First-principles study of molecule/metal interfaces

Ikutaro Hamada

Department of Precision Science and Technology, Graduate School of Engineering, Osaka University, 2-1 Yamada-Oka, Suita, Osaka 565-0871

Carbon-based nanomaterials, such as graphene and nanographene have attracted enormous attention, owing to their fascinating electronic, optical, and magnetic properties. For precise fabrication of nanographene, on-surface synthesis has been developed, in which precursor molecules are thermally induced to react on a surface, and the technique has been proven to be powerful to fabricate graphene based nanostructures. In this work, we propose an alternative method, in which a tip of scanning tunneling microscopy/non-contact-atomic-force microscopy is utilized as a manipulable metal catalyst, which activates cyclodehydrogenation of hydrocarbons [1].

we used diazuleno[1,2-*c*:2′,1′-*g*]phenanthrene (DAPh), as well as 10,10′-dibromo-9,9′-bianthracene (DBBA) adsorbed on a Cu(100) surface, to demonstrate the tip-induced cyclodehydrogenation reaction. To investigate the mechanism of the tip-induced reaction, we performed atomistic simulations based on density functional theory (DFT) with the van der Waals (vdW) density functional (vdW-DF) [2] as implemented in our in-house DFT code STATE [3-6], to describe the interaction between organic molecule and metal accurately.

Experimentally, the DAPh molecule is thermally reacted into a cyclodehydrogenated diazulenopyrene (DAPy), but the reaction intermediate has not been determined. We performed extensive DFT calculations and successfully identified the intermediate as hydro-diazulenopyrenyl (hDAPyr). By using a Cu-terminal tip, we induced the cyclodehydrogenation of hDAPyr to form DAPyr. To understand the reaction mechanism, we used a 10-atom pyramidal model Cu tip over hDAPyr and could reproduce the tip-induced cyclodehydrogenation reaction. Furthermore, we clarified the detailed potential energy surface and by the electronic structure analysis, we revealed the electronic origin of the tip-induced catalytic dehydrogenation reaction.

References

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