First-principles calculations of nano-interfaces of Pd/Au slabs and Au@Pd core-shell nanoparticles

Shingo Tanaka¹, Noboru Taguchi², Tomoki Akita¹, Fuminobu Hori², Masanori Kohyama¹

¹Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), Ikeda 563-8577, Japan
²Department of Materials Science, Osaka Prefecture University, Sakai 599-8531, Japan

Noble metal nanoparticles with core-shell structure play important roles for nano-scale catalysts. The existence of core-shell interface has a large influence on the atomic and electronic structure of the shell region, especially. The Au-Pd bimetallic nanoparticles with higher catalytic activities for hydrogen has been reported [1-5]. Some Au-Pd nanoparticles have a core-shell (Au-core and Pd-shell: Au@Pd) structure. Recently, the fine structure analyses of Au-Pd nanoparticles by analytical transmission electron microscopy (TEM) show the clear Au-core and Pd-shell structure and the lattice expansion of the Pd-shell [6]. In the Pd/Au slabs, there are similar feature of the epitaxial growth and the Pd lattice expansion [7].

In this paper, we have performed the first-principles calculations of nano-interfaces of the Pd/Au slabs and the Au@Pd nanoparticles with adsorbate hydrogens using the projector augmented-wave (PAW) program code QMAS (Quantum MAterials Simulator) [8]. In order to clarify the stable structure near the interface, we first deal with the slab structures. From the adhesive energy analyses of (100) [9] and (111) [10] slab models, the intermetallic configuration near the interface is more energetically stable than the binary separated one. The lattice strained Pd overlayers on Au slabs have large adsorption energies of hydrogens than the unstrained Pd slabs. The adsorption energies of hydrogens are large show the maximum at two Pd overlayers and have strong dependence for the hydrogen adsorption sites. These can be explained by the lattice strain effect and the subsurface interaction effect [11]. The charge density redistribution show the accumulation near the adsorbate hydrogens and the depletion near the Pd atoms which interact with the hydrogens (Fig. 1). Next we deal with the Au@Pd 13-, 55- and 147-nanoparticles. The charge density distribution near the corner atom of Pd-shell is relatively large change. The tendency of charge density redistribution is similar to the slabs. The adsorption energies of hydrogen are large near the corner atoms. The atomic structure of Pd-shell is change befo before and after the hydrogen adsorption. This has a large possibility for higher catalytic activities.

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References
FIG. 1. Charge density redistribution of Pd/Au(100) interfaces with adsorbate hydrogen. The number of Pd overlayers are two. The dark and light transparent region indicate isosurfaces for accumulation and depletion region of the charge density, respectively.

FIG. 2. Charge density redistribution of Au@Pd nanoparticles (N=13) with adsorbate hydrogen. The dark and light transparent region indicate isosurfaces for accumulation and depletion region of the charge density, respectively.