Highly Ordered TiN Nanotube Arrays as Counter Electrode for Dye-sensitized Solar Cells

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Preparation and characterization of TiN nanotube arrays

Firstly, TiO_2 nanotube arrays was prepared by the anodization of metallic Ti foil (>99.7%, 0.25 mm) in a two-electrode cell containing a Pt counter electrode. The anodization was performed at 60 V in a solution of 0.1 wt% NH_4F in ethylene glycol at room temperature for 12 h.[1] Then, the as-prepared TiO_2 nanotube arrays were subsequently calcined at 450°C for 1 h in air to get rid of the ethylene glycol and obtain TiO_2 nanotube arrays with anatase phase. The as-prepared anatase TiO_2 nanotube arrays were further calcined in a tubular furnace at 800 °C for 1 h in ammonia atmosphere with a flow rate of 100 sccm. The structure and morphology of the resultant samples were detected using X-ray diffraction (XRD, Rigaku D/max-2500), scanning electron microscopy (SEM, Hitachi S-3500N), and transmission electron microscopy (TEM, FEI Tecnai 20).

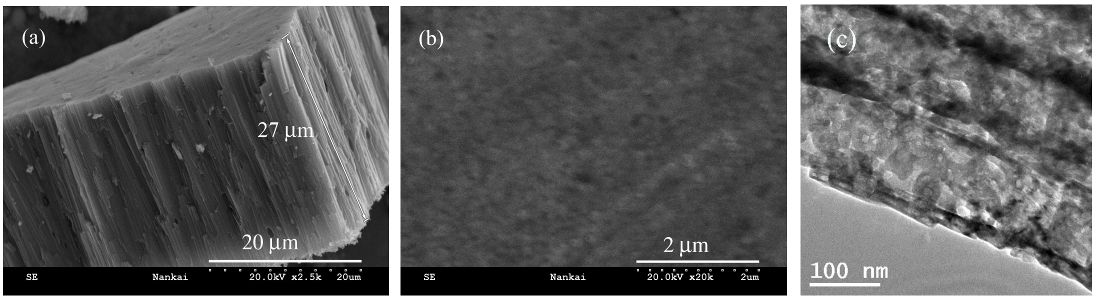

Figure S1. SEM images of full cross-section of mechanically fractured TiN nanotube arrays (a) and of the surface of the FTO/Pt counter electrode (b). A clearer TEM image of TiN nanotubes is shown in Figure S1 (c).

Preparation of FTO/Pt electrode

The mirror-like FTO/Pt (11Ω/sq) electrode was obtained by electrodepositing a platinum layer on the surface of fluorine-doped transparent conductive oxide (FTO, 15Ω/sq, Nippon Sheet Glass).[2]

Sensitized TiO_2 working electrode and device fabrication

Dye-sensized nanoporous TiO_2 film was prepared according to the classical method reported. Dye-sensitized solar cells were assembled by injecting the electrolyte into the aperture between the sensitized TiO_2 porous film electrode and the counter electrode. The liquid electrolyte is composed of 0.05 M I_2, 0.1 M LiI, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), and 0.5 M 4-tert-butyl pyridine (99%, Aldrich) with acetonitrile as the solvent. Surlyn 1702 was used as the spacer between the two electrodes. The two electrodes were clipped together and solid paraffin was used as sealant to prevent the electrolyte solution from leaking. The effective cell size was 0.25 cm^2.

