

A novel nanohybrid of daunomycin and single-walled carbon nanotubes: photophysical properties and enhanced electrochemical activity

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Abstract A nanohybrid adduct of the widely used, functional dye, daunomycin (DM), with single-walled carbon nanotubes (SWNTs) was prepared. Ultraviolet-visible-near infrared and fluorescence spectroscopy and electrochemistry of DM-functionalized SWNTs reveal that DM interacts with SWNTs through strong π - π stacking and there is a significant photo-induced charge-transfer interaction between the two components. Importantly, the novel adduct modified the glassy carbon (GC) electrode to give a much enhanced electrochemical activity than those of DM adsorbed onto not only the bare GC electrode but also the SWNTs-modified GC electrode.

Keywords Daunomycin · Electrochemical · Electron-transfer · Nanohybrid · Single-walled carbon nanotubes

Introduction

Carbon nanotubes (CNTs) have attracted considerable research interests because of their novel structural, electrical properties and potential applications in many fields (Ajayan 1999). Especially their remarkable electronic properties render them attractive candidates for many possible applications as various nanodevices (Tans et al. 1998; Tans and Dekker 2000; Qu et al. 2006). Many CNTs-based devices, such as field-effect transistors (Javey et al. 2004) and biosensors (Lee et al. 2006), have been demonstrated. In recent years, increasing interests are being focused on the rational development of CNTs to fabricate functional nanostructures with novel properties (Christian et al. 2006; Yang et al. 2006). For example, Murakami et al. (2003) has prepared a novel nanohybrid of porphyrin with single-walled carbon nanotubes (SWNTs), which shows a variety of unique chemical, photophysical and biological properties. Recently, Yan et al. (2005) reported a nanomaterial with a polynuclear aromatic electroactive methylene blue functionalized SWNTs, which is very useful for the development of biosensors and photovoltaic cells for practical applications.

We are interested in fabricating novel nanostructures with designed engineering applications for the development of biosensors using SWNTs (Yang et al. 2006; Lu et al. 2006; Yang et al. 2007). We report here a new type of electrochemically nanostructure

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with daunomycin (DM) noncovalently functionalized SWNTs. It is known that the $\pi-\pi$ stacking interaction between the aromatic compounds and SWNTs results in a rather stable adsorption of such kind of compounds on SWNTs surface and the interactions have been characterized by a series of microscopy and spectroscopy (Chen et al. 2001; Yan et al. 2005). DM has multi-aromatic rings which could be used to facilitate the $\pi-\pi$ stacking interaction between it and the walls of SWNTs. More importantly, DM possesses excellent electrochemical properties and has been widely used for many electrochemical studies and applications (Cai et al. 2003). Thus this novel and stable nanohybrid fabricated from DM and SWNTs, with much enhanced electrochemical activity and energy transfer capability, might find applications for the development of novel electronic nanodevices including biosensors and photovoltaic devices.

Materials and methods

Materials

Single-walled carbon nanotubes (SWNTs) were made using our modified arc discharge method (Lv et al. 2005). Daunomycin (DM) and other reagents were commercial products.

Preparation of the DM and SWNTs adduct

SWNTs were purified and shortened using a previously published method (Liu et al. 1998). A typical procedure for the noncovalent functionalization is as follows: 0.25 mg SWNTs were added to 3 μM DM in Milli-Q water (set to pH 8.6 with 8 M NaOH), and then sonicated for 1 h in a cool water bath and then stirred for 40 h at room temperature in dark. The samples were then centrifuged for 90 min at 21,000g. The sediments were washed with Milli-Q water by six sonication–centrifugation (21,000g) cycles in order to remove any free DM. Finally, the samples (referred to here as “DM-SWNTs”, ~0.05 mg) were dispersed in 400 μl Milli-Q water for the following measurements. This yields a clear brown, transparent and homogenous suspension.

The preparation of DM-SWNTs adduct modified electrode and the control ones

Eight microlitre DM-SWNTs suspension was cast on the surface of glassy carbon (GC, diam. = 4 mm) electrode and is referred to as the “DM-SWNTs/GC” electrode.

