

A novel carbon nanotube/polymer composite film for counter electrodes of dye-sensitized solar cells†

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In the development of optoelectronic and electronic devices, it is critically important, but remains challenging to discover new electrode materials to replace the conventional indium and platinum which have obvious disadvantages including high cost, complex fabrication, and chemical instability during the use. To this end, carbon nanotube (CNT)/polymer composite materials may represent one of the most promising candidates due to the combined advantages including high surface area, excellent electrical and electrocatalytic properties, and high stability from CNTs while good flexibility, abundant supply, and easy fabrication from polymers. In the current composite electrodes, however, CNTs are typically interconnected to form networks, and the generated charges have to hop through a lot of boundaries among CNTs. The resulting organic solar cells based on the CNT/polymer composite electrodes showed low efficiencies. Here we have developed a perpendicularly aligned and penetrated CNT/polymer composite film through a simple slicing technique. This novel composite film exhibits good transparency, high flexibility, excellent electrical conductivity, and remarkable electrocatalytic activity, and may be widely used for various electrode materials. As a demonstration, it was used as a counter electrode to fabricate dye-sensitized solar cells with high efficiency.

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Introduction

Due to the complex fabrication and high cost, inorganic solar cells typically based on silicon have been hindered in a wide range of applications.^{1,2} Therefore, increasing attention has recently paid to organic solar cells, which can be fabricated through a low-cost solution process with the possibility of a much lower cost.^{3–6} Indium tin oxide is generally used as the electrode material in the production of an organic solar cell,^{3–8} and platinum as the counter electrode in the case of a dye-sensitized solar cell.^{9–12} However, it is well known that both indium and platinum are expensive due to limited supplies on the earth. The electrode, which is composed of indium tin oxide or platinum, has been generally prepared through a physical vapor deposition where a vacuum is required. In addition, they may suffer instability under extreme conditions. For instance, indium tin oxide is sensitive to acid while platinum may be dissolved in a corrosive electrolyte.¹² In solve the above challenges, it is highly desirable to develop other electrode materials. To this end, carbon nanotube (CNT)/polymer composites

have been widely investigated and proposed as a promising candidate to replace both indium tin oxide and platinum.^{12–25} CNTs show excellent mechanical, catalytic, and electronic properties, *e.g.*, an electrical conductivity of 10^5 S cm⁻¹ at room temperature,^{14–18} while polymers can be flexible, transparent, abundant in source, and easy to fabricate. The CNT/polymer composite electrodes are typically made through a solution or melting process, and CNTs randomly aggregate into network structures during the preparation. Therefore, it remains challenging to control the CNT structure in the composite, and charges also have to be transported among a large number of crossed contacting points with low efficiency. Here we have developed a perpendicularly aligned and penetrated CNT/polymer composite film through a simple slicing technique. This novel composite film exhibits good transparency, high flexibility, excellent electrical conductivity, and remarkable electrocatalytic activity, and may be widely used for various electrode materials. As a demonstration, it was used as counter electrode to fabricate dye-sensitized solar cell with high efficiency.

Experimental section

Materials

Dodecenylsuccinic anhydride, 4,4'-(propane-2,2-diyl) diphenol or epichlorohydrin, 1,2,3-propanetriol glycidyl ethers, dodecenyl succinic anhydride, methyl-5-norbornene-2,3-dicarboxylic anhydride and 2,4,6-tris(dimethylaminomethyl) phenol were

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obtained from SPI Supplies Division of Structure Probe Inc. Fluorine-doped tin oxide (15 ohm per square, transmittance 90%, Nippon Sheet Glass Co., Japan), titanium dioxide slurry (DHS-TPP3, Hydrothermal TiO₂, dispersion phase: terpinol), and Surlyn (DHS-SN1760-500) were ordered from Dalian Hep-tachroma Solartech Co., Ltd.

