

Synthesis, characterization, and electrochemical properties of imidazole derivatives functionalized single-walled carbon nanotubes

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The imidazole derivatives functionalized single-walled carbon nanotubes (SWNTs) were synthesized by a diazonium-based reaction. We have designed and synthesized two imidazole derivatives to modify SWNTs. The resulting products were characterized by Fourier transform infrared (FT-IR) spectroscopy, Raman spectroscopy, ultraviolet visible (UV/Vis) spectroscopy, thermo gravimetric analysis (TGA), energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), and atomic force microscopy (AFM). Electrochemical measurements via a cyclic voltammetry method revealed that the weak intramolecular electronic interactions presented between the attached imidazole derivatives groups and the nanotubes. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: single-walled carbon nanotubes; imidazole derivatives; functionalization; electrochemical properties

INTRODUCTION

Single-walled carbon nanotubes (SWNTs) exhibit excellent mechanical and electrical properties^[1,2] that have emerged as an innovative and new class of nanoscale carbon-based materials currently under intensive investigation.^[3–5] The excitement in this area is, by and large, combining SWNTs with other chemical entities in order to fabricate nanostructures with unique functions^[6–8] and applications.^[9–11] SWNTs are considered as an extended π electron system and can interact with other π electron systems, such as aromatic and heterocyclic molecules. The well-known strong interaction^[12] between aromatic compounds and graphitic sidewalls of SWNTs through effective π - π stacking^[13] can, for example, be exploited to attach chemical and biological substances^[14] to the sidewalls of SWNTs. These interactions have been manifested in solubilization of SWNTs in aromatic solvents^[15] as well as solutions of certain aromatic surfactants and polymers.^[16]

A number of efforts so far have concentrated on the adsorptive π - π electron stacking or charge transfer of organic molecules onto SWNTs sidewalls, such as benzene,^[17,18] naphthalene, or anthracene derivatives,^[19] and small charge-transfer aromatic molecules,^[20] while many researches were involving the covalent linkage of electroactive species. For example, some reports revealed functionalization of SWNTs with electron-donating ferrocene and confirmed that electron transfer occurred from the ferrocene to the photoexcited SWNTs,^[21] and one also succeeded in controlling over electron transfer in tetrathiafulvalene-modified SWNT.^[22] Herein, we report to successfully modify SWNTs with the imidazole derivatives by the covalent method, and explore the intramolecular electronic interaction of imidazole derivatives functionalized SWNTs, using both spectroscopic and electrochemical measurements.

EXPERIMENTAL

The functionalized process of the imidazole derivative-SWNTs is shown in Scheme 1. The SWNTs (outer diameter: 1–2 nm) prepared by a chemical vapor deposition (CVD) process, were produced at Chengdu Organic Chemical Co., Ltd., Chinese Academy of Science. Other reagents were obtained from commercial sources and were used as received. The solvents used were of analytical grade.

Synthesis of 2-(4-aminophenyl)-4,5-di(4,4'-nitrylphenyl)imidazole (1)

Our research group has succeeded in design and synthesis of the imidazole derivatives.^[23]

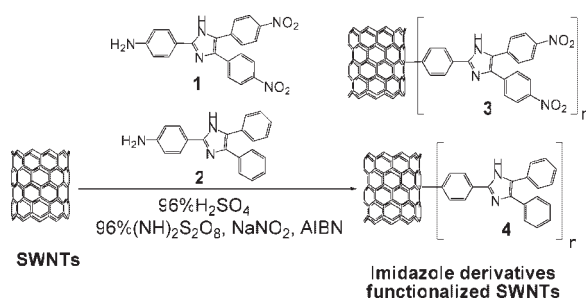
Synthesis of 2-(4-acetaminophenyl)-4,5-diphenylimidazole (1a)

A mixture of benzil (3.7 g), 4-acetaminobenzaldehyde (3 g), ammonium acetate (25.9 g), and acetic acid glacial (50 mL) was refluxed at 118°C for 2 h. Then the dark yellow solution was poured into ice water under stirring, and ammonia was added until an alkalescent solution was attained. The crude product was

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Scheme 1. Scheme for covalent functionalization of SWNTs with imidazole derivatives

collected by filtration and washed several times with water, following by recrystallization from dry ethanol. After drying, 3.4848 g (92%) of **1a** was obtained as a yellow powder. IR: ν_{\max} (cm^{-1}): 3200 ($-\text{NH}-$), 3150 ($-\text{CH}_3$), 1680 ($-\text{CO}-$), 1600 ($-\text{C}=\text{N}-$), 1560, 1500, 1480, 1460 ($-\text{C}_6\text{H}_4-$); $^1\text{H-NMR}$ (DMSO- D_6) δ (ppm): 10.0 (1H, $-\text{C}=\text{N}-$, in imidazole), 8.0 (1H, s, N—H), 7.6–7.9 (4H, m, $-\text{ph}-$), 7.4 (10H, m, $-\text{ph}-$), 2.1 (3H, s, $-\text{CH}_3$).

