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Protein Adsorption on Functionalized Carbon Nanotubes with a Lactobionic Amide Amphiphile

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ABSTRACT: A lactobionic amide amphiphile was synthesized and used to functionalize multiwalled carbon nanotubes (MWNTs). The self-assembly of the amphiphile on the MWNTs was carried out in alcohol/water solutions. The functionalization of the MWNTs was investigated by means of ultraviolet, Raman, and X-ray photoelectron spectroscopies; X-ray diffraction; and high-resolution transmission electron microscopy. It was found that alcohols can promote the self-assembly of the amphiphile on MWNTs and regulate the amount of amphiphile assembled. Lysozyme was adsorbed onto functionalized MWNTs. Circular dichroism (CD) spectra revealed that the conformation of lysozyme underwent no significant alteration upon adsorption.

1. INTRODUCTION

The sidewall surface of pristine carbon nanotubes (CNTs) is highly hydrophobic, and bundles are formed mainly as a result of van der Waals interactions between the sidewalls of the individual tubes.^{1–3} The surface functionality of CNTs is very important for their processing and applications.^{4–6} Covalent and noncovalent modification methods have been developed to improve the solubility and surface functionality of CNTs. Preserving the intrinsic electronic structure and properties requires noncovalent strategies.⁷ Among the noncovalent methods, self-assembly has been demonstrated to be very effective for the attachment of substances to the surface of carbon nanotubes^{8–10} and can provide an excellent route to the creation of novel organizations.¹¹

A variety of materials have been studied for their self-assembly on CNTs, such as polymers^{6,12,13} and biomacromolecules.^{8,14} Self-assembly of surfactants on CNTs is of interest to many researchers. For example, sodium dodecyl sulfate forms supramolecular structures made of rolled-up half-cylinders on the nanotube surface.^{15,16} CNTs coated with the surfactant Triton X-100 can specifically bind to streptavidin.¹⁷ Carbohydrates and their derivatives have been used to construct water-soluble, biocompatible CNTs. Carbon nanotubes wrapped in polysaccharides, such as starch¹⁸ and single-chain schizophyllan and single-chain curdlan,¹⁹ exhibit good water solubility. Carbohydrate derivatives exhibit amphiphilic properties suitable for interactions with CNTs, including pyrene-based glycoconjugates,^{20,21} glycolipids,²² and glycopolymers.^{23–25}

Herein, we report a new approach to the functionalization of CNTs using a lactobionic amide amphiphile that is carried out in alcohol/water solutions. This work demonstrates that alcohol/water solutions are advantageous over pure water for the functionalization of CNTs. Alcohols can promote and regulate the self-assembly of the amphiphile on multiwalled carbon nanotubes (MWNTs). The effect of alcohols on the self-assembly of the amphiphile on MWNTs was investigated. The functionalized MWNTs were found to exhibit good dispersibility in water and to be capable of adsorbing proteins.

2. EXPERIMENTAL SECTION

2.1. Materials. Multiwalled carbon nanotubes were purchased from Shenzhen Nano-Tech Port Co. (Shenzhen, China). Lactobionic acid, hexadecylamine, and lysozyme were purchased from Sigma-Aldrich Chemical Co. (Shanghai, China). Ethyl acetate, acetone, 2-propanol, ethanol, and methanol were obtained from Sinopharm Chemical Reagent Co. (Beijing, China). The chemicals were of analytical reagent grade and were used as supplied.

2.2. Synthesis of *N*-Hexadecyl-*N'*-lactobionylamide (C₁₆LA). The amphiphile C₁₆LA (Scheme 1) was synthesized as follows: Lactobionic acid (2 g) and hexadecylamine (1.34 g) were added to a stirred solution of ethanol (70 mL). The reaction was carried out at room temperature for 12 h, and then the mixture was refluxed at 60 °C for over 12 h. The mixture was filtered under hot conditions to remove the unreacted lactobionic acid. After the filtrate had evaporated, the precipitate obtained was collected, washed with a solution of acetone, and then crystallized from ethyl acetate and ethanol to produce C₁₆LA as a white solid in 55% yield. ¹H NMR (CD₃SOCD₃, 400 MHz): 0.866 (t, 3H), 1.237–1.395 (m, 26H), 1.406 (t, 2H), 2.175 (br s, 1H), 2.501 (m, 1H), 3.596–4.426 (m, 11H), 4.443–5.122 (m, 10H), 7.528–7.547 (t, 1H).