The preparation of the control electrodes was as follows:

- (a) The DM-modified GC electrode was prepared by directly casting 8 μl free DM solution on the surface of GC electrode and is referred to as the “DM/GC” electrode.
- (b) The SWNTs-modified GC electrode was prepared by directly casting 8 μl free SWNTs suspension on the surface of the GC electrode and is referred to as the “SWNTs/GC” electrode.
- (c) The fourth electrode, referred as “DM/SWNTs/GC” electrode, was prepared by first casting 8 μl free SWNTs suspension on the surface of GC electrode, which was then dried in air, and then followed by casting another 8 μl free DM solution onto the surface of the SWNTs-modified GC electrode.

DM and SWNTs concentrations used above were controlled to be the same using UV–vis-NIR spectra.

Electrochemical measurements

Cyclic voltammograms (CVs) measurements were carried out in a standard three-electrode electrochemical cell with a working electrode, a platinum counter-electrode and an Ag/AgCl electrode as reference electrode, in which phosphate buffer (0.05 M, pH 7.4) was electrolyte and KCl (0.1 M) was used as the supporting electrolyte.

Results and discussion

Microscopic and spectroscopic evidence for DM adsorption onto SWNTs

The adduct was confirmed from its transmission electron microscopy (TEM) images (Fig. 1a, b). The surface of SWNTs are clean but the surface of the hybrid material has a much soft coating material, and

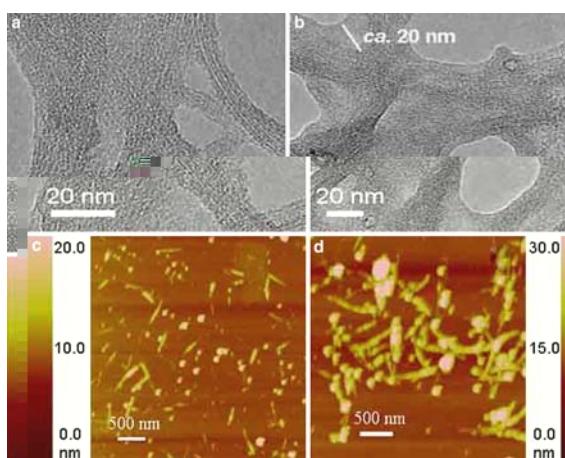


Fig. 1 Typical TEM images of (a) SWNTs, (b) DM-SWNTs adduct and AFM images of (c) SWNTs (vertical scale bar: 20 nm), (d) DM-SWNTs adduct (vertical scale bar: 30 nm)

its thickness in some areas approaches approx. 20 nm. This is indicative of strong interactions in the adduct, as SWNTs adsorb a considerable amount of DM.

Atomic force microscopy (AFM) height measurements, which could provide a reliable measurement of DM-SWNTs diameter, revealed another evidence of DM affinity on to the walls of SWNTs. The height of the nanotubes in Fig. 1c was significantly lower than that of Fig. 1d from the height profiles in the AFM images.

More convincing evidence came from UV-vis-NIR and fluorescence spectroscopy (Figs. 2, 3). In the UV-vis-NIR spectra, free DM solution (Fig. 2a) had a strong absorbance at 481 nm, and that for free SWNTs (Fig. 2b) had unique M_{11} and S_{22} peaks at about 700 nm and 1,000 nm, respectively. The stacking of DM onto the walls of SWNTs was evident from the spectrum of the DM-SWNTs adduct solution (Fig. 2c), which shows both the characteristic absorption peaks of DM and SWNTs simultaneously. Moreover, after forming the adduct, the absorption peaks of both DM and SWNTs all showed a red-shift. For example, the peak of free DM at 481 nm shifted to 490 nm and the peak of free SWNTs at 975 nm shifted to 997 nm in the adduct. These changes are generally believed due to the electron donor–acceptor interaction between the two components (Murakami et al. 2003; Yan et al. 2005; Guldi et al. 2003), namely DM and SWNTs in this study. In the fluorescence spectra (Fig. 3), free DM (Fig. 3a) exhibits a fluorescence emission maximum at

