Supporting information

Enhanced Photoelectrochemical Response of TiO₂ Nanotube Arrays by Simple Surface Air Plasma Treatment

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Experiment section

Synthesis of TiO₂ nanotube arrays

The pristine vertical TiO₂ nanotube arrays were fabricated on titanium foil substrates by a modified potentiostatic anodization process using a power supply (LW10J2, Shanghai) in a two-electrode configuration. Frist, the titanium foils were degreased with acetone, ethanol and deionized (DI) water for about 20 min by ultrasonication, respectively, and dried off with N₂ gas. The clean commercial titanium foil (0.25 mm thick, purity 99.5%, Baoji, China) was served as the working electrode, and the graphite plate was served as a counter electrode. The clean foils were then preanodized in an ethylene glycol solution containing NH₄F (0.5 wt%) at 60 V and 15°C for 2-10 h. The TiO₂ NTs layer was then peeled off by ultrasonication in 1 M HNO₃ aqueous solution. Then the second anodization was performed for 4 h under the same condition, with addition of HF (0.5 vol%). After anodization, the asprepared sample was thoroughly washed by DI water and dried by N₂. As-anodized

TiO₂ NTs were converted to anatase from amorphous by thermal treatment in air at 450° C for 2 h using heating rates of 2°C/min.

Air plasma surface treatment of TiO₂ nanotube arrays

A plasma system (diener electronic Plasma-Surface-Technology) was used to prepare surface modified TiO₂ nanotube arrays samples at room temperature. The power was kept at 98 W, while the chamber pressure was kept at 1.013 bar. The samples were cut into the area of 1 cm \times 3 cm. Then, when the flow rate of air was kept 6 mL/min, the samples were exposed to air plasma for 1 min, 3 min, 5 min, 10 min, 20 min, 30 min and 60 min, respectively. Besides, the samples were exposed to air plasma for 10 min, 4 mL/min, 6 mL/min, 8 mL/min, and 10 mL/min. Note that the treated samples should be immediately conducted about the first round of PEC testing. After then, the samples were stored for different time at room temperature in air under dark for stability measurements.

Characterizations

The morphologies and composition of samples were observed on field emission scanning electron microscopy (FESEM, JSM-6701F, JEOL Inc., Japan) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250xi). X-ray diffraction data were recorded on a X-ray Single Crystal Diffractometer (XRD, X'PERT PRO) with Cu-K α radiation ($\lambda = 1.5418$ Å), 2 θ ranging from 20-80°. The contact angle was measured by a contact angle instrument (DSA100, Germany).

Photoelectrochemical Testing

The PEC measurements were performed using a 3-electrode electrochemical cell, with photoanode as working electrode, an Hg/Hg₂Cl₂ reference electrode and a Pt wire as counter electrode, under simulated sunlight with a 300 W xenon lamp coupled with an AM 1.5G filter (Beijing Perfectlight Technology Co. Lt, PLS-SXE300UV), calibrated to 100 mW/cm², which was measured with a radiometer (CEL-NP2000,

Beijing Au-light Co., Ltd). The effective irradiation area of the photoanode is $1 \times 1 \text{cm}^2$, and its round was sealed with epoxy resin. 0.1 M NaOH aqueous solution (pH = 13) was used as the electrolyte for the PEC measurements. Before PEC measurements, the electrolyte was purged with N₂ for 1 h to remove the oxygen in the electrolyte. Linear sweeps and amperometry (i-t) scans were measured by a CHI660B electrochemical workstation (CHI Co., Shanghai, China), and scan rate is 10 mV/s. The incident photon-to-current conversion efficiencies (IPCE) were tested by a 150 W xenon lamp of SM-25 Hyper Monolight (Japan). The light intensity of the monolight was calibrated with a standard silicon photodiode. The IPCE values are obtained by following equation:

IPCE =
$$\frac{\left(1240 \times j_{ph}\right)}{(\lambda \times I)} \times 100\%$$

where j_{ph} is the steady-state photocurrent density at a specific wavelength, and λ is the wavelength of the incident light. I is the light intensity for wavelength λ at the film surface, I ranges from 0.764 to 3.77 mW/cm² over the spectrum of 300-500 nm.



Fig. S1. (a) XRD patterns of TiO₂ NTs under treatment different time (0 min, 1 min, 3 min, 5 min, 10 min, 20 min). (b) The digital photos and TiO₂ NTs phtoanodes before and after air plasma treatment for 20 min.



Fig. S2. The photocurrent density-time responses measured from TiO_2 NTs after air plasma treatment for 10 min at different air flow rate under the radiation.



Fig. S3. Linear-sweep voltammograms of TiO_2 NTs photoanodes before and after air plasma treatment at 0.15 - 0.30 V vs RHE under 300 W xenon lamp irradiation with an AM 1.5 filter.



Fig. S4. Transient photocurrent responses of TiO₂ NTs photoanodes before and after air plasma treatment for different time from 1 min to 20 min under 300 W xenon lamp irradiation with an AM 1.5 filter.



Fig. S5. (a-d,f) Linear-sweep voltammograms measured from the pristine TiO₂ NTs and plasma-treated TiO₂ NTs before and after storing for different time (2 days, 1 week, 2 week, 1 month, 2 months) in the dark at room temperature. (e) The relationship between photocurrent density values at 1.23 V (RHE) and store time for plasma treated samples.



Fig. S6. High-resolution XPS spectra of (a) survey spectra, (b) Ti 2p, and for TiO₂ nanotubes samples under treatment different time.

Table 1. The XPS data of O 1s and the fitting results showed that the content ofhydroxyl group increased with the increase of air plasma treatment time.

	0min	1min	3min	5min	10min	20min
Ti-O-H(%)	8.61	20.5	22.80	22.86	29.15	37.44
Ti-O-Ti(%)	91.39	79.50	77.20	77.14	70.85	62.56