

Synthesis of β -cyclodextrin-modified carbon nanocrystals and their fluorescent behavior

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Received November 5, 2009; accepted January 19, 2010

Water-soluble β -cyclodextrin (β -CD)-modified carbon nanocrystals (CNCs) have been synthesized by the reaction of CNCs with mono(6-diethylenetriamino-6-deoxy)- β -CD (DETA- β -CD) and comprehensively characterized by ^1H NMR, FT-IR, transmission electron microscopy (TEM) and UV-Vis. DETA- β -CD-modified CNCs (DETA- β -CD-CNCs) are luminescent, and the quantum yield is 8.41%. The photoinduced electron transfer (PET) process between DETA- β -CD-CNCs and (ferrocenylmethyl) trimethylammonium iodide (Fc^+) was investigated by means of fluorescence spectroscopy.

carbon nanocrystals, β -cyclodextrin, supramolecular chemistry, fluorescence

Citation: Jiang Q, Zhang H Y, Liu Y. Synthesis of β -cyclodextrin-modified carbon nanocrystals and their fluorescent behavior. Chinese Sci Bull, 2010, 55: 2835–2839, doi: 10.1007/s11434-010-3252-y

Fluorescent carbon nanocrystals (CNCs) [1–14] are quantum-sized carbon analogues used as biomarkers, bioimaging and bioprobes. CNCs are carbon-based nanomaterials, comparable to fullerenes, carbon nanotubes, graphite and nanodiamonds, which possess fluorescent properties. They are monodispersed in aqueous solution with a scale of 2–10 nm and have high photostability fluorescence. Compared with such semiconductor nanocrystals as CdSe [15], CdTe [16], and CdSe/ZnSe [17], CNCs have lower toxicity to human health or to the environment. As a result, CNCs may be suitable for various applications in chemistry and biology.

Cyclodextrins (CDs) are a class of cyclic oligosaccharides with generally 6–8 D-glucose units linked by α -1,4-glucose bonds. They have the ability to selectively bind various inorganic or organic guests, which leads to widespread applications of CDs not only in pharmaceutical chemistry, food technology, analytical chemistry, chemical synthesis, and catalysis [18–25], but also for constructing molecular devices and machines [26–31]. Therefore, the combination of CNCs with CDs might yield valuable future applications. Here, we

prepared mono(6-diethylenetriamino-6-deoxy)- β -cyclodextrin (DETA- β -CD) modified CNCs (DETA- β -CD-CNCs), which have been characterized by ^1H NMR, FT-IR, transmission electron microscopy (TEM) and UV-Vis, and investigated the photoinduced electron transfer (PET) process between DETA- β -CD-CNCs and (ferrocenylmethyl) trimethylammonium iodide (Fc^+) by means of fluorescence. Importantly, 1-adamantanecarboxylic acid sodium salt (Ad^-) could modulate the PET process between CNCs with Fc^+ .

1 Experimental

1.1 Reagents and instruments

All chemicals were used as received if not special indicated. ^1H spectra were recorded on a Bruker 400M instrument at room temperature, and chemical shifts were recorded in parts per million (ppm). Absorption, fluorescence spectra and fluorescence quantum yields were respectively recorded on a Shimadzu UV-2401PC spectrometer, a Varian Cary Eclipse spectrometer, and FLS920 (Edinburgh Instruments, Edinburgh, UK). FT-IR spectra were obtained from a

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Bruker Tensor 27 instrument, and samples were prepared as pellets using spectroscopic grade KBr. The thermogravimetric analysis was recorded with a RIGAKU Standard type with a heating rate of 10°C/min from room temperature to 700°C. The TEM experiment was performed on a Philips Tacnai G2 20 S-TWIN microscope operating at 200 kV.

