

# Facile and Effective Functionalization of Graphene Oxide by Boron–Oxygen Covalent or Bingel Cyclopropanation Reaction

Weibo Yan\*, Yanfei Xu, and Yongsheng Chen

*Key Laboratory of Functional Polymer Materials and Center for Nanoscale Science and Technology,  
Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China*

Functionalized graphene oxide (GO-BPh<sub>2</sub>), was obtained via one step reaction between triphenyl boron and oxygen-containing groups on graphene sheets. In addition, functionalized graphene oxide (GO-Carbene) was obtained via bingel cyclopropanation reaction of active double bands on graphene sheets. Both functionalized materials can be homogeneously distributed into ortho-dichlorobenzene. They were characterized by FTIR spectroscopy, UV Vis NIR spectroscopy, thermal gravimetric analysis, raman spectra, and X-ray photoelectron spectroscopy (XPS). FTIR, TGA and XPS results prove that phenyl boron has been successfully attached to the graphene sheets by covalent bonds. And the Raman spectra and XPS confirm that many carbon double bands changed into carbon single bands on graphene sheets after cyclopropanation reaction.

**Keywords:** Graphene Oxide, Functionalization, Covalent Grafting, Bingel Cyclopropanation.

## 1. INTRODUCTION

Graphene, with an atomically thin, 2-dimensional structure that consists of sp<sup>2</sup>-hybridized carbons, has attracted enormous interest in the area of solid state electronics<sup>1–4</sup> and composite materials<sup>5–9</sup> due to its fascinating electronic and mechanical properties. Graphene oxide (GO) preferred as the precursor of graphene has been widely studied for its good dispersion in water and mass production with low cost. Despite it shows great potential of application, there are still major challenges ahead. These challenges include the poor solubility of graphene in organic solvent, as many applications such as in the field of organic electronics and polymer composites demand that graphene should be dispersed in organic solvent, especially in weak polar solvent.<sup>10–12</sup>

However, improving the dispersibility of GO or graphene in organic solvents especially in non-polar organic solvents and tailoring its electronic properties at the solid state are the biggest challenges in the practical applications.<sup>13,14</sup> To overcome the first obstacle, so far, many methods have been focused on the non-covalent functionalization through van der Waals forces

or  $\pi$ – $\pi$  interactions,<sup>15–17</sup> or covalent functionalization by reaction with epoxy,<sup>18,19</sup> hydroxyl groups,<sup>20</sup> and conjugated carbon atoms on the basal plane of GO,<sup>21–23</sup> as well as the carboxyl acids on the edges of GO.<sup>24</sup> Effective functionalized method is to introduce large groups onto graphene sheet to prevent the strong  $\pi$ – $\pi$  interaction among the graphene sheets. And many studies showed that the oxygen-containing groups could form the coordinate bond with the metals.<sup>25,26</sup> To date there are only a few reports about the functionalization of GO with non-metal functional groups through covalent grafting,<sup>27–30</sup> the present work addresses this key method.

On the other hand, most common method for functionalized GO focus on the oxygen-containing group such as –OH, –COOH, C=O, and the active carbon double bonds have been neglected. In fact, the active carbon double bonds are very important reactive sites when the energy level of graphene needs to be changed for modifying its electronic properties. Bingel reaction used in fullerene and carbon nanotube chemistry is a cyclopropanation reaction utilizing the active carbon double bonds to obtain methano-fullerene or nanotube derivatives. This reaction is of importance in the field of carbon nano-material field because it allows introduction of useful extensions to the

\*Author to whom correspondence should be addressed.

fullerene sphere or carbon nanotube. These extensions alter their properties for instance solubility, electrochemical behavior, bandgap and therefore widen the range of potential technical applications.<sup>31–33</sup> So, it is very meaningful to further study the functionalized method of GO by bingel cyclopropanation to improve dispersity of graphene sheets.<sup>34,35</sup>

Here, we report two different general and effective methods for the functionalization of GO nanomaterials. One method is carried out by boron-oxygen covalent bonds, which formed by reaction between oxygen-containing groups and triphenyl boron without changing the conjugated structure of GO. The other method is carried out through the bingel [2 + 1] cyclopropanation reaction by addition of exceptionally reactive carbon carbene to active carbon double bonds with changing the conjugated structure of GO. FTIR, Raman, XPS and thermogravimetry analysis (TGA) characterizations confirm the attachment of functional group to the graphene oxide. The attachment of organic molecules has made functionalized GO dispersed stable in organic solvents.

