Heptagons in the Basal Plane of Graphene Nanoflakes Analyzed by Simulated X-ray Photoelectron Spectroscopy

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ABSTRACT: The performance of graphene-based electronic devices depends critically on the existence of topological defects such as heptagons. Identifying heptagons at the atomic scale is important to completely understand the electronic properties of these materials. In this study, we report an atomic-scale analysis of graphene nanoflakes with two to eight isolated or connected heptagons, using simulated C 1s X-ray photoelectron spectroscopy (XPS) to estimate the XPS profiles depending on the density and the position of the heptagons. The introduction of up to 24% of isolated heptagons shifted the peak position toward high binding energies (284.0 to 284.3 eV), whereas the introduction of up to 39% of connected heptagons shifted the calculated peak position toward low binding energies (284.0 to 283.5 eV). The presence of heptagons also influenced the full width at half-maximum (FWHM). The introduction of 24% of isolated heptagons increased the FWHMs from 1.25 to 1.50 eV. However, the introduction of connected heptagons did not increase the FWHMs above 1.40 eV. The FWHMs increased to 1.40 eV for 19% of connected heptagons, but did not increase further as the percentage of connected heptagons increased to 39%. Based on the calculated results, the XPS profiles of graphene nanoflakes containing heptagons with different densities and positions can be obtained. Our precise identification of heptagons in graphene nanoflakes by XPS lays the groundwork for the analysis of graphene.

INTRODUCTION

Graphene has received considerable attention because of its various possible applications in electronic devices and catalyst supports. However, graphene generally contains defects such as heptagons. It is well known that the presence of heptagons changes the structures, electronic states, and reactivity of graphene. Both the number of heptagons per area and the position of heptagons affect the electrical, mechanical, thermal, and chemical properties. Thus, it is essential to clarify the percentage of heptagons and the closeness between heptagons in graphene.

Transmission electron microscopy (TEM) has been used to analyze heptagons in grain boundary and Stone–Thrower–Wales (STW) defects in the basal plane of graphene as well as defects in reduced graphene oxide. However, accurate observation of heptagons is challenging using TEM because graphene structures are changed and/or damaged by the energy of electron-beam irradiation. Heptagons have also been directly observed by scanning tunneling microscopy (STM). However, analyzing positions of heptagons by STM is time-consuming. Heptagons also have been analyzed using Raman, infrared (IR), and nuclear magnetic resonance (NMR) spectroscopies. Although Raman and IR spectroscopies have been utilized to analyze the heptagons in STW defects, peaks originating from only heptagons have not been reported previously. Besides, Raman and IR spectroscopies have disadvantages for quantitative analysis. Furthermore, solid-state NMR spectroscopy requires large amounts of samples for measurements, which are unsuitable for analyzing...
precious nanomaterials. Therefore, more suitable analytical techniques must be developed.

X-ray photoelectron spectroscopy (XPS) can be one of the suitable techniques for quantitatively and qualitatively analyzing heptagons in graphene. Many research groups have separated the main peak in the C 1s spectra of graphene into sp² C and sp³ C peaks, however, the analysis of defects such as heptagons and pentagons has been neglected. Pentagons in graphene nanoflakes (GNFs), analyzed using XPS, were reported by our group in 2015. This computational method was applied to analyze the percentage of pentagons in carbon materials with the aid of an experimental elemental analysis. Recently, graphene nanoribbons with pentagons and heptagons have been synthesized using aromatic compounds, including pentagons and heptagons. However, the peak originating from only heptagons was not reported because reference compounds such as carbon materials with pure heptagons have not yet been synthesized. Hence, computational simulation is necessary to investigate the XPS peak of heptagons in graphene.

