

Synthesis and localized surface plasmon resonance properties of $B8_1$ -type anisotropic crystal structure nanoparticles

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Keywords: Localized surface plasmon resonance; Inorganic nanoparticles; Intermetallic compound; ordered alloy

Localized surface plasmon resonance (LSPR) of metal nanoparticles (NPs) is a unique phenomenon in which free electrons of NPs exhibit collective oscillation due to the resonance with the electric field of incident light. The spherical NPs of group 11 elements (Au, Ag, and Cu) and the alloy NPs containing group 11 elements with *fcc* (face-centered cubic)-based structure have been commonly used for LSPR in the visible region. Recently, we found that the PtIn_2 NPs with *C1* (CaF_2 -type) structure exhibit LSPR in the visible region¹. Crystal structures of most plasmonic NPs are isotropic, such as *fcc* and *C1* structures, with identical atomic arrangements along the x-, y-, and z-axes. In this study, we focused on the visible LSPR of NPs with anisotropic crystal structure, where the atomic arrangement along the z-axis differs from that of the x- and y-axes. We synthesized spherical PtSn NPs with an anisotropic $B8_1$ (NiAs -type) structure (inset in Fig. a), which do not contain any group 11 elements, and investigated their LSPR properties.

XRD, TEM, and HAADF-STEM measurements showed the formation of the desired spherical PtSn NPs with $B8_1$ structure (Fig. a,b). The obtained PtSn NPs showed two characteristic peaks in visible (ca. 380 nm) and near-infrared (ca. 850 nm) regions of the extinction spectrum (Fig. c). Both the refractive index and NPs size dependent LSPR peak shifts suggested that these peaks are derived from the LSPR. We consider that the spherical PtSn NPs exhibit two LSPRs due to their anisotropic crystal structure, especially the contribution from the two types of screening effect, i.e., the oscillation of bound *d* electrons. Calculated photoabsorption of $B8_1$ - $\text{Pt}_{291}\text{Sn}_{306}$ NP also suggested the importance of crystal structure. Plasmonics using such anisotropic materials is expected to be a breakthrough for conventional materials.

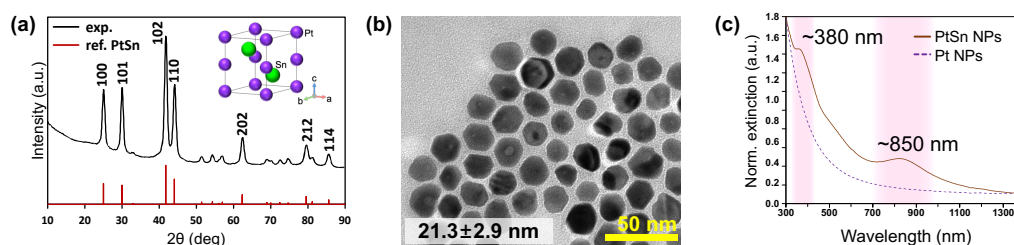


Fig. (a) XRD pattern (Inset : crystal structure) and (b) TEM image of $B8_1$ -PtSn NPs. (c) Extinction spectra of Pt NPs and PtSn NPs.

[1] H. Takekuma, R. Sato, T. Teranishi *et al.*, *Adv. Sci.*, **2024**