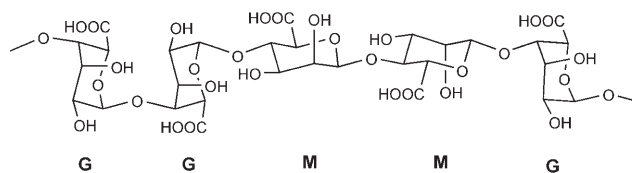


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Cation-Controlled Aqueous Dispersions of Alginate-Acid-Wrapped Multi-Walled Carbon Nanotubes**

Yu Liu,* Peng Liang, Heng-Yi Zhang, and Dong-Sheng Guo

Carbon nanotubes (CNTs) have attracted a lot of attention in recent years due to their possessing unique electronic,^[1] mechanical,^[2] and structural properties,^[3] as well as having potential applications in electronics, nanodevices, and energy storage.^[4] However, exploring the chemistry of CNTs at the molecular level is greatly limited due to their inherently difficult purification and insolubility in water and organic solvents. Therefore, many attempts have been made to improve the solubility of CNTs in common solvents. There are two alternative routes to reach this goal, namely, covalent and noncovalent modification. Direct sidewall attachments of CNTs via oxidation in acidic media,^[5] fluorination,^[2h,6] nitrene addition,^[7] hydrogenation via the Birch reduction,^[6b,8] alkylation,^[9] arylation,^[10] and 1,3-dipolar cycloaddition^[11] have been reported. Chemical functionalization can improve the solubility of CNTs, and maintain their unique properties when coupled to other types of materials, but partially damages the π -conjugate system. In contrast, noncovalent coupling can potentially preserve the unique properties of the nanotubes; this strategy has been widely employed via polymer wrapping and adsorption,^[12] the adsorption of amines^[13] and molecules with large π -systems,^[14] and coating the nanotubes with surfactants such as sodium dodecylsulfate (SDS) or benzylalkonium chloride.^[15] Compared with other systems, biomacromolecules such as starch,^[12c] protein,^[12e] schizophyllan,^[12f] α -GalNAc residues,^[12g] and peptides^[12h] offer considerable advantages due to their biocompatibility. Alginate acid (AA), a natural polysaccharide harvested from brown algae, is an unbranched binary copolymer that is constituted of (1,4)-linked β -D-mannuronic acid (M) and α -L-guluronic acid (G; Scheme 1), and is widely used in the food and pharmaceutical industries, macromolecules, and biological cells.^[16] In this Communication, we utilize AA as a solubilizing agent to prepare AA-wrapped multi-walled carbon nanotube (MWCNT-AA) complexes. Furthermore, the binding behavior of this complex has been comprehensively investigated by NMR

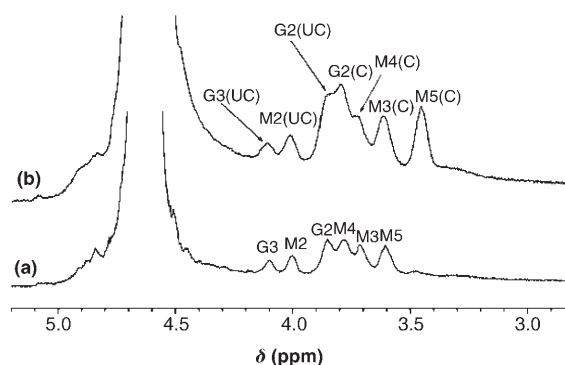


Scheme 1. Molecular structure of AA.

and Raman spectroscopies, thermogravimetric (TG) and differential thermal analysis (DTA), and transmission electron microscopy (TEM). Moreover, preferential precipitation of MWNTs occurs upon the addition of cations, while resolubilization can be achieved when the added cations are trapped using ethylenediaminetetraacetic acid (EDTA).

The MWCNT-AA complex was prepared in 61% yield by treating an aqueous solution of AA with MWCNTs under sonication. The solubility of MWCNT-AA in water ($\approx 3.2 \text{ mg mL}^{-1}$) is similar to that of starched single-walled carbon nanotubes (SWNTs) (3.0 mg mL^{-1}),^[12c] but the ratio (by weight) of MWCNTs to AA in the complex is approximately 58:42, which is larger than that of SWNTs and amylose (1:5). The observations suggest that the amylose homologues are more applicable for wrapping CNTs.