Computational simulations of the XPS profiles of graphene-related materials have been recently employed to clarify the defect structures. Ever since, Proctor and Sherwood and Boutique et al. pioneered simulated XPS for analyzing the functional groups in carbon materials in the 1980s, several groups have calculated and reported the defect structures of graphene-related materials. Recently, our group demonstrated the peak shifts and corresponding full widths at half-maximum (FWHM) of peaks in the XPS profiles of graphene-related materials with various defects, including pentagons, oxygen- and nitrogen-containing functional groups, vacancies, zigzag and armchair edges, sp³-versus sp²-hybridized C atoms, and STW defects. However, to the best of our knowledge, the XPS analysis of pure heptagons in graphene has not been reported.

In this study, the effects of the number, the position, and the connectivity of heptagons on the peak shifts and corresponding FWHMs in the C 1s spectra of GNF were analyzed by simulating the C 1s XPS profiles of GNFs in which some of the hexagons were replaced with isolated or connected heptagons (Figure 1). The highest occupied molecular orbital (HOMO)—the lowest unoccupied molecular orbital (LUMO) gap, work functions, and binding energies were calculated from the optimized structures.

RESULTS AND DISCUSSION

Figure 1 shows the positions of the introduced heptagons, while Figure 2 shows the GNFs with zero, two, four, six, or eight heptagons. Hydrogen-terminated GNF (C100H26) was used as the basic structure (Figure 2a) because the peak position and FWHM of the simulated XPS profile of C100H26 are similar to those of the experimental XPS profile of graphite. For GNF with two or four heptagons (C108H30 and C110H34 respectively; Figure 2b,c), the heptagons were isolated with no neighboring heptagons. For GNF with six heptagons (C124H44; Figure 2d), two sets of three neighboring heptagons were present. For GNF with eight heptagons (C142H44; Figure 2e), each heptagon neighbored two to five other heptagons. These structures mainly include three types of bonding states of carbon atoms: C1 (sp³C–sp³C) in the hexagons; C2 (sp³C–H) at the H-terminated edges; and C3 in the heptagons.

Table 1 shows the calculated gap between HOMO and LUMO of the GNFs with or without heptagons. It has been reported that the HOMO–LUMO gap increases with decreasing the size of graphene and introducing heptagons in graphene. As shown in Table 1, the HOMO–LUMO gap of the GNF with zero heptagons was 0.80 eV, which decreased to 0.23 eV when four isolated heptagons were introduced, as the size of GNF and the number of isolated heptagons increased. However, the HOMO–LUMO gaps of GNRs with four or more heptagons showed opposite tendency in such a way that the HOMO–LUMO gap of GNR with four heptagons (0.23 eV) increased to GNFs with six (0.28 eV)

![Figure 1](image1.png)

**Figure 1.** Numbering of the heptagon positions in the basal plane of GNF. Two heptagons: position 1. Four heptagons: positions 1 and 2. Six heptagons: positions 1, 2, and 3. Eight heptagons: positions 1, 2, 3, and 4.

**Table 1. HOMO–LUMO Gaps of GNF with Heptagons**

| number of heptagons | 0  | 2  | 4  | 6  | 8  |
|---------------------|----|----|----|----|----|
| HOMO–LUMO gap (eV)  | 0.80 | 0.70 | 0.23 | 0.28 | 1.79 |

![Figure 2](image2.png)
and eight heptagons (1.79 eV), with increasing the size of GNF and the number of connected heptagons. This indicates that the connectivity of heptagons affects the electronic properties such as the HOMO−LUMO gap.

Figure 3 shows the C 1s spectra simulated using the structures, as shown in Figure 2. As shown in Figure 3a, the binding energies associated with the C1 and C2 regions (indicated in blue and red, respectively) were 284.0 and 283.7 eV, respectively. The binding energy associated with the C1 region was higher than that associated with the C2 region because the terminal hydrogen atoms donate electrons to the carbon atoms (C2).16,28,29,31 The binding energy associated with the C3 region (indicated by two isolated heptagons in the GNF structure) was 284.7 eV (yellow line in Figure 3b), which