Preparation of the composite film

CNT arrays could be easily synthesized by chemical vapor deposition. Fig. S1† shows the side view of a typical CNT array. Fe (1.2 nm)/Al₂O₃ (5 nm) on silicon wafer was used as the catalyst, ethylene was used as the carbon source (rate of 90 sccm), a mixture of Ar (rate of 480 sccm) and H₂ (rate of 30 sccm) gases was used as the carrying gas, and the reaction was typically carried out at 750 °C. Multi-walled CNTs with a diameter of 9 nm were mainly used in this work (Fig. S2†). Fig. S3† shows a typical Raman spectrum of a CNT array. Fabrication of the perpendicularly aligned and penetrated CNT/resin composite is summarized below. A liquid mixture of dodecenylsuccinic anhydride and 4,4'-(propane-2,2-diyl) diphenol or epichlorohydrin was first prepared, followed by addition of epoxy resin with SPI-Pon 812 (1,2,3-propanetriol glycidyl ethers) and flexibilizer (polyazelaic polyanhydride), dodecenyl succinic anhydride and methyl-5-norbornene-2,3-dicarboxylic anhydride as the curing agents, and 2,4,6-tris(dimethylaminomethyl phenol) as the curing catalyst to produce an embedding solution. A CNT array in a bullet-like mould was then dipped into the embedding solution. The resulting CNT/resin array was sliced to form the perpendicularly aligned and penetrated composite film by a microtome or an ultramicrotome. The composite film can be bent for hundreds of cycles without breaking, which indicates high flexibility. Scanning electron microscopy was further used to investigate the structure stability during the deformation. The aligned structure of CNTs remained after the composite film was bent for more than 100 cycles with a bending angle of ~180°. As the size of the CNT array can be well maintained after incorporation of epoxy resin, the number density of CNT in a composite may be controlled and calculated by that in the as-synthesized array (around 10¹¹ cm⁻²). The electrocatalytic and mechanical characterizations have been provided in Fig. S4 and S5,† respectively. Resistance was measured through a four-probe method with four electrodes connected to the same plane of composite film.

Composite films using conducting polymers

The composite films based on polyaniline or polypyrrole were realized after an electropolymerization by amperometric *i-t* curve method on CHI 660a electrochemical workstation. Firstly, CNT array, platinum wire, and saturated calomel electrode (SCE) were used as working electrode, counter electrode, and reference electrode, respectively. Here the CNT array had been previously treated by an oxygen plasma etching process to have hydrophilic properties. Electropolymerization of aniline was then performed at a potential of 0.85 V vs. SCE for 400 seconds in aqueous solution containing 0.05 M aniline with 1 M H₂SO₄. Electropolymerization of pyrrole was performed at a potential of

0.85 V vs. SCE for 400 seconds in aqueous solution containing 0.15 M pyrrole, 0.2 M NaH₂PO₄, and 1.5 × 10⁻³ M LiClO₄. The composite films were then sliced from the CNT/polyaniline or CNT/polypyrrole array. In the case of polydiacetylene, diacetylenic monomers (*e.g.*, 8,10-heneicosadiynoic acid in this work) were directly incorporated into a CNT array through a solution process similar to epoxy resin, followed by a topochemical polymerization under UV irradiation. The polymerization details can be found in the references. Finally, a composite film was sliced from the CNT/polydiacetylene array. The weight ratio of CNT to polymer is ~1/10.

Fabrication of a dye-sensitized solar cell

The counter electrode was fabricated by paving a penetrated and aligned CNT/epoxy composite film on fluorine-doped tin oxide glass or indium tin oxide coated on polyethylene naphthalate with a drop of alcohol between them, followed by evaporation of alcohol to improve their contact. The working electrode was composed of a layer of nanocrystalline TiO₂ with thickness of 10 μm prepared by a screen printing technology. The electrode was sintered at 500 °C for 30 min and annealed. After the temperature was decreased to 120 °C, it was immersed into 0.3 mM solution of N719 dye in a mixture of dehydrated acetonitrile and *tert*-butanol with volume ratio of 1/1 for about 16 h. The dye-incorporated electrode was carefully rinsed with dehydrated acetonitrile. For a cell fabrication, the cathode and counter electrode with a Surlyn frame as the spacer were sealed by pressing them together at a pressure of about 0.2 MPa and a temperature of 125 °C. The redox electrolyte (composed of 0.1 M LiI, 0.05 M I₂, 0.6 M 1,2-dimethyl-3-*n*-propyl-imidazolium iodide, 0.1 M GuSCN, and 0.5 M 4-*tert*-butyl-pyridine in dehydrated acetonitrile) was then introduced into the cell through the back holes of the counter electrode. Finally, the hole was sealed with the Surlyn and a microscopy cover glass. For the fabrication of a flexible cell, a TiO₂ mixture with 80% anatase and 20% rutile (obtained from Dalian Heptachroma Solartech Co., Ltd.) was added to ethanol with a concentration of 20 wt%. The suspension was coated onto the conducting substrate by a doctor blading method to produce the working electrode.

