

Design and Synthesis of Water-Soluble Photosensitive α -Cyclodextrin and Its Application in Dispersing Carbon Nanotubes

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ABSTRACT: This manuscript describes the use of a novel water-soluble photosensitive α -cyclodextrin modified coumarin (α -CD-C) to disperse carbon nanotubes (CNTs) in water. First, using epichlorohydrin as the bridged unit, water-soluble α -cyclodextrin (α -CD) was introduced to modify 7-hydroxy-4-methylcoumarin and prepare α -CD-C. α -CD-C was characterized with hydrogen nuclear magnetic resonance spectra ($^1\text{H-NMR}$) and High pressure liquid chromatography-mass spectrometry. The photodimerization experiment showed that α -CD-C could photodimerize upon 365 nm irradiation, and then photo-de-crosslink upon the subsequent 254 nm irradiation. Next, α -CD-C was used to disperse CNTs in water. Transmission electron microscope and scanning electron microscope demonstrated that α -CD-C effectively adsorbed onto the surface of CNTs. The α -CD-C is an efficient dispersant for CNTs. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2588–2593, 2013

KEYWORDS: composites; nanotubes; graphene and fullerenes; photochemistry; self assembly

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INTRODUCTION

In recent years, carbon nanotubes (CNTs) have been continuously receiving significant interests in scientific and technological areas due to their excellent properties.^{1,2} However, because of the substantial attraction between CNTs, dispersing CNTs in solvents or polymeric matrices is hindered; hence, CNTs exhibit poor solubility and processability. Significant efforts have focused on the surface modification of CNTs, including the use noncovalent interaction to suspend CNTs in various surfactants or polymers accompanied by the physical processes.^{3,4}

Cyclodextrins (CDs) are captivating molecules, appealing to investigators in both pure research and applied technologies due to their unique physical and chemical merits, which have been under investigated for over 100 years.^{5–7} CDs are well-known to bind with suitable guest molecules in aqueous solutions to form inclusion complexes, which is a useful property for researches in the field of sensor.^{8–12} One of the most important properties of CD is their ability to disperse CNTs in water and organic solvents.¹³ Some research groups have reported the preparation of CNTs/ β -CD composites. Liu et al.¹⁴ have prepared CNTs/ β -CD composites by assembling the β -CD molecules on the surface of CNTs. In their articles, the interaction between CNTs and β -CD was revealed for the first time by using a molecular mechanics method. Zhao et al.¹⁵ prepared pyrene- β -CD decorated CNTs for field-effect transistors as chemical sensors. Although a series

of CNTs/ β -CD composites have been synthesized, less research has been conducted to prepare α -cyclodextrin (α -CD)/CNTs composites, because the cavity size of α -CD is too small to use in host-guest recognition. However, the cavity size of α -CD/CNTs composites would be adequate for gas sensors, allowing the gas to enter the cavity of α -CD and achieving host-guest recognition.

In this article, we report the preparation of novel water-soluble photosensitive α -cyclodextrin modified coumarin (α -CD-C)/CNTs composites. The incorporation of photosensitive groups easily undergoes photodimerization under photoirradiation. This property is important for various applications using the nanocomposites alone or as starting materials, particularly in chemical sensors. Thus, we have prepared stable gas sensors using the novel α -CD-C/CNTs nanocomposites in an ongoing research system. To the best of our knowledge, this report is the first on the use of a water-soluble photosensitive α -CD-C as a dispersant for CNTs. Furthermore, this approach provides an economical solution for dispersing CNTs that is suitable for large-scale production and wider application.

EXPERIMENTAL

Materials

7-Hydroxy-4-methylcoumarin, α -CD, and acetone were obtained from Aldrich and used without further purification. Epichlorohydrin, triphenylphosphine, and NaOH were obtained from

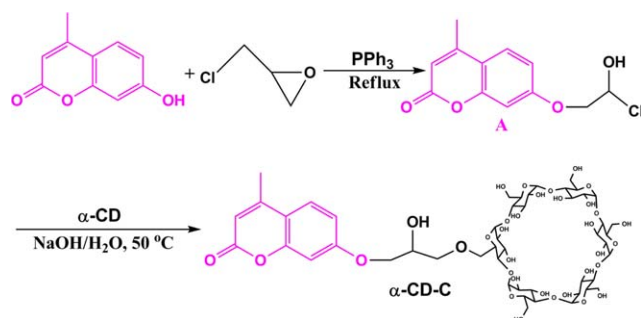


Figure 1. Synthetic route of α -CD-C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

Sinopharm Chemical Reagent, (Shanghai, China). Single walled CNTs (SWCNTs) and multiwalled CNTs (MWCNTs; >95%) were provided by Chengdu Organic Chemicals Institute, Chinese Acad of Sciences, China.