1.2 Synthesis of CNCs

We synthesized CNCs according to previously reported methods [3,10]. CNCs were prepared in an electrochemical cell consisting of a graphite rod working electrode, a Pt slice counter electrode, and a Ag/AgCl reference electrode in a pH 7.0 0.1 mol/L phosphate buffer solution (PBS). The potential on the working electrode was cycled between -2000 mV and 2000 mV at a scan rate of 100 mV/s. When the solution colour changed from colorless to dark yellow, we filtrated the solution through a 0.22 μm filter membrane. After the filtrate was concentrated to ca. 5 mL, it was dialyzed with the membrane (3500 Da) for 24 h to remove the salt. It was dialyzed with the membrane (6000–8000 Da) for 24 h obtaining the part at 3500–8000 Da. After removing the water from the reduced pressure vaporizer and drying it in a vacuum for 24 h, the surface -COOH modified CNCs became a light brown solid. FT-IR: 1730 cm⁻¹; UV-Vis (H₂O) λ_{max} = 360 nm.

1.3 Synthesis of DETA-β-CD-CNCs

1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC·HCl) (73 mg, 0.38 mmol) in 5 mL 150 mmol/L PBS (pH 7.4) and *N*-hydroxysuccinimide (NHS) (52 mg, 0.45 mmol) in 5 mL 150 mmol/L PBS (pH 7.4) were added to the solution of CNCs (40 mg) in 5 mL 150 mmol/L PBS (pH 7.4). The reaction was activated for 20 min at room temperature. DETA-β-CD (400 mg, 0.32 mmol) in 5 mL 150 mmol/L PBS (pH 7.4) was added to the mixture and reacted for 5 h. After the mixture was concentrated to ca. 5 mL, it was dialyzed with a membrane (3500 Da) for 24 h to remove any byproducts and unreacted EDC·HCl, NHS and DETA-β-CD. Water was removed from the reduced pressure vaporizer and then dried in a vacuum for 24 h yielding DETA-β-CD-CNCs 96 mg as light brown solid. ¹H NMR (400 MHz, D₂O): δ = 4.97 (s, 7H, H1_{β-CD}), 3.86–3.77 (m, 28H, H2_{β-CD}), 3.56–3.48 (m, 14H, H3_{β-CD}), 2.97–2.77 (m, 8H, H_a–H_d). FT-IR: 3320, 2924, 1650, 1550, 1081, 1024 cm⁻¹. UV-Vis (H₂O) λ_{max} = 360 nm. H1_{β-CD} is the H-1 proton of DETA-β-CD in DETA-β-CD-CNCs; H2_{β-CD} and H3_{β-CD} are the H-3, H-5, H-6, H-2, and H-4 protons of β-CD in DETA-β-CD-CNCs.

1.4 Determining percent of β-CD in DETA-β-CD-CNCs

1,1'-Dimethyl-4,4'-bipyridinium (MV²⁺; 2.30 × 10⁻⁶ mol,

1.01 mg) and 1.74 mg DETA-β-CD-CNCs were dissolved in 0.5 mL D₂O. The mixed solution was analyzed for the NMR spectrum [¹H NMR (400 MHz, D₂O): δ = 8.91 (s, 4H, H_g), 8.38 (s, 4H, H_f), 4.97 (s, 2.90H, H1_{β-CD}), 4.35 (s, 6H, H_e), 3.86–3.77 (m, 11.60H, H2_{β-CD}), 3.56–3.48 (m, 5.80H, H3_{β-CD}), 2.97–2.77 (m, 3.31H, H_a–H_d)]. H_g is the meta-proton and H_f is ortho-proton in the bipyridine of MV²⁺; H_e is the proton in the methyl of MV²⁺. H1_{β-CD} is the H-1 proton of DETA-β-CD in the DETA-β-CD-CNCs; H2_{β-CD} and H3_{β-CD} are H-3, H-5, H-6, H-2, and H-4 protons of β-CD in DETA-β-CD-CNCs.

2 Results and discussion

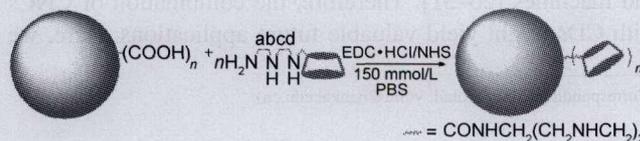
2.1 Synthesis

EDC·HCl was a zero-length crosslinking agent used to couple carboxyl groups to primary amines. By combining EDC·HCl and NHS, the reaction of coupling carboxyl groups to primary amines was accomplished in physiological solutions without adding an organic solvent. Therefore, we selected the surface -COOH-modified CNCs and DETA-β-CD as reactants, in the presence of EDC·HCl and NHS, to yield the DETA-β-CD-CNCs (Scheme 1).