The actual description of the TiO_2 working electrode is presented as follows: Titanium iso-propoxide (30 mL, 98+%, Fluka) was added to nitric acid aqueous solution (0.1 M, 180 mL) under vigorous stirring. After aging at 80 °C for 8 h, the slurry became a translucent blue-white suspension. The resultant colloidal suspension was autoclaved at 240 °C for 12 h to form white milky slurry. The resultant slurry was concentrated, then PEG-20000 (20 wt%) were added to form a TiO_2 colloid (15%). The FTO glass plate was washed with water and ethanol, and treated with 40 mM $TiCl_4$ aqueous solution at 70°C for 30 min to make a good interfacial contact between the TiO_2 layer and the conducting glass plate. Then adhesive tape was used fixed on the four sides of the conducting glass sheet to restrict the thickness and the apparent surface area of porous TiO_2 film. The TiO_2 colloid was spread on the FTO glass plate by using a doctor scraping technique. After drying, a TiO_2 film (12 μm thick) was formed. After calcination at 450 °C for 30 min in air, the TiO_2 film was treated with 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min, and then washed with distilled water. Finally, the porous TiO_2 film was formed by firing the conducting glass sheet at 450 °C for 30 min in air. After cooling to 80 °C, the TiO_2 film was immersed in 2.5×10^{-4} M ethanol solution of Ruthenium 535 bis-TBA (N719, Solaronix SA) for 24 h, then the dye-sensitized TiO_2 film was washed with anhydrous ethanol and dried in moisture-free air.

Photoelectrochemical Performance Measurement

The DSSCs were illuminated by a solar simulator (CHF-XM500, Beijing Trusttech Co. Ltd) under 100 mW/cm^2 (calibrated by a standard silicon solar cell) irradiation. Both the photocurrent-voltage (*I-V*) characteristic curves of the DSSCs under simulated sunlight and the electrochemical impedance spectroscopy (EIS) of the counter electrodes were recorded using an IM6ex (Zahner, Germany) electrochemical workstation. EIS spectra in symmetric cell configuration with two identical counter electrodes with the distance of 50μm, assembled with the similar procedure as described above, were measured. The frequency range was from 100 kHz to 100 m Hz with an AC modulation signal of 20 mV and bias DC voltage of 0.60V.

Preparation, characterization and performance of a TiN particle film and a TiN flat film

A porous TiN particle film was prepared by calcining a TiO_2 nanoparticles film under the same nitridation condition. The TiO_2 nanoparticle film was prepared by coating a layer of TiO_2 paste onto the surface of metallic Ti foil via the doctor scraping technique. The TiO_2 paste were formed of TiO_2 nanoparticles (P25, Degussa AG, Germany) and the same weight of PEG-20000 (polyglycol, M=20000) with the water as solvent. Then the TiO_2 nanoparticle film was calcined at 450 °C for 1 h to get rid of the PEG-20000. The PEG-20000 can increase the porosity of the TiO_2 particle film. The thickness of the TiN particle film was about 27 μm. A TiN flat film was also prepared by directly calcining metallic Ti foil under the same nitridation condition. Figure S2 shows XRD patterns of the TiO_2 particle film and the metallic Ti foil before and after nitridation. After nitridation, the TiO_2 particle film is entirely transformed to the TiN particle film, similar to the case of the TiN nanotube arrays. For the metallic Ti foil, we can find that the diffraction peaks of metallic Ti and TiN coexist, indicating that only partial metallic Ti at the surface layer can be converted into TiN in the nitridation process. SEM images of the obtained TiN films are given in Figure S3. Clearly, the TiN converted from the TiO_2 particle film still keeps a particle morphology (denoted as TiN particle film), while the TiN film from the metallic Ti foil shows a relatively smooth surface (denoted as TiN flat film).

