



# The application of freestanding titanate nanofiber paper for scattering layers in dye-sensitized solar cells

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## ABSTRACT

A titanate nanofiber paper with robust and good flexible property was successfully prepared by alkali hydrothermal synthesis with simple paper-making method. These nanofibers were about 80 nm in diameter and had a typical length in the range of tens of micrometers. Despite the transformation from titanate to TiO<sub>2</sub>-B phase was initially started, such nanofiber paper still kept its original shape and good flexibility after calcinations at 450 °C for 30 min. A solar cell with titanate nanofiber paper as scattering layer yielded an overall conversion efficiency of 4.90% under an incident solar energy of 100 mW/cm<sup>2</sup>, about 27.5% higher than that without nanofiber paper.

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## 1. Introduction

Recently particular interest was paid attention to the organization of one-dimensional (1D) TiO<sub>2</sub> nanostructures, such as nanowires, nanofibers, nanorods and nanotubes, into two-dimensional (2D) paper-like freestanding membranes for new applications [1]. However, large scale practical application has remained a challenge because of the poor strength and brittleness of 2D devices, especially after calcinations.

Dye-sensitized solar cells (DSCs) provide a promising alternative to conventional p–n junction photovoltaic devices because of their relatively high efficiency, simple fabrication process and low cost [2]. The light harvesting enhancements of scattering layers such as large nanoparticles and nanowires have been demonstrated both experimentally [3,4] and theoretically [5] to improve the photovoltaic performance of DSCs. Titanate nanofiber paper composed of flexible titanate nanofiber is similar to 2D paper-like TiO<sub>2</sub> freestanding membranes. Because titanate nanofiber paper has a variable degree of porosity, it can be employed as a very versatile layer for DSCs.

In the present research, we focused on the effects of freestanding titanate nanofiber paper as scattering light layer on the performances of DSCs. First, we developed a freestanding titanate nanofiber paper through alkali hydrothermal synthesis. Then the crystal structure and phase transformation of titanate nanofiber after calcinations were characterized by both X-ray diffraction (XRD) and scanning electron microscope (SEM). Finally, nanofiber paper was applied to assemble

DSC, and the effects of titanate nanofiber paper as a scattering layer were investigated.

## 2. Experimental

Titanate nanofiber was synthesized as follows: 0.20 g of P25 powder (anatase:rutile = 7:3, Degussa, Germany) was introduced into 30 mL of 10 M NaOH alkali solution in a 50 mL Teflon-lined autoclave container [3]. The resulting solution was dispersed by ultrasonic agitation to form a homogeneous suspension. After undergoing a hydrothermal reaction in an oven for 96 h at 200 °C, the resulting white pulp-like paste consisting of titanate nanofibers was then washed with distilled water or dilute hydrochloric acid solution for three times. Subsequently 0.1 wt.% surfactant (Pluronic F-127, Sigma, America) solution was added into the nanofiber suspension with the assistance of ultrasonic cleaning to obtain 10 g/L titanate. The resulting suspension was cast with uniform thickness onto macroscopic template made of stainless grid screen (200 meshes, Sefar, Switzerland) on an ash-free filter paper, and then dried at room temperature to form titanate nanofiber paper. After being covered with another piece of filter paper on top, the titanate nanofiber paper was pressed by using oil pump press machine. The macroscopic template was removed, leaving the titanate nanofiber paper dried in an oven at 150 °C for 10 h.

Photoanodes of DSCs were made of nanocrystalline TiO<sub>2</sub> film onto FTO glass (TEC-15, LOF) using a screen printing method [4] based at the techniques founded by M. Graetzel. Then the as-prepared freestanding titanate nanofiber paper was transferred onto the photoanode under a certain compression. After sintered at 450 °C for 30 min, the resulting photoanode with titanate nanofiber paper was sensitized overnight in 3 × 10<sup>-4</sup> M N-719 dye (Bu<sub>4</sub>N)<sub>2</sub>[Ru(dcbpyH)<sub>2</sub>(NCS)<sub>2</sub>] (Solaronix SA,

