N and F Codoped TiO₂ Thin Films on Stainless Steel for Photoelectrocatalytic Removal of Cyanide Ions in Aqueous Solutions

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Received: March 10, 2016; Revised: December 30, 2016; Accepted: January 25, 2017

N-F codoped TiO₂ films were immobilized on stainless steel sheets through a combined approach involving a dip-coating technique and a hydrothermal treatment, followed by calcination at 400°C in the presence of air. Photocatalyst characterization was conducted using XRD, Raman and UV-VIS spectroscopy as well as SEM. The films were tested in a three-electrode cell for the photoelectrocatalytic degradation of CN-containing compounds. The results showed that the increase in the degradation rate of CN-containing compounds is both influenced by a synergistic effect of the doping agents and strongly dependent on the concentration of CN-containing compounds in the solution. Nitrogen contributed to the enhanced photoactivity under visible light due to the generation of localized states within the band gap of TiO₂, whereas the presence of fluoride improved the superficial properties of the film, which resulted in higher amounts of CN-containing compounds that were degraded by direct charge transfer through the photogenerated holes.

Keywords: Codoped TiO₂, non-metallic doping, photoelectrocatalysis, cyanide oxidation

1. Introduction

Currently, contamination of natural water sources due to industrial toxic waste is one of the major environmental and social global issues. In this sense, the gold mining industry is one of the largest water polluter in the world, due to its heavy use of toxic substances such as cyanide, which are disposed of into natural water sources. Conventional methods for the removal of cyanide involve chemical oxidation with various substances, which include hydrogen peroxide, chloride dioxide, ozonation, and SO₂/air, among others. However, the limitations associated with these methods, such as high cost of reagents and/or equipment as well as the generation of new products with high toxicity, has motivated the study of photoelectrocatalysis as an alternative technique for the detoxification of cyanide waters.

In this context, photoelectrocatalysis (PEC) using semiconductor materials such as titanium oxide (TiO₂), which is low-cost, chemically stable and quantum efficient, has emerged as one of the most promising advanced oxidation processes for the removal of contaminants from natural water sources. In order to perform TiO₂ PEC, photon illumination with a wavelength equal or less than 388 nm is required, which corresponds to the ultraviolet (UV) region and promotes the generation of electron-hole pairs that contribute to the redox process. However, the sunlight spectrum has its maximum radiation between 400-700 nm, and only a small fraction of this range corresponds to UV light. This hinders the ability to use solar radiation in PEC processes on TiO₂ films. Therefore, in order to address this problem and avoid the use of artificial UV lamps, it is essential to develop strategies towards the reduction of the band-gap of the semiconductor.

In this context, doping with non-metallic elements such as N, F, C, S and B has become an attractive alternative because this type of modification results in materials with a low recombination rate, great chemical stability and good response to visible light, relative to metallic doping. Recently, it has been suggested that the use of codoped systems such as N and F, and N and B allow to compensate for the excess charge from substitutional doping with N. Additionally, these codoped materials are effectively used in the charge separation of photogenerated electrons and holes, improving photoelectrocatalytic activity. In this regard, the combination of N and F appears as an interesting doping approach, since it would not only increase the TiO₂ response due to the presence of N, but also would improve the superficial and crystallinity properties of the material due to modification with F. Nonetheless,
the mechanisms of action of N and F as doping agents in TiO$_2$ are strongly dependent on the methods for the synthesis and preparation of the photocatalysts.

Furthermore, even though the use of this type of semiconductor materials for the photoelectrocatalytic oxidation of cyanide represents a promising technology for the decontamination of natural water sources, it has hardly been investigated$^{12-22}$. To our knowledge, the studies reported in the literature primarily deal with the electrooxidation of CN$^-$ by direct electron transfer$^{23,24}$ using expensive electrodes, which compromises the economical feasibility of the process. In the present work, we attempt to gain deeper insights into the CN$^-$ photoelectrocatalytic oxidation processes that involve the use of TiO$_2$ semiconductor films supported on low-cost substrates. Simultaneous doping of TiO$_2$ with N and F was performed and its effect on photoactivity under visible light was evaluated. Moreover, the influence of $e^-\cdot h^+$ pairs and oxidative species such as OH$^*$ radicals on process efficiency was also assessed. The photoelectrochemical studies presented here lay important groundwork needed to accurately understand the mechanisms involved in the photoelectrocatalytic oxidation of cyanide towards the development of low-cost and efficient technologies for the removal of CN$^-$ from contaminated natural water sources.

