Modification of Graphene with Hyperbranched Poly(Ether Ketone) for Heterogeneous Catalyst

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1. Introduction
Graphene, a two dimensional material with single layer sp² hybridized carbon atoms arranged in honeycomb lattice, is of great interest in recent years for its excellent current and heat conduction and surface properties [1]. Single layer graphene is generally prepared by micromechanical cleavage from highly oriented graphite [2]. However, because of its hydrophobic and π-π interaction between the sheets, the graphene sheet is not stable in solvent and tends to re-aggregate to form graphite, which limited its further applications [3]. But the chemical modification is efficient to improve the dispersion and prevent agglomeration [4].

Compared to the single layer graphene, graphene oxide (GO), with a number of OH, COOH and epoxy C-O-C chemical groups, has been widely discussed for surface modification [5]. Small molecules and a large amount of polymers, such as epoxy [6], polyethylene terephthalate [7], polystyrene [8], etc., have been studied as modifiers. The polymer/graphene nanocomposites showed considerable improvements on solubility, dispersion, electronic conductivity, etc. and in all the systems, graphene was dispersed at very low filler loadings in the polymer matrix with strategies containing in-situ intercalative polymerization, solution intercalation and melt intercalation [9]. Moreover, some recent researches utilized a controlled radical polymerization technique and in some of them, GO itself could be a macro-initiator [10].

However, singly layer graphene, with limited defects, shows a low chemical activity that is much harder to be modified by such polymers. To maximize the activity sites, hyperbranched structure is of interest. Our research group has successfully synthesized a novel hyperbranched aromatic poly(ether ketone) (HBPEK) with carboxylic acid terminal groups [11]. Since Friedel–Crafts reaction has been proved for effective functionalization of graphene [12], the carboxylic acid terminal groups of HBPEK can afford a large amount of reaction sites in such reaction and a high loading rate can be expected. Meanwhile, with the help of hyperbranched polymer, the reactive sites for further functionalization are enlarged. The unattached terminals afford a large amount of reactive sites which could be well exposed because of the low entanglement of hyperbranched polymers.

Moreover, our research group has demonstrated the catalytic performances of sulfonic acid terminals on hyperbranched poly(ether sulfone) [13], carboxylic acid terminals on HBPEK [11], and a nitrooxyl radical, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), on HBPEK (TEMPO/HBPEK) [14]. In those studies, the hyperbranched polymers were immobilized onto carbon black or polyimide fine particles to use them as heterogeneous catalysts. If graphene can be used to immobilize them, the flexibility of graphene might contribute to the catalytic activity of resulting materials. In this context, the objective of this study is to demonstrate the modification of graphene with HBPEK followed by the functionalization of the terminals of HBPEK with TEMPO as shown in Fig. 1. Meanwhile, the synthesized material has been tested as a heterogeneous catalyst for the aerobic oxidation of 2-adamatanol.
2. Experimental

2.1. Material synthesis

Preparation of a symmetrical AB$_2$ monomer, 4,4’-(m-phenylenedioxy)-bis(benzenecarboxylic acid), and its polycondensation to form HBPEK have been reported previously [11].

To immobilize HBPEK on graphene, HBPEK (300 mg) was dissolved in 20 mL DMF in the presence of graphene (N002-PDR, Angstron Materials, 60 mg) and PPMA (10 mL), stirred under N$_2$ at 110 °C for 72 h, and then filtered. The product was stirred in DMF at 100 °C for 12 h, and then filtered. This washing process was repeated to obtain HBPEK/graphene.

![Chemical structures and reactions](image)

Fig. 1. Illustration of the synthesis of TEMPO/HBPEK/Graphene and the catalytic reaction of 2-adamantanol.

To immobilize TEMPO on HBPEK/graphene, the HBPEK/graphene (909 mg, corresponding to 1.0 mmol of COOH groups) was mixed with 1-(3-dimethylaminopropyl)-3-ethylcarbodi-imide (EDCI; 186 mg, 1.2 mmol) in 5 mL dichloromethane, followed by stirring for 30 min. 4-amino-TEMPO (188 mg, 1.1 mmol) and 4-dimethylaminopyridine (DMAP) (13 mg, 0.1 mmol) were dissolved in 3 mL dichloromethane and then added to the previous mixture. After stirring at 40 °C for 24 h, the solvent was removed by evaporation and the product washed with water and acetone.

2.2. Measurements

Nuclear magnetic resonance (NMR) (1H, 400MHz) spectra were recorded for samples dissolved in chloroform-$_d$ or dimethyl sulfoxide-$_d_6$ using a JEOL JNM-ECS 400 NMR spectrometer. Fourier-transform infrared (FT-IR) spectroscopy was performed using a spectrophotometer (Jasco, 6100) on KBr pellets.

The ion exchange capacity (IEC) of HBPEK and HBPEK/graphene was determined by titration as follows. 60 mg of sample powder was stirred in a 0.1 M NaOH solution (3 mL) overnight, and then filtered. The filtrate was diluted to 10 mL with deionized water, and titrated with 0.05 M HCl solution.

CHN elemental analysis was performed using a Perkinelmer 2400-II analyzer.

