

Simple and highly efficient direct thiolation of the surface of carbon nanotubes†

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We established a highly efficient and simple method to directly functionalize the surface of carbon nanotubes (CNTs) with thiol groups (–SH). The –SH groups on the surface of the CNTs were characterized using Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), elemental analysis (EA), and transmission electron microscopy (TEM). The TEM indicated that gold nanoparticles (Au NPs) or other metals can be attached to thiolated CNTs (CNT–SHs) through thiol–metal bonding. Hence, the proposed approach can be used for developing self-assembled materials, sensors, catalysts, and CNT nanodevices.

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Introduction

Carbon nanotubes (CNTs) were discovered by Iijima, and have been applied in numerous scientific and technological fields.¹ CNTs exhibit excellent physical, thermal, and electrical properties, which could enable developing one-dimensional nanomaterials for fabricating novel electronic devices.² The carbon nanotube field effect transistor (CNTFET), a CNT application, is considered a next-generation nanotransistor device.³ Recently, Stanford University constructed the first CNT computer, comprising 178 CNTFETs, each containing 10–200 CNTs.⁴ CNTs can also be used to develop support materials for fuel cells and heterogeneous catalysts.^{5–9}

Thiol groups (–SH) exhibit excellent affinity with gold, and have been used for self-assembly and conjugation.¹⁰ Therefore, the applicability of CNTs can be extended using thiolation. CNTs can be modified using noncovalent methods through the π – π interactions between the pyrene derivatives and the

surfaces of the CNT.¹¹ It has been reported that, irrespective of the noncovalent π – π interaction, CNTs can be modified with –SH groups to be able to conjugate with gold nanoparticles (Au NPs).¹² In addition, Dai reported a method to modify CNTs with thiol by noncovalent adsorption of phospholipid molecules, attempting to conjugate CNTs with DNA.¹³ In general, covalent bonding is stronger than noncovalent bonding is. Traditionally, covalent methods to modify CNTs depended on the carboxyl groups introduced by refluxing CNTs with mixed acids (sulfuric and nitric acid).¹⁴ To generate –SH groups on the CNTs, the carboxyl groups on the surfaces of the CNTs can be conjugated with a thiol-containing linker through the amide bond.^{6,15–18} Guo reported a method to functionalize CNTs with –SH groups through an ester bond, allowing Au NPs to attach to the CNTs.¹⁹ However, in these methods, established –SH groups depended on the conjugation of a linker that was not directly modified with –SH groups. Plank reported a method to functionalize single-wall CNTs with thiols by treating the CNT/S mixture with plasma.²⁰ This method was the first direct thiolation of CNTs; however, it requires specific equipment to accomplish the modification and cannot be readily performed in a typical laboratory. Wei reported a method to directly thiolate CNTs by using a series of organic reactions, involving carboxylation, reduction, bromination, and thiolation to produce thiolated CNTs (CNT–SHs) that exhibited 1.92% S based on XPS estimations.⁵ Our group has been researching the surface modification of detonation nanodiamonds (NDs) for several years, and successfully modified NDs using –SH groups. Herein, we present a simple and direct method to functionalize CNTs with –SH groups. In contrast to the plasma method, the proposed method is simple to perform and can be applied to mass production. Furthermore, this method allowed loading more S onto the CNTs than did the method proposed by Wei.

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Therefore, the proposed method enables attaching Au or Pt onto the sidewall of CNTs, producing nanomaterials that could be used as catalysts and sensors.

Experimental section

Chemicals

The multiwall CNTs with an OD < 8 nm and length of 10–30 μm were purchased from Chengdu Organic Chemical Co., Ltd. All chemicals were used as received, without purification. The thiourea and hydrobromic acid were purchased from Sigma Aldrich. The Au NPs (13 nm) were prepared using the citrate reduction of HAuCl_4 . Briefly, an aqueous solution of HAuCl_4 (1 mM, 20 mL) was refluxed at 110 $^\circ\text{C}$, while stirring in an oil bath. A trisodium citrate solution (2 mL of a 38.8 mM aqueous solution) was rapidly added, exhibiting a series of color changes before yielding a wine-red solution. The mixture was refluxed for another 10 min and allowed to cool to room temperature.

Instruments

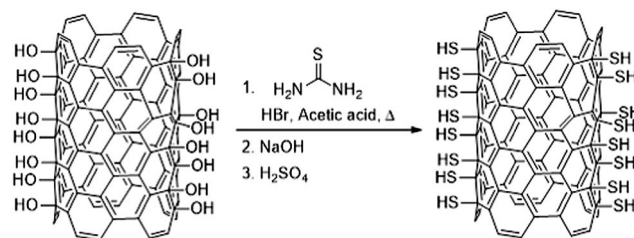
The Raman spectra were obtained using a custom-built micro-Raman system. The excitation source was a 532 nm diode laser. The scattering light was filtered using a long-pass Semrock filter, and the signals were analyzed using a Monochromator DK480. High-resolution transmission electron microscopy (HRTEM) images were recorded using a JEOL JEM-2100F electron microscope operating at 200 kV. X-ray photoelectron spectroscopy (XPS) spectra were obtained using a ULVAC-PHI Quantera SXM, using Al K_α as the X-ray source. The excitation area was 100 \times 100 μm ; the stepsizes for obtaining survey and chemical state spectra were 1.0 and 0.050 eV, respectively.

