

# Spectroscopic Evidence for $\pi$ – $\pi$ Interaction between Poly(diallyl dimethylammonium) Chloride and Multiwalled Carbon Nanotubes

De-Quan Yang, Jean-Francois Rochette, and Edward Sacher\*

Regroupement Québécois de Matériaux de Pointe, Département de Génie Physique, École Polytechnique, C.P. 6079, Succursale Centre-Ville, Montréal, Québec, H3C 3A7, Canada

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The interaction between multiwalled carbon nanotubes (MWCNTs) and aqueous poly(diallyl dimethylammonium) chloride (PDDA) was studied by X-ray photoelectron (XPS) and photoacoustic Fourier transform infrared (PA-FTIR) spectroscopies. We have found that the mild sonication of MWCNTs in aqueous PDDA results in a significant improvement of CNT dispersibility and greatly enhances their adhesion to Au and Si substrates. The MWCNT–PDDA interaction is due to the presence of an unsaturated contaminant in the PDDA chain, as confirmed by both XPS and PA-FTIR, which enters into a  $\pi$ – $\pi$  interaction with the CNTs. Electrostatic group repulsions of the coated CNTs then provide the dispersibility and adhesion.

## Introduction

From their discovery,<sup>1</sup> carbon nanotubes (CNTs) have been of great interest because of their unique structural, electronic, and mechanical properties. However, untreated CNTs show poor dispersibility in liquids and, as a result, are difficult to process, causing delays in their industrial applications (such as high performance CNT nanocomposites<sup>2,3</sup>). There are two main methods of improving the dispersibility: (1) Surface modification via extensive sonication, in the presence of aqueous acids,<sup>4</sup> leading to the introduction of –COOH groups on the CNTs; these groups hydrogen bond to the solvent and, at sufficiently high pHs, the –COO<sup>–</sup> groups formed also cause CNT–CNT repulsion. A major disadvantage of the process is the damage incurred by the CNTs during oxidation, which may result in the loss of their electronic and mechanical properties.<sup>4</sup> (2) Noncovalent bonding with dispersants, via either  $\pi$ – $\pi$  interactions<sup>5–8</sup> or electrostatic interaction between charged chemical groups.<sup>9–12</sup>

$\pi$ – $\pi$  interaction was proposed<sup>13</sup> as an explanation of the attractive interaction of molecules containing  $\pi$  orbitals, in the absence of spectroscopic evidence for HOMO–LUMO interactions. It is, in fact, an electrostatic interaction in which the offset and/or orientation of  $\pi$  orbitals on opposing molecules is such as to maximize the opposing  $\sigma$ – $\pi$  attractive interactions while minimizing the opposing  $\pi$ – $\pi$  repulsive interactions.

Water-dispersible CNTs are of particular interest because of potential biochemical and biomedical applications.<sup>14</sup> Poly(diallyl dimethylammonium) chloride (PDDA, Figure 1a) is a water-soluble quaternary ammonium polyelectrolyte, used in water treatment, paper manufacturing, and the mining industry, as well as in biological applications.<sup>15</sup> It has been found to improve the dispersibility of CNTs in water, and to aid in the formation of CNT thin films for various applications.<sup>9–11,16,17</sup> Those who hold that the interaction between PDDA and CNTs is electrostatic<sup>9–12</sup> consider it to be between the –COO<sup>–</sup> of the CNT and the positively charged PDDA polyelectrolyte backbone.

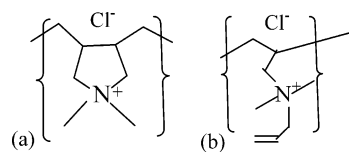


Figure 1. Chemical structure of (a) PDDA and (b) its contaminant.

Here, we report the use of aqueous PDDA in the sonication-aided dispersal of unoxidized (oxygen concentration <3 at %) multiwalled CNTs (MWCNTs). Our X-ray photoelectron (XPS) and photoacoustic Fourier transform infrared (PA-FTIR) spectroscopic data confirm the presence of  $\pi$ – $\pi$  interactions.

