



## Understanding the primary and secondary aggregation states of sputtered silver nanoparticles in thiolate matrix and their immobilization in resin



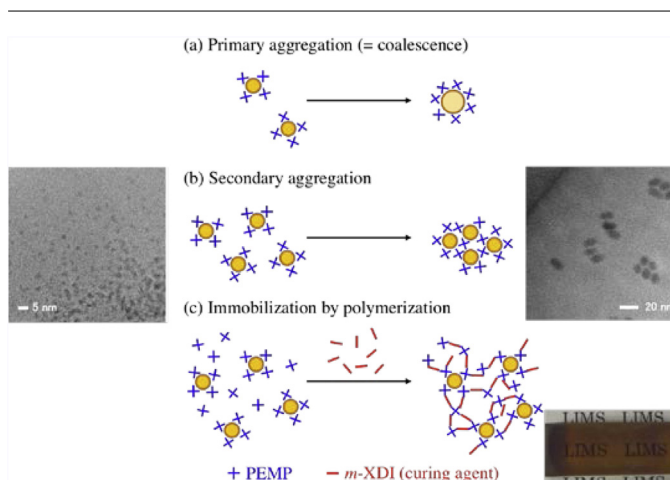
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### HIGHLIGHTS

- Thiolate-protected fluorescent silver nanoparticles were prepared by sputtering deposition onto liquid matrix.
- Main aggregation process was a secondary aggregation with a small contribution from primary aggregation.
- Thiourethane resin was successfully prepared by the polymerization of thiolate matrix.

### GRAPHICAL ABSTRACT



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### ABSTRACT

We report detailed aggregation mechanisms of sputtered silver nanoparticles in a viscous thiolate liquid matrix. Fluorescent silver nanoparticles were prepared by the sputtering deposition over pentaerythritol tetrakis(3-mercaptopropionate) (PEMP). The dependences of extinction, fluorescence and particle size on time were discussed in terms of two possible aggregation mechanisms. The main aggregation process was secondary aggregation, with primary aggregation (core coalescence) making a small contribution. The four thiol groups in the PEMP structure are the driving force determining the predominance of secondary aggregation. Finally, we successfully prepared a thiourethane resin by the polymerization of a thiolate matrix, and complete immobilization of nanoparticles in the resin resulted in no observable degradation of the photophysical properties. The demonstrations presented here will be beneficial in understanding the detailed aggregation mechanism and optical properties of nanoparticles.

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## 1. Introduction

Metal nanoparticles (NPs) and nanoclusters (NCs) have been extensively studied due to their remarkable size-dependent char-

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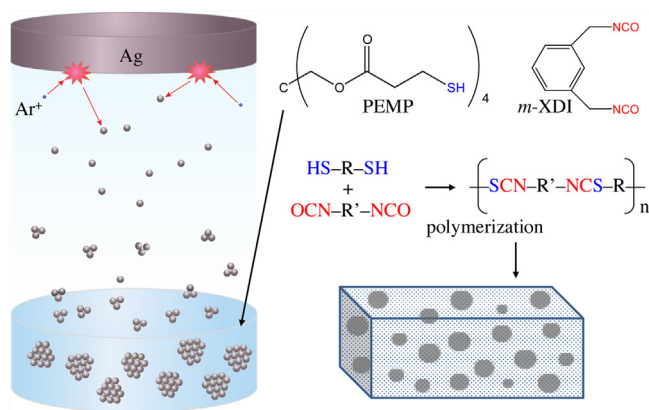
acteristics that make them promising novel materials for catalysis, electronics, and photonics applications. [1–4] Typical preparation of metal NPs or NCs involves chemical reduction of metal ions in solution with a reducing agent such as  $\text{NaBH}_4$ , hydrazine, alcohol, or citric acid. [2] This method has been extensively developed, but is susceptible of contamination from by-products and impurities as excess amounts of reducing agent molecules are used for these reductions. Because complicated, costly and energy-consuming procedures are involved in the purification and separation of products, NP preparations that avoid such contamination are highly valued. Recently-developed methods involving sputtering [5] over liquid matrices to obtain uniform metal NPs has attracted considerable attention for the preparation of colloidal metal NPs. [6,7] Sputtering methods exploit the extremely low vapor pressure of liquid matrices that can be used under high vacuum inside a sputter chamber. In general, ionized argon ( $\text{Ar}^+$ , generated by applying high voltage) attacks the target metal and ejects atoms or atom clusters into the sputter chamber. These small species then coalesce into NPs in the gas phase or at the surface of the liquid matrix (or aggregate further inside the liquid). For this purpose, ionic liquids (which have no vapor pressure) have been used in the early stages of such processes, [7] and other non-volatile liquids such as liquid monomers [8–13] and polymers [14,15] have begun to see use. This sputtering method has promise as a novel environmentally friendly method for the preparation of metal NPs without unnecessary reductants, whereas common chemical reduction methods generate harmful by-products and NPs with limited purity due to their use of reductants. These investigations have enabled the synthesis of metal NPs (mostly Au NPs) with diameters of single to several tens nm. Very recently, we reported a novel methodology to systematically control the diameter of NPs or NCs to within a single nm by the introduction of thiolate ligands through the use of non-volatile mercaptans, as-is or dissolved in a liquid matrix [10,15,16], or using volatile mercaptans that release gas molecules in the chamber [11]. We refer to such systems as *matrix sputtering methods*.