2.2 NMR spectra

There were marked differences in the NMR spectra of DETA-β-CD before and after being attached to CNCs (Figure 1). (1) The H2_{β-CD}, H3_{β-CD} and H_a–H_d in the DETA-β-CD-CNCs were more clearly split than that in the DETA-β-CD. (2) H_a–H_d have a downfield shift of approximately 0.4 ppm. The observations might be attributed to the CONH-group possessing the stronger electron drawing affect than the NH₂- group, leading to H_a–H_d having a downfield shift after the DETA-β-CD was joined with CNCs.

Because the cavity of β-CD does not bind the charged MV²⁺, MV²⁺ was utilized as the inner criterion to estimate the percent of DETA-β-CD in the DETA-β-CD-CNCs. The results obtained indicated that there was ca. 1 × 10⁻⁶ mol DETA-β-CD in 1.82 mg DETA-β-CD-CNCs, i.e., the ratio of the weight of DETA-β-CD moieties in DETA-β-CD-CNCs was ca. 66.7%. In addition, the concentration of DETA-β-CD in DETA-β-CD-CNCs was ca. 1 × 10⁻³ mol/L when 1.82 mg DETA-β-CD-CNCs was dissolved in 1 mL H₂O.



Scheme 1 Synthesis of β-CD-modified CNCs.

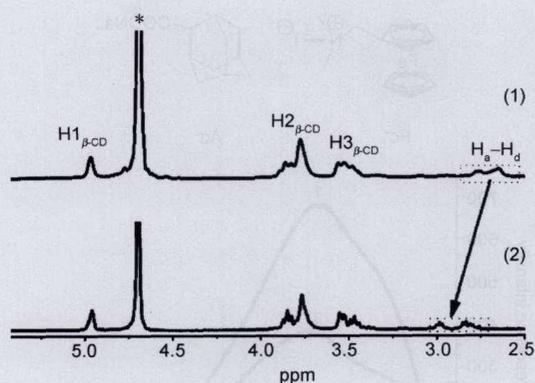


Figure 1 NMR spectra of (1) DETA- β -CD (1×10^{-3} mol/L) and (2) DETA- β -CD-CNCs (1.82 mg/mL) in D_2O (* is H_2O). $H1_{\beta-CD}$ is the H-1 proton of DETA- β -CD in the DETA- β -CD-CNCs; $H2_{\beta-CD}$ and $H3_{\beta-CD}$ are the H-3, H-5, H-6, H-2 and H-4 protons of β -CD in the DETA- β -CD-CNCs.

2.3 FT-IR spectrum

Figure 2 shows that the peak at 1730 cm^{-1} attributed to the C=O stretch vibrations of the -COOH group in the CNCs had nearly disappeared, while two new peaks at 1650 cm^{-1} and 1550 cm^{-1} appeared in the FT-IR spectrum of the DETA- β -CD-CNCs. They are attributed to the C=O stretch vibrations of the -CONH- group. The observation suggests that the -COOH groups on the surface of the CNCs reacts with the -NH₂ of DETA- β -CD to yield the -CONH- group. In addition, the peaks at 3300 cm^{-1} and 2924 cm^{-1} in the DETA- β -CD-CNCs are respectively attributed to N-H stretch vibrations and C-H stretch vibrations, while those of 1081 cm^{-1} and 1024 cm^{-1} are C-O-C stretch vibrations. These observations confirm that DETA- β -CD is covalently connected to the surface of the CNCs.

2.4 TEM

TEM was performed to assess the size and shape of the CNCs and the DETA- β -CD-CNCs. From Figure 3 shows

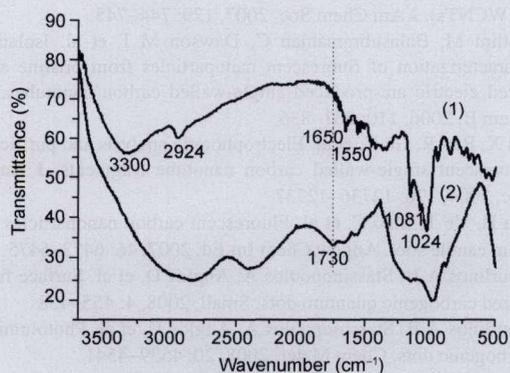


Figure 2 FT-IR spectra of (1) DETA- β -CD-CNCs and (2) CNCs.

