Dye-sensitized solar cell with a titanium-oxide-modified carbon nanotube transparent electrode

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Transparent and conductive carbon-based materials are promising for window electrodes in solid-state optoelectronic devices. However, the catalytic activity to redox reaction limits their application as a working electrode in a liquid-type dye-sensitized solar cell (DSSC). In this letter, we propose and demonstrate a transparent carbon nanotubes (CNTs) film as the working electrode in a DSSC containing iodide/triiodide redox couples. This implementation is realized by inhibiting the charge-transfer kinetics at CNT/redox solution interface with an aid of thin titanium oxide film that facilitates the unidirectional flow of electrons in the cell without sacrificing the electrical and optical properties of CNT. © 2011 American Institute of Physics. [doi:10.1063/1.3610488]

Transparent conducting oxides (TCOs) such as indium-doped tin oxide and fluorine-doped tin oxide are ubiquitously used as window electrodes in optoelectronic devices. However, there exist major technical issues associated with continuing using TCOs as the window electrodes due to their inherent limitations.[1–5] A recent success in the fabrication of optically transparent and electrically conducting thin film from carbon-based materials using carbon nanotubes (CNTs) and grahene has attracted significant attention.[6,7] In comparison to traditional TCOs, these carbon-based materials may allow for substantially reduced costs because of the abundant material source and potentially scalable fabrication from solution process.[8] They are mechanically strong and flexible as well as chemically stable.[9,10] More interestingly, they remain transparent in the near infra-red region, in contrast to TCO.[5,6] As such, CNT and graphene have been demonstrated as the window electrode in a wide range of solid-state applications.[11–15] However, it has not been possible to integrate carbon-based materials as a working electrode in liquid-type dye-sensitized solar cell (DSSC) to date because of their well-known catalytic property to redox reaction. Thus, it has been appropriate to use them as a counter electrode in DSSC to replace expensive Pt.[16] When they are used as a working electrode, however, their catalytic property allows the collected electrons at the working electrode to recombine with I_3^- in the electrolyte by the reaction $I_3^- + 2e \rightarrow 3I^-$, at the electrolyte/working electrode interface. Hence, despite the fact that CNT and graphene have

similar work functions (4.7–4.9 eV and ∼4.6 eV, respectively) to that of conventional TCOs, no liquid-type DSSC with a carbon-based working electrode could be realized so far.

To circumvent this problem, we proposed and employed a facile method for surface modification with thin oxide layer, suppressing the recombination of electrons with I_3^-, as illustrated in Fig. 1, while maintaining the electrical and optical properties of the working electrode made of CNTs. Although this approach would solve the problem, the prerequisites for an ideal oxide used in the modification limits the choice of available materials. For example, a sol-gel processed ZnO film has been proven as a highly transparent, electron-transporting layer in an organic solar cell.[17] However, ZnO is not compatible with acid-containing anatase paste and dye solution. Alternatively, a compact TiO_2 layer by spray-pyrolysis is able to withstand the acid,[18] but heating/pre-heating the substrate at high temperature during film deposition oxidizes the CNTs. Thus, herein, we have modified the CNT film with sol-gel-processed titanium sub-oxide (TiO_x) at low temperature (150 °C). By modifying CNTs with TiO_x, we demonstrated that the efficiency can be tremendously improved.

Our transparent, conductive CNT films were produced by air-gun spray method from the solution containing 0.2 mg/ml single-wall CNT dispersion (Carbon solution, Inc.) and 0.5 wt. % sodium dodecylbenzene sulfonate surfactant in water.[19] Prior to spraying, the mixture was probe-sonicated at 120 W to make a homogenous mixture. After the film deposition, the surfactant was removed by immersion in distilled water for 24 h. Some CNT films were immersed in 98 wt. % sulfuric acid for 30 min to yield doped