2. Experimental

2.1. Preparation of N-F codoped TiO$_2$ films

Semiconductor films were prepared as previously described$^{25}$. Briefly, 5 mL of titanium tetraisopropoxide (TTIP) were dissolved in 5 mL of isopropanol, followed by combination with a second solution consisting of 5 mL of acetyl acetone (AcAc) and 0.6 mL of HNO$_3$ (65%) in 30 mL of distilled water. The resulting mixture was stirred for 12 h at room temperature. After this, 5 mL of triethylamine (TEA) and 0.93 g of NH$_4$F were added as nitrogen and fluorine sources, respectively. Stirring was kept for an additional 12 h. AISI 304 stainless steel substrates were prepared by abrasion with SiC #600 paper followed by cleaning in an ultrasonic bath with ethanol and then acetone, 15 min each time. The films were formed on the metallic substrates by dip-coating and then placed into an autoclave for 4 h at 125 °C. Finally, the photocatalyst films were annealed at 400 °C for 1 h. Following similar procedures as the one described above, four types of films were prepared: i) without doping agents (pristine TiO$_2$), ii) with TEA (TiO$_2$-T), iii) with NH$_4$F (TiO$_2$-NF), and iv) codoped TiO$_2$ (TiO$_2$-TNF). Although the stainless steel is prone to corrosion, it can be used to manufacture photoanodes as long as the semiconductor film deposited on such a substrate is homogeneous, stable chemically and has corrosion protective properties, such as occurs with sol-gel TiO$_2$ coatings$^{25-27}$.

2.2. Characterization of the supported photocatalysts

Grazing angle X-ray diffraction (GAXRD) with an incidence angle of 3° was performed on a BRUKER D8 diffractometer. Additionally, the films were characterized by Raman spectroscopy using a HORIBA Scientific HR LabRAM Evolution equipped with a green laser (532 nm) and a 50X objective. Attenuated reflectance infrared spectroscopy (ATR-FTIR) analyses were performed on a NICOLET IS50 (Thermo Scientific) at a resolution of 4 cm$^{-1}$ with 32 scans and an interferometer speed of 0.4147 cm s$^{-1}$. Moreover, the morphology of the supported photocatalysts was examined by field-emission scanning electron microscopy (FE-SEM) using a FEI QUANTA FEG 650 microscope, and film roughness was evaluated with an AFM Park NX10 microscope using contact mode in 20 μm × 20 μm areas.

2.3. Photoelectrocatalytic oxidation of cyanide solutions

The experiments were performed using a conventional three-electrode cell. AISI 304 stainless steel sheets (4 cm$^2$) coated with the semiconductor films served as the working electrode. A saturated calomel electrode [SCE: Hg/Hg$_2$Cl$_2$ (saturated KCl)] in a Luggin capillary was used as the reference electrode, and the counter electrode consisted of a high purity graphite rod (AGKSP grade, Alfa Aesar). All measurements were carried out on a GAMRY 600 potentiostat. Illumination was provided by a 150 W metal-halide lamp (Phillips MHN-TD UV block) with an integrated UV light filter. 25 mL of solution [NaCN (50, 100 and 250 ppm CN$^-$) + 0.1 M Na$_2$SO$_4$] of pH 11 were used. Solution pH was kept constant by addition of NaOH. The levels of cyanide were measured by duplicate using titration with silver nitrate in a Titrinline Easy automatic titrator (SI analytics). All solutions were prepared using deionized water, and all reagents were analytic grade (Merck).