NMR experiments were used to confirm the interaction of the MWCNTs with AA in aqueous solution. As can be seen from Figure 1, the H-2 protons of the α -L-guluronic

Figure 1. ^1H NMR spectra in D_2O at 298 K: a) AA; b) MWCNT-AA.

acid unit and the H-3, H-4, and H-5 protons of the β -D-mannuronic acid unit in MWCNT-AA display a significant upfield shift (0.036, 0.085, 0.056, 0.141 ppm, respectively) as compared with those of free AA, indicating that the pattern of the interaction of MWCNTs with the M segment in AA is distinctly different from that with the G segment. Two β -D-mannuronic acid units of the M segment can lie on the surface of the MWCNTs, and one of two α -L-guluronic acid units of the G segment can be oriented perpendicularly to the surface of the MWCNTs. The pattern may be imagined as a battlement of the Great Wall of China, in which the M segment is regarded as the crenel, and the G segment as the buttress, as illustrated in Figure 2. This unique binding mode allows the hydrophilic hydroxyl and carboxyl groups in the α -L-guluronic acid unit to be distant from the surface

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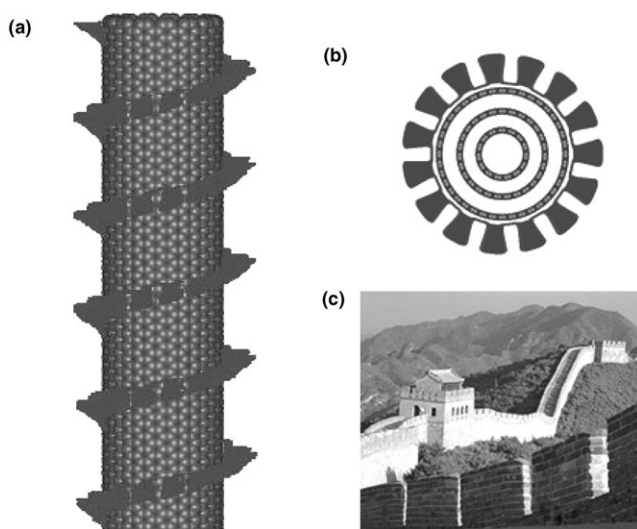


Figure 2. a, b) Schematic representations (from top and side, respectively) of the MWCNT–AA complex; c) a view of the Great Wall of China, highlighting the analogy with the MWCNT–AA complex.

of the nanotube, and hence helps greatly in rendering the MWCNT–AA complex soluble in water.

We performed TEM experiments for a further insight into the size and shape of the wrapped nanotube. The specimens for TEM were prepared by placing one drop of a solution of MWCNT–AA complex onto a carbon-coated copper grid, followed by evaporating the liquid for at least 2 h under vacuum. Figure 3 shows a typical TEM image of the

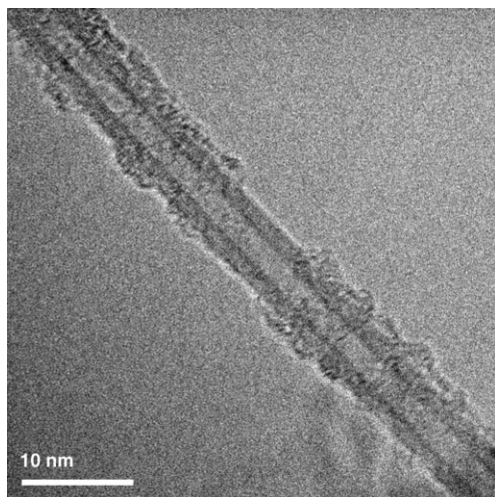


Figure 3. TEM image of the MWCNT–AA complex.

MWCNT–AA complex on the copper grid. We note that the nanotube is partly wrapped by AA. The observation is different from TEM images of water-soluble CNTs mediated by schizophyllan,^[12f] C₁₈-functionalized mucin-mimic-bearing α -GalNAc residues,^[12g] peptides,^[12h] amphiphilic polycations,^[17] and sodium dodecyl sulfate (SDS),^[18] in which CNTs are covered fully by the solubilizing agent.

Raman spectroscopy can provide powerful evidence for the strength of adherence of the chains to the surface of the MWCNTs. The presence of the AA coating affects the vibrational frequencies of tangential movement of the carbon atoms, which is indicative of strong attractive forces between the amylose homologue and the graphite sheet.^[17] The peak in the 1500–1600 cm⁻¹ region is the so-called G band, originating from tangential C–C stretching vibrations both longitudinally and transversally on the CNT axis,^[19] and that in the 1300–1400 cm⁻¹ region is known as the D band, which is attributed to defects and curvature in the nanotube lattice.^[20] Here, the G band shifts to higher wavenumber from 1589 to 1595 cm⁻¹ upon complexation with AA, while the spectral shift of the D band is insignificant (Figure 4). Meanwhile, the intensity ratio of D band to

