



# One-step functionalization of graphene by cycloaddition of diarylcarbene and its application as reinforcement in epoxy composites



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## ABSTRACT

Due to its novel physical, chemical and mechanical properties, graphene has great potential to be applied in composite science. However, the inert chemical structures with low surface energy and low solubility in both organic and aqueous solution are the major bottleneck for real applications. Chemical functionalization of graphene is one of the effective solutions to address the above challenges. In the present study, novel highly reactive diarylcarbene derivative is designed and synthesized. Different to previous approaches, this diarylcarbene derivative contains reactive epoxy groups, which can serve as anchoring sites for further modification. Then, reactive epoxy groups are introduced to graphene via one-step diarylcarbene cycloaddition. The modification is observed spectroscopically, and the obtained graphene (DC-GR) can be well-dispersed in organic solvent, such as acetone and dichloromethane. In order to further verify the effectiveness of modification, we use DC-GR as reinforcement to enhance epoxy resin. Both thermal and mechanical properties of the composites are improved significantly at low DC-GR content loading. The enhancement is believed to be attributed to the strong interfacial interactions between DC-GR and the matrix via epoxy groups. This study provides alternate strategy to modify the graphene, which will greatly expand the application field of graphene in composite science.

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## 1. Introduction

Although the concept of graphene has been proposed since the 1940s, the explosive interest of graphene is aroused by the 2004 paper of Geim and Novoselov [1]. After this discovery, the unique and superior properties of graphene open up a broad range of applications, including energy storage, drug delivery systems, transistors, sensors, and nanocomposite materials [2–5]. Despite the high potentials of graphene, two major shortcomings are the inert chemical structures with low surface energy and its low solubility in both organic and aqueous [6]. Chemical functionalization of graphene is one of the effective solutions to address the above challenges. Since graphene is a planar sheet sp<sup>2</sup> carbon materials, it is less reactive compared to two other nano allotropes its:

fullerenes and carbon nanotubes [7]. It is therefore not surprising that much work on graphene modification has been achieved using highly reactive intermediates [8]. The reactive species, including radicals, carbenes, nitrenes, and arynes, can form covalent adducts in graphene and enhance its properties for real applications.

Carbene is a highly reactive intermediate. The reactivity of carbenes with C–H and X–H (X = O, N, and S) by bond insertion, and with C=C double bonds by addition reactions, would be expected to modify nanocarbon materials. In fact, dichlorocarbene [9,10], diarylcarbene [11], modified diazirines [12], dipyriddyimidazolide nucleophilic carbene [13], and fluorinated olefins [14] have been used to introduce adducts to carbon nanotubes in previous work. Most recently, Chua and coworkers have successfully modified graphene with dichlorocarbene [15]. However, there are several limitations restrict its application, including the need for volatile and highly reactive carbenes, high reaction temperature, and metal catalysts. Moreover, the carbene synthesis usually needs drastic reaction conditions, which requires the carbene precursor don't contain reactive functional groups. Otherwise, the reactive groups will take place relevant reaction and no longer exist after the

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carbene preparation. Against this background, we have developed a novel and mild approach to form diarylcarbene with representative epoxy groups. This diarylcarbene derivative introduces functional groups to graphene via carbene reaction, which can be further derivatized to get more controllable structure and better composites. To the best of our knowledge, as only few carbene functionalizations of graphene have been reported, it is imperative to extend the study to provide alternate strategy to suit different applications.

Epoxy resins are a class of high overall performance thermosetting polymers that have wide applications. Recently, a lot of attention has been given to graphene/epoxy resin composites [16–22]. As chemical oxidation is the most widely used approaches for modification of graphene, we think it is worthwhile to use diarylcarbene modified graphene as reinforcement to enhance the properties of epoxy resin. The reactive groups (epoxy groups) not only led the better dispersibility of graphene, but also enable stronger interfacial interactions between the graphene and the matrix.

## 2. Experimental section

### 2.1. Materials

The 4,4'-dihydroxybenzophenone, tosylhydrozone, epichlorohydrin, graphite, hydrazine hydrate, KOH, MgSO<sub>4</sub>, NaNH<sub>2</sub> and common solvent were products of Aladdin, China. Epoxy resin (Araldite resin LY5052) was the matrix material and supplied by Vantico Co., Ltd., UK, as well as the curing agent (Aradur hardener HY5052).

### 2.2. Synthesis of compound a

Starting material, 4,4'-dihydroxybenzophenone (2.14 g, 10 mmol), was stirred with KOH (1.12 g, 20 mmol) and methanol (50 mL) in a 250 mL round-bottom flask. When the reagents were completely dissolved in the reaction solvent, excessive epichlorohydrin (15.64 mL, 200 mmol) was added. After carrying out reaction at 60 °C overnight, the reaction solution was washed with water. A product was extracted from the aqueous solution using a sufficient amount of dichloromethane. After drying with MgSO<sub>4</sub>, the solvent was removed under vacuum. The resulting crude compound a was washed by cold ethanol and dried. Yield: 92%. The characterization spectra were shown in Fig. S1. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, δ): 2.73, 2.88, 3.34, 3.97, 4.25, 6.92, 7.72 ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz, δ): 44.6, 49.9, 68.8, 114.1, 132.2, 161.7, 194.6 ppm. IR: 2931, 1636, 1600, 1578, 1507, 1252, 1171, 1030, 912, 851 cm<sup>-1</sup>. MS *m/z* (%): 327.0 (100).

