



# A new photoanode architecture of dye sensitized solar cell based on ZnO nanotetrapods with no need for calcination

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## ABSTRACT

We introduce a photoanode architecture in dye sensitized solar cell comprising building blocks of ZnO nanotetrapods with a mean arm diameter of 40 nm and arm lengths of 500–800 nm. This photoanode features a decent roughness factor up to 400, good network forming ability and limited electron-hopping interjunctions. Even without calcination, a power conversion efficiency up to 3.27% (under  $100 \text{ mW cm}^{-2}$ ) has been achieved at a film thickness of  $31.2 \mu\text{m}$ . The avoidance of the calcination step is an outstanding feat for flexible solar cells. We have also employed impedance spectroscopy to interpret the solar cell performance features.

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## 1. Introduction

Dye sensitized solar cell (DSSC) is one of the most successful devices that takes advantage of nanostructures to accomplish efficient solar-to-electric power conversion [1]. In such photoelectrochemical cells, the key component is typically a highly porous  $\text{TiO}_2$  nanoparticle photoanode originally invented by Oregan and Gratzel in 1991 [2]. Recently, great efforts have been directed to exploring new photoanode architectures in place of the porous  $\text{TiO}_2$  nanoparticles films, in the hope to further understand the inner working of DSSC system and enhance its performance [3]. Some on the list include  $\text{TiO}_2$  nanotube [4]/nanowire [5] arrays, ZnO nanorod [6]/nanotube [7] arrays synthesized by various methods. An important common feature of all these photoanode architectures is the vectorial electron transport pathway perpendicular to the charge collecting substrates, and the resulting generally superior electron collection, which is critical for high performance DSSCs [3,6]. Up to now, the  $\text{TiO}_2$  nanotube arrays photoanode has attained up to about 7% power conversion efficiency [4], whereas no more than 1.7% power conversion efficiency has been reported so far for ZnO nanorod [6] or nanotube arrays photoanodes, mainly limited by dye adsorption due to their relatively low roughness factors (*RF*).

Herein, we propose a photoanode architecture for DSSC based on ZnO nanotetrapods with a branched structure. This work is an outgrowth of our recent success on the growth of nearly monodi-

persed, well crystallized ZnO nanotetrapods with arm diameters much thinner than 100 nm [8], and indeed much thinner than the ZnO tetrapods reported previously in literature [9]. Several design benefits can be envisaged for such a photoanode. First, the thin arm diameter of our ZnO nanotetrapods promises a decent *RF*. Second, the ZnO nanotetrapods, being of a branched structure by nature, are amenable to be assembled into connected network with a good mechanical strength. Such a network structure can maintain the characteristics of a vertically aligned nanorod arrays by significantly reducing the many electron-hopping interjunctions existing in the porous nanoparticle films. Indeed, some of the expectations above have already been born out from our initial experiments as described as below.

