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Physico-chemical studies of amorphous carbon nanotubes synthesized at low temperature

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1. Introduction

Carbon nanotubes (CNTs) have undeniably attracted great attention since their early discovery [1,2]. CNTs appear to be one of the most important materials due to their unique structures, which gives extraordinary strength, excellent electrical properties and efficient thermal conductivity. Due to these unique properties, CNTs are suitable for a tremendously diverse range of applications. In addition, their optical properties are also significant, which leads to various optical and electronic applications [3]. Various growth techniques for CNTs such as arc discharge, laser vapourization, pyrolysis, plasma-enhanced and thermal chemical vapour deposition (CVD) have been well established [4-6]. Previous works were mostly focused on either multi-walled carbon nanotubes (MWCNTs) or single-walled carbon nanotubes (SWCNTs). However, conventional techniques such as arc discharge and CVD may also be employed to synthesize α -CNTs [7,8]. In addition, other methods have been developed which include anodic aluminium oxide (AAO) template and solvothermal methods. Catalysts are not required in these approaches. The dimensions of nanotubes such as diameter, length, graphitization degree and orientation of graphene layer can be manipulated by controlling the shape of the AAO template [9,10]. The solvothermal method has been used to obtain α -CNTs from ferrocene in benzene to significantly reduce

ABSTRACT

This work provides better understanding on the nature of amorphous carbon nanotubes, which are synthesized via a simple chemical route. Amorphous carbon nanotubes (α -CNTs) are successfully synthesized by heating a mixture of ferrocene and ammonium chloride at temperature as low as 200 °C and are treated with hydrochloric acid. Transmission and field emission scanning electron microscopy techniques are performed to examine the morphology and dimension of the samples. X-ray diffraction tests confirm the amorphous structure of the nanotubes. The Fourier transform infrared spectroscopy and Raman studies indicate that the treated α -CNTs consist of many defective walls and are more amorphous compared with the untreated α -CNTs. Ultraviolet–visible absorption studies reveal that the untreated and treated α -CNTs exhibit plasmon absorbance with high bandgaps of 4 eV and 4.35 eV, respectively.

the synthesis temperature. However, longer reaction duration and poisonous reagents are inevitable in this approach [11,12]. In general, requirements of high synthesis temperature and pressure, complicated processing steps, catalyst supports, longer synthesis period or expensive costs may still the major drawbacks arising from the above-mentioned techniques [7–13].

The optical properties of CNTs have been investigated for a relatively long time, which include absorption, photoluminescence and Raman characteristics [14,15]. However, the exploitation of the desirable optical properties of these nanoscopic carbon cylinders is necessary as the fundamental understanding of how these functional properties are affected by the morphological characteristics of the inherent CNTs remain elusive. Literature survey indicates that relatively few optical absorption studies are carried out and almost exclusively involve SWCNTs [6]. In comparison to crystalline CNTs, amorphous CNTs (α -CNTs) are gradually receiving attention due to their simple synthesis conditions. Additionally, α -CNTs have gained increasing interest due to their potential development in field-emission display devices and nanodevices such as gaseous adsorbents and catalyst supports. These applications are possible due to the defects within their amorphous walls [16,17].

The optical properties of CNTs typically possess several key features, from long to short wavelengths (low to high energy). The first spectral feature refers to vibrational transitions due to carbon–carbon bond stretches whereas the other pertains to vibrationally active modes in the infra-red (IR) [18]. Band-gap transitions have been observed at the near infra-red–visible–ultraviolet

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(NIR-vis-UV) regions within a wavelength range of 2500–350 nm, and are affected by both specific diameter and chiralities of CNTs. Strong absorptions are also present at significantly higher energy, i.e. in the UV and far-UV regions, due to plasmon resonance [19,20].

In this paper, α -CNTs are synthesized via a simple chemical route [16,17]. The low temperature synthesis is capable of eliminating the potential disadvantages associated with the aforementioned growth techniques. The goal of the present work is to examine the optical properties of α -CNTs using ultraviolet-visible (UV-vis), Fourier transform infrared (FTIR) and Raman spectrometers. Morphological, structural and elemental studies are also carried out by using transmission electron microscope (TEM), field emission scanning electron microscope (FESEM), energy-dispersive X-ray spectrometer (EDX) and X-ray diffractometer (XRD). The results are subsequently correlated with those obtained from optical studies.

