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Chemical modification of graphene oxide with carbethoxycarbene under microwave irradiation

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ABSTRACT

The structure of graphene oxide (GO) enables it to act as the olefin in cyclopropanation reaction with ethyl diazoacetate (EDA) under microwave irradiation. This versatile synthetic method offers a powerful method for the rapid chemical modification of GO. The attachment of carbethoxycarbene (CEC) to GO was confirmed by the results of FTIR, XPS, Raman, and UV–vis analysis.

1. Introduction

Graphene oxide (GO) has attracted increasing attentions in recent years because of its hydrophobic basal plane and abundant hydrophilic oxygen-containing groups including epoxy, hydroxyl, carboxyl and carbonyl groups, leading to its facile modification and wide application in various aspects as an exciting material [1–4]. GO has a large theoretical specific surface area, high intrinsic mobility, high Young's modulus, good thermal and electrical conductivity [5]. These features suggest that GO is a powerful material for energy storage, biological and chemical sensors [6]. However, the intrinsic zero band-gap energy and low solubility in both organic and aqueous solvent are two of the most prominent challenges that hold GO back in many fields [7]. Chemical functionalization has proven to be an effective method which renders GO a more versatile precursor for a wide range of applications [8].

Until now, the most well-known model of GO is the one pronounced by Lerf and Klinowski (Figure 1) [9]. The double bonds between the carbon atoms of GO are likely either aromatic or conjugated. So far, chemical modification of GO has been mainly focused on the graft of the polar groups onto the surface of graphene, for instance, epoxy [10], and carboxylic acid groups [11]. However, due to the structure of planar sheet, GO is facing the challenge of less reactivity in chemical reactions. Taking carbon nanotubes for example, chemical functionlization of sp^2 carbon materials have been widely investigated [12]. As far as we know, only a few chemical functionalizations of graphene/GO based on the sp^2 carbon were reported, such as 1,3-dipolar cycloaddition [13], Diels–Alder addition [14] nitrene addition [15], and aryne addition [16]. These chemical functionalizations of graphene/GO enable sp^2 hybrid carbon to convert to sp^3 hybrid carbon at the edge or defect sites of the graphene planar sheet.

The addition of carbenes (i.e. dichlorocarbene and diarylcarbene) to the carbon materials, such as sidewalls of the carbon nanotubes, has been investigated for many years [17–19]. Cyclopropanation reaction, as a powerful synthesis method, has been extensively used in the cycloaddition of alkenes with diazocompounds [20]. After the releasing of nitrogen, carbenes are generated from diazocompounds and could insert into the double bond of alkenes to form the cyclopropane derivatives. Considering the hybrid sp^2 carbon of GO planar sheet which is similar to that of alkene, the cyclopropanation reaction of GO with diazocompounds is quite possible. As a green and efficient method, microwaves are used in many chemical researches of carbon materials due to their strong microwave (MW) absorption ability [21-24]. Carbon nanotubes (CNTs) and fullerene have been successfully functionalized under MW irradiation [25,26]. Herein, we present the first example of chemical functionalization of GO with carbethoxycarbene (CEC) that is generated from ethyl diazoacetate (EDA) under MW irradiation (Figure 1), and the final product was named as CECGO.

2. Experimental

2.1. Preparation of GO

GO was prepared through a modified Hummers method using natural graphite powder as the starting material. The synthetic procedure was described as follows: graphite (6 g) and sodium nitrate (3 g) were added into a 1000 ml flask at 0 °C. Then, concentrated H_2SO_4 (150 ml) was slowly added dropwise into the flask under continuously stirring, keeping the temperature of the reaction mixture at 5 °C for 2 h. Subsequently, 22 g of $KMnO_4$ was added in batches and the reaction temperature was maintained at about 10 °C. After that, the reaction temperature was elevated to 35 °C and stirred for 2 h. After the accomplishment of reaction, 270 ml of water was poured slowly into the solution with vigorous stirring to obtain dark brown suspension. The suspension was

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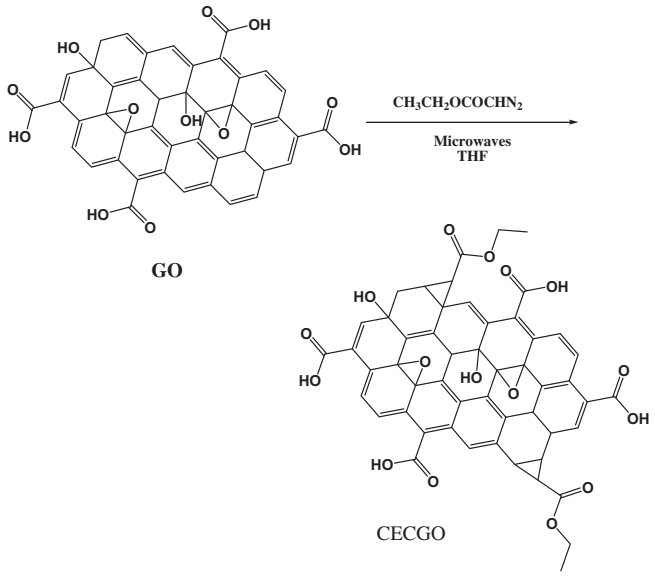

Figure 1. The attachment of carbethoxycarbenes on GO under microwave irradiation.

