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BRIEF COMMUNICATION

Covalently β-cyclodextrin modified single-walled carbon nanotubes: a novel artificial receptor synthesized by 'click' chemistry

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Abstract Novel β-cyclodextrin covalently modified single-walled carbon nanotubes have been synthesized via a 'click' coupling reaction. The product was fully characterized with Raman, FTIR, XRD, UV-Vis-NIR spectra as well as TEM and TGA measurements. The effective functionalization via 'click' coupling has set up a facile and versatile route for modular preparation of SWNTs based functional materials. The inclusion complexation behavior of this artificial receptor with quinine has been investigated in aqueous solution by fluorescence spectroscopy.

Keywords Carbon nanotube · Cyclodextrin · 'Click' chemistry · Chemical modification · Colloids

Introduction

Single-walled carbon nanotubes (SWNTs) exhibit unique mechanical and electrical properties and are of great interest in the applications of photovoltaic devices, field emission displays and ultrahigh-strength materials (Dresselhaus et al. 2001). The studies of SWNTs in biomedicine field have also drawn much attention in recent years. In order to overcome the strong intertube van der Waals interaction (~40 k_BT/nm) (Girifalco et al. 2000) to improve their solvent dispersibility and endow SWNTs with new properties, various modification methods (i.e., noncovalent modification and covalent modification) have been investigated (Tasis et al. 2006; Lu and Chen 2005). Noncovalent modification can maintain the nanotube's electronic structure and its process is relatively simple, but the choices of surfactants are rather limited and condensed aromatic compound with large π-systems, a kind of organic mutagenic carcinogen (e.g., pyrene) is often used (Tasis et al. 2006). Covalent modification can introduce a wide range of functional groups on nanotube's surface and is more stable to environment changes than noncovlant modification. Furthermore, covalently functionalized SWNTs samples are substantially less cytotoxic than surfactant stabilized SWNTs and the samples become much less cytotoxic with the increase of the functionalization degree (Sayes et al. 2006). Thus through covalent modification, the dispersibility, cytotoxicity and biocompatibility of SWNTs can be significantly improved. In addition, through endocytosis functionalized SWNTs can carry smaller molecules into cells, which makes them potential drug delivery systems and facilitate their application in biomedicine research (Liu et al. 2007). Covalent modified SWNTs,

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which can carry *cis*-[$Pt(NH_3)_2Cl_2$] and complexed siRNA into tumor cells and silence the targeted gene, have been recently reported by Feazell et al. (2007) and by us (Yang et al. 2006; Zhang et al. 2006).

β-Cyclodextrin (*β*-CD), an oligosaccharide consisting seven D-glucose units linked by α-1,4-glucose bonds, is well-known to encapsulate various organic and biological guests within their hydrophobic cavities in aqueous solution, which enables them to be successfully utilized as drug carriers and enzyme mimics. So the combination of *β*-CD and carbon nanotubes is expected to generate significant and interesting object for supramolecular chemistry, biomedicine and nanodevice construction. However, most of the reported CD/nanotube systems have been concentrated on the electrochemistry of noncovalently CD modified multi-walled carbon nanotubes (MWNTs) (He et al. 2006; Wang et al. 2004) and the formation of hydrogel or complexes of noncovalent CD/SWNT systems (Ogoshi et al. 2007; Wang and Chen 2007; Ikeda et al. 2004). As far as we know, covalently bonded CD–SWNTs hybrids have not been reported yet. As one of the most effective 'click' reactions, Cu(I) catalyzed Huisgen 1,3-dipolar cycloaddition has been widely used in organic synthesis and material research for its high selectivity, mild reaction conditions, high yield and simple purification steps (Binder and Sachsenhofer 2007; Li et al. 2005). In this work, we report the first synthesis of novel *β*-CD covalently modified SWNTs nanohybrid through 'click' coupling (Fig. 1). The product was fully characterized with Raman, FTIR, XRD, UV-Vis-NIR spectra, TGA and TEM measurements. As *β*-CD immobilized on SWNTs is supposed to show drug binding abilities, the interaction of obtained *β*-CD covalently modified SWNTs with alkaloid was probed by fluorescence spectroscopy.