2.3. Catalytic reaction

The catalytic performance of the materials was determined using a Shibata Chemist Plaza CP100 multi-reactor system equipped with 6-mL reactors. 2-adamantanone (1.0 mmol), nitric acid (67%, 0.1 mmol) and the catalyst (TEMPO content: 0.04mmol) were mixed with 2 mL of 1,4-dioxane in the reactor, and stirred at 60 °C for 10–12 h with an oxygen balloon. The products were quantified using a Shimadzu GCMS-QP2010 Plus instrument equipped with a TC-FFAP column (0.25 mm × 30 m). The conversion was calculated based on the peak area ratio of 2-adamantanone against the internal standard (naphthalene). The product yield was calculated based on the peak area ratio of 2-adamantanone against the internal standard.

For catalyst recycling, the reaction mixture was diluted to 40 mL with acetone, filtered, and washed with acetone, and then the residue was used for the next cycle after drying and weighing.

3. Results and discussion

3.1. Synthesis of TEMPO/HBPEK/graphene

The synthesized HBPEK has a weight-average molecular weight ($M_w$) of 74000 measured by gel permeation chromatography [11], and an ion exchange capacity (IEC) of 2.5 mmol g$^{-1}$ which calculated by titration.

The HBPEK loading on graphene was
determined by titration of carboxylic acid terminals on HBPEK. The IEC of HBPEK was 2.5 mmol g⁻¹, while that of HBPEK/graphene was 1.1 mmol g⁻¹. The HBPEK loading on graphene was calculated as 44 wt%.

Then, 4-amino-TEMPO was immobilized on HBPEK/graphene to functionalize the material. The TEMPO units were linked by amide bonds with the help of carboxylic acid terminals of HBPEK.

The results of CHN elemental analysis for graphene, HBPEK/graphene and TEMPO/HBPEK/graphene were shown in Table 1. The TEMPO loading rate is calculated as 0.96 mmol g⁻¹ from the nitrogen content.

### Table 1. CHN elemental analysis result of graphene, HBPEK/graphene and TEMPO/HBPEK/graphene

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Elemental analysis / wt%</th>
<th>TEMPO loading / mmol g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>90.6 0.3 0.2</td>
<td>-</td>
</tr>
<tr>
<td>HBPEK/graphene</td>
<td>80.6 0.6 0.6</td>
<td>-</td>
</tr>
<tr>
<td>TEMPO/HBPEK/graphene</td>
<td>76.4 2.2 2.9</td>
<td>0.96</td>
</tr>
</tbody>
</table>

3.2. Catalytic performance

The synthesized catalysts were tested as a catalyst for the aerobic oxidation of 2-adamantanol. Table 2 compares the catalytic performances of TEMPO/HBPEK and TEMPO/HBPEK/graphene. The turn over numbers (TON) of the TEMPO unit were calculated from the yield of 2-Adamantanone. The blank test without catalyst resulted in a quite low yield. The TEMPO/HBPEK, which is still a homogenous system, can reach a high yield with a TON of 21. The TEMPO/HBPEK physically mixed with graphene was also tested as a control group of TEMPO/HBPEK/graphene, which showed a TON of 3. TEMPO/HBPEK/graphene shows a lower catalytic activity with a TON of 5. The decrease of activity is caused by the insolubility of TEMPO/HBPEK/graphene, which forms a heterogeneous system. But its TON is still higher than that of the blank test and control group.

Receyclability of TEMPO/HBPEK/graphene was tested under a condition at 60 °C for 10 h. The conversion of each run was controlled to lower than 50% to avoid the over-dose of TEMPO unit. The TEMPO/HBPEK/graphene was collected by filtration and used for the next run after washing them with acetone. Fig. 2 shows the collected yield and TON of each run.

The collected yields of TEMPO/HBPEK/graphene kept over 90% even after the 5th run. The TON of TEMPO/HBPEK/graphene initially is around 5, and then became stable only with a slightly decrease run by run.

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### Table 2. Catalytic performances of TEMPO/HBPEK and TEMPO/HBPEK/graphene

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TEMPO unit / mmol</th>
<th>Yield / %</th>
<th>Conv. / %</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0</td>
<td>1.3</td>
<td>2.2</td>
<td>-</td>
</tr>
<tr>
<td>TEMPO/HBPEK</td>
<td>0.04</td>
<td>84.5</td>
<td>90.3</td>
<td>21</td>
</tr>
<tr>
<td>TEMPO/HBPEK + graphene</td>
<td>0.04</td>
<td>12.8</td>
<td>18.1</td>
<td>3</td>
</tr>
<tr>
<td>TEMPO/HBPEK/graphene</td>
<td>0.04</td>
<td>18.3</td>
<td>23.3</td>
<td>5</td>
</tr>
</tbody>
</table>

*a* 2-Adamantanol (1.0 mmol), nitric acid (67%, 0.1 mmol), catalyst (TEMPO content: 0.04mmol), 1,4-dioxane(2 mL), 60 °C, 12 h, with oxygen balloon.  
*b* 20 mg of graphene.

![Fig. 2. Recycling test of TEMPO/HBPEK/graphene](image)

Based on these experimental results it can be concluded that TEMPO/HBPEK/graphene exhibits certain catalytic activity and fairly good recyclability in the aerobic selective oxidation of 2-adamantanol.

4. Conclusion

We have demonstrated that hyperbranched poly(ether ketone) can be used for the modification of graphene with a polymer loading of 44 wt%. The material can be used as a heterogeneous catalyst for aerobic oxidation after functionalizing it with TEMPO. The catalyst shows a good recyclability and stability for at least 5 runs.
Acknowledgement

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References