



Enhanced photoinduced electron transfer by multiwalled carbon nanotubes in self-assembled terpyridine polymer networks



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ABSTRACT

In this study, self-assembled Ru-containing polymer-MWNTs hybrid thin films were synthesized using metal-ligand (terpyridine, (tpy)) interactions. The subsequent deposition of tpy and Ru-functionalized polymer (tpy-PVA-Ru) with metal ions such as Zn(II) or Cu(II) and tpy-functionalized MWNT resulted in photoactive polymer-MWNTs hybrid thin films. The photoinduced electron transfer from Ru complexes in the polymer films to the indium tin oxide electrode was observed. Although Cu(II)-tpy linkages produced thicker hybrid films owing to the stronger binding energy than those of the Zn(II)-tpy linkages, the photocurrents of the hybrid films with Cu(II) were much smaller than those with Zn(II), probably attributed to the slower electron hopping rates inside the films. However, the anodic photocurrents increased with the inclusion of the MWNTs layer; the polymer-MWNTs hybrid films fabricated by Cu(II) and Zn(II) show 2.2- and 1.4 folds enhanced photocurrent when compared to the thin films without MWNTs. Potential-step chronoamperometry showed that the electron hopping rate constants significantly improved with the inclusion of MWNTs, which may have provided an efficient electron transfer pathway.

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1. Introduction

Photoelectrochemical systems have drawn significant attentions owing to their application in water splitting, solar energy conversion, and photocatalysis [1,2]. In such systems, metal-ligand complexes, for example, metal-2,2':6',2''-terpyridine (tpy) complexes, play an important role. They exhibit intriguing optoelectronic properties and thus can be utilized as photosensitizers for solar cell and water splitting [3,4], molecular assembly [5–7], and sensors [8]. The photoinduced electron transfer involving metal-ligand complexes is known to be effective in efficient photoelectrochemical systems [9].

2,2':6',2''-Terpyridine is one of the extensively utilized ligands in organometallic chemistry owing to its high binding affinity to various metals. Furthermore, tpy can be used in layer-by-layer self-assembly (LBL-SA) for metal-ligand interactions [10,11]. LBL-SA

offers several advantages such as possibility of self-repair, thermodynamic stability, and controllability of film properties. By the LBL-SA method based on the metal-ligand interactions, the facile assembly of polymer films, with interesting optical and electrical properties can be prepared [10,12]. Previously, we reported that the interaction between metal ions and a tpy ligand affects the growth rate of thin film deposition, and such interaction can also control the electron hopping rate inside the polymer films. The photocurrent generated in the polymeric thin films with Zn(II)-tpy interactions was much higher than other films because the apparent diffusion rate constant of photoinduced electrons in the polymeric thin films with Zn(II) was larger than those with other metal ions [13].

In order for efficient electron transfer in photoelectrochemical systems, we hypothesized that electron conductor such as carbon nanotubes (CNTs) may provide facile diffusion pathways for photoinduced electrons. CNTs have been used in various fields, because of their high charge mobility. For example, they have been used in hybrid films for photoelectrochemical devices by functionalizing with various chemical groups to enhance photoelectric

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conversion efficiency *via* offering an electron transfer pathway [14–18]. Although several examples of self-assembled polymer materials based on the metal–ligand interactions have been reported [19,20], hybrid materials using the metal–ligand interactions between the polymer and CNTs to enhance the electron-hopping rate have not much studied. Several research groups synthesized a tpy moiety and used it for functionalization of CNTs. The modified CNTs with tpy groups provide a binding site for metal ions and successfully fabricate multilayer films by the LBL-SA method. Moreover, they have potential for CNTs-based stimuli-responsive materials [21], metal sensing [22], and enhancing photoactivity [14,23]. Herein, self-assembled polymer–CNT hybrid films were successfully synthesized using the tpy ligand. The photoinduced electrons from the Ru complexes were transferred to an indium–tin-oxide (ITO) electrode, and the anodic photocurrent increased with CNT layers. The electron-hopping rate was measured via potential-step chronoamperometry, and the electron-hopping rate constant (k_{app}) was matched well with the photocurrent densities.

2. Experimental

2.1. General

FT-IR spectra were measured with a Bruker Optik, Vertex70 spectrometer. UV–Vis spectra were obtained using a UV-1800 ENG 240V, SOFT spectrometer. The surface image of the self-assembled films was observed by a field emission scanning electron microscopy (FE-SEM, JEOL JSM 7100F). The thickness of films was measured by an Alpha-Step IQ Surface Profiler (KLA-Tencor). The photocurrent experiment and potential step chronoamperometry were performed on an Epsilon electrochemical analyzer (EC epsilon, BASi).