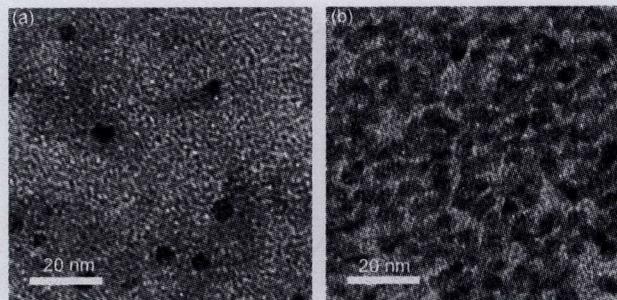


Figure 3 TEM images of CNCs (a) and DETA- β -CD-CNCs (b).

that both the size and compactness for CNCs and DETA- β -CD-CNCs are different. The particle size of CNCs are on a scale of 3.1–5.1 nm, while that of the DETA- β -CD-CNCs are 4.6–6.6 nm. The corresponding diameter distributions are illustrated in Figure 4. The height of β -CD is about 0.79 nm, so the extra diameter of the DETA- β -CD-CNCs in excess of about 1.5 nm may be attributed to the β -CDs attached to the surface of the CNCs. The observation of the closer distance among particles in the DETA- β -CD-CNCs may be a consequence of the more readily facilitated interaction between cyclodextrins than between CNCs.

2.5 Fluorescent behavior of DETA- β -CD-CNCs

When the DETA- β -CD-CNCs were excited with wavelengths of 350–550 nm, the emission wavelengths changed from 450 to 600 nm (Figure 5). Different from the 460 nm emission wavelength of the DETA- β -CD-CNCs excited at 365 nm, the emission wavelength of the CNCs was 550 nm at the same excited wavelength, as shown in Figure 6. Correspondingly, the color of the CNCs aqueous solution was light yellow while that of the DETA- β -CD-CNCs was blue green. In addition, we also measured their quantum yields, which were 1.05% for the CNCs, and 8.41% for the DETA- β -CD-CNCs. One reasonable explanation is that the DETA- β -CD modified to the CNCs may passivate the surface of the CNCs, resulting in a hypsochromic emission and a higher quantum yield [17].

β -CD binds both Fc^+ and Ad^+ , but the corresponding

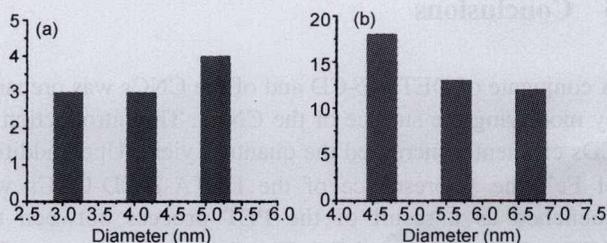


Figure 4 Diameter distributions of CNCs (a) and DETA- β -CD-CNCs (b) particles in TEM.

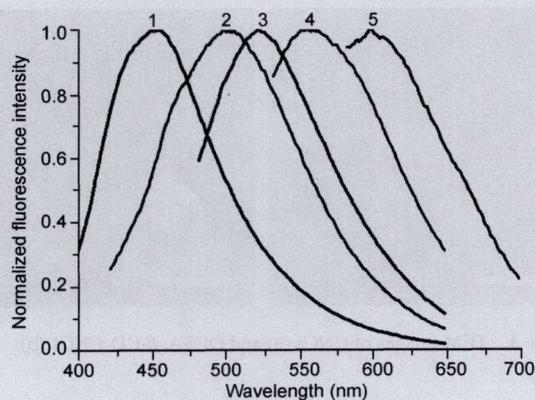


Figure 5 Normalized emission wavelengths at different excited wavelengths of the DETA- β -CD-CNCs in H₂O. (1) 350 nm; (2) 400 nm; (3) 450 nm; (4) 500 nm and (5) 550 nm.