| number of heptagons | 0  | 2 | 4 | 6 | 8 |
|---------------------|----|---|---|---|---|
| ratio of the number of carbon atoms (C1:C2:C3) | 100:26:0 | 64:30:14 | 54:34:28 | 44:38:42 | 42:44:56 |
| percentage of C3/% | 0 | 13 | 24 | 34 | 39 |
| whole C 1s spectrum (C1 + C2 + C3) | peak top/eV | 284.0 | 284.1 | 284.3 | 284.4 | 283.5 |
| | FWHM/eV | 1.25 | 1.35 | 1.50 | 1.45 | 1.40 |
| C1 (hexagon) | peak top/eV | 284.0 | 284.3 | 284.4 | 284.3 | 283.5 |
| | peak shift of C1 from C1 of GNF/eV | 0 | 0.3 | 0.4 | −0.1 | −0.5 |
| | FWHM/eV | 1.15 | 1.20 | 1.25 | 1.20 | 1.20 |
| C2 (C−H) | peak top/eV | 283.7 | 283.8 | 284.0 | 284.1 | 283.2 |
| | peak shift of C2 from C1/eV | −0.3 | −0.5 | −0.4 | −0.2 | −0.3 |
| | FWHM/eV | 1.15 | 1.15 | 1.25 | 1.20 | 1.20 |
| C3 (heptagon) | peak top/eV | 284.7 | 284.7 | 284.6 | 283.7 |
| | peak shift of C3 from C1/eV | 0.4 | 0.3 | 0.3 | 0.2 |
| | FWHM/eV | 1.20 | 1.20 | 1.20 | 1.30 |
| work function/a/eV | 3.98 | 3.84 | 3.56 | 3.51 | 4.27 |
| averaged number of electrons of one carbon atom on one heptagon | 5.997 | 5.998 | 6.000 | 6.001 |

"Work function: energy difference between HOMO level and vacuum level. Averaged number of electrons of one carbon atom on one heptagon: the calculated method is shown in Supporting Information."
was the highest binding energy among the C1, C2, and C3 regions owing to the electron-donating nature of the heptagons (Figure S1). All the structures used in this study showed the same tendency (Table 2 and Figure 3).

According to our previous study, the introduction of isolated pentagons does not influence the shifts in the peak positions of the C 1s spectra of GNFs, whereas the introduction of connected pentagons shifts the peak positions to lower binding energies. Moreover, the peak position in the C 1s spectra is influenced by the environment surrounding the pentagons. The peak position originating from a pentagon surrounded by five hexagons is lower than that originating from a pentagon surrounded by three hexagons.

Heptagons have an electron-donating nature toward hexagons, whereas pentagons have an electron-withdrawing nature. Thus, we expected the peak shifts of the C 1s spectra upon the introduction of heptagons to be oppositely correlated to those with pentagons. However, this opposite correlation was not observed. The peak position in the C 1s XPS profile of GNF (284.0 eV) shifted to a higher binding energy (284.3 eV) upon introducing four isolated heptagons (with 24% of isolated heptagons; Figures 2 and 3, Table 2) and shifted to a lower binding energy (283.5 eV) upon introducing eight connected heptagons (with 39% of connected heptagons; Figures 2 and 3, Table 2). This trend of heptagons is the same as that of pentagons. The reason for this unexpected similarity can be explained based on the work function.

The work functions were calculated from the energy differences between the HOMO and vacuum level. The work functions were 3.98, 3.84, 3.56, 3.51, and 4.27 eV for GNF with zero, two, four, six, and eight heptagons, respectively (Table 2). The work function decreased with the addition of up to six heptagons, but increased when eight heptagons were introduced. In the same manner, the peak positions increased with the addition of up to six heptagons, but decreased when eight heptagons were introduced (Figures 3 and 4a, Table 2). This is because the C 1s orbitals and valence band edge neared the atomic nucleus and the energy required for removing electrons from the carbon atoms in GNFs with connected heptagons was lower than that for GNF without heptagons.