2. Experimental

2.1. Materials and sample preparation

In this work, all as-prepared α -CNT samples were synthesized via a modified reduction process. Briefly, 8 g of ammonium chloride (NH₄Cl) and 16 g of ferrocene (Fe(C_5H_5)₂) were mixed homogeneously. The mixture was transferred into a Parr reactor, with a capacity of 125 mL. The Parr reactor was sealed and heated to 200 °C inside a furnace. The heating process was maintained at 200 °C for 30 min. Following this, the Parr reactor was cooled down to room temperature and the mixture was taken out and labelled "untreated α -CNTs". In addition, a portion of the untreated sample was soaked and washed with concentrated hydrochloric acid (HCl) (5 M), followed by methanol (CH₃OH) (99.8%) and purified water $(>15.0 \text{ M}\Omega \text{ cm})$ for several times. The sample was subsequently filtered and collected on a nylon filter membrane $(0.2 \ \mu m)$ with the aid of a pump. Dehydration was carried out using a vacuum oven at 80 °C for 10 h to obtain the final sample, which was labelled "treated α -CNTs". Both untreated and treated samples were then ready for further characterizations.

2.2. Characterizations

2.2.1. Morphological, elemental and structural studies

Both untreated and treated samples (α -CNTs) were observed under TEM and FESEM for qualitative analysis on their surface morphologies and microstructures. The TEM (LIBRA® 120, Germany) was operated at an accelerating voltage of 120 kV. The FESEM (AURIGA, ZEISS, Germany) was operated at an accelerating voltage of 10 kV, with a working distance of 3.5– 4.5 mm. The FESEM images were generated by a backscattered electron detector. An EDX spectrometer equipped in the FESEM was used for elemental analysis of the α -CNTs at room temperature. Structural analysis was carried out using XRD (SIEMENS D5000, German) with Cu-K α X-ray of wavelength 1.54056 Å at 60 kV and 60 mA. The diffraction was conducted with Bragg angles between 5° and 100°.

2.2.2. Optical studies

Ultrasonication was performed on a sample for 1 h using methanol as the solvent in order to provide better dispersion for the sample. The ultraviolet ray absorption was then recorded using UV–vis spectrophotometer (Cary Win UV 50, Australia). By using a 1 cm quartz cuvette, the optical absorption and transmittance measurements were then scanned at a slow rate over the range of 190–800 nm (ultraviolet, infrared, visible and adjacent regions). Raman characteristics of the α -CNTs were examined using Raman microscope (RENISHAW, United Kingdom). The He–Ne laser was excited on the nanotubes with a wavelength of 633 nm. FTIR spectroscopy (PerkinElmer, Spectrum 400, USA) was carried out within the range of 400–4000 cm⁻¹ to study the attachment of bonding groups in the nanotubes.

3. Results and discussion

3.1. FESEM, TEM and EDX results

Fig. 1 presents both low and high magnification FESEM images of nanotubes prior to treatment with hydrochloric acid, i.e. untreated α -CNTs [21]. The magnified structure can hardly be recognized as nanotubes as the structure has irregular shapes with a disordered arrangement. Some of the nanotubes agglomerated heterogeneously. Additionally, the surface of the nanotubes is rough, indicating the presence of many defects within the structure. However, it can be seen that the nanotubes have uniform diameters and open ends after being treated with diluted acid, as shown in Fig. 2. The nanotubes in this sample exist in bundles. The tubular shape of the nanotubes is more apparent due to the removal of residual reactants (Fe and NH₄Cl) by purification treatment with diluted acid.

Fig. 3 shows that the dominant element in both untreated and treated α -CNTs is carbon. Impurities such as Fe, O, N, and Cl elements are present in both samples and their respective weight percentages are presented in Table 1. It is expected that both N and Cl originate from the unreacted NH₄Cl compound (one of the starting materials) during reaction. The traces of Fe may have originated either from the ferrocene compound or from the inner body of the stainless steel Parr reactor. The presence of oxygen indicates that the samples are oxidized to some extent. The soaking



Fig. 1. FESEM images of untreated α -CNTs under different magnifications: (a) 5000× and (b) 20,000×.



Fig. 2. FESEM images of treated α -CNTs under different magnifications: (a) 10,000× and (b) 20,000×.



Fig. 3. EDX spectra of: (a) untreated and (b) treated α -CNTs.

and washing treatments substantially reduced the foreign elements such as N, Cl and Fe.