Experiment

Raman spectra were measured by a Renishaw inVia Raman microscope with the 514 nm line of an Ar ion laser as an excitation source. FTIR spectra were obtained with a BRUKER TENSOR 27 instrument. UV-Vis-NIR spectra were obtained with a JASCO V-570 spectrometer. Fluorescence spectra were obtained with a VARIAN Cary Eclipse fluorimeter and were taken in aqueous phosphate (NaH_2PO_4–Na_2HPO_4) buffer solution of pH = 7.40 at 25 °C. ^1H NMR spectra were recorded on a Bruker (300 MHz) spectrometer using TMS as the internal standard. Mass spectra were acquired on a LCQ Advantage ESI ion trap spectrometer (ThermoFinnigan). Melting points were obtained on a digital melting point instrument (X-4, Beijing Tech Instrument Co., Ltd) and are uncorrected. Filtration was performed through a nylon membrane (Whatman International Ltd, England, 0.2 μm, 47 mm). Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku D/max-2500 diffractometer with Cu Kα radiation. For thermogravimetric analysis (TGA), a NETZSCH STA 409PC instrument was used, and sample was heated in dry nitrogen flow (20 sccm) at a rate of 5 °C min^{-1}. Transmission electron microscope (TEM) images were obtained on a FEI TECNAI-20 instrument operated at 100 kV.

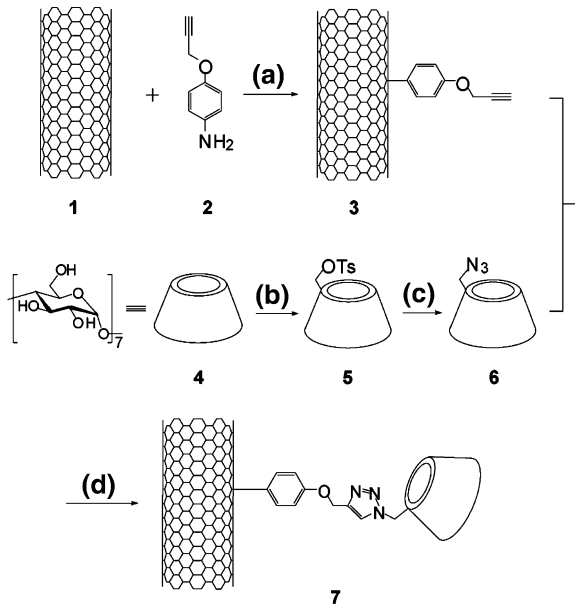

Fig. 1 Synthesis of *β*-CD covalently modified SWNTs. Reagents and conditions: (**a**) isoamyl nitrite, *o*-dichlorobenzene, acetonitril, 60 °C, overnight; (**b**) *p*-toluenesulfonyl chloride, NaOH, H_2O, rt, 2 h; (**c**) NaN_3, H_2O, 80 °C, 5 h; (**d**) CuI, DBU, DMF, 70 °C, 48 h

SWNTs sample was purchased from Shenzhen Nanotech Port Co. Ltd. (synthesized by chemical vapor deposition method) and was purified according to the reported method (Furtado et al. 2004). Acetonitrile and *o*-dichlorobenzene (ODCB) were distilled from calcium hydride before use. *N,N*-Dimethylformamide (DMF) was distilled freshly from anhydrous

calcium sulfate. All other chemicals (AR) obtained from commercial sources were used without further purification.

p-(2-Propynyloxy)-benzenamine **2** was prepared by the reported procedures (Agag and Takeichi 2001). *p*-Nitrophenol was etherified with propargyl bromide and then reduced by $SnCl_2 \cdot 2H_2O$ in concentrated HCl (37%) and 1,4-dioxane. The crude product **2** was purified by column chromatography to afford white crystals. ^{1}H NMR (300 MHz, $CDCl_3$) ppm: δ = 6.83 (d, 2H, J = 9.0 Hz), 6.65 (d, 2H, J = 8.7 Hz), 4.61 (d, 2H, J = 2.4 Hz), 3.41 (br, 2H), 2.49 (t, 1H, J = 2.4 Hz). ESI-MS: calcd. for $C_{10}H_{13}NO_2$ (M + CH_3OH) 179.09, found 179.04 $[M + CH_3OH]^+$. FTIR (KBr) cm^{-1}: v = 3433, 3350 (s, NH_2), 3261 (s, C≡C–H), 2115 (w, C≡C).

