Large-scale Floated Single-Crystalline TiO_2 Flower-like Films: Synthesis Details and Applications

Supporting Information

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1. Synthesis of nanorod arrays directly on FTO

The nanorod arrays directly grown on FTO was made by a facile hydrothermal method described by Liu et al[1]. In a typical process, the FTO was ultrasonic cleaned with acetone, ethanol and deionized (DI) water for 15 minutes each and dried in nitrogen firstly. 20 ml DI water and 20 ml concentrated hydrochloride acid (36-38 wt %) were mixed and then 0.5 ml titanium butoxide was added into the solution. After a piece of FTO glass was put into Teflon-lined stainless steel autoclave with the conducting side downward, the reaction solution was transferred into the reactor. Then it was heated to 150 °C for 12 h. After the reaction, the solution was naturally cooled to the room temperature and the FTO glass was covered with a layer of nanorods shown in Fig. S1.

2. Transfer of the flower-like films onto FTO as photoanodes

In this experiment, titanium butoxide was used as the paste. A clear FTO was first coated with a thin layer of TBT (titanium butoxide) by scrape coating, and then a piece of film was rapidly transferred onto the FTO. After that, the sample was annealed at 500 °C for 15 min with a ramp of 2°C/min.

As a contrast, a DSSC based on the TiO_2 linking layer made from the annealing of titanium butoxide was fabricated. The characteristic was shown in Fig.S2.

3. Transfer of the flower-like films onto photoanodes as scattering layers

The TiO_2 nanoparticle paste was fabricated as the reference[2]. The film with the thickness of 4 μm was made by the doctor-blade method. After the doctor-blade, the flower-like film immediately covered the nanoparticle film and then they were stored in an ethanol atmosphere for 3 min before drying at 125 °C for 6 min. After that the film with the scattering layer was annealed at 500 °C for 15 min as the same as the film without the scattering layer.

4. Dye desorption experiments

The dye desorption experiment was conducted by immersing the dye loading photoanodes into a 0.1 mol/L NaOH ethanol solution (with the volume ratio of ethanol and water 1:1) for 12 h.

5. DSSC assembly

After the TiO2 films used as photoanodes was kept at 80 °C for 30 min, they were immersed in a 0.25 mM N719 ethanol solution for 24 hours to adsorb adequate dye. The solution composed of 0.1 M LiI, 0.6 M 2-dimethl-3-n-propylimidazolium iodide (DMPII), 0.05 M I_2, 1 M 4-tert-butylpyridine (TBP) in methoxyacetonitrile was used as the electrolyte. The counter electrode (FTO glass coated with platinum) and the photoanode was attached by a 25 μm surlyn film with the space between the two electrodes filled with the electrolyte.

