Contact Potential Difference of Au/TiO$_2$(110) Model Catalysts Measured by Kelvin Probe Force Microscopy

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Contact potential difference (CPD) of Au/TiO$_2$ model catalysts was measured by Kelvin probe force microscopy (KFM). The CPD of Au particles was lower than that on the TiO$_2$(110) surface and the difference of CPD between them increased with the particle height. By applying the parallel disk model, the work function difference and the charge density at the Au/TiO$_2$ interface were estimated to be 0.19 eV and 0.01 C/m$^2$, respectively. We have previously measured local barrier height (LBH) of Au/TiO$_2$ by scanning tunneling microscopy. From the results of CPD and LBH measurements, we found a possibility that the localized charge at the Au/TiO$_2$ interface plays some role in the catalytic activity of Au catalysts.

Keywords: Kelvin probe force microscopy; Scanning tunneling microscopy; Surface electronic phenomena; Gold; Titanium oxide; Catalysis

I. INTRODUCTION

Since Au is chemically very stable and it does not lose metallic luster even after long term exposure to air, Au had been regarded as being catalytically inert. In 1987, Haruta and co-workers have discovered that Au nanoparticles, supported on metal oxides, exhibit novel catalytic activity such as low-temperature CO oxidation [1]. The catalytic activity of Au is strongly dependent on the particle size and the kind of metal oxide supports, which suggests that the nano-sized interface between Au and supports plays an important role for the activity [2-4]. In order to clarify this nano-hetero interface effect, experimental and theoretical researches have been performed on the Au/TiO$_2$ model catalyst [5, 6].

Among them, the STM research by Goodman et al. is important [7]. They discovered the correlation between the activity and the quantum size effect (QSE) of Au particles. Taking into account the importance of extra electrons [8], we considered that this phenomenon is related to the charge distribution at the Au/TiO$_2$ interface. Therefore, we have performed local barrier height (LBH) measurement by STM and found that the QSE is correlated with work function difference (WFD) between Au particles and a TiO$_2$ substrate [9, 10]. However, since LBH measurement is strongly influenced by the tip condition (e.g. work function, structure), it was difficult to evaluate the charge distribution at the interface quantitatively. In this research, we performed CPD measurement by Kelvin probe force microscopy (KFM), and estimated the WFD and the charge density on the Au/TiO$_2$ model catalysts.

II. EXPERIMENTAL

All experiments were performed in an UHV-SPM system (JSTM-4500XT, JEOL) equipped with an UHV-AFM chamber. The base pressure was 2 $\times$ 10$^{-8}$ Pa. Substrates used were polished TiO$_2$(110) single crystals. The cross-linked (1 x 2) surfaces were obtained by repeated cycles of Ar$^+$ sputtering (3 keV, 5-10 min) and annealing (800°C, 10-30 min). Gold was deposited by vacuum evaporation with the substrate being kept at room temperature. Platinum coated cantilevers (NSC12/Pt, Mikromasch) with a spring constant of 14 N/m and a resonance frequency of 300 kHz were used. Tip-sample distance was controlled in FM mode. The cantilever was oscillated with an oscillation amplitude of about 36 nm with constant excitation energy, and frequency shift was set with the procedure described in the Appendix. KFM was performed by a KFM control system (TM-57600FUPG, JEOL), and CPD signal was detected by an external lock-in amplifier (LI5640, NF Electronic Instruments). The modulation voltage and frequency for CPD measurement are 0.5 V$_{p-p}$ and 1 kHz, respectively. The images were analyzed using WSxM software. In the CPD images, dark contrast represents lower electric potential.

III. RESULTS AND DISCUSSION

Figure 1 shows (a, c) topographies and (b, d) simultaneously obtained CPD images of Au/TiO$_2$ samples, taken by KFM. The height of the Au particles shown in (a) and (c) was 0.18-1.21 and 0.75-3.77 nm, respectively. The CPD images show that the electric potential of the Au particles (indicated by arrows) is lower than that on the TiO$_2$ surface and larger particles have much lower potential. Figure 2 shows the particle size dependence of CPD of the Au particles shown in Fig. 1. The CPD value in this plot is defined as the difference from the value measured on the TiO$_2$ surface. When particle height is 3-4 nm, the CPD of the Au particles is about 0.14 V. Then,
it decreases with height down to zero.

