

## 論文内容の要旨

論文題目 **Matrix Sputtering Synthesis of Inorganic Nanoparticles  
for Development of Optically Functional Materials**

(マトリックススパッタリング法による無機ナノ粒子の合成と  
光機能性材料への展開)

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### Introduction

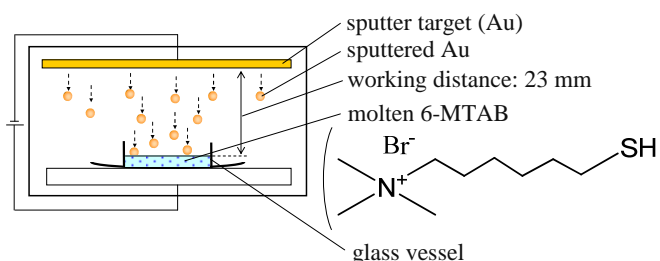
Inorganic nanoparticles (NPs) such as metal NPs, metal oxide NPs, and quantum dots are attracting considerable interest as optical materials and for use in electrical devices and biosensors because of their unique optical and electronic properties. Various *in-situ* preparation methods of metal NPs to control and uniform their size have been demonstrated. However, the methods require multistep processes including purification and fractionation using ligand exchange, centrifugal filtration and/or polymer gel electrophoresis. In addition, it is an onerous task to remove by-products completely. Recently, simple processes for preparing metal NPs that do not produce by-products have been demonstrated. These processes are based on vacuum metal evaporation using a limited number of low-vapor-pressure liquids at room temperature. For example, metal NPs were produced by vapor deposition in silicone oils and by sputtering deposition in ionic liquids. However, nanometer-order size control and high dispersibility of metal NPs in various matrices have not been achieved using the vacuum methods.

In this study, I developed a new vacuum method of inorganic NP preparation, which I term molten matrix sputtering (MMS). Using this method, water-soluble luminescent AuNPs exhibiting a large Stokes shift were synthesized. Furthermore, AuNPs/thiourethane and

AuNPs/urethane hybrid optical resins were prepared using the matrix sputtering method. The AuNPs thus prepared were characterized using various methods and their optical properties were analyzed.

### MMS synthesis of water-soluble luminescent AuNPs with a large Stokes shift

The MMS method is illustrated in Figure 1. Temperature control of the disperse medium was introduced during sputtering deposition of MMS. Specifically, disperse media that are in solid state at room temperature were heated above their melting points to keep them in liquid state

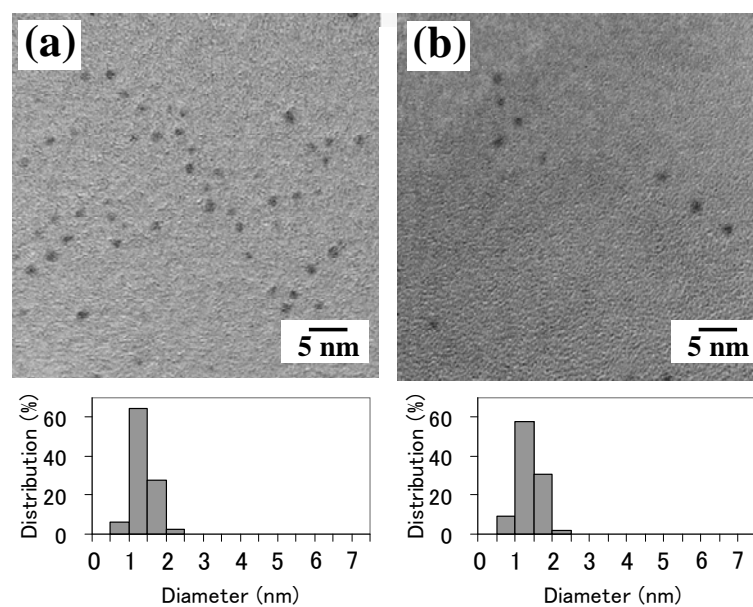


**Figure 1.** Schematic diagram of the MMS system.

during sputtering. The MMS method can apply to many kinds of disperse media in solid state at room temperature.

A molten (6-mercaptohexyl)trimethylammonium bromide (6-MTAB) (m.p. 83 °C) was heated at 110 °C for 3 min in a vessel, and then sputtering deposition into molten 6-MTAB was carried out. AuNPs could be prepared with sputtering times of 5–20 min. The samples obtained were then dispersed into 3 mL of water (these samples are referred to as s-AuNPs).

