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Nitrogen-containing graphene analyzed by X-ray photoelectron spectroscopy

Yasuhiro Yamada *, *Jungpil Kim*, *Shintaro Matsuo*, *Satoshi Sato*

Graduate School of Engineering, Chiba University, 1-33 Inage, Yayoi, Chiba 263-8522, Japan

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ABSTRACT

X-ray photoelectron spectroscopy (XPS) has been commonly used to determine the nitrogen-containing functional groups of graphene. However, reported assignments of C1s shifts of nitrogen-containing functional groups are unclear. Most works discuss peak shifts of only N1s spectra and C1s shifts and the full width at half maximum (FWHM) are excluded. Thus, peak shifts and FWHMs of C1s and N1s XPS spectra of graphene with nitrogen-containing functional groups such as pyridinic, phenanthroline-like, $sp^2C–NH_2$, $sp^3C–NH_2$, pyrrolic, imine, pyridazine-like, pyrazole-like, $sp^2C–CN$, $sp^3C–CN$, and valley quaternary nitrogen (Q–N) on edges and $sp^3C–NH_2$, center amine, and center Q–N in the basal plane were simulated using density functional theory calculation. Main peaks of C1s spectra were shifted positively and negatively by the electron-withdrawing and electron-donating functional groups, respectively. FWHMs of the main peaks of C1s spectra were influenced by mainly electron-withdrawing functional groups on edges and most functional groups in the basal plane. $Sp^2C–NH_2$ on zigzag edges is suggested as a reference functional group to adjust the N1s spectra because influence of the functional group on the shift of main peak and the FWHM of C1s spectrum was small.

1. Introduction

Graphene has been intensively and extensively studied for various applications such as catalyst supports [1–3], catalysts [3–5], ligands for coordination of metal ions [6,7], electronic materials for fuel cells [8,9], solar cell [9], super capacitors [10,11], lithium-ion batteries [12], and bio materials [13–15] especially since Geim and Novoselov demonstrated the usefulness of graphene [16,17]. One of commonly used methods to improve the properties of graphene is introduction of nitrogen atoms [1,2,8,9,18]. Varieties of nitrogen-containing functional groups such as pyridinic, pyrrolic, amine, and quaternary nitrogen (Q–N) have been introduced. Because the types of nitrogen-containing functional groups play an important role to improve various properties, the accurate assignments and introduction of aimed single nitrogen-containing functional groups are essential for the future of graphene.

X-ray photoelectron spectroscopy (XPS) is among the most commonly used analytical methods for nitrogen-containing functional groups of carbon materials such as graphene [18]. Owing to the efforts of many researchers, the assignments of nitrogen-containing functional groups have been experimentally revealed. For example, Ishitani et al. analyzed carbon fibers and assigned four types of peak shifts as $sp^3C–CN$ (400 eV), pyridinic (so-called N-6, 399 eV), imino (401 eV), and nitroso (403 eV) groups [19]. Proctor et al. assigned a peak at ca. 400 eV as an amine group [20]. Pels et al. [21] and Jansen et al. [22] added various nitrogen-containing functional groups such as pyrrolic and pyridone-like groups (so-called