## 2. EXPERIMENTAL DETAILS

### 2.1. Materials

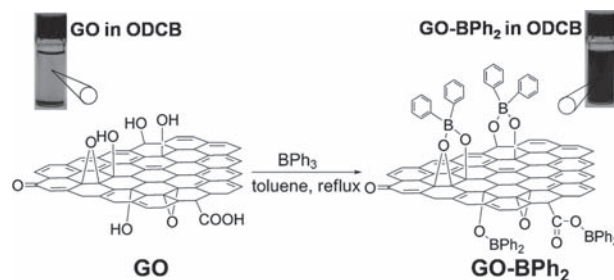
Graphite was obtained from Qingdao Huarun Graphite Co. Graphene oxide was prepared by modified Hummers' method.<sup>36</sup> Triphenyl boron was obtained from Aldrich. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and Diethyl bromomalonate were obtained from Aldrich. Sodium and *n*-Decyl alcohol were obtained from third chemical company in Tianjin city (China). All manipulations were carried out under a dry argon atmosphere using the standard Schlenk techniques, and all solvents were purified by standard procedures before use.

### 2.2. Preparation of BPh<sub>2</sub>-Functionalized Chemically Converted Graphene Oxide Sheets

As demonstrated in Figure 1, GO (20 mg) was dispersed in dry toluene (50 mL) by ultrasound for 30 minutes, and then triphenyl boron (200 mg) was added. The mixture was allowed to reflux at 110 °C for 24 hours under argon. After that, the functionalized product was obtained by centrifuged, and washed with toluene and then dried under vacuum. The product GO-BPh<sub>2</sub> has good solubility in ODCB with maximum solubility, 1.0 mg mL<sup>-1</sup>.

### 2.3. Functionalization of Graphene Oxide by Bingel Cyclopropanation Reaction

As demonstrated in Figure 2, first, a suspension of GO (20 mg) was obtained by sonication for 0.5 hour in dry ortho-dichrobenzene (ODCB) (30 mL) and then GO reacted with an excess of 1,8-diazabicyclo[5.4.0]undecene (DBU) (860 mg, 4.2 mmol) and Diethyl bromomalonate (1005 mg, 5.7 mmol) under argon at ambient temperature for 3 days. The homo-dispersed brown solution

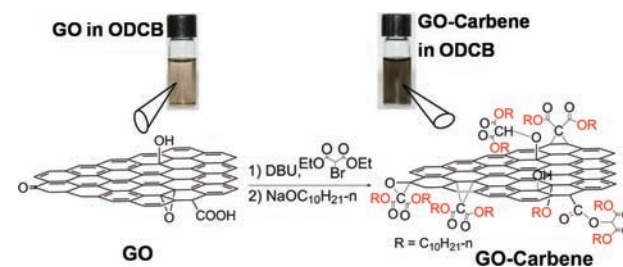


**Figure 1.** Scheme for the functionalization of GO by covalent grafting reaction with BPh<sub>3</sub> and inserted photo with GO/GO-BPh<sub>2</sub> (1.0 mg mL<sup>-1</sup>) dispersed in ODCB.

was obtained. The mixture was centrifuged, and then obtained solid (intermediate product) was washed with dry ODCB and THF successively. At last, the intermediate product obtained by centrifugation was dispersed in dry THF (20 mL) at once, then excess fresh prepared *n*-Decyloxide sodium was added, and then the mixture was stirred at room temperature under argon for 2 days. The mixture was centrifuged and the obtained solid was dispersed in C<sub>2</sub>H<sub>5</sub>OH, centrifuged to wash away un-reacted *n*-Decyloxide sodium and byproducts. Then the black solid was obtained after drying under vacuum. The product GO-Carbene has good solubility in ODCB with maximum solubility, 0.6 mg mL<sup>-1</sup>.

