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Surface functionalization of multi-walled carbon nanotubes via electron reduction of benzophenone by potassium metal

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ABSTRACT

The covalent sidewall functionalization of multi-walled carbon nanotubes (MWCNTs) via the electron reduction of benzophenone by potassium metal is reported. Fourier transform infrared spectroscopy (FTIR) results show that diphenylcarbinol (DPC) groups were successfully grafted to the MWCNTs sidewalls after 10 days of reaction time. Raman and UV–vis spectroscopies reveal the presence of covalent sidewall functionalization. The percentage of residues for DPC-MWCNTs was found to be lower than that for pristine MWCNTs, which indicates the existence of functional groups on the sidewalls of DPC-MWCNTs. It is shown that the sidewall of the DPC-MWCNTs was covered by non-uniform layer of DPC, as observed by transmission electron microscopy (TEM). Results from Raman spectroscopy, FTIR, TGA, UV–vis spectroscopy and TEM confirm that the functionalization of the covalent sidewalls of MWCNTs was successfully performed by this method.

1. Introduction

Carbon nanotubes (CNTs), discovered in 1991 [1] by Iijima, are of keen interest to material scientists due to their remarkable physical, mechanical, chemical and electronic properties, which exceed those of many other materials [2–5]. Such properties make carbon nanotubes ideally suitable as the “ultimate material” for next-generation composites [6]. These properties are attractive for applications in many scientific and technological fields, such as polymer composites [7], electronic structures [8] and biological systems [9]. Although several studies have focused on producing nanocomposites [2–4], many practical challenges concerning their properties remain, compromising the full realization of their enormous potential. For example, many experiments indicate that carbon nanotubes in composites are weaker or only slightly stronger than the neat matrix [10]. This has been found to be primarily due to a combination for several factors, namely poor CNT dispersion, inadequate alignment, and weak interfacial bonding [11]. It was reported that covalent sidewall functionalizations can be used to overcome some of these difficulties [11,12].

In order to improve the properties of CNTs, several methods for sidewall functionalization have been developed, such as the addition of carbine [13], fluorine [14] and potassium. Covalent sidewall functionalization of single wall carbon nanotubes (SWCNTs) by one-electron reduction of benzophenone by potassium has been carried out by Wei and Zhang [15]. This functionalization process is reported to have successfully introduced diphenylcarbinol groups onto the sidewalls of the nanotubes. In this study, a similar method was repeated on multi-walled carbon nanotubes (MWCNTs), and due to the slight differences between SWCNTs and MWCNTs, the optimal reaction time has also been investigated.

2. Experimental

2.1. General

Multi-walled carbon nanotubes (MWCNTs) with a purity of >95%, outer diameters of <10 nm and lengths of 1–2 μm were supplied by ShenZhen Nanotech Port Co., Ltd., China. The chemicals used in this study were toluene (supplied by J.T. Baker), benzophenone (supplied by Fluka) and potassium, ethanol and dried ethanol (supplied by Merck). Structural characterization of MWCNTs was done using a Renishaw invia Raman Spectroscope. Ar^+ lasers with a wavelength of 514 nm were used to characterize the functionalized MWCNTs and pristine MWCNTs. FTIR spectra in KBr pellets were recorded on a PerkinElmer Spectrum One FTIR spectrometer. Thermal study was carried out using thermogravimetric analysis (TGA) (PerkinElmer Pyris 6 instrument) at a heating rate of 10 °C/min in a nitrogen environment. Ultraviolet–visible (UV–vis) spectra were measured using a PerkinElmer Lambda 35 UV–vis spectrometer. The morphology of the samples was analyzed by transmission electron microscopy (TEM), with a Philips CM12 equipped with an analysis Docu Version 3.2 image analysis system.

2.2. Preparation of diphenyl-carbinol-functionalized MWCNTs (DPC-MWCNTs)

A solution consisting of 30 mg of MWCNTs and 40 mg of potassium (40 mg) in 150 ml toluene was ultrasonicated for 10 min, and then 0.179 g of benzophenone were added to the solution. The mixture was stirred at 80 °C in a nitrogen environment for 12 h. Afterwards, an additional 255 mg of benzophenone and 56 mg of potassium were added to the mixture. The mixture was further stirred for 5 days and 10 days at 80 °C and cooled at room temperature. Dried ethanol was then added to