* *Corresponding author:* Fax: +81 43 290 3376.
E-mail address: y-yamada@faculty.chiba-u.jp (Y. Yamada).
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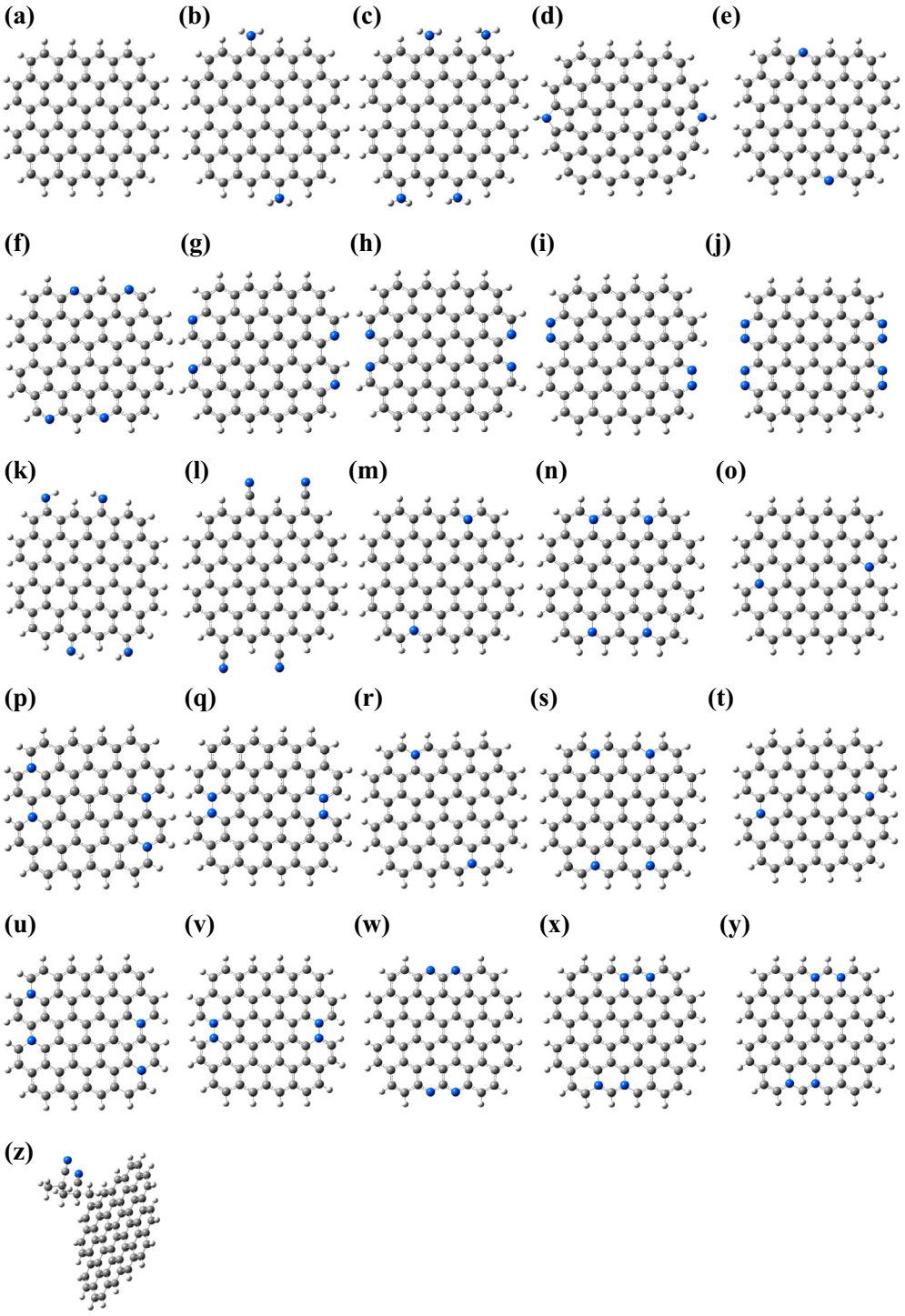

Fig. 1 – Modeled structures of graphene with functional groups on edges. All the edges were terminated by hydrogen atoms unless functional groups or other defects were present. (a) Twenty hydrogen atoms on edges, where white and gray spheres indicate hydrogen and carbon atoms, respectively. (b) Two $sp^2C–NH_2$ groups on zigzag edges, where blue spheres indicate nitrogen atoms. (c) Four $sp^2C–NH_2$ groups on zigzag edges. (d) Two pyrrolic groups on armchair edges. (e) Two pyridinic groups on zigzag edges. (f) Four pyridinic groups on zigzag edges. (g) Four pyridinic groups on armchair edges. (h) Two phenanthroline-like groups on armchair edges. (i) Two pyridazine-like groups on armchair edges. (j) Four pyridazine-like groups on armchair edges. (k) Four C═N—H on zigzag edges. (l) Four $sp^2C–CN$ on zigzag edges. (m) Two valley Q–Ns on zigzag edges. (n) Four valley Q–Ns on zigzag edges. (o) Two valley Q–Ns on armchair edges. (p) Four valley Q–Ns on armchair edges. (q) Four valley Q–Ns on armchair edges next to each other. (r) Two valley amine groups on zigzag edges. (s) Four valley amine groups on zigzag edges. (t) Two valley amine groups on armchair edges. (u) Four valley amine groups on armchair edges. (v) Four valley amine groups on armchair edges next to each other. (w) Two pairs of pyridinic groups on zigzag edges. (x) Four valley Q–Ns next to each other on zigzag edges. (y) Four valley amine groups next to each other on zigzag edges. (z) Two $sp^3C–CN$ on zigzag edges. (A colour version of this figure can be viewed online.)