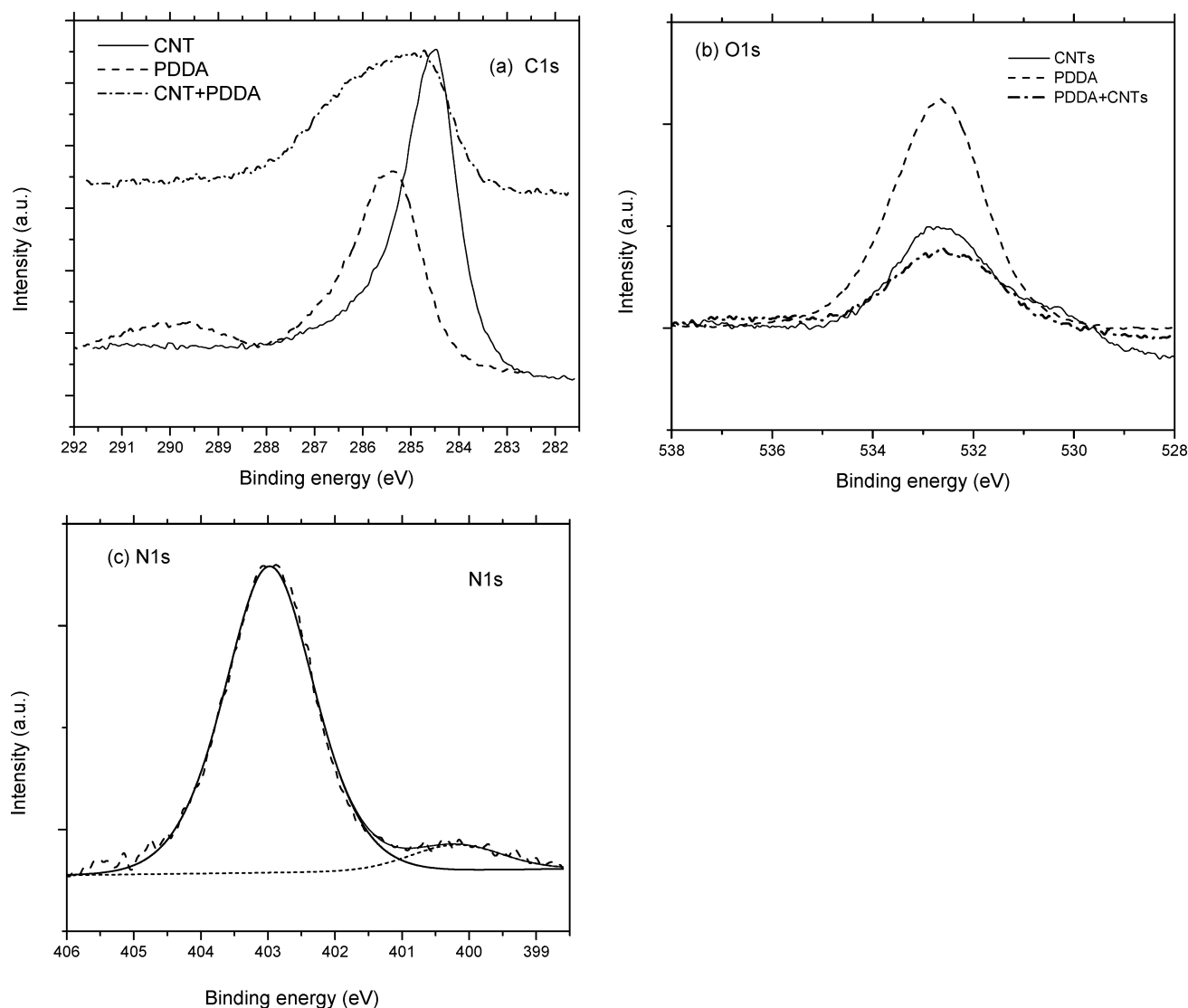
## Experimental Section

MWCNTs (95% purity, diameter 10–20 nm, length 1–5  $\mu$ m) were obtained from Nano-Lab, Brighton, MA. The PDDA (MW 200 000–350 000) was obtained from Aldrich-Sigma, St. Louis, MO, and diluted in deionized water. The mixture to be sonicated was prepared in a 10 mL vial, by adding 25  $\mu$ L of 20% aqueous PDDA and 0.5 mg of MWCNTs in 5 mL of deionized water. To create a homogeneous dispersion in the 0.1% PDDA solution, the mixture was sonicated for 15 min. Samples so produced were stable to agglomeration for at least several weeks. A thin layer deposited onto glassy carbon electrodes<sup>15</sup> showed good electrical behavior and functioned well as an electrochemical biosensor.

The samples for XPS analysis were prepared by dropping and drying onto the substrate (200 nm Au/10 nm Ti evaporated onto a native oxide-covered Si (100) wafer). The PA-FTIR samples were similarly deposited onto cleaned Si wafers. Sample drying was carried out in atmosphere for one week or under mechanical vacuum for 3 days.