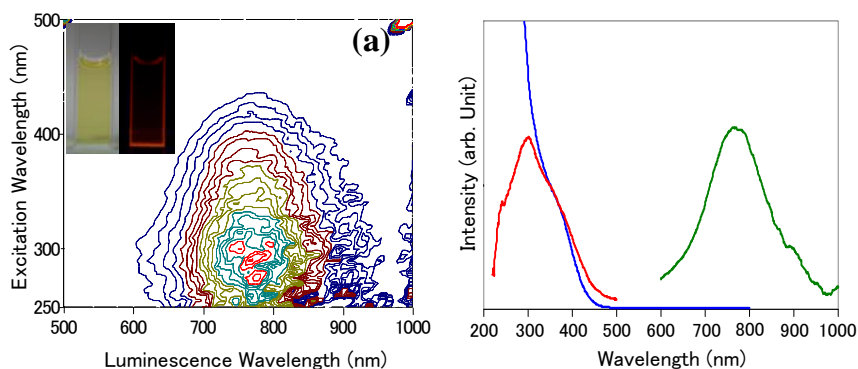
Figure 2 shows transmission electron microscope (TEM) images and size-distribution histograms of s-AuNPs produced with sputtering times of 5 min and 20 min. The average sizes of the s-AuNPs for both sputtering times are 1.3 nm with a very narrow distribution ( $\pm 0.3$  nm). These results suggest that s-AuNPs do not grow in 6-MTAB; rather, additional nucleation occurs so that the number of s-AuNPs increases with increasing



**Figure 2.** TEM images and size-distribution histograms of s-AuNPs produced with sputtering times of (a) 5 min and (b) 20 min.

sputtering time. Careful observation of molten 6-MTAB during sputtering revealed that the local concentration of s-AuNPs close to the surface became very high. The strong adsorption of the thiol group of 6-MTAB to the sputtered species (i.e., Au atoms and/or clusters) could suppress the growth and aggregation of s-AuNPs.

Figure 3a shows 3D photoluminescence (PL) spectra of s-AuNPs produced with a sputtering time of 20 min. s-AuNPs that formed with different sputtering times have similar spectral profiles and PL peak wavelengths. This result is in good

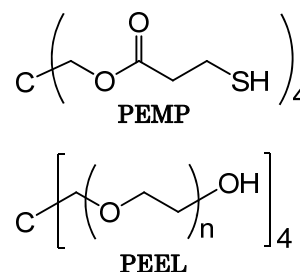


**Figure 3.** (a) Three-dimensional PL spectra of s-AuNPs produced with sputtering time of 20 min. Inset shows photographs of s-AuNPs for 20 min under (left) daylight and (right) 365-nm UV radiation. (b) Optical absorption (blue), PL (green), and PLE (red) spectra of s-Au NPs for 20 min.

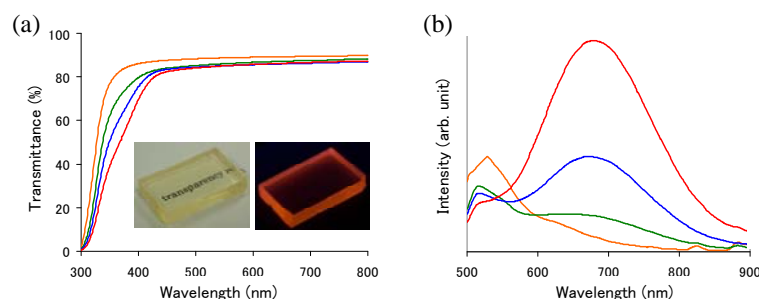
agreement with the similar size distributions of s-AuNPs produced using different sputtering times. Figure 3b shows a UV-Vis absorption spectrum of s-AuNPs in which the absorbance increases continuously as the wavelength decreases from 350 nm; in contrast, its PL excitation (PLE) spectrum has a peak at around 300 nm. It is a fascinating result that excitation with UV radiation at 300 nm gives a low-energy emission at 770 nm that extends to the near-IR region. The Stokes shifts of the s-AuNPs exhibit large values (2.4–2.7 eV).

