

**TiO₂ nanotubes formed in aqueous media:
Relationship between morphology, electrochemical
properties and the photoelectrochemical performance
in water oxidation**

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TiO₂ nanotubes have gain great attention due to the easy forming, highly ordered structure, directional pathway for electron transport and prominent photoelectrochemical performance shown in water oxidation and pollutant degradation [1-2].

Different electrolytes (aqueous and organics) have been employed to obtain TiO₂ nanotube arrays with tailored pore diameter, tube length, and packing [1-2]. The TiO₂ nanotubes formed in fluoride containing aqueous electrolytes are normally short due to the high chemical etching [1-2]; however, these films are highly ordered, adherent and require lower imposed voltage than those formed in organic media.

Despite the continuously increased research work, there are still some gaps related to the different parameters controlling the photoelectrochemical performance of the nanotube arrays obtained by anodization in fluoride containing media [3-4]. Particularly the semiconductor properties and their relationship with the processing variables during anodization, have been scarcely explored [5].

In the present work anodic TiO₂ nanotubes were obtained in two different electrolytes (0.1 M HClO₄ plus 0.05 M HF or 0.05 M NH₄F) by imposing a potentiostatic pulse (10 V, 15 V, 20 V and 25 V) during 1 h. The obtained films were cleaned in an ultrasonic bath, left to dry in air and then heat treated at 450 °C during 30 min to obtain anatase. The pore diameter and tube length were estimated from SEM images. The electrochemical properties of the films were characterized in the dark in a three-electrode cell employing electrochemical impedance spectroscopy and cyclic voltammetry in 0.1 M HClO₄ aqueous solution. The photoelectrochemical performance towards water oxidation was carried using an Hg lamp (100W) by means of open-circuit measurements, linear voltammetry and chronoamperometry.

The formation potential and the fluoride salt employed in the anodization showed to be preponderant in the film morphology, particularly the pore diameter (Figure 1 a), and the semiconductor properties of the formed film (Figure 1 b). The aforementioned was attributed to the increase in the fluoride ion insertion in the TiO₂ lattice probably caused by the NH₄⁺ ions adsorption in the TiO₂ surface [6]. The variation in the photoelectrochemical performance of the films correlates well with the changes in the semiconductor properties (Figure 1 c), showing a higher performance for the films growth in NH₄F electrolyte. The different relation between morphology, electrochemical properties and photoelectrochemical performance will be discussed; however, the electronic properties seem to be the determining factor.

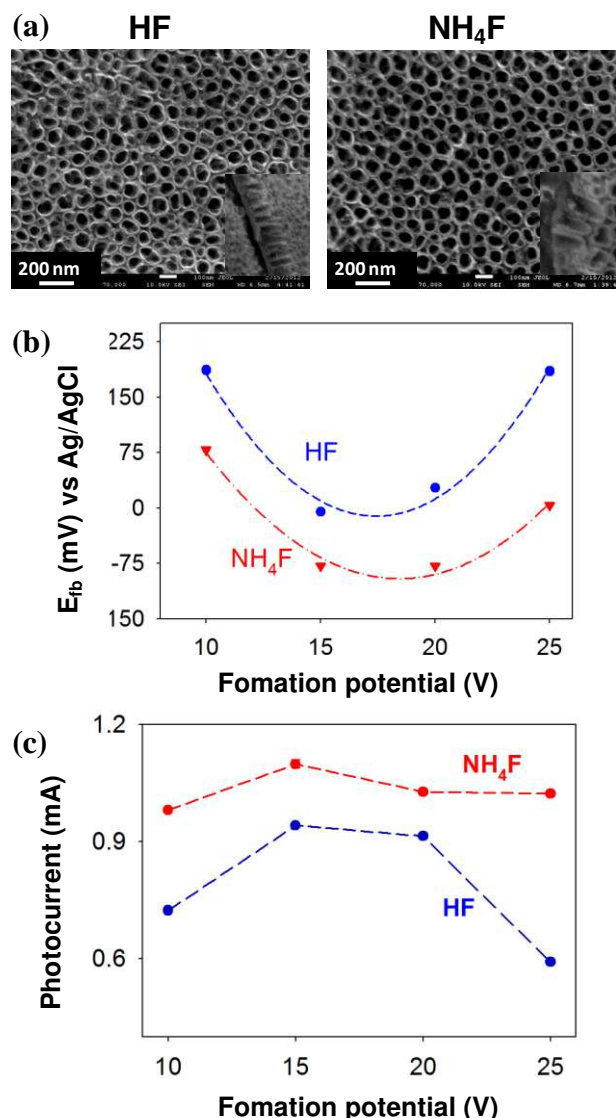


Figure 1. (a) SEM images obtained for the anodic TiO₂ nanotubes formed in 0.05 M HF and 0.05 M NH₄F at 15 V. (b) Variation of the flat band potential (E_{fb}), estimated from Mott-Schottky, with the formation potential employed to growth the film. (c) Photocurrent registered during water oxidation, at a potentiostatic pulse of 1.25 V vs Ag/AgCl (3 M KCl), as a function of the formation potential employed to growth the film.

References

- [1] S. Rani, S.C. Roy, M. Paulose, O.K. Varghese, G.K. Mor, S. Kim, S. Yoriya, T.J. LaTempa and C.A. Grimes, *Phys. Chem. Chem. Phys.* **12**, 2780 (2010).
- [2] P. Roy, S. Berger, and P. Schmuki, *Angew Chem Int Ed.* **50**, 2904 (2011).
- [3] S. Liang, J. He, Z. Sun, Q. Liu, Y. Jiang, H. Cheng, B. He, Z. Xie and S. Wei, *J. Phys. Chem. C*, **116**, 9049 (2012).
- [4] B. Liu, K. Nakata, S. Liu, M. Sakai, T. Ochiai, T. Murakami, K. Takagi and A. Fujishima, *J. Phys. Chem. C*, **116**, 7471 (2012).
- [5] S. Ait Alí Yahia, L. Hamadou, A. Kadri, N. Benbrahim and E.M.M. Sutter, *J. Electrochem. Soc.* **159**, K83 (2012)
- [6] P. Acevedo-Peña, D. Valdez and I. González, *J. Electrochem. Soc.* To be submitted.