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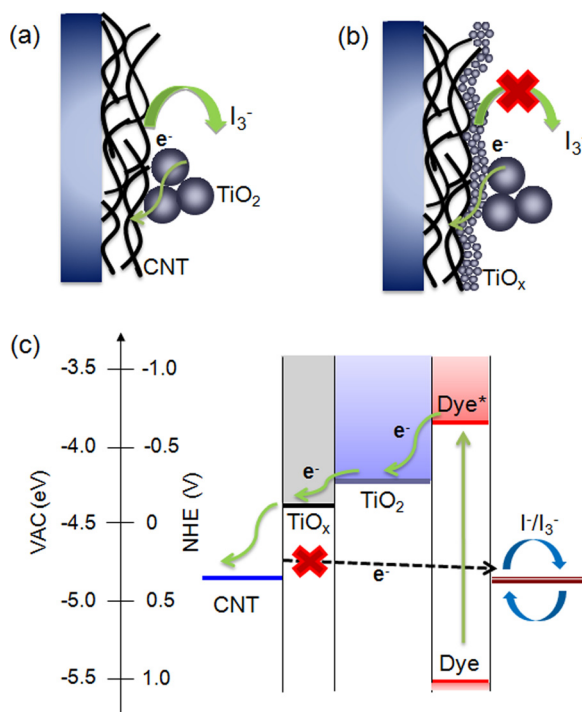
FIG. 1. (Color online) Schematic of (a) recombination of electrons with I_3^- at the CNT/electrolyte interface in the case of bare CNT electrode, (b) inhibiting the charge-transfer kinetics at the interface by using a thin TiO_x layer, (c) unidirectional flow of electrons in the liquid-type DSSC with the TiO_x-modified-CNT working electrode, showing the energetics of the individual components used in the cell.

CNT films. A number of well-entangled and interconnected CNTs with a general diameter of 10-25 nm were observed in the resultant film under scanning electron microscopy (SEM) (Fig. 2(a)). The relationship between the sheet resistance and the optical transmittance of the doped and undoped CNTs at the optical wavelength of 600 nm is shown in Fig. 2(b). Generally, the doped CNT film yields higher transmittance compared to the undoped one at the same sheet resistance. The optimum combination of sheet resistance and transmittance occurs for
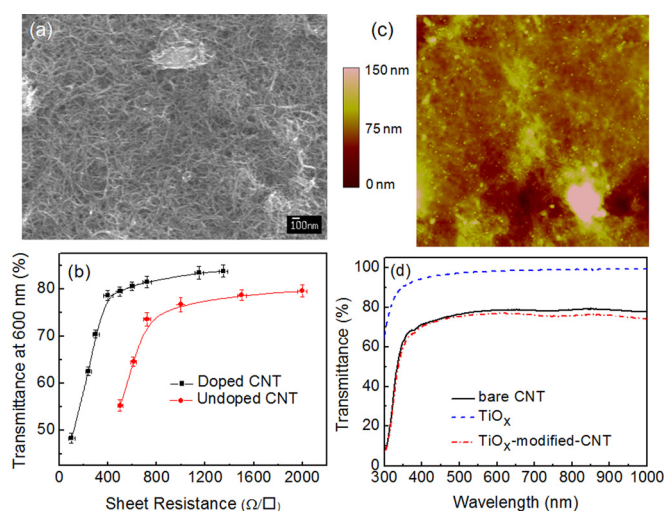

FIG. 2. (Color online) (a) SEM image of a typical CNT film deposited by air-gun spray. (b) The sheet resistance vs. optical transmittance of the doped and undoped CNT film. (c) AFM image of TiO_x coated CNT film ($8.0 \times 8.0 \ \mu m^2$). (d) Typical optical transmittance spectra of the bare CNT, TiO_x, and TiO_x-modified-CNT films.

400-450 $\Omega/\square$ while the corresponding transmittance is around 75%-78%. Hence, the doped CNT film with a sheet resistance $400 \pm 20 \ \Omega$ was chosen for our device fabrication.

