Thionine-mediated chemistry of carbon nanotubes

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Abstract

Thionine can be employed as a kind of useful functional molecule for the non-covalent functionalization of carbon nanotubes, as it shows a strong interaction with either SWNTs or MWNTs. Attachment of thionine molecules onto the sidewalls of carbon nanotubes would improve the solubility and lower the thermal stability of original carbon nanotubes. More importantly, it may functionalize the surface of carbon nanotubes with rich NH_2 groups and therefore open up more opportunities for the surface chemistry of carbon nanotubes. It has been proved that through the modification of small thionine molecules, other kinds of species such as cytochrome C and TiO_2 nanoparticles could be easily and selectively introduced onto the surface of carbon nanotubes. With this approach, SWNTs or MWNTs can be tailored with desired functional structures and properties.
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1. Introduction

Surface chemistry modifications are useful and critical to manipulate the properties of carbon nanotubes and develop their potential applications [1–4]. Recently, some attempts have been made to attach biological molecules such as, peptide [5], enzymes [6], antibodies [7] and DNA [8] onto the sidewalls of SWNTs to fabricate highly sensitive biosensors, and to anchor quantum dots [9] and semiconductive nanoparticles [10] on SWNTs to form nanojunction structures for the development of nanoelectronic and optical devices. Chemical processing of carbon nanotubes with desired functionalized surfaces and manipulated properties will be thus important. Refluxing in oxidative acids [11], aniline solution [12], or reacting with highly active species [13–19] are generally used routes for the covalent functionalization of carbon nanotubes at ends or/and side-walls. As carbon nanotubes are chemically inert, covalent functionalization of carbon nanotubes is often difficult and uncontrollable, and its efficiency often largely depends upon the concentration of defective sites in nanotube structures [2]. In a sense, through covalent functionalization, it is easy to destroy the sp^2 structures of carbon nanotubes, thereby diminishing their pristine mechanical and electronic properties. In contrast, non-covalent functional strategies seem a more friendly and effective alternative for this purpose. Some molecules including small gas molecules [1], anthracene derivatives [20–22], and polymer molecules [3,23] have been found liable to absorb onto or wrap around SWNTs. The presence of such non-covalent interactions may modify the native conductance, semiconductivity and solubility of carbon nanotubes remarkably. As a result, it may be potentially useful for the chemical tailoring of carbon nanotubes [1–3]. In this present study, we found that carbon nanotubes, especially single-walled nanotubes had a strong interaction with thionine molecules. Thonine is a small planar molecule and has two $-NH_2$ groups symmetrically distributed on each side. Functionalization of carbon nanotube with thionine molecules has been shown to be very simple and useful for further introducing other molecules onto tube surfaces and enriching the chemistry of carbon nanotubes.

2. Experimental

The SWNT sample used in this work was synthesized by methane CVD using MgO supported Fe catalysts as described in a previous study [24]. The purity of SWNTs

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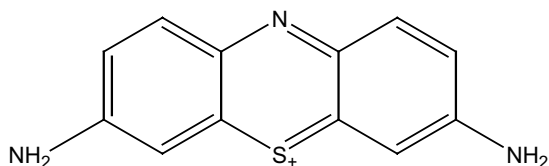*E-mail addresses:* jzhang@chem.pku.edu.cn (J. Zhang), lzf@chem.pku.edu.cn (Z. Liu).

Fig. 1. The chemical structure of thionine.

was higher than 90% after purification in 37% HCl. For adsorption procedures, SWNT aqueous suspension were mixed and sonicated with thionine (purchased from Shanghai chemical company and used as received, the chemical structure was shown in Fig. 1) solution (10 mg/ml) at room temperature for at least 12 h. The carbon nanotube samples were then filtered with a 1.2 μm diameter pore membrane, thoroughly rinsed with the solvent and dispersed in a desired solvent or on a silicon surface for characterization. Adsorption and subsequent introduction of other kinds of molecules onto nanotubes were preferably carried out directly on the substrate surface, as it may avoid some possible influence on the modified carbon nanotubes during further procedures. TGA was conducted using a sample of about 5 mg which was heated at a rate of 10 °C/min from 30 to 800 °C in airflow.