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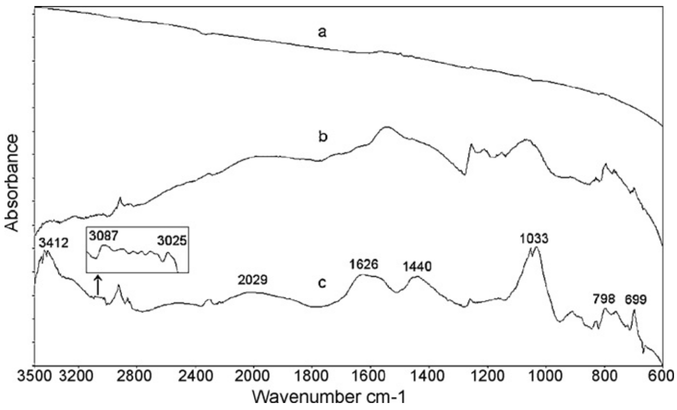

Fig. 1. FTIR spectra of (a) Pristine MWCNTs, (b) DPC-MWCNTs (5 days) and (c) DPC-MWCNTs (10 days).

stop the reaction. The mixture obtained was filtered and flushed with a large amount of ethanol and water. The resulting functionalized MWCNTs were collected and then dried in a vacuum oven at 80 °C. The reaction products were characterized by Raman scattering, UV–vis, FTIR, TGA and TEM.

3. Results and discussion

In order to determine a suitable reaction time for the MWCNT surface functionalization process, FTIR was utilized to measure the possible bonding on the nanotubes surface. Two samples with different reaction times were investigated in this study, which were reacted for 5 days and 10 days. Fig. 1 exhibits the FTIR spectroscopy of pristine MWCNTs and DPC-MWCNTs reacted for 5 days and 10 days. Fig. 2 shows the possible interaction mechanism between DPC-MWCNTs. For functionalized of MWCNTs reacted for 10 days (Fig. 1(c)), many peaks were observed, which are related to possible bonding at the surface of the MWCNTs. The weak C–H stretching vibrations in the 3000–3100 cm^{-1} range are characteristic of the phenyl groups of DPC in functionalized MWCNTs. The band at 3412 cm^{-1} can be ascribed to O–H stretching of the grafted DPC. Several absorptions in the 1600–2000 cm^{-1} range are a fingerprint, which is assigned to the phenyl-ring substitution overtones [16]. Absorption at 1440 cm^{-1} is assigned to phenyl ring stretching [15]. The band at 1033 cm^{-1} was ascribed to the C–O stretching vibration. Furthermore, several absorptions in the 675–870 cm^{-1} range are assigned to phenyl ring substitution bands [16]. For the 5-day functionalization process sample (Fig. 1(b)), no obvious peaks were observed at 3412 and 1033 cm^{-1}, which refer to O–H and C–O stretching vibrations, respectively. This indicates that a 5-day reaction time for this functionalization process is insufficient. Hence, the following characterization by Raman spectroscopy, UV–vis spectroscopy, TGA and TEM will focus on the sample prepared for 10 days.

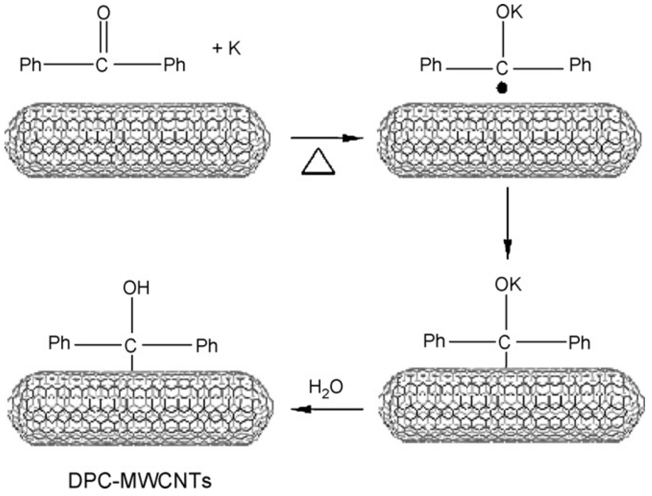

Fig. 2. Chemical reaction for the preparation of DPC-MWCNTs [15].