3. Results and discussion

3.1. Characterization of the photocatalyst films

In the context of photoelectrochemistry, and especially for macroelectrolysis purposes, it is essential to ensure that the working electrode is stable and exhibits appropriate structural properties. This is particularly crucial when working with semiconductor films supported on substrates of different nature, as it is the case in the present studies (TiO$_2$/stainless steel). Therefore, SEM characterization was performed in order to evaluate the morphology of the synthesized films (Figure 1). The representative SEM images in Figure 1 evidence the superficial line patterns associated with SiC paper abrasion during preparation of the metal.
substrates. Despite this, all four types of films appeared to have a crack-free, homogeneous and compact structure, features that are required for their use as photoanodes since they favor their stability and increase corrosion resistance of the metal substrate\textsuperscript{25,26,28,29}.

Figure 1. SEM images for (a) pristine TiO\textsubscript{2}, (b) TiO\textsubscript{2}-T, (c) TiO\textsubscript{2}-NF and (d) TiO\textsubscript{2}-TNF films.

Additionally, AFM images obtained for the films in contact mode (20 μm × 20 μm area) are shown in Figure 2. As it can be noted, polishing patterns caused by abrasion with SiC paper (# 600) are present on all the films. However, some agglomerates are observed as a function of the composition of the films. Average (R\textsubscript{a}) and root mean squared (R\textsubscript{q}) roughnesses are tabulated in Table 1. The addition of TEA seems to promote the increase of roughness (TiO\textsubscript{2}-T and TiO\textsubscript{2}-TNF); while NH\textsubscript{4}F appears to favor the formation of more homogeneous and thicker films, which increases their corrosion protective character\textsuperscript{27}.

Figure 2. AFM images for the synthesized films on stainless steel: a) pristine TiO\textsubscript{2}; b) TiO\textsubscript{2} T; c) TiO\textsubscript{2} NF and d) TiO\textsubscript{2} TNF.

Grazing angle X-ray diffraction (GAXRD) patterns for the different films are shown in Figure 3. All four samples were subjected to hydrothermal treatment for 4 h followed by calcination at 400°C. As it can be observed in Figure 3, anatase is the only TiO\textsubscript{2} crystalline phase that is present, which is known as the phase with the highest activity in photocatalytic processes\textsuperscript{1}. Moreover, the intense peak associated with Fe content in stainless steel was detected, due to the thin nature of the TiO\textsubscript{2} films. Some additional diffraction peaks associated with iron nitride (FeN\textsubscript{0.0324}) were also observed for the TiO\textsubscript{2}-NF sample.

Figure 3. X-ray diffraction patterns for pristine TiO\textsubscript{2}, TiO\textsubscript{2}-T, TiO\textsubscript{2}-NF and TiO\textsubscript{2}-TNF films after hydrothermal treatment and annealing at 400 °C.

The optical response of semiconductor materials can be related to the presence of energetic states within their band-gap, which are induced by defects and/or the effect of doping elements on the structure of TiO\textsubscript{2}. Such localized states are generated above the lower limit of the valence band (type p doping) or below the upper limit of the conduction band (type n doping) and are responsible for the absorption of less energetic light. This allows the activation of TiO\textsubscript{2} under visible light\textsuperscript{9-20}. Figure 4 shows the UV-VIS spectra for the films, which reveal that modifications with the doping agents significantly affected the visible light absorption of the TiO\textsubscript{2}-NF and TiO\textsubscript{2}-TNF samples. Using the Kubelka-Munk modified function (see Figure 4 insert) the band-gap values for each photocatalyst were estimated\textsuperscript{30} as follows: 3.2 eV for pristine TiO\textsubscript{2}, 3.1 eV for TiO\textsubscript{2}-T and 2.9 eV for both TiO\textsubscript{2}-NF and TiO\textsubscript{2}-TNF. These results indicate that when TEA is used alone, the insertion of N in the oxide network is not stable to heat treatment, which leaves anionic vacancies.

| Material       | Roughness | Roughness |
|----------------|-----------|-----------|
| Pristine TiO\textsubscript{2} | R\textsubscript{a} (nm) | R\textsubscript{q} (nm) |
| TiO\textsubscript{2}-T | 112.7 | 140.5 |
| TiO\textsubscript{2}-NF | 28.2 | 34.7 |
| TiO\textsubscript{2}-TNF | 57.2 | 68.9 |

Table 1. Roughness measurements for TiO\textsubscript{2} and modified TiO\textsubscript{2} films supported on stainless steel.
in the material. On the other hand, modification with either NH₄F or TEA and NH₄F resulted in more thermally stable doping of TiO₂, and therefore, produced a material that can effectively use visible light in photo-assisted electrochemical processes for the degradation of contaminants.

