WELL-ALINGNED AND CONDUCTIVE CARBON-NANOTUBE/TiO_2 FILM FOR FLEXIBLE PHOTOELECTRODE

Jiangtao Di and Qingwen Li

Suzhou Institute of Nano-tech and Nano-bionics, Chinese Academy of Sciences, Suzhou 215123, China

Introduction

Carbon nanotube (CNT) film has attracted considerable interest as it combines high electrical conductivity, optical transparency and good flexibility, while being low-cost [1]. Organic solar cell using CNT film as electrode has shown solar-to-electricity conversion efficiencies comparable to that using ITO [2, 3]. Solution routes for the preparation of CNT film typically need the dispersion of CNTs into solution under ultrasonication and with the aid of surfactant, which could shorten the CNTs and involve contamination. As an effective alternative, CNT film directly drawn from a spinnable CNT array has shown unique advantages [4]. For example, CNTs in the film have larger aspect ratio, not contaminated by surfactant. Moreover the transparency and conductivity can be readily modulated by physically depositing conductive metals on the CNT film [5]. For the fabrication of flexible optoelectronics, photoactive layers such as poly(3 -hexylthiophene), TiO_2 typically are coated on CNT film physically. Due to the poor surface wettabbility of CNT, it is a challenge to get well-connected interface between the CNT film and its guest. Moreover, the CNT itself, especially the single-walled carbon nanotube, has noticeable absorption in the visible region, which may lower the absorption efficiency of the photoactive layer. Covering the photoactive layer out of CNT could be a effective approach as this design can promise better solar absorption and more effective radical charge transport from the out layer to CNT. In this paper we report the synthesis of CNT/TiO_2 film based on this design. The film was prepared by depositing TiO_2 on to CNT film by chemically vapor deposition. The film is transparent and conductive. Directly using such film as photoelectrode in water-splitting cell and dye-sensitized solar cell (DSSC) has been investigated.

Experimental

Materials
Titanium isopropoxide, and tetrabutylammonium iodide, LiI, I_2 and 4-tert-butylpyridine were obtained from Adamas Reagent Co. Ltd. and used without purification. Other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd.

Growth of carbon nanotube array
The growth of spinnable CNT array was according to the method reported elsewhere [6]. Briefly, 30 nm Al_2O_3 buffer layer was deposited onto a silicon wafer with 600 nm-thick SiO_2 layer by electron beam evaporation, followed by depositing 1 nm Fe films upon the Al_2O_3 layer. Growth of the CNT arrays was carried out in a 5-inch tube furnace using a chemical vapor deposition method. Argon containing 6% hydrogen was used as the forming gas and ethylene as the carbon source. Typically, 100 sccm forming gas was feed through the furnace till the temperature ramping up to 750 ℃. CNT started to grow by introducing 100 sccm ethylene. The CNT growth was maintained for 10 min followed by switching off the carbon source while maintaining the forming gas till the furnace cooled down to room temperature.

Preparation of the CNT/TiO_2 film
CNT sheet was pulled out of the array with the help of a plane blade and fixed on a scaffold. To deposit TiO_2 on the CNT sheet, titanium isopropoxide (TTIP) was vapored at 200 ℃ and the gas was introduced to a hot region of 400 ℃ in a tube furnace by argon flow. The CNT sheet was then coated with TiO_2 layers in the furnace, forming a CNT/TiO_2 core/shell film.

Fabrication and test of water-splitting cell and DSSC
The photoresponse of the CNT/TiO_2 film was investigated in a two-electrode photoelectrochemical cell. 1 M Na_2SO_4 aqueous solution was used as the electrolyte and Pt wire as the counter electrode. A 500 W Xe lamp with intensity of 100 mW/cm^2 was served as the light source. The performance measurement of the cell was carried out on a CH Instruments potentiostats (CHI 660C).

The CNT/TiO_2 film was transferred on a PET film with the aid of a drop of ethanol. A copper foil with a square opening was adhered to the top of the film followed by covering the copper foil with a 25-μm Surlyn 1702 film (DuPont). The as-formed electrode was treated at 100 ℃ in vacuum for 1 h and then soaked in a 0.5 mM solution of commercially available N719 dye in ethanol overnight at room temperature. FTO/PEN film with a electrochemically deposited Pt film was used as the counter electrode. The dye-covered electrode and the counter electrode were assembled into a cell and sealed by of thickness 60 μm. Acetonitrile solution consisting of 50 mM I_2, 0.1 mM LiI, 0.5 mM tetrabutylammonium iodide, and 0.5 M 4-tert-butylpyridine in acetonitrile was used as the electrolyte. The cell was tested on a on a Keithley 2612 source meter under simulated air mass 1.5 global (AM 1.5 G) full sunlight intensity.

Results and Discussion

Fig. 1a shows a photograph of a self-supporting long CNT film that has been drawn from a spinnable array. Under the CNT sheet is the copper wire scaffold used to support the sheet for TiO_2 deposition. Figure 1b shows scanning electron microscopy (SEM) image of the joint between the CNT sheet and the array where the array is drawn into sheet. The CNT sheet shows good alignment along the drawing direction (Fig. 1c). Moreover, the CNT film is transparent (transmittance >85 % between 400 and 700 nm). In the film, CNT bundles are interconnected by small CNT bundles, promising a continuous array film with conductivity. The sheet resistance of the CNT film was measured as 1.2 KΩ/□ which can be further lowed down by 10% after the TiO_2 deposition as result of the contact resistance between CNTs being reduced.

