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Letter to the Editor

Synthesis and characterization of a graphene–C₆₀ hybrid material

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ABSTRACT

A graphene–C₆₀ hybrid material has been synthesized using a chemical coupling method between graphene oxide and pyrrolidine fullerene. The formation of this hybrid material was verified by Fourier transform infrared spectroscopy, thermal gravimetric analysis and high-resolution transmission electron microscopy. Raman spectroscopy suggests a strong interaction between the C₆₀ cage and the graphene sheet. X-ray photoelectron spectroscopy demonstrates that one C₆₀ molecule is covalently attached for every ~130 carbon atoms of the graphene–C₆₀.

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Graphene, with a two-dimensional (2D) structure consisting of sp²-hybridized carbon, has attracted a tremendous amount of attention in recent years due to its unique electrical properties, which stem from its semi-metallic nature and 2D structure [1]. This unique nanostructure holds great promise for potential applications in many technological fields, such as lithium batteries [2]. In the meantime, other allotropic carbon nanomaterials, such as fullerenes, have been continuously attracting strong interest in many areas of science and technology due to their unique chemical and physical properties [3]. C₆₀ and the higher fullerenes display remarkable chemical reactivity. Various hybrid materials created by organic functionalization of fullerenes have generated intense attention, driven by the possibility of combining some of the outstanding properties of the fullerenes with those of other interesting materials, such as photoactive and/or electroactive units, including small organic molecules, polymers and carbon nanotubes (CNTs). For example, Nasibulin et al. [4] prepared a CNTs–C₆₀ hybrid material which showed a high cold electron field emission efficiency, thus making it attractive for many electronic applications. Delgado et al. [5] have

recently described the synthesis of hybrid conjugated single-walled carbon nanotubes (SWCNTs)-fullerene materials. The presence of attached fullerenes in the SWCNTs could improve the mechanical properties of the SWCNTs and tune the electronic and optical properties of the fullerene derivative, a subject of great interest for many optoelectronic applications. Therefore, we expect that a hybrid material combining graphene and fullerene may lead to some novel electronic/optoelectronic or other properties for many potential applications, including solar cells or optical limiting devices. Herein, we report a graphene–C₆₀ hybrid material via a simple coupling reaction between graphene oxide (GO) [6,7] and pyrrolidine fullerene [8].

The synthesis procedure for the graphene–C₆₀ hybrid is shown in Fig. 1. GO was prepared according to a modified hummers method [6]. The GO was confirmed to exist as individual sheets in solution [7]. The sizes of the GO sheet are mainly distributed between 200 and 500 nm determined by a statistical analysis using atomic force microscopy (AFM). Pyrrolidine fullerene (1) was prepared by a photochemical reaction between amine acid esters and C₆₀ [8]. First, GO

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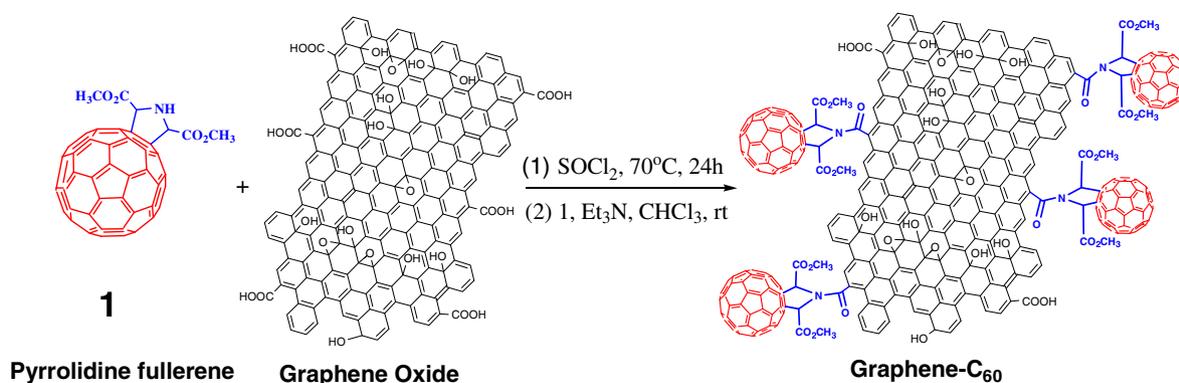


Fig. 1 – Synthesis procedure of the graphene-C₆₀ hybrid material.

was reacted with SOCl_2 to obtain acyl-chloride functionalized GO [9]. Then a condensation reaction between pyrrolidine fullerene and the acyl-chloride functionalized GO was performed using a similar method as previously described in the literature [10]. The graphene-C₆₀ hybrid obtained was investigated by Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, thermal gravimetric analysis (TGA), high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS).