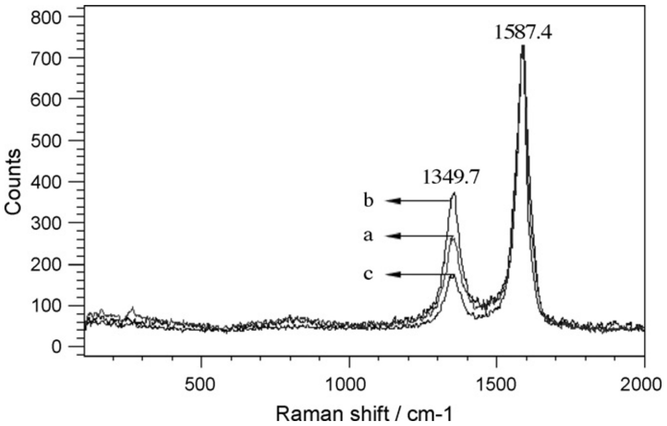

Fig. 3. Raman spectra of: (a) Pristine MWCNTs, (b) DPC-MWCNTs and (c) DPC-MWCNTs after TGA.

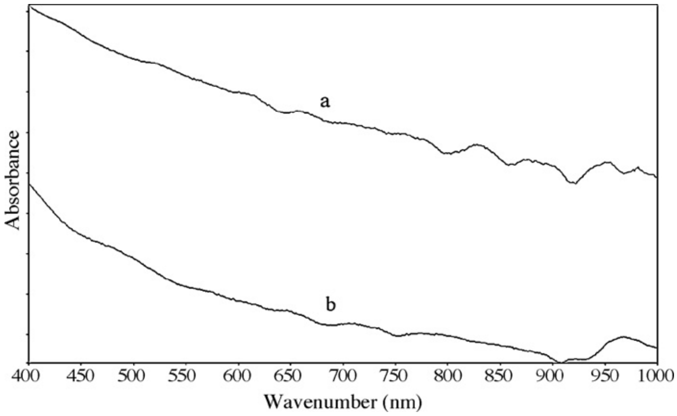

Fig. 4. UV–vis absorption spectroscopy in dimethylformamide: (a) Pristine MWCNTs and (b) DPC-MWCNTs.

Fig. 3 shows the Raman spectra of (a) pristine MWCNTs and (b) functionalized MWCNTs (DPC-MWCNTs). Sample (c) refers to functionalized MWCNTs (DPC-MWCNTs) after heating in a nitrogen

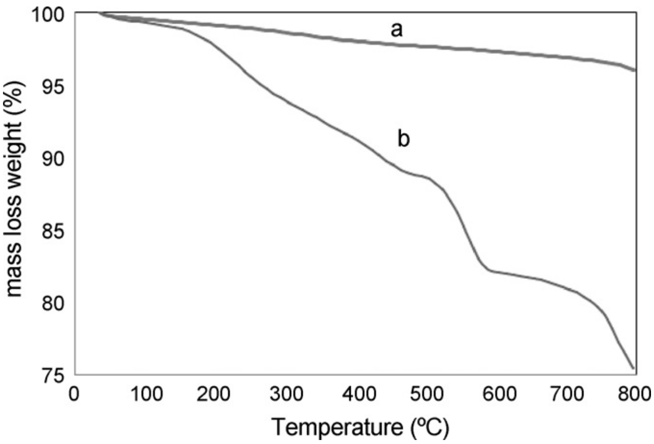

Fig. 5. TGA result for (a) Pristine MWCNTs and (b) DPC-MWCNTs.

