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Marked Adsorption Irreversibility of Graphitic Nanoribbons for CO_2 and H_2O

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Supporting Information

ABSTRACT: Graphene and graphitic nanoribbons possess different types of carbon hybridizations exhibiting different chemical activity. In particular, the basal plane of the honeycomb lattice of nanoribbons consisting of sp^2-hybridized carbon atoms is chemically inert. Interestingly, their bare edges could be more reactive as a result of the presence of extra unpaired electrons, and for multilayer graphene nanoribbons, the presence of terraces and ripples could introduce additional chemical activity. In this study, a remarkable irreversibility in adsorption of CO_2 and H_2O on graphitic nanoribbons was observed at ambient temperature, which is distinctly different from the behavior of nanoporous carbon and carbon blacks. We also noted that N_2 molecules strongly interact with the basal planes at 77 K in comparison with edges. The irreversible adsorptions of both CO_2 and H_2O are due to the large number of sp^3-hybridized carbon atoms located at the edges. The observed irreversible adsorptivity of the edge surfaces of graphitic nanoribbons for CO_2 and H_2O indicates a high potential in the fabrication of novel types of catalysts and highly selective gas sensors.

A serious shortage of minor metals has triggered active research activity dedicated to the search for alternative materials for catalysts,[1] sensors,[2] electrodes,[3,4] and magnetic applications.[5] Especially, alternative and low-cost catalytic materials have been demanded for the conservation of scarce metals.[1,6] Generally speaking, a prominent catalyst must possess both a high surface area and a high specific activity. Graphene[7,8] and carbon nanotubes[9−11] appear to be good candidates for the development of alternative catalysts able to replace expensive and scarce metals. In particular, graphene and open (uncapped) single-walled carbon nanotubes (SWCNTs) exhibit large surface areas of ~2630 $m^2\ g^{-1}$. SWCNTs could also vary from semiconductor to metal by modification of the tube chirality,[12,13] whereas the structure of edge terminations (zigzag or armchair) governs the electronic properties of graphitic nanoribbons.[14−16] Interestingly, the surface catalysis phenomenon originates from the unique electronic structure of each catalyst material. Therefore, graphitic nanoribbons (GNRs) and SWCNTs have a high potential to become excellent and efficient catalysts. In addition, an excellent catalyst is associated with nanoscale molecular sites such as terraces and step structures or nanopores. In this context, GNRs with widths of a few nanometers possess inherent terraces and step structures in addition to their characteristic reactive edges.[17−20] More interestingly, GNRs have an inherent mixed-valence structure of sp^2- and sp^3-hybridized carbon atoms because edge carbon atoms and in-plane carbon atoms display sp^3 and sp^2 hybridizations, respectively.[21] It is well-known that the mixed-valence structure plays an essential role in the unusual catalysis of transition-metal oxides.[22−24] Consequently, a pioneering study of the surface activity of GNRs needs to be carried out in order to design alternative catalysts able to replace expensive and scarce metals.

Table 1. Surface Areas and Crystallite Sizes of Graphite Nanoribbons (GNRs) and Carbon Blacks (CBs)

sample	surface area ($m^2\ g^{-1}$)	crystallite size (nm)
GNRs	59	11
w-CB	87	35
i-CB	74	30

In this study, we observed a remarkable irreversibility in the adsorption of CO_2 and H_2O on chemical vapor deposition (CVD)-grown GNRs, indicating the presence of highly reactive surface sites. The GNR samples were synthesized by an aerosol pyrolysis process using ferrocene/thiophene/ethanol solutions. The detailed procedure has been reported elsewhere.[17,18] Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images and Raman spectra of GNRs are given in Figures S1 and S2 in the Supporting Information. To compare the performance of our GNRs, we also studied two types of carbon blacks (CBs), whose surfaces are mainly covered

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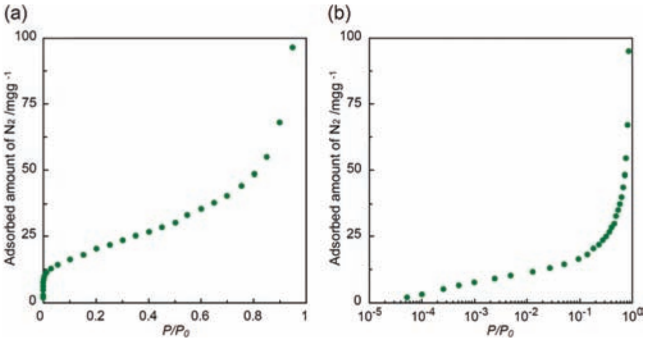

Figure 1. N_2 adsorption isotherms for GNRs at 77 K. P/P_0 is expressed using a linear scale in (a) and a logarithmic scale in (b).