The aggregation/growth mechanism in sputtering processes is different from common chemical reduction methods. Aggregation is one of the most important phenomena in physical chemistry, and efforts have been made to understand the aggregation/growth mechanism of atoms, clusters or nanoparticles in homogeneous liquid systems (especially in aqueous solutions). [17] Growth mechanisms of metal NPs produced via sputtering (without thiolate ligands) have been previously investigated, showing that metal NPs coalesce mainly in the gas phase and on the surface of the liquid matrix [14,18], and then further coalesce and grow within the liquid. However, the aggregation mechanism is still unknown when thiolate ligands are present in the liquid matrix. Our matrix sputtering method, a promising novel technique for precise controlling the size and photophysical properties of high-purity metal NPs, involves such thiolate ligands. Here, we report detailed mechanisms and aggregation behavior of sputtered silver nanoparticles in a thiolate liquid matrix.

## 2. Experimental

### 2.1. Materials

Pentaerythritol tetrakis(3-mercaptopropionate) (PEMP, Aldrich) was used as the liquid matrix in the matrix sputtering synthesis. Water was purified using an Organo/ELGA Purelabo system (>18 M $\Omega$  cm). Ag target (99.99%) of 50 mm $\phi$  size was supplied by Tanaka Precious Metals (Tokyo).



**Fig. 1.** Schematic illustration of the matrix sputtering method, chemical structures of PEMP and *m*-XDI, and polymerization scheme.

### 2.2. Matrix sputtering synthesis of Ag NPs in PEMP and polymerization

A custom-designed magnetron sputter was used for matrix sputtering to prepare the Ag NPs. In order to remove unwanted gas, water, and other volatile molecules from PEMP, solutions were baked at 80 °C for 1 h while stirring under reduced pressure with a rotary vacuum pump before use. No bubbles were observed in the vacuum chamber during sputtering, which may affect the sputter rate and subsequent structures of the obtained NPs. After being allowed to cool to room temperature, 13 g of PEMP was added into a 60 mm $\phi$  glass petri dish. Ag sputter deposition was carried out at a current of 30 mA under 10 Pa of Ar in the sputter coater. This experimental procedure is illustrated in Fig. 1. During the sputter deposition, the PEMP surface was positioned 40 mm from the Ag target, and the sputtering deposition was carried out for 20 min.

Polymerization of this obtained PEMP dispersion was used to form thiourethane. We used *m*-xylylene diisocyanate (*m*-XDI) as a curing agent, and dibutyl tin dichloride (DBC) as a catalyst for polymerization. In brief, the obtained PEMP dispersion containing Ag NPs was mixed with *m*-XDI at a molar ratio of  $[\text{PEMP}]/[\text{m-XDI}] = 1/2$ . DBC (100 ppm to PEMP) was added, and the mixture was degassed for 20 min using a rotary pump. The solution was put in a polypropylene container, and kept for 15 h at 25 or 50 °C. The obtained resin was cut into 10 mm  $\times$  10 mm pieces using a Buehler IsoMet 4000, and polished with a Marumoto Struers S5629. 2 mm  $\times$  10 mm samples were prepared for optical measurements.

### 2.3. Characterization

Immediately after the sputtering deposition, UV-vis extinction spectra were measured using a spectrophotometer (Jasco, V-630, 250–800 nm) with a 1 mm quartz cell. Fluorescence spectra of the obtained Ag NP dispersions were measured using a fluorescence spectrophotometer (Jasco, FP-6600) with a 10 mm quartz cell. NP shapes and size were studied using transmission electron microscopy (TEM, Hitachi H-9500) at an acceleration voltage of 300 kV. TEM samples were prepared by drop-casting from a NP dispersion of PEMP diluted with acetonitrile onto collodion-coated copper grids and then dried overnight. Size distributions were calculated from measurements of 200 particles in a fixed area of a TEM image.

## 3. Results and discussion

After the sputtering deposition of Ag into PEMP, we obtained a light yellow dispersion as shown in the inset in Fig. 2. [13] First,

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