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A novel conversion of inert carbon nanotubes to highly dispersed fibres

X. TANG, Y. ZHAO, Q. JIAO*, Y. CAO

School of Chemical Engineering and the Environment,
Beijing Institute of Technology, Beijing 100081, P. R. China

Multiwalled carbon nanotubes were functionalized with alkyl groups and transformed to form highly dispersed carbon nanofibres (CNFs) in ethylenediamine via the Benkeser reaction. The functionalized CNFs were characterized by transmission electron microscopy, scanning electron microscopy, Raman, infrared spectroscopoy as well as thermogravimetric analysis. The functionalized CNFs with long alkyl chains can be highly dispersed in universal solvents such as ethanol, toluene and N, N-dimethylformamide. The conversion mechanism has been investigated and the electrophilic reagents were proposed as key factors affecting the conversion degree.

Keywords: *carbon nanotubes; carbon nanofibres; characterization methods; functionalization*

1. Introduction

Carbon nanotubes (CNTs) are of great interest, stemming from their extraordinary structural, electronic and mechanical properties [1–3]. Many applications based on this unique material have been proposed such as mechanically reinforced composites [4], field-emission transistors [5], bio- and chemical sensors [6], and many others [7, 8]. In order to realize these potential applications, chemical modifications [9–13] to the surface of CNTs should be performed, to improve their solubility and dispersion in solvents. Over the past few years, many chemical reactions have emerged in the sidewall or endcap functionalization of CNTs; a subject having been extensively reviewed [14–16].

Recently, the chemical functionalization of CNTs using the Benkeser reaction was studied and single-walled carbon nanotubes (SWNTs) with alkyl and aryl groups have been successfully functionalized in ethylenediamine, which undergoes a convenient, scalable and moderate process [17]. In contrast with SWNTs, multiwalled carbon nanotubes (MWNTs) are easier to produce, more economical and have been widely

*Corresponding author, e-mail: jiaoqz@bit.edu.cn

used in large-scale consumer applications such as CNT-reinforced polymer composites [18]. Herein, this convenient route has been extended to the functionalization of MWNTs. Fortunately, inert MWNTs can also be functionalized with alkyl groups under Benkeser's condition. It is very interesting that in this reaction most of the MWNTs are transformed into disordered carbon nanofibres (CNFs) which also show good dispersibility in common solvents. To the best of our knowledge, this novel conversion has not been reported in other chemical reactions involving CNTs [9–16].

2. Experimental

In a typical experiment, 30 mg of MWNTs and 40 cm^3 of ethylenediamine were mixed in a flask. The mixture was rigorously stirred under argon at ambient temperature. After 20 min, when the solution became visually homogeneous, pieces of lithium (100 mg) were added in batches until the dark blue colour disappeared. Then hexadecyl iodide was added dropwise to the mixture. The reaction mixture was then stirred for about 3 h. The resulting dark solution was diluted with ethanol, followed by filtering over a 0.2 μm polycarbonate membrane. The dark solid obtained was washed thoroughly with ethanol and deionized water, and dried overnight in a vacuum oven at 80 °C to produce the functionalized product (30 mg).

A comparative experiment was conducted, and followed the same reaction procedure as earlier, except for the substitution of *tert*-butanol for hexadecyl iodide. The product was isolated as a black solid (30 mg).

Raman spectra were acquired using a Renishaw in via-reflex Raman microscope with a laser light wavelength of 532 nm. Fourier transform infrared (FTIR) data were recorded on a Perkin Elmer FTIR spectrometer. Thermogravimetric analyses (TGA) were carried out on a Pyris-1 thermogravimetric analyzer (Perkin Elmer, USA) with the heating rate of 10 °C/min and in nitrogen diluted air atmosphere. TEM images were obtained on a JEM-1200EX electron microscope operating at an accelerating voltage of 100 kV. HRTEM images were acquired using a JEM 2010 high resolution transmission electron microscope at the accelerating voltage of 120 kV.

3. Results and discussion

MWNTs were subjected to Benkeser reduction conditions in ethylenediamine, with an excess of hexadecyl iodide as the electrophile. The morphology of the MWNTs before and after the reaction was investigated by high resolution transmission electron microscopy (HRTEM) and scanning electron microscopy (SEM). As shown in Figs. 1 and 2, pristine MWNTs (p-MWNTs) show a smooth tube structure with regular graphite sheets. However, the hexadecylated products exhibit a disrupted structure with disordered carbon nanofibre features wrapped by some amorphous materials, which can be ascribed to the organic groups covalently attached to their sidewalls. Nearly all of the hexadecylated products observed display these new fibre fea-

tures; they have an average diameter of 15–25 nm and lengths ranging from hundreds of nanometers to micrometers (Figs. 1, 2).