XPS analysis was carried out in a VG ESCALAB 3 Mark II, using nonmonochromated Mg K $\alpha$  X-rays (1253.6 eV). The base pressure in the analysis chamber was less than 10<sup>–10</sup> Torr. High-resolution spectra were obtained at a perpendicular takeoff angle, using a pass energy of 20 and 0.05 eV steps, at an instrument resolution of  $\sim$ 0.7 eV. After Shirley background removal, the component peaks were separated by the VG Advantage V1.62 (Thermo VG Scientific) program. All peaks were energy

\* Address correspondence to this author. E-mail: edward.sacher@polymtl.ca. Phone: (514) 340-4711, ext. 4858. Fax: (514) 340-3218.



**Figure 2.** XPS results: (a) C1s spectra of PDDA, pristine CNTs, and their mixture; (b) O1s spectra of PDDA, pristine CNTs, and their mixture; and (c) N1s spectrum of the mixture.

calibrated to the Au4f<sub>7/2</sub> peak at 84.0 eV. Peak energies and widths previously found applicable were used for the separation of the spectral components.

PA-FTIR spectra were obtained using a He-purged MTEC 300 photoacoustic cell in a Bio-Rad FTS 6000 spectrometer, at a spectral resolution of 4 cm<sup>-1</sup>. The 5 kHz modulation frequency used probed the entire sample thickness.

## Results

C1s, O1s, and N1s XPS spectra are found in Figure 2. The C1s spectrum of the CNTs used here, Figure 2a, has been analyzed<sup>18</sup> and found to consist of four peaks, at the same energies, and with the same attributions, as those in highly oriented pyrolytic graphite (HOPG).<sup>19</sup> However, for reasons of comparison with PDDA, as is made clear in Table 1 and the accompanying text, we use here four peaks, at 284.5, 285.9, 287.3, and 291.5 eV. Changes in component positions on increasing the PDDA concentration in the PDDA/CNTs mixtures were all within experimental error ( $\pm 0.01$  eV).

The C1s spectrum of PDDA, in Figure 2a, was separated into three peaks (Table 1), at 286.0, 287.1, and 290.9 eV, the latter a shake-up. The positions of the major peaks are clearly in error for the following reasons: (1) The peak intensity ratio of the

**TABLE 1: C1s Component Peak Positions<sup>a</sup>**

CNTs	PDDA	(PDDA/CNT) <sup>b</sup>
284.5		284.6
285.9	286.0 (1) <sup>c</sup>	286.0
287.3	287.1 (0.22) <sup>c</sup>	287.1
291.5	290.9	

<sup>a</sup> Energy in eV. <sup>b</sup> Mixture made from 25  $\mu$ L of 20% aqueous PDDA and 0.5 mg of MWCNTs in 5 mL of deionized water. <sup>c</sup> Relative peak intensities.

major peaks, 1:0.22, makes no sense. (2) A perusal of the group inductive constant compilation in Table 1 of Hansch, Leo, and Taft<sup>20</sup> indicates that the inductive effect of quaternary amines is felt over long distances along carbon chains; this suggests the existence of multiple XPS peaks in the C1s spectrum of PDDA, differing in binding energy, for the  $\alpha$ -carbons, the  $\beta$ -carbons, etc. (3) A methylene group adjacent to a quaternary amine is more electronegative than a methyl group so attached,<sup>21</sup> suggesting that the  $\alpha$ -methyl and  $\alpha$ -methylene groups have XPS peaks at different energies. Unfortunately, our present ignorance of how best to separate the PDDA spectrum restricts our ability to proceed further.

The higher C1s binding energy of the PDDA spectrum is due to the presence of the positive charge at the N atom and its

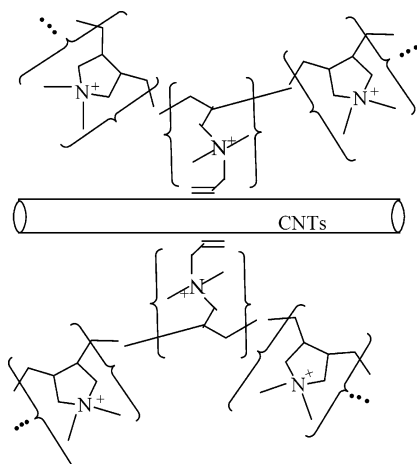


Figure 3.  $\pi$ - $\pi$  PDDA/CNT interaction.

