



Assembly of fullerene particles on carbon nanotubes through poly (acryloyl chloride)

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ABSTRACT

Multiwalled carbon nanotubes (MWCNTs)/fullerene composites were prepared through a facile method. Poly (acryloyl chloride) (PACl) was first grafted onto oxidized MWCNTs through the reaction between the acyl chloride groups of PACl with the hydroxyl groups on the surface of MWCNTs. The PACl with multiple acyl chloride groups provided more active points for further reactions. Subsequently, the remaining acyl chloride groups of PACl were allowed to react with the hydroxyl groups of fullerenes leading to the covalent attachment of the latter onto the grafted PACl chain. The MWCNTs/fullerene composites thus obtained were characterized using Fourier transform infrared spectrometer (FTIR), transmission electron microscopy (TEM), and thermal gravimetric analysis (TGA).

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1. Introduction

The carbon nanotube based composites had recently attracted considerable research interests for their excellent mechanical and electrical properties [1]. Li et al. reported a novel method of preparing Pt/carbon nanotube complexes by adsorbing the Pt nanoparticle precursors onto surface of 1-aninopyrene modified carbon nanotubes via electrostatic interactions [2]. Shi et al. reported that the nanoparticles of CdS were in situ bound to the carboxy groups on the surface of MWCNTs through chemical-solution route [3]. Sainsbury and Fitzmaurice assembled titanium dioxide and silica nanoparticles to the surface of MWCNTs modified by phosphonic acid or alkoxy silane [4]. Delgado et al. prepared conjugated hybrid of fullerene and single-wall carbon nanotube by amidation of acid functionalized single-wall carbon nanotubes with an amine functionalized fullerene derivation [5]. Among the nanotube/inorganic particle composites mentioned above, the carbon nanotube/fullerene composite has attracted extensive attention because of the excellent mechanical and electrical properties [6]. For carbon nanotube/fullerene composites thus obtained, however, only several fullerene particles were grafted onto the end of carbon nanotubes due to a few functionalized sites. The quantity of fullerene particles grafted onto the carbon nanotube surface was too few to exhibit the optimum properties of obtained composites [5,7].

In this paper, a methodology to introduce a large quantity of fullerene indirectly onto carbon nanotubes was proposed, using poly (acryloyl chloride) as the bridges between carbon nanotubes and fullerenes. Firstly the oxidized multiwalled carbon nanotubes (MWCNTs) were grafted by multifunctional PACl [8], which resulted in the encapsulated MWCNTs and subsequently the fullerenes were grafted covalently to the surface of MWCNTs via the PACl, which resulted in the generation of MWCNTs/fullerene composite. Since PACl provided numerous reactive sites, a large quantity of fullerenes could be assembled surrounding the MWCNTs.

2. Experimental

2.1. Materials

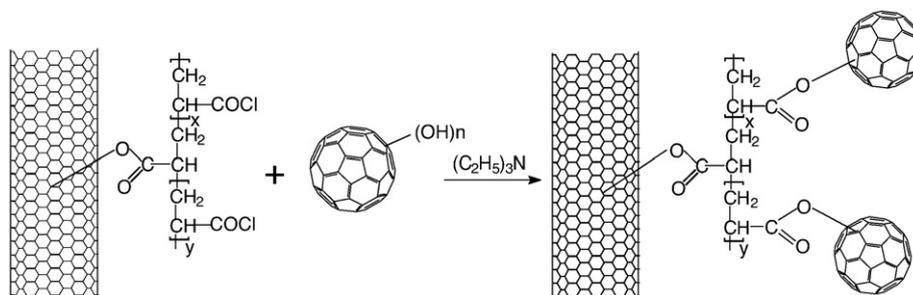
MWCNTs (purity $\geq 95\%$, diameter 10–20 nm and length 0.5–500 μm) were provided by Shenzhen Nanotech Port, China. The fullerene was obtained from Materials and Electrochemical Research Corporation (MER, USA). Acryloyl chloride (97%) was purchased from Acros Organic. 2,2'-azobutyronitrile (AIBN), dimethyl sulfoxide (DMSO), 1,4-dioxane (99%), tetrahydrofuran (THF, 99%), concentrated sulfuric acid (98%) and concentrated nitric acid (70%) were provided by Vas Chemicals of China.