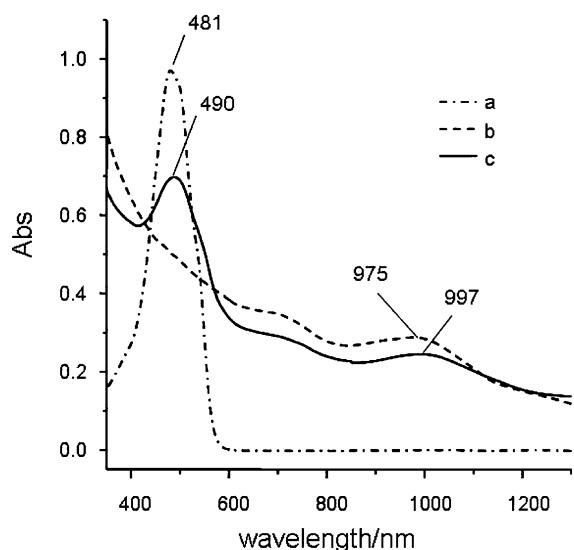


Fig. 2 UV-vis-NIR spectra of (a) DM, (b) SWNTs and (c) DM-SWNTs adduct in water

592.7 nm when excited at 480 nm. However, upon excitation at the same wavelength (480 nm), DM-SWNTs (Fig. 3b) exhibits ~85% quenching of its emission band. Furthermore, the emission band of DM shifts from 592.7 nm to 594.6 nm for DM-SWNTs adduct. These results are consistent with our earlier study for the adducts of ferrocene (Yang et al. 2006) and porphyrin (Guo et al. 2006) with SWNTs and imply the presence of a photo-induced electron-transfer process (Guo et al. 2006; Baskaran et al. 2005).

Electrochemical property of the hybridization adduct

From the results for the photophysical studies above, we considered that this adduct might show enhanced electrochemical activity due to the photo-excited electron-transfer. We thus investigated the electrochemical property of DM-SWNTs and found, indeed, it showed much enhanced electrochemical activity. Figure 4 compared the typical CVs using the four different electrodes, the adduct of DM-SWNTs modified electrode (Fig. 4d) and the three control electrodes: DM/GC (Fig. 4a), SWNTs/GC (Fig. 4b) and DM/SWNTs/GC (Fig. 4c) electrodes. In Fig. 4a, for the electrode modified directly with free DM, the

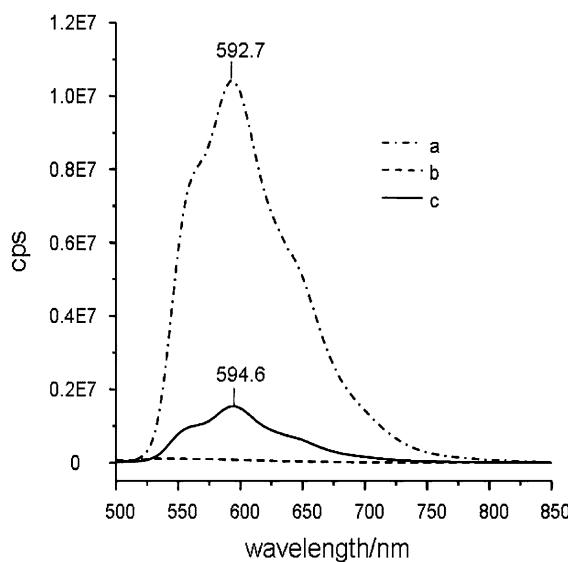


Fig. 3 Steady-state fluorescence of (a) DM, (b) SWNTs and (c) DM-SWNTs adduct in water at $\lambda_{ex} = 480$ nm. Both DM and SWNTs concentrations were all controlled to be the same using UV-vis-NIR spectra

typical redox couple of peaks with cathode and anode peak potentials at -0.64 V and -0.61 V were observed. These are the characteristic peaks of DM based on its quinine portion of the molecule (Lü 2003). The GC electrode modified with SWNTs exhibited a featureless peak in this potential range (Fig. 4b). Whereas the DM-SWNTs adduct modified GC electrode displayed a pair of much stronger redox peaks (Fig. 4d).

