

# Electronic state modification of Cu nanoparticles on TiO<sub>2</sub>(110) : Effect of oxygen exposure

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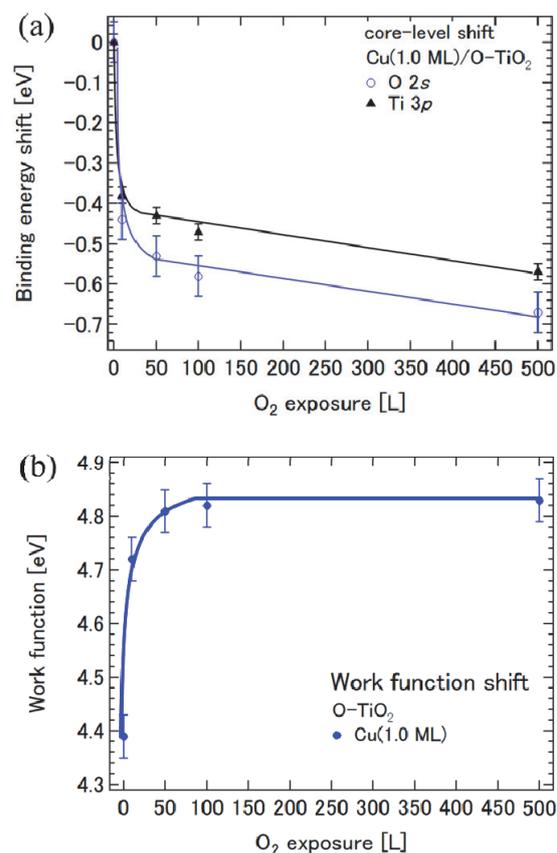
It is well known that Cu based catalysts, both pure and supported on metal-oxides, are used in reactions such as water gas-shift, methanol oxidation, methanol synthesis, and so on [1]. So far several models have been proposed to explain the emerging catalytic activities for Cu/metal-oxide. In spite of many efforts, however the mechanism leading to strong catalytic activities of Cu nanoparticles is still a debatable issue. The structure and morphology of supported metal particles are critical role in determining catalytic activity. Scanning tunneling microscopy (STM) studies have shown that the morphologies of supported nanoparticles on TiO<sub>2</sub>(110) can change dramatically upon exposure to adsorbate gases [2].

In the previous study, we have found the charge transfer between nanoparticles and substrates by measuring the core level shifts and the work functions. In this work, we have measured the electronic properties of oxygen-exposed Cu nanoparticles by photoelectron and photo-induced secondary electrons emission spectroscopy using synchrotron radiation light.

The experiments were performed at beamline 8 named SORIS set up at Ritsumeikan university SR center. We use the rutile TiO<sub>2</sub>(110) which have oxygen rich surface (O-TiO<sub>2</sub>). The O-TiO<sub>2</sub> were prepared by 0.75 keV Ar<sup>+</sup> sputtering and annealing at 870 K for 10 min in UHV, then expose to oxygen as 2000 L (1 L=1.0×10<sup>-6</sup> Torr·s). Cu was deposited onto the O-TiO<sub>2</sub> surfaces using MBE. The deposition rate was 0.08 ML / min (1 ML=1.76×10<sup>15</sup> cm<sup>-2</sup>).

Fig. 1 (a) and (b) show core level shift and work function for Cu(1.0 ML)/TiO<sub>2</sub>(110) as a function of amount of O<sub>2</sub> exposure, respectively. All the O 2s and Ti 3p lines shifted toward a lower binding energy side with increasing the amount of O<sub>2</sub> exposures. The binding energy shift of Ti 3p and O 2s core levels were 0.53 eV and 0.43 eV after the O<sub>2</sub> exposure of 50 L, respectively. The work function increase abruptly by a small amount of O<sub>2</sub> exposure.

The higher binding energy shifts of Ti 3p and O 2s core level and the decreasing work function indicated that the band is bent upward such as the p-n heterojunction. It was formed Cu<sub>x</sub>O by oxidation of Cu nanoparticles.



**Fig. 1** (a) Binding energy shifts of O 2s and Ti 3p observed for Cu/TiO<sub>2</sub>(110) as a function of the amount O<sub>2</sub> exposures. (b) Work functions measured from secondary electrons emission spectra for Cu/TiO<sub>2</sub>(110) as a function of O<sub>2</sub> exposures.

## References

- [1] J. M. Thomas, W. J. Thomas; *Principles and Practice of Heterogeneous Catalysis*; VCH: (New York, 1997)
- [2] J. Zhou, Y. C. Kang, and D. A. Chen, *J. Phys. Chem. B* **2003**, 107, 6664