### 2.4. Measurement and Characterization

Fourier transform infrared spectroscopy (FT-IR) spectra were obtained using a Bruker Tensor 27 spectrometer. All IR samples were prepared as pellets using spectroscopic grade KBr. UV vis NIR spectra were obtained with a Jasco V-570 spectrometer, and UV vis spectra were recorded on a Varian Cary 300 spectrophotometer. Thermal gravimetric analysis (TGA) was used by Netzsch STA 409PC with heating rate of 5 °C min<sup>-1</sup> from room temperature to 1000 °C under N<sub>2</sub>. Raman spectra were measured by a Renishaw inVia Raman microscope at room temperature with the 514-nm line of an Ar ion laser as an excitation source. XPS spectra were recorded using a Kratos Axis Ultra DLD spectrometer employing a monochromated Al-Kα X-ray source ( $h\nu = 1486.6$  eV),



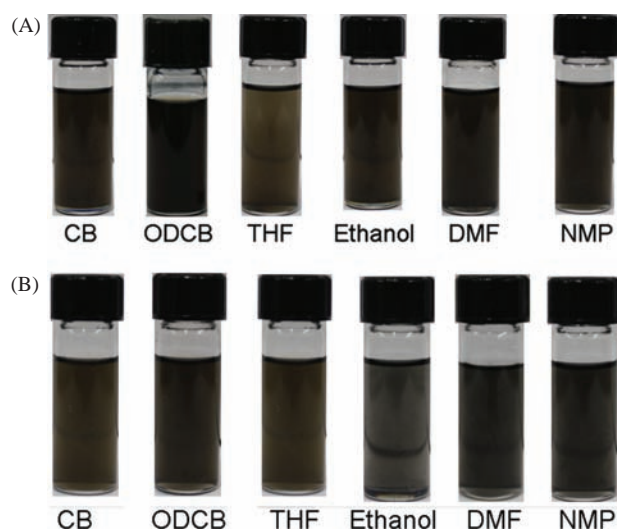
**Figure 2.** Scheme for the functionalization of GO by bingel reaction with carbon carbene, followed by interesterification reaction, inserted photo with GO/GO-Carbene (0.6 mg mL<sup>-1</sup>) dispersed in ODCB.

hybrid (magnetic/electrostatic) optics and a multi-channel plate and delay line detector (DLD).

### 3. RESULTS AND DISCUSSION

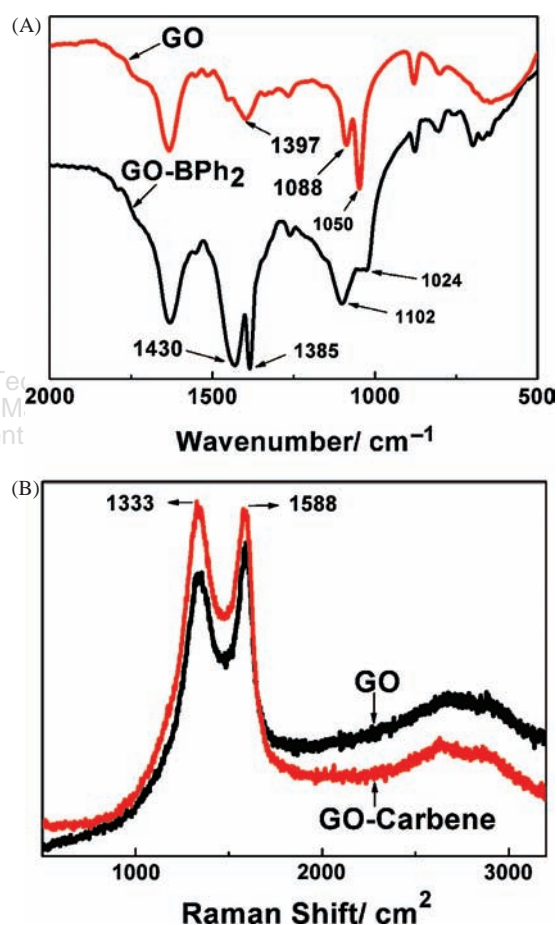
GO was prepared according to the modified hummers method.<sup>36</sup> As shown in Figure 1, triphenyl boron could form the covalent bonds with the adjacent oxygen and could also react with carboxyl and isolate hydroxyl to release benzene. The phenyl boron functional groups can be probably on both the edge and the surface of GO and the functionalized GO is highly soluble in non-polar, ODCB without aggregation, as shown in Figure 3(A). Except the non-polar organic solvent, the product GO-BPh<sub>2</sub> also can be dispersed in polar organic solvents such as DMF, NMP, as shown in Figure 3(A), with a little precipitate in THF or ethanol solution of 1.0 mg mL<sup>-1</sup>.

