Electronic state changes of Cu nanoparticles on reduced TiO$_2$(110) by oxygen exposure

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It is well known that Cu based catalysts are used in the reactions such as water gas-shift, methanol oxidation, CO oxidation, and so on. In spite of many efforts, however, the mechanism leading to strong catalytic activities of Cu nanoparticles is still a debatable issue. In previous study, we have found the oxidation of Cu nanoparticles on oxygen-rich TiO$_2$(110) (O-TiO$_2$) by measuring the core-level shifts and the work functions. In this work, we have measured the electronic properties of oxygen-exposed Cu nanoparticles on reduced TiO$_2$(110) (R-TiO$_2$) by photoelectron and photo-induced secondary electrons emission spectroscopy using synchrotron radiation (SR) light.

The photoelectron spectroscopy (PES) measurements were performed at beamline 8 named SORIS set up at SR center, Ritsumeikan University, Ti 3$p$ and O 2$s$ spectra were obtained by irradiating SR light of 120 eV. Secondary electron spectra were obtained with a bias voltage of -3.0 eV. The all measurements were performed at room temperature (RT) under ultrahigh vacuum (UHV) of $\sim$1 $\times$ 10$^{-7}$ Pa. The R-TiO$_2$ were prepared by Ar$^+$ sputtering and annealing at 870 K for 10 min in UHV. Cu was deposited on the clean surfaces at RT with a Kundsen cell under UHV condition. The deposition rate was 0.055 ML/min. Here, 1 ML means 1.77 $\times$ 10$^{15}$ atoms/cm$^2$, corresponding to the areal density of Cu(111).

Figure 1 shows Ti 3$p$ and O 2$s$ spectra for Cu (0.5 ML)/R-TiO$_2$ as a function of oxygen exposure. It is clearly seen that the binding energies of both the O 2$s$ and Ti 3$p$ lines shift toward a lower binding energy side.

Figure 2 shows the binding energy shifts of Ti 3$p$ and O 2$s$ and the change of work function as a function of oxygen exposure for Cu (0.5 ML)/R-TiO$_2$ and R-TiO$_2$. The electronic state change for R-TiO$_2$ indicates an upward band bending by changing to O-TiO$_2$ after O$_2$ exposure [1]. The electronic state for Cu (0.5 ML)/R-TiO$_2$ changes more significantly than that for R-TiO$_2$. These results indicate that Cu nanoparticles oxidized to Cu$_2$O by oxygen exposure and then the additional upward band bending is caused by a p-n junction between Cu$_2$O and TiO$_2$ substrate.

References