### Click Preparation of AuNPs-Dispersed Optical Resins Using the Matrix Sputtering Method

The low vapor pressure of pentaerythritol tetrakis(3-mercaptopropionate) (PEMP) enables matrix sputtering. Sputtering deposition of Au into PEMP was carried out with sputtering times of 5–15 min at room temperature (these samples are referred to as AuNPs/PEMP). The absorption spectra of AuNPs/PEMP are similar to those of s-AuNPs. AuNPs/PEMP also show luminescence at *ca.* 690 nm.



The thiourethane resins embedded with AuNPs (AuNPs/thiourethane) were prepared from curing the mixture solutions of AuNPs/PEMP and *m*-xylylene diisocyanate (*m*-XDI). The transmittance spectra of AuNPs/thiourethane hybrid resins exhibit good transparency at wavelength longer than 450

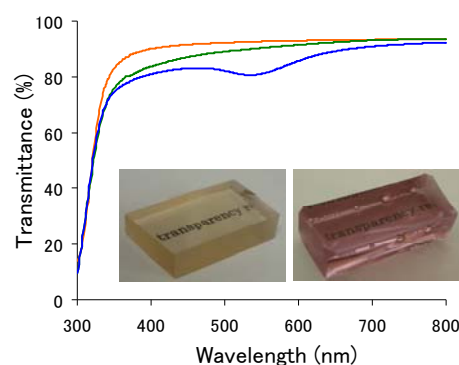


**Figure 4.** Transmittance (a) and PL (b) spectra of AuNPs/thiourethane resin (thickness: 1.3 mm) with sputtering time of 0, 5, 10, and 15 min for orange, green, blue, and red curves, respectively. Inset shows photographs of AuNPs thiourethane resin (c) with sputtering time of 15 min under daylight (left) and 365-nm UV radiation (right).

nm, and no surface plasmon absorption peaks around 530 nm are observed (Figure 4a). No

growth and aggregation of AuNPs was observed during polymerization *ca.* 130 °C. A high angle annular dark field scanning transmission electron microscope (HAADF-STEM) image of AuNPs/thiourethane hybrid resin agrees with the UV-Vis spectrum. The luminescence of AuNPs/thiourethane resins is kept at around 690 nm as well as AuNPs/PEMP (Figure 4b). This indicates that the thiol group of PEMP which can strongly bind to sputtered Au surface is responsible to keep the same optical properties of AuNPs/PEMP in the resins.

AuNPs/pentaerythritol ethoxylate (PEEL) was synthesized by the matrix sputtering, and then Au NPs/urethane hybrid resin was obtained immediately by its polymerization with *m*-XDI (fresh-AuNPs/urethane resin). The resin shows good transparency with brownish tint. Its UV-Vis transmittance spectrum shows little surface plasmon band (Figure 5), which is consistent with the size of fresh-AuNPs/PEEL from the TEM image ( $2.1 \pm 0.7$  nm). The difference of the sizes of AuNPs/PEMP and fresh-AuNPs/PEEL can be attributed to the difference of the coordination affinities of thiol and hydroxy groups to gold surface. The weak interaction between the hydroxy group and gold surface allowed coalescence of AuNPs in PEEL with the passage of time. The size of AuNPs/PEEL after 65 days (matured-AuNPs/PEEL) from the TEM image is  $4.5 \pm 3.4$  nm. The UV-Vis spectra of matured-AuNPs/PEEL and its hybrid resin exhibit surface plasmon absorption peaks at around 520 nm (Figure 5a). In addition, once the resin was formed, no further UV-Vis spectral change was detected, indicating no more coalescence and aggregation of AuNPs in the solid matrix.



**Figure 5.** UV-vis transmittance spectra of urethane (orange), fresh-AuNPs/urethane (green), and matured-AuNPs/urethane (blue) for 3 min (thickness: 1.3 mm) (inset: photographs of fresh (left) and matured (right) AuNPs/urethane)

## Conclusion

I developed a simple method, MMS, for synthesizing water-soluble luminescent AuNPs. The obtained AuNPs have a uniform size, a narrow size distribution and a luminescence with a large Stokes shift for all the sputtering times used in this study. In addition, AuNPs/thiourethane and AuNPs/urethane hybrid resins with good transparency were prepared by the matrix sputtering method. AuNPs/thiourethane resins do not show surface plasmon absorption but red luminescence. In contrast, AuNPs/urethane resins exhibit surface plasmon absorption, of which intensity can be tuned by change the size of AuNPs/PEEL with time before polymerization. This study expands the possibilities to obtain various functionalized NPs and their hybrid materials.