3. Results and discussion

Thionine is a kind of purple dye, which can be easily dissolved in water and ethanol. When a few drops of thionine solution (2 mg/ml) were added to a SWNT suspension, the purple color of the solution would soon disappear in a few mins, implying that carbon nanotubes showed a strong tendency to absorb thionine molecules. It was observed that more than 2 mg thionine could be absorbed by 1 mg tube sample. The high adsorption capacity of SWNTs, on one hand, can be understood with the fact that SWNTs exhibit higher specific surface areas owing to their hollow and tubular structures. On the other hand, the high quantity of thionine absorbed by SWNTs may be partly due to the adsorption of thionine aggregates. Similar results could also be obtained with MWNTs. When carbon nanotubes have the possibilities to interact with other molecules, it may result in different results. For macromolecules, such as polymers or biological molecules, they could probably wrap around tubes or stand on the sidewalls of tubes [2,8]. In the case of small molecules, the situation would be quite different, small molecules could not only cover the side-walls of individual MWNTs (typical diameter range from 10 to 20 nm), but also be able to penetrate into the interior of the tubes. This can be clearly confirmed by TEM characterization (no micrographs are shown). Some black spots or blocks

could be observed in the tubes after their interaction with thionine molecules. They often moved or disappeared in the interior of the tubes under e-beam irradiation. The movement and disappearance of these black spots was evidently attributed to the evaporation of absorbed thionine solution or thionine molecules themselves.

Fig. 2 shows the UV spectra of thionine solution and thionine modified SWNTs suspended solution. Pure thionine aqueous solution has two characteristic adsorption peaks, one in visible region around 600 nm, the other located in UV region around 250 nm. The two peaks can be also observed in thionine modified SWNTs solution, indicating the presence of thionine molecules on SWNTs. Moreover, the obvious red shift for the peak at 600 nm and blue shift for the other peak at 250 nm provide the further evidence on the interaction between SWNTs and thionine molecules. In addition, as shown in Fig. 3, the similar Raman spectra of SWNTs and thionine coated SWNTs revealed that the there was little harm to the native structure and properties of thionine molecules after its interaction with SWNTs. It thus implied that their strong interactions ought to
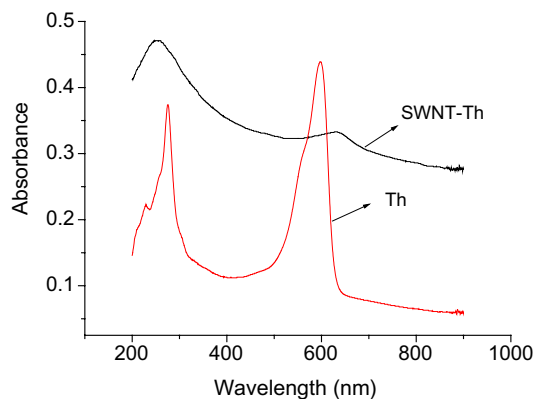

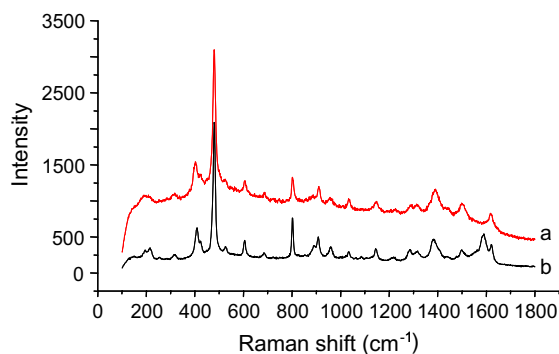Fig. 2. UV spectra of thionine and thionine modified SWNTs solutions.

Fig. 3. Raman spectra of thionine (a) and thioinine coated SWNTs (b).

result from a π–π stacking force between these two kinds of conjugated frames.