2.3. Preparation of the Amphiphile/MWNT Composite. MWNTs were purified as reported elsewhere²⁶ by refluxing in an aqueous solution of 2.6 M HNO₃ at 70 °C for 45 h. The nanotube suspension was diluted and washed with doubly distilled water and then filtered through a 0.8-μm polycarbonate membrane. The samples were dried at 80 °C under a vacuum. The self-assembly of the amphiphile on MWNTs was carried out in different solutions of water mixed with alcohol, including methanol, ethanol, and 2-propanol. In each case, 60 mg of C₁₆LA was added to 40 mL of alcohol/water solutions and sonicated for 20 min. Then, 20 mg of purified MWNTs was added to the mixture, and the sonication was continued for 1 h. The mixture was centrifuged at 12000 rpm for 30 min, yielding

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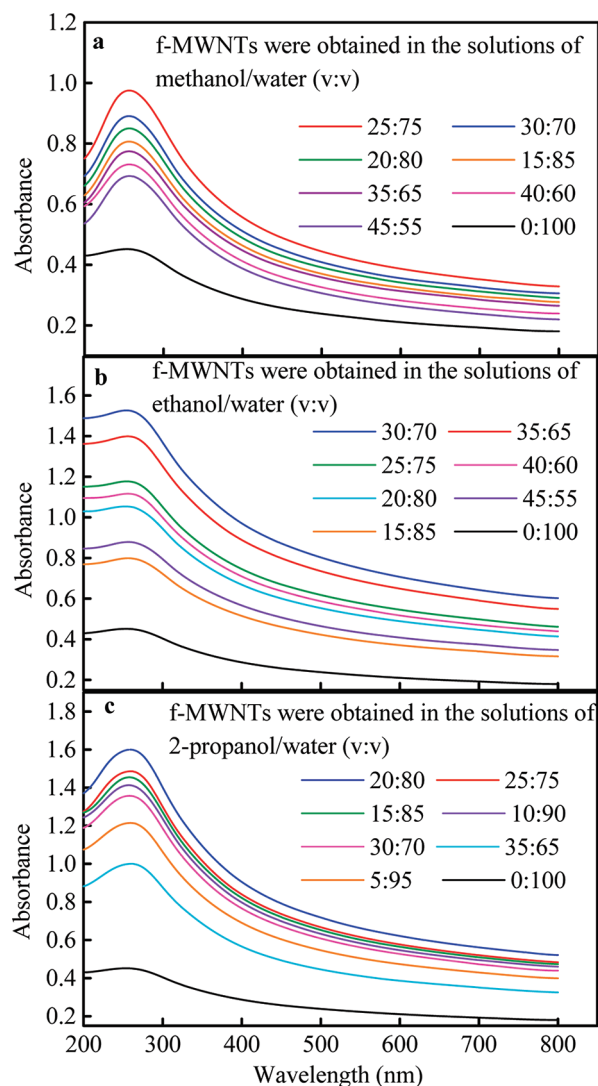
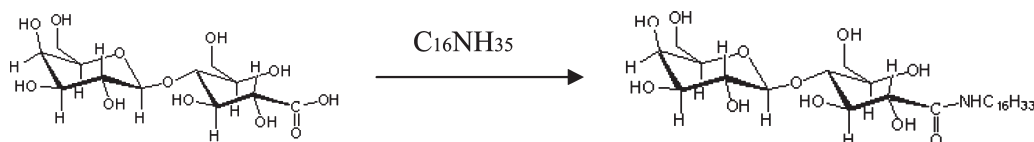
Scheme 1. Reaction Scheme of the Synthesis of *N*-Hexadecyl-*N'*-lactobionylamide

Figure 1. UV-vis absorbance spectra of f-MWNTs dispersed in water, where the f-MWNTs were obtained by the self-assembly of C_{16} LA on MWNTs in alcohol/water solutions containing the alcohols (a) methanol, (b) ethanol, and (c) 2-propanol.

well-suspended MWNTs coated with the amphiphile. The suspension was filtered through a $0.45\text{-}\mu\text{m}$ membrane and rinsed with water to remove unbound amphiphile. The functionalized MWNTs (f-MWNTs) were lyophilized to eliminate traces of alcohol and water.

