

## Mesoporous titania film as photoanodes for cathodic protection of stainless steel

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### Introduction

Recently, the mesoporous TiO<sub>2</sub> films has been widely investigated for the application to dye-sensitized solar cells, photocatalyst as well as self-cleaning materials due to their unique properties such as high surface area, highly ordered porous structure, suitable morphology and semiconducting behavior. In this abstract, the mesoporous anatase TiO<sub>2</sub> films with ordered structures were prepared on FTO conducting glass substrates. Moreover, the photoelectrochemical properties of the mesoporous TiO<sub>2</sub> films were also investigated.

### Experimental

The mesoporous TiO<sub>2</sub> thin films were synthesized using the method combining dip-coating and evaporation-induced self-assembly. The FTO conducting glass (SnO<sub>2</sub>:F, 15 Ω/sheet, 10 mm×30 mm×2 mm) was used as substrates. The surface and cross section morphologies of mesoporous TiO<sub>2</sub> thin films were observed using field emission scanning electron microscopy (FE-SEM, LEO-1530). Moreover, the small-angle X-ray diffraction (SAXD) was used to determine the mesostructure of mesoporous TiO<sub>2</sub> thin films, with 2-theta ranged from 0.5° to 3°. All X-ray data were collected by X'pert X-ray diffractometer (XRD, X'pert PRO, Panalytical, Netherlands) using CuKα1 radiation ( $\lambda = 1.54056\text{\AA}$ ) at 40 kV and 30 mA. The photoelectrochemical measurements were performed using PARSTAT2273 Advanced Electrochemical System connected to an Omni-λ 300 grating spectrometer with a LSXS-500 Xe lamp as the illumination source. The TiO<sub>2</sub>/FTO electrode was served as a photoanode in the photoelectrochemical cell while the coupled 304SS electrode as the working electrode in the corrosion cell.

### Results and discussion

The results showed that the 350°C calcined TiO<sub>2</sub> films exhibited the ordered mesopores (about 10 nm in diameter) with a six-fold symmetry arrangement (Fig. 1). Moreover, the cross sectional image also confirmed that a hexagonally packed mesoporous microstructure with an ABAB stacking sequence was observed in the 350°C-calcined TiO<sub>2</sub> films, and the thickness of this film was about 200 nm. SAXD patterns of the mesoporous TiO<sub>2</sub> films on FTO substrates indicated that the film calcined at 350°C exhibited stronger (002) and (004) diffraction peaks than that of calcined at 500°C.

WAXD patterns of the samples calcined at 350°C and 500°C showed that all of the diffraction peaks in both samples matched well with the anatase TiO<sub>2</sub> (JCPDS No. 21-1272). This indicated that the mesoporous walls in the films were consisted of the anatase TiO<sub>2</sub> crystallites. Moreover, the intensity of diffraction peaks was greatly strengthened as the calcination temperature increased from 350 to 500°C, which suggested that the higher crystallinity was obtained in the sample calcined at 500°C than that of calcined at 350°C.

The photoelectrochemical measurements indicated that the mesoporous TiO<sub>2</sub> films could result in the more negative photopotential values than that of the TiO<sub>2</sub> films

without mesoporous structures (Fig 2 left). Therefore, the mesoporous TiO<sub>2</sub> films could offer a more effective photogenerated cathodic protection for 304SS due to their ordered mesostructures.

The mesoporous TiO<sub>2</sub> film calcined at 350°C showed a very weak photocurrent peak in the wavelength of 300–400 nm, whereas the mesoporous TiO<sub>2</sub> films calcined at 500°C exhibited two distinct photocurrent peaks located in the ultraviolet-light range of 300–400 nm and the visible-light range of 600–750 nm, respectively (Fig 2 right). Previous study reported that the TiO<sub>2</sub> films codoped with elemental N and F could result in a visible-light response in the wavelength range of 600–750 nm. The mesoporous TiO<sub>2</sub> films in this study could readily adsorb the N<sub>2</sub> in atmosphere under the aerated condition. Therefore, the photocurrent peak could also be observed in the visible-light range for the mesoporous TiO<sub>2</sub> films.

Tafel polarization curves of 304SS coupled with the mesoporous TiO<sub>2</sub> films and the control TiO<sub>2</sub> films both under the white light illumination and in the dark indicated that the electrode potential of each sample was shifted to a more negative value under illumination by white light. Moreover, the mesoporous TiO<sub>2</sub> films calcined at 500°C exhibited the maximum negative photopotential and the largest photocurrent, which agreed well with the OCP and the photocurrent spectra results. The electrochemical parameters of the Tafel polarization curves fitted by the analytical program revealed that the polarization current density of the mesoporous TiO<sub>2</sub> films calcined at 500°C increased by 5 orders of magnitudes than that of calcined at 350°C. It was also indicated that the more photogenerated electrons were produced in the ordered mesoporous TiO<sub>2</sub> films calcined at 500°C than that of calcined at 350°C.

### Conclusions

More negative photopotential was observed for the mesoporous TiO<sub>2</sub> films compared to the TiO<sub>2</sub> films without mesoporous structures. Besides, the mesoporous TiO<sub>2</sub> films calcined at 500°C exhibited the more negative photopotential and larger photocurrent than that calcined at 350°C. The mesoporous TiO<sub>2</sub> films could provide the effective photogenerated cathodic protection for 304SS.

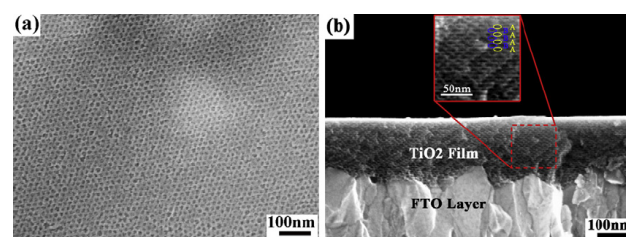


Fig. 1. The surface and cross sectional morphologies of the mesoporous TiO<sub>2</sub> films

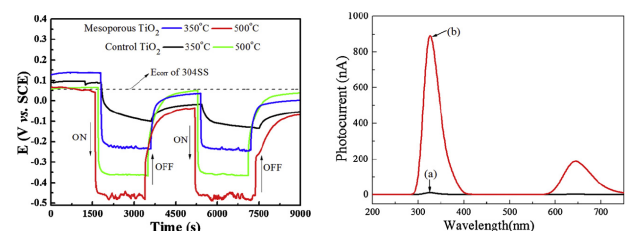


Fig. 2. (left) the OCP changes in the coupled electrodes between TiO<sub>2</sub> films and 304SS under illumination by intermittent white light. (right) the photocurrent spectra of the mesoporous TiO<sub>2</sub> films.