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Synthesis of Cu-Au nanoparticles by two-step gamma-ray irradiation reduction method

Motoaki Tanaka[1], Shintaro Toda[1], Toshiyuki Matsui[1], Akihiro Iwase[1], Noboru Taguchi[2], Shingo Tanaka[2], Qiu Xu[3] and Fuminobu Hori[1*]

1) Osaka Prefecture University, Gakuen-cho1-1, Sakai, 599-8531 Osaka, Japan
2) National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka 563-8577, Japan
3) Research Reactor Institute, Kyoto University, Kumatori, Osaka 590-0494, Japan

1 Introduction

Copper nanoparticles are key materials for various industrial fields, because of its electrical and optical properties. Copper is rich in natural resources compare to other metals on earth; even so, it is important to control the size and shape of copper particles for electric and photonic devices. Generally, copper particles of microns have been synthesized using chemical reduction methods. However, they are easy to oxidize and re-dissolved since their high surface activity, so that it is difficult to fabricate copper particles below nanometer size without surface oxidation. Previously, we have successfully synthesized pure copper particles with an average size of about 20 nanometers diameter by gamma-ray irradiation reduction method [1]. However, they are stable in argon gas atmosphere. In this study, we attempted to synthesize gold stabilized copper nanoparticles by one step reduction of gold and copper ions in aqueous solution under gamma-ray irradiation reduction field.

2 Experiment

Aqueous solutions of 1.0mM gold complex ($NaAuCl_4 \cdot 2H_2O$) and 1.0mM Cu^{2+} ion of copper complex ($(CH_3COO)_2Cu \cdot H_2O$) with a cationic surfactant of sodium dodecyl sulfate (SDS) and a radical scavenger of 8.5 vol% ethylene glycol (EG) were prepared. An aqueous solution was poured into a polystyrene container and was purged with argon gas for 10 minutes. After degassing, they were irradiated with gamma-ray at Kyoto University Research Reactor Institute. Total dose of gamma-ray irradiation was 20 kGy with the dose rate of 2.0 kGy/h. All irradiated solutions were examined by using an UV/vis absorption spectrophotometer (Shimadzu UV-2550) in the wavelength range of 200-800nm. The size and the structure of the synthesized particles were characterized by transmission electron microscope (TEM) on JEOL JEM-2000FX and energy dispersive X-ray spectrometry (EDS). The samples for TEM were prepared by dispersing the all products on carbon films with a molybdenum mesh by dropping the solutions and were dried in vacuum.

In order to investigate stability of synthesized particles, after samples exposed to air for 2months, samples were characterized by UV/vis absorption spectrophotometer, TEM and X-ray Photoelectron Spectroscopy (XPS) at KEK-PF BL-27A. The samples for XPS were prepared by dropping samples on germanium and dried in vacuum.

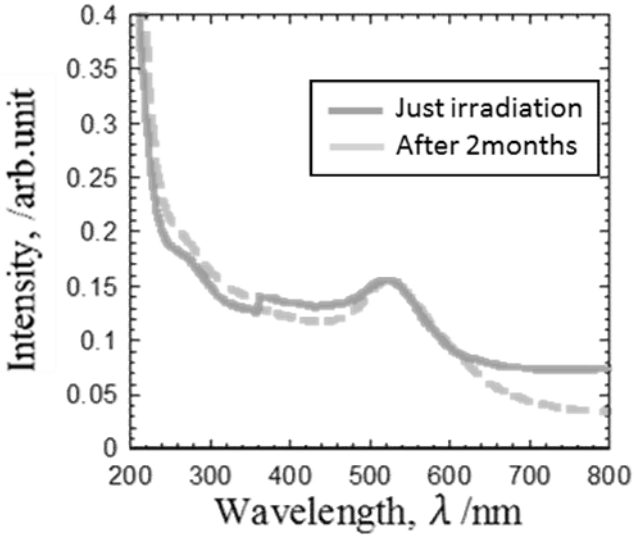

Fig.1 UV/vis spectra of solutions just irradiated by gamma-ray irradiation and 2 months after.

3 Results and Discussion

Figure 1 shows the UV/vis absorption spectra of aqueous solutions after gamma-ray irradiation. In case of the solid line, this graph has one peak around 520 nm. The peak around 520 nm corresponds to the surface plasmon resonance from pure Au nanoparticles. After 2 months, in case of the broken line, peak doesn't change. It shows that nanoparticles in samples didn't change for 2 months.

Figure 2 shows TEM images of nanoparticles just after irradiation and 2months after irradiation. From left figures, the shape of nanoparticles is spherical and its mean diameter is about 11nm. Even after 2 months, from right figure, the shape of nanoparticles kept spherical and nanoparticles didn't form aggregation. The structure of synthesized nanoparticles can be estimated as a core shell (Au-core Cu-shell) type nanoparticle by EDS analysis (Fig. 3). We suppose the mechanism of this structural nanoparticles is that Au ions are reduced faster than Cu ions because of difference in redox potential. So first Au