2.4. Determination of the Saturation Adsorption of Lysozyme on the Functionalized MWNTs. Lysozyme at concentrations ranging from 0.02 to 0.15 mg/mL was added to aqueous solutions of f-MWNTs (0.075 mg/mL). The mixtures were then shaken at $25\text{ }^{\circ}\text{C}$ in an incubator shaker at 150 rpm for 4 h. The

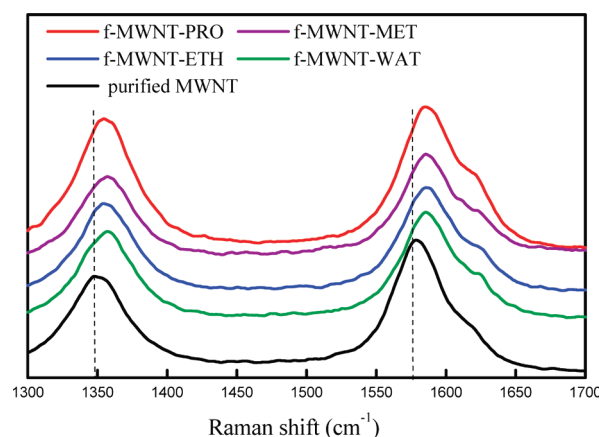


Figure 2. Raman spectra of f-MWNTs obtained by the self-assembly of C_{16} LA on MWNTs in alcohol/water solutions (v:v) and in water: f-MWNT-PRO in 2-propanol/water (20:80), f-MWNT-ETH in ethanol/water (30:70), f-MWNT-MET in methanol/water (25:75), f-MWNT-WAT in water.

nanotube-lysozyme suspension was washed with doubly distilled water by filtering through a polycarbonate membrane ($0.2\text{ }\mu\text{m}$). The lysozyme content was measured using the micro bicinchoninic acid (micro BCA) assay (Pierce Biotechnology). The BCA working reagent was prepared by mixing 50 parts of reagent A with 1 part of reagent B. A protein concentration standard curve was prepared with concentrations ranging from 0.0 to 0.80 mg/mL achieved by serial dilutions of BSA supplied with the BCA assay kit. Toward that end, $20\text{ }\mu\text{L}$ of each protein standard solution and each unknown sample were pipetted into a 96-well micro plate. Then, $200\text{ }\mu\text{L}$ of the BCA working reagent was added to each well, and the plate contents were mixed thoroughly on a plate shaker for 30 min. The plate was incubated at $37\text{ }^{\circ}\text{C}$ for 30 min. After being cooled to room temperature, the plates were read for absorbance at a wavelength of 562 nm using an automated microplate reader (ThermoLab System, Helsinki, Finland). The protein standard curve was used to determine the concentration of each unknown sample. The saturation adsorption of protein onto f-MWNTs was determined through the detection of lysozyme in the filtrate, which was based on average values taken from triplicate measurements of three adsorption operations. The relative changes in adsorption capacities were below 2.0%.

2.5. Characterization. Ultraviolet-visible (UV-vis) spectra were recorded on a Shimadzu UV2550-PC spectrophotometer. X-ray diffraction (XRD) patterns were obtained with a Rigaku D/Max 2500 VBZ+/PC powder diffractometer using a Cu target at 35 kV and 30 mA. The powder diffractograms were obtained at a scan rate of $1^{\circ}/\text{min}$ from $2\theta = 5^{\circ}$ to $2\theta = 90^{\circ}$. Raman spectra were recorded using a Renishaw InVia apparatus (514.5 nm , $E_{\text{laser}} = 2.41\text{ eV}$).

