

Characterization of alloy nanoparticles synthesized by gamma and electron irradiation reduction

Fuminobu HORI¹, Kemeng ZHU¹, Tomoko YAMADA¹, Toshiyuki MATSUI¹, Akihiro IWASE^{1,2}, Qiu Xu³

¹Osaka Metropolitan University, Gakuen-cho1-2, Sakai, Osaka, 599-8570, Japan

²The Wakasa-wan Energy Research Center, Tsuruga, Fukui, 914-0192, Japan

³KURRI, Kyoto University, Nishi 2, Kumatori-cho, Sennan-gun, Osaka 590-0494, Japan

1 Introduction

Catalysts are indispensable in reaction processes related to the development of new energetic materials and their importance is increasing. Therefore, there is a need to develop catalysts that are highly functional yet resource-saving. In this context, nanoparticles are attracting attention. Nanoparticles ability to exhibit novel electrical, optical, magnetic, and chemical properties due to the quantum size effect when the size of the material is reduced and the diameter is about the de Broglie wavelength of an atom. Many of the NPs currently in use nano-sized to increase the efficiency of their specific surface area, and inexpensive base metals are attracting attention for their ability to both conserve resources and provide high functionality. However, base metals are difficult to reduce in water and difficult to stabilize. In our previous work, it is found that base metal ions can be easily reduced and fabricate nano size materials by the irradiation reduction method using electron and gamma ray [1]. The base metals can be reduced by the difference in redox potential of metals, and NPs can be stabilized by alloying of the base metals by noble metals or something other elements. Therefore, the aim of this study is to synthesize stable alloy NPs containing base metals and characterize them. In the present work, we have tried to synthesize more than ternary alloy systems containing Ni, Cu, Ag, and Au.

2 Experimental

Aqueous solutions with various ternary combination of a given concentration of metal complexes (combination of AgAuCu and AgCuNi), $((\text{CH}_3\text{COO})_2\text{Cu}\cdot\text{H}_2\text{O})$, AgNO_3 , NiCl_2 , $\text{Na}[\text{AuCl}_4]$ and $\text{PdCl}_2\text{NaCl}_3\text{H}_2\text{O}$ with an additive of polyvinyl (PVP) and 8.5 vol% ethylene glycol were prepared. The ratio of all ion concentration was adjusted to the ratio of 0.5 to 2.0 in the solution. The solution was argon gas purged and sealed into polystyrene vessels. They were irradiated at about 300 K with 1.17 and 1.33 MeV gamma-rays from ^{60}Co radio active source at gamma irradiation facility in KURRI, Kyoto University. The total dose was fixed to 10 kGy with the dose rate of 1.0 kGy/h. Also, same solutions were irradiated 8 MeV electron with total dose of 10kGy in about 60 sec by linear accelerator at same facility. After irradiation, the samples were measured for UV-vis absorption and X-ray diffraction. The structures for all colloidal products were examined by X-ray absorption fine structure (EXAFS) near the Cu K-edge and X-ray photoelectron spectroscopy (XPS) at BL-27 KEK-Photon

Factory, X-ray diffraction and 200 kV transmission electron microscope JEOL 2000FX.

3 Results and Discussion

Fig. 1 shows the photograph of water solutions including Ag, Au, Cu and Ni ions before and after gamma and electron irradiation. After electron and gamma-ray irradiation, the color of solutions was clearly changed, and their color is not also the same. It is considered that these unique colors originated from different type of particles formation, such as size and the state of alloy phase.