Synthesis of thiolated carbon nanotubes

A mixture of hydroxyl CNTs (CNT-OHs, 300 mg) and thiourea (11.4 g, 150 mmol) in hydrobromic acid (25 mL) and glacial acetic acid (50 mL) was stirred under reflux for 48 h. The hot reaction mixture was poured in small portions into a cold (ice bath) 15% aqueous NaOH solution (600 mL), and stirred overnight at room temperature. The reaction mixture was acidified with 50% aqueous H_2SO_4 to pH = 2–3, maintaining a temperature less than 10 $^\circ\text{C}$. The pellets were rinsed several times with distilled water, and separated using centrifugation at 8000 rpm. The CNT-SHs were dried in a vacuum oven at 50 $^\circ\text{C}$ for 24 h.

Results and discussion

CNT-OHs were obtained by reducing CNT-COOH with lithium aluminum hydride (LiAlH_4), which also reduced the carboxyl groups on the surface of the CNTs. The hydroxyl groups of the CNTs were replaced with $-\text{SH}$ groups by treatment with thiourea in the presence of hydrobromic acid and acetic acid (Scheme 1). In acidic conditions, the hydroxyl groups are protonated and the S atom of the thiourea is attacked, replacing the hydroxyl groups with $-\text{SH}$ groups (see ESI Scheme S1†).



Scheme 1 Directly thiolated onto the surface of CNT.

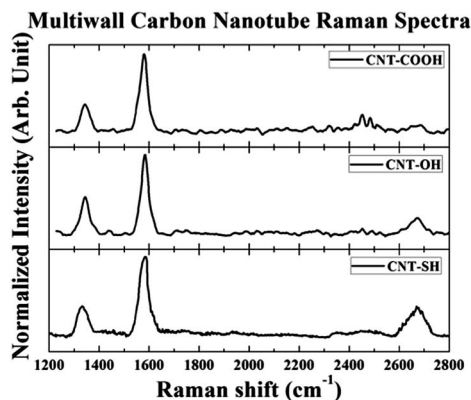


Fig. 1 The Raman spectra of the carbon nanotube.

CNT-SHs were characterized using TEM, elemental analysis (EA), Raman spectroscopy, and XPS spectroscopy. Raman spectroscopy revealed a major graphite peak at 1580 cm^{-1} and a disorder carbon peak at 1350 cm^{-1} (Fig. 1). The characteristic signal of the $-\text{SH}$ group was observed at 2670 cm^{-1} , indicating the successful introduction of $-\text{SH}$ groups onto the surfaces of the CNTs.

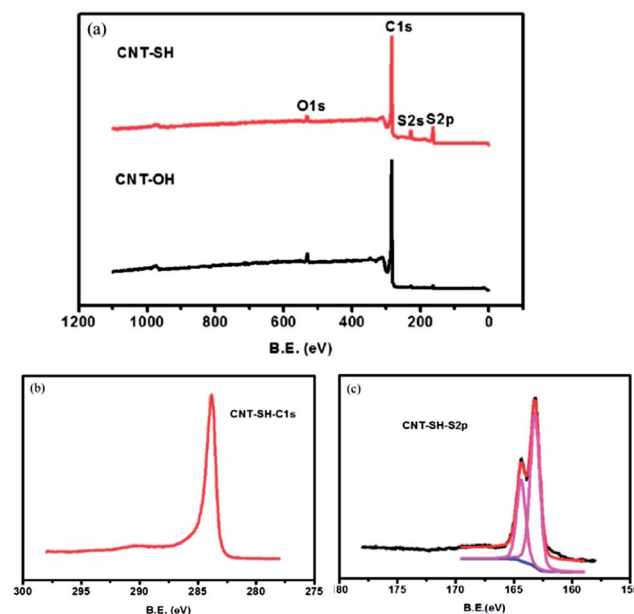


Fig. 2 XPS spectra of (a) CNT-OH and CNT-SH; (b) CNT-SH $\text{C}_{1\text{s}}$; and (c) CNT-SH $\text{S}_{2\text{p}}$.