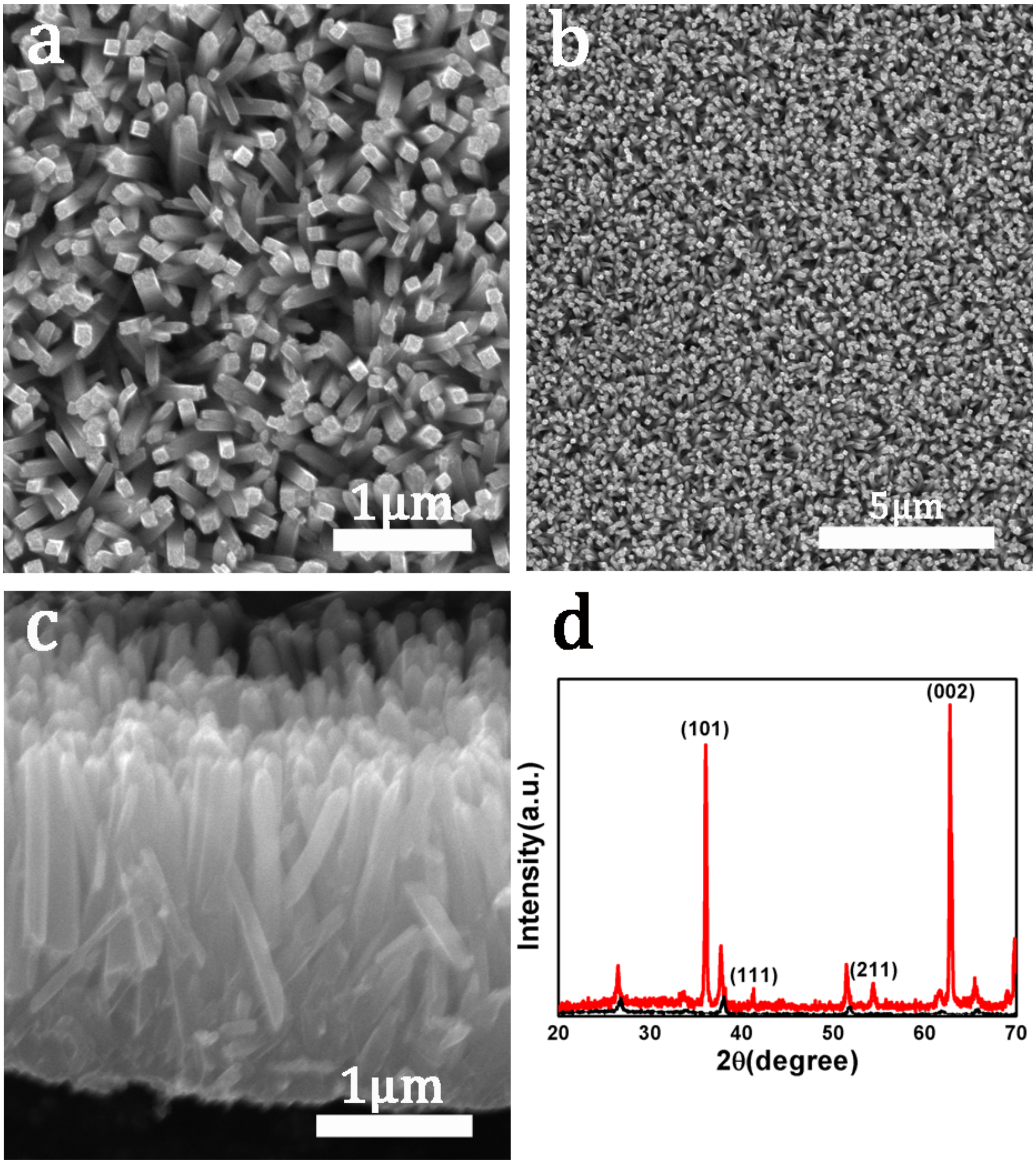

Fig.S1 Rutile TiO2 nanorod arrays directly grown on the FTO: (a-b) Top view with different magnification; (c) the section view; (d) the corresponding XRD pattern with the black line corresponding to the FTO without nanorods.

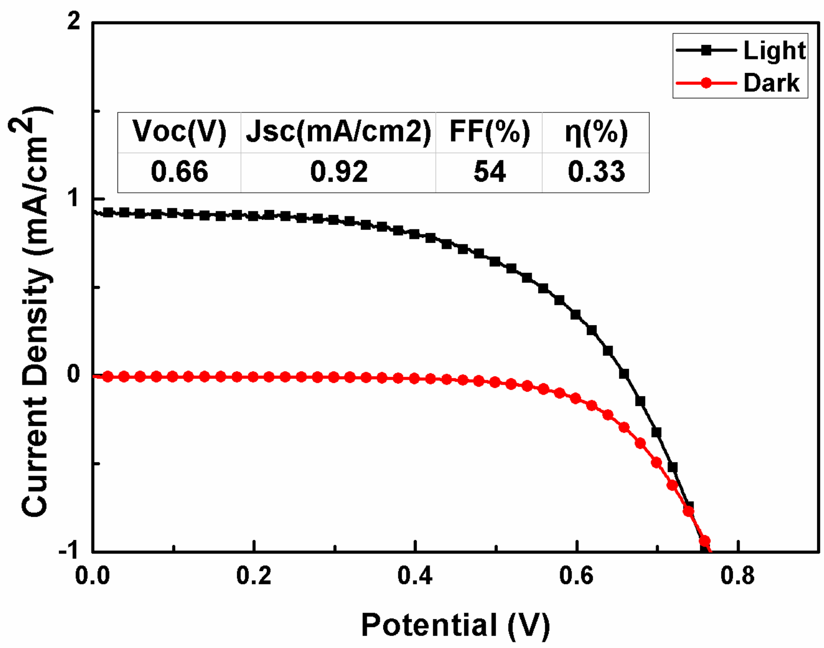

Fig.S2 Characteristic of DSSC made from the titanium dioxide linking layer.

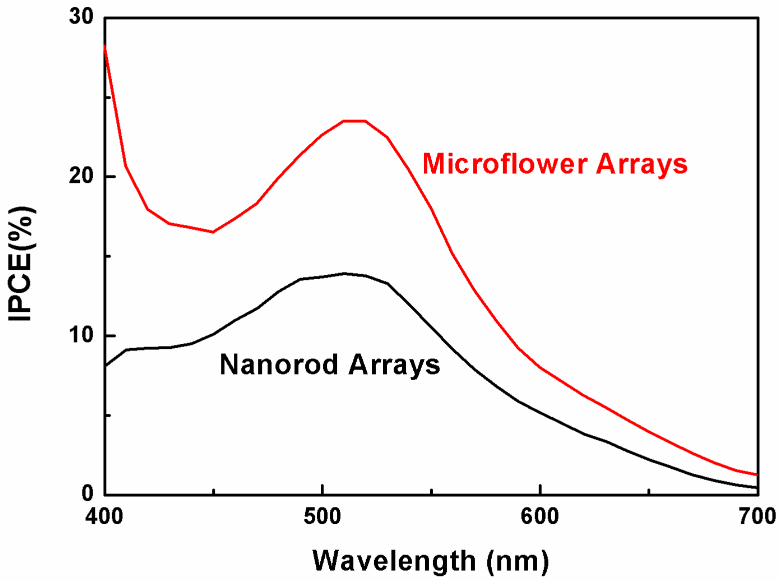

Fig.S3 IPCE values of different DSSCs as a function of wavelength; no correction was made for reflection losses.

6. IPCE Test

IPCE (incident photon to current conversion efficiency) measurements of MFDSSC and NRDSSC were performed with a 500W Xenon lamp using Spectra-300i Meter Triple Grating Monochromator/Spectrograph (Acton Research Corporation) with the results shown in Fig.S3.

7. Discussion about the factors influencing the short-circuit current

There are three main factors determining the short-circuit current: light harvesting capacity, electron injection efficiency and electron collection efficiency. As the TiO_2 nanorods which made up microflowers were synthesized at a chemical environment similar to that of TiO_2 nanorod arrays directly growth on the substrate, and they are both rutile, they may have similar surface states and electron injection efficiency. The linking layer in the micro-flower DSSC can increase the series resistance and decrease the short circuit current, resulting in lower electron collection efficiency. However, compared to nanorod-based DSSC, a much enhanced short current was obtained by microflower-based DSSC, which indicates that light harvesting efficiency could have much more effect on the short-circuit current.

References:

1. B. Liu and E. S. Aydil, *Journal of the American Chemical Society*, 2009, **131**, 3985-3990.
2. S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Gratzel, M. K. Nazeeruddin and M. Gratzel, *Thin Solid Films*, 2008, **516**, 4613-4619.