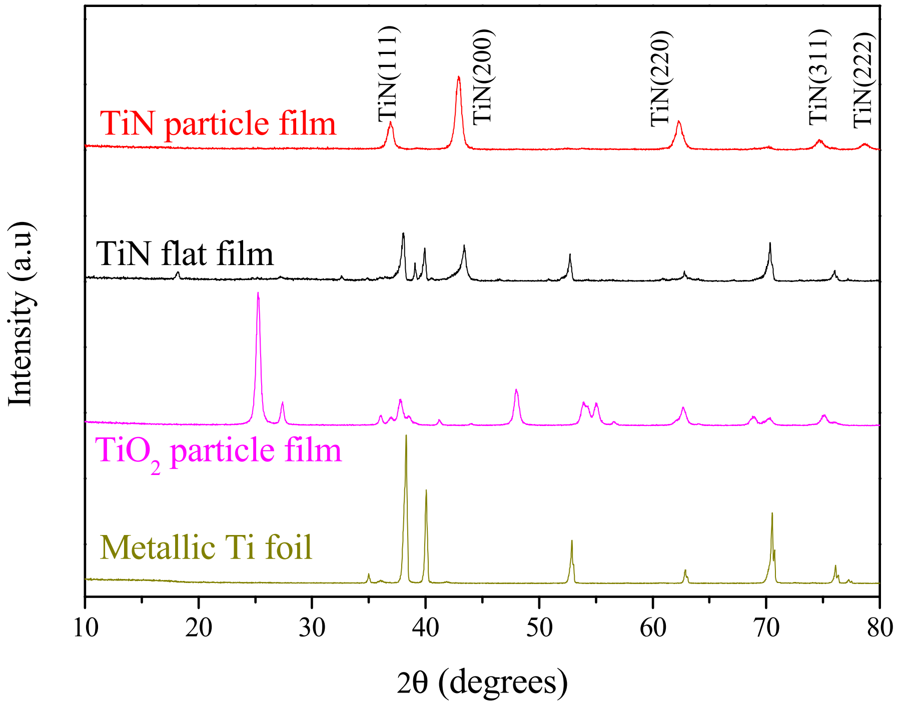

Figure S2. XRD patterns of TiO_2 particles film, metallic Ti foil, and their nitrided products (TiN particle film and TiN flat film).

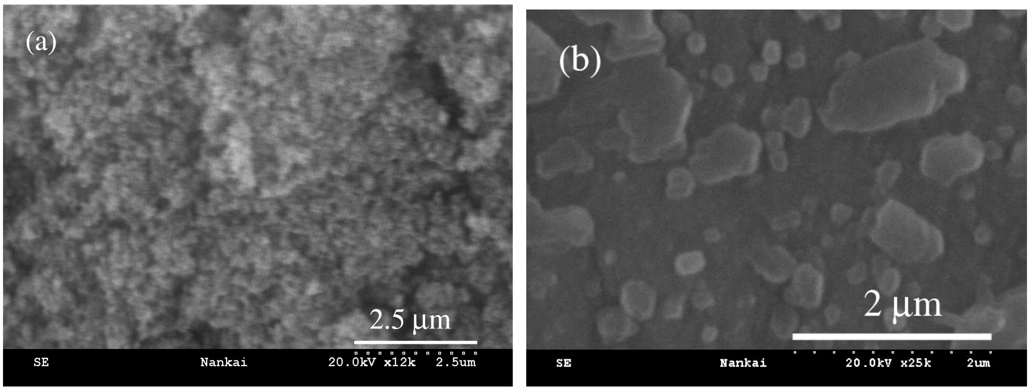

Figure S3. SEM images of porous TiN particles film (a), TiN flat film (b).

