Transfer of asymmetric free-standing TiO_2 nanowire films for high efficiency flexible dye-sensitized solar cells

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ABSTRACT

A free-standing TiO2 nanowire thin film was prepared using the doctor-blade method. The film is composed of big and small nanowires on each side. The big nanowires have the functions of weakening adhesion to its original substrate, supporting the film after lift-off, and acting as a scattering layer in the final solar cells, whereas the small nanowires provide large surface area for dye loading and good adhesion to the flexible substrate for photoelectron collection. A high efficiency of 5.47% was obtained for flexible dye-sensitized solar cells fabricated by transferring the nanowire films onto ITO–PEN substrates.

The mechanically stable and sturdy film have other applications area such as water splitting, photo catalytsis, etc. In addition, modifications can be made to the film to strengthen / weaken its adhesion to the substrate, allowing for various applications.

Keywords: Flexible Dye-sensitized solar cell, free standing film, TiO_2 nanowires, lift-off, transfer

1 INTRODUCTION

Light-weight and flexible dye-sensitized solar cells (DSSCs) have attracted increased attention in recent years because they are highly desirable as portable power supplies, and they can be manufactured *via* low cost and high productivity roll-to-roll mass production.

However, good interconnection between TiO_2 particles in DSSCs usually requires sintering process at temperatures that are much higher than the melting point and decomposition temperature of commonly used plastic flexible substrates. As a result, several ‘‘low temperature sintering’’ methods have been reported to develop flexible DSSCs on plastic substrates. However, the performances of these low-temperature sintered devices are generally not comparable to those with high temperature sintering.

An alternative strategy to fabricate flexible DSSCs is to transfer high-quality, high-temperature sintered TiO_2 films onto flexible substrates. However, common reported transfer methods usually require complex lifting-off processes and pretreatment on substrates.[1] Moreover, the lifted TiO_2 films are mechanically fragile, which prevents their large-scale applications. In this contribution, we report a method to produce robust and free-standing asymmetric TiO_2 NW films which can be automatically lifted off from its original substrate, and be readily attached to flexible substrates (Fig. 1).

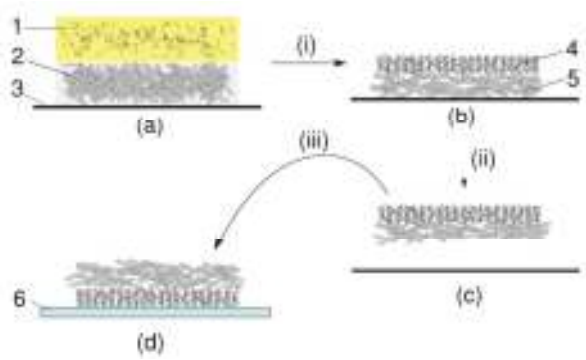

Figure 1 Illustration of the designed fabrication and transfer procedure using free-standing film method. (1) small nanowire paste; (2) big nanowire paste; (3) glass substrate; (4) small nanowire layer; (5) big nanowire layer; (6) flexible substrate. (i) High temperature treatment; (ii) cooling down to room temperature; (iii) transfer. (a) One layer of (2) and one layer of (1) formed on a piece of (3) using the doctor-blade method. (b) After (i), a free-standing film with layered structure was formed. (c) During (ii), the free-standing film automatically lifted off from (3). (d) The free-standing film was transferred onto a piece of (6) with small nanowires attached to substrate

2 EXPERIMENT

The NWs were synthesized according to literature reports. [2]The obtained NWs were converted to doctor-blade pastes,[3] spread onto glass substrates with big NWs directly attached to the glass substrate and small NWs on the top, and then sintered at 550 ^{o}C for 30 min. Upon cooling down to room temperature, the film was automatically lifted off from glass substrate without any visible cracks.

Photocurrent–photovoltage (I–V) measurements were conducted under 100 $mWcm^{-2}$ AM1.5 conditions, and a mask was used to keep the active area to be 0.158 cm^2.