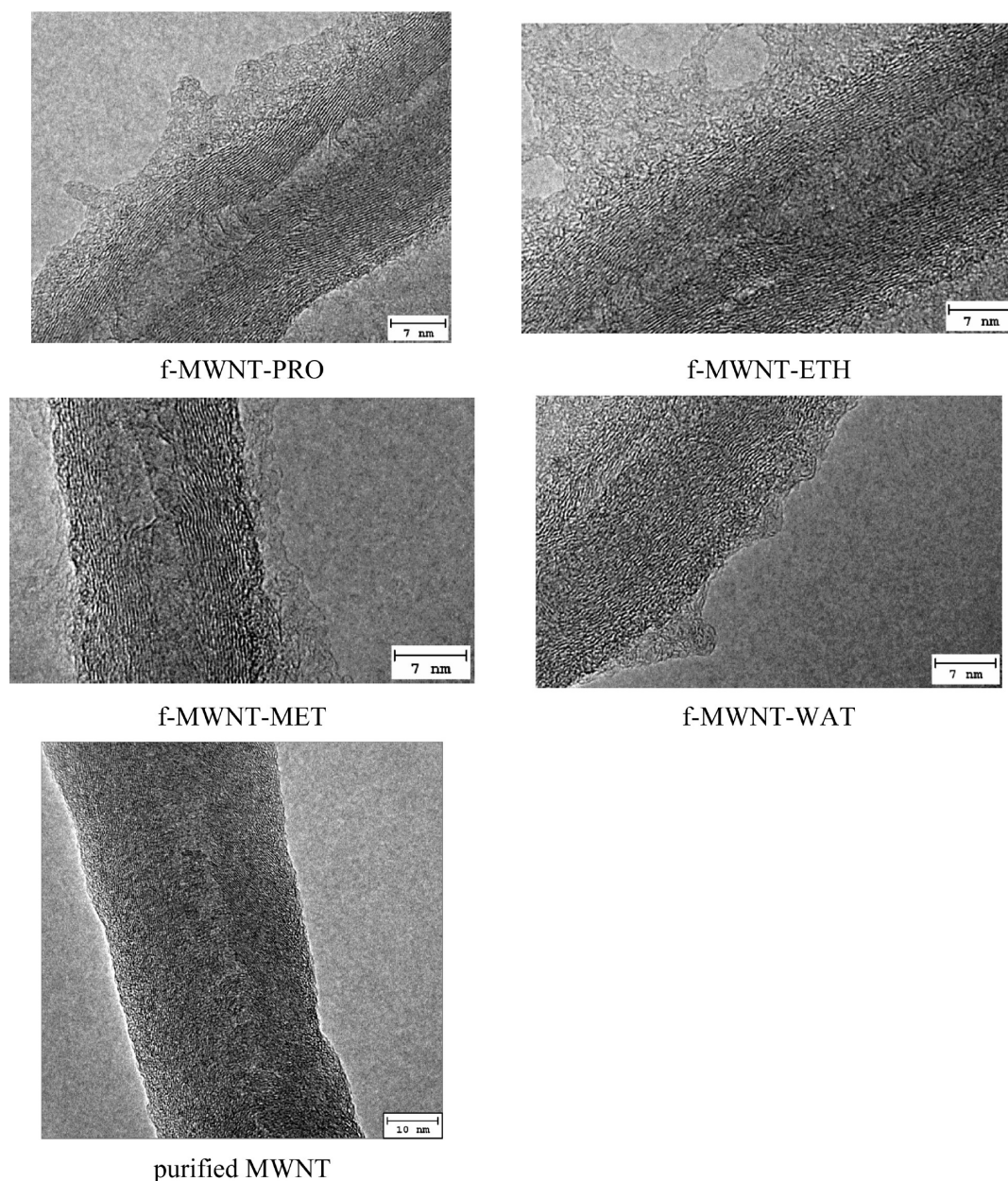


Figure 3. HRTEM images of f-MWNTs obtained by the self-assembly of C₁₆LA on MWNTs in alcohol/water solutions (v:v) and in water: f-MWNT-PRO in 2-propanol/water (20:80), f-MWNT-ETH in ethanol/water (30:70), f-MWNT-MET in methanol/water (25:75), f-MWNT-WAT in water. The HRTEM image of purified MWNTs is also shown.