After its interaction with thionine molecules, the SWNT solid sample became fluffier and the solubility in water or other kinds of organic solvents was improved as well. As shown in Fig. 4, the as-prepared long SWNTs are always entangled and are difficult to separate and disperse in water. After being modified by thionine molecules, however, SWNTs could be better wetted and dispersed in aqueous solution. We also found that the adsorption capacity of SWNTs in aqueous solution was obviously higher than that in ethanol solution, and some of the absorbed thionine molecules could be washed away when a SWNT sample was rinsed with ethanol. It is suggested that the numbers of thionine molecules on the surface of individual SWNTs could be intentionally manipulated by the selection of solvents.
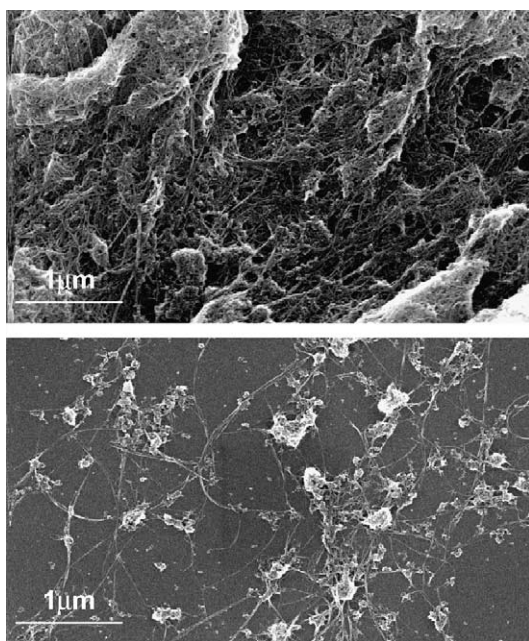
On the other hand, the thermal stability of SWNTs was remarkably decreased after their interaction with thionine molecules. Fig. 5 shows the TGA and its differential curves of pristine SWNTs and modified SWNTs. The evident weight loss of pristine SWNTs started around 480 °C and ended at 700 °C with a combustion peak temperature at 571 °C. When SWNTs were functionalized with thionine in aqueous solution (noted as Th-SWNT), the weight loss at less than 400 °C mainly arose from the contribution of absorbed thionine molecules. Starting from 400 °C, the contribution of SWNTs became dominant. The evident weight loss however ended around 570 °C, much lower than that of pure SWNTs [20]. Two sharp combustion peaks were observed at 471 and 492 °C in its TGA curve, and neither of the characteristic peaks of SWNTs and thionine was found. If the adsorption event happened in ethanol, where a lower amount of thionine molecules were absorbed onto SWNTs, the TGA curve was similar to that obtained from aqueous solution. Only one combustion peak emerged at 480 °C, near to the result of thionine modified SWNTs in aqueous solution, but also quite lower than that of pristine SWNTs, confirming that the average thermal stability of SWNTs was greatly diminished by the introduction of thionine molecules. If 50% (weight ratio) thionine was mechanically mixed with SWNTs thoroughly (noted as Th + SWNT), the resulting combustion peak temperature of this system was at 540 °C, showing that the thermal stability of SWNTs was destroyed less severely in contrast to the results of thionine functionalized SWNTs. Similar results could be also obtained with multi-walled carbon nanotube samples. Therefore, it could be concluded that the oxidation reaction of carbon nanotubes was greatly enhanced by the adsorption of thionine molecules. Future studies are underway to determine the origin of this process.

The introduction of NH_2 containing thionine molecules on the sidewall of carbon nanotubes may open up more opportunities for their further chemical processing.

Fig. 4. SEM images of SWNTs before (upper) and after (down) the adsorption of thionine molecules.
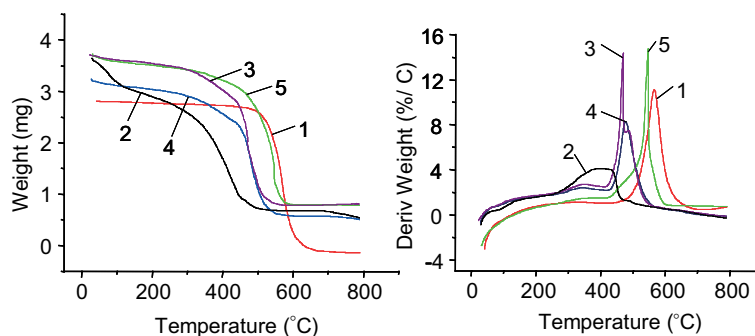

Fig. 5. TGA and its differential curves of SWNTs modified with thionine molecules, (1) SWNT products; (2) pure thionine; (3) SWNTs interacted with thionine in aqueous solution; (4) SWNTs interacted with thionine in ethanol; (5) thionine mechanically mixed with SWNTs.

To illustrate this fact, SWNTs were first well dispersed on a silicon surface, then immersed in 50 mM thionine solution in ethanol, 20% glutaraldehyde solution, and cytochrome C solution in sequence, with the silicon wafers being washed thoroughly with water or ethanol and dried in air before they were dipped in another solution. The results of AFM characterization showed that protein molecules were successfully, densely and uniformly attached onto the sidewalls of each of individual SWNTs (Fig. 6(a)). The attachment of protein molecules onto SWNTs was achieved via a condensation reaction between thionine and protein molecules. If without thionine adsorption step, fewer protein molecules were attached onto SWNTs. Similar results could be observed with MWNT sample (Fig. 6(b)). When a few drops of glutaraldehyde solution and cytochrome C solution were successively added into pure and modified MWNT suspended solutions respectively, protein molecules were found accumulating on the sidewalls of most of modified tubes. However, no protein molecules were captured onto pure tubes, their clusters were found randomly scattered around tubes. Therefore, thionine functionalization offers more possibilities to enrich the surface chemistry of carbon nanotubes. During this process, glutaraldehyde was used as a bifunctional reagent [25]. If without glutaradehyde, we see proteins randomly scattered on a TEM grid (micrographs not shown).