Mono-6-deoxy-6-azido-β-cyclodextrin **6** was prepared according to the method reported by Muderawan et al. (2005). β-Cyclodextrin **4** reacts with *p*-toluenesulfonyl chloride to produce mono-6-(*p*-toluenesulfonyl)-β-cyclodextrin **5**. **5** was added to the solution of NaN_3 and stirred at 80 °C for 5 h, then **6** was precipitated by addition of acetone. m.p. 205 °C (decomp.). ^{1}H NMR (300 MHz, d_6-DMSO) ppm: δ = 4.83–4.87 (m, 7H), 3.55–3.65 (m, 28H), 3.22–3.43 (m, 14H). ESI-MS: calcd. for $C_{42}H_{69}N_3NaO_{34}$ (M + Na) 1182.37, found 1182.46 $[M + Na]^+$. FTIR (KBr) cm^{-1}: v = 2105, 2038 (s, N_3)

Purified SWNTs **1** (50 mg, 4.17 mmol of carbon) was sonicated for 2 h in 40 mL ODCB. To this suspension was added 1.21 g **2** (8.23 mmol) in 10 mL of acetonitrile. After transfer to a septum-capped flask and bubbling with nitrogen for 10 min, 1.50 g (12.80 mmol) of isoamyl nitrite was quickly added and the suspension was stirred at 60 °C under nitrogen overnight. The resulting mixture was diluted with 10 mL DMF and filtered through nylon membrane. The collected solid was washed with DMF until the filtrate became colorless. Sonication and redispersion was repeated in DMF and then in ether. The product was dried in a vacuum at 60 °C for 10 h to give alkyne modified SWNTs **3** as a black powder (58 mg).

Alkyne functionalized SWNTs **3** (12 mg) were dispersed in 15 mL DMF by sonication for 5 min and bubbling with nitrogen for 10 min. Then 232 mg azide-functionalized cyclodextrin **6** (0.20 mmol), 38 mg CuI (0.20 mmol) and 1.52 g DBU (10.00 mmol) were added. The reaction mixture was evacuated and refilled with nitrogen three times followed by stirring under nitrogen at 70 °C for 48 h. After cooling to room temperature, the mixture was diluted with 10 mL of DMF, sonicated for 5 min, and filtered through nylon membrane. The product was sonicated and redispersed in DMF, KI aqueous solution (1 mol L^{-1}) respectively and then washed thoroughly with water and acetone. 13 mg β-CD covalently modified SWNTs **7** was obtained as black powder after drying under vacuum overnight.

Results and discussion

Purified SWNTs was reacted with *p*-(2-propynyloxy)-benzenamine in ODCB using diazotization-coupling procedure to produce alkyne-functionalized SWNTs (**3**, Fig. 1). This in situ diazotization-coupling to SWNTs founded by Bahr and Tour (2001) allows for effective functionalization without the use of unstable aryl diazonium salts and has been widely used in chemical modification of carbon nanotubes (Shi et al. 2006). Then alkyne-functionalized SWNTs **3** and β-CD azide **6** were coupled in DMF via [3 + 2] Huisgen cycloaddition between the alkyne and azide groups using CuI/DBU as catalyst, following the protocol reported by Li et al. (2005), yielding β-CD functionalized SWNTs (**7**, Fig. 1). CuI and DBU were used as catalysts instead of $(PPh_3)_3CuBr$ to make the reaction process at relatively low temperature to avoid dehydration of β-CD, and they were removed by washing with KI aqueous solution and DMF. Excess β-CD azide **6** was used for high conversion and can be easily removed by washing with water. Compare to SWNTs which is completely insoluble in water, the CD–SWNTs nanohybrid **7** was water dispersible due to the hydrophilic nature of β-CD, and can form a clear, dark solution with no discernible particulate materials. **7** was dispersible in high polar solvents such as water, DMSO and DMF, but not in methanol and acetone. The dispersibility of CD–SWNTs nanohybrid **7** is in accordance with β-CD and indicates the existence of β-CD to some extent.

