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Synthesis, fine structure, and formation mechanism of metal and metal alloy nanoparticles via sputtering onto liquid polymers

「液体高分子へのスパッタリングによる金属・合金ナノ粒子の合成、微細構造、生成機構」

Solid solution alloy (SSA) nanoparticles are particles in nanoscale regime containing a single phase of metals completely miscible in solid state. They offer a tool to realize new and/or synergistic properties which single constituents do not have. However, it is challenging to synthesize SSA nanoparticles of various metal systems, especially those contain miscibility gaps or intermetallics in the bulk. Recently developed vacuum sputter deposition onto a non-/low volatile liquid has some unique features. The sputter deposition generates metal atoms/clusters from the bulk metals and allows for random combinations and alloying. Meanwhile, the low volatile liquid can capture and control particle growth to form nanoparticles. Hence, the particle formation by this technique is unique compared to that in chemical synthesis and/or bulk alloy fabrication. We have been using sputter deposition onto liquid polymer to synthesize metal and SSA nanoparticles and aiming to elucidate the fine alloy structures and particle growth mechanism.

Fine-structure of sputtered binary nanoparticles

Using co-sputter deposition onto liquid polyethylene glycol (PEG) (Fig. 1), we attained binary SSA nanoparticles of below 3 nm for various metals no matter they are miscible (e.g., Au/Ag), form intermetallics (e.g., Au/Cu, Ag/Pt, Cu/Pd, Cu/Pt), or possess a large miscibility gap (e.g., Au/Pt) in the bulk. Their composition was varied in almost entire range by

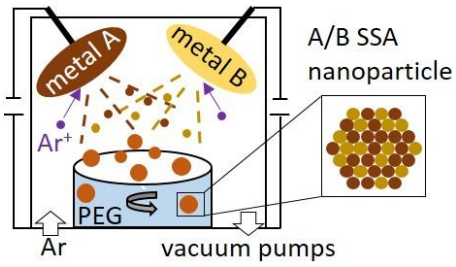

Fig. 1. Co-sputtering onto PEG

adjusting the sputter currents. XRD results reveals fcc structure of Au/Pt nanoparticles with the (111) peak shift from that of Au to Pt for an increase of Pt atom % (Fig. 2a, *Langmuir* 2020). Fine structure analysis with atomic resolution high-angle annual dark field (HAADF) imaging in scanning-electron microscope (STEM) coupled with energy dispersive X-ray spectra (EDS) further confirmed SSA structure in a single Au/Pt nanoparticle (Fig. 2a). In intermetallic systems, such as Au/Cu, the sputtered nanoparticles exhibited a random mixing, e.g., Au and Cu, in atom columns (Fig. 2b, *Langmuir* 2017), suggesting the formation of SSA instead of intermetallics. These small SSA nanoparticles are in on-going study and expected to deliver interesting catalytic properties.

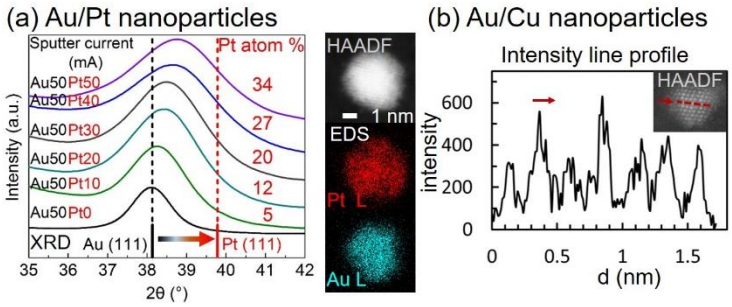

Fig. 2. (a) XRD and STEM-EDS maps of SSA Au/Pt and (b) intensity line profile of a SSA Au/Cu nanoparticle.

Particle growth mechanism

The particle growth in liquid was traced. By measuring particle size for various deposition period and time, we obtained experimental evidence of the particle growth in both the surface and inside the liquid. Besides, impact of the liquids on size, structure, composition distribution, and aggregation of nanoparticles was elucidated. The physiochemical properties of the liquids, particularly their binding strength to particles relatively compared with metal-metal interaction, were demonstrated as a control factor. Small particles and stable dispersions were obtained with stronger binding strength of the liquid to metal, which is in line with the trend in chemical synthesis.

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