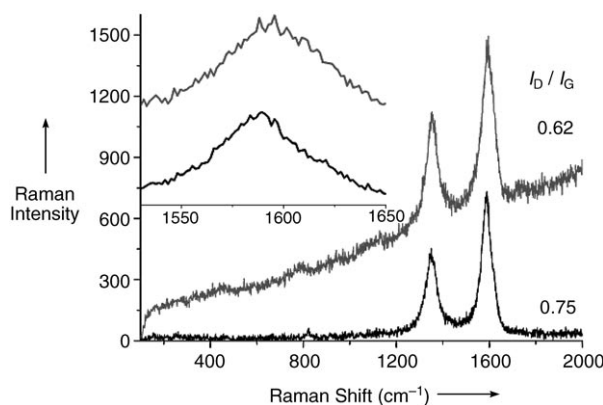


Figure 4. Raman spectra (excited with a 514.5-nm laser) of MWCNTs (black) and the MWCNT–AA complex (gray).

G band (I_D/I_G) increases from 0.62 for raw MWCNTs to 0.75 for the complex. The up-shift of the G band peak is indicative of the strong attachment of AA to MWCNTs due to an increase in the elastic constant of the harmonic oscillator of the AA-coated MWCNTs.^[17] The observation that the position of the D band does not change, implies that AA does not covalently attach to MWCNTs,^[10b,21] and the enhancement of the D band can be attributed to field disturbance and physical strain in the graphite skeleton caused by AA coating^[22] or some damage to the grapheme sheet caused by sonication treatment used to disperse the nanotubes.^[17] Because the D/G ratio has a linear relation with the inverse of the in-plane crystallite dimension,^[23] the increase of the D/G ratio suggests that the degree of long-range-ordered crystalline perfection of the MWCNTs decreases after being wrapped by AA.

The thermal behavior of the MWCNT–AA complex, along with its constituent parts was studied from room temperature to 800 °C in flowing oxygen (Figure 5). DTA results show that the combustion temperature of AA is 418 °C, and that of the MWCNTs is 558 °C. However, for the MWCNTs wrapped with AA, the corresponding temperature is lower than that of the naked MWCNTs, but higher than that of AA, reaching 466 °C. Hence, we can deduce that the thermal stability of MWCNTs decreases after being wrapped by AA. Comparing the thermogravimetric curves of MWCNTs

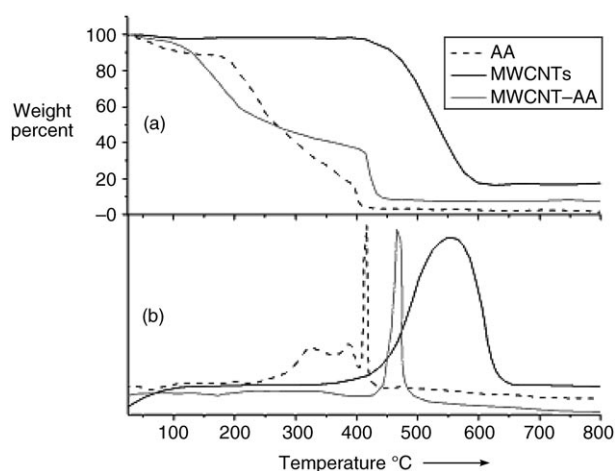


Figure 5. a) Thermogravimetric analysis and b) differential thermal analysis of AA, MWCNTs, and MWCNT-AA.

and MWCNT-AA, it is notable that the amount of residual catalyst metals in the MWCNTs reduces from 17.7 wt.% in the raw MWCNTs to no more than 7.7 wt.% in the complex. That is to say, the raw MWCNTs are purified during the wrapping process.