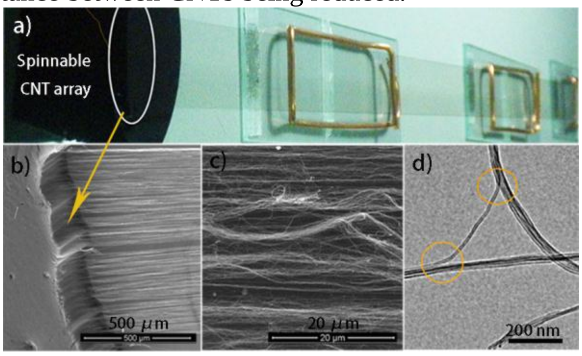

Fig. 1. (a) Carbon nanotube sheet being drawn from a 2-inch spinnable carbon nanotube array. (b), SEM image showing the drawing process of the CNT sheet. (c) SEM image of the CNT sheet. (d) TEM image of the CNT sheet demonstrating that the CNTs are interconnected.

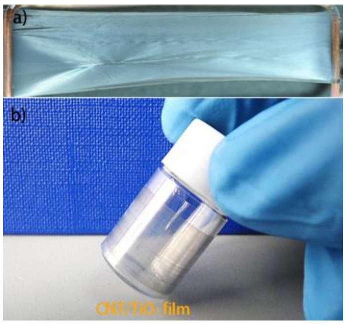

Fig. 2. (a) A free-standing CNT/TiO_2 film on a scaffold. (b) The CNT/TiO_2 film wrapped on a vial.

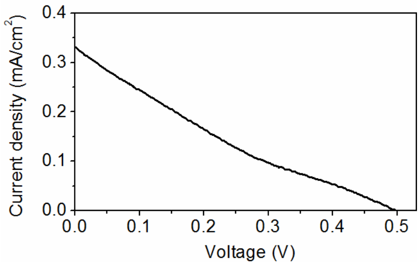

Fig. 3. *I-V* plots of the water-splitting cell based on the CNT/TiO_2 electrode.

Fig. 2a shows photograph of a CNT/TiO_2 film focused on its surface. The film is shinning and become slightly white after the TiO_2 deposition. The CNT/TiO_2 film is flexible and can be transferred to other substrates. Fig. 2b shows a CNT/TiO_2 film wrapped around a small vial with a diameter of 1 cm. Its transparency is illustrated by the visibility of the background.

Fig. 3 shows the *I-V* characteristics for the water-splitting cell illustrated by a Xe lamp with a light intensity of 100 mW/cm^2. The cell has a short-circuit photocurrent density of 0.33 mA/cm^2 with an open-circuit voltage of 0.49 V, calculated filling factor of 0.19, and overall power conversion efficiency of 0.03%.

The low conversion efficiency of the water-splitting cell can be attributed to the large band gap (3.0-3.2 eV) of TiO_2 which means that large content of solar light can not be absorbed. We further use dye to help the CNT/TiO_2 film absorb visible light. DSSC based on the film was then assembled.

Fig. 4b shows the *I-V* characteristics for the solar cells prepared with CNT/TiO_2 under AM 1.5 illustration (100 mW/cm^2). DSSC based on such composite film shows a noticeable improvement compared to the water-splitting cell, with short-circuit photocurrent density being 0.8 mA/cm^2, an open-circuit voltage being 0.52 V, calculated filling factor of 0.34, and overall power conversion efficiency of 0.14%. We think the efficiency of our cell can get improved by enhancing the conductivity of the CNT/TiO_2 film which is closely related to the filling factor of the cell.

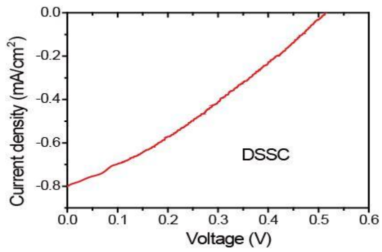

Fig. 4. *I-V* plots of the DSSC based on the CNT/TiO_2 electrode.

Conclusion

CNT sheet directly drawn from spinnable arrays are used as template for TiO_2 deposition, leading to the formation of CNT/TiO_2 film endowed with transparency and conductivity. Moreover, the CNT/TiO_2 film shows potentials applying in flexible optoelectronics.

References

(1) Wu, Z.; Chen, Z.; Du, X.; Logan, J. M.; Sippel, J.; Nikolou, M.; Kamaras, K.; Reynolds, J. R.; Tanner, D. B.; Hebard, A. F. *Science* **305** (2004) 1273-1276.

(2) van de Lagemaat, J.; Barnes, T. M.; Rumbles, G.; Shaheen, S. E.; Coutts, T. J.; Weeks, C.; Levitsky, I.; Peltola, J.; Glatkowski, P. *Appl. Phys. Lett.* **88** (2006**)** 233503.

(3) Tenent, R. C.; Barnes, T. M.; Bergeson, J. D.; Ferguson, A. J.; To, B.; Gedvilas, L. M.; Heben, M. J.; Blackburn, J. L. *Adv. Mater.* **21** **(**2009) 3210-3216.

(4) Zhang, M.; Fang, S.; Zakhidov, A. A.; Lee, S. B.; Aliev, A. E.; Williams, C. D.; Atkinson, K. R.; Baughman, R. H. *Science* **309** (2005) 1215-1219.

(5) Feng, C.; Liu, K.; Wu, J. S.; Liu, L.; Cheng, J. S.; Zhang, Y.; Sun, Y.; Li, Q.; Fan, S.; Jiang, K. *Adv Funct Mater* **20** (2010**)** 885-891.

(6) Li, Q. W.; Zhang, X. F.; DePaula, R. F.; Zheng, L. X.; Zhao, Y. H.; Stan, L.; Holesinger, T. G.; Arendt, P. N.; Peterson, D. E.; Zhu, Y. T. *Adv. Mater.* **18** (2006**)**, *18*, 3160-3163.