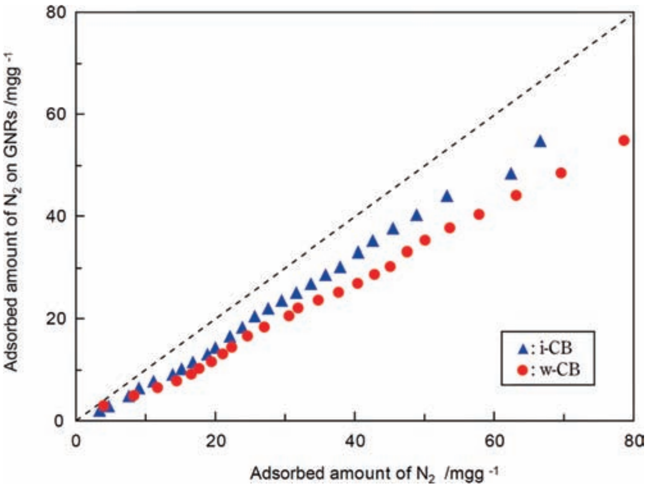

Figure 2. Comparison plots of N_2 adsorption isotherms of GNRs against CBs of different crystallinity at 77 K. When the interaction energy of the CB with N_2 is identical to that of the GNRs, the comparison plot is given by the broken line.

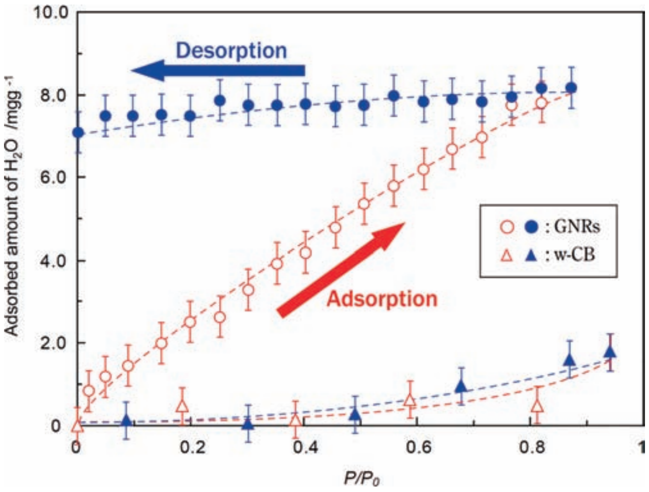

Figure 3. Adsorption isotherms of H_2O on GNRs and well-crystalline CBs at 298 K.

with the basal planes of sp^2-hybridized carbon atoms. In particular, we studied the adsorption characteristics of well-crystalline CB (w-CB) (acetylene black, DENKA Co.) and ill-crystalline CB (i-CB) (oil furnace black, Mitsubishi Chem. Co.).[25] The surface areas and crystallite sizes of GNRs and CBs (Table 1) were determined by N_2 adsorption at 77 K and powder X-ray diffraction (Cu Kα, 30 kV). The N_2 adsorption isotherm was measured by the volumetric method using an Autosorb MP-1 analyzer (Quantachrome Instruments) at 77 K. The CO_2 adsorption was measured at 303 K using a laboratory-designed gravimetric method as well as a volumetric method (BELSORP-max, BEL Japan, Inc.). The H_2O adsorption isotherm of GNRs of 6.0 μg order was measured using the quartz-balance method (BEL-QCM, 9 MHz-oscillator, BEL Japan, Inc.) with a flowing H_2O/He mixture at 297 K. Thermal desorption analysis was carried out using the BEL-QCM after H_2O adsorption. Prior to the adsorption measurements, GNRs and CBs were preheated in vacuo at 383 K for N_2 and CO_2 adsorption and in a He flow at 353 K for CO_2 adsorption using the BEL-QCM.

