High energy XPS analysis of Ag-diacetylene hybrid nano-particles related to plasmon damping

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It is well-known that electric field enrichment by the surface plasmon excitation on a metal is useful to enhance nonlinear optical properties. Nanometer-sized metal particle is the most suitable material to realize nonlinear optical properties owing to its large surface area and quantum confinement effect. Masuhara et al. succeed to synthesize core-shell type hybridized nanocrystals using the co-reprecipitation procedure [1]. They used acetylene monomer which were composed of 1,6-di(N-carbazolyl)-2,4-hexadiyne (DCHD), and covered Ag nano particles. They found that the surface plasmon in this hybridized Ag/diacetylene nanoparticles was damped by the polymerization of diacetylene after ultra violet (UV) light irradiation. Our motivation to analyze hybridized nano-crystal is to reveal the origin of plasmon damping mechanism for Ag/diacetylene nano crystals and realize the long-life hybrid nanocrystal with intense surface plasmon.

In this work, we have focused attention on the core Ag structure before/after polymerization of diacetylene. For this, we have measured high energy XPS spectra of this nanocrystal to evaluate the electronic structure of hybrid nano crystal, especially core Ag particles on which surface plasmon exists. High energy XPS experiment was done at the BL15XU beamline of SPring-8. Photon energy was set to be 4750 eV. Figure 1 shows the valence band XPS spectra of core Ag of hybrid nano crystals before/after UV irradiation. In Fig.1, it can be concluded that we observed no difference between valence band XPS spectra of Ag core covered with monomer-diacetylene and Ag core covered with polydiacetylene. However, there is difference between hybrid nano crystal and Ag metal. These data indicated as follows: " 4d band narrowing", "5s band enrichment", "broadening of Fermi edge", "Fermi edge shift to higher binding energy".

Combination of high energy XPS analysis with the L_3MM Auger XANES analysis at Ag L_3 edge revealed that there were no change of electronic structure of overall Ag core before/after UV irradiation and "4d band narrowing" and other phenomena mentioned above come from the cluster size effect of Ag cluster. These cluster size effect is visible under the condition that cluster is smaller than 4 nm. Muvlaney [2] showed theoretically that the surface plasmon on these small clusters is easily damped owing to the shrinking space of the surface plasmon. We can conclude that plasmon damping of Ag/diacetylene nano crystals is caused by the instability of surface plasmon on tiny cluster smaller than 4nm.

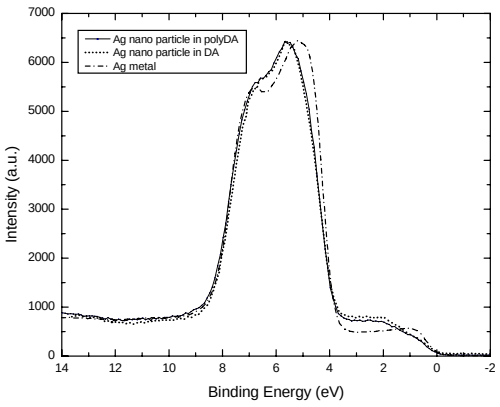

Figure 1 Valence band XPS spectra of core Ag of hybrid nano crystals before/after UV irradiation. Valence band spectrum of Ag metal is also indicated as a reference. X-ray energy was 4750 eV.

[1] Masuhara et al. Jpn. J. Appl. Phys. **40** (2001) L1129-L1131.
[2] P. Mulvaney: *Langmuir*, **12**, 788 (1996).