The addition of glucosidases to starch-wrapped carbon nanotubes results in the precipitation of SWNTs from aqueous solution.^[12c] Herein, the aqueous solution of MWCNT-AA is very stable to the addition of alkali-metal cations (Li^+ , Na^+ , K^+), while the addition of alkaline-earth-metal cations (Mg^{2+} , Ca^{2+} , Ba^{2+}), transition-metal cations (Zn^{2+} , Co^{2+} , Ni^{2+} , Fe^{3+} , Cu^{2+}), heavy-metal cations (Pb^{2+} , Ag^+), and lanthanoid cations (La^{3+} , Eu^{3+} , Tb^{3+}) to the solution leads to either the precipitation of the nanotubes (for Mg^{2+} , Ca^{2+} , Zn^{2+} , Ni^{2+} , Tb^{3+}) or to a floccular precipitate containing the nanotubes after treatment for 10 min. These observations are consistent with phenomena observed when adding these cations to an aqueous solution of AA, that is, the addition of Mg^{2+} , Ca^{2+} , Zn^{2+} , Ni^{2+} , or Tb^{3+} ions makes the original cloudy solution of AA become clear, and the addition of the other eight cations yields a floccular precipitate. When we added an aqueous solution of EDTA to the above bottles, the nanotube precipitates containing Zn^{2+} and Ni^{2+} ions, as well as the floccular precipitates containing Co^{2+} , Pb^{2+} , La^{3+} , and Eu^{3+} ions disperse after shaking, while the rest do not disperse. These phenomena are attributed to differences in the binding abilities of these cations with EDTA and AA. Typically, the binding constant of Zn^{2+} with AA ($\log K = 3.98^{[24]}$) is much lower than that with EDTA ($\log K = 16.4^{[25]}$), which results in EDTA “carrying off” the binding Zn^{2+} ions with AA, and allowing the “released” AA to rewrap around the nanotubes. In contrast, the binding constant of Ca^{2+} with AA ($\log K_1 = 6.12$, $\log K_2 = 4.01^{[26]}$) is more similar to that with EDTA ($\log K = 11.0^{[25]}$), which means that EDTA does not remove the Ca^{2+} ions from AA.

To conclude, we have demonstrated that AA can efficiently solubilize MWCNTs in aqueous solution because of the unique “Great Wall of China” binding mode between the MWCNTs and the amylose homologue, and the high

ratio of MWCNTs to AA as well as the TEM images suggest that part of the hydrophobic surface of the nanotubes is still naked in the aqueous phase, which is useful for preserving its intrinsic physical and chemical properties, in the same way as systems that involve chemical functionalization. Furthermore, the addition of alkaline-earth-metal, transition-metal, heavy-metal, and lanthanoid cations to the AA-wrapped nanotubes results in the precipitation of MWCNTs from aqueous solution, while EDTA can redisperse MWCNTs previously precipitated with Zn^{2+} , Ni^{2+} , Co^{2+} , Pb^{2+} , La^{3+} , or Eu^{3+} ions in water. This cycle mediated by specific cations has potential application in aqueous biological systems and medicinal chemistry.

Experiment Section

General: AA was purchased from Qingdao Brightmoon Seaweed Industry Co., Ltd. MWCNTs produced by the CVD method were obtained from Chengdu Organic Chemistry Co., Ltd, Chinese Academy of Sciences. NMR spectra were recorded on a Varian Mercury VX300 instrument. Raman spectra were recorded on a Renshaw inVia Raman microscope. The thermogravimetric (TG) and differential thermal analysis (DTA) were recorded with a RIGAKU Standard type apparatus at a heating rate of $20^\circ\text{C min}^{-1}$ from room temperature to 800°C . Transmission electron microscopy (TEM) experiments were performed using a Philips Tacnai G² 20 S-TWIN microscope operating at 200 kV.

Preparation of MWCNT-AA: An AA stock solution was prepared by filtrating saturated an aqueous solution of AA through a polytetrafluoroethylene (PTFE) membrane filter (0.45 μm), and stored in a refrigerator (4°C). Open-ended MWCNTs (90 mg) were dispersed in the AA stock solution (30 mL, containing 65.4 mg of AA) by agitation, followed by mild ultrasonication for 40 min. A black residue separates from the AA-wrapped MWCNTs on centrifugation at 4000 rpm for 15 min. After centrifugation and decantation, the aqueous solution was concentrated by evaporation to provide the crude product. This material was washed twice with deionized water to give a black solid (94.5 mg, yield 61.0%). The product can be dissolved in water up to a concentration of 3.2 mg mL^{-1} . The resultant solution (10 mL) was added to 1 mL of aqueous ZnCl_2 (0.1 mol L^{-1}) and MWCNTs precipitated from the solution. After collection by centrifugation, the solid was dried in vacuo overnight. The ratio of MWCNTs to AA (w/w) in the complex is approximately 58:42.

Keywords:

alginate acid • carbon nanotubes • cations • noncovalent interactions • oligosaccharides

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(equivalent to 1.25 mm of the monomeric units) in the sample cell (1.4227 mL volume). A control experiment was performed to determine the heat of dilution by injecting a solution of ZnSO_4 into pure water containing no alginic acid. The dilution enthalpy was subtracted from the apparent enthalpy obtained in each titration run, and the net reaction enthalpy was analyzed by using the "one set of binding sites" model.

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