The N_2 adsorption isotherm of GNRs at 77 K is shown in Figure 1. The N_2 adsorption isotherm is of typical IUPAC type II (Figure 1a), indicating no nanoporosity. Figure 1b shows that the N_2 adsorption increased gradually with the N_2 pressure below $P/P_0 = 10^{-1}$ and then increased steeply above $P/P_0 = 5 \times 10^{-1}$ as a result of multilayer adsorption. The N_2 adsorption was completely reversible without any adsorption hysteresis. The N_2 adsorption isotherm of GNRs was then compared with those for two types of CBs in order to understand the surface nature of the GNRs. Figure 2 depicts the comparison plots for the N_2 adsorption isotherms. Here the ordinate and abscissa denote the adsorbed amounts for the GNRs and the CB, respectively. If the GNR samples display a N_2 adsorptivity identical to that of the CB, the comparison plot should give a diagonal shown by the broken line. However, both comparison plots deviate downward from the diagonal, clearly indicating that GNRs interact more weakly with N_2 molecules than do the CBs. Furthermore, the comparison plot with the w-CB sample (higher-crystallinity CB) provides a greater downward deviation. Consequently, the GNR surfaces are distinctly different from the basal planes of CBs. As the GNR surface consists of sp^3-hybridized carbon atoms located at the edges and sp^2-hybridized carbon atoms situated on the terraces [~1:1 ratio according to X-ray photoelectron spectroscopy (XPS)],[18] the edge surfaces of the GNRs are less active for N_2 than the basal planes consisting of sp^2-hybridized carbon atoms.

Thus, the edge carbon surface appears to be inert toward inert molecules such as N_2. N_2 adsorption at 77 K stems from the dispersion interaction, whose strength is dominated by the atomic density of the solid surface. As the carbon atomic density of the basal plane is larger than that of the edge plane, N_2 molecules are more strongly adsorbed at 77 K on the basal planes than on the edge surfaces. However, it is expected that dipolar H_2O molecules and CO_2 molecules with their large quadrupole moment[26] could interact more strongly with the edge surface than N_2 does. The H_2O adsorption isotherms of GNRs and w-CB at 303 K are of the Freundlich type, and for the GNRs, almost no desorption occurs even near $P/P_0 = 0$ (Figure 3). This remarkable irreversibility of H_2O adsorption on GNRs is noteworthy. On the contrary, H_2O adsorption amount on w-CB is nil, although the specific surface areas of the two carbon samples are not so different from each other. Even nanoporous carbon does not show any irreversibility in H_2O adsorption near ambient temperature.[27−33] The H_2O adsorption isotherm of nanoporous carbon with pore widths in the range 0.7−1.4 nm has a predominant

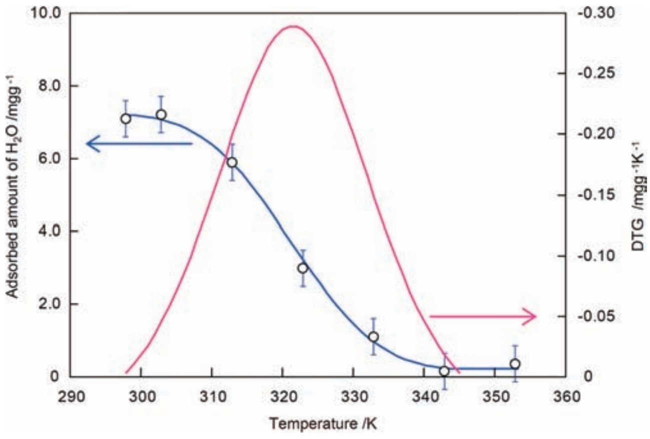

Figure 4. Thermal desorption (blue) and differential thermal desorption (red) profiles of H_2O adsorbed on GNRs.

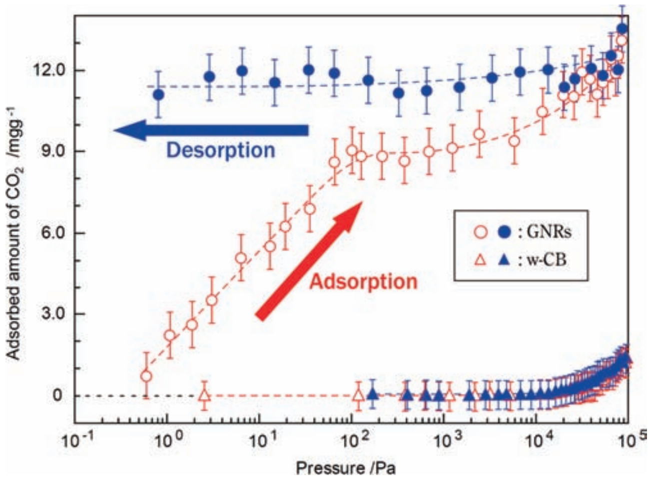

Figure 5. Adsorption isotherms of CO_2 on GNRs and well-crystalline CBs at 303 K.