X-ray photoelectron spectroscopy (XPS) data were acquired using a Thermo VG ESCALAB250 X-ray photoelectron spectrometer, which was operated at a pressure of 2×10^{-9} Pa using Mg K α X-rays as the excitation source. Data analysis was carried out with Thermo Advantage XPS software.²⁷ All XPS spectra were referenced to the main C 1s hydrocarbon peak at 284.9 eV binding energy. A Shirley background²⁸ was used in all curve fitting.²⁹ Elemental compositions were calculated using an O 1s relative sensitivity factor (RSF) of 2.50 relative to C 1s²⁹ and a N 1s RSF of 1.73 relative to C 1s.

Samples for measuring circular dichroism (CD) spectra were prepared with a lysozyme solution (0.05 mg/mL) and a solution of f-MWNTs (0.09 mg/mL). The samples were shaken at 4 °C for 4 h. CD spectra (190–320 nm) were recorded on a JASCO

J-810 CD instrument in a cell with a path length of 1.0 cm. Measurements were performed at a scanning speed of 1000 nm/min and a resolution of 1.0 nm. The spectra were corrected by subtracting the background of f-MWNTs. Ten spectra were accumulated and averaged for each sample.

3. RESULTS AND DISCUSSION

The dispersibility of f-MWNTs in water was investigated by measuring UV–vis spectra, where higher UV–vis absorbance means greater aqueous dispersibility of the f-MWNTs. Figure 1 shows the UV–vis absorbance spectra of f-MWNTs in water. As can be seen, the MWNTs functionalized in alcohol/water solutions had better dispersibility in water than those obtained

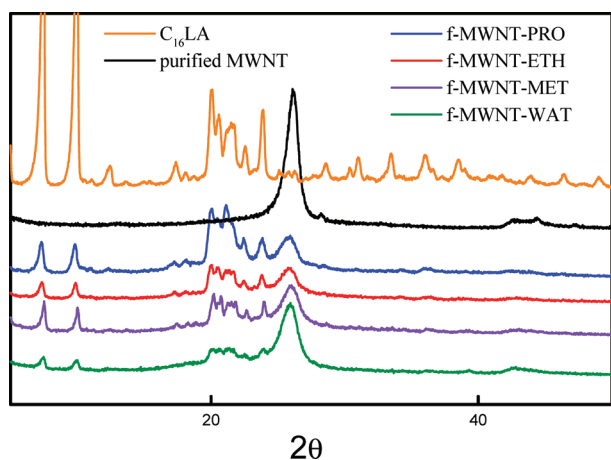


Figure 4. XRD patterns of C₁₆LA, purified MWNTs, and f-MWNTs obtained by the self-assembly of C₁₆LA on MWNTs in alcohol/water solutions (v:v) and in water: f-MWNT-PRO in 2-propanol/water (20:80), f-MWNT-ETH in ethanol/water (30:70), f-MWNT-MET in methanol/water (25:75), f-MWNT-WAT in water.

in pure water (black line for the ratio 0:100 in each plot). These results indicate that, for the functionalization of MWNTs with C₁₆LA, alcohol/water solutions are advantageous over pure water. The results also demonstrate that the alcohol concentration has an effect on the functionalization of MWNTs, suggesting that the functionalization of MWNTs with C₁₆LA in alcohol/water solutions can be regulated by changing the alcohol concentrations. C₁₆LA has a hydrophilic sugar head group and a long hydrophobic chain. Because of intermolecular hydrogen-bonding and hydrophobic interactions, C₁₆LA molecules tend to self-assemble to form aggregates in water. Alcohols have been demonstrated to be effective cosolvents for alkyl polyglycosides.³⁰ Molecular simulations have indicated that short-chain alcohols can act as cosurfactants, directly influencing the properties of surfactant aggregates.³¹ These are possible reasons that C₁₆LA is better solubilized in the alcohol/water solutions than in pure water and that the C₁₆LA aggregates are reduced. This facilitates the interaction of the hydrophobic chains of C₁₆LA with the MWNTs. The following mechanism for the self-assembly of C₁₆LA on MWNTs is possible: C₁₆LA molecules are adsorbed on MWNTs, with the nonpolar groups attached to the surface of the MWNTs and the sugar head groups oriented toward the bulk solution. The chain–chain and hydrogen-bonding interactions between the C₁₆LA molecules are the driving forces for the assembly of C₁₆LA on the MWNTs. Some C₁₆LA molecules are able to incorporate into the C₁₆LA–CNT complex by simultaneous hydrophobic and hydrogen-bonding interactions. The surface of the CNT–amphiphile complex becomes hydrophilic in the final adsorption state.