Synthesis of α -CD-C

In a flask equipped with a stirrer and a reflux condenser, 7-hydroxy-4-methylcoumarin (50 g, 0.28 mol) were mixed with 110 mL epichlorohydrin (1.2 mol) and the catalyst triphenylphosphine (0.2 g). The suspension was stirred under reflux at 110°C for 24 h. After cooling to room temperature, the liquid was decanted from the flask. The epichlorohydrin was removed by distillation and the chlorinated 7-hydroxy-4-methylcoumarin was poured into a large number of petroleum until the product was purified clean enough. Finally, powders were obtained by drying *in vacuo* at 40°C; the yield was 90%. Then, the obtained powders (13.40 g, 0.05 mol) were mixed with 40 mL NaOH (20 wt %) aqueous solution, and α -CD (9.72 g, 0.01 mol) was added to the solution. After further reacting at 50°C for 48 h, 100 mL of ultra-pure-water was added into the reaction system immediately and the resulting mixture was stirred quickly while cooling to the room temperature, then the mother liquid was collected and a gray solid was obtained. Finally, the product was obtained after heating at 40°C for 24 h using a vacuum drying oven. The yield of α -CD-C was 50 wt %. The synthetic route of α -CD-C can be shown in Figure 1.

Structure Characterization of α -CD-C

As shown in Figures 2 and 3, the structure of α -CD-C was characterized by ^1H NMR and HPLC-MS. The signals for methylene protons appear at 3.73–3.52 ppm (16H, CH_2). The signals at 6.74–6.69 and 7.68 ppm are assigned to the aromatic protons relative to benzene group (1H, 2H, ArH). The peaks at

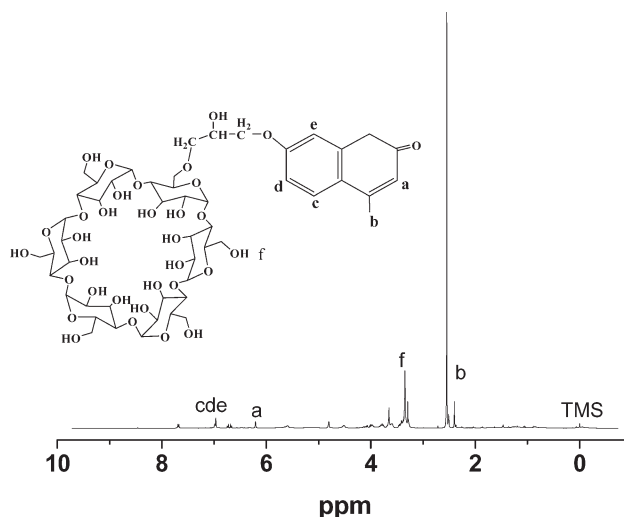


Figure 2. The ^1H -NMR of α -CD-C in *d*-DMSO.

4.22–4.04 (6H, OH) and 5.54–5.80 (5H, OH) ppm are ascribed to the oxyhydril group. Moreover, the signals for $[\text{s}]\text{OH}$ in CD appear at 4.53 ppm (6H, OH in CD). The peaks at 4.80 (1H, CH), 4.01–3.91 (7H, CH) and 3.87–3.75 ppm (6H, CH) are ascribed to $[\text{s}]\text{CH}$ group. The signals at 2.55 ppm is ascribed to methyl group (3H, CH_3). High pressure liquid chromatography-mass spectrometry (HPLC-MS): $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (4 : 1); column HYPER-SIL C18, $25 \times 2.1 \text{ cm}^2 \times 5 \text{ m}$; flow = 0.25 mL/min; m/z ($[\text{M} + \text{Na}]^+$) = 1227.3. Anal. Calcd. for $\text{C}_{49}\text{H}_{72}\text{O}_{34}$: C 48.84; H 6.02. Found: C 48.85; H 6.11.