Fig. 4 shows the untreated α -CNTs at room temperature under different magnifications. The nanotubes have straight dimensions, whereby the outer and inner diameters of α -CNTs are estimated to be about 90 and 65 nm, respectively. The length of the nanotubes is about 8–10 μ m. The average length and diameter of the α -CNTs are in good agreement with the FESEM images (Figs. 1 and 2). The nanotubes are completely amorphous, which agrees well with the XRD patterns presented in Fig. 5. On the other hand, Fig. 4(a) indicates that the untreated α -CNTs are surrounded by the unreacted NH₄Cl salt, which corresponds to its XRD pattern shown in Fig. 5, where all diffraction peaks are attributable to the NH₄Cl phase (JCPDS 73-0365). This compound is removed after

Table 1

Weight and atomic percentage of elements within untreated and treated samples.

Sample		Elements				
		С	0	Cl	Fe	Ν
Untreated α -CNTs	wt%	43.78	9.92	12.20	23.98	10.12
	at%	63.27	10.77	5.97	7.45	12.54
Treated α -CNTs	wt%	82.30	6.02	10.18	1.50	0
	at%	90.85	4.99	3.81	0.36	0

soaking and washing with acid. Nanotubes are clearly observed (Figs. 2 and 4(b)) as the NH₄Cl phase is absent within the treated α -CNTs (Fig. 5). The XRD pattern of treated α -CNTs is very broad with low intensity, although some residual reactant of Fe₂O₃ is still present within the sample.

3.2. FTIR study

FTIR study was performed on the α -CNTs by fabricating pellets from their powders. Based on Fig. 6, both the treated and untreated α -CNTs exhibit peaks at 1360 and 1259 cm⁻¹, which correspond to C=O vibrational bands. Additionally, the peaks at 1588 and 1582 cm⁻¹ also indicate the presence of C=C vibrational bands due to internal defects [16]. An additional band in the 2800–3500 cm⁻¹ region is observed only in the treated α -CNTs, which corresponds to the presence of hydroxyl group (-OH). This band is associated with amorphous carbon, which forms bonds easily with oxygen and hydrogen. The OH peak may be due to exposure of the sample to air. The amorphous walls of the nanotubes have many defects, which absorb moisture conveniently. On the other hand, the OH peak for untreated CNTs is hardly observed due to the relatively lower intensity. This indicates that a lesser extent of amorphous walls was formed during growth for the untreated α -CNTs, since this sample is not completely amorphous (Fig. 5).



Fig. 4. TEM images under different magnifications: (a) untreated α -CNTs 10,000×, (b) treated α -CNTs 12,500× and (c) 31,500×.

3.3. Raman analysis

Fig. 7 shows the Raman spectra for both untreated and treated α -CNTs. It is apparent that two broad bands are present in the Raman spectra, which correspond to the D and G bands of graphite.





The D band appears at 1372 cm^{-1} for the untreated sample, and at 1350 cm⁻¹ for the treated sample. The D-band is attributed to the Raman-inactive A_{1g} in-plane breathing vibration mode. The Dband can be assigned to the vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite, and thus being associated with the presence of defects within the hexagonal graphitic layers [22]. The G band appears at 1576 cm⁻¹ in the untreated sample, and at 1570 cm^{-1} in the treated sample. The G band is attributed to the Raman-active E_{2g} in-plane vibration mode, which is related to the vibration of sp^2 bonding within the carbon atoms in a two dimensional hexagonal lattice, such as in a graphite layer. Nanotubes with crystalline structures consisting of hexagonal carbon lattice display the same vibration. [21,23]. For treated α -CNTs, the relative intensity of D-band is larger than that of the G-band. The G-band (1570 cm^{-1}) is also broader than that of the untreated α -CNTs. The intensity ratio for D-band to G-band (I_d / I_{g}) is also larger. Therefore, the treated α -CNTs are more amorphous since they have defective tube walls made of disordered carbon. In fact, the G-band is hardly observed, revealing that the treated α -CNTs have a higher degree of disorder after the soaking and washing treatment. The Raman spectra correlate well with the XRD spectra (Fig. 5).



Fig. 6. FTIR spectra of α -CNTs at room temperature.



Fig. 7. Raman spectra of α -CNTs at room temperature.