Table 2 shows the calculated C1 peak shifts of GNFs with heptagons in comparison to the calculated C1 peak position of GNF without heptagons. It also shows the calculated peak shifts from C1 to C2 and C3. The C1 peak positively shifted from 284.0 to 284.4 eV as the number of heptagons increased from zero to six and negatively shifted to 283.5 eV with eight heptagons. The peak shift from C1 to C2 for GNF without heptagons was −0.3 eV and that for GNFs with two to eight heptagons ranged from −0.2 to −0.5 eV, indicating that the shift from C1 to C2 was small, irrespective of the introduced number and the connectivity of heptagons.

The peak shifts from C1 to C3 for GNFs with two, four, six, and eight heptagons were 0.4, 0.3, 0.3, and 0.2 eV, respectively (Table 2 and Figure 3). The decrement in peak shifts from C1 to C3, that is, from 0.4 to 0.2 eV, can be explained by averaging...

Figure 4. Dependency of work function, the number of electron on carbon atoms and FWHM of C 1s, and the peak positions of C 1s spectra on the number of heptagons. (a) Correlation between work functions and peak tops on the number of heptagons. (b) Correlation between averaged numbers of electrons of 1 carbon atom on 1 heptagon and peak shifts of C3 from C1 on the number of heptagons. (c) Correlation between FWHMs and peak tops on the number of heptagons.
the number of electrons in one carbon atom of one heptagon. The average numbers of electrons in one carbon atom of one heptagon were 5.997, 5.998, 6.000, and 6.001 in GNFs with two (Figure S1), four, six, and eight heptagons, respectively (Table 2 and Figure 4b). The average number of electrons was obtained by adding the number of electrons (6.000) in the carbon atoms to the negative value of the Mulliken charge.

The number of heptagons in the GNF influenced the FWHMs of the C 1s spectra in addition to the peak position. The calculated FWHM of the entire C 1s spectrum (1.25 eV for GNF including peaks originating from C–H bonding) in Table 2 and Figure 4c was equal to the actual FWHM of the entire C 1s spectrum of graphite (1.25 eV).16 The FWHM increased to 1.35, 1.50, 1.45, and 1.40 eV upon the introduction of two, four, six, and eight heptagons, respectively (Table 2 and Figure 4c). The reason for the small FWHM of the calculated and actual C 1s spectra of GNF (1.25 eV) is the absence of heptagons. Increasing the number of heptagons increases the number of different C–C bonding states; thus, the FWHMs increased, in a similar way to those in the C 1s spectra of graphene with other defects, including pentagons16 and oxygen,28 or nitrogen-containing functional groups.29

Figure 5. Optimized structures of GNF with connected heptagons (a–c) and their C 1s XPS profiles (d–f). (a,d) GNF without heptagons. (b,e) GNF with two heptagons. (c,f) GNF with four heptagons.

Figure 6. Dependence of peak tops and FWHMs of whole C 1s spectra on density of heptagon (C3). (a) Dependence of peak tops on the number of isolated and connected heptagons. (b) Dependence of FWHMs on the number of isolated and connected heptagons.
GNFs with zero, two, or four connected heptagons (Figure 5) were simulated to confirm the effect of the connectivity of heptagons on the peak shifts and FWHMs of the C 1s spectra. The peak position of the entire C 1s spectrum (284.0 eV) shifted to a lower binding energy (283.7 eV) with the inclusion of up to four connected heptagons (with 34% of connected heptagons, Figures 5 and 6a and Table 3) and shifted to 283.5 eV in GNFs with eight connected heptagons (with 39% of connected heptagons, Figure 6a). In terms of FWHMs (Figure 6b), when 24% of isolated heptagons was introduced, the FWHM increased from 1.25 to 1.50 eV. However, by introducing connected heptagons, the FWHM increased up to 1.40 eV. The FWHMs became larger when introducing connected heptagons, whereby 34% of the carbon atoms are in connected heptagons, Figure 5c, C1:C2:C3 = 26:28:28.

