

## Theoretical and Experimental Studies of Metal/Inorganic Materials Interfaces for Energy and Environmental Applications

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In various energy and environmental technologies such as environmental catalysts, fuel cells, lithium batteries, hydrogen storage devices, and thermal barrier coatings, surfaces and interfaces of materials play essential roles. Especially, metal/inorganic materials interfaces are involved in key functions in various devices. Novel catalytic activities often occur at metal/oxide interfaces. Chemical reactions coupled with electron and ion transport occur at such interfaces in fuel cells and lithium batteries. Thus understanding and design of metal/inorganic materials interfaces are crucial. For this purpose, the combination between microscopic observations and first-principles calculations is quite effective. In this paper, we present our recent combined researches of metal/inorganic materials interfaces [1].

Au/TiO<sub>2</sub> systems exhibit high catalytic activity of low-temperature CO oxidation when the Au-particle size is less than 2-3nm [2]. The mechanism to activate gold is exciting, where heterogeneous or nano-size effects seem to be important. By the combination between electron microscopy observations [3] and first-principles calculations [4], we showed that the *interface stoichiometry* is an essential factor. For Ti-rich or O-rich Au/TiO<sub>2</sub> interfaces, there occur large interfacial adhesion and great changes in the electronic structure of Au atoms. This picture was supported by scanning-probe microscopy observations [5]. Recently, we have obtained HAADF-STEM images with atomic-column resolution for Au particles on TiO<sub>2</sub> surfaces with several orientation relationships [6]. We have performed first-principles calculations of realistic models of the Au/TiO<sub>2</sub> interfaces from the observed configurations, and examined the effects of *interface stoichiometry* in details. We discuss the catalytic activity from the relation between the *interface stoichiometry* and the reaction path around the peripheral regions of Au-particle/TiO<sub>2</sub> contact.

Au/CeO<sub>2</sub> catalysts with high activity for water-gas-shift reactions are also quite interesting, where novel structural changes of Au particles on CeO<sub>2</sub> surfaces have been found by the electron microscopy [7]. Smaller Au particles disappear during the observation, through layer-by-layer diffusion remaining only one Au layer on the CeO<sub>2</sub> surface. Then the Au particles recover at the same positions after the electron beam is turned off. This kind of behaviors of Au particles seem to be dominated by the oxidation state of CeO<sub>2</sub> namely the O vacancy formation in the bulk and surfaces, and the strong contact at the interface should be also involved. Recently, HAADF-STEM images of Au/CeO<sub>2</sub> systems with atomic-column resolution revealing the interface configurations have been obtained [8], for which the first-principles calculations are now being performed so as to understand the behavior of Au particles and the catalytic activity.

Metal/Al<sub>2</sub>O<sub>3</sub> interfaces are used in various systems such as catalysts, electronic devices and thermal barrier coatings. For this system, the *interface stoichiometry* is also crucial. It is easy to construct the stoichiometric Al-terminated metal/Al<sub>2</sub>O<sub>3</sub>(0001) interfaces and the O-rich O-terminated metal/Al<sub>2</sub>O<sub>3</sub>(0001) interfaces by changing the termination planes, and the relative stability depends on the atmosphere, namely atomic chemical potentials. The adhesion and intrinsic mechanical properties of Cu/Al<sub>2</sub>O<sub>3</sub>(0001) and Ni/Al<sub>2</sub>O<sub>3</sub>(0001) interfaces have been examined via first-principles tensile testing simulations [9]. In the stable configurations, the adhesion at the Al-terminated interfaces is dominated by image-charge-like interactions via the charge redistribution in the metallic side, while the strong metal-O bonds with both ionic and covalent characters dominate the O-terminated ones. The latter features are examined by the comparison with electron microscopy observations of Cu/Al<sub>2</sub>O<sub>3</sub>(0001) interfaces [10].

The O-terminated interfaces reveal quite larger tensile strength than the Al-terminated ones, and the failure of the O-terminated interfaces occurs in the metallic side, while the metal-Al interfaces are easily broken in the Al-terminated ones. The first-principles examination of tensile behaviors is useful to develop the effective interatomic potentials for large-scale simulations of metal/oxide interfaces [11].

The performance of the proton-exchange membrane fuel cells (PEFC) is dominated by the electrode catalysts consisting of Pt particles supported on carbon materials. In order to attain high efficiency and durability of the electrode, design and control of nano structures of the Pt/C systems are essential. For this purpose, the combination between electron microscopy observations and first-principles calculations is quite effective. Recently, we have applied the electron microscopy observation to the electrode catalysts of PEFC and clarified the detailed features of degradation [12]. In the first-principles calculations [13], by dealing with the interactions between graphene sheets and various kinds of Pt configurations such as atoms, small clusters, planes and so on, the overall features of Pt-C interactions have been clarified, which can be used to design nano-scale structures of the Pt/C electrode systems via phase-field models [14].

Finally, we introduce our recent development of the computational techniques for interface researches. In dealing with mechanical properties of material interfaces by first-principles calculations, the analysis using the local energy density [15] and stress density [16] within the density-functional theory should be quite effective, although there has been rare successful coding. Our group is now engaged in the development of a new *ab initio* code QMAS (Quantum MATERIALS Simulator) [17], and the formulation and coding of the energy and stress densities in the framework of the PAW (projector augmented wave) scheme have been successfully performed. This has been successfully applied to interface systems.

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