Dispersion of CNTs with α -CD-C

A schematic drawing of the α -CD-C decorated CNTs hybrids is shown in Figure 4. First, small amounts of CNTs (MWCNTs or SWCNTs) and α -CD-C were ground in a mortar and pestle with the dropwise addition of H_2O (1 g). After grinding for 1 h, the resulting black powder was transferred to a bottle with the dropwise addition of H_2O (9 g). Finally, the dispersion of CNTs was obtained. The masses (g) of each component are (MWCNTs/ α -CD-C/ H_2O) 0.02/0/10, 0.02/0.01/10, and (SWCNTs/ α -CD-C/ H_2O) 0.02/0/10, 0.02/0.01/10, designated as samples A, B, C, and D, respectively.

Analysis and Characterization

Hydrogen nuclear magnetic resonance spectra (^1H -NMR) and were measured on a Bruker AV-300 spectrometer with chemical

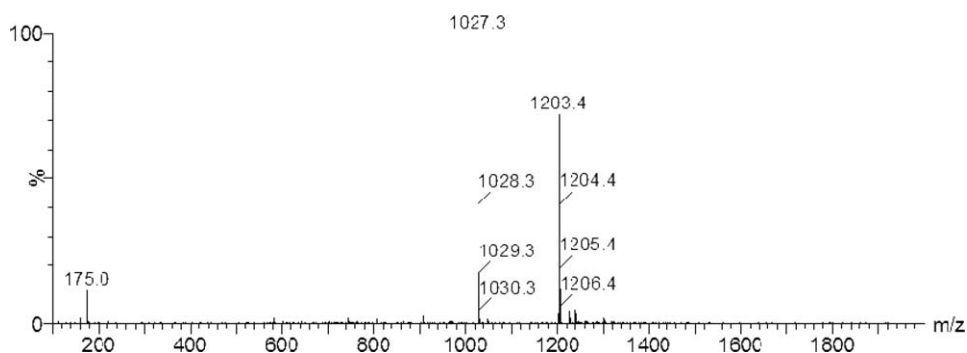


Figure 3. HPLC-MS of α -CD-C.

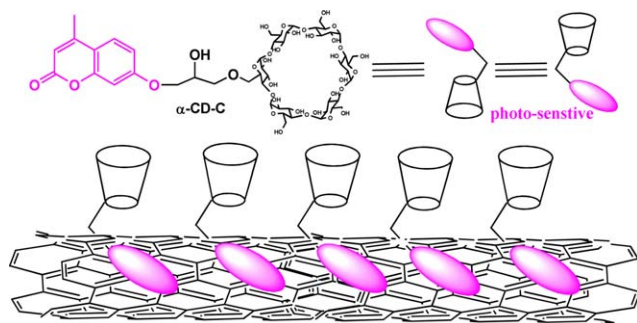


Figure 4. Scheme for the α -CD-C decorated CNTs hybrids. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

