



# Microwave-Assisted thiol-ene click chemistry of carbon nanoforms



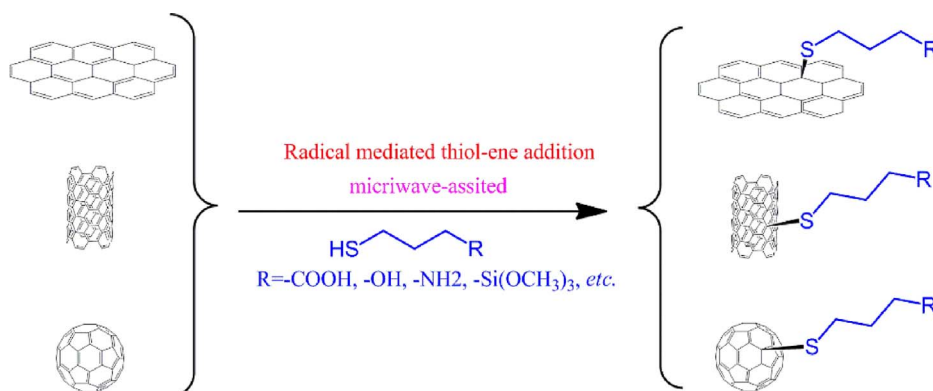
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## GRAPHICAL ABSTRACT

Carbon nanoforms (CNFs, fullerenes, nanotubes, and graphene) have played important roles in the fields of material science and nanocomposite. We provided a novel strategy to obtain functional CNFs via microwave-assisted thiol-ene click chemistry.



## ARTICLE INFO

**Keywords:**  
Microwave  
Fullerene  
Carbon nanotube  
Graphene  
Thiol-ene

## ABSTRACT

Carbon nanoforms (CNFs, including graphene, carbon nanotube and fullerene) were functionalized via microwave-assisted thiol-ene click chemistry. Different functional CNFs with  $-\text{COOH}$ ,  $-\text{NH}_2$ ,  $-\text{NH}_3\text{Cl}$ ,  $-\text{Si}(\text{OCH}_3)_3$ , alkyl and furyl groups were obtained and characterized by XPS, EDS, TGA, Raman spectroscopy and MALDI-TOF MS. Microwave was much more efficient to promote reactions than traditional thermal method. XPS confirmed the binding energy of C-S-C (163.3eV) the modified CNFs. Raman spectroscopy showed increasing  $I_D/I_G$  and  $A_D/A_G$  of graphene and CNT after thiol-ene addition reaction. The result of MALDI-TOF MS indicated that the thiol-containing molecules were attached on fullerene. All these results indicated the successful thiol-ene click reactions between CNFs and thiol-containing molecules under microwave. TGA analysis results showed the mass loss of the modified CNFs, which provided that AIBN and 3-mercaptopropionic acid were the most efficient initiator and monomer, respectively. In summary, the microwave-assisted thiol-ene click reaction provided a powerful chemical tool for the preparation of functional CNFs materials.

## 1. Introduction

Carbon nanoforms (CNFs) have played important roles in the fields

of material science and nanocomposite [1–4]. Since the emergences, CNFs are regarded as one of the next-generation nano fillers for polymer nanocomposites [5], due to their unique chemical and physical

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<http://dx.doi.org/10.1016/j.colsurfa.2017.08.018>

Received 29 June 2017; Received in revised form 15 August 2017; Accepted 17 August 2017

Available online 24 August 2017

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properties [6,7]. For example, fullerene C<sub>60</sub> is a good trapper for radical [8]. The mechanical properties of carbon nanotubes are expected to be an ideal carbon fiber [9,10]. Graphene displays remarkable physico-chemical properties [11–13]. However, the high inertness of CNFs has limited their applications in many different areas, such as energy storage, electrode in supercapacitor, battery and reinforcement in polymer nanocomposite [14,15]. To modify CNFs via an efficient chemical or physical way was urgency.

Click chemistry, termed by Sharpless and coworkers [16], is an excellent chemistry widely used in synthesizing functional polymers and modifying nanomaterials for its efficiency, versatility, simplify and mild reaction conditions [17]. However, only a few literatures were reported about modifying CNFs via click reaction. Horacio J. Salavagione and co-worker [18] modified graphene by low molecular weight SH-terminated polyethylene (PE). Yusuf Yagci et al. [19] obtained fullerene-capped polystyrene by using the thiol-ene click-chemistry approach. In our previously work [20], trimethoxysilane terminated PE (TMS-PE) and trimethoxysilane modified multiwall carbon nanotube (TMS-MWNT) is prepared through radical mediated thiol-ene addition reaction, and is used to obtain PE covalently grafted multiwall CNT (PE-Si-MWNT) carbon nanotubes. However, the chemical inertness of C=C bond of CNFs blocked the activity of the thiol-ene reaction, and it usually accompanied by low reaction efficiency.

Recently, microwave-assisted synthesis is a novel efficient technology that has been widely used in organic synthesis [21]. CNFs are excellent microwave-absorbing material. Vazquez and Brunetti [22] found that microwave irradiation for multifunctionalized carbon nanotubes reduced the reaction time and improved the degree of functionalization than those obtained by conventional thermal method. Huang and coworkers [23] successfully utilized chitosan to functionalize multi-walled carbon nanotube via condensation reaction between –NH<sub>2</sub> and –COOH under the microwave irradiation within 1 h, which is more effective than conventional methods. Langa and co-worker [24] used microwave irradiation to assist the Dies-Alder reaction of fullerene and o-quinodimethane in mild reaction conditions. The results showed that microwave heating had overcome the shortcoming of conventional thermal method which need long heating time. Microwave opened the door for the functionalization of CNFs with a simply and efficiently method as compared to traditional thermal method.

