Supporting Information

Work function lowering of graphite by sequential surface modifications: nitrogen and hydrogen plasma treatment

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Figure S1 The $I_D/I_G$ of Raman spectra on HOPG after N (black) or Ar (red) plasma treatment.

Here, we show the time evolution of defect amount change as plasma treatment. The amount of introduced defects by N plasma was almost saturated to 0.4 of $I_D/I_G$ after 1 hour treatment. Since the results of Ar plasma showed similar tendency, it can be inferred that $I_D/I_G$ of Ar plasma also increases only up to approximately 0.4. The saturation of $I_D/I_G$ can be explained that defect introduction and etching of the surface by long-time plasma treatment are in equilibrium and the defect amount became saturated.
Figure S 2 Raman spectra of HOPG samples: pristine HOPG (black), HOPG treated by Ar plasma for 10 min (red), HOPG treated by N plasma for 10 min (green), HOPG treated by H plasma for 10 min (blue), HOPG treated by N plasma for 30 min followed by H plasma treatment for 10 min (light blue). All spectra have been normalized with respect to the intensity of G peak (1581 cm$^{-1}$).

To investigate difference of defect introduction by plasma species, Raman spectra of the plasma treated HOPG were compared. An increase of the D peak (1353 cm$^{-1}$) is observed after all kinds of plasma treatment, which means the plasma treatment introduces defects on HOPG surface. These defects are derived from vacancies, hetero doping, and sp$^3$ bonding carbon atoms. The I$_D$/I$_G$ of hydrogenated HOPG (blue) was increased to around 0.7 just by irradiating H plasma for 10 min, which is much larger than
that of N and Ar plasma (Figure S 1). Previous reports said defect of sp³ bond shows larger $I_D/I_G$ than that of vacancy and N doping $^{1,2}$. Therefore, the large increase in $I_D/I_G$ by H plasma should indicates the formation of sp³ structure of hydrogenation. On the other hand, the N + H plasma treated HOPG showed smaller D peak than H plasma HOPG. That is because the many surface carbon atoms were replaced with nitrogen atoms due to its highly doping amount, and the amount of sp³ carbon decreased.

Figure S 3 The work function change of HOPG as a function of H plasma treatment time. The Black line indicates a pristine HOPG, and the red line indicates a damaged HOPG, in which a defect of $I_D/I_G$ ~0.2 was introduced in advance by irradiating Ar plasma for 10 min.
Here, we will discuss an effect of sample defect on hydrogenation and work function of HOPG. After H plasma treatment for 80 min, the \(I_D/I_G\) of pristine HOPG has increased to 1.45, indicating that defects are introduced with the plasma processing time. The increase of vacancy by plasma treatment relaxes strain from hydrogenated sp\(^3\) bond, which promotes additional hydrogenation and further reduces the work function of HOPG. On the other hand, the work function of the damaged HOPG reaches the minimum value in a shorter time than that of pristine HOPG. This result suggests introducing defects contributes to the reducing work function as a result of promoting hydrogenation in early stage. In later stage, however, there was no remarkable difference in the reached work function values, both in the initial and hydrogenated states. This result indicates that the work function is not directly influenced by defects, but by hydrogenation and nitrogen doping.

The downward shift of work function for the present p-HOPG was 0.8 eV which is smaller than the 1.5 eV of diamond. It should be because of an insufficient sp\(^3\) conversion of graphite surface. The formation of hydrogenated sp\(^3\) bond on graphite surface causes lattice tension originated of different lattice constant, which should restricts further hydrogenation. This limited hydrogenation results larger work function of graphite than that of diamond. Introduction of a large amount of vacancies by long time plasma
treatment would relieve this tension. This is reason why our result showed lower work function than 4.0 eV of the previous study\(^3\), and why it took a long time until the work function of p-HOPG became the lowest.

Figure S 4 (a-d) Change of XPS N1s spectra of HOPG sample after repetitive annealing and plasma hydrogenation. The blue, green, and red peak components are indicate of graphitic, pyridinium, and pyridinic N components. (e) Change of work function at each hydrogenation and annealing process.

In order to investigate the effect from hydrogen plasma on N dopant in detail, we conducted an experiment to repeat hydrogenation/dehydrogenation on the N doped HOPG. First, N plasma irradiation was conducted under a high temperature condition of
600°C to produce N-doped graphene in which only graphitic and pyridinic N exist (a).

This thermal treatment removes pyrrolic N that contributes p electron into the π system\(^5\).

At this time, in order to increase the amount of doping, plasma treatment was carried out at a power of 200 W which is much stronger than the usual power of 10 W. The pyridinic N component was hydrogenated and changed into pyridinium N after the H plasma treatment (b). When this sample was annealed again at 600°C under a vacuum of \(1 \times 10^{-5}\) Pa, hydrogen atoms desorbed and pyridinium N returned to pyridinic N (c). At this time, since an etching effect to edge sites removed a part of pyridinic N, the proportion of graphitic N component increased from 60% to 67%. By repeating these treatments, desorption of pyridinic N progressed, and the ratio of graphitic N increased up to 86% after the H plasma treatment for a total 10 minutes and annealing (d).