Figure 2 shows the Raman spectra of **1**, **3** and **7**. They all exhibit the characteristic radial breathing mode at ~200 cm^{-1} (RBM band), disorder mode at ~1350 cm^{-1} (D-band) and tangential mode at ~1590 cm^{-1} (G-band), which verifies the existence

and structural integrity of SWNTs (Bahr and Tour 2001). The disorder mode involves the resonance-enhanced scattering of an electron via phonon emission by a defect that breaks the basic symmetry of the graphene plane. Thus relative intensities of D-band to G-band can reflect the relative amount of sp^3 hybridized carbon converted from sp^2 hybridized carbon on SWNTs, and can be used to estimate the degree of functionalization (Strano et al. 2003). It can be clearly seen that relative intensities of D-band increased after *p*-(2-propynyloxy)phenyl group functionalization (Fig. 2a and b), indicating the diazotization-coupling was carried out successfully on SWNTs' side walls (Bahr and Tour 2001). As the 'click' coupling occurs at the alkyne group attached on SWNT's surface and the SWNT framework was untouched, the relative intensity of D-band to G-band of **7** remained approximately the same as that of **3** (Fig. 2b and c).

As is shown in Fig. 3a, purified SWNTs **1** show no characteristic IR absorptions as reported (Li et al. 2005). After diazotization-coupling, the IR spectrum of alkyne modified SWNTs **3** exhibits the characteristic absorptions of terminal alkyne group at 2127 and 3260 cm^{-1} which respectively correspond to the stretching vibration of C≡C and C–H (Fig. 3b). As phenyl was introduced as a linker in **3**, the absorptions of phenyl framework vibration can be also seen at 1600–1450 cm^{-1}. In the IR spectrum of CD–SWNTs **7** (Fig. 3c), the characteristic strong absorption of C–O stretching vibration of *β*-CD at 1221, 1173, 1102 and 1030 cm^{-1} can be clearly seen

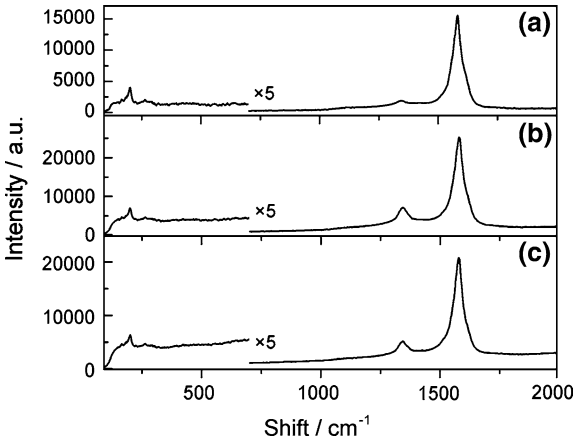

Fig. 2 Raman spectra (514 nm excitation) of SWNTs **1** (**a**), alkyne modified SWNTs **3** (**b**) and CD–SWNTs **7** (**c**)

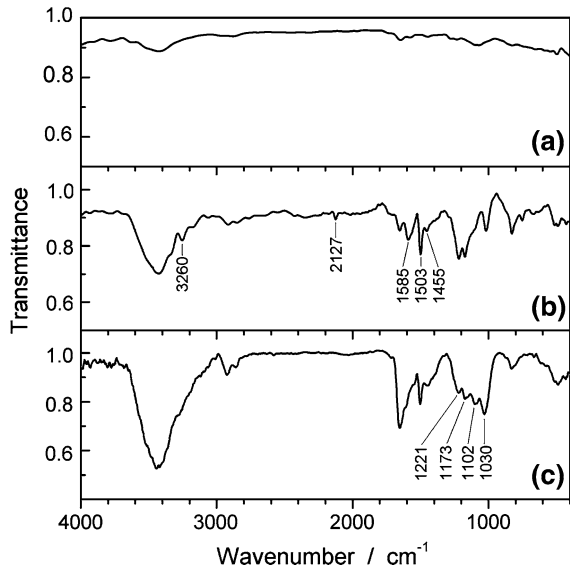

Fig. 3 FTIR spectra (KBr pellet) of SWNTs **1** (**a**), alkyne modified SWNTs **3** (**b**) and CD–SWNTs **7** (**c**)

and the relative intensity at ~3400 cm^{-1} increased greatly due to the existence of a huge amount of hydroxyl groups in *β*-CD, which is in accordance with the earlier studies (Na et al. 2006). In the meantime, the absorptions at 2127 and 3260 cm^{-1} disappeared, indicating most of the alkynes in **3** have reacted with azide-CD through 'click' coupling. These results show the existence of *β*-CD and validate the covalent modification of SWNTs. The UV-Vis-NIR spectrum (not shown) of **7** in water showed typical SWNTs continuous absorption extended to near-IR region, indicating the homogeneous dispersion of SWNTs in water (Dresselhaus et al. 2001). As a character of SWNT's covalent diazotization modification, the loss of the van Hove singularities caused by disturbed *π* system is also observed (Bahr and Tour 2001).