Electrochemical impedance spectroscopy was carried out in the dark using an Autolab workstation. The results are fitted with a reported model. [4]

3 RESULTS AND DISCUSSION

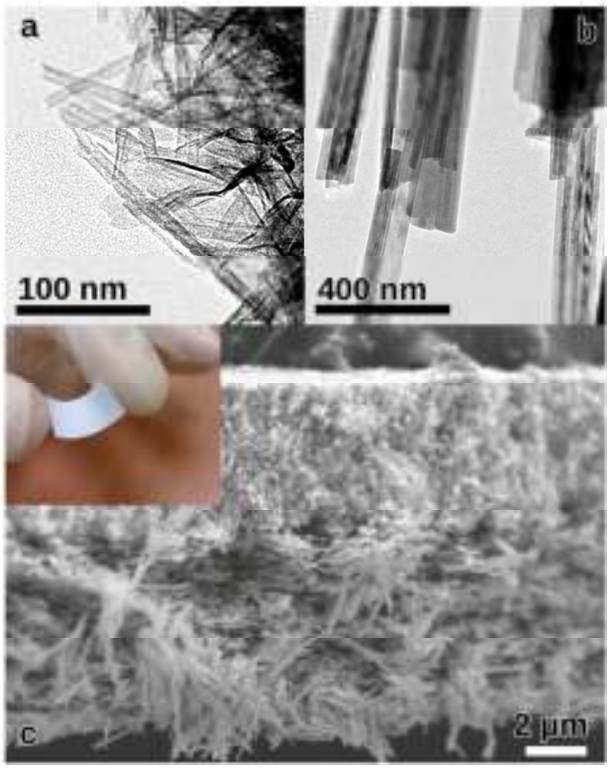

Figure 2a and b: TEM image of as-synthesized small and big NWs. c: Cross sectional FESEM image of a piece of free-standing flexible TiO_2 NW film (inset figure), showing layered structure with small and big NWs on the top and bottom, respectively.

The transmission electron microscopy (TEM) images of small and big NWs are shown in Fig. 2a and b, respectively. The lengths of the small NWs are ~200 nm, and the diameters are ~10 nm, while the big NWs are several micrometers long and ~100 nm in diameter. Fig. 2c shows a piece of free-standing flexible TiO_2 film (inset picture) and its cross-sectional field emission scanning electron microscopy (FESEM) image. The film has a layered structure: the upper layer contains small NWs, while the bottom layer is composed of big NWs. From the cross-sectional image, the thicknesses are determined to be ~6.5 µm and ~5.5 µm for layers containing big and small NWs, respectively.

Specifically for use in the fabrication of DSSCs two modifications were applied to the films in order to improve the device performance: 1) the films were treated with 80 mM $TiCl_4$ aqueous solution at 70 ^oC for 30 min and 2) Degussa P25 TiO2 nanoparticles were mixed with small NWs (wt% = 50%)[5] to improve surface area for dye adsorption.

A photoanode was fabricated by first attaching a piece of NW film to FTO-glass with the small NW side facing the substrate, then pressing the attached film for one minute at room temperature under a pressure of 0.6 t cm^2, and finally immersing it into D149 dye solution for 2 h at room temperature. The dye solution contained 0.5 mM D149 and 0.5 mM chenodeoxycholic acid in acetonitrile and tert-butanol mixture (v/v 50/50). The DSSCs were assembled by clipping the photoanode and pyrolysis platinum electrode together, using a 25 mm hot melt film as the spacer. The electrolyte contained 0.6 M 1-butyl-3-methyl imidazolium iodide(BMII), 0.05 M I2, 0.1 M LiI and 0.05 M 4-tert-butylpyridine, in a mixture of valeronitrile and acetonitrile (v/v 15/85).

The representative device was named as device A. The performance of device A is shown in Fig. 3. Device A has a light-to-electrical efficiency (η) of 6.24% with a short circuit photocurrent density (J_{SC}) of 12.1 mA cm^{-2}, an open circuit photovoltage (V_{OC}) of 0.740 V and a fill-factor (FF) of 69.7%.