Synthesis of 2-(4-acetaminophenyl)-4,5-di(4,4'-nitrylphenyl)imidazole (**1b**)

A solution of **1a** (3.4848 g) in oil of vitriol (42 mL) was added to the nitric acid (14 mL) under stirring. After retaining for 20 min, the mixture was poured into water under stirring. Then NaOH (50 mL of a 5% aqueous solution) was added until a neutral pH was attained. The yellow precipitate was collected by filtration and recrystallized from dry ethanol/chloroform (1:1 v/v). 1.3366 g (53%) of **1b** was obtained as a yellow powder after dried. IR: ν_{\max} (cm^{-1}): 3456 ($-\text{NH}-$), 3106, 2984 ($-\text{CH}_3$), 1673 ($-\text{CO}-$), 1600 ($-\text{C}=\text{N}$), 1597, 1519, 1494, 1409 ($-\text{C}_6\text{H}_4-$), 1341 ($-\text{NO}_2$); $^1\text{H-NMR}$ (DMSO- D_6) δ (ppm): 13.5 (1H, m, $-\text{C}=\text{N}-$, in imidazole), 7.7 (1H, s, N—H), 8.3–8.7 (8H, m, $\text{ph}-\text{H}$), 7.8–8.2 (4H, m, $\text{ph}-\text{H}$), 2.1 (3H, s, $-\text{CH}_3$).

Synthesis of 2-(4-aminophenyl)-4,5-di(4,4'-nitrylphenyl)imidazole (**1**)

A mixture of **1b** (1.3366 g), KOH (1 g), water (4 mL), methanol (8 mL), and tetrahydrofuran (THF) (10 mL) was refluxed for 10 min, following adding 100 mL hot water, and retained for another 20 min. Then 6 M HCl was added with stirring until a neutral pH was attained. When the solution was alkaline with saturated aqueous NaHCO_3 the crude product was collected on filter paper, then dissolved in THF and the organic solvents was distilled to obtain 0.9 (66%) of dried **1** as a brownish red powder. IR: ν_{\max} (cm^{-1}): 3460, 3370 ($-\text{NH}_2$), 1612 ($-\text{C}=\text{N}-$), 1596, 1508 ($-\text{ph}-$), 1340 ($-\text{NO}_2$). $^1\text{H-NMR}$ (DMSO- D_6) δ (ppm): 13.4 (1H, m, $-\text{C}=\text{N}-$, in imidazole), 8.8–8.2 (m, 8H, $-\text{ph}-$), 8.0–7.7 (m, 4H, $-\text{ph}-$), 7.2 (s, 2H, $-\text{NH}_2$).

Synthesis of 2-(4-aminophenyl)-4,5-diphenylimidazole (**2**)

Synthesis of 2-(4-nitrophenyl)-4,5-diphenylimidazole (**2a**)

A mixture of benzil (1.6 g), 4-nitrobenzaldehyde (1.2 g), ammonium acetate (10.6 g), and acetic acid glacial (50 mL) was

refluxed at 118°C for 4 h. Then the dark yellow solution was poured into ice water under stirring, and ammonia was added until a neutral pH was attained. The red precipitate was collected by filtration and washed several times with water. Following re-crystallization from dry ethanol, 2.2 g (92%) of **2a** was obtained as a dark yellow powder. IR (KBr): ν_{\max} (cm^{-1}): 1582, 1512, 1485, 1442 ($-\text{ph}-$), 1337 ($-\text{NO}_2$), 1601 ($-\text{C}=\text{N}-$); $^1\text{H-NMR}$ (DMSO- d_6) δ (ppm): 12.2 (1H, N—H), 8.4 (4H, s, $-\text{ph}-\text{NO}_2$), 7.2–7.8 (10H, m, $-\text{ph}$).