2.2. Materials

The synthesis of the polymer with terpyridine (tpy) and di-terpyridyl ruthenium (tpy-PVA-Ru) was described previously. The composition is $n \approx 0.01$, $m \approx 0.01$, $x = 0.12$, $y = 0.83$ and remains carboxyl group $z \approx 0.03$ (Fig. 2) with molecular weight of 18,000 kDa [13]. Zinc perchlorate ($Zn(ClO_4)_2 \cdot 6H_2O$), copper perchlorate ($Cu(ClO_4)_2 \cdot 6H_2O$), tetrabutylammonium hexafluorophosphate (TBAPF₆), and multi-walled carbon nanotubes (MWNTs, O.D. 6–9 nm and length 5 μ m, >95%) were purchased from Sigma–Aldrich.

2.3. Functionalization of MWNTs

Pristine-MWNTs (300 mg) were added to a mixture of conc. H_2SO_4 and HNO_3 (180 mL, 3:1 v/v). The mixture was allowed to stir at 60 °C for 8 h. Then, the resulting mixture was centrifuged to be filtered and washed with distilled water until pH of the filtrate was 7 and then washed with MeOH [22]. The acid-treated MWNT-COOH (200 mg) was mixed with $SOCl_2$ (20 mL) under a reflux condenser for 24 h, remaining excess $SOCl_2$ was removed under reduced pressure. The obtained MWNT-COCl was washed with anhydrous THF and benzene several times. To a mixture of MWNT-COCl (100 mg) dispersed in anhydrous chloroform (10 mL) was added 3-([2,2':6',2''-terpyridin]-4'-yloxy)propan-1-amine (50 mg) under nitrogen atmosphere. The reaction mixture was allowed to reflux at 70 °C accompanied by mechanical stirring for 24 h. The resulting mixture was vacuum-filtered through a 0.22 μ m polycarbonate membrane three times to obtain tpy-MWNT [21,22]. Yield = 142 mg (95%).

2.4. Preparation of self-assembled polymer-MWNTs hybrid thin films

A cleaned quartz slide and ITO glass were immersed in polyethyleneimine (PEI) solution (5 mg/mL) for 20 min, in polystyrene sulfonate (PSS) solution (5 mg/mL) for 20 min, in metal solution (10 mM), in polymer solution (1 mg/1 mL) for 2 min, and then ultrasonicated mixture tpy-MWNT (0.5 mg/mL) in water for 2 min, respectively. After each adsorption cycle, water rinsing and N_2 drying were performed. These processes can be repeated until the desired number of bilayers of PVA-Ru/CNT is obtained. All layer-by-layer procedures were carried out at room temperature using distilled water [11,24].

2.5. Photocurrent and potential step chronoamperometry measurements

The photocurrent experiment and potential step chronoamperometry (PSCA) were performed on an Epsilon electrochemical analyzer in a three-electrode cell configuration consisting of a quasi-internal Ag wire as a reference electrode submerged in 0.01 M $AgNO_3$ /0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) and anhydrous CH_3CN , a ITO-coated glass electrode as a working electrode and the Pt coil as a counter electrode. The photocurrent measurement carried out at a constant applied potential under light irradiation.

3. Results and discussion

In order to enhance the photocurrent efficiency, tpy-functionalized multiwalled carbon nanotubes (MWNTs) were designed and synthesized to fabricate self-assembled polymer-MWNTs hybrid thin films. In the first step, MWNTs were functionalized to carboxylic acid groups using nitric acid and sulfuric acid, followed by the formation of the acyl chloride in the presence of thionyl chloride through the known procedures [21,22,25]. The desired tpy-functionalized MWNTs (tpy-MWNT) were obtained from coupling reaction of acyl chloride with an amine-terminated tpy derivative by using a common amidation method (Scheme 1) [26]. Structures of the intermediates and final product were analyzed by FT-IR spectroscopy (Fig. 1), confirming the formation of carboxylic acid groups and amide groups including tpy moieties.

Photoactive polymer-MWNTs hybrid thin films were fabricated via the LBL-SA method utilizing interactions between metal and tpy ligand. Cu(II) and Zn(II) were selected as the metal ions for assembly because in our previous study without using MWNTs, the

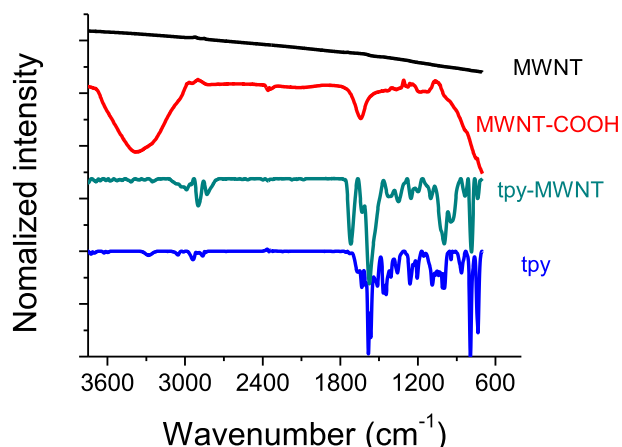


Fig. 1. FT-IR spectra of MWNT, MWNT-COOH, tpy-MWNT, and tpy.

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