

HIERARCHICAL TiO₂ BRUSH TYPE NANOSTRUCTURES FOR EFFICIENT PHOTOELECTROCHEMICAL WATER SPLITTING

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ABSTRACT

In this work, we developed a new type of nanostructured photoanode for a photoelectrochemical water splitting. The photoanode is based on hierarchical brush Titanium dioxide (TiO₂) nanostructures (BTNs), which were fabricated by our recently reported Glancing Angle Deposition and Oxidation (GLADOX) technique. The maximum incident photon-to-current efficiency (IPCE) of the BTNs photoanode was around 22% in the UV region and around 5% in the VIS light. The integral IPCE of the BTNs measured under bias of 0.5V under UV light illumination was 30 times higher compared to the photoanode based on TiO₂ nanorods and about 200 times higher compared to the one based on TiO₂ flat film. These results demonstrate that the brush TiO₂ nanostructures is a promising material for effective hydrogen generation via photocatalytic water splitting.

KEYWORDS

TiO₂ nanostructures, Glancing Angle Deposition, photoelectrochemical water splitting, fuel cell.

INTRODUCTION

Due to the wide spreading of personal electronic devices there is an increasing demand for high energy portable power sources. Micro fuel cells (MFC) are considered as a good candidate for this purpose, because they can provide much higher energy density than existing electrochemical batteries. However, the reliance of MFCs on external hydrogen source limits their use in portable devices.

In response to this issue, we proposed a new concept device that combines an MFC with on-chip micro-fluidic system for hydrogen generation via photoelectrochemical water splitting (Fig. 1). The device consists of two parts: internal fuel generation and the fuel cell. The both parts are integrated in one closed system based on two microchannels which are bridged by the system nanochannels arrays (for efficient H⁺ transfer and separation). The fuel generation part contains an integrated TiO₂ based photoanode and a Pt cathode. The fuel cell part consists of a composite Pt-Pd anode and a Pt cathode. The working principle is based on four steps:

- I. $\text{H}_2\text{O} + h\nu \rightarrow 1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$;
- II. $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$;
- III. $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$;
- IV. $1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$,

Our laboratory has already reported new critical findings about enhanced proton mobility [1] and high Laplace pressure in extended nanochannels [2], which enable efficient H⁺, O₂ and H₂ separation [3]. We also demonstrated on-chip photocatalytic water splitting system based on TiO₂ flat film photoanode integrated with the separation system, in which hydrophilic nanochannels were used for H⁺ transfer and hydrophobic micro channels were used for gas-liquid separation [4]. However, the flat TiO₂ films had low specific surface that resulted in low IPCE of about 0.016%. The motivation of this work was to enhance the photocatalytic activity of our photoanode through the modification of the TiO₂ morphology toward higher specific surface with higher density of catalytic centers and toward better response to the solar light in both UV and visual part of the solar spectrum.

EXPERIMENT

TiO₂ films of three different morphologies: flat film, nanorods (NRs) and brush nanostructures (BTNs) were fabricated on indium tin oxide flat films with Au interlayer (ITO/Au/ITO) on fused silica substrates. TiO₂ flat film and TiO₂ NRs were prepared directly by reactive r.f magnetron sputtering of Ti in a mixture of O₂/Ar at 0.1-0.2Pa in normal and glancing angle deposition (GLAD) regimes, respectively (Fig.1a). The details on the GLAD method can

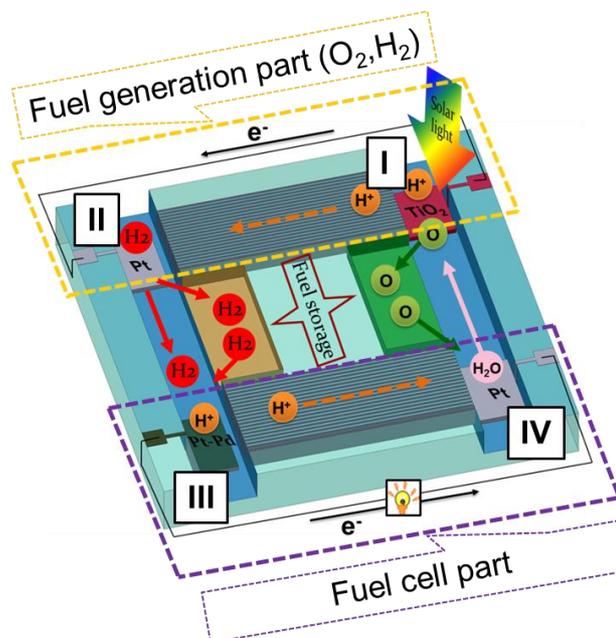


Figure 1. Conceptual sketch of the proposed micro/nano fluidic self-recharging fuel cell device.