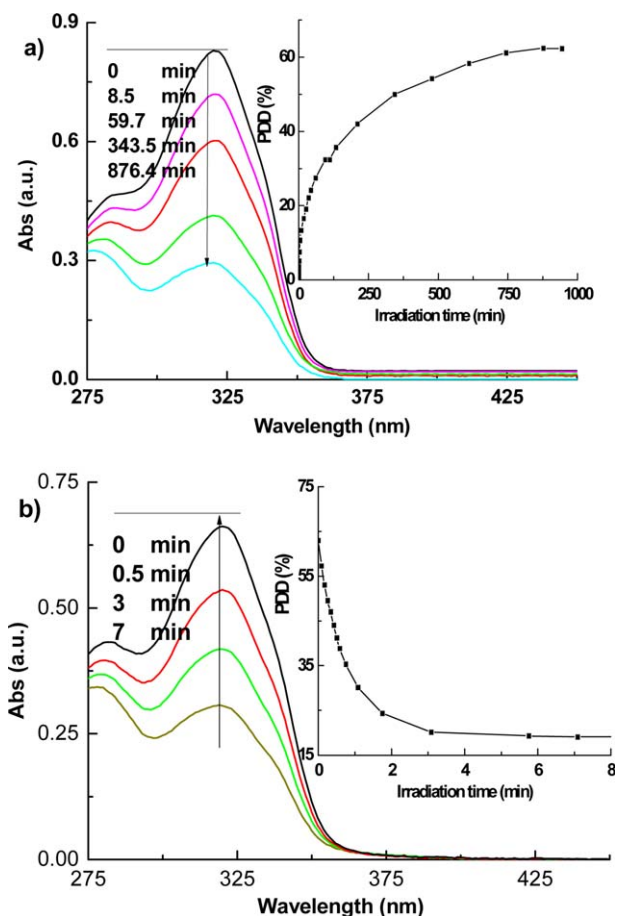


Figure 5. UV-vis spectra of α -CD-C (0.125 mg/mL \times 2 mL) upon 365 nm (a) and 254 nm irradiation (b); the insets indicate the photodimerization degree versus irradiation time. The concentration of α -CD-C solution was 0.125 mg/mL and the temperature was 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

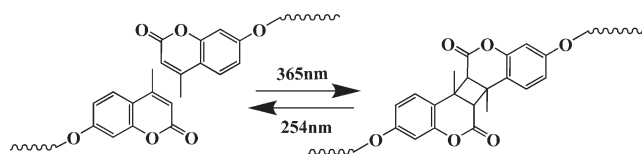


Figure 6. The photoreversible dimerization of coumarin groups upon UV irradiations.



Figure 7. Water dispersions of MWCNTs (a) without dispersants (b) with α -CD-C, and of SWCNTs (c) without dispersants (d) with α -CD-C. The images were taken after one month storage. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

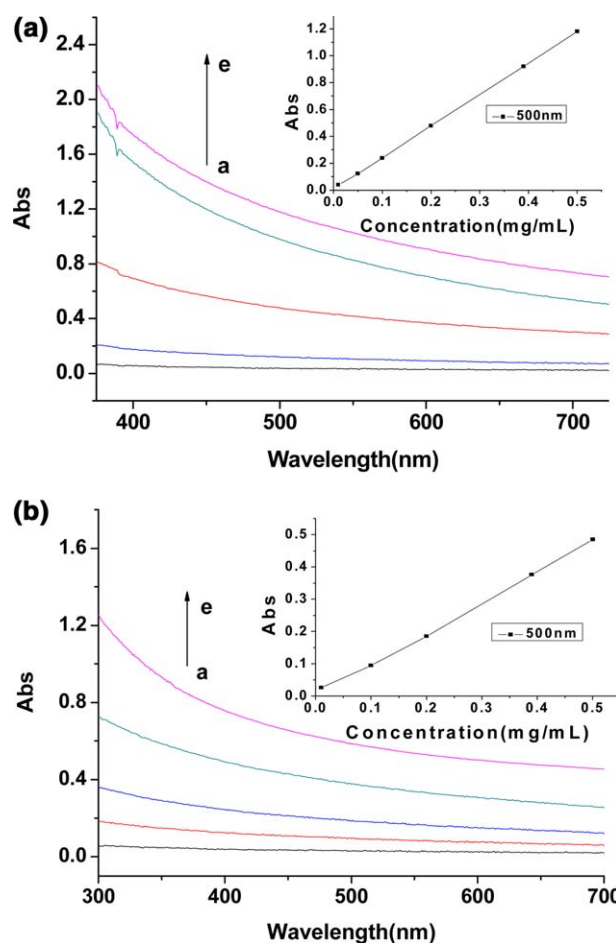


Figure 8. UV-vis absorption spectra of α -CD-C dispersed CNTs in H₂O with concentrations of (a) 0.01, (b) 0.1, (c) 0.2, (d) 0.4, and (e) 0.5 mg/mL. The inset is the plot of absorbance intensity (500 nm) versus solution concentration. (a) MWCNTs and (b) SWCNTs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