TABLE 2: Relative Concentrations (atomic %)

samples	carbon	oxygen	nitrogen
pristine MWCNTs	97.4	2.6	0
PDDA	53.6	46.2	0.2
PDDA/MWCNTs	83.6	13.6	2.8

effect on the various C atoms of the repeat unit. The shake-up, evident in the PDDA spectrum at  $\sim 290$  eV, is due to the presence of  $\sim 2$ – $3\%$  of the unsaturated impurity in Figure 1b,<sup>22</sup> formed during the polymerization of the monomer: its presence indicates that the concentration of the impurity is sufficiently high for orbital overlap, permitting  $\pi^* \leftarrow \pi$  transitions to occur; such shake-up peaks are invariably found for unsaturated polymers.<sup>23</sup>

The C1s spectrum of the mixture, in Figure 2a, is composed of three peaks (Table 1), at the positions already found for both the CNTs and the PDDA, with the shake-up peak absent. The fact that no shake-up is visible for the mixture indicates that all the unsaturated impurity present in the mixture has bound to the CNTs; the shake-up peak of the CNTs, at  $\sim 291$  eV, is small, and difficult to see,<sup>19</sup> as is that of the CNTs in the mixture. The absence of a shake-up, even when the amount of PDDA is doubled (Table 1), indicates that, even here, all the unsaturated impurity is used to bond to the CNTs, presumably in the form seen in Figure 3, or that the unsaturated impurity in the bonded PDDA cannot participate in orbital overlap.

The O1s spectra are found in Figure 2b, where it is seen that not only are the MWCNTs partially oxidized by the presence of  $-\text{OH}$  and  $-\text{C}=\text{O}$  groups (the relative oxygen concentration is less than 3 atomic %)<sup>24</sup> but that PDDA also contains oxygen. This is, in fact, due to several factors: first, the instability of  $\text{Cl}^-$  in aqueous solution: over time, as indicated by our XPS spectral study, the N:Cl ratio diminishes as the  $\text{Cl}^-$  reacts with  $\text{H}^+$  and is lost as HCl gas (N:Cl for our PDDA solution was 16:1). PDDA chloride thus becomes PDDA hydroxide, the presence of whose  $-\text{OH}$  is manifested in the O1s peak. A second reason appears to be the large amount of water of hydration retained by the PDDA.

The O1s shoulder, at  $\sim 531$  eV, seen in the CNT spectrum, comes from the Au–O of the substrate,<sup>24</sup> seen through the cracks in the poorly wetting CNT film; its absence on PDDA treatment demonstrates the increased wettability resulting from the treatment. The superposition of the PDDA O1s spectra with that of the mixture indicates that the CNTs were not further oxidized to  $-\text{COOH}$  by the sonication.<sup>24</sup>

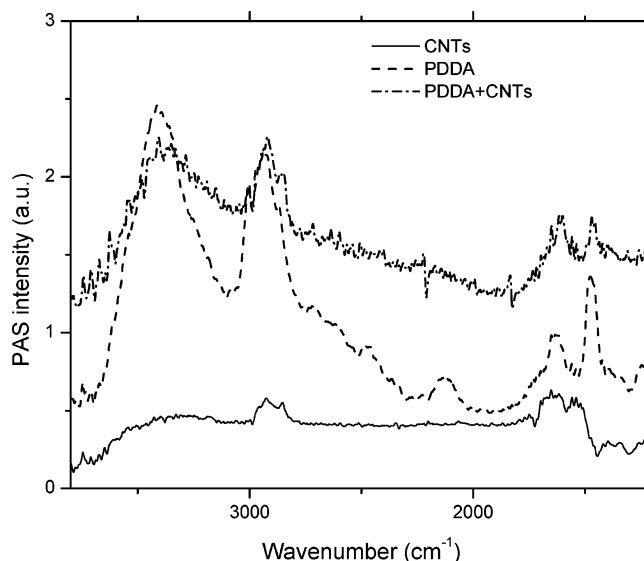


Figure 4. PA-FTIR spectra of PDDA, pristine CNTs, and their mixture.

TABLE 3: IR Peak Attributions

PDDA	CNTs	PDDA/CNT	attributions <sup>a</sup>
3417		3408, decrease	$\nu_{\text{OH}}$
3005–2750	2958–2852	3007–2850	$\nu_{\text{CH}_n}$
2124			?
1635	1649	1610	$\delta_{\text{C}=\text{C}}$
1476		1469, decrease	$\delta_{\text{C}=\text{C}}$

<sup>a</sup> Reference 26, in  $\text{cm}^{-1}$ .

