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A facile method to modify carbon nanotubes with nitro/amino groups

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ABSTRACT

Nitro groups (–NO_2) have been introduced on the surface of multi-walled carbon nanotubes (MWCNTs) by treatment with a mixture of concentrated H_2SO_4/HNO_3 solution at low temperature (60 °C). Such a low-temperature treatment simultaneously can well prevent MWCNTs from the structural damage. From the nitro-modified MWCNTs, MWCNTs can be readily modified with amino groups by reduction of nitro groups. The prepared amino-modified MWCNTs are highly soluble in polar solvents such as dimethylformamide (DMF), alcohol and acetone. Further, as a demonstration, MWCNTs can be functionalized with guest objects, provided by the strong bonding ability of amino groups.

1. Introduction

Carbon nanotubes are found to be extremely promising materials in various fields such as nanoelectronics, catalysis, material science and biological system, due to their unique electronic, chemical and mechanical properties [1–4]. In many applications, the introduction of functional groups on CNTs is necessary. For CNT-reinforced polymer composites, the organic groups on CNTs can improve the dispersion and homogeneity of the CNTs within the host ploymer and can efficiently enhance the nanotube–polymer interaction [5–8]. For CNT-supported catalysts, the functionalities are highly useful for anchoring active objects and/or creating catalytic centers [9,10]. When CNTs are employed in biological field, the functional groups on them can be used to immobilize bioguests [11,12] and to create biological discrimination [13]. For more examples, the functional groups introduced on CNTs are also useful for further chemical functionalizing [14] and/or assembling CNTs [15,16].

The organic functionalities introduced on CNTs usually are carboxyl (–COOH) [14,17], fluorine (–F) [18], amino groups (–NH_2) [19–21], hydroxyl (–OH) [22], carbonyl (–C=O) [17], and so on. Among these functional groups attached to CNTs, the amino group shows unique properties for further functionalizing and/or assembling CNTs. Amino groups can improve the solubility of CNTs in many solvents. More importantly, the amino group, due to its chemical versatility, should be a useful precursor for surface modification of CNTs through reacting with other organic molecules, polymers and biological systems [5].

However, to date, reports concerning amino group-modified carbon nanotubes are very limited due to the relatively difficulty of the modification. Stevens et al. [23] have exploited an approach to obtain the sidewall amino-modified single-walled carbon nanotubes (SWNTs) through fluorination and subsequent reactions with terminal diamines. Recently, Gromov et al. [19] have reported a three-step amino-modification process involving the formation of chloroanhydrid from carboxylic, amidation, the Hofmann rearrangement of carboxylic acid amides. Brinson and co-workers [5] have introduced amino groups to SWNTs through a four-step reaction route, involving oxidation of CNTs, reduction of the carboxyl group to hydroxymethyl, transformation into aminomethyl groups through phthalimide coupling and hydrolysis. However, due to strongly corrosive conditions, the fluorination process involved in the report of Stevens et al. is difficult to manipulate. And the later two approaches available involve fussy reaction steps and are difficult to control.

Here, we describe a facile methodology for introducing amino/nitro groups on MWCNTs. The MWCNTs are first modified with nitro groups via nitration reaction, which is one of the basic organic reactions. The nitro groups on MWCNTs can be then efficiently converted to amino groups by a simple reduction reaction. We also demonstrate that the amino groups can be used to facilitate linking guest objects, such as perylene derivatives via bonding to MWCNTs with imide bonds.

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2. Experimental

2.1. Materials and solvents

Pristine MWCNTs (purity > 95%) are purchased from Tsinghua University of China. The carbon nanotubes have a diameter of approximate 20 nm and a length of at least 2 μm. Concentrated sulfuric acid (H_2SO_4), concentrated nitric acid (HNO_3), acetic acid, iron powder (Fe), *N*-methyl kelopyrrolidide, *n*-butylamine and 3,4;9,10-perylenetetracarboxylic dianhydride (PTCDA) are all analytical grade and used as received.

2.2. Modification of MWCNTs with nitro groups

Adding 30 ml concentrated sulfuric acid solution slowly into 27 ml concentrated nitric acid solution, the resulting mixed acid (H_2SO_4/HNO_3 = 10/9, vol/vol) was cooled down to room temperature with cold water. Typically, 500 mg pristine MWCNTs and 20 ml cooled mixed acid solution were added into a three-necked flask and sonicated for 5 min. The mixed acid was dropped slowly into the flask through a filling funnel. Simultaneously, the reaction system was heated up to 60 °C and stirred for 90 min at 60 °C (80 °C and 90 °C are also used). Then the mixture was diluted and cooled with 600 ml of distilled water to terminate the reaction. The resulting suspension was then filtered through a glass sand-cored funnel (G4, porous size: 3–4 μm), washed with distilled water until pH 7 and dried at 60 °C overnight under vacuum. The MWCNTs treated in mixed acid at 60 °C was denoted as MWCNTs-NO_2.