2.2. Synthesis of MWCNTs/fullerene composites

The fullerene was prepared using the method proposed by Chiang et al. [9]. The pristine MWCNTs were hydroxylated with a concentrated $\text{H}_2\text{SO}_4\text{--HNO}_3$ mixture (1:1 v/v) [10]. Poly (acryloyl chloride) (PACl) was synthesized by radical polymerization of acryloyl chloride at 53 °C in 1,4-dioxane in the presence of 2,2'-azobutyronitrile

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Scheme 1. The schematic representation of the synthesis of MWCNTs/fullerenol composites.

(AIBN) for 48h with nitrogen atmosphere in Schlenk tube [11]. The PACI thus obtained was introduced into the suspension of acid treated MWCNTs in 1,4-dioxane and kept stirring for 48h under nitrogen atmosphere. The solid product was collected after filtration, washed 5 times with THF. PACI-grafted MWCNTs were obtained. The fullerenols were suspended in DMSO by sonicating for 60 min. The suspension and triethylamine were introduced into PACI-grafted MWCNTs suspension in DMSO and subsequently kept stirring for 48h at 60 °C under N_2 . The solution was filtrated and washed 5 times with THF. The final product was dried under vacuum for 10h at 70 °C. The reaction process was presented in Scheme 1.

2.3. Characterization

Fourier transform infrared spectra (FTIR) were conducted on a Nexus 670 FT-IR spectrometer. The microstructure of products was observed by TEM (JEM100CX). Thermal gravimetric analysis (TGA) was conducted on a STA 449C instrument at a heating rate of 10 °C/min in a nitrogen flow.

3. Results and discussion

FTIR spectra of PACI-grafted MWCNTs were shown in Fig. 1. The C–H stretch vibration of PACI backbone was detected at 2950 cm^{-1} as a broad and weak absorption peak (Fig. 1a), while the 1759 and 1806 cm^{-1} are characteristic peaks of the C=O stretch vibration of ester and acyl chloride respectively [8]. The FTIR feature in Fig. 1a suggested that the PACI was attached to the surface of MWCNTs (Scheme 1). Fig. 1c shows the

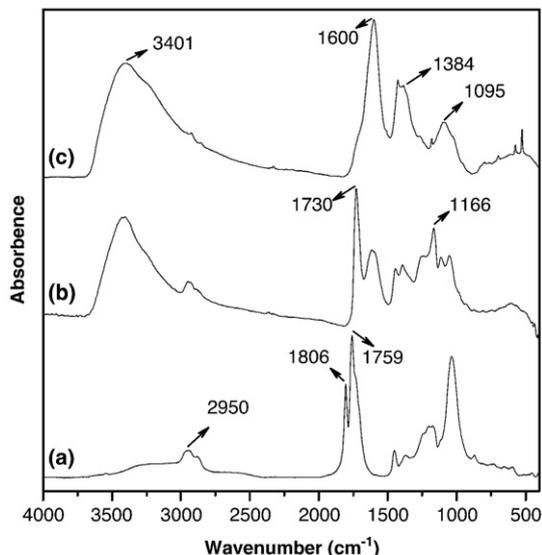


Fig. 1. FTIR spectra of (a) PACI-grafted MWCNTs; (b) MWCNTs/fullerenol composites; (c) fullereneol.

features of fullereneol: a broad hydroxyl group related absorption band (3401 cm^{-1}), C=C bands (1600 cm^{-1}), O–H bending vibration (1384 cm^{-1}) and a C–O stretching band at 1095 cm^{-1} [12]. In Fig. 1b, the peak 1730 cm^{-1} was attributed to the C=O stretching vibrations of the ester carbonyl group, which resulted from the reaction between PACI-grafted MWCNTs and fullerenols. While the appearance of an intense absorption peak ($C-O$, 1166 cm^{-1}) indicates the formation of ester linkage between fullerenols and PACI-grafted MWCNTs. The disappearance of the C=O stretching vibration of acyl chloride (1806 cm^{-1}) indicates that most of the acyl chloride must have been consumed during this reaction. Moreover, the changes of broad hydroxyl band of fullereneol into a sharp band in the MWCNTs/fullerenol composites also demonstrated that the fullerenols were covalently attached to the MWCNTs.