In order to further confirm the covalent linkage mode and eliminate the possible physical adsorption of *β*-CD on SWNT's surface, a control experiment was carried out. Alkyne modified SWNTs **3** was reacted with *β*-CD azide **6** under the same conditions but without the 'click' coupling catalyst (CuI/DBU). The SWNTs obtained show the same IR spectrum as **3** without the absorption of *β*-CD, indicating that 'click' coupling did not occur and the *β*-CD noncovalent adsorption on SWNT's surface can be excluded.

The powder XRD patterns of SWNTs **1**, β-CD **4** and CD–SWNTs **7** were illustrated in Fig. 4. SWNTs **1** display three typical peaks at $2\theta = 26$, 44 and 51° (Fig. 4a) (Karim et al. 2006). β-CD **4** show diffractograms consistent with their crystalline nature (Fig. 4b) (Liu et al. 2005). In Fig. 4c, we can still find the corresponding peaks of **1** and **4** indicating the existence of the two components in CD–SWNTs **7**. But the spectrum of **7** has a different pattern to a simple sum of the spectra of **1** and **4** in 10–30° area, where the peaks associated with β-CD have shifted and the relative intensities altered significantly. These results can be rationalized for that the covalent linkage of β-CD to SWNTs makes CD's conformation reorient to some extent and the crystalline form of CD changed (Liu et al. 2005).

From above spectroscopic measurements and the result of control experiment, the β-CD covalent modification upon the surface of SWNTs can be confirmed. The effective functionalization via 'click' coupling will provide a facile and versatile route for modular preparation of SWNTs based functional materials.

TEM images in Fig. 5 show the surface morphology of SWNTs before and after functionalization. Unlike the smooth sidewall of unmodified SWNTs, the image of CD–SWNTs **7** shows the existence of amorphous soft materials on the surface of SWNTs, indicating the presence of β-CD (Ogoshi et al. 2007; Li et al. 2005; Zeng et al. 2005). In order to evaluate the degree of functionalization, TGA measurement for CD–SWNTs were taken under nitrogen. The weight loss curve shows a typical pattern of functionalized SWNTs with a weight loss of 36% at 860 °C, which corresponds to a ratio of one functional group in 190 carbon atoms of the SWNTs framework.

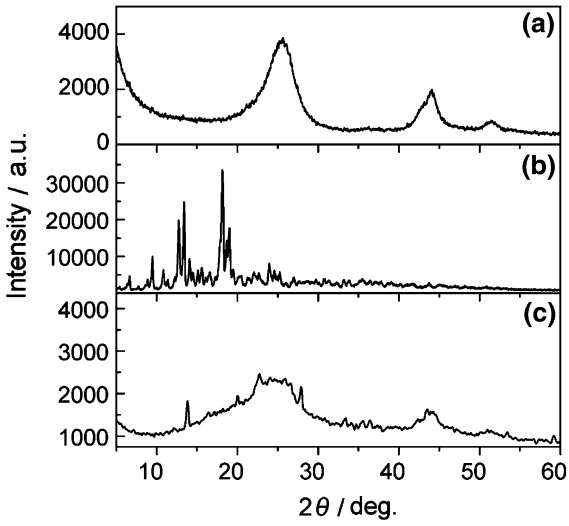

Fig. 4 The X-ray powder diffraction (XRD) patterns of SWNTs **1** (**a**), β-CD **4** (**b**) and CD–SWNTs **7** (**c**)