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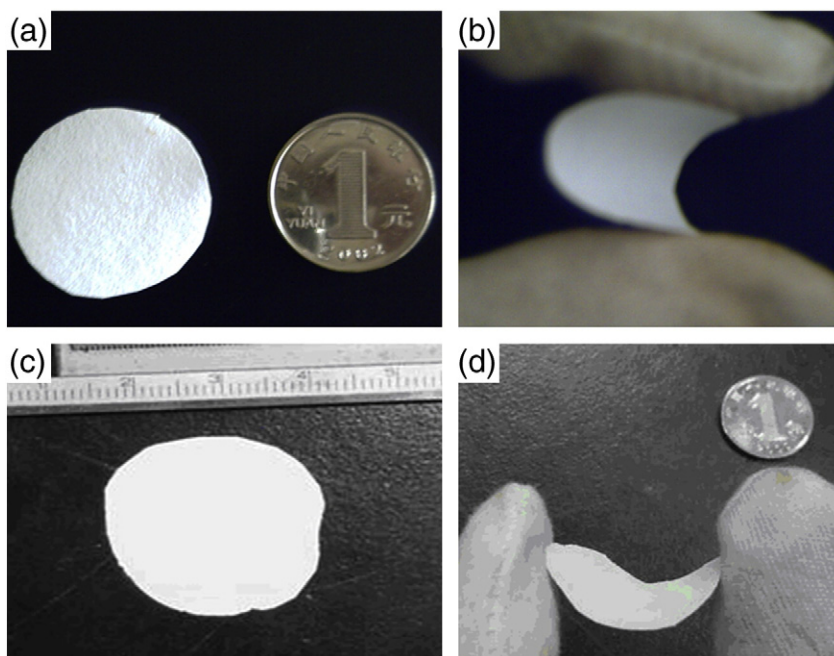


Fig. 1. Robust and flexible titanate nanofiber paper: (a) as-prepared flat and (b) as-prepared bended paper, (c) flat paper and (d) bended paper after calcinations at 450 °C for 30 min.

Switzerland) solution. The dye-sensitized photoanode was sandwiched together with a platinum-coated FTO counter electrode by insertion of a hot-melt type polyethylene surlin film to assemble a sandwich-type cell. The electrolyte (50 mM iodine ( $I_2$ ), 500 mM lithium iodide (LiI), and 500 mM *tert*-butyl pyridine dissolved in 3-methoxypropionitrile) was employed. The active area of the DSCs was 0.196 cm<sup>2</sup>. For comparison, the reference DSC without titanate nanofiber paper as scattering layer and another reference DSC with only titanate nanofiber paper as photoanode (without spreading TiO<sub>2</sub> paste on FTO) were fabricated with other parameters same as above.

### 3. Results and discussion

As shown in Fig. 1, a large-scale flexible titanate nanofiber paper with a diameter of 24 mm was fabricated purely from long inorganic functional nanofibers which were synthesized by alkali hydrothermal

reaction. The thickness of nanofiber papers was basically controlled by adjusting the nanofiber concentration and amount of the suspension followed by a compressive stress. The titanate nanofiber papers used in this paper were about 10 μm in thickness and 0.01–0.015 g/cm<sup>2</sup> in weight. The as-prepared titanate nanofiber paper is robust and highly flexible, with no obvious change in its shape after repeated bending as shown in Fig. 1(a) and (b). Even after calcination at 450 °C for 30 min, such titanate nanofiber paper still kept its original shape and good flexibility, and could be freely handled by hands and trimmed with scissors as shown in Fig. 1(c) and (d). This enables the nanofiber papers to be formed into various modules for larger commercial applications.

SEM (Superscan SSX-550, Japan) images of the titanate nanofiber paper are illustrated in Fig. 2. It was found that the titanate nanofiber paper was formed by overlapping and interpenetrating of long nanofibers with typical lengths in the range of tens of micrometers to hundreds of micrometers as shown in Fig. 2(a). And a high-resolution

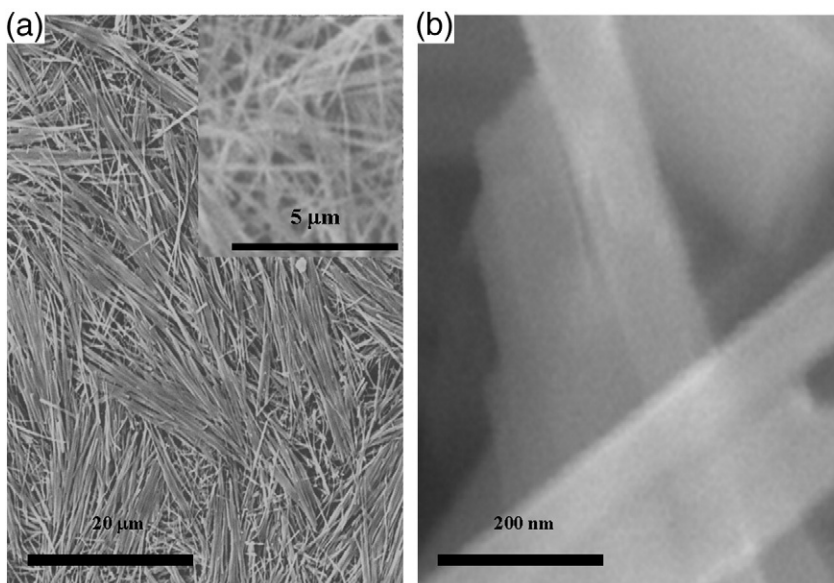


Fig. 2. SEM images of the titanate nanofibers paper in different magnification factor.

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