ABSTRACT

Graphene was functionalized via non-covalent π–π interactions with 1-pyrenebutanoic acid, succinimidyl ester (PBASE). The functionalized graphene (PBASE-G) was able to be dispersed in tetrahydrofuran (THF) and fluorescence intensity measured for the resulting dispersion was found to be enhanced as compared to a solution of only PBASE in THF. A possible explanation for the increase in emission intensity is that energy transfer occurs from graphene in the excited state to pyrene in the ground state. UV-visible absorption spectra obtained showed that the reaction condition needs to be optimised as amount of PBASE adsorbed on graphene was found to be much lesser than the initial quantity of PBASE used.

INTRODUCTION

Chemical oxidation of graphite\(^1\) is considered the most suitable route for the large scale production of graphene, a single graphitic sheet. This method involves the reduction of graphene oxide to graphene and graphene obtained from reduction of graphene oxide tends to aggregate and form back graphite due to insolubility in most common solvents.\(^6\) In order to prevent this, various methods have been studied and reported.\(^3,4,5\) One method is to utilize π–π interactions to non-covalently functionalize graphene and produce stable dispersions in a desired solvent. Aqueous dispersion of graphene has been achieved through method\(^8\) and in this study, a similar method is employed to functionalize graphene in order to demonstrate that graphene can be dispersed in the organic solvent, tetrahydrofuran (THF), and characterize the properties of the functionalized graphene.

EXPERIMENTAL PROCEDURES

Synthesis of Functionalized Graphene via π–π interactions

Graphite oxide was synthesized from natural graphite powder by a modified Hummers method.\(^1,2\) The graphite oxide obtained was mixed in N,N-dimethylformamide (DMF) and sonicated till a clear, homogeneous graphene oxide (GO) dispersion (0.1 mg mL\(^{-1}\)) was obtained. A pyrene derivative “1-pyrenebutanoic acid, succinimidyl ester” (PBASE) was used to functionalize graphene. Functionalized graphene (PBASE-G) was prepared by adding 4mg of PBASE (10 μmol) into 20 mL of GO dispersion. Hydrazine monohydrate (100 μL, 2 mmol) was then added to the mixture to reduce GO to graphene at 80 °C for 24 h. After reduction, a homogeneous black dispersion was obtained. The obtained dispersion was mixed with ethanol (100 mL) and centrifuged to obtain a black precipitate after pouring the supernatant away. The black precipitate is dried in a vacuum dessicant and redispersed in THF for characterization (See Figure 1).

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Synthesis of PBASE-GO

For comparison purpose, PBASE-GO was synthesized using the same method as PBASE-G except the starting quantity of PBASE was changed and hydrazine monohydrate was not used since reduction was not required. There were 3 samples made: PBASE-GO (2:1), PBASE-GO (1:1) and PBASE-GO (1:10). The ratio indicates a ratio with respect to weight, that is in the case of PBASE-GO (2:1), 4 mg of PBASE was added to 20 mL of GO dispersion (2 mg of GO).

Characterization of PBASE-G and PBASE-GO

X-ray photoelectron spectroscopy (XPS) was performed for PBASE-G with a Phobios 100 electron analyzer (SPECS GmbH), using an unmonochromated Mg KR X-ray source (1253.6 eV). The pass energy of the hemisphere analyzer was set at 50 eV for wide scan and 20 eV for narrow scan, while the takeoff angle was fixed normal to the sample. UV-visible absorption spectra and fluorescence spectra of PBASE-G and the 3 PBASE-GO samples were measured using Shimadzu UV-2450 Spectrophotometer and PerkinElmer LS 55 Fluorescence Spectrometer respectively. Concentration of PBASE-G and PBASE-GO dispersions used for absorption and fluorescence measurement was 25 μg/ml.

RESULTS AND DISCUSSION

Figure 1. From left to right: Image of PBASE-G solid, PBASE-G dispersion in THF (0.1mg mL⁻¹), reduced-GO and THF.

Figure 2. (left) C1s XPS spectra of GO, PBASE-G and reduced-GO

Figure 3. (right) UV-visible absorption spectra of PBASE-G and PBASE-GO samples

Reduced GO (2nd from right) seen in Figure 1 was made under the same conditions as PBASE-G except the addition of PBASE. It can be observed that the reduced-GO could not dissolve in THF and the precipitate settled down at the bottom. On the other hand, PBASE-G added to THF yielded a clear, gray solution with no precipitate.

The reduction of GO to graphene was evident when comparing the C1s XPS spectra (Figure 2) of GO and PBASE-G. The right peak of GO at 287eV was due to the oxide...
species\textsuperscript{8} present and the marked reduction in intensity of this peak in PBASE-G indicates a high degree of reduction. Also, XPS spectra of reduced-GO and PBASE-G coincide indicating that reduction process was not hindered by the presence of PBASE.