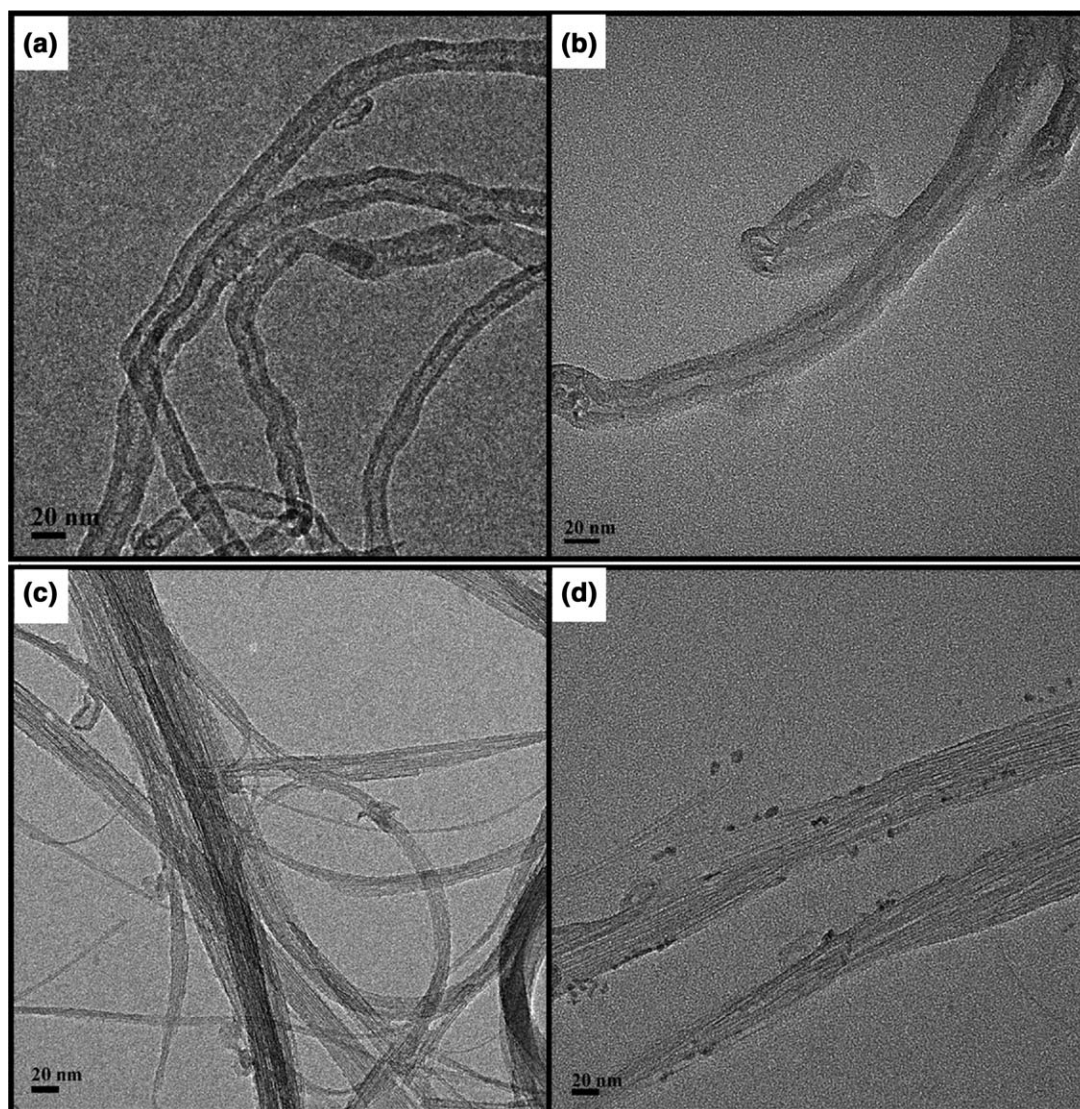


Figure 9. TEM images of MWCNTs (a) without dispersants (b) with α -CD-C and SWCNTs (c) without dispersants (d) with α -CD-C. CNTs : α -CD-C = 1 : 2 (weight ratio).

shifts reported in ppm (in DMSO- d_6 ; TMS as internal standard). HPLC-MS(MS) analysis of α -CD-C was performed using a nanoflow UPLC system (Waters, Milford, MA) coupled to a high resolution QTOF Premier mass spectrometer (Waters, Milford, MA). The UV-vis spectra were recorded on a TU-1901 spectrophotometer (Beijing Purkinje General Instrument). The high-resolution transmission electron microscopy (HR-TEM) images were obtained on a JEOL-2010 transmission electron microscope. A Hitachi S-4800 scanning electron microscope (SEM; produced in Japan), was adopted to observe surface morphologies of the samples.