hysteresis; the adsorbed H_2O could be completely desorbed at $P/P_0 = 0$. The water adsorbed in ultramicropores with widths of <0.7 nm is desorbed at $P/P_0 = 0$, although the adsorption behavior is different from nanoporous carbon having pore widths of >0.7 nm. The different types of H_2O adsorption isotherms on carbon materials that have only a few surface functional groups are given in Figure S3. Consequently, the edge carbon surface is not hydrophobic but hydrophilic. The interaction of H_2O molecules with the GNR surface was examined using thermal desorption analysis, as shown in Figure 4. H_2O molecules were desorbed with an increase in temperature and became completely desorbed above 340 K; the peak of the differential thermal desorption profile was observed at 323 K. Therefore, H_2O molecules were not chemically adsorbed, irrespective of the explicit adsorption irreversibility observed at 298 K. H_2O molecules should be adsorbed via hydrogen bonding through the surface functional groups on the edge carbon surfaces or via dipolar interactions with the edge surface. The amount of irreversibly adsorbed H_2O at 298 K was 7 mg g^{-1} (0.39 mmol g^{-1}), which corresponds to 25 m^2 g^{-1} using the H_2O molecular area of 0.106 nm^2 at 303 K.[34] The surface area occupied by irreversibly adsorbed H_2O molecules was ~42% of the total surface area (59 m^2 g^{-1}), which is close to the ratio of sp^3-hybridized carbon atoms with respect to the total number of carbon atoms. H_2O molecules should be selectively adsorbed only on the edge surfaces, which thus exhibit the characteristic hydrophilicity.

A striking irreversibility in CO_2 adsorption on GNRs at 303 K was also observed (Figure 5). CO_2 adsorption gradually increased with increasing CO_2 pressure up to 10^2 Pa, reaching a plateau over the pressure range 10^2–10^4 Pa. Subsequently, a further increase in adsorption was observed. The adsorption and desorption behavior of GNRs is noteworthy; almost no desorption was observed. Hence, CO_2 was strongly adsorbed on the GNR surface. Interestingly, CO_2 was not adsorbed on w-CB below 10^4 Pa at 303 K; the adsorption amount near 10^5 Pa was only 2 mg g^{-1}. The CO_2 adsorbed on w-CB at higher pressure was completely desorbed below 0.01 Pa at 303 K. The irreversibly adsorbed amount of 11.5 mg g^{-1} (0.26 mmol g^{-1}) for GNRs corresponds to a surface area of 22 m^2 g^{-1}, which is ~37% of the total surface area, similar to the value for H_2O adsorption. Here the surface area occupied by the irreversibly adsorbed CO_2 was evaluated using the CO_2 molecular area of 0.142 nm^2 at 195 K.[34] The irreversible adsorptivity of CO_2 should be also associated with the edge carbon atoms of the ribbon, since the surface area occupied by adsorbed CO_2 is also close to the surface area consisting of sp^3-hybridized carbon atoms located at the ribbon edges. Since GNRs exhibit many corner atoms at the steps in the edges, the presence of the plateau of 9 mg g^{-1} should be associated with the activity of those corner carbon atoms. As CO_2 molecules do not form hydrogen bonds with the surface functional groups on the edge surfaces, the GNR edge surfaces should have an electron-acceptor nature and thereby interact with CO_2 through weak charge-transfer interactions.[35]

In conclusion, the irreversible adsorptivity of the carbon edges for CO_2 and H_2O was observed for CVD-grown GNRs, which is distinctly different from the adsorption behavior of the sp^2-hybiridized carbon basal planes. The edge surfaces of GNRs should contain dangling bonds that give rise to weak charge-transfer interactions with donor molecules and/or strong surface electric fields that could interact with the molecular dipole of H_2O and large molecular quadrupole of CO_2. We believe that the edge ribbon surfaces should be studied further since GNRs appear to have an extreme and novel potential as efficient catalysts and may able to replace some of the existing metals. Also, GNRs should be promising for applications in electronics.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. TEM and SEM images of GNRs, Raman spectra of GNRs and carbon materials, adsorption isotherms of H_2O on porous carbons and CB, and complete refs 3 and 18. This material is available free of charge via the Internet at http://pubs.acs.org.

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