in the photocatalytic performance of coatings. N-S co-doped TiO₂ films coated on titanium showed better PCA than on stainless steel, because on this last substrate α-Fe₂O₃ and α-FeOOH poison the films. The solution proposed herein to improve the photocatalytic activity of N-S co-doped TiO₂ films supported on stainless steel is not useful for practical applications in photo(electro)catalysis, due to low PCA of modified TiO₂ photocatalyst, but indeed constitutes a way to solve the detrimental effect of metal diffusion. Accordingly, is suggested the formation of a thermodynamic stable layer (diffusion barrier) between stainless steel support and the film to avoid the iron diffusion. In the case of titanium substrate, depending on the extent of hydrofluoric acid pickling, the photocatalytic activity of modified anodic TiO₂ films can be modulated.
Figure 4. (i) Photocurrent transient behaviour and the corresponding (ii) discoloration of 4.5 ppm solution of methyl orange by sol−gel N-S co-doped TiO₂ electrodes in 0.1 M Na₂SO₄. Electrodes: (a) P-SS, (b) CC-SS, (c) H/P-SS, (d) H-SS, (e) CC-Ti, (f) PC(10s)-Ti, and (g) PC(20s)-Ti. Volume of solution 50mL, stirring rate 800rpm, UVA-vis illumination and an applied potential of 0.65V vs Ag/AgCl.

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