

## HIGH ENERGY XPS AND XANES ANALYSIS OF Ag-DIACETYLENE HYBRID NANOPARTICLES RELATED TO PLASMON DAMPING

It is well known that electric field enrichment by surface plasmon excitation on a metal is useful for enhancing nonlinear optical properties. A nanometer-sized metal particle is the most suitable material for realizing nonlinear optical properties owing to its large surface area and quantum confinement effect. Neeves and Birnboim have suggested that hybrid nanocrystals constructed of a core-sphere and spherical-shell have an attractive nonlinear optical susceptibility [1].

Masuhara *et al.* succeeded in synthesizing core-shell type hybridized nanocrystals using the co-precipitation procedure [2]. They used diacetylene monomers which were composed of 1,6-di(N-carbazolyl)-2,4-hexadiyne (DCHD), and covered Ag nanoparticles. They found that the surface plasmon in these hybridized Ag/diacetylene nanoparticles was damped by the polymerization of diacetylene after ultraviolet (UV) light irradiation. Figure 1 shows the transmission electron microscope (TEM) image for Ag-diacetylene hybridized nanocrystals and the visible absorption spectral change of hybridized nanocrystals with UV irradiation [3]. It was clearly observed that the absorbance peak of the surface plasmon (marked with LSP in Fig. 1(b)) of the Ag core was damped while that of an exciton (marked with EA in Fig. 1(b)) of the polydiacetylene shell increased. The surface plasmon peak eventually disappeared after 10 minutes of UV irradiation.

Neeves and Birnboim [1] showed theoretically that the simple coupling between the optical properties of metal and polystyrene decreases the intensity of the surface plasmon peak in some cases. However, according to their calculation, the surface plasmon remains as a consequence of coupling and the decrease in the surface plasmon peak coincides with the drastic energy shift of the plasmon. It should be noted that the experimental result in Fig. 1(b), which showed

plasmon annihilation and no energy shift of the surface plasmon during plasmon damping, is significantly different from Neeves and Birnboim's theoretical analysis results. This peculiar phenomenon leads us to consider other mechanism of plasmon damping.

In this work, we have focused attention on the core Ag structure before/after diacetylene polymerization. For this, we have measured the high energy XPS spectra of these nanocrystals to evaluate the electronic structure of hybrid nanocrystal, especially core Ag particles on which a surface plasmon exists. Ag-diacetylene nanocrystals were dispersed on a Si wafer. The detailed process of synthesizing nanocrystals is described in ref. [2]. The high energy XPS experiment was performed at beamline BL15XU. The photon energy was set to be 4750 eV (the maximum analyzing energy is 4800 eV for the XPS machine at BL15XU). Figure 2 shows the valence band XPS spectra of the Ag core of hybridized nanocrystals before/after UV irradiation. The valence band XPS spectrum of Ag metal is also indicated as a reference. In Fig. 2, it can be concluded that we observed no difference between the valence band XPS spectra of the Ag core covered with monomer-diacetylene and the Ag core covered with polydiacetylene. However, there is a difference in valence band XPS spectra between the hybrid nanocrystal and the Ag metal. These results can be summarized as follows: "4d band narrowing", "5s band enrichment", "broadening of Fermi edge", and "Fermi edge shift to higher binding energy." Usually, these types of phenomena are explained on the basis of two models. One is a chemical reaction of core Ag with other elements (such as carbon and oxygen). The other is a cluster size effect. The cluster size effect has been well investigated for simple metal clusters on a substrate. For example, Roulet *et al.*

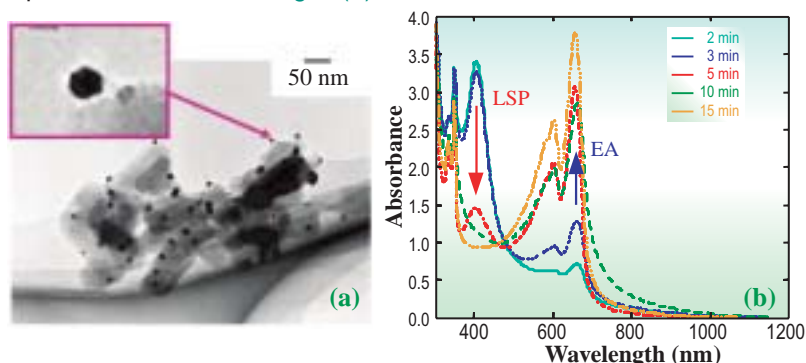


Fig. 1. TEM image of Ag-diacetylene hybridized nanocrystals (a) and its absorption spectral change during solid-state polymerization of diacetylene by UV irradiation (b) [3]. The inset of Fig. 1(b) indicates the irradiation time of UV.

discussed that the *d* valence-band width of XPS spectra for Au clusters on a NaCl(100) substrate becomes narrower with decreasing cluster size, and the critical size for band narrowing is 4 nm (about 10<sup>3</sup> atoms in a cluster). Tanaka *et al.* pointed that a 3.8 nm Ag cluster on HOPG substrate has a broad Fermi edge of UPS spectra [4].