**Table 3. Calculated Peak Shifts and FWHMs of C 1s Spectra and Work Function of Structures in Figure 5a–c**

| number of heptagons | 0 | 2 | 4 |
|---------------------|---|---|---|
| ratio of the number of carbon atoms (C1:C2:C3) | 66:20:0 | 36:24:14 | 26:28:28 |
| percentage of C3/% | 0 | 19 | 34 |
| whole C 1s spectrum (C1 + C2 + C3) | peak top/eV | 284.0 | 283.9 | 283.7 |
| FWHM/eV | 1.25 | 1.40 | 1.40 |
| C1 (hexagon) | peak top/eV | 284.0 | 283.9 | 283.7 |
| FWHM/eV | 1.15 | 1.20 | 1.20 |
| C2 (C−H) | peak top/eV | 283.7 | 283.7 | 283.4 |
| FWHM/eV | 1.15 | 1.20 | 1.20 |
| C3 (heptagon) | peak top/eV | 284.3 | 283.9 | |
| FWHM/eV | 1.25 | 1.20 | |
| work function*/eV | 4.59 | 4.68 | 4.87 |

*Work function: energy difference between HOMO level and vacuum level.

The peak positions and FWHMs in the XPS profiles of GNFs with two (Figure 2b) or four (Figure 2c) isolated heptagons or two (Figure 5b), four (Figure 5c), six (Figure 2d), or eight (Figure 2e) connected heptagons were calculated and used to determine the positions and the number of heptagons. The experimental C 1s XPS profile of graphite was used in this simulated study using the data in our previous report.16 The peak position and FWHM were 284.0 and 1.25 eV, respectively.16 GNFs with heptagons were simulated based on these experimental results.

**CONCLUSIONS**

Introducing heptagons to the basal plane of GNF shifted the peak positions and altered the FWHMs in the C 1s XPS profile. In the calculated C 1s spectra, the binding energy originating from the heptagons was higher than that originating from the hexagons because of the electron-donating nature of the heptagons. The introduction of isolated heptagons shifted the peak position of the simulated spectra to higher binding energies. The positive peak shifts of the calculated C 1s spectra were related to the decrement of the work function. The FWHM of the C 1s spectrum of GNF (1.25 eV) increased up to 1.50 eV as the percentage of isolated heptagons increased up to 24% because the number of different states of C−C bonds was maximized. The introduction of connected heptagons in GNFs shifted the peak positions of the C 1s spectra to lower binding energies. In addition, the FWHMs increased as the percentage of connected heptagons increased up to 19% (1.40 eV), but did not increase further when the percentage of connected heptagons increased to 39%. These results indicate that the number and the position of heptagons in graphene can be analyzed based on the peak shifts and FWHMs of the spectra.

**METHODS**

Gaussian 09 quantum chemistry software was used for all calculations.35 The ground-state geometry was fully optimized using the B3LYP/6-31G(d) basis set in the gas phase, and the HOMO−LUMO gaps were calculated from the optimized structures. The XPS profiles were simulated using population analyses with the B3LYP/6-31g(d) basis set to calculate the electronic energy levels from HOMO to C 1s; details are provided in the Supporting Information and our previous papers.16,17,28,36

The peak positions and FWHMs in the XPS profiles of GNFs with two (Figure 2b) or four (Figure 2c) isolated heptagons or two (Figure 5b), four (Figure 5c), six (Figure 2d), or eight (Figure 2e) connected heptagons were calculated and used to determine the positions and the number of heptagons. The experimental C 1s XPS profile of graphite was used in this simulated study using the data in our previous report.16 The peak position and FWHM were 284.0 and 1.25 eV, respectively.16 GNFs with heptagons were simulated based on these experimental results.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05717.

Experimental details; simulated C 1s XPS profiles of structures before applying asymmetric Voigt function; and Mulliken charge distribution (PDF)

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**Notes**

The authors declare no competing financial interest.

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