Fig. 2 displays the XPS spectra of the CNT-SHs; this was used to evaluate the surface modification. The main peak (C_{1s}) was observed at 283.85 eV, and the S_{2s} and S_{2p} peaks were observed at 228 and 164 eV, respectively. The peak fitting results revealed that S_{2p} was contributed by the $S_{2p}^{1/2}-H$ at 164.35 eV and $S_{2p}^{3/2}-H$ at 163.2 eV. The surface composition of the CNTs was also determined using XPS, which indicated a 6.55% atomic percentage of S. EA confirmed the substantial increase in the S content of the CNT-SHs after thiolation (Table 1).

To confirm the presence of -SH groups in the CNTs, we treated the thiolated CNTs with Au NPs (experiment set), then discarded the supernatant contained residue of Au NPs by centrifuge and washed the pellets (CNT-S-Au) with deionized water. The pellets were collected by centrifuge again and then redispersed in deionized water with same volume. The aqueous solution of CNT-S-Au was detected the characteristic UV absorption of Au (Fig. 3). Compared to the characteristic UV absorption of Au NPs (control set, the concentration of Au NPs was equal to that of experiment set), the decreased intensity of CNT-S-Au was due to most of Au NPs were removed during the step of discarding supernatant. The TEM image in Fig. 4 provides solid evidence of the conjugation of the Au NPs on the surfaces of the CNTs.

Herein, we proposed a method to functionalize the surface of CNTs with -SH groups. This method was based on a simple functional group transformation, which can be easily and efficiently performed in any laboratory without special equipment. The -SH groups of the CNTs exhibited a high affinity for Au, Pd, and Pt; thus, soft sulfides and soft metals can be used as CNT support catalysts. The findings proved that Au NPs were attached to the surfaces of the CNT-SHs. Moreover, -SH groups directly modified the CNT sidewall, without requiring a linker, minimizing the contact resistance between the CNTs and NPs.⁵ Compared with Wei, who successfully modified CNTs with -SH groups, yielding a 1.92% S content, we developed a simple and

Table 1 Elemental composition (%) of functionalized CNT

	N%	C%	H%	S%
CNT-COOH	0.366	87.340	1.031	0.173
CNT-OH	0.309	88.089	0.959	0.166
CNT-SH	0.169	58.243	0.333	37.059

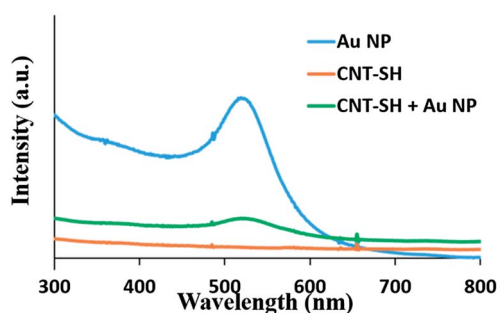


Fig. 3 The UV-Vis spectra of the thiolated CNT treat with gold nanoparticles.

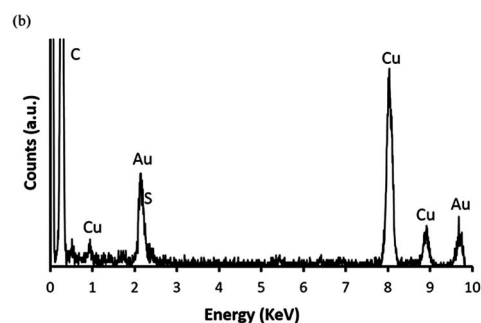
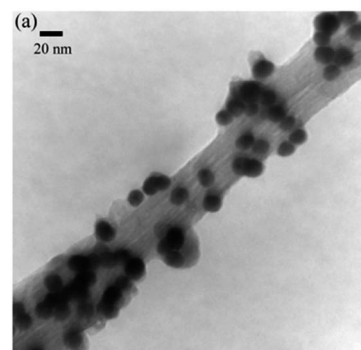


Fig. 4 The TEM image of the CNT-SH treat with gold nanoparticles (Au-CNT). (a) CNT-S-Au; (b) EDS pattern of CNT-S-Au on the surface of copper holey carbon support grid.

efficient method that yielded a S content as high as 6.55%. We provided a new strategy to functionalize CNTs and develop new nanomaterials for use in catalyst support or sensor nanodevices.

Conclusions

In conclusion, we reported a simple method to thiolate the surfaces of CNTs. Thiolated CNTs exhibited abundant surface -SH groups, enabling reactions with Au NPs and simple conjugation with thiol affinity functional groups. The functionalized CNTs were characterized using various spectroscopic measurements namely, EA, TEM, UV-Vis, XPS, and Raman spectroscopy. According to our results, the -SH groups enabled modifying the CNT surfaces, yielding an XPS-estimated atomic percentage of S of 6.55%. The TEM results provide the solid evidence of the gold nanoparticles were self-conjugated onto the surface of carbon nanotubes through the thiol-metal bonding. Hence, this approach can be used to functionalize CNTs, facilitating their attachment to other nanostructures. The proposed technique can be applied for conjugating Au NPs in sensors and attaching Pt or Pd to catalysts.

Acknowledgements

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