Synthesis of 2-(4-aminophenyl)-4,5-diphenylimidazole (**2**)

A mixture of **2a** (1.22 g) in ethanol/water (2:1 v/v, 50 mL), iron powder (1.57 g), and 38% HCl (1–2 drop) was refluxed at 80°C for 6 h. The iron scruff was removed by filtration before the filtrate was heated to boiling. The reaction agents were removed by distillation and drying to yield 0.8 g of **2**. IR (KBr): ν_{\max} (cm^{-1}): 3471, 3340 ($-\text{NH}_2$), 1608, 1509, 1480, 1445 ($-\text{ph}-$), 1633 ($-\text{C}=\text{N}-$); $^1\text{H-NMR}$ (Acetone- D_6) δ (ppm): 13.4 (1H, N—H), 6.8 (2H, s, $-\text{NH}_2$), 7.4–7.6 (10H, m, $-\text{ph}$), 7.8 (4H, $-\text{ph}-$).

Functionalization of SWNTs with imidazole derivatives (**3** and **4**)

A mixture of 96% H_2SO_4 (30 mL), SWNTs (20 mg), and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (20 g) was homogenized using an adjustable magnetic blender at a lower speed. Once the mixture was visibly dispersed (no large particulates were visible), the resulting imidazole derivative (**1** or **2**, 0.4 mmol) was added and homogenization was continued for 10 min in order to effectively disperse the imidazole throughout the mixture. This was followed by adding NaNO_2 (0.11 g) and azobisisobutyronitrile (AIBN, 0.06 g). The mixture was then placed in an oil bath at 80°C and homogenization was continued for 2 h. The suspension was poured over 100 g of ice, and the mixture was filtered using a 0.22 μm membrane. The functionalized products (**3** and **4**) were then washed with large amount of acetone and DMF, and then dried.

$^1\text{H-NMR}$ spectra were recorded on a Varian Unity AS600 spectrometer (600 MHz for ^1H). The chemical shifts were reported by using the residual solvent signal as an indirect reference to TMS: acetone- D_6 2.1 ppm (^1H), DMSO- D_6 2.4 ppm (^1H). Fourier transform infrared (FT-IR) spectra were recorded by using KBr as the background on a Perkin-Elmer Spectrum One spectrometer. Thermo gravimetric analysis (TGA) was obtained on a Perkin-Elmer TGA-7 Instrument. Samples of about 5 mg were heated at a rate of 10°C/min to 800°C under a flow of nitrogen. Raman spectra were recorded on a LabRAM HR 800 UV spectrometer equipped with a 632.8 nm He–Ne radiation. Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX) were obtained on a Philip Technai-20 instrument operating by depositing a dilute DMF solution of the raw materials and functionalized nanotubes, on a 200 mesh holey micro grid. Atomic force microscopy (AFM) images were taken on a Nanoscope IIIa instrument by depositing a dilute DMF solution of the materials on single crystal silicon. The electrochemical properties of pristine SWNTs and imidazole derivatives functionalized tubes were investigated in saturated solution of DMF containing 0.1 M $\text{nBu}_4\text{NClO}_4$ in an argon atmosphere on a CHI660A Electrochemical apparatus. IR and NMR spectra of the above imidazole derivatives were given at the Supporting Information.

RESULTS AND DISCUSSION

FT-IR spectra of the functionalized SWNTs were obtained to determine the chemical groups on the nanotubes. In the spectrum of the pristine SWNTs (Fig. 1(a)a and (b)a), the infrared absorption is extremely low. The typical FT-IR spectra of imidazole derivatives functionalized SWNTs (Fig. 1(a)b and (b)b) show some characteristic peaks, which are assigned as follows: The peaks at 3000–2900 and 1600–1400 cm^{-1} characterize the aromatic C—H symmetric stretches of phenyl groups attached to the SWNTs. The peak at about 1638 cm^{-1} (Fig. 1(a)b and (b)b) belongs to the —C=N— bend absorbs. And the peak at 1283 cm^{-1} (Fig. 1(a)b) is the characteristic peak of the nitril groups, which is similar to the spectrum of **1**.