Figs. 2 and 3 show the UV-vis light absorption spectra of each colloidal solution after electron and gamma-ray irradiation. Clear different absorption profile appears in each solution. The clear absorption peaks of Ag-Cu-Ni (400 nm) and Ag-Au-Cu (520 nm) close to the surface plasmon resonance absorption (SPR) of pure Ag and Au

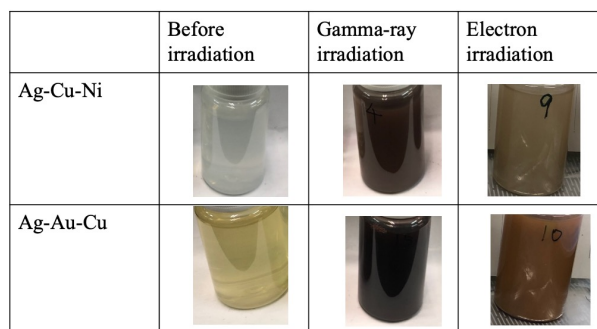


Fig.1 Photographs of water solutions including metal ions before and after gamma-ray and electron irradiation.

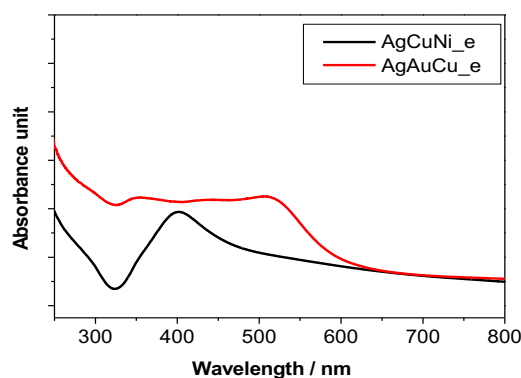


Fig.2 UV-vis light absorption spectra of (Ag, Au, Cu) and (Ag, Cu, Ni) solution after gamma-ray irradiation.

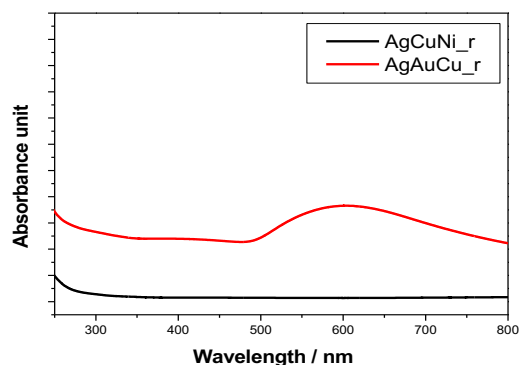


Fig.3 UV-vis light absorption spectra of (Ag, Au, Cu) and (Ag, Cu, Ni) solution after electron irradiation.

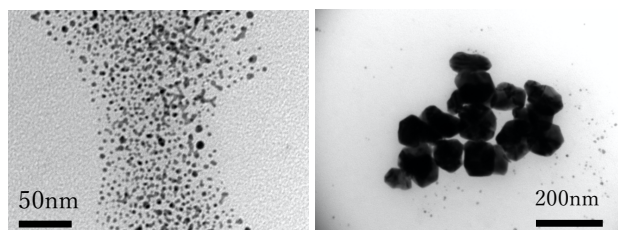


Fig.4. TEM images of products in (Ag, Au, Cu) solutions synthesized by (a) electron and (b) gamma-ray irradiation.

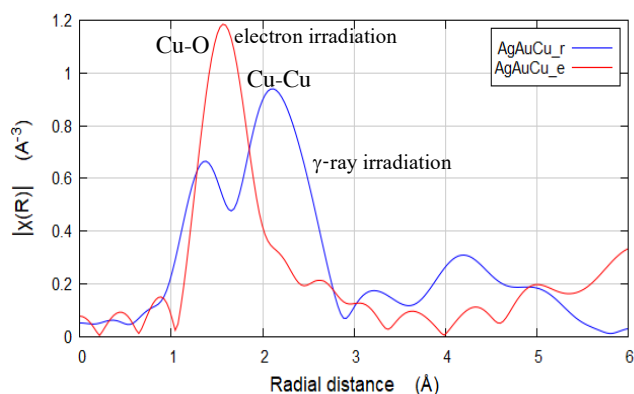


Fig. 5 EXAFS spectra near Cu K-edge of electron and gamma-ray irradiated (Ag, Au, Cu) solution.