RESULTS AND DISCUSSION

UV-vis Spectra of α -CD-C

Figure 5 shows that when the α -CD-C solution was exposed to UV light at 365 nm, the absorption of coumarin moieties at \sim 320 nm decreased continuously with time, indicating the

occurrence of dimerization [Figure 5(a)]; the inset provides the increase in the dimerization degree as estimated from the change in absorbance at 320 nm. Subsequently, when the cross-linked solution of α -CD-C was illuminated by a UV lamp (254 nm, 1.25 W, and placed at .7 cm from the solution), the opposite process, that is, the photocleavage of coumarin dimers, occurred as indicated by the recovery of the absorption at 320 nm [Figure 5(b)]. The decrease in the dimerization degree is also shown in the inset. These results demonstrate that the photo-reversible dimerization of α -CD-C can be controlled through changing the UV-vis spectra and the process can be shown in Figure 6.^{16–18} However, only about 50% of the coumarin restored to the initial structure. The results show that in the alternate illumination conditions, reaction to light only partially reversible. The reason is that when the α -CD-C solution was exposed to UV light at 254 nm, the photochemical reaction element exists in homeostasis between photocrosslinking and

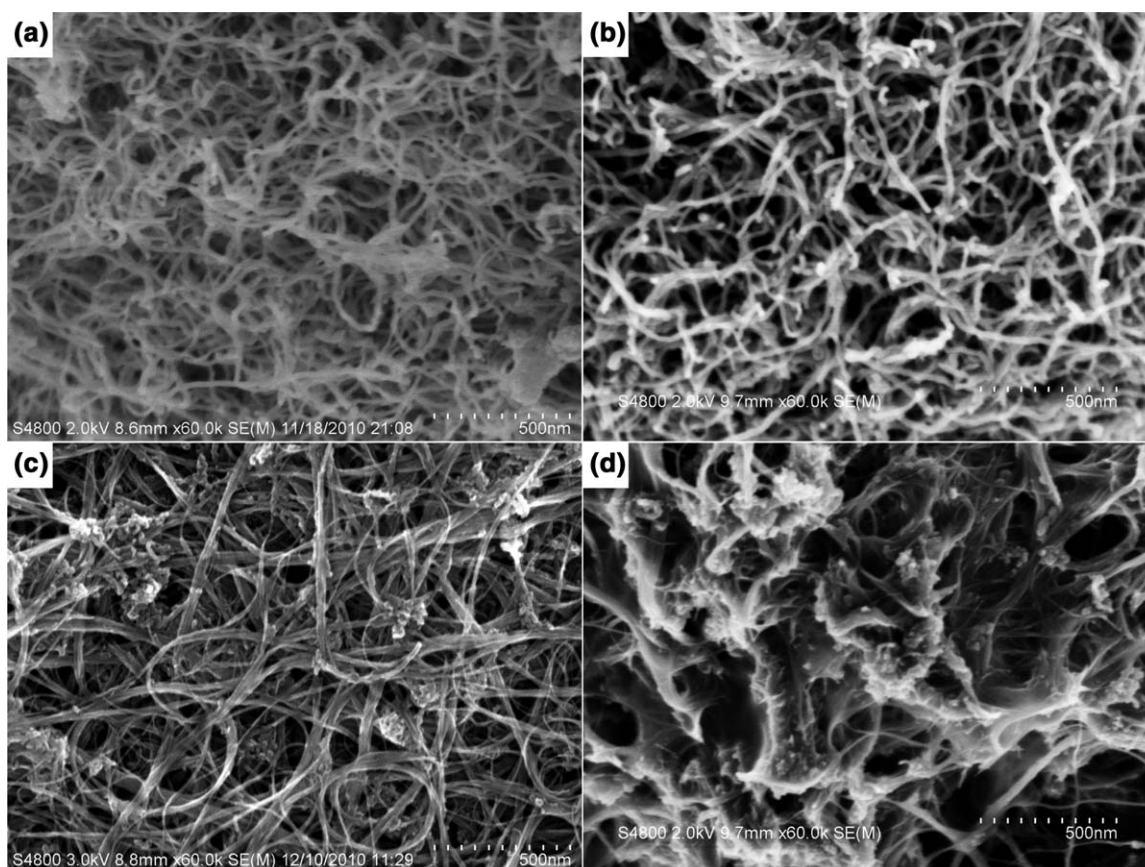


Figure 10. SEM images of MWCNTs (a) without dispersants (b) with α -CD-C and SWCNTs (c) without dispersants (d) with α -CD-C. CNTs : α -CD-C = 1 : 2 (weight ratio).

photocleavage of coumarin.^{17,18} In addition, through the comparison with our previous results, it is found that the water soluble α -CD-C required more time than the hydrophobic coumarin.