Raman spectra, on the other hand, give confirmative evidence to the functionalization of SWNTs. Pristine SWNTs (seen in Fig. 2a) exhibit a stronger C—C tangential mode band at 1578 cm^{-1} (G) and a weak band at 1317 cm^{-1} (D) attributed to sp^3 -hybridized carbon in the hexagonal framework of the nanotube walls. After functionalization the disorder mode band near 1320 cm^{-1} (D) shows a significant enhancement in intensity (shown in Fig. 2b and c). However, a decrease in the relative intensities, using the G band (at 1584 and 1586 cm^{-1}) as an internal reference, of these bands was observed upon diazonium-based reaction. This behavior has previously been observed in some related systems.^[24] In addition, the G band is noticeably upfield shifted by about 8 cm^{-1} in the spectra of the **3** and **4**

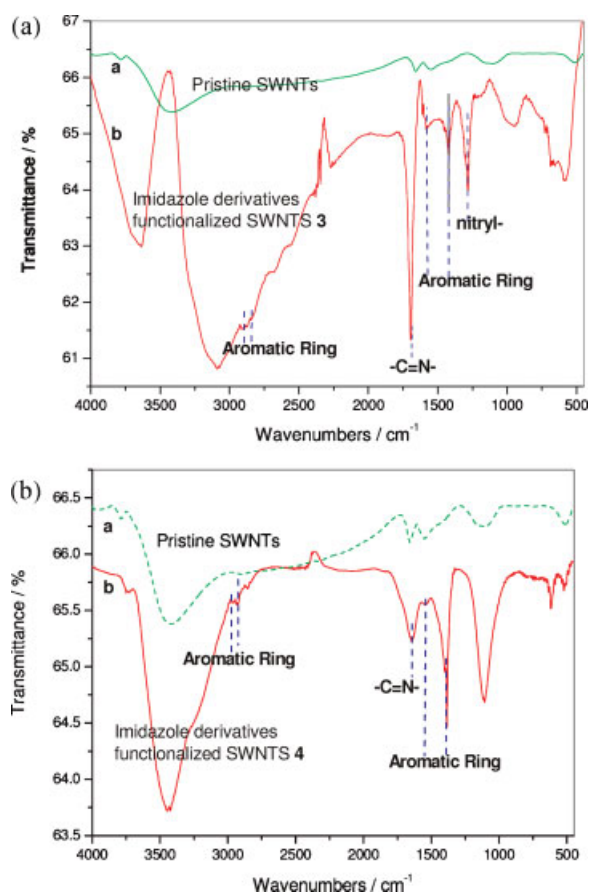


Figure 1. FT-IR spectra of the pristine SWNTs (dot line in (a) and (b)) and imidazole derivatives functionalized SWNTs (a) **3** and (b) **4** (solid line).

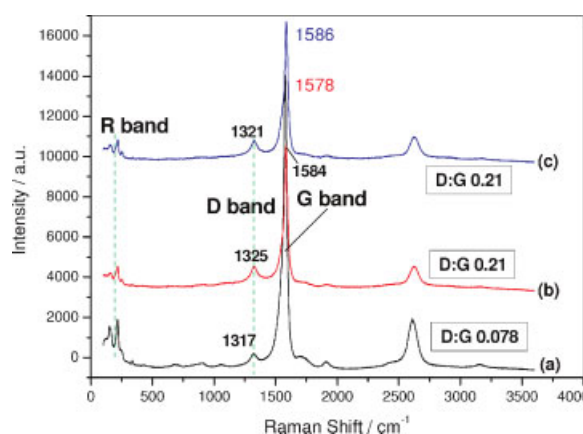


Figure 2. Raman spectra (excited by 632.8 nm radiation) of (a) the pristine SWNTs, (b) the imidazole derivatives functionalized SWNTs **4**, and (c) the imidazole derivatives functionalized SWNTs **3**

nanoconjugates relative to that seen in the pristine SWNT (Fig. 2a). The slight differences between the relative intensities of the D and G bands (seen in Fig. 2) give indications of the extent of disorder introduced in the functionalization steps. The D:G ratio is quite low in the pristine SWNTs, while the D:G ratio of the functionalized tubes **3** and **4** are significantly higher, as expected as the groups are attached to the sidewalls of the nanotubes.

Functionalization of the nanotubes has also been investigated by TGA under nitrogen. The TGA trace showed that the weight loss of the pristine SWNTs between 150 and 550 $^{\circ}\text{C}$ is only 3%, and the inflection at $\sim 500^{\circ}\text{C}$ indicates the tube decomposition (Fig. 3a), while the imidazole derivatives functionalized SWNTs **3** and **4** (Fig. 3b and c) exhibit a weight loss of 21 and 38% in the same temperature range. TGA indicates that both **3** and **4** nanoconjugates all show a similar behavior upon heating. As expected, the increased weight loss compared to their respective precursors comes from the covalent linkage of the imidazole derivatives moieties to the sidewalls of the nanotubes.

