Surrounding gas effect on diffusion and adsorption of a single metal atom on heteroatom-doped graphene

Shun Hasegawa, Yuji Kunisada, Norihito Sakaguchi

Graduate School of Engineering, Hokkaido University,
Kita 13 Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan
hsgwsyun@eis.hokudai.ac.jp

Recently, metal sub-nanoclusters have drown a great deal of attention in various fields, such as catalysts and hydrogen storage materials, thanks to their unique properties. For practical use of sub-nanoclusters, support materials are required to allow sub-nanoclusters to adsorb stably and keep their sizes for a long time, because the properties of sub-nanoclusters strongly depend on their sizes. Graphene is one of promissing support materials as it has high mechanical-chemical durability, relative surface area and electron conductivity. However, graphene surface is highly inert, which causes agglomeration of sub-nanoclusters and degrades their properties. On the other hand, it has been reported that heteroatom doping into graphene improves durability of metal clusters on graphene. Actually, we have revealed that heteroatom-doped graphene supresses metal atom (Pt, Fe) agglomeration [1,2]. In this study, we investigated the effect of surrounding gas on diffusion behaviors and adsorption states of a metal atom to find proper dopants which can supress agglomeration of sub-nanoclusters in practical environment.

We performed DFT calculations using the Vienna ab initio Simulation Package (VASP). A supercell contains 4×4 graphene and vacuum layer of 25 Å with periodic boundary conditions to separate their periodic images in the perpendicular direction to a graphene sheet. We adopted Pt and Fe atoms as metal atoms; H and H_2 as environmental gas. Doped graphene was modeled by substituting one carbon atom in graphene lattice with one dopant atom, i.e. B, N, O, Si, P and S.

Figure 1 shows the diffudion barriers of single Pt and Fe atoms on pristine and doped graphene. From Fig.1 (a), we can find that the diffusion barriers of Pt atoms decrese in the cases that H or H_2 exist in the system compared to that in vacuum system. A noteworthly fact is that Pt atoms on graphene easily diffuse on pristine graphene. This means that atmosphere containing H will enhance agglomeration of Pt sub-nanoclusters on pristine graphene in short duration and degrades Pt sub-nanoclusters property rapidly. However, doped graphene, especially O-, Si- and P-doped graphene have large diifision barriers of Pt atoms even under H atmosphere. We revealed that Pt atoms bond to prisitine graphene through weak covalent bond, and H and H_2 weaken this interaction between Pt atoms and pristine graphene. On the other hand, O-, Si- and P-doped graphene strongly interact Pt atoms through dangling bond, therfore O-, Si- and P-doped graphene keep high Pt atom diffusion barriers even in atmosphere containing H or H_2 gas, therefore they are suitable supports for Pt sub-nanocluster. On the othe hand, H and H_2 dose not affect the diffusion barriers of Fe atoms so much. This is becouse H and H_2 interact with Fe atoms weekly, and do not weeken bond between Fe atoms and graphene. Therefore, suitable supports for Fe sub-nanoclusters are B-, O-, Si-, P-doped graphene which show high diffusion barrier in the vacuum. We will also discuss about adsorption states of metal atoms on graphene and effect of other gas, such as O and OH.

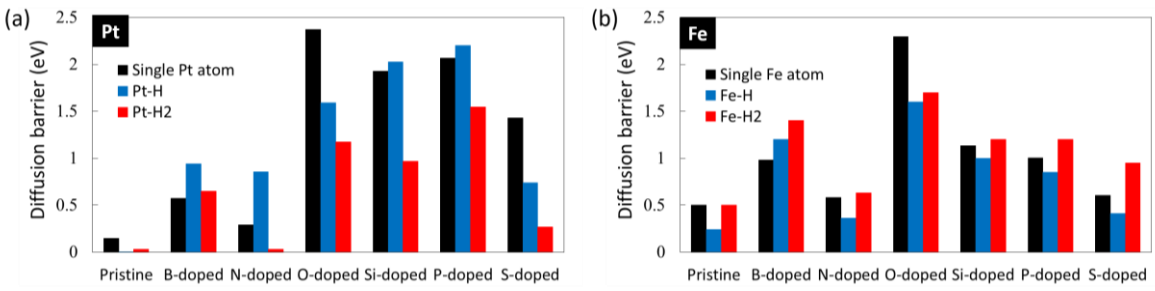

Figure 1. Diffusion barrier of (a) Pt and (b) Fe atom on pristine and doped graphene. Black, blue and red bar shows the result in vacuum, H atmosphere and H2 atmosphere respectively.

References: [1] S. Hasegawa, Y. Kunisada, N. Sakaguchi, J. Phys. Chem C **121**, 17787 (2017)
[2] S. Hasegawa, Y. Kunisada, N. Sakaguchi, e-JSSNT, accepted.