3.4. UV-vis analysis

According to the UV–vis transmittance spectra shown in Fig. 8, it is clear that overall, the transmittance intensity of the treated α -CNTs in solution is lower than that of the untreated α -CNTs. This shows that the treated α -CNTs are well-dispersed in the solution and have better dispersion characteristics compared to the untreated α -CNTs.

Both treated and untreated α -CNTs exhibit similar UV-vis behaviour as shown in Fig. 9. Both samples have intense absorption peaks at 256 nm (4.85 eV) and 253 nm (4.90 eV), respectively. The absorption energy for both samples is consistent with those in previous reports [14,24]. In general, both absorption bands are due to transitions between spikes in density of states within the electronic structure of the tubes. It is believed that the results are attributed to the π plasmon absorbance. This phenomenon is associated with collective excitations of π electrons which occur at around 310–155 nm (4.0–8.0 eV) in the CNTs' π - π * electron transition. In other words, this absorption peak is due to plasmon resonance in the free electron cloud of the nanotube π electrons [14,19,25].

The band gaps (E_g) for the α -CNTs were estimated using Tauc/ Davis–Mott model based on optical absorption measurements as this is an important parameter for opto-electronic applications [26]. In this model, the relation between E_g and optical absorption for an amorphous material is expressed by Eq. (1):

$$(\alpha h\nu)^n = B(h\nu - E_g) \tag{1}$$

where *B* is a constant, $h\nu$ is the photon energy of the incident light and *n* is the characterization index for the type of optical transition. The absorption coefficient (α) is defined by the Lambert–Beer law given by Eq. (2):

$$\alpha = -\ln\left(\frac{A}{t}\right) \tag{2}$$

where *A* is the absorbance and *t* is the sample thickness. The optical band gaps can be obtained from the extrapolation of the best linear portion of the curves for $(\alpha h\nu)^n$ versus $h\nu$, at α equals zero near the band edge region.

The presence of a metallic element (remaining Fe) in both samples is believed to modify the electronic states and optical transitions of the nanotubes, which results in allowed transitions rather than forbidden transitions [26]. Hence, an index value of n = 3 is selected to obtain a suitable Tauc and Davis–Mott plot for both samples, as presented in Figs. 10 and 11. The E_g for untreated α -CNTs is estimated to be 4 eV, which is lower than that of treated α -CNTs, having a value of 4.35 eV. Both samples are found to have higher bandgaps than that of crystalline nanotubes [27,28].



Fig. 8. UV-vis transmittance spectra for the α -CNTs at room temperature.



Fig. 9. UV-vis absorbance spectra of α -CNTs at room temperature.



Fig. 10. Tauc and Davis–Mott plots for $(\alpha h \nu)^3$ as a function of $h\nu$ for untreated α -CNTs.



Fig. 11. Tauc and Davis–Mott plots for $(\alpha h\nu)^3$ as a function of $h\nu$ for treated α -CNTs.

There are no absorption bands in the visible region, as observed in the wavelength range of 400–800 nm (Fig. 9). This behaviour differs from the observation of a previous study [15], whereby three small peaks were detected. In this study, the α -CNTs do not demonstrate Van Hove singularities (VHS). The initial density of the electronic states is low and thus, absorption of light does not occur at longer wavelengths [29]. VHS refers to well-spaced and symmetric structures that are not possible in amorphous nanotubes. Instead, VHS appears in the local density of states of SWNTs due to the one-dimensional (1D) nature of the conduction electron states [26].

4. Conclusions

 α -CNTs have been successfully synthesized via a relatively simple technique. TEM, FESEM and XRD observations confirm that the nanotubes with open ends are composed of amorphous structures. The nanotubes are found to have straight morphologies with a length of 8–10 μ m. The average inner and outer diameters are estimated to be approximately 65 and 90 nm, respectively. FTIR study shows the presence of both C=C and C=O bonds without any vibrational bands related to crystalline nanotubes. The detection of hydroxyl groups implies that the walls of the nanotubes are amorphous, with the introduction of numerous defects. A lesser extent of amorphous walls is formed for untreated α -CNTs. There is a higher degree of disorder in the structures (more amorphous) of the treated nanotubes after being soaked and washed with diluted acid, as indicated by the Raman spectra. This is attributed to the higher intensity of the D-band compared with the G-band. The α -CNTs demonstrate the π plasmon absorbance (E_{π}) phenomenon in the UV region, which is characteristic for most crystalline CNTs. The α -CNTs also have a higher estimated bandgap compared to crystalline CNTs.

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