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# A resonance Raman study of carboxyl induced defects in single-walled carbon nanotubes

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## ARTICLE INFO

### Article history:

Received 25 June 2008

Received in revised form

12 August 2010

Accepted 16 August 2010

### Keywords:

Carboxylation

Resonance Raman spectroscopy

Single-walled carbon nanotubes

Defects

Haeckelites

## ABSTRACT

Changes in the vibrational response of single-walled carbon nanotubes (SWCNTs) resulting from the introduction of structural defects on their body were studied using resonance Raman spectroscopy. Structural defects were introduced on the SWCNTs by subjecting them to carboxylation for different intervals of time. Various Raman modes were observed, including the D, G<sup>+</sup>/G<sup>-</sup>, G' modes, and new defect induced modes were identified. Weaker vibrational modes corresponding to Stone–Wales defects with specific structures known as Haeckelites were identified. These modes were compared with the theoretically calculated modes and correlated to O<sub>5,6,7</sub> and R<sub>5,7</sub> Haeckelite structures.

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## 1. Introduction

Carbon nanotubes possess metallic or semi-conducting properties depending on the angular symmetry of their graphene sheet [1–4]. While, conceptually, the conjugated structure is regarded as a singular  $\pi$ -continuum, nanotubes may possess many defects on their body. The presence of these defects can take away from the highly conductive (thermal or electronic) nature of the nanotubes [5]. The nanotubes become more reactive at these defect sites and, consequently, more prone to functionalization [1,6–8]. At the defect sites, bonds are formed through alteration of the  $\pi$ -continuum and the introduction of pentagons and heptagons known as Haeckelites.

These defects are subtle and only form a small part of the nanotube body. However, resonance Raman spectroscopy can be used to detect the presence of these structural defects [9]. Over the last few decades, spectroscopy has been extensively used in characterizing structures of carbon nanotubes [9]. Additionally, spectroscopy can be used to detect any changes in nanotube structure brought forth by chemical modifications made through self-assembly or conventional covalent bonding of the nanotubes with other molecules. Such chemical functionalization of nanotubes,

has changed the perception of this nanomolecular conducting wire and elevated the potential uses of nanotubes beyond basic transport into the realms of coating, transducers and sensors [10].

Purification processes such as hydrothermal treatment [11], microinflation [11,12], solvent extraction and chemical functionalization [23–25] are applied to the raw material of SWCNTs to remove residual catalyst and amorphous carbon. One of the most common processes used over the last decade is carboxylation, also known as acid treatment. However, this process not only removes amorphous carbon from the soot that contains nanotubes, but also introduces defects along the nanotube body. Therefore, it is important to identify these defects and understand the changes in nanotube properties brought about by their presence.

In this work we report the resonance Raman spectroscopic characterization of SWCNTs with defects induced by carboxylating the nanotubes for various periods of time. The position and intensity of the Raman modes, their line-shape analysis and the appearance of new defect induced modes are used to identify the structural alterations in the SWCNTs body.

## 2. Experimental

Pristine arc discharge SWCNTs (nanolegde) (10 mg) were acid-treated using 7 ml of concentrated sulfuric acid and 3 ml of concentrated nitric acid. The suspension was sonicated for

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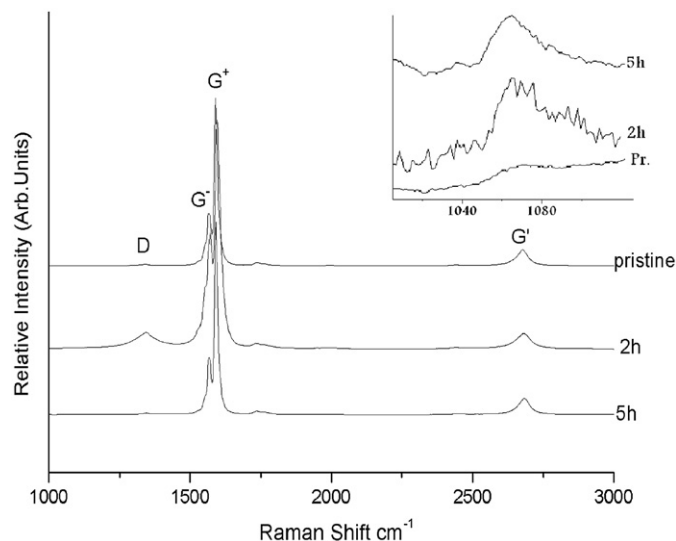
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different time periods (2 and 5 h). Following carboxylation, they were diluted by de-ionized water, filtered and washed with distilled water repeatedly until no acidity was observed. The residual material was collected, dried at room temperature and the normalized Raman spectra collected using the Renishaw Raman spectrometer (RE O2). All normalized peak parameters were obtained by least-square Lorentzian fitting line [1,7,13–15]. In order to monitor the change in the Raman spectra, three different laser wavelengths were used as the excitation source: Ar+ laser (514 nm, 2.41 eV, 20 mW), He-Ne laser (633 nm, 1.96 eV, 11 mW) and diode laser (785 nm, 1.58 eV, 380 mW). Their power was kept below 1 mW to avoid heating the samples. An acquisition time of 50s for each sample is used to allow for a reasonable signal to noise ratio in the Raman spectra. Raman spectra of five different spots on the sample were taken and averaged between 1000 and 3000  $\text{cm}^{-1}$ .