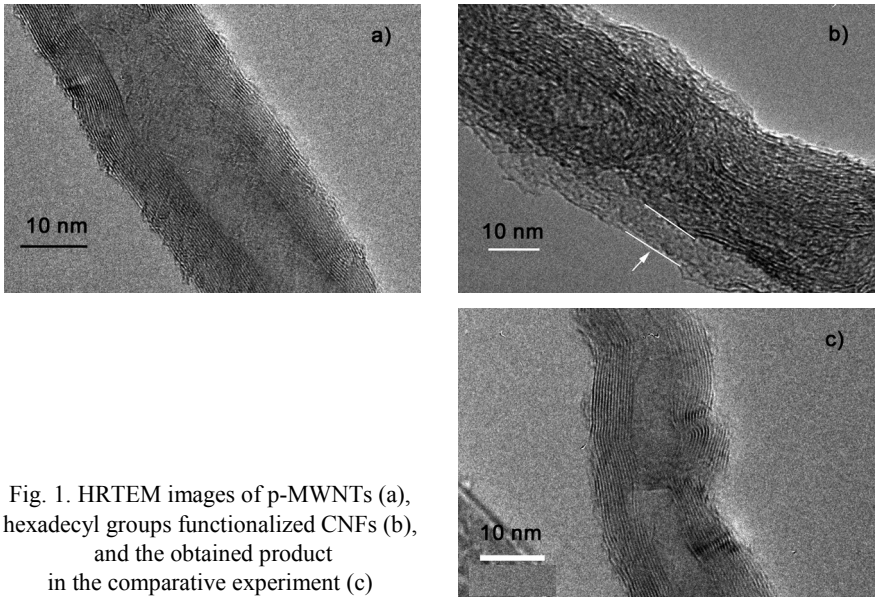

Fig. 1. HRTEM images of p-MWNTs (a), hexadecyl groups functionalized CNFs (b), and the obtained product in the comparative experiment (c)

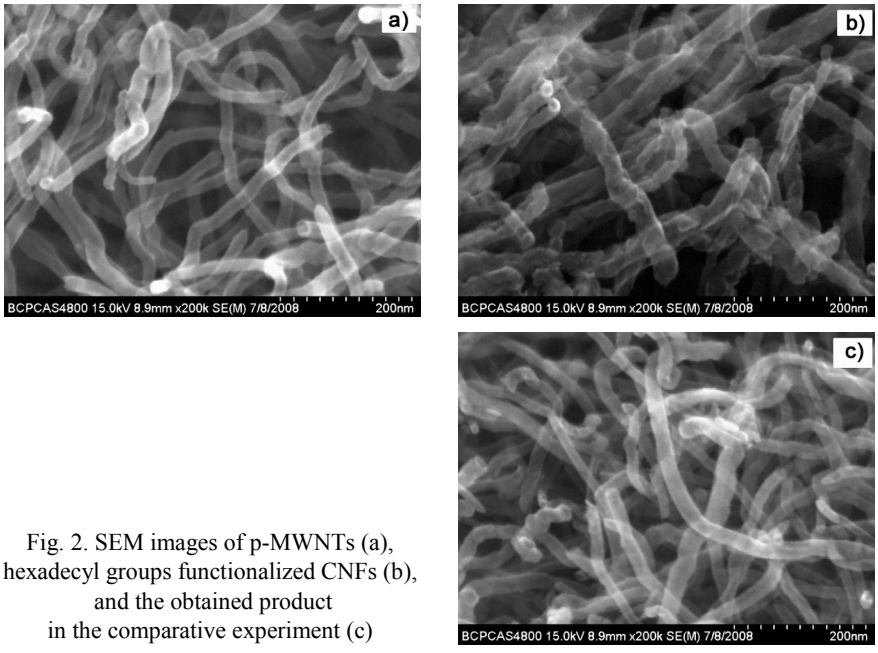

Fig. 2. SEM images of p-MWNTs (a), hexadecyl groups functionalized CNFs (b), and the obtained product in the comparative experiment (c)

The functionalization and morphological transformation was confirmed by Raman spectra (Fig. 3a). The intensity ratio of the disorder band (D band) to the tangential

band (G band) (I_D/I_G) for p-MWNTs and hexadecyl groups functionalized carbon nanofibres (f-CNFs) was increased from 0.77 to 1.17. This significant enhancement of the I_D/I_G ratio is related to the presence of defects, as well as of nanoparticles and amorphous carbon in the functionalized product which resulted from the reduced Benkeser procedure. Additionally, the linewidth of the D band is also broadened at about 50 cm^{-1} as compared with those of p-MWNTs, which further suggests the formation of CNFs [19–21] , and is in agreement with the HRTEM observations.

