

Title	電子移動を利用した多元金属ナノ粒子の特性制御と新奇バイオ/化学センシングプローブへの応用
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## Abstract

Plasmonic metallic nanoparticles have been explored extensively in terms of their fundamental and practical applications such as for optoelectronic devices, optical metamaterials, sensors, and solar cells as well as many others. During the past decade the concomitant rapid development of plasmonics into a vibrant sub-area of nanotechnology has focused almost entirely on Au and Ag as (nano) plasmonic metals. Ag provides high enhanced-Raman activity, while the Au provides excellent chemical stability and a great reactivity with sulfur containing biomolecules, which has inevitably led to the combination of Au and Ag in a single nanoparticle system. The synthetic approach to Au-Ag nanoparticles still has many obstacles. Aqueous synthesis techniques for Ag nanoparticles are advantageous for biological applications because the resulting nanoparticles can often be used directly, yet these techniques typically provide unstable Ag nanoparticles of low monodispersity, or with a size that is difficult to control. In addition, it is still challenging to synthesize well-defined uniform Ag@Au nanoparticles because the Ag core is easily etched away due to the galvanic replacement reaction between Au ions and the Ag metal cores which causes gaps in the Au shell or hollow sections at the interface of the core and the shell. In my research, Au@Ag core-shell nanoparticles were demonstrated to have better chemical stability and very high SERS activity together with tunable size, shell thickness and plasmonic properties. Moreover, Ag in the shell also could suppress the galvanic replacement reaction allowing the formation of double shell (Au@Ag)@Au nanoparticles without any defects or gaps in the structure. All of these attractive aspects arise from the electron transfer phenomenon which has been shown to occur in the Au-Ag system.

By extending this phenomenon to other silver based NP systems, insight can be gained into how to manipulate the particle structure and composition towards the desired characteristics. With this goal in mind, we created a series of different sized platinum particles and coated them in silver shells of various thicknesses. In this case, platinum was chosen as a core material because of its status as a noble metal, its *fcc* crystal structure (the same as for silver), and its chemical similarity to gold. The resulting particles were characterized in terms of their structural/composition properties, and then the electronic properties of these probes were analyzed by using X-Ray Photoelectron Spectroscopy. The results demonstrate that the electronic transfer phenomenon can be extended to a wide range of heterostructure systems, and provides insight into how to exploit electronic transfer to create silver based sensing probes with enhanced robustness, high optical/plasmonic activity and plasmonic characteristics that can be tuned for a desired application.

Electron transfer or charge transfer phenomenon is very attractive as a route to manipulate the properties of materials and also presents a complex challenge. Understanding the mechanism of operation and its effect to materials characteristics can lead us to systematically design materials with distinct characteristics for specific applications. My PhD research attempted to make clear the controllability of electron transfer phenomenon specifically in multi-metallic nanomaterials. In order to have the full picture of electron transfer phenomenon, we clarify the interaction among three noble metals (Ag, Au and Pt) by comparing Au-Ag, Pt-Ag and Au-Pt in homogeneous and heterogeneous nanostructure. This fundamental research will provide scientists with a useful tool in understanding, designing and controlling the properties of metallic nanomaterials. In addition, nanoparticles which are composed of Au, Ag or Pt are promising not only in biosensing and diagnostics applications but also are a good candidate for medical – therapy or catalyst applications.

*Keywords: noble metal, heterostructure, nanoparticle, electron charge transfer, biosensor.*