Characterization

Structures of the perpendicularly aligned CNT/resin composite were characterized by scanning electron microscopy (Hitachi FE-SEM S-4800 operated at 1 kV). Raman measurements were performed on Renishaw inVia Reflex with excitation wavelength of 514.5 nm and laser power of 20 mW at room temperature. The dye-sensitized solar cells were measured by recording *J-V* curves with a Keithley 2400 Source Meter under illumination (100 mW cm⁻²) of simulated AM1.5 solar light coming from a solar simulator (Oriel-94023 equipped with a 1000 W Xe lamp and an AM1.5 filter). The stray light was shielded by a mask with an aperture which was a little smaller than the working electrode. The EIS measurements were performed on CHI 660a electrochemical workstation (Shanghai, China) under AM 1.5 illumination. Mechanical measurements were performed by a Hengyi Table-Top Universal Testing Instrument.

Results and discussion

CNT arrays were first synthesized through a chemical vapor deposition followed by incorporation of polymers.²⁶ Fig. 1a schematically shows the structure of a CNT/polymer array. The aligned and penetrated CNT/polymer film was then sliced from the top or bottom of the composite array. The fabrication detail and characterization have been provided in the ESI (Fig. S1–S3†). The thickness of composite film may be accurately tuned from tens to hundreds of nanometers by an ultramicrotome and from less than 1 micrometer to hundreds of micrometers by a microtome. Both single-walled and multi-walled CNTs are available for this fabrication method. Here multi-walled CNTs are investigated due to their easy synthesis, and epoxy resin is mainly explored as a model polymer. The resulting composite film was flexible. A composite film (Fig. 1a) with thickness of $\sim 40 \mu\text{m}$ can be scrolled into different morphologies, *e.g.*, the curved one in Fig. 2b. Scanning electron microscopy confirms that CNTs are penetrated and aligned with CNT number density of around 10^{11} cm^{-2} (Fig. 2c and d). The composite film exhibited excellent electrical properties. The resistivity perpendicular to the CNT-aligned direction was measured to be $10^{-2} \Omega \text{ cm}$, while the electrical resistivity parallel to the CNT-aligned direction achieved $10^{-4} \Omega \text{ cm}$. Therefore, this composite film may show a high performance in the electrode application. Here it had been used as counter electrode in replacement of platinum to fabricate dye-sensitized solar cell.

Fig. 1b schematically shows a typical cell structure, where a layer of nanocrystalline TiO_2 on fluorine-doped tin oxide (FTO) was used as the working electrode, a composite film on FTO was used as counter electrode, and *cis*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis(tetrabutylammonium) (also called N719) was used as the dye. To realize this structure, both electrodes with a Surlyn frame as the spacer were sealed, followed by injection of the redox electrolyte. The resulting dye-sensitized solar cell is expected to show a high performance according to the working mechanism.^{13,27,28} Open ends of CNTs can more effectively catalyze reduction reaction of I_3^- ions compared with their side walls which had been generally used by others.^{29,30} The aligned structure of CNTs with high electrical conductivity further improved the charge separation and transport compared with the randomly dispersed CNTs.^{13,31–34}

Dye-sensitized solar cells using these composite films ranging from 10 to 40 μm in thickness were fabricated and

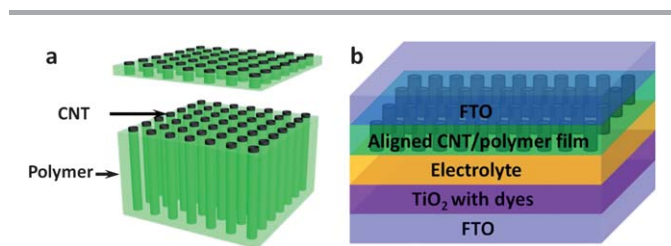


Fig. 1 (a) A schematic illustration of fabrication of the perpendicularly aligned and penetrated CNT/polymer composite film. (b) The structure of a dye-sensitized solar cell using the composite film as a counter electrode.