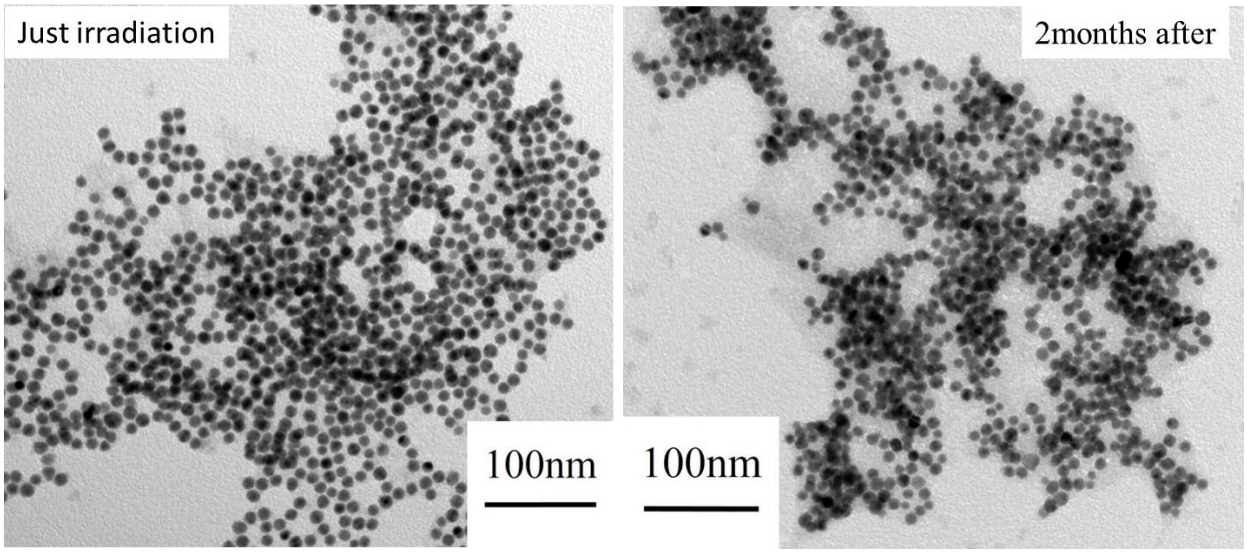

Fig.2. TEM images of nanoparticles just irradiated and 2months after irradiation.

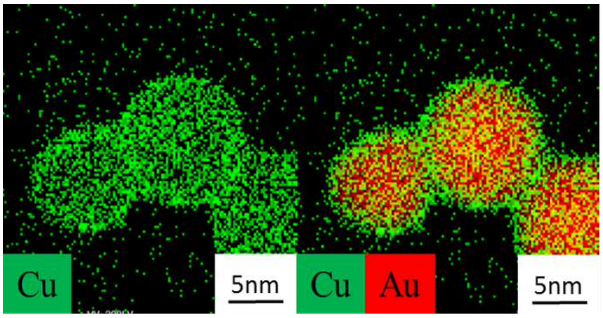

Fig.3. EDS images of solutions just irradiated by gamma-ray irradiation.

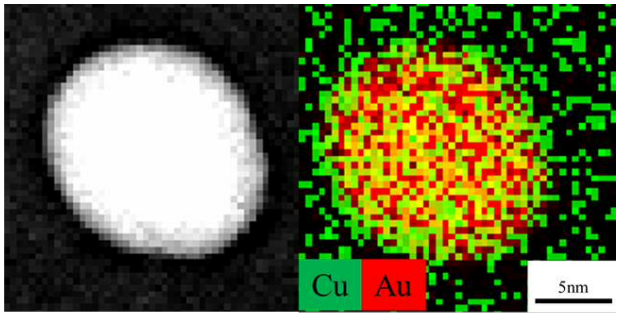

Fig.4. EDS images of solutions 2months after irradiation by gamma-ray irradiation.

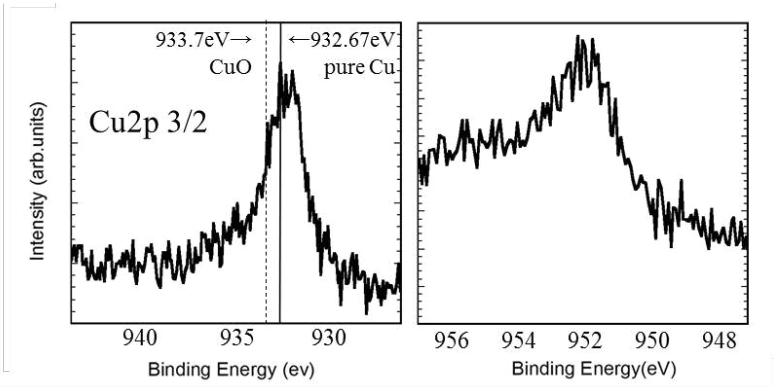

Fig5. XPS of solutions exposed to air for 2months

cores are formed, next Cu are synthesized on surface of Au core. Figure 4 shows EDS results of nanoparticles exposed to air for 2 months. Nanoparticles kept Au-core Cu-shell structure and were found to be stable in air.

Figure 5 shows XPS spectra of solutions exposed to air for 2 months. From this figure, a peak was found around 932.67 eV, which is originated from pure Cu metal. On the other hand, other peaks correspond to CuO(933.5~934.0eV) were not observed. This result means that Cu shell on Au core obtained resistance to oxidation. We found even if Cu shell are thin, Cu shell are stable than pure Cu nanoparticle in air.

There is a possibility core-shell nanoparticles get resistance to oxidation by interact of core-shell structure.

References

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* horif@mtr.osakafu-u.ac.jp