These results suggest the following two points. (1) Pyridinic N has high reactivity with hydrogen, and then H plasma treatment can change almost all pyridinic N into pyridinium N. (2) Hydrogen bonded pyridinium N is unstable, and part of it is decomposed with nitrogen atoms when hydrogen atoms are desorbed by thermal heating. In the point (1), as mentioned in the main text, the theoretical calculation said that hydrogen atom is more likely to bond at the pyridinic nitrogen atom than the surrounding carbon atom\(^6\). For this reason, most of pyridinic N has possibly changed to pyridinium N. Regarding point (2),
reports on decomposition of pyridine ($C_5H_5N$) molecule should be useful for understanding about desorption of nitrogen atoms with dehydrogenation. Pyridinium N with hydrogenated sp$^3$ carbon in our study has a similar structure of piperidine ($C_5H_{11}N$). Schwartz has reported that heating pyridine in a hydrogen-containing atmosphere forms piperidine, in which C - N bonds are broken and rings are opened, and then finally decompose into the molecules of NH$_3$. Exposing to an active hydrogen plasma promotes chemical reactions like such heating under a hydrogen atmosphere. In our N doped HOPG samples, therefore, it can be thought that H plasma eventually desorbs the doped nitrogen as NH$_3$, and decomposes pyridinic N in the similar process in the study of piperidine.

In addition, we should mention that core level depth (binding energy) might be shifted with Fermi level shift, because the binding energy is calculated from Fermi level. However, in our analysis of N 1s peak fitting, the apparent change of the N 1s binding energy was not observed. It is because the work function is changed not only by Fermi level shift but also by vacuum level shift. While the Fermi level shift changes the binding energy, the vacuum level shift by the surface dipole layer does not change that. Therefore, we consider that a large portion of the work function change was caused by the decrease of vacuum level.
We investigated the surface state of HOPG after thermal dehydrogenation. Before the annealing, hydrogenated HOPG showed $I_D/I_G \sim 0.79$ (black). After dehydrogenation (red), defects of about $I_D/I_G \sim 0.14$ are still left. Elias et al. reported that hydrogen atoms are eliminated by heating above 350 °C\textsuperscript{9}. In addition, the reduced work function also returned to its original state. These facts indicate the residual D peak does not originate from hydrogenated-$sp^3$ bonds, but originated from vacancies. It is reported that carbon atoms are removed together with hydrogen desorption in the form of CH$_4$ when graphene is etched by hydrogen plasma\textsuperscript{10,11}. Likewise, carbon desorption seems to be occurred...
even in the dehydrogenation process, and finally leave vacancies. It can be explained a reason why the D peak remains in graphene even after desorption of hydrogen atoms.

Figure S 6 The change of N doping amount and component ratio of graphitic N/ total N after repeat of H plasma treatment and annealing.

By repeating H plasma treatment and annealing, the total amount of nitrogen decreases, and the proportion of graphitic N can be increased. This is because the nitrogen atoms of pyridinic and pyridinium N, which are dopant at the edge of the graphene lattice, are more reactive and desorbable \(^{10,11}\), whereas the nitrogen atoms of the graphitic N, dopant at inside of graphene lattice, are more stable. We have succeeded in tuning dopant species by repeating hydrogenation and annealing.
Figure S 7. (a) The change of work function of HOPG samples, in which initial N doping amount and dominant doping sites were variously changed. The dominant component types and initial doping amounts are shown with each plot. (b-e) Initial N 1s XPS spectra of each plot.

In order to investigate the N-doping condition that contribute to the lowest work function, HOPG samples with various initial states were hydrogenated. Comparing with the doping amounts, the work function greatly decreases as the doping amount is larger, and the sample with the largest doping amount (black line in (a), (b)) reached the lowest work function. On the other hand, in order to investigate the influence from the doping sites, we made specimens having different graphitic/pyridinic ratio by means of introducing prior defect 12. One sample had dominant graphitic N (red line in (a), (c)) and the other sample had larger pyridinic N (green line in (a), (d)). In the initial state, graphitic N dominant sample (red line) had a lower work function, but pyridinic N dominant sample (green line) had a higher work function. The both samples, however, similarly reduced their work functions by H plasma treatment. This result indicated all kinds of doped nitrogen became n-type dopants by hydrogenation and reduced work function. In this way, since hydrogenation eventually change the all kinds of dopants to electron donor, the work function is more effectively reduced when the doping amount is larger.
In addition, we would like to discuss comparison of other nitrogen-contained carbon materials. In our study, the graphite surface disordered by long time plasma irradiation should be similar to amorphous carbon nitride (a-CN). Photoelectron spectroscopy cannot measure a-CN due to its insulation, while its work function could be estimated as 5.2 eV using Kelvin Probe Force Microscopy (KPFM)\textsuperscript{13}. We had obtained consistent results in heavily doped graphite, which showed the work function of 5.2 eV when doping amount was 32%. In addition, there is a report about hydrogenated a-CN surface. Although its work function was not directly measured by KPFM, Saitoh \textit{et al.} reported that the work function of field emission characteristics was greatly reduced by hydrogenation \textsuperscript{14}.

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