Next, we turn to the description of the functionalized GO with carbene. In the previous review of “Graphene Oxide Chemistry,” Ruoff et al. has discussed the structure of GO in detail.<sup>12</sup> Although even to this day no unambiguous model exists, it is rational that the double bonds were likely either aromatic or conjugated, as shown in Lerf–Klinowski model of GO. As we all known, conjugated alkenes connected with aromatic ring, carboxyl acid and carbonyl group were more reactive to carbene than the aromatic carbon double bonds. Carbene also could react with the oxygen-containing groups such as OH, COOH through O–H insertion reaction, as shown in Figure 2. GO could not disperse in ODCB and aggregate even after by sonication, but after functionalization, the solubility of GO-Carbene in ODCB was greatly improved and it can disperse in ODCB homogeneously with the maximum concentration, 0.6 mg mL<sup>-1</sup>. It also can be well dispersed in polar organic solvents, as shown in Figure 3(B).



**Figure 3.** (A) Photograph of GO-BPh<sub>2</sub> dispersing in different solvents ([GO-BPh<sub>2</sub>] = 1.0 mg mL<sup>-1</sup>), (B) Photograph of GO-Carbene dispersing in different solvents ([GO-Carbene] = 0.6 mg mL<sup>-1</sup>).

The functionalization of GO is further confirmed by FT-IR spectroscopy. As shown in Figure 4(A), in the spectrum of GO, the strong band at 1390 cm<sup>-1</sup> was attributed to the stretching vibration of C–O in the epoxy O–C–O, which is converted to the strong band at 1430 cm<sup>-1</sup> arising from the C–O and 1385 cm<sup>-1</sup> arising from the B–O stretching vibration of covalent bond C–O–B–O–C.<sup>37</sup> And the strong bands at 1050 cm<sup>-1</sup>, 1088 cm<sup>-1</sup> arising from the stretching vibration of C–O in C–O–H on the GO sheets, were converted to the C–O stretching vibration at 1024 cm<sup>-1</sup> and 1102 cm<sup>-1</sup> of C–O–B in the spectrum of GO-BPh<sub>2</sub>, indicates the B–O covalent bond was formed.



**Figure 4.** (A) FTIR spectra of GO and GO-BPh<sub>2</sub>. In the spectrum of GO, the strong band at 1390 cm<sup>-1</sup> was attributed to the stretching vibration of C–O of the O–C–O, which is converted to the strong band at 1430 cm<sup>-1</sup> arising from the C–O and 1385 cm<sup>-1</sup> arising from the B–O stretching vibration of covalent bond C–O–B–O–C. And the strong bands at 1050 cm<sup>-1</sup>, 1088 cm<sup>-1</sup> arising from the stretching vibration of C–O in C–O–H on the GO sheets, were converted to the C–O stretching vibration at 1024 cm<sup>-1</sup> and 1102 cm<sup>-1</sup> of C–O–B in the spectrum of GO-BPh<sub>2</sub>, indicates the B–O coordinate bonds were formed. (B) Raman spectra of GO and GO-Carbene. The ratio of the intensities ( $I_D/I_G = 1.02$ ) for GO-Carbene is markedly increased compared with that ( $I_D/I_G = 0.91$ ) of GO, indicating the break of C=C and the formation of many sp<sup>3</sup> carbons.

