Structural Analysis of Nitrogen-doped Graphene Nanoribbons with Zigzag and Armchair Edges by Infrared and Raman Spectroscopy

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Nitrogen-doped graphene nanoribbons (N-GNRs) have been expected to be applied to catalysts and electrodes.[1] Although structural analysis of the edges and nitrogen-containing functional groups (N-groups) is an important issue for improving the properties of these materials, the analytical methods of N-GNRs are limited to some spectroscopies and microscopies, and the simultaneous determination of substituted positions by nitrogen(N) and the types of N-groups is challenging. Infrared (IR) spectroscopy has long been utilized as one of conventional analytical techniques to determine basically functional groups of carbon materials.[2] Raman spectroscopy has become the primary method for studying GNRs because of its ease of use, effectiveness, and sensitivity to structural details.[3] In this study, N-GNRs with various N-groups at various introduced positions were analyzed by simulated IR and Raman spectra and analytical methods of substituted positions of N and the types of N-groups in N-GNRs were provided.

Four kinds of reference compounds were analyzed by IR and the peak positions were verified by vibration analysis of Gaussian 16 (B3LYP/6-31g(d)). Primary amine (NH_2), pyrrolic N, and pyridinic N were introduced into the GNRs model with zigzag and armchair edges, as well as secondary amine (NH) and quaternary NH (Q-NH) on the edge position, N (Valley N) and quaternary N (Q-valley N) on the valley position, and N (Basal N) and quaternary N (Q-basal N) on the basal plane, were calculated in the same way as above.

The introduction of N on zigzag GNRs shifted the peak positions of sp^2C-H stretching vibration to higher wavenumbers in the order of pyrrolic N > Q-valley N > Valley N > Q-basal N > Basal N > Pyridinic N > NH_2 > Q-NH but shifted the peak positions of sp^2C-H stretching vibration for NH to lower wavenumber. The introduction of N-groups such as Q-basal N, Basal N, Q-valley N, and Valley N shifted the peak positions of sp^2C-H stretching vibration in armchair GNRs to higher wavenumbers, whereas that of N-groups such as NH_2 and Pyridinic N shifted the peak positions to lower wavenumbers. In addition, the introduction of N-groups such as Q-NH and NH in armchair GNRs shifted the peak positions of sp^2C-H stretching vibration to both higher and lower wavenumbers. Since this tendency of armchair GNRs was different from zigzag GNRs, edge structures and the types of N-groups can be distinguished by focusing on peak positions of sp^2C-H stretching vibration.

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