Further confirmation of GO to graphene in the synthesis of PBASE-G can be seen from the UV-visible absorption spectra (Figure 3). The tail absorption of PBASE-GO (2:1) shows a steeper decrease in intensity as compared to the tail absorption of PBASE-G which indicates an increase in the extent of conjugation from GO to graphene.\textsuperscript{3}

UV-visible spectra also indicate that the degree of functionalization of graphene was very low. Table 1 lists the values of expected and actual absorbance value. Expected and actual absorbance values were calculated by the below equation:

\[
A_{\text{expected}} = \frac{W_{\text{PBASE}}}{W_{\text{PBASE}} + W_{\text{GO}}} \times A_{\text{PBASE}} \tag{1}
\]

\[
A_{\text{actual}} = A_{343.6\text{nm}} - A_{400.0\text{nm}} \tag{2}
\]

Where \( W \) is the weight of the chemical added for reaction; \( A_{\text{PBASE}} \) is the absorbance of PBASE solution in THF (25 \( \mu \text{g/mL} \)) measured at wavelength of 343.6nm; \( A_{\text{actual}} \) is a corrected absorbance value corresponding to PBASE absorption in the solution; \( A_{343.6\text{nm}} \) is the measured absorbance value for the solution at 343.6nm and \( A_{400.0\text{nm}} \) is an estimate of absorbance value corresponding to graphene absorption at 343.6nm. Comparison of values showed that less than 5\% of PBASE added was functionalized on graphene (or GO), therefore reaction needs to be optimized for future studies.

Table 1. Comparison table for expected vs measured absorbance and emission values

<table>
<thead>
<tr>
<th></th>
<th>PBASE-GO (1:10)</th>
<th>PBASE-GO (1:1)</th>
<th>PBASE-GO (2:1)</th>
<th>PBASE-G</th>
<th>PBASE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expected UV absorbance ( (A_{\text{expected}}) )</td>
<td>0.19</td>
<td>1.07</td>
<td>1.42</td>
<td>1.42</td>
<td>2.14</td>
</tr>
<tr>
<td>Actual UV Absorbance ( (A_{\text{actual}}) )</td>
<td>0.01</td>
<td>0.02</td>
<td>0.042</td>
<td>0.043</td>
<td>2.14</td>
</tr>
<tr>
<td>Expected emission intensity ( (I_{\text{expected}}) )</td>
<td>16</td>
<td>32</td>
<td>67</td>
<td>68</td>
<td>3396</td>
</tr>
<tr>
<td>Actual emission intensity ( (I_{\text{actual}}) )</td>
<td>115</td>
<td>205</td>
<td>439</td>
<td>494</td>
<td>3396</td>
</tr>
</tbody>
</table>

Figure 4. Fluorescence spectra (excitation wavelength at 340nm) of PBASE, PBASE-G and PBASE GO in THF.
Based on $A_{actual}$, the concentration of PBASE in each solution can be obtained with the assumption that Beer-Lambert’s Law is followed. From the concentration calculated, fluorescence intensity can be predicted as stated in Table 1. From fluorescence spectra obtained (Figure 4), it has been observed that monomer emission intensity is enhanced by approximately 7 times (see Table 1) when PBASE is adsorbed on graphene or GO.

A possible explanation for this phenomenon is that energy transfer occurs from excited state graphene (or GO) to ground state PBASE. PBASE excited via energy transfer de-excites through photon emission, increasing emission intensity. Quenching of the excimer emission$^{7,8}$ at around 480nm when pyrene derivatives are functionalized on graphene via $\pi-\pi$ interactions has been commonly reported in literature, however, the effect on monomer emission$^7$ at 377nm has not been reported before. This new phenomenon may have potential applications in optoelectronic devices where PBASE-G or similar composite materials can act as a donor-acceptor pair.

**CONCLUSION**

Graphene was successfully functionalized, via $\pi-\pi$ interactions, using PBASE. Functionalized graphene (PBASE-G) synthesized was able to be dispersed in THF without being precipitated out like non-functionalised graphene. UV-visible absorption spectra obtained indicate that there is a low level of functionalization and optimization is required to ensure efficient use of PBASE in subsequent reaction. Fluorescence studies indicate that monomer emission intensity of PBASE was stronger by approximately 7 times when in the presence of graphene (or graphene oxide). A possible explanation for this enhancement of emission intensity may be the excitation of PBASE through energy transfer from excited state graphene (or graphene oxide) to ground state PBASE.

**REFERENCES**