

## Photoelectron Intensity from Cu Nanoparticles on HOPG

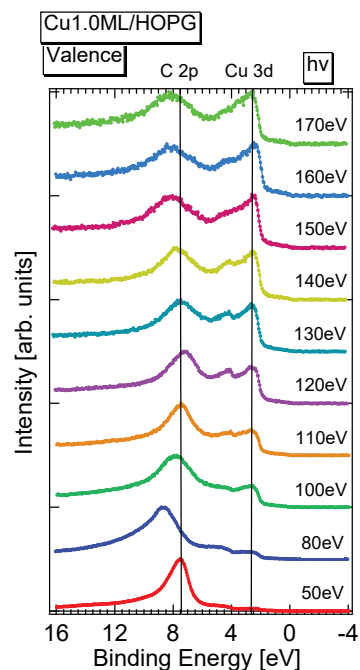
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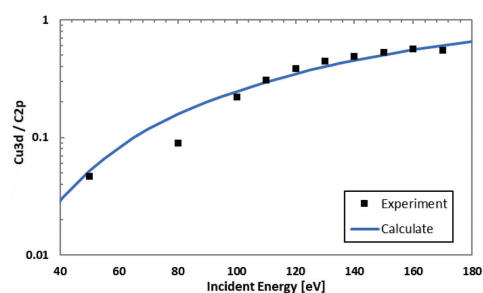
Cu based catalysts exhibit strong catalytic activities for methanol oxidation, water-gas shift reaction, and so on. Therefore, Cu nanoparticles on several substrates have been studied. Recently, Yang *et al.* have found that Cu and carbon material catalyst works for a new reaction that products ethanol from CO<sub>2</sub> [1]. Due to this catalyst's novelty, it is important to elucidate the interface electronic structure between Cu and carbon. In this work, we have studied the electronic structure of Cu/HOPG by photoelectron spectroscopy (PES). Since photon energy can be continuously varied using synchrotron radiation (SR) light, we have examined how much information about the electronic structure of Cu nanoparticles and HOPG substrates can be obtained from the PES valence band spectra as a function of incident photon energy.

The experiments were performed at beamline 8 named SORIS system set up at SR center, Ritsumeikan University. HOPG substrate was prepared by cleavage in atmosphere before entering ultrahigh vacuum (UHV) chamber. After that, HOPG was annealed at 673K for 30 minutes to remove surface contaminations. Cu deposition was performed by MBE method, and the deposition rate was 0.055 ML/min. Here, 1.0 ML means  $1.77 \times 10^{15}$  atoms/cm<sup>2</sup>, corresponding to the areal density of Cu(111). Then, valence band spectra for Cu/HOPG (Cu 3*d* and C 2*p*) were obtained by irradiating SR light of 50 eV to 120 eV at room temperature under UHV of  $\sim 5 \times 10^{-8}$  Pa.

Figure 1 shows valence band spectra for Cu (1.0 ML)/HOPG as a function of incident photon energy. Cu 3*d* electronic structure appears around the binding energy of 2.5 eV, while that of C 2*p* appears around the binding energy of 7.5 eV [slight energy shifts come from the (*k<sub>z</sub>*) band dispersion of graphite]. We find that Cu 3*d*/C 2*p* intensity ratio increases as increasing incident photon energy. Since the photoelectron intensity changes due to the effect of cross section, we estimate the cross-section ratios of Cu 3*d*/C 2*p* [2] together with the experimental intensity ratios by the spectral decomposition, as summarized in Fig. 2 (the estimated cross-section ratios are multiplied by some factor). We found that the photon energy dependence of the experiment results agrees with that of the calculated cross-section ratios. Therefore, in order to investigate the valence band electronic structure of Cu nanoparticles on HOPG by PES, higher photon energy, such as 130 eV, is suitable.



**Fig. 1** Valence band spectra (Cu 3*d* and C 2*p*) for Cu (1.0 ML)/HOPG as a function of incident photon energy.



**Fig. 2** Cu 3*d*/C 2*p* intensity ratio as a function of incident photon energy. Markers and solid curve are experimental and theoretical results, respectively.

### References

- [1] Y. Song, R. Peng, D.K. Hensley, P.V. Bonnesen, L. Liang, Z. Wu, H.M. Meyer III, M. Chi, C. Ma, B.G. Sumpter, and A.J. Rondinone, *ChemistrySelect*, **1**, 6055 (2016).
- [2] J.J. YEH and I. LINDAU, *Atomic Data and Nuclear Data Tables* **32**, 1 (1985).