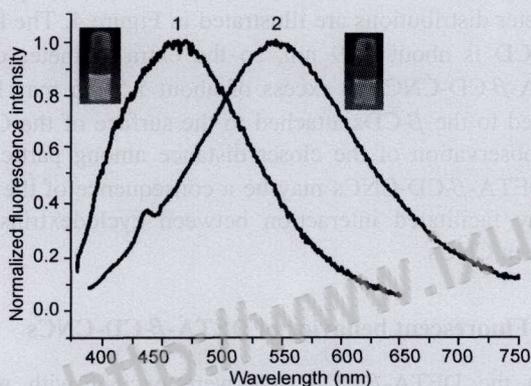


Figure 6 Normalized emission wavelengths of (1) DETA- β -CD-CNCs and (2) CNCs excited at 365 nm in H₂O.

binding constants (K_S) are different ($K_S = 2900 \text{ M}^{-1}$ [32] for β -CD- Fc^+ , and $K_S = 39500 \text{ M}^{-1}$ for β -CD- Ad^- [33]). Upon addition of Fc^+ to the aqueous solution of the DETA- β -CD-CNCs, a quenching process was observed, indicating that the PET process took place upon irradiation. When Ad^- was added to the aqueous solution of DETA- β -CD-CNCs/ Fc^+ , it ejected Fc^+ from the cavity of β -CD in the DETA- β -CD-CNCs, leading to the PET process being suppressed accompanied by a fluorescent intensity increase, as shown in Figure 7.

3 Conclusions

A conjugate of DETA- β -CD and of the CNCs was prepared by modifying the surface of the CNCs. The introduction of CDs efficiently increased the quantum yield. Upon addition of Fc^+ , the fluorescence of the DETA- β -CD-CNCs was quenched as a result of the PET process between the DETA- β -CD-CNCs and Fc^+ . The fluorescence increased in the presence of AD^- by ejecting Fc^+ from the cavity of the CDs of DETA- β -CD-CNCs. Benefiting from various func-

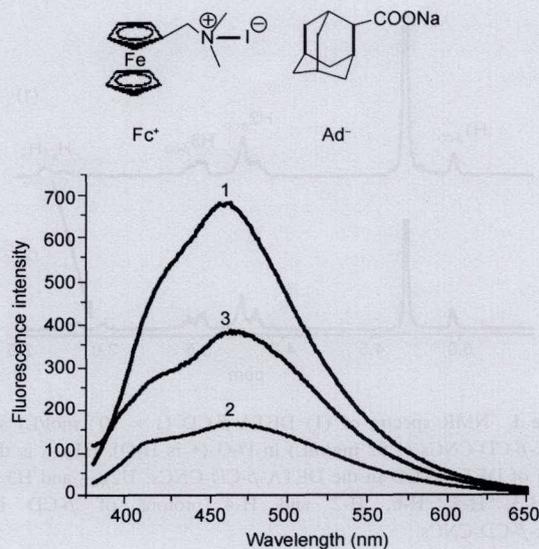


Figure 7 The structures of Fc^+ and Ad^- (upper) and the emission spectra of the DETA- β -CD-CNCs (1.82 mg/mL) on addition of Fc^+ and Ad^- in H₂O (lower). (1) DETA- β -CD-CNC (1.82 mg/mL); (2) DETA- β -CD-CNC (1.82 mg/mL) and Fc^+ ($2 \times 10^{-3} \text{ mol/L}$); (3) DETA- β -CD-CNC (1.82 mg/mL), Fc^+ ($2 \times 10^{-3} \text{ mol/L}$) and Ad^- ($2 \times 10^{-3} \text{ mol/L}$). Excited: 360 nm; emission: 460 nm.

tions of the CDs and CNCs, such a system might have applications in chemistry and biology.

This paper is dedicated to Professor LIU YouCheng on the occasion of his 90th birthday. This work was supported by the National Basic Research Program of China (2006CB932900) and the National Natural Science Foundation of China (20932004 and 20972077).

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