Raman spectroscopy is a powerful tool for identifying the structure defects of graphene-based materials. The variation of the relative intensities of *G* (the *E* 2g mode of sp<sup>2</sup> carbon atoms) and *D* (the symmetry A 1g mode) bands in the Raman spectra of the GO usually reveals the change of the electronic conjugation state. Among the process of functionalization, there was no remarkable change of the position of the peaks. As depicted in Figure 4(B), while the ratio of the intensities ( $I_D/I_G$ ) showed that after functionalization, the ratio of the intensities ( $I_D/I_G$ ) of the samples increased, which indicated that some sp<sup>2</sup>-carbons were converted to sp<sup>3</sup>-carbons on the graphene sheets.<sup>38</sup> It proved the successful addition reaction of carbene to active carbon bond on GO sheet.

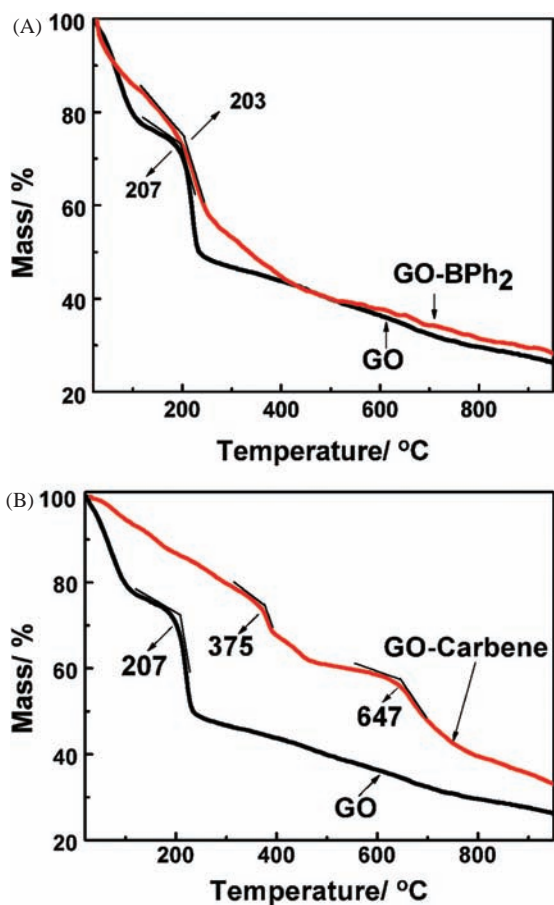
The successful functionalization of GO with BPh<sub>3</sub> was also reflected in TGA curves. As shown in Figure 5(A), the GO shows weight loss was attributed to the absorbed water below 120 °C. Then a large weight loss (23%) with onset temperature at 207 °C can be attributed to the removal of the groups (–OH and –COOH) from the GO sheets.<sup>39</sup> And the GO-BPh<sub>2</sub> showed a similar weight loss (~40%) to GO below 400 °C, which is attributed to the removal of the functional groups (including: O<sub>2</sub>BPh<sub>2</sub>/OBPh<sub>2</sub>/O<sub>2</sub>BPh).

It was estimated according to the mass ratio from TGA of GO-BPh<sub>2</sub>. The degree of functionalization for GO-BPh<sub>2</sub> was estimated to be one functional group per ~25 graphene carbons. The curves show that after functionalization, GO-BPh<sub>2</sub> has a little better thermal stability than GO, but the functional groups are easy to remove as the oxygen-containing groups on GO. That shows that the GO-BPh<sub>2</sub> material is easy to restore to graphene structure under low temperature condition.