Fig. 7. TEM and AFM characterization of thionine modified MWNTs (a) and SWNTs (b and c) showing strong interaction with TiO$_2$ nanoparticles.

Other kinds of inorganic molecules could be also attached onto the surface of carbon nanotubes. Owing to the unique interaction between TiO$_2$ nanoparticles and NH$_2$-terminated contained thionine [26], TiO$_2$ nanoparticels with particle sizes less than 10 nm were preferentially absorbed onto modified MWNTs instead of pure tubes when a TiO$_2$ suspension solution was dropped into carbon nanotube suspended solutions (Fig. 7(a)). In addition, as –NH$_2$ functionalized surface was found specific to tetra-n-butyl titanium (TBT) precursors [27], thionine modified individual SWNTs may serve as useful sites or templates for the formation of thin nanowire materials. Thionine modified SWNT sample on silicon surface was intentionally immersed into TBT/isopropyl alcohol solution, washed and then put into distilled water to hydrolyze adsorbed Ti precursor molecules. Fig. 7(b and c) show the AFM images of hydrolyzed SWNTs, where it could be observed that each individual SWNTs was densely surrounded by a layer of Ti oxide particles, no matter how thin or how thick the tubes were. Under this condition, this would be another feasible route to prepare Ti oxide nanotube materials. The versatility of this method can be extended to other systems in which the target molecules have specific interaction with NH$_2$ groups.
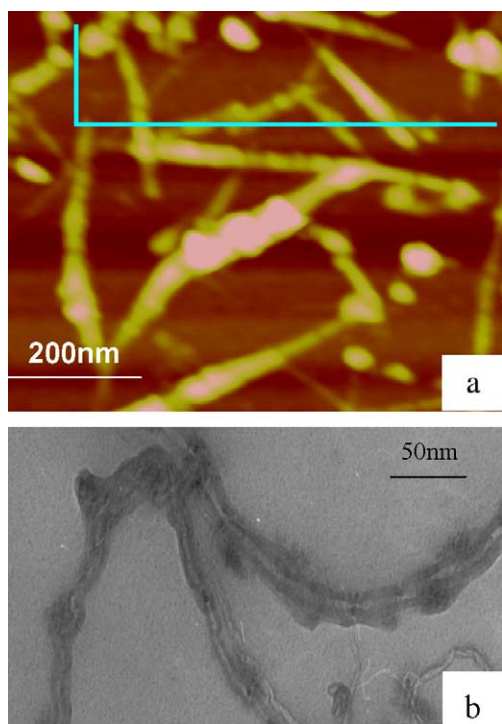

Fig. 6. AFM image of SWNTs (a) and SEM image of MWNTs (b) after their interaction with cytochrome C molecules, inset is a contact AFM image of SWNTs coated with adsorbed thionine molecules.
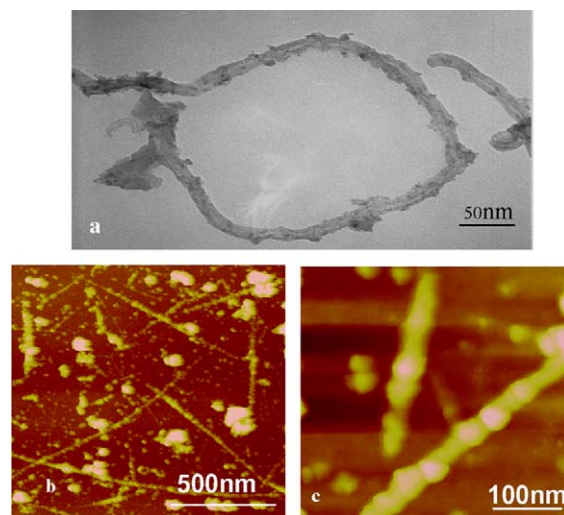
4. Conclusions

Thionine molecules were found to show a strong interaction with individual SWNTs. Interaction with thionine molecules would improve the solubility of carbon nanotubes in some solvents and greatly decrease their thermal stability as well. Modification with thionine enriched the surfaces of individual SWNTs with NH$_2$

groups, which would open up more opportunities for anchoring other molecular species such as protein molecules and semiconductive nanoparticles onto SWNTs, and accordingly this strategy would be available for building various SWNT based heterojunction structures.

Acknowledgements

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