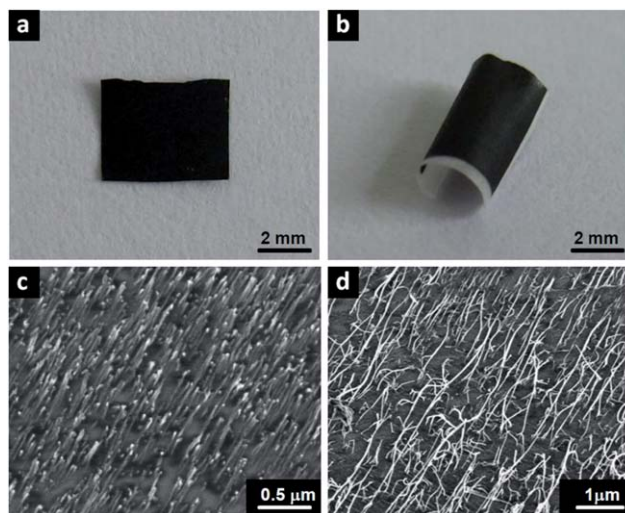


Fig. 2 Perpendicularly aligned and penetrated CNT/resin composite film. (a and b) Photographs of a composite film with different morphologies. (c) Scanning electron microscopy (SEM) image from a top view. (d) SEM image from a side view.

tested under AM1.5 illumination. Fig. 3 shows typical J - V curves for the described cells. For convenience, four main parameters, *i.e.*, open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (FF), and energy conversion efficiency (η) are summarized and compared in Fig. 4. The open-circuit voltage remains unchanged (Fig. 4a), while both short-circuit current density and fill factor decrease (Fig. 4b and c) with the increasing thickness of composite film as a higher thickness results in a higher electrical resistance. For a platinum electrode, the resulting dye-sensitized solar cell typically exhibited a V_{OC} of 0.75 V, J_{SC} of 11.77 mA cm^{-2} , and FF of 0.57 (Fig. S6†). As a comparison, the cell derived from the composite film with thickness of 10 μm without optimization showed slightly decreased V_{OC} and FF but increased J_{SC} under the same conditions. The cell efficiency based on the composite film is close to that based on the platinum electrode.

To further understand the dependence of short-circuit current density and fill factor on the thickness of composite film, electrochemical impedance spectroscopy was also used to

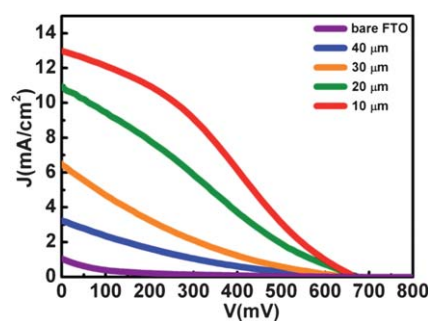


Fig. 3 J - V curves of dye-sensitized solar cells using bare FTO and perpendicularly aligned and penetrated CNT/resin composite films with different thicknesses as counter electrodes measured under AM1.5 illumination.

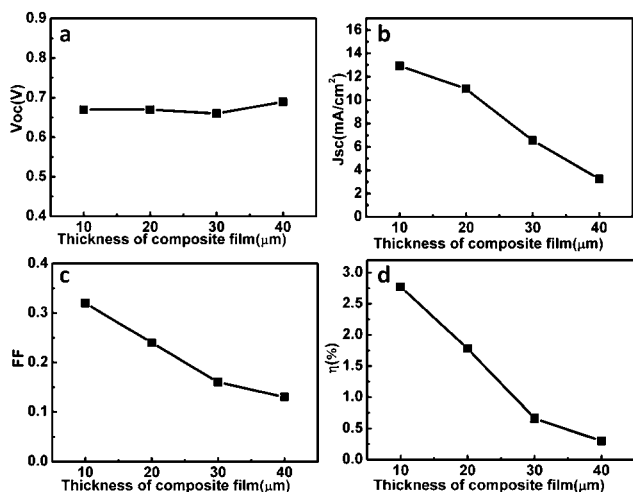


Fig. 4 Parameters of the dye-sensitized solar cell using perpendicularly aligned CNT/resin composite films with different thicknesses as counter electrodes measured under AM1.5 illumination. (a) Dependence of the open-circuit voltage on film thickness. (b) Dependence of the short-circuit current density on film thickness. (c) Dependence of the fill factor on film thickness. (d) Dependence of the energy conversion efficiency on film thickness.

