3F14

炭素ドープによる h-BN 表面活性領域拡大に関する理論的研究

（[1] 北大院理，[2] 京大 ESICB [3] NIMS, GREEN）　○高 敏 [1,2]，王奔 [1]，足立 将 [1], Lyalin Andrey [3], 武次徹也 [1,2,3]

Large active area of h-BN Monolayer induced by carbon doping

([1]Hokkaido Univ., [2] Kyoto Univ., ESICB [3] NIMS, GREEN) ○ Gao Min [1,2], Wang Ben [1], Adachi Masashi [1], Lyalin Andrey [3], Taketsugu Tetsuya [1,2,3]

The catalytic reactions with molecular oxygen have attracted lots of interests due to its various crucial industrial chemical processes, such as selective oxidation and epoxidation, exhaust gas emission control for automotive applications, oxygen reduction reaction in fuel cells, and so on. Extensive efforts are devoted to the development of effective catalytic materials for oxygen activation. Currently, most of the industrially used catalysts are based on precious transition metals (Pt, Pd, Ru, etc.). Therefore, the development of effective, cheap and environment friendly catalysts based on the nonprecious abundant elements is an emerging task for commercial market. Recently, we have demonstrated theoretically [1] and proved experimentally that even inert and catalytically inactive materials, h-BN can be functionalized to become active catalysts at nanoscale [2]. Our findings open new and yet unexplored routes to design effective catalyst based on materials that have never before been considered for catalytic applications.

In the present work, we performed a systematic theoretical investigation of the catalytic activity of the C doped *h*-BN monolayer toward a reaction with molecular oxygen reactant. It is demonstrated that C doping into B position on the *h*-BN monolayer (C_B@*h*-BN) produces n-type semiconductor material with noticeable catalytic activity in the large area extended far away from the C impurity [3]. The adsorption energy of O_2 on C_B@*h*-BN decreases slowly as shown in Fig. 1a with the increasing in distance from the C impurity, while O_2 remains to get electron from C_B@*h*-BN (Fig. 1b) and highly activated. It is shown that a small energy gap between the occupied defect level and the

bottom of the conduction band leads to functionalization of the large area around the defect. Therefore, to design effective BN-based catalyst using atomic doping one should introduce occupied defect states in a close vicinity of the bottom of the conduction band.

To investigate the catalytic activity of C_B@*h*-BN, the oxygen reduction reaction [3] and oxidation reactions of CO and C_2H_4 are considered. All these reactions can occur even at the sites far from the doped C atom. Such effects were not observed for *h*-BN monolayer doped with different atoms such as B, N, Al, Si, Ge, Ni, Pt, Pd, and Au where O_2 adsorbs only in the close vicinity of the dopant. Therefore, even small concentration of C dopants can functionalize the large surface area of h-BN monolayer, making it a promising catalytic material.

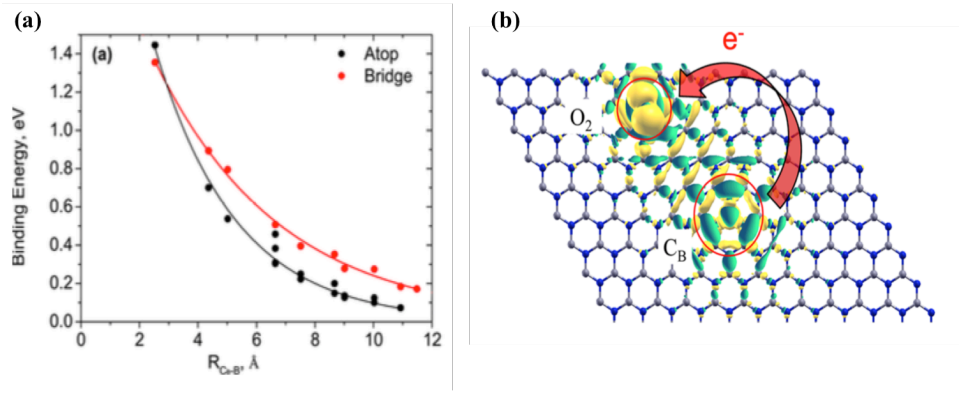

Fig. 1 (a) Dependence of the binding energy and on the adsorbed O_2 as a function of distance $R_{CB\text{-}B}$ between the C_B dopant center and the active site for O_2 adsorption on C_B@h-BN. (b) Isosurface of the electron density difference induced by interaction of O_2 molecule with the C_B@h-BN surface, i.e. ρtot(O_2/ C_B@h-BN) − ρtot(O_2) − ρtot(C_B@h-BN).

[1] Lyalin A.; Gao M.; Taketsugu T. *Chem. Rec.* **2016**, in press.

[2] Uosaki, K.; Elumalai, G.; Noguchi, H.; Masuda, T.; Lyalin, A.; Nakayama, A.; Taketsugu, T. *J. Am. Chem. Soc*. **2014**, 136, 6542−6545.

[3] Gao M.; Adachi M.; Lyalin A.; Taketsugu T. *J. Phys. Chem. C* **2016**, in press (DOI: 10.1021/acs.jpcc.5b12706)