In this paper, we focus on the functionalization of CNFs assisted by microwave irradiation, including the reaction condition, the structure of thiol-containing molecules, and the kinds of CNFs. A series of functional CNFs were prepared via thiol-ene click reactions between CNFs and thiol-containing molecules. The thiol-containing molecules were covalently grafted onto the surface of CNFs via S-C bonds. The introduction of different polarity groups on surface of CNFs will improve their inertness, and extend their applications for many areas, such as polymer nanocomposites ect.

## 2. Experimental

### 2.1. Materials

Benzoyl peroxide (BPO, 98%) was purchased from Sinopharm Chemical Reagent Co, Beijing; 1, 1'-azobis(cyclohexanecarbonitrile) (ABCN, 98%), furfuryl mercaptan (FM, 98%), 3-mercaptopropionic acid (MPA, 98%), 2, 2'-azobis(2-methylpropionitrile) (AIBN, 98%), 2, 2'-azobis(2-methylbutyronitrile) (AMB, 98%), *tert*-butyl peroxybenzoate (TBPB, 98%), cysteamine hydrochloride (CHI, 98%) and L-cysteine hydrochloride anhydrous (LCHA, 98%) were purchased from Aladdin Industrial Inc; cysteamine (CM, 96%), *n*-octadecyl mercaptan (nOM, 98%) and 3-mercaptopropyltrimethoxysilane (MPTS, 97%) were purchased from J & K Scientific; graphene sheet was purchased from the Six Element (Changzhou) Materials Technology Co., Ltd; Carbon nanotubes was purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences; Fullerene was purchased from Suzhou Dade

Carbon Nano technology Co, Ltd.

### 2.2. Analytical techniques

TGA analysis was performed at a heating rate of 20 °C min<sup>-1</sup> in nitrogen atmosphere from 50 to 700 °C on Perkin-Elmer TGA-1 instrument. X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALab 250Xi using 200 W monochromated Al K $\alpha$  radiation. The 500  $\mu$ m X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about 3  $\times$  10<sup>-10</sup> mbar. Typically the hydrocarbon C1 s line at 284.2 eV from adventitious carbon is used for energy referencing. Scanning electron microscope (SU1510, Hitachi High-Tech Corporation, Japan) equipped with electron-dispersive X-ray spectroscopy (EDS) was used to obtain the elemental analysis. The samples with no gold coated were observed with secondary electron mode at a 15 kV accelerating voltage. Elemental analysis was conducted on the selected section of the scale by EDS to verify the element content. Raman spectra were recorded on a LabRAM Aramis, Raman spectrometer at 532 nm wavelength incident laser light.

### 2.3. General procedure for thiol-ene click reactions of CNFs

About 0.5 g of CNFs was dispersed in 150 ml of THF or toluene (for C<sub>60</sub>) with a mount of thiol-containing molecule (1e.q.) and radical initiator (0.13 e.q.) by ultrasonication for 1 h in a microwave glass vessel. Subsequently, the mixture was placed in the center of a MAS-I microwave oven (Sineo Microwave Chemistry Technology (China) Co, Ltd.) with a refluxing system outside, and then irradiated by microwave (350W) at 70 °C for hours under stirring. Or the mixture was placed in an oil heating bath and stirred under particular temperature for hours. The obtained solution was dealt via centrifuge and then poured out the supernatant liquor. For C<sub>60</sub>, the crude solution was dealt via reduced pressure distillation to remove the tremendous toluene and the product was precipitated by methanol. The collected black solid was washed with ether three times until supernatant liquor was clear. The product was dried under vacuum at 50 °C for 24 h.

## 3. Results and discussion

### 3.1. Functionalization of graphene by MPTS

At first, the modification of graphene sheets by 3-mercaptopropyl-trimethoxysilane (MPTS) was studied. The synthesis details of G-MPTS are listed in Table 1. XPS analysis was carried out to confirm the structure of G-MPTS. The S2p spectra of G-MPTS (Fig. 1) showed the C-S-C at the binding energy of 163.37eV corresponding to the literature [25]. The C1 s spectra of G-MPTS could be deconvoluted into two peaks corresponding to carbon atoms in different functional groups: C–C (nonoxygenated carbon, 284.33eV) and C–O–Si (285.27eV). The overall spectrum is shown in Fig. S1 in the Supporting Information. The XPS results indicated that MPTS was covalently linked to graphene sheets through thiol-ene reaction between MPTS and the double bond of graphene sheet. In the FTIR spectra of pure graphene and functional

**Table 1**  
Synthesis details and results of G-MPTS.

Sample	Initiator	Heating	Time /hour	Weight loss /%	Functional group coverage <sup>a</sup>
G-MPTS1	BPO	CT <sup>b</sup>	8	3.34	332
G-MPTS2	BPO	MVI <sup>c</sup>	1	8.39	126
G-MPTS3	AIBN	CT	8	7.27	147
G-MPTS4	AIBN	MVI	1	10.60	97
G-MPTS5	ABCN	MVI	1	5.00	219
G-MPTS6	AMB	MVI	1	4.07	271
G-MPTS7	TBPB	MVI	1	6.94	154

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