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Fabrication of Unique Stripe-Shaped Mesoporous TiO_2 Films and the Performance as a Novel Photo-Assisted Catalyst Support for DMFC

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Experimental Details

Materials

All the reagents were of analytical purity and used without further purification. Pluronic F127 (EO106PO70EO106, EO = ethylene oxide, PO = propylene oxide) was purchased from Sigma-Aldrich Corporation. $TiCl_4$, sulfuric acid, ethanol, methanol, potassium hydroxide and chloro platinic acid were purchased from Sinopharm Chemical Reagent Limited Corporation.

Synthesis of the mesoporous TiO_2 film

FTO glass plates were thoroughly cleaned by sonication for 30 min in the following solvents successively: acetone, aqua regia and deionized water.

A typical solution was prepared by the slow addition of the $TiCl_4$ into an ethanolic solution of the template in the molar ratio $1TiCl_4$:22EtOH:0.005F127. To this mixture was slowly added water ($10H_2O$:1Ti). Films were deposited at room temperature by spin-coating FTO glass at a spinning rate of 1500 rpm for 30 s under a controlled atmosphere of 70 % relative humidity (RH). Then films were aged at room temperature and RH in the 60-70 % range for at least 2 days, and they were heated at 60, 100, 130 ℃ for 24 h at each temperature. Calcination were done in air at 400 ℃ (ramp of 1 ℃ /min) for 2 h.

The TiO_2 films without mesopore structure were prepared following the similar method without F127 being added.

Electrodeposition of Pt on the mesoporous TiO_2 film

In a typical experiment, a three-electrode system was used, with the mesoporous TiO_2 films as working electrode, a platinum electrode as counter electrode, and a saturated calomel electrode (SCE) as reference electrode. Electrodeposition was carried out in the solutions of 0.5 M H_2SO_4 containing 50 mM H_2PtCl_4. Potentiostatic pulse electrodeposition was used to deposit Pt on the mesoporous TiO_2 films. For pulsed electrodeposition, rectangular potential pulses were used. During each pulse, a potential of -0.3 V versus SCE was applied for 1 s, followed y a potential of +0 V versus SCE being applied for 3 s. The number of consecutive pulses was 100, with the effective electrodeposition time of 100 s.

Characterization

X-ray diffraction (XRD) patterns were recorded by a Bruker D8 ADVANCE diffractometer using Cu Kα radiation (λ = 0.154056 nm). Transmission electron microscopy (TEM, FEI Tecnai G2) operating at 200 kV was applied to characterize the morphology of the mesoporous materials. Samples obtained by scratching the films from the substrate were embedded ethanol and ultrasonic dispersed. The field emission scanning electron microscopy (FE-SEM/EDXS) images were recorded on a Hitachi S-4800 microscope with an accelerating voltage of 5 kV, to observe the surface and cross-section image of the films.

Electrochemical and photoelectrochemical measurement

Photoelectrochemical reactions were carried out in the quartz beaker (50 mL) sing a Pt electrode as the counter electrode and a saturated calomel electrode (SCE) as the reference

electrode. An 8 W UV light was employed as a UV excitation source (the wavelength range of 265 nm). Cyclic voltammetry characteristics of the Pt/TiO_2 films electrodes were monitored in 1.0 M CH_3OH + 0.5 M KOH aqueous solution with and without UV illumination. All photoelectrochemical measurements were performed on a CHI 660C electrochemical workstation at a temperature of 298 K.

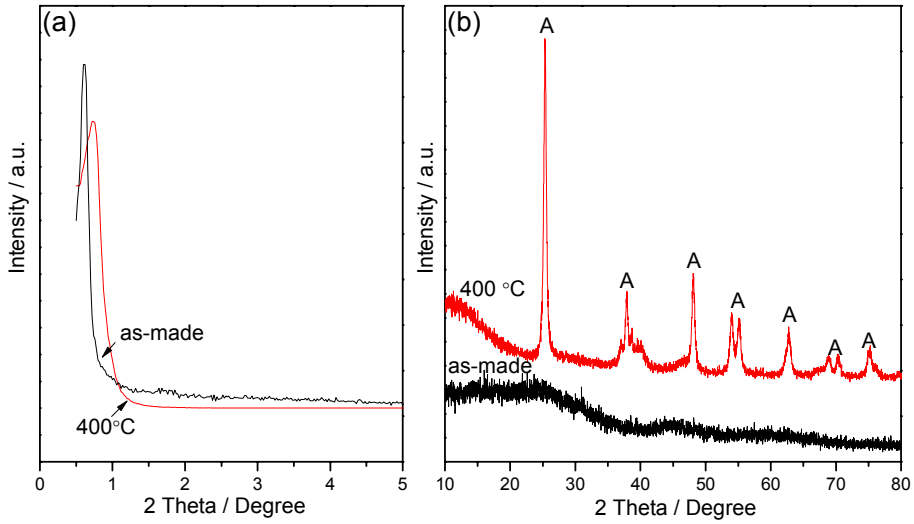

Figure S1. Small-angle (a) and wide-angle (b) XRD pattern of as made TiO_2 film and calcined at 400 ℃