nanoparticles are observed after electron irradiation. In the case of gamma irradiation, a clear absorption peak corresponding to the position close to the SPR of pure Cu nanoparticles is observed only in the Ag-Au-Cu solution. All of these peaks do not exactly match for the authorized SPR of pure metal nanoparticles. This may be caused by the formation of complex alloy particles. Also, color depth is clearly different for electron and gamma-ray irradiation. This is thought to be due to the difference in the reduction rate of metal ions. That is, especially in case of Ag-Cu-Ni with gamma-ray irradiation, characteristic SPR peak does not appear but the color of solution is very dark. It is known that the amount of radicals generated is proportional to the absorbed dose due to irradiation, and since the absorbed dose rate is lower in gamma-ray irradiation than in electron irradiation, particles grow slowly and become larger in gamma-ray irradiation [2]. Therefore, this is considered

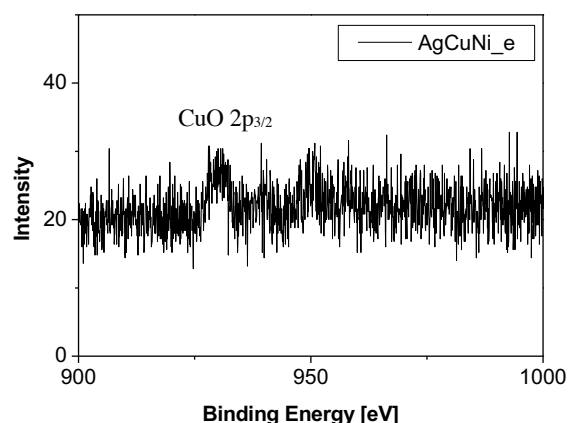


Fig.6 XPS spectra for the product in (Ag, Cu, Ni) solution.

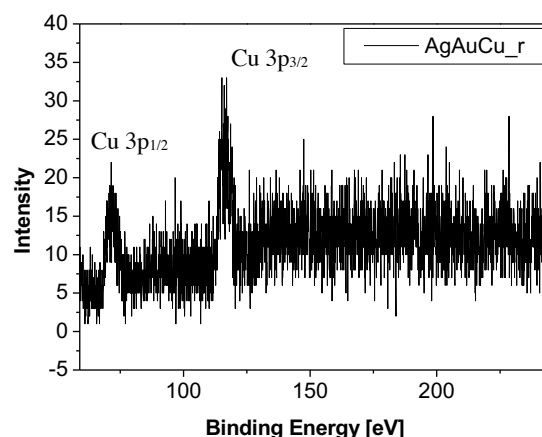


Fig.7 XPS spectra for the product in (Ag, Au, Cu) solution.

that the pure metal and/or complex particles were coarsened to the extent that surface plasmons did not appear because the reaction proceeded slowly by gamma-ray irradiation.

As shown in Figure 5, EXAFS spectrum shows that the local atomic order of the particles is quite different by electron and gamma irradiation (Ag, Au, Ni), and it was found that copper is oxidized by electron irradiation. Figures 6 and 7 show XPS spectra focused on the bonding of Cu atoms in the nanoparticles produced by irradiation. From these results, we found that Cu metal particle by gamma-ray irradiation and Cu oxidation products by electron irradiation are formed mainly. More local complex states of those particles are now examined.

Acknowledgement

The authors are also grateful to Dr. Y. Baba, Dr. Y. Okamoto, and Dr. N. Usami for their help for experiments at BL27.

References

- [1] N.Taguchi *et al.*, Rad. Phys. and Chem. **78** 1049 (2009).
- [2] N.Maeda *et al.*, Mater. Res. Symp. Proc. 900E 0900-006-16.1 (2020).

*horif@omu.ac.jp