The results from Raman characterization are shown in Figure 6. As it can be observed, all the film samples exhibited the characteristic bands for the vibrational modes of the anatase phase: E₈ (148 cm⁻¹), B₁g (396 cm⁻¹), A₁g (513 cm⁻¹) and E₇ (638 cm⁻¹)³⁵. Relative to pristine TiO₂, a slight shift in the main band of the E₈ mode (148 cm⁻¹) was observed for the doped samples. This could be due to the presence of structural defects in the TiO₂ network. The red shift observed for TiO₂-T (E₈ = 146 cm⁻¹, see Figure 6 insert) can be associated with a variation in the crystal size³⁵,³⁶. On the other hand, the blue shift detected for TiO₂-NF (E₈ = 152 cm⁻¹) and TiO₂-TNF (E₈ = 153 cm⁻¹) has been previously attributed to distortions in the TiO₂ crystal network caused by the presence of N and F, which increase the vibration energy of the E₈ mode³⁵,³⁶.

3.2. Semiconducting properties

In order to evaluate the impact of the modifying agents on the semiconducting properties of the synthesized thin films, Mott-Schottky (M-S) plots were generated at a frequency of 400 Hz (Figure 7)³⁷. A positive slope in the linear region of the M-S plots can be observed for all cases, which indicates the n-type behavior of the films. The linear region in Figure 7 was fitted to equation (1) (solid line) in order to estimate the flat-band potential (Eᵦ) and donor density (Nₗ) of the formed films, which are summarized in Table 2:

\[
\frac{1}{C_{sc}^2} = \frac{2Nₗ}{εᵣε₀F} \left( Eᵦ - Eₚ - \frac{RT}{F} \right) \tag{1}
\]
in the donor density \( (N_d) \), which indicated the generation of defects such as oxygen vacancies in the material\(^{8,10}\). On the other hand, \( \text{NH}_4\text{F} \) doping (\( \text{TiO}_2\)-NF) displaced the flat band potential towards positive values, with a slight decrease in \( N_d \) compared to what was measured for the pristine samples. This behavior could be related to the compensating effect associated with the presence of F, which prevents the generation of new defects such as oxygen vacancies when N and F are simultaneously incorporated in the \( \text{TiO}_2 \) structure\(^{13}\). Moreover, it is well known that fluorine chemisorption onto a \( \text{TiO}_2 \) surface changes the surface acidity of the material, which could explain the variation in the \( E_{\text{fb}} \) values relative to pristine \( \text{TiO}_2 \). Furthermore, band diagrams were sketched from \( E_{\text{fb}} \) measurements, see Figure 7b. The valence band position (VB), derived by adding the band-gap energy (measured from UV-vis spectra in Figure 4), shows a slight displacement toward lower potential values for N-modified films. This behavior indicates that N2p states are being generated by the incorporation of N in the \( \text{TiO}_2 \) lattice, as it has been previously proposed\(^4\).