Fig. 2 shows the FTIR spectra of GO, pyrrolidine-C₆₀ and the graphene-C₆₀ hybrid. As shown in Fig. 2, the notable FTIR feature of GO is the absorption band corresponding to the carboxyl stretching at 1730 cm^{-1} . The peak at 1630 cm^{-1} is attributed to the deformation of the O-H band of the strongly intercalated water absorbed by GO. The peak at 1746 cm^{-1} in the pyrrolidine-C₆₀ is the vibration of the $-\text{COOCH}_3$ group. The graphene-C₆₀ hybrid has two main peaks at 1725 and 1636 cm^{-1} . The broad peak at 1725 cm^{-1} may be attributed to the overlapping of the remaining carboxyl group in the graphene and the ester group in the pyrrolidine-C₆₀. Also, there is a new peak at 1636 cm^{-1} in the graphene-C₆₀ hybrid, which can be assigned to the amide carbonyl stretching mode [11]. This indicates that C₆₀ is chemically attached to the graphene sheet.

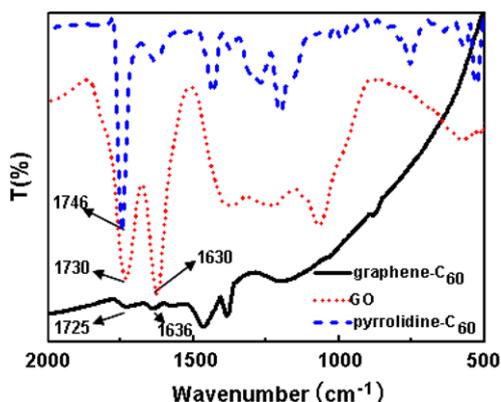


Fig. 2 – FTIR spectra of GO (dotted line), pyrrolidine fullerene (dashed line) and graphene-C₆₀ (solid line). The peak at 1636 cm^{-1} in the graphene-C₆₀ hybrid material is the amide carbonyl stretching mode, indicating that C₆₀ is chemically attached to the graphene sheet.

Raman spectroscopy of the GO, pyrrolidine-C₆₀ and graphene-C₆₀ hybrid was also conducted, as shown in Fig. 3. The GO shows an intense tangential mode (G band) at 1600 cm^{-1} , with a disordered-induced peak (D band) at 1354 cm^{-1} . The spectrum of the pyrrolidine-C₆₀ contains the pentagonal pinch mode, $A_g(2)$ mode at 1469 cm^{-1} , and additional H_g modes are seen at 1574 and 1424 cm^{-1} . The graphene-C₆₀ hybrid shows three peaks at 1603 , 1352 and 1482 cm^{-1} . The peaks at 1603 and 1352 cm^{-1} can be attributed to the G and D bands of the graphene sheet. The peak at 1482 cm^{-1} should be assigned to the $A_g(2)$ mode of the C₆₀ cage, which is shifted by 13 cm^{-1} compared with the pyrrolidine-C₆₀. This relative shift sufficiently suggests a strong interaction between the C₆₀ cage and the graphene sheet [5].

Fig. 4 shows the TGA curves of the GO, pyrrolidine-C₆₀ and graphene-C₆₀ hybrid. The GO shows a large weight loss (30%) with an onset temperature at 200 °C , which can be attributed to the removal of the functional groups ($-\text{OH}$ and $-\text{COOH}$) from the GO [7]. For the pyrrolidine-C₆₀, a weight loss of 15% occurred at an onset temperature of 237 °C , which can originate from the breakdown of the $-\text{COO}-$ group in the pyr-

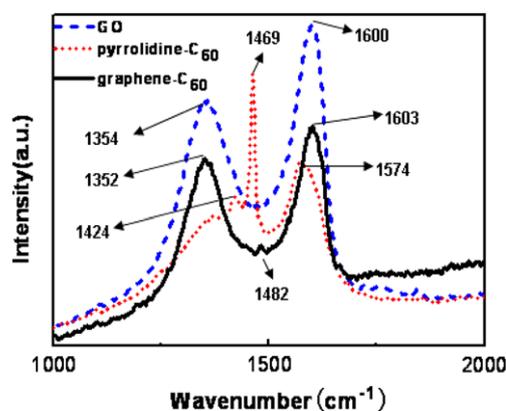


Fig. 3 – Raman spectra of GO (dashed line), pyrrolidine fullerene (dotted line) and graphene-C₆₀ (solid line) excited at 514 nm . The peak at 1482 cm^{-1} in the graphene-C₆₀ is the $A_g(2)$ mode of the C₆₀ cage, which is shifted by 13 cm^{-1} compared with that of the pyrrolidine-C₆₀. This relative shift sufficiently suggests a strong interaction between the C₆₀ cage and the graphene sheet.