The N1s spectrum of the mixture, in Figure 2c, shows a principal peak at  $\sim 403$  eV, due to  $\text{N}^+$ , and a second component, at  $\sim 400$  eV ( $\sim 7\%$  of the total), due to an uncharged side product; it is identical with the N1s spectrum of pure PDDA, which is omitted. Since the N atoms of both PDDA (Figure 1a) and its contaminant (Figure 1b) are positively charged, they cannot be distinguished using the N1s spectrum.

The relative concentrations of C, N, and O, for the three types of samples, were determined from the XPS spectra, using sensitivity factors previously determined. They are found in Table 2. The higher than expected oxygen concentrations for PDDA and the mixture confirm the presence of PDDA hydroxide and water of hydration. The unexpectedly high amount of water absorption in the PDDA, as seen in the relative oxygen concentrations for PDDA and the mixture, in Table 2, is due to the fact that PDDA is able to absorb up to several hundred times its volume of water.<sup>25</sup> As seen in Table 2, the relative concentration of N increases, from 0.2% in aqueous PDDA to 2.8% when mixed with MWCNTs. This is probable due to the decrease of PDDA hydration, as suggested by a corresponding decrease in the relative concentration of O, in also seen in Table 2.

The PA-FTIR spectra are found in Figure 4. The peak attributions<sup>26</sup> are found in Table 3, and are in partial disagreement with those previously published.<sup>27</sup> As expected, the PDDA hydroxide and water of hydration manifest a strong O–H stretching peak at  $\sim 3410$   $\text{cm}^{-1}$ , which persists in the mixture. What is particularly interesting is the loss of the unattributed peak, at  $\sim 2120$   $\text{cm}^{-1}$  on mixing; as well, there is a corresponding shift of the peak at  $1635$   $\text{cm}^{-1}$  to  $1610$   $\text{cm}^{-1}$ , along with an intensity decrease of the peak at  $\sim 1470$   $\text{cm}^{-1}$ , both latter peaks attributed to  $\delta_{\text{C}=\text{C}}$ . This indicates that the activities of these vibrational modes are reduced/modified in the mixture, due to PDDA–CNT interaction.

## Discussion

The evidence we have presented here makes untenable the suggestion<sup>9–12</sup> that PDDA-CNT interaction is electrostatic, between charged chemical groups. This evidence includes the following: (1) The retention of the C1s component of the CNT at 284.5 eV on mixing, which is not to be expected when  $\text{—COO}^-$  groups on the CNT are able to delocalize their charge into the alternant hydrocarbon structure of the CNT; indeed, one of the research groups suggesting electrostatic interaction<sup>11</sup> noted the unexpected paucity of  $\text{—COO}^-$  groups available on their single-walled CNTs, a situation we found to be true on our MWCNTs.<sup>24</sup> (2) The disappearance of the C1s shake-up of PDDA, on mixing with the CNTs, is unexpected for electrostatic interaction between charged chemical groups. Indeed, the disappearance of the shake-up constitutes direct evidence for  $\pi$ – $\pi$  interaction. (3) The PA-FTIR spectra of the CNTs and the mixture show the absence of  $\text{—COO}^-$  groups on the CNTs (expected at  $\sim 1730\text{ cm}^{-1}$ ), necessary for electrostatic interaction, and the presence of contaminant  $\text{C}=\text{C}$  unsaturation on the PDDA polymer (Figure 1b), which is involved in  $\pi$ – $\pi$  interaction with the CNTs.

Thus, the  $\pi$ – $\pi$  interaction of the PDDA and the CNT serves to coat the CNT with positively charged polyelectrolyte, which causes not only CNT-CNT electrostatic repulsion but also CNT hydrophilicity. In a similar fashion, the increased CNT adhesion to substrates, such as Au and Si, is due to the electrostatic interaction between substrate  $\text{Au-O}^-$  and  $\text{SiO}^-$  groups,<sup>24</sup> and the positively charged PDDA.

## Conclusions

We have demonstrated that the interaction of PDDA and CNTs is due to  $\pi$ – $\pi$  interaction, and serves to coat the CNTs with a polyelectrolyte that enhances dispersibility and substrate adhesion through subsequent electrostatic interactions.

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