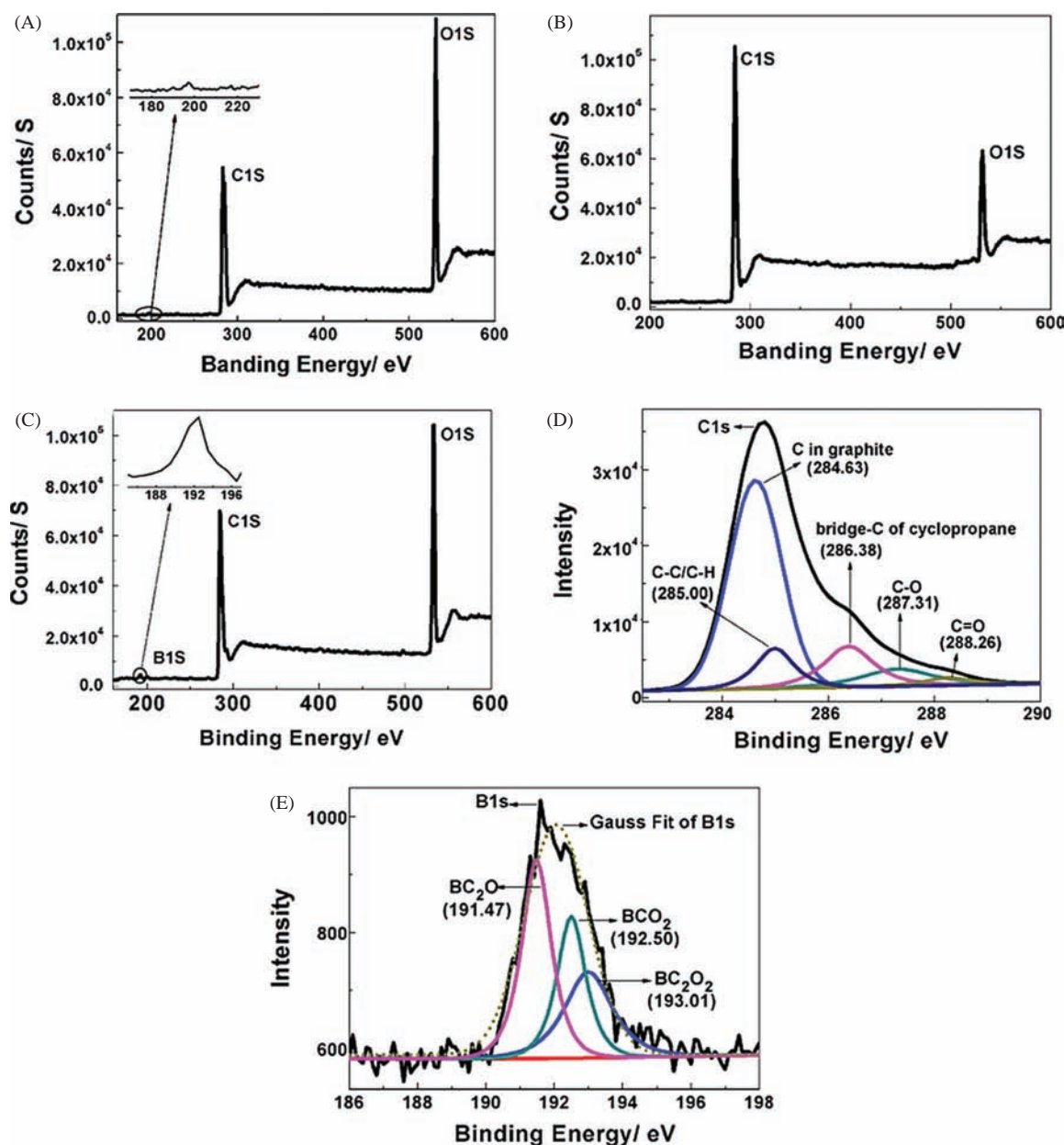
The successful functionalization of GO with carbene addition was also reflected in TGA curves as shown in Figure 5(B). The GO shows weight loss (23%) is attributed to the absorbed water. Then a large weight loss (23%) with onset temperature at 207 °C can be attributed to the removal of the groups (–OH and –COOH) from the GO sheets.<sup>39</sup> And the GO-Carbene shows the similar weight loss to GO below 200 °C, mainly the removal of adsorbed solvent. After 200 °C until 375 °C, it is attributed to the weight loss (13%) of groups produced by the reaction between oxygen-containing groups and carbene. And from 375 °C to 470 °C, GO-Carbene shows a weight loss (13%) which can be attributed to the removal of the groups connected with graphene sheet by C–C bond. Moreover, high temperature pyrolysis of GO-Carbene is similar to GO after 470 °C and attributed to pyrolysis of the carbon skeleton of graphene.<sup>40</sup> The degree of functionalization for GO-Carbene was estimated to be one functional group per ~58 graphene carbons. These results demonstrate that after functionalization, GO-Carbene has better thermal stability than GO.