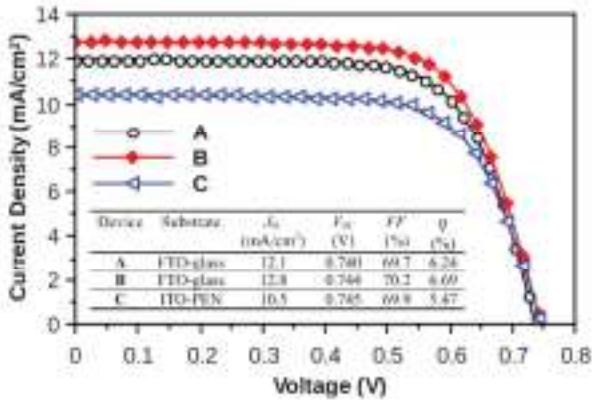

Figure 3 Performances of the devices. A: Transferred onto glass substrate. B: Non-transferred. C: Transferred onto flexible substrate.

As a control, devices B were fabricated with exactly the same structure and film thicknesses as device A, but using the conventional method instead, ie without transfer. A TiO_2 film was prepared by spreading the NW pastes onto a FTO-glass substrate using the doctor-blade method with the big NWs on top of the small ones, which was followed by high-temperature sintering and $TiCl_4$ treatment. All the other procedures were identical to those for device A. As shown in Fig. 3, these devices have an average g of 6.69%, a J_{SC} of 12.8 mA cm-2, a V_{OC} of 0.744 V and an FF of 70.2%. It is found that the energy conversion efficiency of a transferred device, A, is similar to the one fabricated with a standard method, B. This suggests that the qualities of the sintered TiO2 films are successfully retained by this transfer method. With the small NW attached to the glass substrate in device B, the film did not automatically lift off

after sintering. In contrast, with the big NW attached to the glass substrate in device A, the film was not firmly adhered to the substrate after sintering. This suggests that the big NWs are the key for the TiO2 film to lift-off automatically after sintering.

Electrochemical impedance analysis was performed to understand the differences between devices A and B. The devices were measured in the dark with forward biases between 0.55 V and 0.75 V. [4, 6]The measured impedance spectra were then fitted with a reported transmission line model. From the fitting results (Fig 4), it is found that R_{CO} (the resistance at TiO_2/substrate interface) of a transferred device was only slightly higher than that of the non-transferred one (A vs. B: 2.56 V vs. 1.61 V at V_{OC}). This finding is interesting, because the TiO2 film in device A is attached to the glass substrate by pressing while that in device B is directly sintered on the glass substrate. The strong adhesion formed between the film and substrate in device A by means of pressing alone is believed to be due to the NW film's intrinsic flexibility and softness which aid in forming multiple strong connection points between itself and the glass substrate.

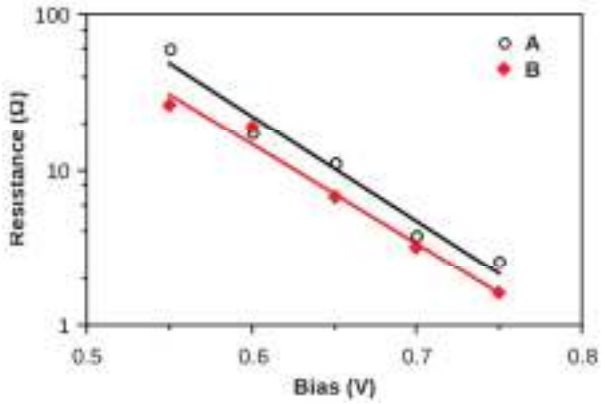

Figure 4 Fitted R_{CO} v.s. bias voltage of devices transferred onto FTO-glass

Using the fabrication conditions on FTO-glass substrate, we further fabricated a flexible DSSC on ITO–PEN substrate, with the glass based counter electrode replaced by ITO–PEN with 100 nm platinum. As shown in Fig. 3, this device (device C) has an η of 5.47% with a J_{SC} of 10.5 mA cm22, a V_{OC} of 0.745 V and a FF of 69.9%. Compared to device A, device C has a lower performance mainly due to the drop of photocurrent, which is in turn possibly caused by the stronger light absorption of the plastic substrate in device C as compared to the FTO-glass substrate used in device A.

4 CONCLUSIONS

In this study, an asymmetric free-standing flexible TiO2 film was prepared using the simple doctor-blade method. Flexible DSSCs were fabricated by transferring the free-standing films onto ITO–PEN substrates, without any pretreatment on the substrate required. Electrical impedance analysis showed good connection between the transferred film and its substrate. The free-standing and mechanically robust TiO_2 film may find other exciting applications where these mechnically properties are highly desired.

5 REFERENCES

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