

Supporting Information

Suitability of GaP Nanoparticles as a Surface-Assisted Laser Desorption/Ionization Mass Spectroscopy Inorganic Matrix and Their Soft Ionization Ability

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EXPERIMENTAL Details

Preparation of GaP NPs. GaP NPs were prepared by the gas evaporation method similar to that previously reported.¹ A vacuum chamber was first evacuated to 2.7×10^{-3} Pa and then filled with Ar gas of 1.6×10^4 Pa. Small GaP crystals were evaporated from a tungsten basket in Ar gas. The NPs grown along the convection of Ar gas were deposited on a stainless steel (SUS304) substrate ($2\text{ cm} \times 2\text{ cm} \times 1\text{ mm}$) placed 5 cm above the heater. The thickness of the NP layer was *ca.* 0.2 mm.

Preparation of Metal NPs. Metal NPs were prepared by the chemical reduction processes. Pt NPs were obtained by dropwise addition of NaBH_4 into aqueous H_2PtCl_6 .¹ Au and Ag NPs were prepared by NaBH_4 reduction in the presence of trisodium citrate. The aqueous solutions of 1-mL $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ of 0.2 mM and 1-mL trisodium citrate of 0.4 mM were dissolved in 98 mL of water. An aqueous solution of 6-mL NaBH_4 of 8 mM was slowly added at a speed of 1 mL/min under vigorous stirring at room temperature. The resultant solution was kept under vigorous stirring for 30 min at room temperature. Ag NPs were synthesized according to the same condition mentioned above, except for the use of AgNO_3 .

Characterization. Scanning electron microscopic (SEM) images of the SALDI substrate surface before and after mass measurement were taken with a JEOL FE-SEM: JSM-6701F.

SALDI-TOF-MS measurement. SALDI-TOF-MS measurements were performed with a Shimadzu/Kratos AXIMA-CFR time-of-flight mass spectrometer equipped with a pulsed nitrogen laser (337 nm) in the positive reflectron mode or the linear mode. The analyte ions were accelerated at 20 kV under delayed extraction conditions.

A GaP-NP-deposited stainless sample plate was fixed to a stainless steel sample plate holder by using double-sided conductive carbon tape. The 1- μ L PEG solution (1 mg/mL) with a cationization agent of NaI was spotted onto the substrate and dried under reduced pressure. One hundred laser shots were used to acquire the mass spectra.

Survival yield (SY) measurements of thermometer ion.² Benzyl chloride was mixed with 3 mL of anhydrous pyridine (pyridine/benzyl chloride molar ratio: 20:1). This mixture was heated in a water bath for 5 h at 60°C. Excess pyridine was removed by vacuum evaporation. The compounds with BP-Cl (1-4-chlorobenzylpyridinium) were confirmed by SALDI-MS analysis and used without further purification. A stock solution of BP-Cl (0.166 mM) was prepared in methanol.