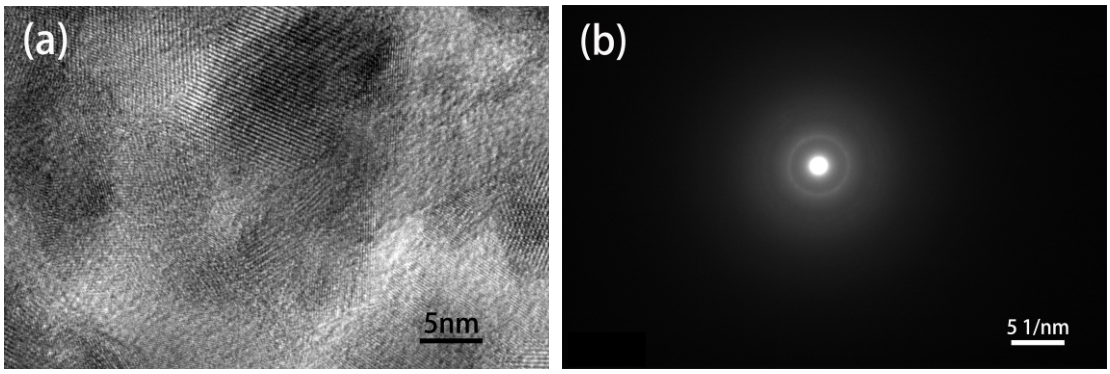

Figure S2. HR-TEM (a) and electron diffraction (b) images of the mesoporous TiO_2 film

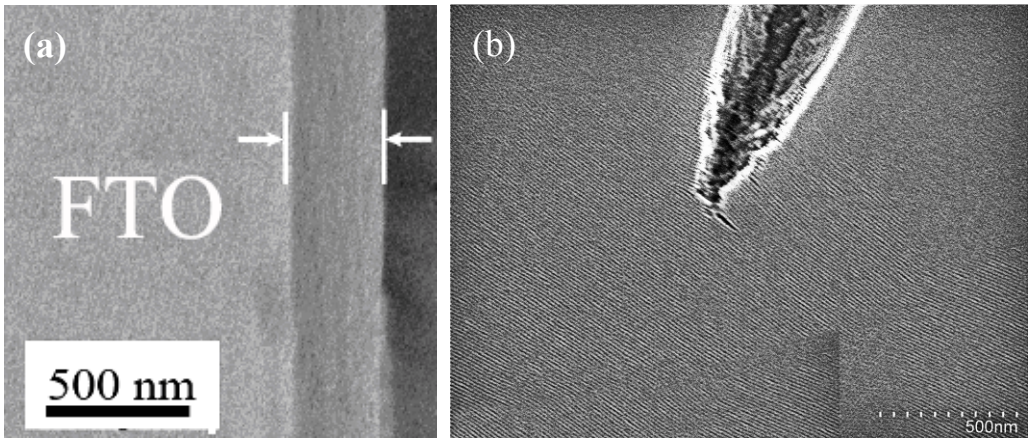

Figure S3. The section thickness(a) and the FE-SEM image(b) of the mesoporous TiO_2 film

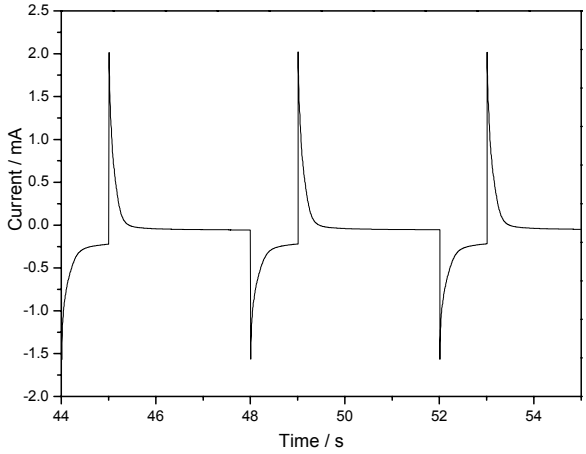

Figure S4. Pt electrodeposition curve by potentiostatic pulse electrodeposition method