In another control CV measurement (Fig. 4c), where the DM/SWNTs/GC electrode was prepared by casting the same volume free DM solution onto the surface of SWNTs-modified GC electrode used for the measurement in Fig. 4b, the height of the reduction peak was significantly lower than that of DM-SWNTs (Fig. 4d). Comparing Fig. 4c with 4d, though both use the same concentration of DM and SWNTs on the surface of electrodes, the two electrodes show very different enhancement of the electrochemical signal. This may be because of the different interactions between DM and SWNTs on the two electrodes. In the electrode modified with the adduct of DM-SWNTs, the interaction between the two components in the homogenous adduct is more efficient in enhancing electron transfer compared with that for the electrode prepared by casting the DM solution and the SWNTs suspension on GC electrode surface sequentially. This

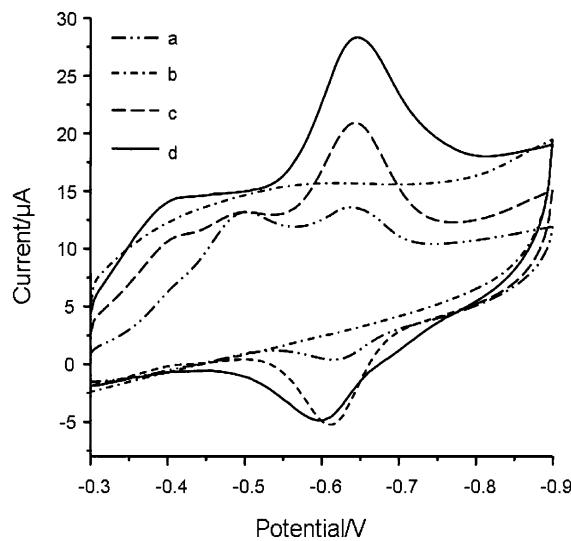


Fig. 4 Cyclic voltammetry curves of (a) DM, (b) SWNTs, (c) DM/SWNTs and (d) DM-SWNTs modified GC electrodes in a standard three-electrode electrochemical cell with a working electrode, a platinum counter-electrode and an Ag/AgCl electrode as reference electrode at a 50 mV/s scan rate, in which phosphate buffer (0.05 M, pH 7.4) was electrolyte and KCl (0.1 M) was used as the supporting electrolyte. Both DM and SWNTs concentrations were controlled to be the same using UV-vis-NIR spectra. The preparation of the four electrodes was as follows: (a) Casting $8 \mu\text{l}$ free DM solution on the surface of GC electrode (b) Casting $8 \mu\text{l}$ free SWNTs suspension on the surface of GC electrode (c) First casting $8 \mu\text{l}$ free SWNTs suspension on the surface of GC electrode, which was then dried in air, and then followed by casting another $8 \mu\text{l}$ free DM solution onto the surface of SWNTs modified GC electrode and (d) Casting $8 \mu\text{l}$ DM-SWNTs adduct suspension on the surface of GC electrode

better interaction is expected significantly to enhance the redox reaction current and thus offers a better sensitivity and a lower detection limit for the widely used for amperometric detection.

In conclusion, a nanohybrid of DM-SWNTs adduct with noncovalently bonded DM with SWNTs has been synthesized and characterized by microscopy and spectroscopy. The UV-vis-NIR and fluorescence results and electrochemical experiments suggest that there is strong $\pi-\pi$ stacking interaction between DM and SWNTs. The excellent electrochemical and photo-induced electron-transfer activity of DM-SWNTs adduct could thus offer another way to prepare novel carbon nanotubes-based nanodevices for applications such as biosensors and photovoltaic cells. Additional experiments are underway for

gaining further insights into the $\pi-\pi$ stacking interaction between DM and SWNTs.

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