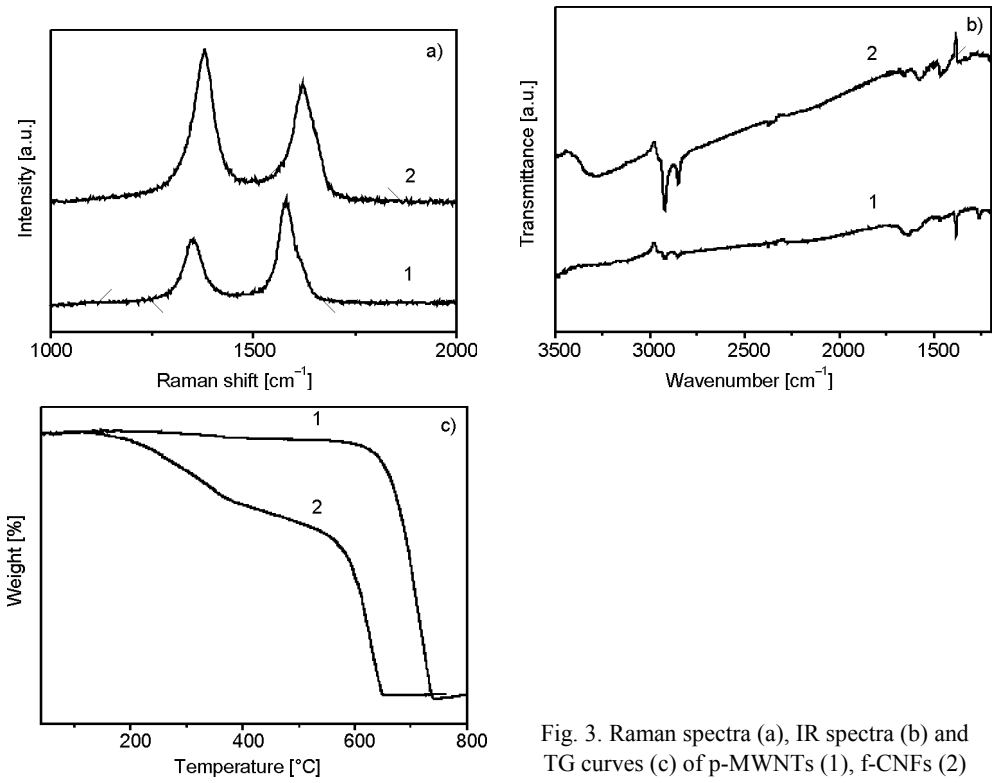

Fig. 3. Raman spectra (a), IR spectra (b) and TG curves (c) of p-MWNTs (1), f-CNFs (2)

The obtained f-CNFs were further characterized by IR spectroscopy (Fig. 3b). The f-CNFs show typical C–H stretching modes at 2920, 2850 cm^{-1}, as well as a C–H deforming mode at 1460 cm^{-1}: these were not found in the p-MWNTs and should come from the long hexadecyl groups attached to the sidewall of the CNFs. Since the reduced product was functionalized with hexadecyl groups, the surface property of f-CNFs could be altered significantly, which was confirmed by the dispersion measurements. As expected, f-CNFs exhibit good dispersibility in toluene, N, N-dimethylformamide (DMF) and ethanol. Figure 4 shows the dispersed states of the p-MWNTs and f-CNFs via sonication for 3 min in these solvents. Dispersed p-MWNTs are easily aggregated, however, f-CNFs are stable as homogeneous black suspensions. As is

known, highly dispersed f-CNFs can also be used as excellent polymer fillers in the field of polymer nanocomposites [22, 23].

The TGA curve (Fig. 3c) of the f-CNFs reveals a 23% weight loss in the range of 200 to 400 °C, which can be attributed to the decomposition of the functionalized hexadecyl groups. The ratio of carbon to hexyadecyl group is estimated to be 62:1, which is identical to that of dodecyl groups functionalized MWNTs reported by Tour et al. [12]. The temperature ascribed to the decomposition of their own structural backbone for f-CNFs is in the range of 550–650 °C, and that is much lower than the corresponding range for p-MWNTs, which is about 600-740 °C. This indicates that the obtained f-CNFs have poor thermal stability. It also provides further evidence of the structural alteration of MWNTs during this Benkeser reaction.

