

Fe-doped TiO₂ nanotube array films for Photocathodic protection of stainless steel

Rong-Gui Du*, Yan-Feng Zhu, Juan Zhang, Hai-qing Qi, Lu Xu, and Chang-Jian Lin

State Key Laboratory for Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, Fujian 361005, P. R. China

TiO₂ semiconductor materials have attracted great interest in the academic world due to their photocatalytic activity and other special photoelectrochemical properties. In the area of corrosion control, the application of TiO₂ films to the photocathodic protection of metals has inviting prospects (1-3). However, due to the wide band gap of the TiO₂ semiconductor, it is only excited by ultraviolet light ($\lambda < 387$ nm), and only 3-4% solar energy can be utilized. Therefore, it is expected to improve the photoelectric conversion performance of TiO₂ films by preparing TiO₂-based composite films (2-5).

In this work, our intention is to prepare a Fe-doped TiO₂ composite nanotube film on titanium substrates for achieving a significant photocathodic protection effect on stainless steel in a corrosive NaCl solution.

Ti plates (purity 99.9%) with dimensions of 15 mm×10 mm×0.1 mm were used as specimens. The highly ordered TiO₂ nanotube array films on the pre-cleaned Ti plate specimens were prepared in a 0.5 wt% HF solution by an anodic oxidation method at 20 V for 30 min with a Pt plate counter electrode. Then the specimens were annealed at 450 °C for 2 h and then naturally cooled down. The Fe-doped TiO₂ nanotube films were prepared in a mixed solution containing 0.5 wt% HF and 0.10 M Fe(NO₃)₃ by the same method as in the 0.5 wt% HF solution.

The morphology and composition of the as-prepared TiO₂ nanotube films were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The results showed that the prepared TiO₂ film was composed of the ordered nanotube array (Figure 1). The average inner diameter and length of the tubes were about 90 nm and 400 nm, respectively. The XRD result revealed that the film mainly consisted of anatase form of TiO₂. The surface analyses also showed that the morphology of the prepared Fe-doped TiO₂ nanotube film was similar to that of the pure TiO₂ nanotube film, and that the doped film contained Fe.

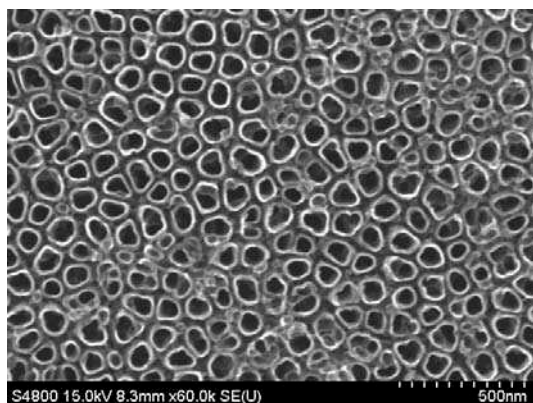


Figure 1. Typical SEM image of the TiO₂ nanotube array film prepared in a 0.5 wt% HF solution.

The photocathodic protection effects of the prepared films on stainless steel were evaluated by electrochemical

techniques (3). When 304 stainless steel in a 0.5 M NaCl solution was coupled to the TiO₂ film in a 0.4 M Na₂SO₄ solution, its interfacial reaction resistance and the electrode potential decreased steeply under ultraviolet illumination. The results indicated that lots of photoelectrons were transferred to the steel so as to lead to the cathodic polarization, which indicated that TiO₂ nanotube films could produce a good photocathodic protection effect on the steel. Especially the potential of 304 stainless steel coupled to the Fe-doped TiO₂ film decreased by 450 mV under illumination under the same experimental conditions, and remained lower than its corrosion potential after the light was cut off for about 6 h, showing a better photocathodic protection effect than that of the pure TiO₂ film.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 21073151, and 21173177), the National High Technology Research and Development Program of China (2009AA03Z327).

References

1. J. Yuan, S. Tsujikawa, *J. Electrochem. Soc.* 142, 3444 (1995).
2. M. J. Zhou, Z. O. Zeng, L. Zhong, *Corros. Sci.* 51, 1386 (2009).
3. J. Zhang, R. G. Du, Z. Q. Lin, Y. F. Zhu, Y. Guo, H. Q. Qi, L. Xu, C. J. Lin, *Electrochim. Acta* 83, 59 (2012).
4. M. J. Zhou, Z. O. Zeng, L. Zhong, *Mater. Corros.* 61, 324 (2010).
5. T. Tatsuma, S. Saitoh, Y. Ohko, A. Fujishima, *Chem. Mater.* 13, 2838 (2001).
6. Y. F. Zhu, R. G. Du, W. Chen, H. Q. Qing, C. J. Lin, *Electrochem. Commun.* 12, 1626 (2010).