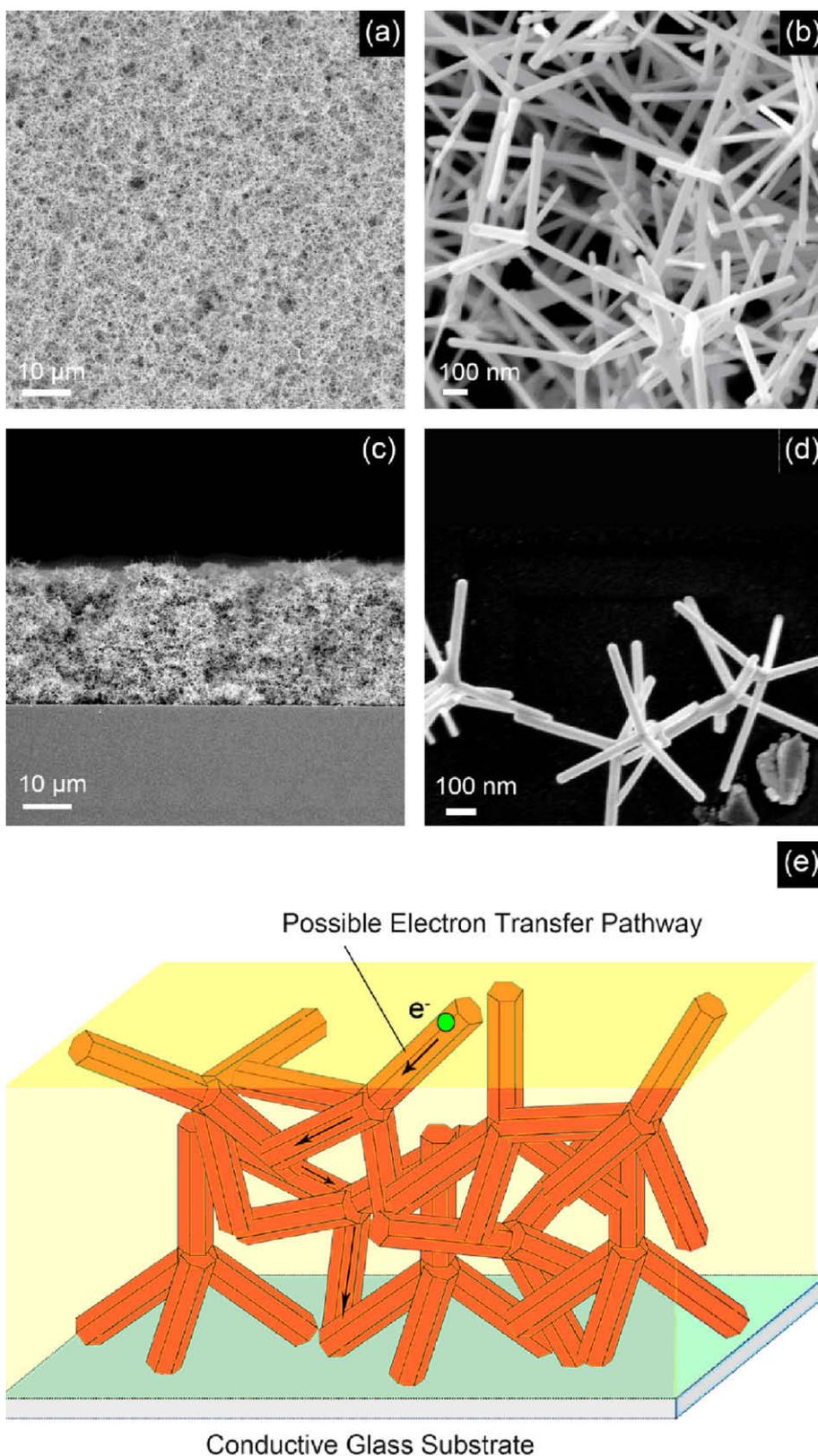
## 2. Experimental

The ZnO nanotetrapod powder was synthesized by the metal vapor transport-oxidation method we reported previously [8], except for small modifications for high loading of Zn source and thus high yield of the ZnO nanotetrapod product. For ZnO nanotetrapods film preparation, 0.4 g of ZnO nanotetrapods powder was first dissolved in 8 ml of 1-butanol to form a sufficiently viscous paste. Then the doctor blade technique was employed to spread this paste onto a conductive glass substrate (FTO-coated glass,  $14 \Omega \text{ square}^{-1}$ ). After totally dried in a vacuum oven at room temperature over night, the films were immersed in 0.1 mM ethanol solution of N719 dye at  $60^\circ\text{C}$  for 75 min to adsorb dye sensitizer.

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Solar cell test was carried out under  $100 \text{ mW cm}^{-2}$  light intensity illumination using an Oriel solar simulator (450 W, AM 1.5G) as the light source. Active electrode area was  $0.196 \text{ cm}^2$ . Electrolyte

composition was 0.5 M LiI, 0.05 M  $\text{I}_2$  and 0.5 M 4-tertbutylpyridine in an acetonitrile and valeronitrile mixed solvent (85:15 by volume).



**Fig. 1.** Structural characteristics of a  $30 \mu\text{m}$  thick ZnO nanotetrapods film. (a–d) SEM images viewed from top (a), at high resolution (b), in cross-section (c), and at the detailed inter-tetrapod connections (d). (e) Schematic showing a possible electron transport pathway across the ZnO nanotetrapod film. The sample in (d) was from a residue left on an FTO-glass substrate after scratching away a nanotetrapods film.

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