### 3.3. Photoelectrocatalytic oxidation of cyanide

Synthesized films were used as photoanodes in a conventional three-electrode cell to perform the photoelectrocatalytic oxidation of cyanide in synthetic solutions. All experiments were carried out in solutions of pH 11. Solution pH was kept constant by addition of 0.1 M NaOH to avoid the generation of hydrogen cyanide. In order to determine the most favorable potentiostatic conditions for the photoelectrocatalytic oxidation of cyanide, TEA and \( \text{NH}_4\text{F} \) modified \( \text{TiO}_2 \) films (\( \text{TiO}_2\)-TNF) were used to degrade 100 ppm of \( \text{CN}^- \) at different potentials for 120 min (see Figure 8). As shown in Figure 8, the percentage of degraded \( \text{CN}^- \) increases proportionally with the imposed potential, exceeding 50% cyanide oxidation when a potential of 0.97 V Vs SCE is reached. However, beyond this point, cyanide degradation drops drastically to undetectable levels at 1.1 V Vs SCE. When looking at the currents that were registered during the experiment, a different trend is observed: there is a monotonic increase of the current followed by a change in the slope of the curve in the interval of potentials where maximum percentage \( \text{CN}^- \) degradation is achieved (0.95 to 0.97 V). This response indicates that potentials above 0.97 V favor an additional process that reduces the efficiency of \( \text{CN}^- \) degradation, which is possibly the oxidation of water. Based on these findings, a potential of 0.97 V Vs SCE was selected for the photoelectrocatalytic oxidation of the cyanide solutions.

Once the appropriate potential was selected, four different film samples were prepared (pristine \( \text{TiO}_2 \), \( \text{TiO}_2\)-T, \( \text{TiO}_2\)-NF and \( \text{TiO}_2\)-TNF) for the PEC oxidation of 100 ppm of \( \text{CN}^- \) during 150 min, as shown in Figure 9.

The kinetic curves in Figure 9a reveal that the highest degradation rate was achieved on the \( \text{TiO}_2 \) films modified with TEA and \( \text{NH}_4\text{F} \) (\( \text{TiO}_2\)-TNF), which allowed for up to

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**Table 2.** Donor density \( (N_d) \) and flat band potential \( (E_{\text{fb}}) \) estimated from Figure 7.

| Sample  | \( N_d \times 10^{22} \) cm\(^{-3} \) | \( E_{\text{fb}} \) mV Vs SCE |
|---------|---------------------------------|------------------------------|
| \( \text{TiO}_2 \) | 2.4 | -33 |
| \( \text{TiO}_2\)-T | 11.7 | -49 |
| \( \text{TiO}_2\)-NF | 1.4 | 61 |
| \( \text{TiO}_2\)-TNF | 1.1 | 71 |

where \( N_d \) is Avogadro’s number (\( 6.02 \times 10^{23} \) mol\(^{-1} \)), \( N_d \) (cm\(^{-3} \)) is the donor density, \( F \) is the Faraday constant \( (\sim 9.65 \times 10^4 \) C mol\(^{-1} \)), \( \epsilon_r \) is the relative permittivity \( (50) \), \( \epsilon_0 \) is the permittivity of vacuum \( (8.8542 \times 10^{-12} \) F cm\(^{-1} \)), \( E_{\text{fb}} \) \( (V) \) is the potential at which the measurement was carried out, \( E_{\text{fb}} \) \( (V) \) is the flat-band potential, \( R \) is the gas constant \( (8.314 \) JK\(^{-1} \) mol\(^{-1} \)), and \( T \) is the absolute temperature \( (\sim 298 \) K). The third term in parentheses can be assumed to be negligible at room temperature, relative to the other terms.

As seen in Table 2, relative to pristine \( \text{TiO}_2 \), TEA modification of \( \text{TiO}_2 \) (\( \text{TiO}_2\)-T) resulted in a slight shift towards more negative values of \( E_{\text{fb}} \) with a nearly five-fold increase.
for the present studies, the magnitude of the current varied significantly among samples despite the fact that all films exhibited similar morphology. As shown in Figure 9b, the oxidation process occurs at a higher rate on the TiO$_2$-TNF and TiO$_2$-NF films, relative to pristine TiO$_2$ and TiO$_2$-T. These results are consistent with what was observed for the kinetic curves and confirm that simultaneous modification of TiO$_2$ with TEA and NH$_4$F results in a codoped material with a higher ability for photoelectrocatalytic oxidation of CN$^-$, relative to pristine or individually modified TiO$_2$.