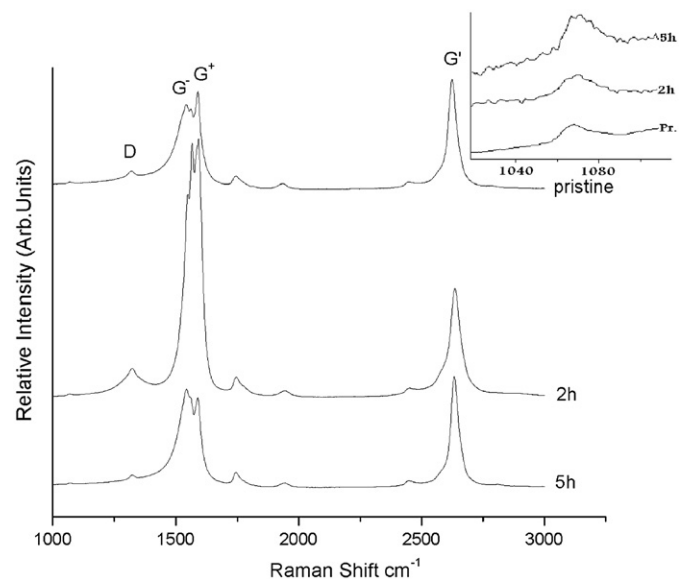
### 3. Analysis

#### 3.1. G modes

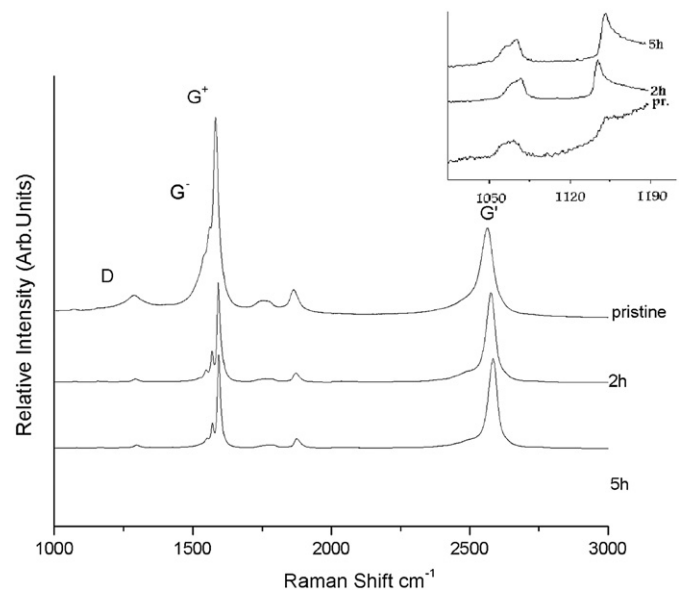
The tangential modes ( $G^+$  and  $G^-$  modes) observed for SWCNTs provide useful information regarding the composition of the SWCNT samples. Unlike graphite, where the G band is one broad peak, the G band for SWCNTs is split into several peaks (Figs. (1)–(3)) due to cylindrical tubular and curvature effect [16]. Although Raman positions of the tangential modes are not as sensitive toward SWCNT diameter as the RBM mode, their line shapes are highly revealing with respect to the type of nanotubes (semi-conducting or metallic) present [16]. Accordingly, a narrow and symmetric line shape has been assigned to resonances for semi-conducting tubes whereas broad and asymmetric profiles were due to metallic tubes [14,16,27–30]. Therefore, the line shape of the 2 h acid-treated sample indicates that semi-conducting nanotubes are in resonance with the 514 nm excitation laser line, while metallic nanotubes are in resonance with 633 nm excitation laser line (Figs. 1 and 2). The line broadening in the latter was attributed to the coupling between phonons and free electrons in the nanotubes with metallic characteristic which directly related to defects introduction to the nanotubes [16]. The intensity increase of the  $G^+$  band is attributed to the intercalation



**Fig. 1.** Raman spectra for the three samples in the range 1000–3000  $\text{cm}^{-1}$  at 514 nm excitation wavelength. The inset shows the Haackelite modes observed in the three samples.



**Fig. 2.** Raman spectra for the three samples in the range 1000–3000  $\text{cm}^{-1}$  at 633 nm excitation wavelength. The inset shows the Haackelite modes observed in the three samples.



**Fig. 3.** Raman spectra for the three samples in the range 1000–3000  $\text{cm}^{-1}$  at 785 nm excitation wavelength. The inset shows the Haackelite modes observed in the three samples.

of acid molecules among the nanotubes as well as the oxidative defects induced by the acid treatment. While, the most prominent shift in the  $G^-$  mode line can be observed for 5 h sample, which can be explained by the behavioral change of the G band. The G band developed from two structural components with single sharp peak to one structural component with strong Breit-Wigner-Fano (BWF) line showing a highly metallic behavior. This line shape modification could be related to a loss of the metallic character of the tubes that restored in the 5 h acid-treated sample [17].

Doping the nanotubes with acid causes an up shift in both the  $G^+$  and the  $G^-$  modes. The magnitude of the shift changes strongly with excitation energy, which depends on the specific type of the nanotube that is in resonance with the excitation energy (Table 1 [23,28,30]).

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