be found elsewhere [5]. The hierarchical brush TiO_2 nanostructures (BTNs) were fabricated by our recently reported Glancing Angle Deposition and Oxidation (GLADOX) technique [5, 6]. In particular, 200 nm Ti layer was firstly sputtered on the ITO/Au/ITO/fused silica glass substrate in normal configuration. Then the stage position was switched to the GLAD regime, which resulted in the fabrication of well-separated Ti nanorods (Fig. 2(a)). The Ti nanorods were converted to brush TiO_2 nanostructures via anodic oxidation in 0.3wt% solution of NH_4F in ethylene glycol under anodization potentials of 20V at 19°C (Fig. 2 b). The as grown amorphous TiO_2 flat films, nanorods and BTNs were transformed to crystalline Anatase by annealing at 450°C in oxygen atmosphere, which was confirmed by XRD analysis. The photoelectrochemical characterization was conducted in a three-electrode cell by using DY2300 potentiostat and a tunable light source provided by a 500W Xenon lamp and a grating monochromator.

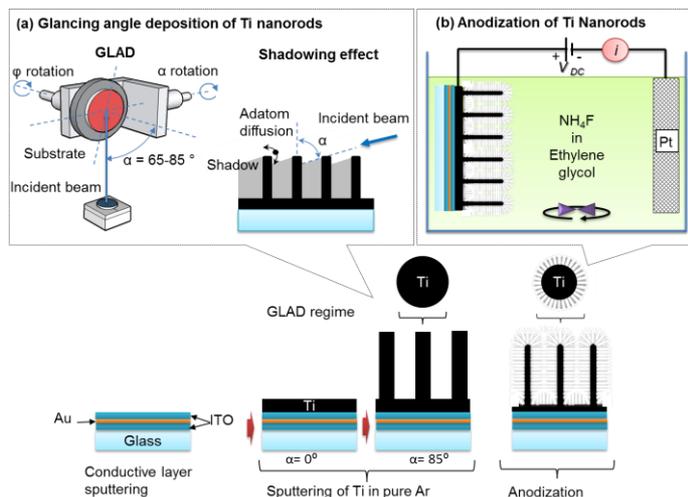


Figure 2. Fabrication of TiO_2 BTNs by combination of GLAD (a) and anodization (b).

RESULTS AND DISCUSSION

The morphologies of TiO_2 photoanodes are shown in Figure 3. The TiO_2 flat film (Fig. 3a) consists of dense-packed grains with high surface roughness most probably originated from a high deposition rate in the transition deposition mode. The photoanode prepared by GLAD of TiO_2 mainly consists of individual NRs with the diameter of around 50-70 nm, which are well-separated from each other (Fig. 3b). BTNs of TiO_2 fabricated by GLADOX consist of small TiO_2 nanotubes arranged in shells around central cores (Fig. 3c). The initial Ti nanorods, which served as precursors for BTNs are shown in Fig. 3d. We performed a series of experiments to find conditions that control the conformal growth of TiO_2 nanotubes on the walls of Ti NRs. The anodization potential of 20V was found to promote formation of small NTs with the diameter of around 10-20 nm. By using appropriate anodization time we were able to precisely control the conversion ratio of Ti nanorods into BTNs. As a result, the highly porous material that consists of brush TiO_2 nanostructures with thin Ti cores was formed (Fig. 3c).

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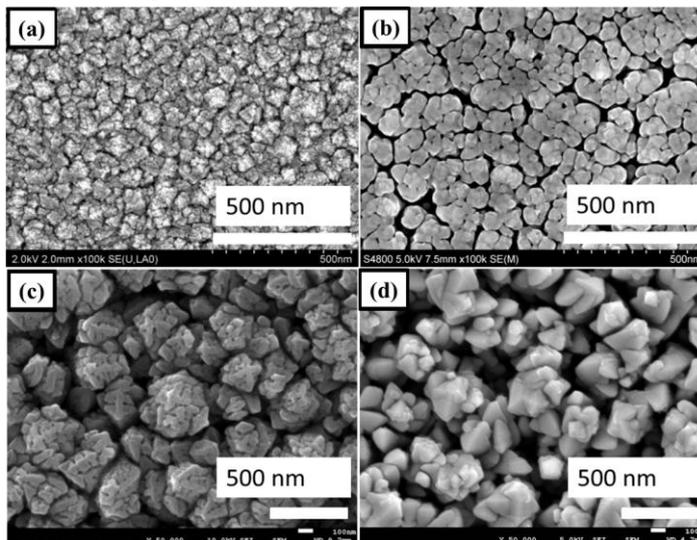


Figure 3. SEM images of a TiO_2 flat film (a), TiO_2 NRs (b) and BTNs TiO_2 (c) prepared by GLADOX. Ti nanostructure before the anodization (d).