characterize the dye-sensitized solar cell. Four cells fabricated from composite films with thicknesses of 10, 20, 30, and 40 μm are compared in Fig. 5. The equivalent circuit is also demonstrated in Fig. 5.³⁵ Here the serial resistance (R_s) is the combined resistance of electrolyte and electrode, while the resistances of R_{ct1} , R_{ct2} , and R_{diff} (the real part of diffusion impedance, *i.e.*, Z_w) correspond to the electrochemical reaction at the counter electrode in the high-frequency region, the charge transfer at $\text{TiO}_2/\text{dye}/\text{electrode}$ interfaces in the middle-frequency region, and the Warburg diffusion process of I^-/I_3^- ions in the electrolyte in the low-frequency region, respectively. Therefore, the catalytic capability of composite film as counter electrode is reflected by R_{ct1} (the first semicircle at the high frequency). Obviously, the first semicircle decreases in size with the decreasing thickness of composite film in Fig. 5. The decreased first semicircle indicates the acceleration of the electron transfer at the CNT/

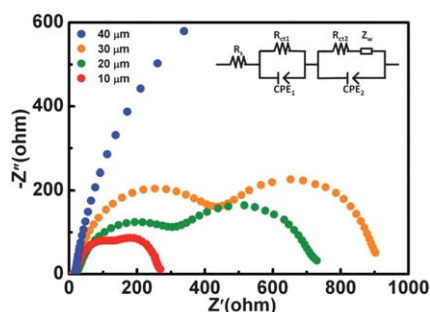


Fig. 5 Equivalent circuit and Nyquist plots of the dye-sensitized solar cell using perpendicularly aligned and penetrated CNT/resin composite films with different thicknesses as counter electrodes measured under AM1.5 illumination. The frequencies ranged from 0.1 to 100 kHz with an applied voltage of -0.8 V. Here R_s , R_{ct1} , R_{ct2} , Z_w , and CPE stand for serial resistance, charge-transfer resistance at the counter electrode, charge-transfer resistance at $\text{TiO}_2/\text{dye}/\text{electrode}$ interfaces, diffusion impedance, and constant phase element, respectively.

electrolyte interface. This is consistent with the enhanced fill factor due to decreased series resistances. The decreased series resistance with the decrease in the film thickness may be also responsible for the improved short-circuit current density.^{28,36}

The energy conversion efficiencies of the solar cells are summarized in Fig. 4d. Obviously, the efficiencies increase with the decreasing thicknesses of the composite films. Currently, the cell efficiency is $\sim 2.77\%$ in the case of a composite film with thickness of 10 μm . Note that a dye-sensitized solar cell using bare FTO (without composite film) has a very low efficiency ($\sim 0.04\%$) in Fig. 3, so the composite film plays the critical role in the cell performance. It should be also emphasized that the dye-sensitized solar cell based on the perpendicularly aligned and penetrated CNT/resin film has not been optimized with regard to the material used, the composite structure, and the device architecture. In fact, we found that the energy conversion efficiency could be greatly improved when a thinner composite film of hundreds of nanometers was used. In addition, the conversion efficiency could be also greatly improved by increasing the CNT number density, selecting the other polymer such as conducting polymer, and modifying the CNT surface for a better compatibility with polymer. For instance, the as-synthesized CNT array typically had a number density of 10^{11} cm^{-2} , which remained unchanged after the formation of composite film. The number density of CNTs in composite film could be increased up to tens of times and tuned by pressing the as-synthesized array from one side or both sides (Fig. S7[†]). In another instance, three conducting polymers, *i.e.*, polyaniline, polypyrrole, and polydiacetylene, had been used to produce composite films with better electrical properties (Fig. S8[†]). The above two approaches can improve the electrical properties of composite film. More efforts are underway to optimize the composite film and cell architecture for a higher efficiency.

Perpendicularly aligned and penetrated CNT/polymer composite films have also been used as counter electrodes to fabricate flexible dye-sensitized solar cells (Fig. S9[†]). A representative J - V curve of a flexible cell using a composite film as the counter electrode is shown in Fig. S10[†]. The values of V_{oc} , J_{sc} , and FF are 0.67 V, 3.69 mA cm^{-2} , and 0.32, respectively. The energy conversion efficiency of the flexible cells can be as high as the rigid cells by improving the fabrication process.

Conclusions

In summary, we have prepared perpendicularly aligned and penetrated CNT/polymer composite films as effective electrode materials. When they were used as counter electrodes, the resulting dye-sensitized solar cells showed high efficiencies. This penetrated and aligned structure can be also be extended to various conductive one-dimensional nanostructures including nanorods and other nanotubes besides CNTs to develop a new family of general electrode materials.

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