Raman spectra of the purified MWNTs and f-MWNTs are shown in Figure 2. The D-band at 1348 cm^{−1} and the G-band at 1576 cm^{−1} were obviously observed for the purified MWNTs.^{32,33} For the f-MWNTs, the D- and G-bands are blue-shifted. This is because of strong interactions between the C₁₆LA molecules and the nanotubes increase the energy necessary for vibrations and shift the Raman band to higher frequencies.³⁴ The increase in the D-/G-band intensity ratio also can be attributed to strong interaction between the sugar head

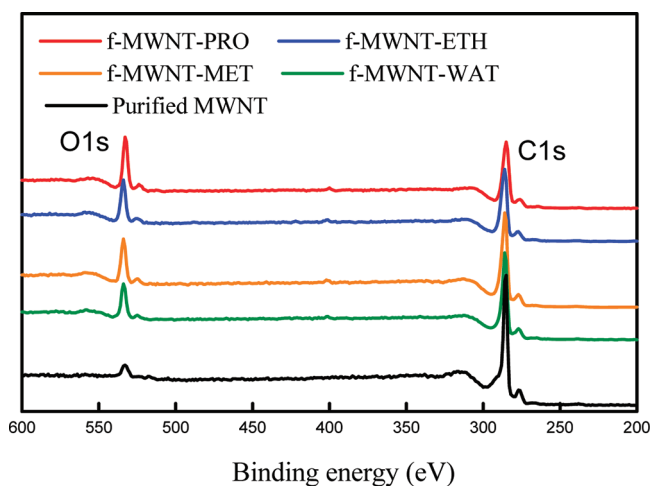


Figure 5. XPS spectra of f-MWNTs obtained by the self-assembly of C₁₆LA on MWNTs in alcohol/water solutions (v:v) and in water: f-MWNT-PRO in 2-propanol/water (20:80), f-MWNT-ETH in ethanol/water (30:70), f-MWNT-MET in methanol/water (25:75), f-MWNT-WAT in water.

groups of the C₁₆LA molecules and the local defects of the f-MWNTs.^{35,36} The f-MWNTs were imaged by high-resolution transmission electron microscopy (HRTEM). As shown in Figure 3, the thick layers of C₁₆LA confirm the self-assembly of C₁₆LA on the MWNTs.

Compared to the XRD patterns of f-MWNTs (Figure 4), the XRD pattern of C₁₆LA (orange) exhibits more peaks. This indicates that the symmetry of the crystal structure of C₁₆LA increases after its self-assembly on MWNTs.³⁷ This is probably due to the interactions between the C₁₆LA molecules and the f-MWNTs, which induce a conformational change in C₁₆LA upon its self-assembly on the MWNTs. The number of the peaks around 21° in the XRD pattern of f-MWNT-WAT (olive) is smaller than the numbers of such peaks in the other cases, suggesting that the C₁₆LA self-assembled on the MWNTs in water gave a more symmetrical crystal structure.

X-ray photoelectron spectroscopy (XPS) is a powerful tool for the investigation of functionalized MWNTs.^{38,39} Figure 5 shows the XPS spectra of the MWNTs functionalized in different alcohol/water solutions. Compared to that of purified MWNTs, the spectra of f-MWNTs show an increase in oxygen intensity. This is attributed to the oxygen atoms in the amphiphile. The intensities of the oxygen and carbon peaks indicate that the amount of C₁₆LA self-assembled on the MWNTs was highest for the 2-propanol/water solution; the amount of C₁₆LA assembled on the MWNTs in pure water was lowest.