We studied the photoresponse of the different photoanodes by measuring their incident photon-to-current efficiencies (IPCE) (Fig. 4a). The maximum IPCE (~22%) in the UV region was observed for the BTNs photoanode and was 30 times higher compared to photoanode based on TiO_2 nanorods and about 200 times higher compared to the one based on TiO_2 flat film. This indicates that the UV light was effectively used even on one micrometer thick BTNs. Beside those BTNs demonstrated an enhancement of IPCE in the visible region starting from 580nm, which reached the maximum value of 5% at 770 nm and resulted in the solar to hydrogen conversion efficiency of 0.45% with respect to the whole solar spectrum (Fig. 4d). The high IPCE in the UV region is attributed not only to the high specific surface of BTNs, but also to their hierarchical morphology, which promote electron transfer from the nanotubes to the Ti cores and then to the conducting substrate. The efficient electron transfer significantly reduces the recombination losses and thus promotes excessive concentration of the reactive holes at the semiconductor/electrolyte interface, as illustrated in Fig. 4(e). In addition, the metallic Ti cores inside BTNs act as effective light scatterers that promote light trapping inside the photoanode. Although the origin of the enhanced photoresponse of the BTNs photoanode to the visual light is not clear, the most probable explanation is plasmon resonance absorption facilitated by Au interlayer embedded into the ITO film. The IPCE enchantment in the visual region can be observed for the TiO_2 NRs as well, though the effect is much smaller than in the case of BNTs. This suggest that there is an emergent synergy between BTNs and ITO/Au/ITO that enables effective utilization of the

plasmonic effect, in which Ti cores inside the BTNs play an important role.

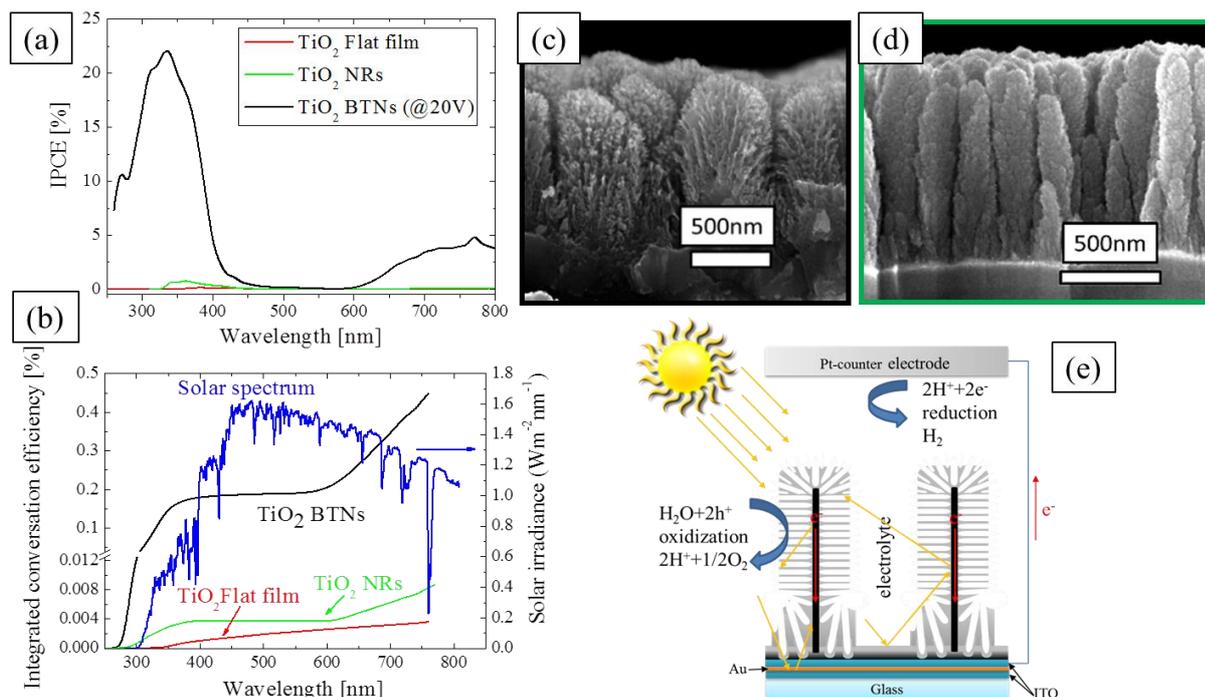


Figure 4. (a) IPCE action spectra of the TiO₂ flat film, NRs and BTNs, measured at 0.5V vs Ag/AgCl. (b) Integrated solar conversion efficiency of the photoanodes based on TiO₂ flat film, NRs and BTNs by the integration of measured IPCE at standard AM1.5 solar illumination according to ref. [7]. (c-d) SEM cross section images of TiO₂ NRs and BTNs. (e) Schematic representation of the electron transport in BTNs photoanode and illustration of the principle of light trapping.

CONCLUSIONS

In summary, we developed a new type of nanostructured photoanode for a photoelectrochemical water splitting, which is based on hierarchical brush TiO₂ nanostructures (BTNs). The photoanode demonstrated an excellent IPCE in the UV region, which was attributed to the high specific surface of BTNs, reduced recombination losses and effective light scattering by Ti cores inside the BTNs. In addition, BTNs photoanode demonstrated an increase of photocurrent in the visible region, which can be attributed to plasmon resonance absorption effect.

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