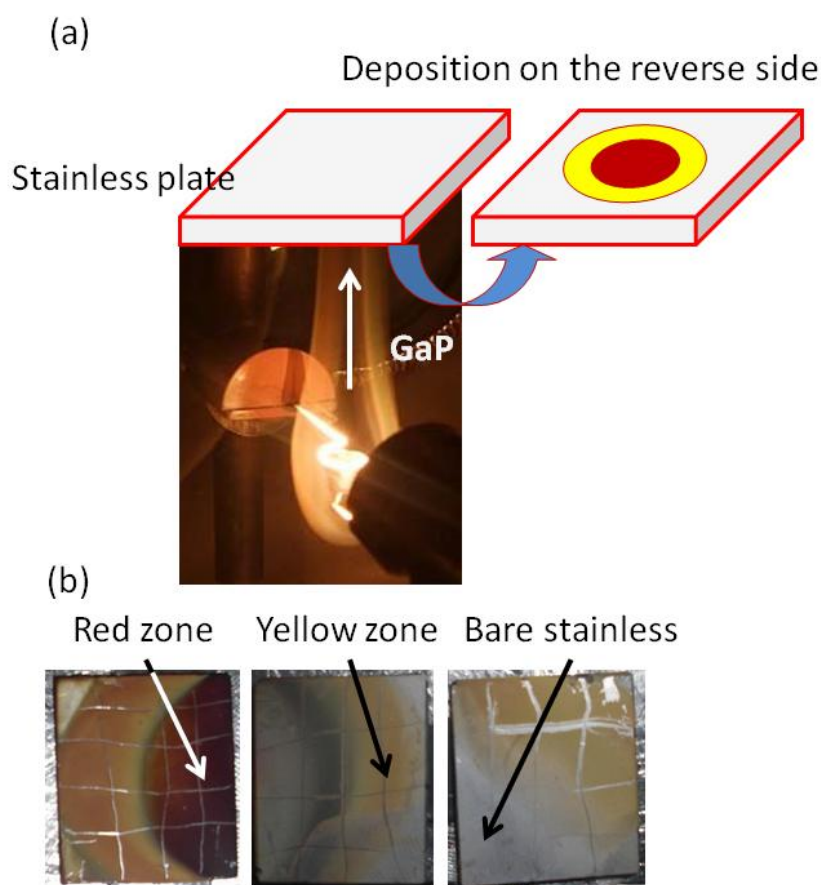


Figure S1. a) A schematic illustration of the gas-evaporation method to produce GaP NPs. GaP NPs were directly deposited on the stainless plate. b) Photograph of typically obtained GaP NPs substrate on a stainless plate. The red NP zone, yellow NP zone, and bare stainless zone are shown by arrows.

Calculated absorption spectra of GaP NPs with various diameters.

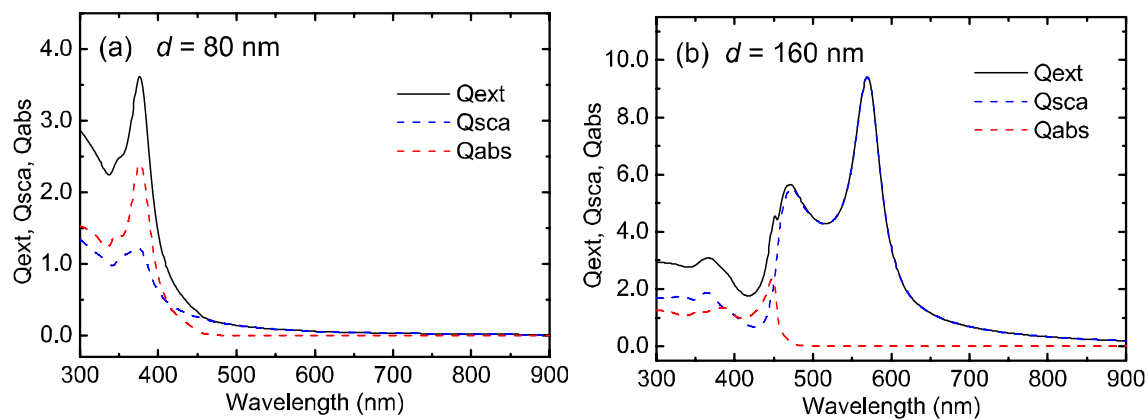


Figure S2. Results of Mie calculations,³ calculated optical spectra of GaP nanoparticles with the diameter of (a) 80 nm and (b) 160 nm. Qabs: absorption cross section, Qsca: scattering cross section, and Qext: extinction cross section. $Q_{\text{ext}} = Q_{\text{abs}} + Q_{\text{sca}}$.

References

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2. H.-M. Kim, S. Hayashi, K. Yamamoto, *Jpn. J. Appl. Phys.*, 1995, **34** (Suppl. 34-01), 40.
3. G. Mie, *Ann. Phys.*, 1908, **25**, 377.