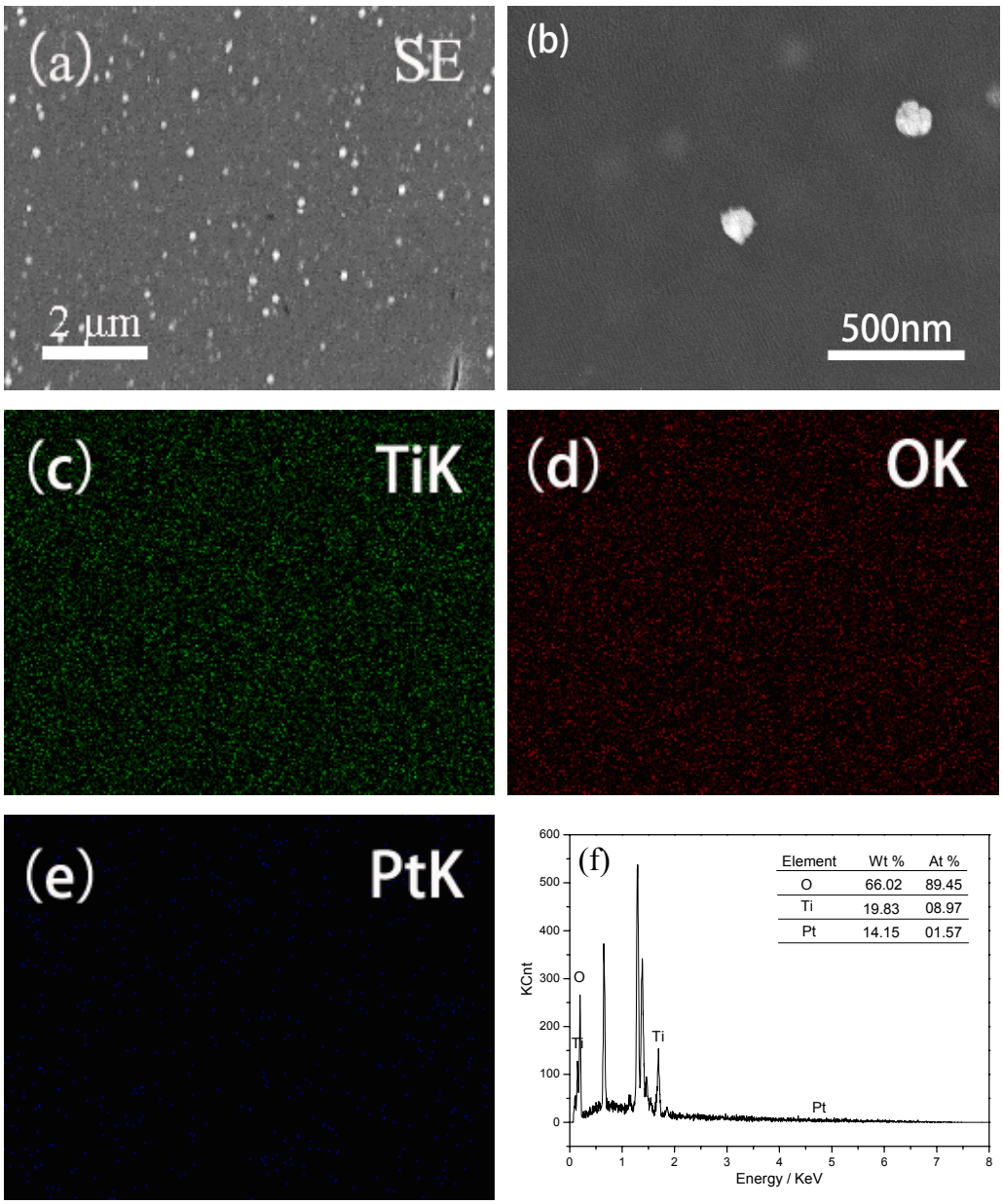

Figure S5. SEM/EDXS mapping of the mesoporous TiO_2film

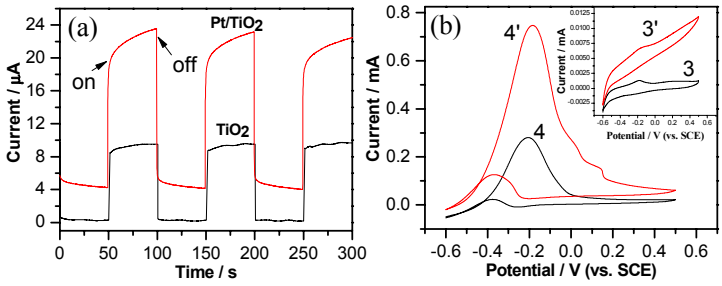

Figure S6. Photocurrent response and cycle voltammetry of the bare TiO_2 film electrode and Pt/TiO_2 film electrode with and without UV irradiation