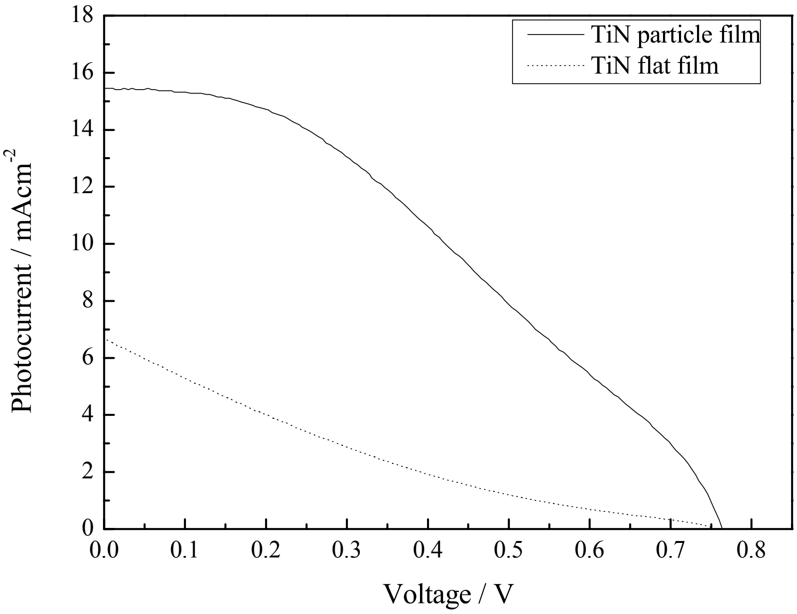

Figure S4. I-V characteristics of DSSCs with different counter electrodes of TiN particle film and TiN flat film. Figure S4 shows *I-V* characteristics curves of the dye-sensitized solar cells using the TiN particle film and the TiN flat film as counter electrodes. The corresponding photovoltaic performance parameters are listed in Table S1. The DSSC using the TiN particle film has a close V_{OC} and I_{SC} values to the DSSC using the TiN nanotube arrays, but a lower *FF* and η. The results demonstrate the positive effect of the nanotube array morphology on photoelectrochemical performance.

Table S1. Photovoltaic performance parameters of DSSCs with different counter electrodes

Counter electrode	V_{OC} (V)	J_{SC} (mA/cm^2)	*FF*	η (%)
TiN particle film	0.760	15.45	0.36	4.24
TiN flat film	0.755	6.68	0.172	0.87

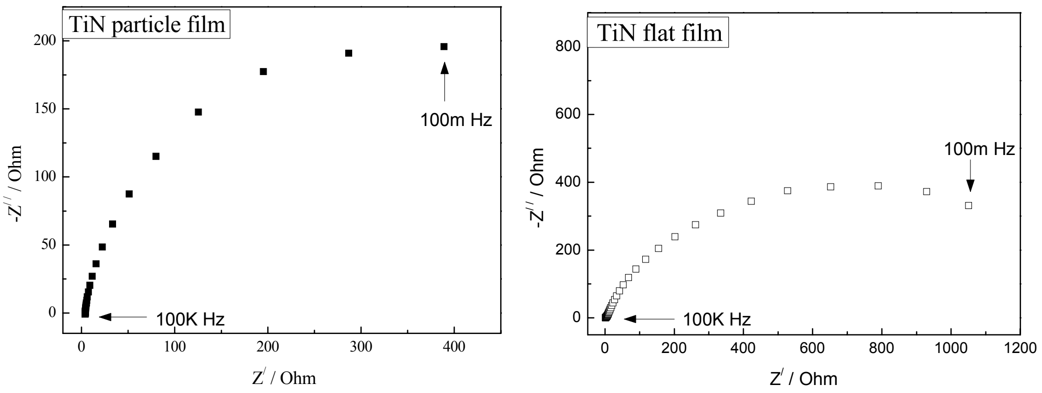

Figure S5. Nyquist plots of the symmetric cells with two identical counter electrodes. The frequency range was from 100 kHz to100m Hz.

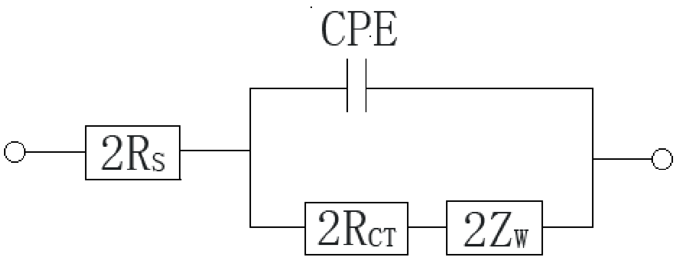

Figure S6. Equivalent circuit of EIS from the symmetric cell.[3]

Table S2 Simulated parameters of EIS from CE-CE cells

Sample	R_s (Ω)	CPE-T (F)	R_{CT} (Ω)	Z_{W-R} (Ω)
FTO/Pt	21.88	1.07×10^{-4}	7.38	8.34
TiN nanotube arrays	5.68	2.15×10^{-2}	1.51	104.9

References

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