In order to analyze this size dependence, we applied the parallel disk model which Sasahara et al. have reported [11, 12]. In this model, the charge distribution at the particle/support interface is approximated as the parallel disk capacitor, and the potential difference between the electrodes is expressed by

\[
V = \frac{\sigma}{2e_0} \left( \sqrt{R^2 + h^2} - \sqrt{R^2 + (h + d)^2 + d} \right),
\]

(1)

where \( \sigma, R, d \) and \( h \) are the charge density on the electrodes, the radius of the electrodes, the inter-electrode distance and the tip-sample distance. By fitting Eq. (1) to the plots in Fig. 2, \( \sigma \) and \( h \) were obtained as 0.01 C/m^2 and 0.73 nm, respectively. Herein, we substituted the particle height into \( R \) (assuming the hemispherical shape of the particles), and assumed that \( d = 0.33 \) nm from the result of transmission electron microscopy [13]. In addition, when \( R \) is infinity, Eq. (1) is reduced to \( V = (\sigma/2e_0)d \). With \( \sigma = 0.01 \) C/m^2 and \( h = 0.73 \) nm, the WFD between Au and TiO_2 was calculated to be 0.19 V. The work functions of bulk Au and TiO_2 are 5.4 and 5.3 eV, respectively. Therefore, taking into account that the TiO_2 substrates used were strongly reduced during the sample preparation procedure, the calculated WFD value is appropriate. Moreover, the result of Au/TiO_2 was consistent with the result of Pt/TiO_2 reported by Sasahara et al. From their results, the charge density at Pt/TiO_2 interface is estimated to be 0.05 C/m^2. Since the bulk WFDs of Au/TiO_2 and Pt/TiO_2 are 0.1 and 0.3 eV, respectively, the charge densities for Au and Pt particles estimated from the CPD measurements are well correlated with the bulk WFDs. However, it should be noted that with respect to charge polarity, their result is opposite to our result.

The energy diagram shown in Fig. 3 represents the correlation between the electric charge and the QES at the Au/TiO_2 interface, which was revealed from the CPD and previously performed LBH measurements. From the LBH measurement, we found: when a Au particle is larger than 0.4 nm, its electronic structure is metallic, and electrons transfer from TiO_2 to Au due to the WFD between them; when the particle is smaller than 0.4 nm, the QSE appears and the charge transfer disappears. From the CPD measurement, we estimated the value of WFD to be 0.19 eV. Since the parallel disk model was well applicable to the CPD analysis, it is inferred that the electrons were localized at the interface with the charge density of 0.01 C/m^2. Taking into account that (1) large metallic particles (e.g. 5 nm diameter) show the catalytic activity [4], (2) the catalytic activity is dependent on perimeter length of the interface [14], and (3) the catalytic activity decreases with occurrence of QSE [7], the result shown in Fig. 3 is consistent with the extra electron model [8], i.e. the localized charge at the interface possibly affects the catalytic activity of Au catalysts. However, the estimated value of the charge density is very small (0.01 C/m^2 = 0.0045 electrons/Au-atom). In addition, the charge transfer from stoichiometric TiO_2 to Au particles should be smaller than this value, because work function of stoichiometric TiO_2 is larger than that of reduced TiO_2. Therefore, in order to clarify whether such small charge density affects the catalytic activity, further experimental and theoretical analysis should be indispensable.

![FIG. 1](image1.png) (a, c) Topographies and (b, d) simultaneously obtained CPD images of Au particles on TiO_2(110) surfaces. Frequency shifts were 30.6 Hz in (a, b) and 17.1 Hz in (c, d). The height of the Au particles shown in (a) and (c) is 0.18-1.21 and 0.75-3.77 nm, respectively. White arrows indicate Au particles. Dark color in the CPD images represents lower CPD value.

![FIG. 2](image2.png) CPD of the Au particles shown in Fig.1 plotted as a function of the particle height. The CPD value is defined as the difference from the value measured on the TiO_2 surfaces. The red line is the fitting curve of Eq. (1) using the parallel disk model. Assuming the inter-electrode distance d of 0.33 nm, the charge density \( \sigma \) and the tip-sample distance \( h \) are estimated to be 0.01 C/m^2 and 0.73 nm, respectively.
IV. CONCLUSION

From the results of the CPD and the LBH measurements, we succeeded in analyzing the charge density at the Au/TiO$_2$ interface quantitatively. The results suggest the possibility that the localized charge at the interface induced by the WFD plays some role in the catalytic activity of Au catalysts. However, since the estimated charge density was very small, further experimental and theoretical analysis should be required in order to clarify the influence of the charge. In addition, we found the difference between CPD and LBH measurements: CPD was excellent in quantitativity, while LBH is excellent in spatial resolution and sensitivity. Therefore, complementary use of these methods enables us to reveal nanoscale charge distribution more quantitatively.

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Appendix A: Procedure for setting the frequency shift

In KFM, the CPD value is dependent on operation mode and feedback parameters because a realistic probe tip has a finite size and shape. For example, Glatzel et al. have found that distance dependence of measured CPD value in AM mode is smaller than that in FM mode [15]. In our research, KFM measurement was performed in FM mode. Therefore, in order to compare the data obtained with different tips or samples, it is necessary to optimize the frequency shift more carefully. We calculated the standard deviation (SD) of CPD for all pixels in a CPD image. Figure 4 shows the frequency-shift dependence of the SD of the CPD images obtained at the same position as shown in Fig. 1(b). The SD of the images increases with frequency shift and reaches a steady value at the frequency shift of 30.6 Hz. At the larger frequency shifts (more than 40 Hz), the SD increases rapidly because feedback control of tip-sample distance became unstable. In this research, we selected the frequency shift where the SD value reached a steady value (indicated by an arrow).


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