The morphology of the samples was observed with TEM. Fig. 2a showed that the oxidized MWCNTs' surface was relative smooth and clean. In contrast, the edge of PACI-grafted MWCNTs (Fig. 2c) became blurred, indicating that the surface of MWCNTs was wrapped by the PACI [8]. For the cohesive hydrogen bonds among fullereneol particles, the fullerenols aggregated into cluster as shown in Fig. 2b [13]. From the TEM image of the Fig. 2d, it is clear to discern that the fullereneol particles were hanged on the surface of MWCNTs. From all of the results above, it is reasonable to believe that the fullerenols were assembled onto the surface of MWCNTs through the reaction between the hydroxyl groups of fullereneol and the acyl chloride groups of PACI.

TG analysis of the samples was shown in Fig. 3. Under N_2 atmosphere the fullereneol (Fig. 3b) exhibited a steady mass loss from 100 to 800 °C [14]. In Fig. 3c, the PACI-grafted MWCNTs show significant weight loss ($380\text{--}440\text{ °C}$) that resulted from the thermal

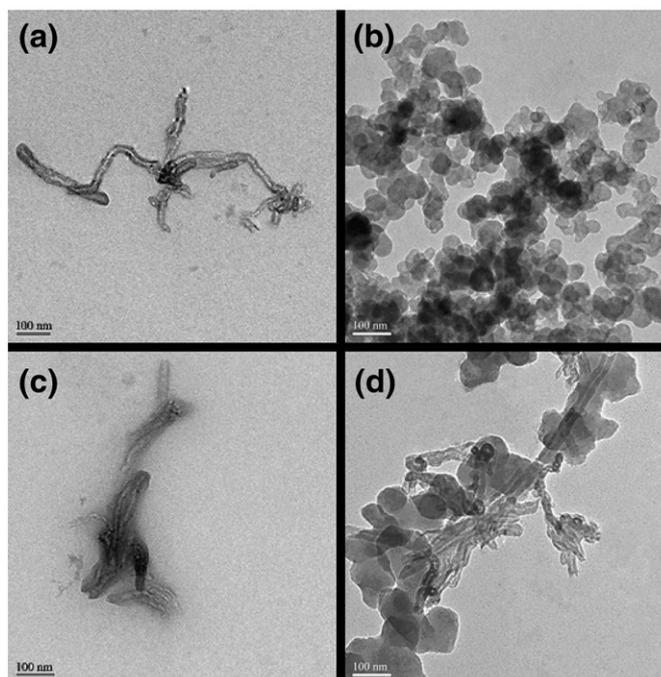


Fig. 2. Representative TEM images of (a) oxidized MWCNTs, (b) fullerenols, (c) PACI-grafted MWCNTs, and (d) MWCNTs/fullerenol composites.

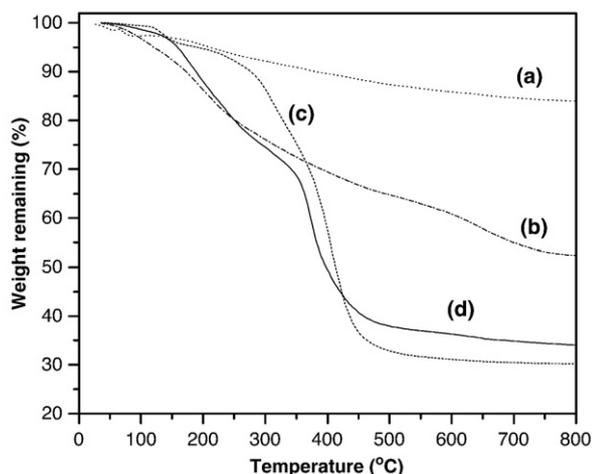


Fig. 3. TG curves of (a) oxidized MWCNTs, (b) fullerene, (c) PACI-grafted MWCNTs, and (d) MWCNTs/fullerene composites.

degradation of PACI. As shown in Fig. 3d, besides the weight loss of PACI occurring at about 400 °C, the initial weight loss after 100 °C resulted from the presence of fullerenols.

4. Conclusion

We successfully prepared a MWCNTs/fullerene composite via poly (acryloyl chloride) (PACI). The FTIR and TEM analyses revealed that the fullerene spheres were assembled onto the surface of MWCNTs. The

MWCNTs/fullerene composites may have the potential application in the fields involving fullerene and carbon nanotube.

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