The two products were well dispersed in some organic solvents, extremely in DMF. Dispersed concentration of 0.75 mg/mL was obtained in DMF under sonication for 15 min (Fig. 4a). The

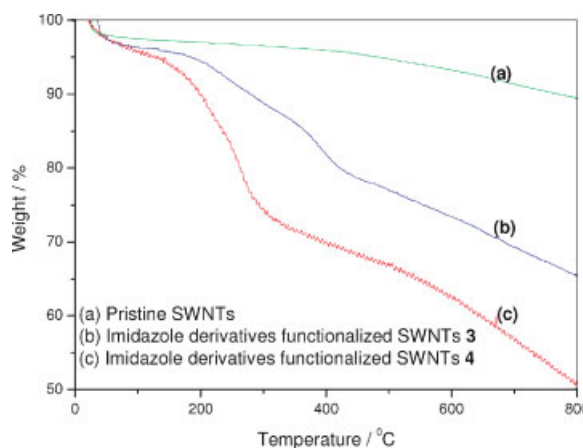


Figure 3. TGA of (a) the pristine SWNTs, (b) the imidazole derivatives functionalized SWNTs **3**, and (c) the imidazole derivatives functionalized SWNTs **4**

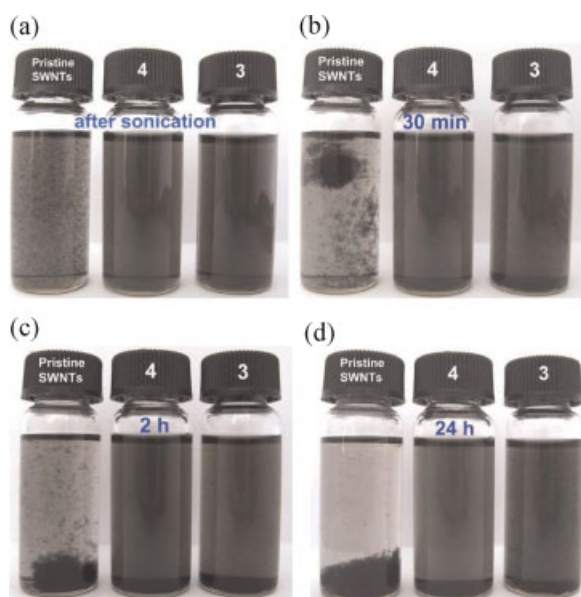


Figure 4. The optical images showing dispersion stability of (a) the pristine SWNTs and the functionalized SWNTs after sonication in DMF for 15 min, retaining (b) 30 min, (c) 2 h, and (d) 24 h

experiment of stability showed very few SWNTs precipitation after prolonged standing (24 h) under ambient conditions, whereas the pristine nanotubes precipitated, just after sonication, to the bottom of the container (seen in Fig. 4b–d).

Both functionalized SWNTs and pristine SWNTs were dispersed in DMF by ultrasonication used for ultraviolet visible (UV/Vis) measurement. The trace of pristine SWNTs (Fig. 5(a)a and (b)a) show the distinct van Hove singularities, which have recently been spectroscopically assigned by nanotube structure of individualized material. Upon covalent functionalization (disruption of the electronic structure), the electrons are localized and all of the transitions disappear (trace of imidazole derivatives functionalized SWNTs, **3** and **4**). The complete loss of singularities corresponds to the covalent functionalization, which disrupts the extended π -conjugation of nanotubes.

Complementary, EDX spectroscopy together with TEM determine the presence of the imidazole derivatives functional group (Fig. 6). EDX spectrum is a powerful tool for the analytical investigation of carbon-rich hybrid materials. The EDX spectrum of imidazole derivatives functionalized SWNTs shows that except from carbon and oxygen, nitrogen are detected as 5.3 and 2.9 wt% for **4** and **3**, respectively. The high-magnification TEM image (Fig. 6a and b, inset) shows the functionalized SWNTs with uneven, disorder sidewall, indicative of the imidazole derivative groups.