TiO_x sol-gel was prepared by refluxing 1 ml of titanium (IV) isopropoxide, 5 ml of 2-methoxyethanol, and 0.5 ml of ethanolamine in a three-necked flask under argon environment at $80 \,^\circ C$ for 2 h and $120 \,^\circ C$ for 1 h.[20] The prepared sol-gel was spin-coated onto the CNT film at 3000 rpm. The thickness of the film was controlled by diluting with 2-methoxyethanol. Subsequently, the samples were heated at $150 \,^\circ C$ for 1 h in air. The precursor was hydrolyzed and converted to TiO_x during heating in air. The elemental composition of Ti and O, cross-checked by X-ray photoelectron spectroscopy, is 41.9% and 56.6%, respectively. Hence, the film is considered as titanium sub-oxide, rather than titanium dioxide. As seen from atomic force microscopy (AFM) image (Fig. 2(c)), the resulting TiO_x film is composed of myriad nano-sized colloids, completely covering the underlying CNT bundles. The modification of CNT film with ultra-thin TiO_x layer slightly affects the sheet resistance of the overall electrode. The sheet resistance of TiO_x-modified-CNT film increases only to $550 \pm 20 \ \Omega/\square$ with a 10-nm-thick TiO_x film from $400 \pm 20 \ \Omega/\square$ for the bare CNTs. More interestingly, TiO_x film is highly transparent in visible region as well as the near infra-red range and, hence, the transmittance of bare and modified CNT films is nearly the same (Fig. 2(d)).

To demonstrate that TiO_x-modified-CNT films serve as potential window electrodes for liquid-type DSSCs, we fabricated a DSSC using porous TiO_2 as the wide-bandgap semiconductor, cis-diisothiocyanato-bis(2,2′-bipyridyl-4′-dicarboxylato)ruthenium(II) bis(tetrabutylammonium) (Solaronix) as the sensitizer, I^-/I_3^- solution as the electrolyte, Pt as the counter electrode, and TiO_x-modified-CNT/bare CNT as the working electrode. The J-V characteristics of the cells with the bare CNT electrode and the TiO_x-modified-CNT electrode ($TiO_x \sim 10$ nm) under illumination of AM1.5G simulated solar light (100 mW/cm^2) are shown in Fig. 3. The short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and power conversion efficiency (PCE) of the cell using the bare CNT electrode are 0.281 mA/cm^2, 0.057 V, 23%, and nearly 0%, respectively, and the cell is therefore almost nonfunctional. By modifying CNTs with TiO_x,
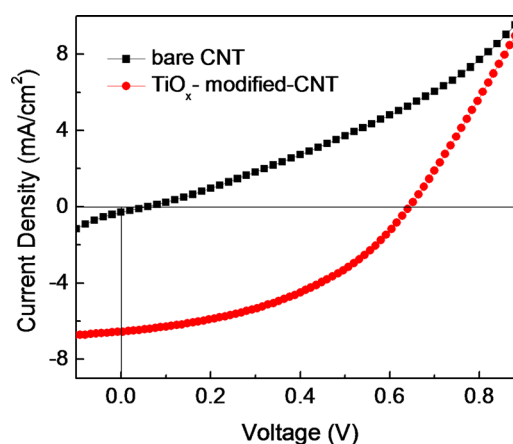

