Covalent sidewall functionalization of single-walled carbon nanotubes via one-electron reduction of benzophenone by potassium

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Abstract

We report a method for covalent sidewall functionalization of single-walled carbon nanotubes via one-electron reduction of benzophenone by potassium. The reaction of a potassium atom with a benzophenone molecule results in transferring one electron from the potassium to the benzophenone, forming a radical anion, which adds readily to nanotubes. Raman and UV–vis spectroscopy confirm unambiguously that covalent functionalization has taken place. ATR-FTIR spectroscopy shows that diphenylcarbinol groups have been grafted onto the sidewalls of nanotubes. The degree of functionalization was measured by thermogravimetric analysis (TGA).

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1. Introduction

Single-walled carbon nanotubes (SWNTs) have been intensively investigated over the last several years due to their unique chemical and physical properties [1]. However, realistic application of these materials has been limited by many difficulties [2], such as poor solubility and weak adhesion with other materials. Covalent sidewall functionalizations can be used to overcome some of these difficulties [3]. As compared with fullerenes, the reactivity of the sidewalls of nanotubes is much lower due to the significantly lower sidewall curvature [4]. Only relatively harsh reaction conditions or ‘hot’ addends are suitable for covalent sidewall attacks to SWNTs [4]. Several methods for sidewall functionalization have been developed, such as addition of fluorne [5], carbenes [6] or azomethine ylides [7]. Addition of radicals generated from organic peroxides [8], 4-methoxyphenylhydrazine [9], heptadecafluorooctyl iodides [10] or diazonium salts [11] has also been reported. Despite these impressive progress, a simpler, cheaper and more convenient method is still appealing. We report here the covalent functionalization of SWNTs via one-electron reduction of benzophenone by potassium, as outlined in Fig. 1. The reaction of a potassium atom with a benzophenone results in transferring one electron from the potassium to the benzophenone, forming a radical anion [12], which adds readily to nanotubes. This method is simple, and the reactant is easily accessible. The resultant diphenylcarbinol-functionalized SWNTs (DPC-SWNTs) offer a wider variety of possible reaction for further modification.

2. Experiments

The purified SWNTs used (Aldrich Co.) have an average diameter of 1.1 nm with high purity (≥90%). In a typical experiment, SWNTs (30 mg) and potassium (40 mg) in 150 ml toluene were transferred into a flask. After the solution was sonicated for 10 min, 0.179 g of benzophenone was added. The mixture was stirred at 80 °C under N2 for 12 h, and then additional benzophenone (255 mg) and potassium (56 mg) were added. The mixture was further stirred for four days at 80 °C and then cooled at room temperature. Anhydrous ethanol was added to stop the reaction. The obtained mixture was filtered and flushed with a large amount of ethanol and water. The resulting
Functionalized SWNTs were collected on a glass flake and then dried in vacuum at 80°C. The reaction products were characterized by Raman scattering, UV–vis spectroscopy, ATR-FTIR and thermogravimetric analysis (TGA).

3. Results and discussion

Raman spectroscopy is a powerful tool for characterization of both SWNTs and their covalent sidewall derivatives [13]. The purified SWNTs exhibit a tangential mode at 1560 cm⁻¹ (G band) and diameter-dependent radial breathing modes (RBMs) at 140–253 cm⁻¹ (Fig. 2). The disorder mode at 1313 cm⁻¹ (D band), attributed to sp³ hybridized carbon atoms in the benzenoid framework of the carbon nanotube walls [6], is widely used as a measure of covalent sidewall functionalization. After functionalization (Fig. 2b), the intensity of the D band was greatly enhanced. This increase in D band intensity is due to the covalent binding of the addends leading to many sp³ defects in the sidewalls [4]. Fig. 2 also shows that after heating the DPC-SWNTs in N₂ atmosphere to remove the addends, the intensity of D band dramatically decreases, suggesting the restoration of the pristine structure upon heating [14]. This observation is in accord with previous reports on the covalent sidewall functionalized SWNTs [14,15]. The RBM bands (140 cm⁻¹ and 253 cm⁻¹) become weak after functionalization (Fig. 2b), probably because the addition of the functional groups disrupts the radial breathing oscillation of the nanotubes [13,16]. A RBM band at 218 cm⁻¹ was observed in the DPC-SWNT samples upon 632.8 nm excitation (Fig. 2b), indicating the presence of nanotube bundles in the DPC-SWNT samples [17,18].

The covalent sidewall functionalization of SWNTs was also evidenced by UV–vis absorption spectroscopy in dimethylformamide (Fig. 3). Unlike the purified SWNTs, the van Hove singularities are absent in the spectrum of DPC-SWNTs. The loss of the van Hove singularities is indicative of covalent sidewall functionalization [14].

The degree of functionalization was measured by TGA (Fig. 4) in the 50–800°C range (nitrogen flow, ΔT = 10°C/min). For purified SWNTs, the weight loss of 6% is attributed to the removal of the oxidized carbon groups in the purified SWNTs [9]. The overall weight loss is 16.5% for the DPC-SWNTs. The increased weight loss (10.5%) is attributed to the presence of functional groups (DPC) on the DPC-SWNTs. The degree of coverage is not high (about 1 DPC in 120 carbon atoms). However, one grafted DPC molecule can provide three functional groups (two phenyl groups and one carbinol group). This endows DPC-SWNTs with a wider variety of possible reaction for further modification, for example, the carbinol groups could be further derivatized by esterification, and the phenyl groups could be sulfonated in oleum.

FTIR spectroscopy using an ATR accessory has proven to be very informative for studying the functional groups attached to the sidewalls of SWNTs [13]. Fig. 5 shows the ATR-FTIR spectroscopy of DPC-SWNTs. The weak
C–H stretching vibrations in the 3000–3070 cm\(^{-1}\) range are characteristic of the phenyl groups of the DPC in the functionalized samples. The band at 3330 cm\(^{-1}\) is ascribed to the O–H stretches of the grafted DPC, and several absorptions in 1400–1600 cm\(^{-1}\) are assigned to phenyl ring stretches [19]. The band at 1150 cm\(^{-1}\) was ascribed to the C–O stretching vibration, and the band at 1210 cm\(^{-1}\) was assigned to C–O stretching or the O–H bending mode [20,21]. These evidences further confirmed the attachment of DPC onto the sidewalls.

In summary, we successfully developed a simple method for covalent sidewalls functionalization of SWNTs via one-electron reduction of benzophenone by potassium, as confirmed by Raman scattering, UV–vis spectroscopy, TGA and ATR-FTIR. A wide variety of radical anions can be generated via one-electron reduction of ketones by reducing metals [12,22]. In principle, these radical anions are also feasible for functionalization of SWNTs, which could lead to a large variety of functionalized SWNTs. The attached diphenylcarbinol groups are suitable for further modification. Further functionalization of DPC-SWNTs and incorporation of them into polymer matrix are under investigation currently.

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