To further illustrate the successful functionalization of GO, X-ray photoelectron spectroscopy (XPS) was performed on GO, GO-BPh<sub>2</sub> and GO-Carbene samples. Figures 6(A)–(C) show the survey data of the solid samples and the higher resolution spectra of the O1s, and C1s areas in both samples with B1s of GO-BPh<sub>2</sub>. The XPS results indicate the mass ratio of carbon/oxygen (C:O) in GO-Carbene sample is 3.9:1, with that of 1.9:1 in GO. It can be thought that the content of carbon in GO-Carbene sample increased compared with that in starting material, GO, after many long alkyl chain attaching onto the GO sheets. It also demonstrates that through this method, we can obtain the high degree functionalized GO sheets. The mass ratio of carbon/oxygen/boron (C:O:B) is 2:1:0.06, which indicates the B-containing groups have been attached onto GO sheets by B–O covalent bond.

The higher resolution data of C1s area of the GO-Carbene are shown in Figure 6(D). It clearly indicates five components corresponding to carbon atoms in different functional groups: the C in graphite (BE, 284.63 eV), the C in C–C/C–H in alkyl chain (BE, 285.00 eV), the bridge C of the cyclopropane (BE, 286.38 eV), C–O–C (BE, 287.31 eV,) and the carbonyl C (BE, 288.26 eV).<sup>41</sup> The new components of C 1s, such as C–C/C–H in alkyl chain (BE, 285.00 eV), the bridge C of the cyclopropane (BE, 286.38 eV), strongly indicating that the GO sheets



**Figure 5.** (A) TGA spectra of GO and GO-BPh<sub>2</sub>; (B) TGA spectra of GO and GO-Carbene obtained with a heating rate of 5 °C min<sup>-1</sup> under purified nitrogen gas flow.



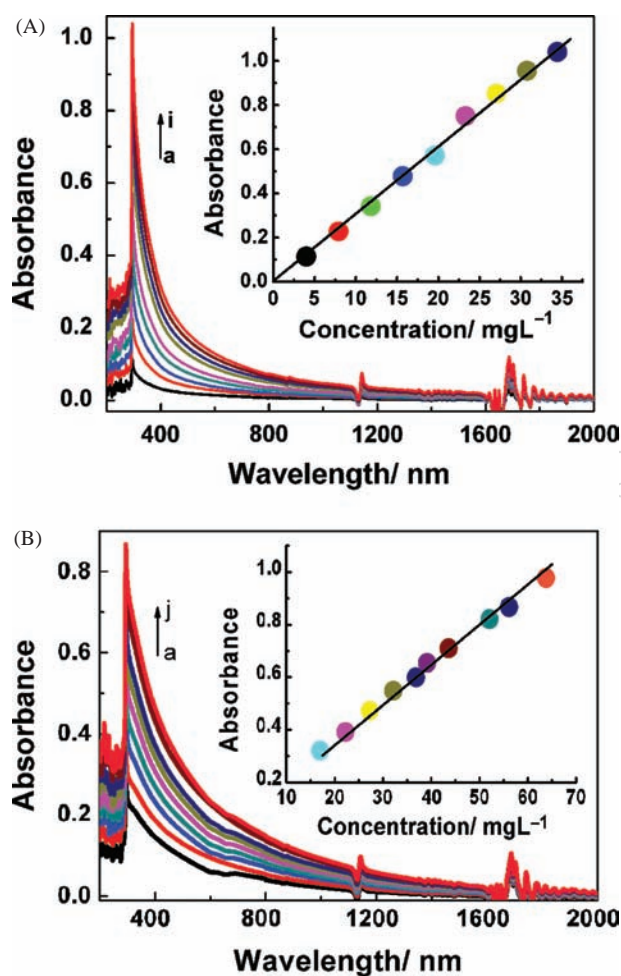
**Figure 6.** XPS characterization of carbon bonding state in GO-Carbene and boron bonding state in GO-BPh<sub>2</sub>. The survey curves of (A) GO, (B) GO-Carbene and (C) GO-BPh<sub>2</sub>, inset: the higher resolution curves of the boron area. (D) The higher resolution curves of C1s in GO-Carbene; (E) the higher resolution curves of B1s in GO-BPh<sub>2</sub>.

have been successfully functionalized by bingel cyclopropanation reaction. This is consistent with our raman spectra analysis.