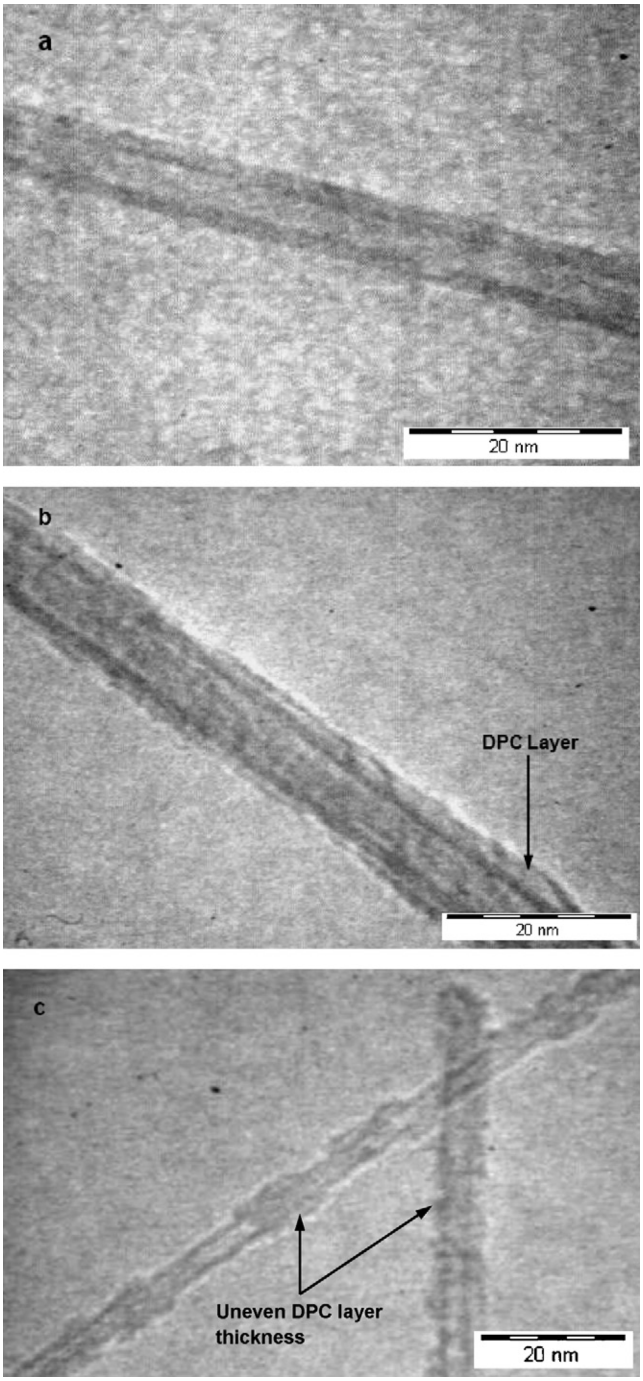

Fig. 6. TEM image of (a) Pristine MWCNT (at ×100k magnification), (b) DPC-MWCNT (at ×100k magnification) and (c) DPC-MWCNT (at ×60k magnification).

atmosphere to remove the surface functionalized materials on the carbon nanotubes. In general, it is observed that these three samples exhibit a tangential mode (G band) at 1587.4 cm^{-1} and a disorder mode (D band) at 1349.7 cm^{-1}; however, the latter has a different intensity of the D band. It has been reported that the intensity of the D band is generally governed by the presence of amorphous carbon, graphitic impurities [17] and sp^3 hybridized carbon atoms in the benzenoid framework of the carbon nanotube walls. In general, the D band is widely used to measure covalent sidewall functionalization [15]. The higher D band intensity of the DPC-MWCNTs, sample (b), is greatly increased compared to samples (a) and (c); it has been reported that this is due to the many sp^3 defects that exist on the sidewalls of MWCNTs [15]. On the other hand, the Raman spectrum for sample (c) exhibits the lowest intensity D band, suggesting a restoration of the pristine structure upon heating [15].

Fig. 4 shows the UV–vis absorption spectroscopy results for pristine MWCNTs and functionalized MWCNTs (DPC-MWCNTs). It is observed that the Van Hove singularities are found to be weak after functionalization of MWCNTs, which is not true of the pristine MWCNTs. The weakening of the Van Hove singularities in DPC-MWCNTs indicates quite a substantial sidewall functionalization [18]. The degree of funtionalization was measured by TGA and is shown in Fig. 5. It is observed that the weight loss of the pristine MWCNTs and DPC-MWCNTs at 800 °C is 4% and 24.5%, respectively. It is apparent that the thermal stability of DPC-MWCNTs is lower compared to pristine MWCNTs. This is in accordance with previous work [12,19], where it was reported that increased weight loss and decreased thermal stability can be attributed to the presence of functional groups on the sidewalls of DPC-MWCNTs.

TEM images of pristine MWCNTs and DPC-MWCNTs are presented in Fig. 6. Pristine MWCNT exhibit smooth surface (as shown in Fig. 6a). After modification and reaction, the surface of the individual MWCNT (Fig. 6b and c) is found to be wrapped by an uneven layer of DPC, indicating that the DPC successfully attached to the sidewall.

4. Conclusions

Functionalization of MWCNTs using one-electron reduction of benzophenone by potassium has been investigated in this study. With this method, the covalent sidewall of multi-walled carbon nanotubes was successfully functionalized by diphenylcarbinol, as confirmed by Raman scattering, UV–vis spectroscopy and FTIR. TEM images indicated the existence of a non-uniform DPC layer on the surface of the MWCNTs.

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