As seen in Figure 10a, increasing CN$^-$ concentrations increased the quantity of degraded cyanide in both photoelectrocatalytic (PEC) and electrocatalytic (EC) processes. Figure 10 shows that the amount of oxidized cyanide was directly related to the magnitude of the registered currents, according to Faraday’s law of electrolysis. Moreover, regardless of the contaminant initial concentration, illumination resulted in higher CN$^-$ removal and therefore higher currents were generated, relative to the process without illumination (Figure 10b). This is associated with the generation of electron-hole pairs on the surface of the semiconductor$^5$. As it has been previously reported in the literature$^5,22-24$, photocatalytic oxidation of CN$^-$ on TiO$_2$ occurs primarily due to direct charge transfer.

Furthermore, ln C/C$_0$ vs time curves obtained at different initial cyanide concentrations, and the kinetic constant for a pseudo-first order reaction versus the initial cyanide concentration are plotted in figures 10c and 10d, respectively. The higher k values were obtained at the lowest cyanide concentration, which indicates that photoelectrocatalytic process could be employed more efficiently at a low pollutant concentration, as it has been stated for photocatalytic processes$^3$.

Since TiO$_2$ modification with fluoride generally results in an increased generation of OH$^-$ radicals for both photocatalytic
(PC) and photoelectrocatalytic (PEC) processes, the effect of OH\(^+\) radicals on PEC cyanide degradation was evaluated. In order to do this, 80 mM of tert-butanol (t-BuOH) was added to the CN\(^-\) solution\(^{39}\). A constant potential of 0.97 V Vs SCE under illumination for 150 min was used as well. Figure 11 shows the results for the TiO\(_2\)-TNF and TiO\(_2\)-T films. The kinetic curves indicate a small decrease in CN\(^-\) degradation when OH\(^+\) radicals are inhibited by t-BuOH, due to the fact that oxidation occurs primarily by direct electron transfer.

Several researchers have associated the photocatalytic oxidation of CN\(^-\) on TiO\(_2\) with a direct charge transfer process\(^{39-43}\). Nonetheless, it has also been reported that such photocatalytic oxidation could also take place through indirect mechanisms at the semiconductor/electrolyte interface. These indirect mechanisms are due to the presence of adsorbed hydroxyl ions that form OH\(^+\) radicals or caused by a homogeneous phase reaction with the OH\(^+\) radicals that diffuse into the cyanide solution\(^1\). These OH\(^+\) radicals react with the CN\(^-\) ions to give cyanate ions (OCN\(^-\)) and formamide (HCONH\(_2\))\(^{39}\). However, most authors report that for the carbon balance after degradation, the sum of CN\(^-\) and OCN\(^-\) ion concentrations is constant and properly fits the mass balance\(^{39,40}\). For this reason, indirect oxidation mechanisms do not seem feasible, or do not take place at significant magnitudes during the photocatalytic oxidation of CN\(^-\).

4. Conclusions

TiO\(_2\) modification using nitrogen and fluoride precursors (TEA and NH\(_4\)F) revealed a higher degree of crystallinity of the anatase phase and superior absorption of visible light, relative to pristine TiO\(_2\). This modification probably favored a direct oxidation mechanism through the holes trapped on the catalyst (=Ti-O\(^+\)), which resulted in a more efficient use of visible light to generate electron-hole pairs.

The results from the PEC experiments showed that TEA and NH\(_4\)F modified TiO\(_2\) photoanodes (TiO\(_2\)-TNF) achieve a significant degradation percentage of cyanide (> 60%) in diluted solutions (100 ppm) in just 150 min, when an optimal potential of 0.97 V Vs. SCE is used. Furthermore, it was found that the generation of OH\(^*\) radicals during TiO\(_2\) modification with fluoride does not have a significant effect on the PEC degradation of CN\(^-\) ions, which takes place by direct electron transfer. Cumulatively, these results indicate that the increase in percentage degradation of cyanide can be associated with a more efficient use of visible light due to a reduction in the band-gap of TiO\(_2\) in the presence of NH\(_4\)F and TEA.

5. Acknowledgements

The authors would like to acknowledge financial support from COLCIENCIAS (Project 1102-521-28875) and Universidad Industrial de Santander (DIEF Ingenierías Fisicoquímicas, Project 9416). The authors would also like to thank Dr. Hugo A. Estupiñán from Universidad Nacional de Colombia (Medellín) for technical assistance with AFM measurements.

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