### 2.3. Synthesis of compound b

Added 2.0 mmol compound a to EtOH/tetrahydrofuran (10/10 mL) in a 50 mL round-bottom flask. Then 4.0 mmol tosylhydrozone was added to the above solution. The mixture was heated to reflux (80 °C) for 48 h, then the solvent was removed in vacuum. The compound b was purified by column. Yield: 65%. The characterization spectra were shown in Fig. S2. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, δ): 2.34, 2.72, 3.30, 3.67, 4.24, 6.72, 6.94, 7.26, 7.69, 10.01 ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz, δ): 21.6, 44.6, 50.0, 69.6, 114.1, 123.7, 127.8, 129.6, 132.2, 144.1, 154.2, 161.7 ppm. IR: 2927, 1599, 1509, 1246, 1160, 1031, 912, 837, 731, 665 cm<sup>-1</sup>. MS *m/z* (%): 495.2 (100).

### 2.4. Synthesis of compound c

The compound b (0.25 mmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub>

(10 mL). NaNH<sub>2</sub> was added (2.5 mmol) to this solution and the reaction mixture was stirred in dark at room temperature for 6 h. Upon completion of the reaction (monitored by TLC), the reaction was stopped to give a purple solution. As the compound c is unstable, it can't obtain the correct NMR and MS spectrum under the high energy testing condition. However, the FT-IR spectrum was collected immediately after the reaction was completed (Fig. S3). The characteristic peaks at 2023, 912 cm<sup>-1</sup> were observed and resulted from the presence of diazo and epoxy groups of compound c. The results indicated that the tosyl groups were removed from the compound b and the diazo groups were successfully generated after the base treatment. Moreover, the epoxy groups were still remained in compound c, which would be further introduced to graphene.

### 2.5. Treatment of graphene with diarylcarbene

Graphene oxide was synthesized by the modified Hummers method. The graphene oxide was reduced by typical reduction procedure using hydrazine hydrate to get reduced graphene oxide (GR). The GR was added into the above solution containing compound c. The solvent was removed under vacuum. The mixture was heated at 100–120 °C to generate diarylcarbene. The color was changed from violet to light yellow in 20 min. The diarylcarbene modified graphene (DC-GR) was washed with acetone and water for several times to remove the impurity and adsorbed compounds.

### 2.6. Preparation of epoxy/DC-GR composites

The obtained DC-GR was dispersed in acetone (0.5 g/L) by ultrasonic assistant for 0.5 h. The epoxy precursor was added to the above suspension and treated by sonication for another 2 h. To remove the acetone, the mixture was put into oven at 80 °C for 24 h. Subsequently, the hardener HY5052 was introduced at mass ratio of 38:100 to epoxy resin and mildly stirred at room temperature. The mixture was degassed for 1 h under vacuum, then the mixture was transferred to an open mold and cured at 80 °C for 10 h, then 130 °C for 10 h to get the composite samples.

### 2.7. Characterization and measurement

Characterization of organic compounds was done using the following equipment and settings. Infrared (IR) spectra were recorded on Bruker Tensor 27 FT-IR spectrometers. Nuclear magnetic resonance (NMR) was recorded on Bruker AVF400 (400 MHz) spectrometer. Mass spectra (MS) were obtained with a Fisons Platform spectrometer with electrospray ionisation (ESI).

FT-IR (Bruker, Tensor 27) and Raman spectra (Horiba JobinYvon, France) were used to characterize the functionalized graphene. X-ray photoelectron spectroscopy (XPS) was performed on a lab built spectrometers at 10<sup>-9</sup>–10<sup>-10</sup> Torr, with an Al K-α X-ray source (1486.6 eV). The solid state NMR spectra were obtained by Bruker AVF500 (500 MHz) spectrometer. Transmission electron microscope (TEM, JEM-2100F) and atomic force microscope (AFM, Sounding Housing SPA 400) were used to characterize the morphology and structure of the graphene.

The tensile properties of epoxy/DC-GR composites were carried out with an Instron 4301 at a crosshead speed of 2 mm/min. At least five samples were tested to obtain average values. Scanning electron microscope (SEM, S-4800, Hitachi Instrument) was used to characterized freeze-fractured surface of the composites. Thermogravimetric analysis (TGA) were performed with a thermogravimetric analyzer (Netzsch STA449C) from room temperature to 700 °C at a heating rate of 10 °C/min.

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