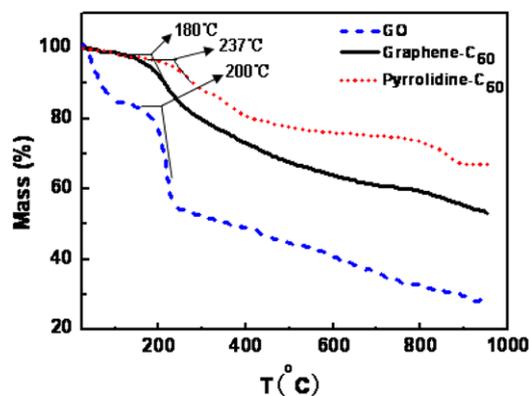


Fig. 4 – TGA curves of GO (dashed line), pyrrolidine- C_{60} (dotted line) and graphene- C_{60} (solid line). All the samples were running under purified nitrogen gas flow with a 5 °C/min heating rate. The graphene- C_{60} hybrid shows decreased onset temperature compared with GO and pyrrolidine- C_{60} , indicating that new chemical bonds are formed between the graphene sheet and C_{60} .

rolidine- C_{60} . The graphene- C_{60} hybrid exhibits an onset temperature of 180 °C due to the decomposition of the amide carbonyl group (-CON-), which shows less thermal stability compared with the -COO- (-COOH and -COOCH₃) groups. The decreased onset temperature of the graphene- C_{60} compared with its parent species indicates that new chemical bonds are formed and C_{60} is chemically bonded onto graphene.

The HRTEM of the as prepared GO sheet is shown in Fig. 5a, which shows a clear edge contour. The image of the graphene- C_{60} hybrid is shown in Fig. 5b. There are some C_{60} molecules with a size of ~0.8 nm attached on the edge of the graphene sheet. In this paper, the reaction between the graphene and C_{60} originates from the -COOH group of GO, which is transferred to -COCl by SOCl₂. The -COOH groups are mainly distributed on the edge of GO [12], so we can see a preferential distribution of the C_{60} cages on the edge of the graphene sheet.

Finally, we also performed the XPS analysis for both GO and the graphene- C_{60} . Based on the atomic ratio of C to N determined by XPS in the graphene- C_{60} , it is estimated that one C_{60} molecule is covalently attached for every ~130 carbon atoms in the graphene- C_{60} (see the Supporting information). In contrast, no trace of the N1s peak can be found in the XPS spectrum of GO. This further verifies the formation of the amide bond in the graphene- C_{60} .

In conclusion, we have synthesized a graphene- C_{60} hybrid material by a simple coupling reaction. This material was investigated using spectral analysis, TGA, HRTEM images and XPS. In view of the unique electronic properties of both graphene and C_{60} , this material could conceivably exhibit unique electronic and optical properties. For instance, taking advantage of the electron-accepting feature of C_{60} and the high electron transport capability of graphene, this hybrid material may find application in solar cells (as the acceptor material). Further work on the application of this hybrid material is currently under way.

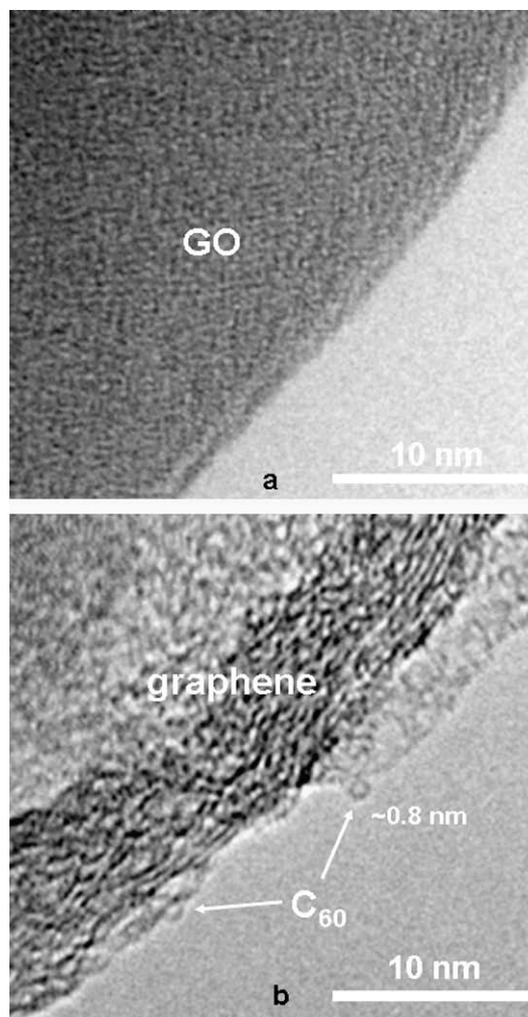


Fig. 5 – HRTEM images of GO (a) and graphene- C_{60} hybrid (b). The images were acquired from samples deposited onto a holey carbon support film.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.carbon.2008.10.018](https://doi.org/10.1016/j.carbon.2008.10.018).

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