Size-dependent electronic structure of Au nanoparticles

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Due to their peculiar properties, gold nanoparticles (NPs) have attracted much attention in not only fundamental physics, but also in application fields, such as catalysis, optical- and electronic devices, medicinal use, and so on. The size-dependent electronic structure of Au NPs is an indispensable input to fully comprehend the origins of the peculiar properties, e.g., the magnetic property of these materials [1], and a lot of spectroscopy studies have been reported over the last decade [2-4]. However, the spread of the NPs size and/or the low energy-resolution of the photoemission equipment used in these former studies prevent to obtain detailed information on the electronic states, especially the electronic states of valence band, of Au NPs. Recently, a method to synthesize Au NPs with a certain number of Au atoms, i.e., magic numbers, has been reported [5]. The use of these thiolate-protected Au NPs together with high-resolution photoemission equipment will allow us to obtain a proper understanding on the size-dependent electronic structure of Au NPs.

In this paper, we will present our results on the electronic states of the valence band region and that of the Au 4f core-level, measured for Au NPs with magic numbers of 25, 38, and 144. Photoemission measurements were carried out at the APE beamline of Elettra synchrotron, Italy, and the beamline 13 of Saga Light Source, Japan, under UHV condition and sample temperature of room temperature. Two components originating from the core-Au and surface-Au were observed in the Au 4f spectra, and the size-dependent intensity ratios of these components show agreement with those reported in the literature [4]. That is, the relative intensity of the shell-Au increases as the size of NP decreases. However, in contrast to the Au 4f core-levels, the valence bands measured at photon energy of 700 eV in the present study look different from those measured at 1253.6 eV in ref. 4. The better resolved spectra obtained from the higher energy resolution used in the present study allowed us to analyze the electronic state of the valence region in more details. We will also discuss the change in the electronic states of Au 5d, and discuss the origin of the magnetism of Au NPs.

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