Dispersion of CNTs with α -CD-C

Figure 7 presents the water dispersions of CNTs with α -CD-C in water. The black-colored solution of CNTs with α -CD-C is visually nonscattering, and no precipitation was observed after one month standing. In contrast, the same concentration of CNTs dispersed in water without the α -CD-C began to precipitate immediately after sonication and completely settled within 0.5 h, as shown in Figure 7(a,c).

Bundled CNTs are not active in the UV-vis region.¹⁹ Only individual CNTs absorb in this region. Therefore, dispersion of CNTs (MWCNTs or SWCNTs) can be characterized using UV-vis absorption spectroscopy. We measured the UV-vis absorbance of the CNTs aqueous dispersions with different CNTs concentrations and the results are shown in Figure 8. The concentration of CNTs dissolved or dispersed into the solution was determined using the specific extinction coefficient of CNTs at 500 nm, $\epsilon_{500} = 28.6 \text{ cm}^2/\text{mg}$,²⁰⁻²² in the Lambert-Beer law. As shown, the intensity of the absorbance increases with the increasing CNTs concentration and the dependence of absorbance on concentration at 500 nm obeys Beer's law (the inset of

Figure 8), indicating that the CNTs surface were modified by α -CD-C and that the dispersion of CNTs depend on the concentration.

Morphology Characterization

Figure 9 presents the TEM images of α -CD-C dispersed CNTs in water. From the images shown in Figure 9(a) (MWCNTs) and Figure 9(c) (SWCNTs), it can be clearly observed that the nanotubes without dispersant are characterized by regions of thick, aggregated CNTs ropes caused by the large van der Waals forces. The surfaces of these CNTs were inhomogeneously distributed on the grid, with tubes localized only at isolated regions.²³ In contrast, well-separated nanotubes are observed for the dispersions of CNTs with α -CD-C, as shown in Figure 9(b) (MWCNTs) and Figure 9(d) (SWCNTs). The distribution of the CNTs on the grid becomes highly uniform, which can be attributed to the α -CD-C breaking up the bundles into suspension of smaller bundles. The addition of α -CD-C enhances the suspension stability by overcoming the van der Waals force through steric hindrance. The TEM images demonstrate that the both kinds of CNTs can be well dispersed individually by α -CD-C in water solution, indicating the efficacy and the applicability of this approach.

Figure 10 shows typical SEM images of the CNTs [Figure 10(a,c)] and water dispersions of CNTs with α -CD-C [Figure 10(b,d)]. The pristine CNTs exhibited a clustered or bundled

surface morphology similar to a reptile chain [Figure 10(a,c)].²⁴ The obtained composites of CNTs and α -CD-C were much thicker than the raw CNTs, and homogeneous CNTs with a diameter of 20–40 nm were observed at high magnification. The α -CD-C-dispersed CNTs were tightly covered by a thick layer of α -CD-C [Figure 10(b,d)]. The SEM analysis shows that the CNTs were well wrapped by the α -CD-C, primarily through non-covalent interactions.

CONCLUSIONS

We have successfully designed and synthesized a novel water-soluble photosensitive α -CD-C. The photo-reversible dimerization of α -CD-C upon UV irradiations was researched, followed by the presentation of a facile and efficient approach to disperse CNTs in water using the α -CD-C. The resulting CNTs water dispersions showed that the CNTs were well dispersed in the water phase and a very stable suspension was obtained. Their good dispersing behavior, easy synthesis and low cost makes the α -CD-C an attractive dispersant for CNTs. In addition, the water dispersions of CNTs could be used as nano-composites alone or as starting materials for various applications such as sensor, coating, and wastewater treatment.

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