2.3. Modification of MWCNTs with amino groups through reduction of MWCNTs-NO_2

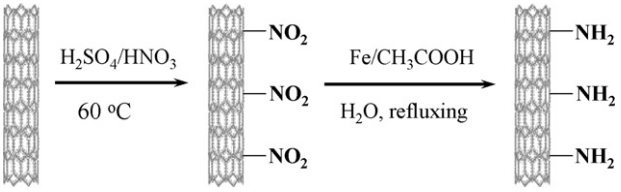
Typically, 1 g iron powder, 2 ml acetic acid and 50 ml distilled water were added into a three-necked flask. The mixture was stirred and refluxed for 10 min to activate iron into ferrous acetate. Then 200 mg MWCNTs-NO_2 were added into the reaction system and refluxed for 1 h. After the reaction finished, the superfluous iron was separated from the reaction mixture by a magnet. The resulting mixture was then filtered through a glass sand-cored funnel (G4, porous size: 3–4 μm), washed with hydrochloric acid (0.01 N), distilled water and dried at 60 °C overnight under vacuum. The as-obtained product was named as MWCNTs-NH_2.

2.4. Grafting perylene derivative onto MWCNTs-NH_2

N-butyl-3,4;9,10-perylenetetracarboxylic momoanhydride monoimid (SBPTCD) was synthesized via the reaction between PTCDA and *n*-butylamine as reported before [24]. 100 mg MWCNTs-NH_2 and 30 mg SBPTCD were added in *N*-methyl kelopyrrolidide. The reaction mixture was sonicated for 5 min and then was refluxed for 40 h under N_2 ambience. After the reaction finished, the reaction mixture was filtered through a glass sand-cored funnel (G4, porous size: 3–4 μm), washed with sodium hydroxide solution (0.01 N) and distilled water. The resulting product was dried in a vacuum oven at 60 °C overnight. The as-obtained hybrid was denoted as MWCNTs-SBPTCD.

2.5. Characterization

Element analysis result was obtained on a Vario EL element analyzer. Fourier transform infrared (FTIR) spectra were carried out on a Nicolet 380 spectrometer using KBr pallets at ambient temperature. Transmission electron microscopy (TEM) images were obtained on a JEM-2010 transmission electron microscope. UV–vis absorption spectra were performed on a Shimadzu UV–vis–NIR spectrophotometer (UV-3600).



Scheme 1. Reaction paths for introduction of nitro groups on MWCNTs and transformation of the nitro groups to amino groups.

3. Results and discussion

As well known, there are many atomic defects on the surfaces of MWCNTs [25]. The structure of these defect edges is similar to that of benzene which is very active with respect to electrophilic substitution, which provides general ways to modify MWCNTs. The nitration of aromatic compounds is a basic organic reaction to introduce –NO_2 on benzene, and the reduction of –NO_2 to –NH_2 can be carried out in stoichiometric ratio. Following these ways, MWCNTs can be easily modified with nitro/amino groups, as shown in Scheme 1.

To modify MWCNTs with nitro groups, a 10:9 (vol/vol) mixture of concentrated H_2SO_4 (98%)/HNO_3 (70%) was used. The mixed acid treatment was previously used to purify [26], cut [27] and introduce oxygen-containing functional groups on CNTs [28,29], based on an oxidation reaction, which usually occurs at high temperatures (*e.g.* 80 °C, 90 °C). As shown in Fig. 1, the strong oxidative ability of mixed acid and the high-temperature conditions result in heavy oxidation of MWCNTs, which displaying significant weight loss, similar to the situation reported previously [30]. Under the high temperatures, although minority of nitro groups are also introduced on MWCNTs, (shown in Fig. 2a and b, bands centered at 1384 cm^{-1} and 1558 cm^{-1}, which are the characteristcs of–NO_2 [31,32]), the majority of groups introduced on MWCNTs are carboxyl groups (band centered about 1714 cm^{-1} [33] in Fig. 2a and b). Considering that the nitration of benzene is usually performed at low temperature (50–60 °C), we modify MWCNTs with nitro groups at 60 °C.

As shown in FTIR spectra (Fig. 2), the pristine MWCNTs shows obvious vibrational band centered at 1558 cm^{-1}, which is associated with stretching of carbon nanotube backbone C=C [34]. Compared with pristine MWCNTs (Fig. 2d), the sample treated

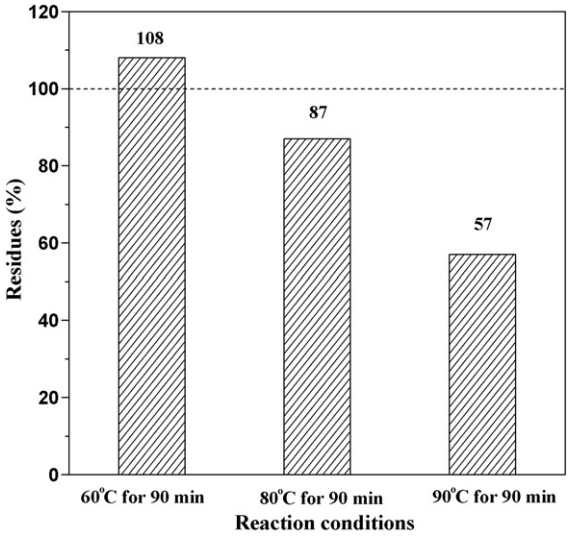


Fig. 1. Residual yields of mixed acid-treated MWCNTs as a function of treatment conditions.