In Fig. 2, we could not identify which model mentioned above is the actual one. We have, therefore, performed Ag-element-specific spectroscopy for checking a chemical reaction of Ag. Usually, one measures a chemical shift of XPS inner-shell peaks for checking the chemical reaction, but a sharp Ag 3*d* XPS peak is not sensitive to the chemical reaction. Therefore, we have measured the X-ray absorption near edge structure (XANES) spectra at the Ag L<sub>3</sub> edge by detecting Ag L<sub>3</sub>MM Auger peaks, since the XANES spectra of Ag are very sensitive to a chemical reaction [5]. Figure 3 shows the XANES spectra of the Ag L<sub>3</sub> edge for hybridized nanocrystals before/after sufficient UV irradiation. The XANES spectrum of Ag metal [5] is also indicated in Fig. 3 as a reference. These data led us to recognize that the Ag core of hybridized nanocrystals was metallic and stable before/after UV irradiation.

Since XANES spectra clarified that the overall Ag core was metallic, we can conclude that the XPS valence band of the Ag core shown in Fig. 2 is caused by the cluster size effect. It should be noted that this cluster size effect is visible under the condition that the cluster size is smaller than about 4 nm as mentioned above. However, TEM data (e.g. in Fig. 1) showed that the average size of the overall Ag core was roughly estimated to be 15 nm. We considered with much interest that the Ag core is a lump of clusters smaller than 4 nm from the viewpoint of electronic structure.

It is well known that a plasmon comes from a collective oscillation of conduction electrons, and its intensity is dependent on the electron mean free path of conduction electrons. Muvlaney stated that conduction electrons are largely scattered by the

surface with decreasing size of the metal cluster, and a smaller mean free path dependent on the cluster size results in the stronger plasmon damping [6]. This means that the shortening of electron mean free path on the Ag core's surface of hybridized nanocrystals results in the stronger damping of the surface plasmon when Ag core size is unchanged. It should be noted that this type of plasmon damping phenomenon, which shows a vanishingly small plasmon peak shift and enables plasmon annihilation as a consequence, is consistent with the experimental result in Fig. 1. According to Muvlaney's study, a cluster size less than 4 nm is small enough for us to take account of plasmon damping. Since the overall Ag core of hybridized nanocrystals remained metallic after UV irradiation, we had better consider a part of the Ag core surface which cuts off surface plasmon oscillation spreading over the small cluster surface. We explained as a hypothesis that the surface plasmon damping of hybridized nanocrystals after UV irradiation is caused by the generation of spots, where the interface of the Ag core and diacetylene is non-metallic, on the Ag core surface by the UV irradiation. These spots might be coming from a local chemical reaction or a local optical-property-mixing at part of the interface of the Ag core and the diacetylene shell.

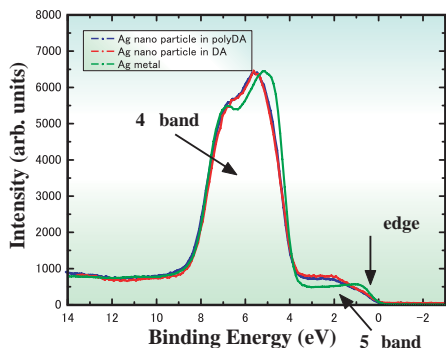


Fig. 2. Valence band XPS spectra of core Ag of hybridized nanocrystals before/after UV irradiation [3]. The valence band XPS spectrum of bulk Ag metal is also indicated as a reference. The X-ray energy was 4750 eV.

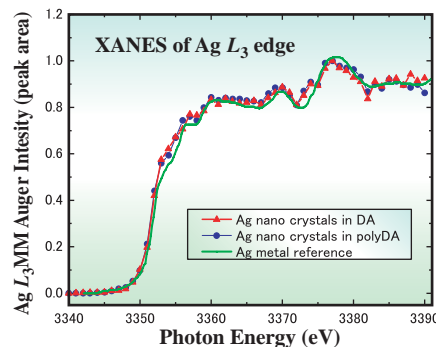


Fig. 3. XANES spectra of Ag L<sub>3</sub> edge for hybridized nanocrystals before/after UV irradiation. The XANES spectrum of Ag metal [5] is also indicated as a reference.

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