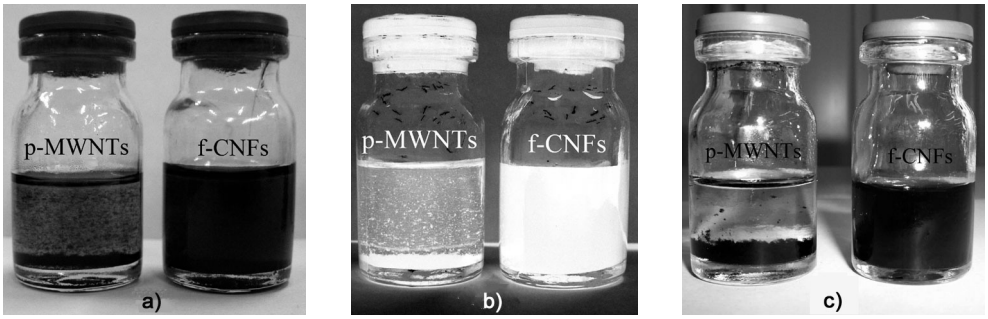

Fig. 4. p-MWNTs and f-CNFs suspensions in toluene (a), DMF (b), and ethanol (c) for variable times after 3 min of sonication. Time since sonication is 30 min (a), 5h (b), 7 days (c)

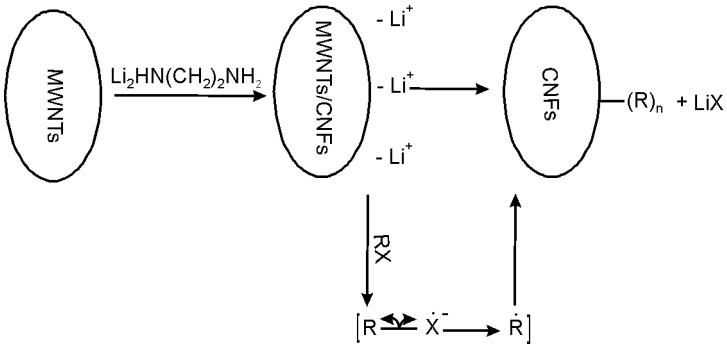

Fig. 5. Proposed mechanism of the conversion process

The mechanism of this interesting conversion from inert MWNTs to highly dispersed f-CNFs seems to be complicated. A preliminary study of the conversion process was undertaken. A comparative experiment was conducted in the absence of an electrophile. When hexadecyl iodide was replaced with a proton source, the tube structures were almost fully preserved (Figs. 1c, 2c). As mentioned above, nearly all the MWNTs are transformed into CNFs when hexadecyl iodide was used. Therefore, the electrophilic reagent plays an important role in the structural conversion. If reagents

with different electrophilic strengths were used, the degree of structural conversion to the final product would differ accordingly, thus resulting in materials with different chiralities and potential uses in electronic applications. Billups et al. [13] proposed that a single electron transferring (SET) mechanism occurs for their reductive alkylation of SWNTs (Birch reaction), including the formation of SWNTs salts and alkylation step in tandum. Mindful of Billups's investigations, we propose that our Benkeser reaction may experience the same process, as shown in Fig. 5. Because the fibre structure cannot be formed without the electrophile in the Benkeser reaction (findings from the comparative experiment), it is concluded that the structure conversion takes place at the alkylation step, rather than the reduction step (salts formation step). The lithiation of the MWNTs causes them to disperse well in ethylenediamne and leaves enough reaction sites for the addition of radicals. Then, the addition of alkyl radicals to the MWNTs may occur not only at the inner graphite layers but also at the outer ones of the MWNTs, which results in the structural deterioration of the MWNTs, and thus yields the functionalized CNFs.

4. Conclusions

A novel conversion of inert MWNTs to highly dispersed CNFs, functionalized with alkyl groups, was developed under the Benkeser reaction, which was confirmed and characterized by TEM, SEM, Raman, IR and TG analyses. The high dispersibility of the CNFs in common solvents was observed in the dispersion experiment. Consequently, this makes then potentially good candidate materials for use as fillers in polymer composites. Preliminary investigations indicate that the conversion takes place at the alkylation step. Investigations on the detailed dynamics of the conversion mechanism, in order to explore the viability of exploiting the considered materials in various fields of electronics, would be the aim of our subsequent research. However, the complexity of the conversion process would make this a highly challenging task.

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