The functionalized MWNTs, namely, f-MWNT-PRO, f-MWNT-ETH, f-MWNT-MET, and f-MWNT-WAT, were used to adsorb lysozyme. The saturation adsorptions of lysozyme onto the f-MWNTs are 560, 598, 673, and 750 μg of lysozyme/mg for f-MWNT-PRO, f-MWNT-ETH, f-MWNT-MET, and f-MWNT-WAT, respectively. The resultant saturation adsorptions might be due to the differences in the interactions of the f-MWNTs with the lysozyme. Knowledge of the conformational change of the lysozyme adsorbed on the f-MWNTs can be helpful in better understanding the interactions of the lysozyme with the f-MWNTs. For this purpose, the same amount of lysozyme (concentration of 0.05 mg/mL) was used for adsorption onto the functionalized MWNTs (concentration of 0.09 mg/mL).

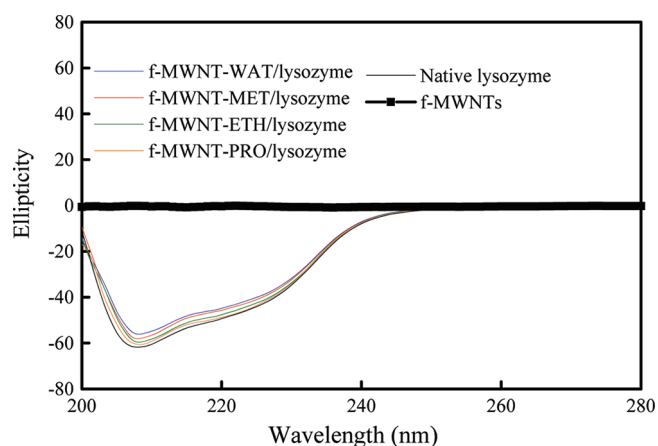


Figure 6. CD spectra of the native lysozyme and the lysozyme interacting in water with f-MWNTs obtained by the self-assembly of C₁₆LA on MWNTs in alcohol/water solutions (v:v) and in water: f-MWNT-PRO in 2-propanol/water (20:80), f-MWNT-ETH in ethanol/water (30:70), f-MWNT-MET in methanol/water (25:75), f-MWNT-WAT in water.

The lysozyme was completely adsorbed onto the f-MWNTs, as the ratio of 0.05:0.09 was smaller than the saturation adsorption ratios. The structural change of the lysozyme upon adsorption was monitored by measuring CD spectra. Figure 6 shows the CD spectra of the lysozyme interacting with f-MWNTs in water. Information on the structural change of the lysozyme can be obtained from the intensity differences between the colored lines (immobilized lysozyme) and the black line (native lysozyme). Figure 6 shows that the lysozyme structure was well preserved upon adsorption. On the other hand, there are some differences in intensity between the colored lines, arising from the difference in the interactions between the lysozyme and the f-MWNTs. In water (neutral conditions), the lysozyme has an overall positive charge. The sugar head groups of the C₁₆LA molecules on MWNTs can thus have a hydrophilic–ionic interaction with the lysozyme. In addition, the lysozyme can have a hydrophobic interaction with the surface of f-MWNTs that are not covered by C₁₆LA. The adsorption of lysozyme onto purified MWNTs was performed under the same conditions as used for the f-MWNTs. The saturation adsorption of lysozyme onto the purified MWNTs was 230 μ g of lysozyme/mg of MWNT. This value is much smaller than those in the cases of f-MWNTs. Possibly, this is because the purified MWNTs aggregated during the adsorption of lysozyme, so that lysozyme was adsorbed onto MWNT bundles rather than individual MWNTs. In addition, the lysozyme adsorbed on purified MWNTs presented a relatively greater conformational change. This is possibly because the interaction of the lysozyme with the hydrophobic surface of the purified MWNTs is stronger than that between the lysozyme and the hydrophilic–hydrophobic surface of the f-MWNTs.

4. CONCLUSIONS

In alcohol/water solutions, MWNTs were functionalized with the lactobionic amide amphiphile. It was found that the amphiphile can self-assemble on the MWNTs and that the functionalized MWNTs have a good dispersibility in water. The alcohols can promote the self-assembly of C₁₆LA on MWNTs and regulate the amount of self-assembled C₁₆LA on the MWNTs.

The structure of lysozyme adsorbed on f-MWNTs was well-preserved, indicating good biocompatibility of the f-MWNTs. The regulation of the alcohol for the self-assembly of C₁₆LA on CNTs allows for the formation of designed amphiphile–CNT composites that can be used for protein adsorption.

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