

Electronic Supplementary Information

Photoelectrochemical reforming of biomass for hydrogen generation

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Experimental Section

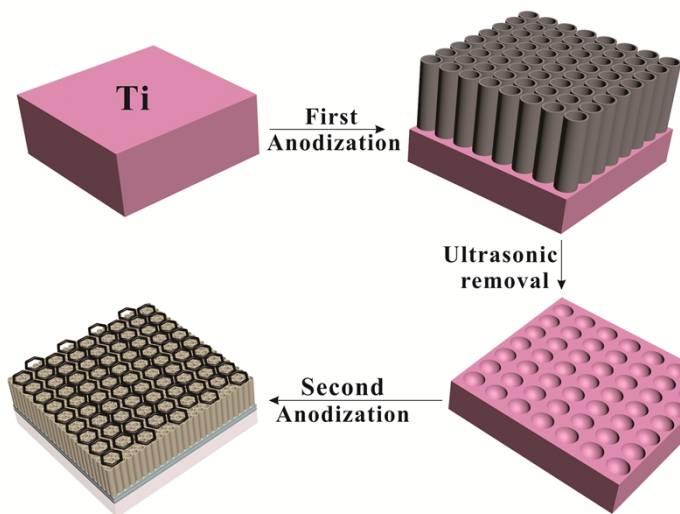
Chemicals and materials

A 2 mm thick titanium sheet (99.6%, Strem Chemicals) was cut into pieces of 25 × 10 mm². Ethylene glycol (EG), ammonia fluoride (NH₄F), potassium hydroxide (KOH), and glucose were purchased from Acros Organics and used as received. All aqueous solutions were prepared using deionized (DI) water with a resistivity of 18.2 MΩ cm prepared by Millipore system.

Preparation of the TiO₂ NTs

The hierarchical TiO₂ NTs were fabricated by a two-step anodization process. Prior to anodization, the Ti sheets were first degreased by sonicating in ethanol and room-temperature DI

water, followed by drying in pure nitrogen stream. The anodization was carried out using a conventional two-electrode system with the Ti sheet as an anode and a Pt mesh (Aldrich, 100 mesh) as a cathode respectively. All electrolytes consisted of 0.5 wt% NH_4F in EG solution with 2 vol% water. All the anodization was carried out at room temperature. The anodization processes have been illustrated in **Scheme S1**. In the first-step anodization, the Ti sheet was anodized at 60 V for 60 min, and then the as-grown nanotube layer was ultrasonically removed in DI water. The same Ti sheet then underwent the second anodization at 80 V for 10 min. After the two-step anodization, the prepared TiO_2 NTs sample was cleaned with DI water and dried off with N_2 gas. The as-anodized TiO_2 NTs was annealed in air at $450\text{ }^\circ\text{C}$ for 1 h with a heating rate of $5\text{ }^\circ\text{C min}^{-1}$.



Scheme S1. Two-step anodization synthesis of the hierarchical TiO_2 NTs.

Characterization of the TiO_2 NTs

The morphologies of the TiO_2 NTs were determined by field-emission scanning electron microscope (FESEM, FEI Quanta 600). The crystalline structure of the samples was analyzed by

X-ray diffraction (XRD, Bruker D8 Discover diffractometer, using Cu K α radiation, $\lambda = 1.540598 \text{ \AA}$). The diffuse reflectance UV-vis adsorption spectra were recorded on a spectrophotometer (Shimadzu, UV 2550), with fine BaSO₄ powder as reference. Photoelectron Spectroscopy (XPS) data were collected by an Axis Ultra instrument (Kratos Analytical) under ultrahigh vacuum ($<10^{-8}$ torr) and using a monochromatic Al K α X-ray source operating at 150 W. The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 and 20 eV, respectively. Binding energies were referenced to the C 1s binding energy of adventitious carbon contamination which was set at 284.8 eV.

PEC performance of TiO₂ NTs in presence and absence of glucose

The PEC performances of the TiO₂ NTs in presence and absence of glucose were evaluated using a three-electrode configuration with the TiO₂ NTs electrode, Ag/AgCl electrode and Pt mesh as working, reference and counter electrode, respectively. The supporting electrolyte used was 1 M KOH solution. The potentials of the photoelectrodes were controlled by a potentiostat and were reported against reversible hydrogen electrode (RHE) following the equation below:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + E^{\circ}_{\text{Ag/AgCl}} \text{ with}$$
$$E^{\circ}_{\text{Ag/AgCl}} = 0.1976 \text{ V at } 25 \text{ }^{\circ}\text{C} \quad (1)$$

The scan rate for the linear sweep voltammetry (LSV) was 5 mV s^{-1} . The transient photoresponse was evaluated under chopped light irradiation (light on/off cycles: 60 s) at a fixed electrode potential of 1.23 V vs RHE. The photocurrent was measured under an irradiation from a 300 W Xe lamp (PLS-SXE300, PE300BF). The intensity of the light source was calibrated with a Si diode (Model 818, Newport) to simulate AM 1.5G illumination (100 mW cm^{-2}). The electrochemical impedance spectra (EIS) were measured using a PGSTAT 302N Autolab Potentiostat/Galvanostat (Metrohm) equipped with a frequency analyzer module (FRA2) with an

excitation signal of 10 mV amplitude. The impedance *vs* frequency spectra were acquired at the open circular potential of the system both in dark and under illumination condition. Afterward, impedance *vs* potential measurement at a fixed frequency of 5k Hz in dark was performed to determine the carrier density.

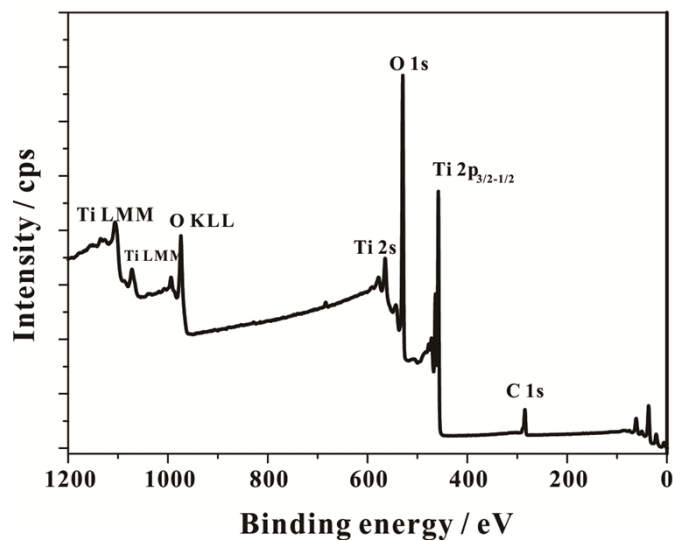


Fig. S1 XPS survey of the TiO₂ NTs.