The presence of SWNTs in all the studied samples was corroborated by means of AFM analysis (Fig. 7), which permitted a more detailed insight into the imidazole derivatives functionalized SWNTs nanoconjugates. The samples were prepared by dispersing solution of imidazole derivatives functionalized SWNTs in DMF on single crystal silicon wafers. This technique allowed us to visualize very thin bundles (several hundreds of nanometers long and 3–10 nm in diameter) as well as individual tubes (1.5–3 nm in diameter). This characteristics are fundamentally different from those of the pristine SWNTs, which exhibit thick and long bundles exclusively even after sonication.

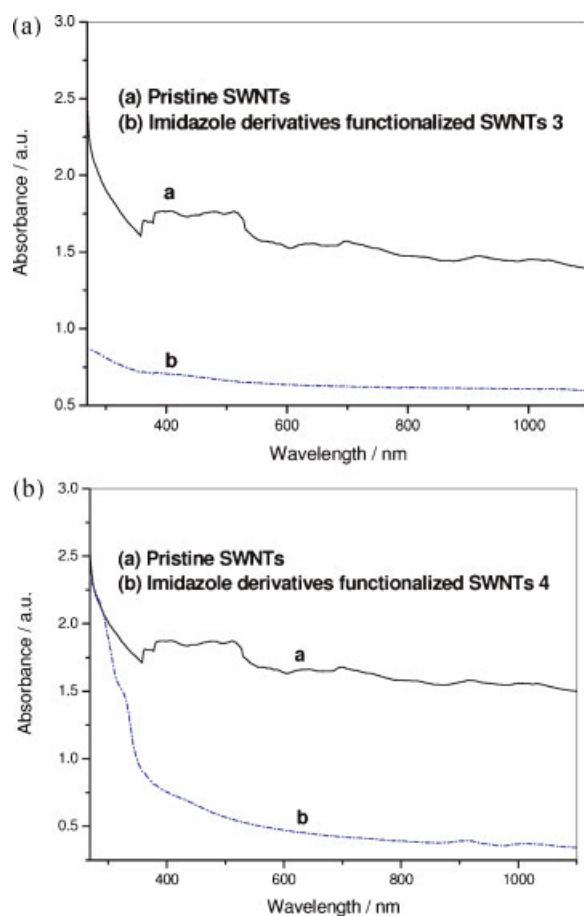


Figure 5. UV/Vis/NIR spectra of the imidazole derivatives functionalized SWNTs (a) **3** and (b) **4**

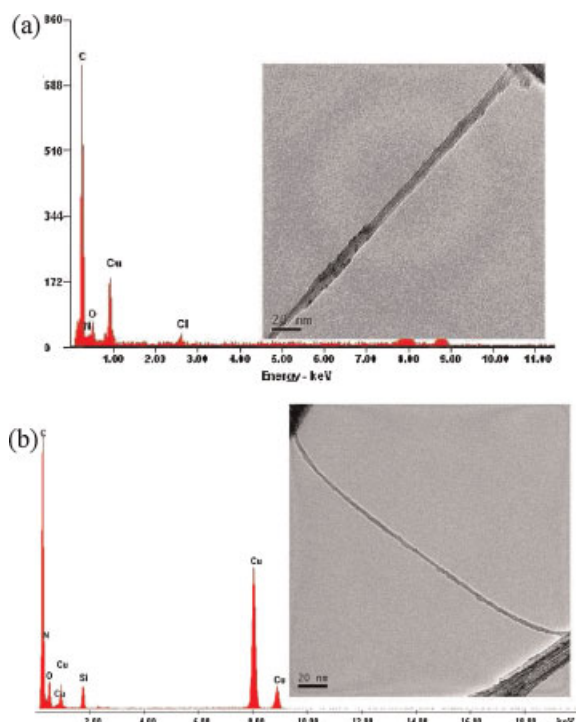


Figure 6. EDX spectra and TEM images (inset) of the imidazole derivatives functionalized SWNTs (a) **3** and (b) **4**

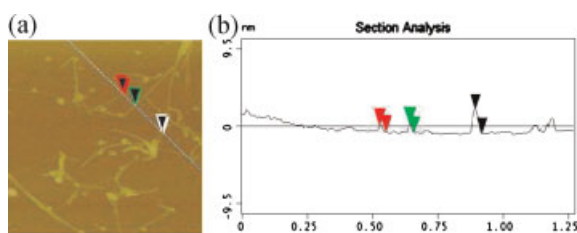


Figure 7. (a) AFM image of the imidazole derivatives functionalized SWNTs **4**; (b) section analysis of the functionalized SWNTs. The vertical distance is between 1.5 and 3.0 nm