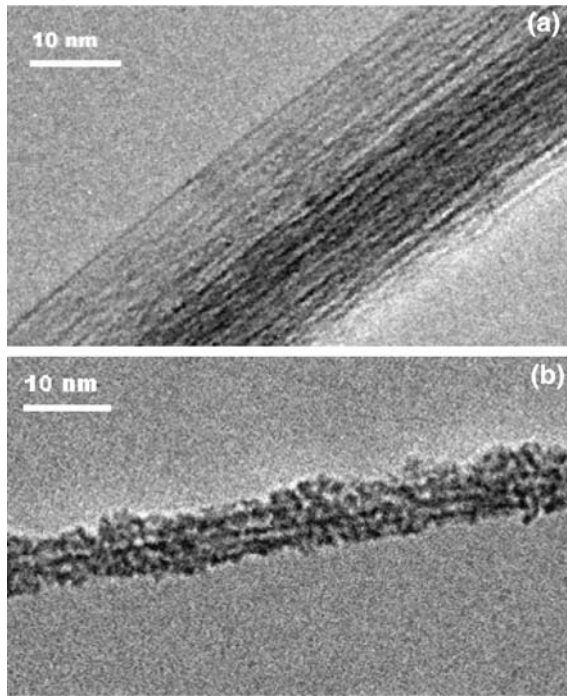

Fig. 5 TEM images of purified SWNTs **1** (**a**) and CD–SWNTs **7** (**b**)

Cinchona alkaloids, which have been successfully used as antimalarials, are well known for their bioactivity and pharmacology properties. Their application in antiarrythmics and antitumor drugs have also been reported (Honigsbaum 2001; Kuhlmann et al. 2003). In order to probe the recognition ability of CD–SWNTs **7** for medicinal purpose, quinine was selected as a drug molecule model and the association of quinine with **7** was examined using fluorescence spectroscopy (Chen et al. 2006; Liu et al. 2003). As can be seen in Fig. 6, the strong fluorescence of quinine around 384 nm in aqueous buffer solution (pH = 7.40, human plasma pH) gradually decreased with the addition of **7** (Fig. 6 inset). The quenching phenomena can be interpreted by two reasons: (i) the interaction between lone pair electrons on quinine's

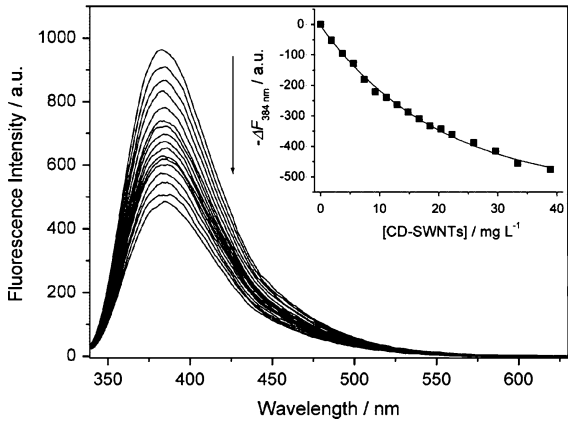

Fig. 6 Fluorescence spectral changes of quinine (2.34×10^{-5} mol L^{-1}) upon addition of **7** (0–39 mg L^{-1} from top to bottom) in aqueous buffer solution (pH = 7.40, 25 °C). Inset: differential fluorescence intensity (ΔF) versus the concentration of CD–SWNTs **7** relationship. The excitation wavelength is 330 nm

nitrogen heteroatom and the cyclodextrin interior cavity with high electron density could deactivate the guest molecule and result in a decrease of the number of fluorescing species in solution (Liu et al. 2003); (ii) the effective electron/energy transfer between the π-systems of quinine and SWNTs helps to quench the fluorescence, which additionally increases the binding ability of this nanohybrid to drugs. The cooperative binding derived from CD and SWNTs helps to increase the complex ability of SWNTs hybrid to guests. Analogous inclusion complexation induced by CD inclusion and large π-systems interaction of carbon related materials was also observed in reported β-CD–C_{60} systems (Chen et al. 2006).

Conclusion

In summary, we have prepared a novel β-CD covalently modified SWNTs hybrid through a facile and versatile modular 'click' reaction. The spectroscopic data collected clearly indicate the covalent fuctionalization and fluorescence quenching results show its binding ability to guests as an artificial receptor. With better biocompatibility and the rich guest recognition property derived from cyclodextrin, this CD–SWNT hybrid is expected to provide a promising approach for materials researches and nanoscale drug hosting and delivery platform. Further investigation on drug and biomolecules targeted delivery is currently in progress.

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