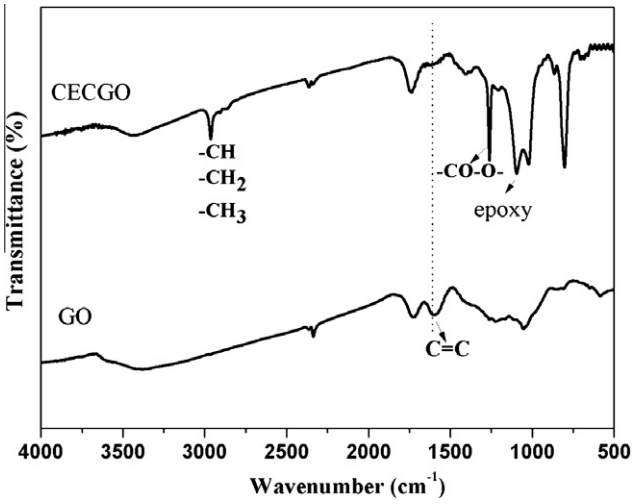

Figure 2. FTIR spectra of GO and CECGO.

treated further by adding the mixture of H_2O_2 (21 ml, 30%) and water (165 ml) to remove the residual permanganate and MnO_2. The resulting suspension has bright yellow color and was separated by vacuum filtration. The yellow–brown GO powders were washed for four times with warm (40 °C) diluted HCl (3%, 450 ml) solution, and dried at 60 °C in oven.

2.2. Experiment equipment

A multimode microwave oven (WBFY-21, 2450 MHz, 800W) was used in the study.

2.3. Chemical functionalization procedure of GO

0.2 mg GO was dispersed in THF by sonication for 60 min to yield a homogeneous yellowish brown dispersion of GO. And, 20 ml of 0.1 mg/ml GO suspension and 0.01 mol ethyl diazoacetate (EDA) were mixed in a 50 ml round bottom flask. With a condenser, the mixture was irradiated for 30 min at the microwave power of 800 W. After that, some black solid were found in the

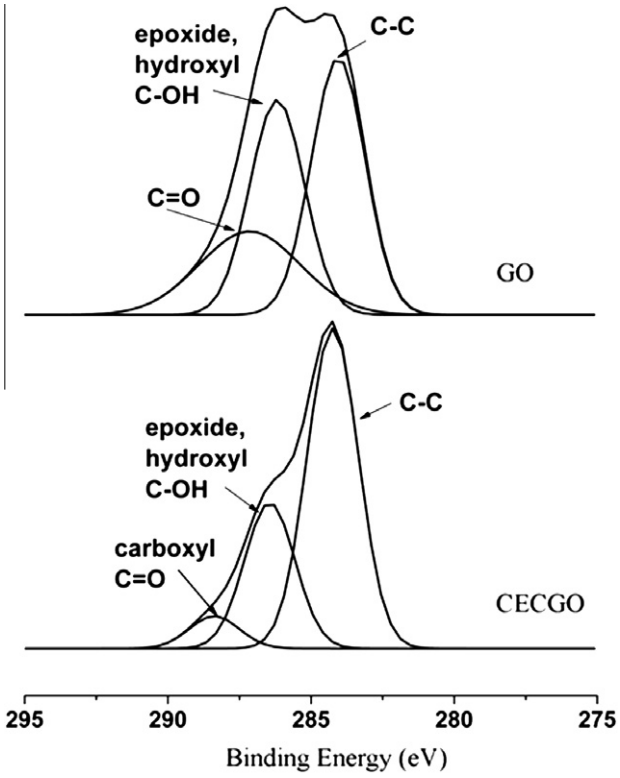

Figure 3. X-ray photoelectron spectroscopy spectra of GO and CECGO.

Table 1
The C 1s peak position and the relative atomic percentage of various functional groups in GO, CECGO.

	Binding energy (eV) (relative atom percentage %)			
	C=C (sp^2)	C–C (sp^3)	C–O/C–O–C	C=O/O–C=O
GO	284.8 (40.7)		286.7 (34.6)	288.3289.6 (24.7)
CECGO	284.2 (64.6)		286.4 (29.0)	288.4 (6.4)

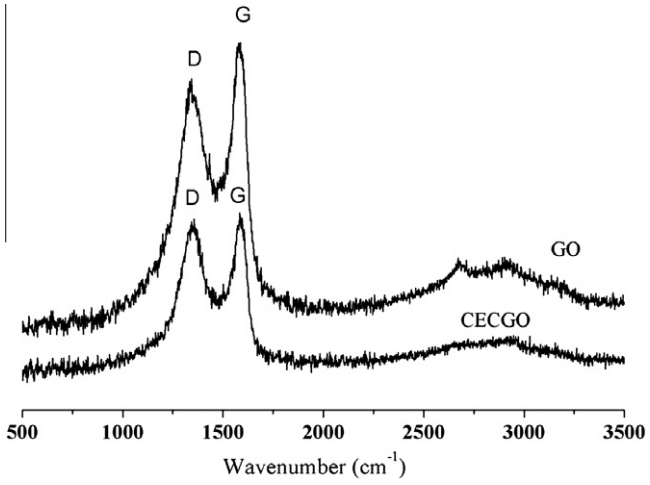

Figure 4. Raman spectra of GO and CECGO in aqueous.