The electrochemical properties of imidazole derivatives functionalized SWNTs (**3** and **4**) were investigated in saturated solutions of DMF containing 0.1 M $n\text{Bu}_4\text{NClO}_4$ in a nitrogen atmosphere. Comparing with the pristine SWNTs, the Cyclic voltammograms of imidazole derivatives functionalized SWNTs (**3** and **4**) display a continuum of diffusion-controlled cathodic

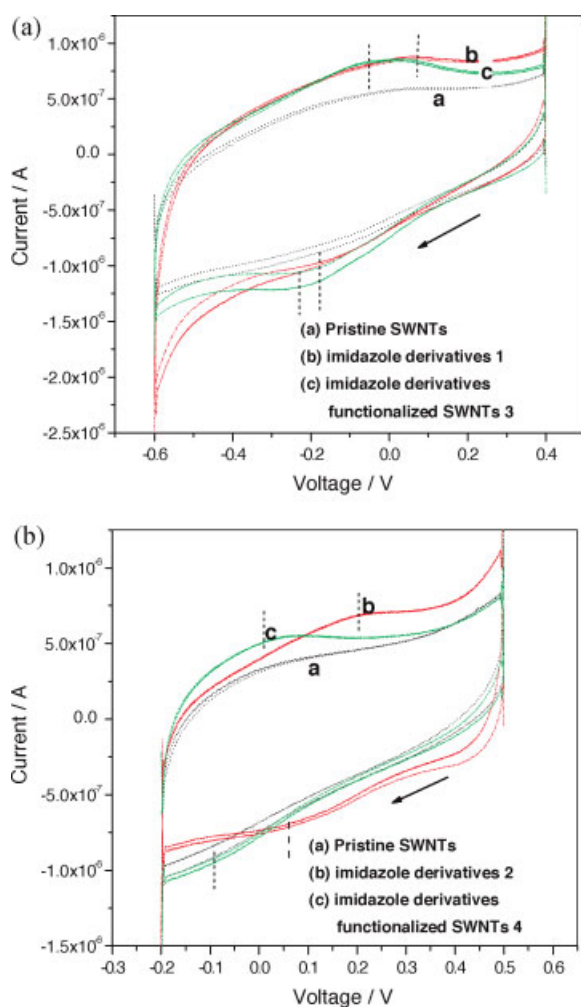


Figure 8. Cyclic voltammetry measurement of (a) the imidazole derivatives **1** and functionalized SWNTs **2**, (b) imidazole derivatives **2**, and functionalized SWNTs **4**. Saturated solution in a 0.1 M $n\text{Bu}_4\text{NClO}_4/\text{DMF}$ solution under N_2 , sweep rate 0.1 V/s, temperature 25 °C, a glassy carbon as a working electrode, Ag/AgNO_3 as a reference electrode, and Pt wire as a counter electrode

current, with an onset at around -0.184 and -0.025 V respectively, which is attributed to the reductive charging of the functionalized SWNTs where the tubes behavior as electron acceptor, and the imidazole derivatives groups behavior as electron donor.^[25] Single one-electron and chemically reversible oxidation processes are clearly discernible for **3** and **4**. We assign them to imidazole derivatives-centered processes, even though they are positively shifted relative to the reference systems (Fig. 8, imidazole derivatives **1** and **2**). These shifts are likely a result of weak intramolecular electronic interactions between the electroactive units in the nanoconjugates. In contrast, **3** and **4** reveal different potential-shifts ($\Delta\text{EA} < \Delta\text{EB}$, Fig. 8) for the single one-electron transfer reductions, which attributes to the strong acceptor groups ($-\text{nitril}$) on the imidazole derivatives substitutes of **3**. The $-\text{nitril}$ groups make the electron on the imidazole derivatives units of compound **3** not so easily transport to the SWNTs, so that the intramolecular electronic interaction of **4** is stronger than that of compound **3**.

CONCLUSION

We have described the synthesis, characterization, and electrochemical properties of imidazole derivatives functionalized SWNTs. The imidazole derivatives functional groups have been successfully attached onto the nanotubes surface by diazonium-based reaction, which is analyzed by their FT-IR, Raman, UV/Vis EDX spectroscopy, TGA curve, and demonstrated by TEM, SEM image. Importantly, voltammetry measurements results showed the intramolecular electronic interaction between SWNTs and imidazole derivatives functional groups.

Acknowledgements

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