FIG. 3. (Color online) J-V characteristics of liquid-type DSSC with the bare CNT electrode and the TiO_x-modified-CNT electrode under simulated solar irradiation of AM1.5G (1 sun).
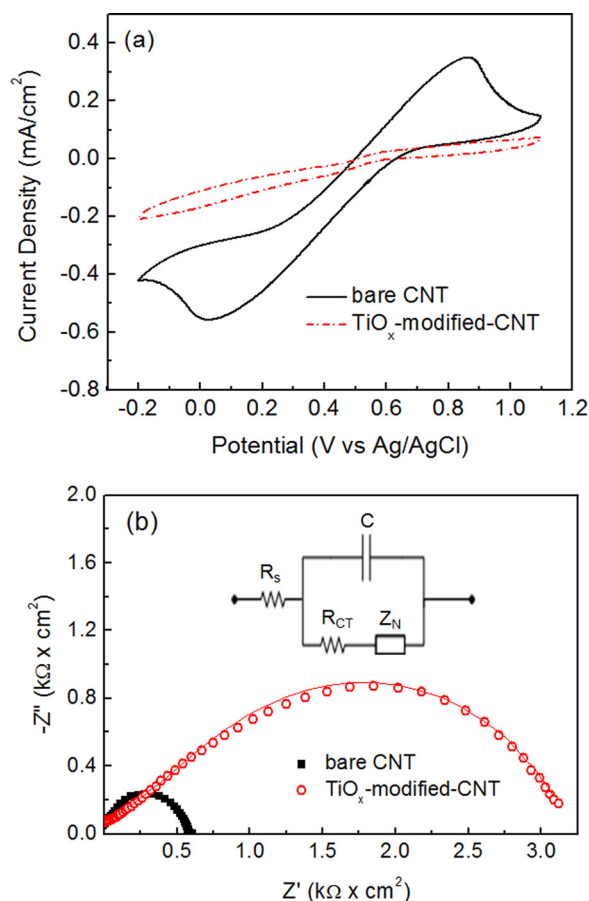
FIG. 4. (Color online) (a) Cyclic voltammograms of the bare CNT and TiO$_x$-modified-CNT electrodes at a scan rate of 10 mV/s. (b) The Nyquist plots of the electrodes at a bias of 300 mV. The frequency range was from 0.1 to 100 kHz. Inset is the equivalent circuit used in fitting data. Pt plate and Ag/AgCl were used as the counter and reference electrodes, respectively, in all electrochemical tests.

however, the PCE of the cell significantly improves to 1.8% with J_{sc} of 6.547 mA/cm^2, V_{oc} of 0.644 V, and FF of 43%.

To further understand the role of TiO$_x$ in the CNT-electrode-based DSSC, we studied the electron-transfer properties of the electrodes using cyclic voltammetry (CV). Fig. 4(a) shows the CV response of the electrodes in 0.1 M KCl solution containing 5.0 mM K$_3$Fe(CN)$_6$ at a scan rate of 10 mV/s. The bare CNT electrode shows a quasi-reversible characteristic with a cathodic peak of 0.56 mA/cm^2 at a reduction potential 0.026 V and an anodic peak of 0.35 mA/cm^2 at an oxidation potential 0.86 V, suggesting that there is electron-transfer between the CNTs and the redox system. In contrast, neither cathodic nor anodic peak was observed in CV response of TiO$_x$-modified-CNT electrode, indicating that the electron transfer between the CNTs and the redox species is blocked by TiO$_x$. We also conducted electrochemical impedance spectroscopy to evaluate charge-transfer resistance (R_{CT}) at the electrode/electrolyte interface. Fig. 4(b) shows the Nyquist plots of a three-electrode system in an electrolyte containing 0.05 M I$_2$ and 0.5 M LiI in aqueous solution. The plots were fitted with the equivalent circuit model (inset Fig. 4(b)). R_{CT} indicates the electron transfer resistance between the electrode and electrolyte. The Nernst diffu-

sion impedance (Z_N) describes the diffusion of I$_3^-$ in electrolyte while R$_s$ stems from the ohmic resistance of the electrolyte and electrodes.[21,22] From the fitted data, R$_{CT}$ of TiO$_x$-modified-CNT electrode was found to be 2.513 k$\Omega \cdot$cm^2 while that of bare CNT electrode was only 311.4 $\Omega \cdot$cm^2. Because R$_{CT}$ varies inversely with the I$_3^-$ reduction activity of the electrode, the larger R$_{CT}$ of TiO$_x$-modified-CNT film suggests that the reduction of I$_3^-$ at the CNT/electrolyte interface is largely suppressed by TiO$_x$.

In conclusion, we proposed and demonstrated the feasibility of carbon-based transparent, conductive film made of CNTs as the working electrode in a DSSC containing redox solution, enabled by surface modification of CNTs using TiO$_x$, which serves as a retardation medium to electron-transfer kinetics at the CNT/electrolyte interface without degrading the electrical and optical properties of CNTs. As a result, the power conversion efficiency of 1.8% has been realized. With further optimization in the sheet resistance and transmittance, carbon-based window electrodes could offer a viable low-cost alternative to conventional TCOs in both solid-state and liquid-type optoelectronic devices.

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