The survey (Fig. 6(A)) of GO shows the absence of any detectable amounts B 1s (XPS band is B1s usually found between 180 and 200 eV depending on the chemical environment). As shown in the inset of Figure 5(C), a weak band of B 1s appears ca. 191.60 eV, with assigning to B–C.<sup>42</sup> Compared with GO, the survey of GO-BPh<sub>2</sub> shows the presence of B 1s originating from B–Ph group with the C/B weight percentage 1/0.03, indicating that the covalent functionalization of GO successfully occurred.

The higher resolution data of B 1s area of the GO-BPh<sub>2</sub> are shown in Figure 5(E). It could be seen that the curve of the B 1s is not smooth, with many burrs because of the small atom weight of boron and low degree functionalization of GO sheets. It clearly indicates three components corresponding to boron atoms in different functional groups: the B in BC<sub>2</sub>O of O–BPh<sub>2</sub> groups (BE, 191.47 eV), the B in BCO<sub>2</sub> of Ph–BO<sub>2</sub> groups (BE, 192.50 eV), the B in BC<sub>2</sub>O<sub>2</sub> of Ph<sub>2</sub>BO<sub>2</sub> groups (BE, 193.01 eV).<sup>43</sup> It indicates that the GO sheets have been successfully functionalized by oxygen-boron coordinate bonds. This is consistent with our IR spectra analysis.

Apart from the visual observation, solution-phase UV-Vis-NIR spectroscopy (Fig. 7(A)) is used to determine the solubility of GO-BPh<sub>2</sub> and GO-Carbene in ODCB. The absorptions (at 294 nm) for the GO moiety<sup>44</sup> were plotted against concentration and a good linear relationship was obtained with an *R* value of 0.99. The absorbance of solutions of GO-BPh<sub>2</sub> at other wavelengths was also consistent with the Beer's law. These results demonstrate that GO-BPh<sub>2</sub> has good solubility in ODCB with maximum solubility, 1.0 mg mL<sup>-1</sup>. Solution-phase UV-Vis-NIR spectroscopy (Fig. 7(B)) can be used to determine the solubility of GO-Carbene.<sup>45</sup> The absorptions (at 296 nm) for



**Figure 7.** (A) Concentration dependence of UV absorption of GO-BPh<sub>2</sub> in ODCB, (Concentrations are 3.98, 7.92, 11.82, 15.69, 19.61, 23.30, 27.05, 30.77, 34.45 mg L<sup>-1</sup> from a to i, respectively). Shown in the inset is a plot of optical density at maximal absorption position (294 nm) for the GO moiety versus concentration. The straight line in the plot in the inset is a linear least-square fit to the data, indicating GO-BPh<sub>2</sub> was dissolved homogeneously. (B) Concentration dependence of UV absorption of GO-Carbene in ODCB, (Concentrations are 18.87, 24.69, 30.30, 35.71, 40.94, 43.48, 48.43, 53.22, 57.85, 62.33 mg L<sup>-1</sup> from a to j, respectively). Shown in the inset is a plot of optical density at maximal absorption position (296 nm) for the GO moiety versus concentration. The straight line in the plot in the inset is a linear least-square fit to the data, indicating GO-Carbene was dissolved homogeneously.

the GO moiety<sup>44</sup> were plotted against concentration and a good linear relationship was obtained with an *R* value of 0.99. The absorbance of solutions of GO-Carbene at other wavelengths was also consistent with the Beer's law. These results demonstrate that the functionalized GO are homogeneously dispersed in ODCB, with maximum solubility similar with results reported (1.0 mg mL<sup>-1</sup> in DMF).<sup>46</sup>

#### 4. CONCLUSIONS

In summary, we have successfully developed two new and simple methods to obtain functionalized chemically converted graphene oxide nanosheets. One method is via *c* covalent grafting reaction between organic boron and oxygen-containing group on the GO, the other is through the reaction between carbene and carbon double bands on the GO sheets. The results clearly indicate that the functionalized GO sheets have good solubility in organic solvents, such as ODCB, which would open up a wide range of possibilities for efficient chemical derivatives of GO or graphene, graphene-based organic electronics and polymer composite materials.

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