Formation mechanism of metal nanoparticles studied by XAFS spectroscopy and effective synthesis of small metal nanoparticles

Tsunehiro Tanaka [a,*], Junya Ohyama [b], Kentaro Teramura [a], Yutaka Hitomi [c]

[a] Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan
[b] Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan
[c] Department of Molecular Chemistry and Biochemistry, Faculty of Science and Engineering, Doshisha University, Kyotanabe 610-0321, Japan

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ABSTRACT

Recently, we studied and developed two useful synthesis methods of metal nanoparticles. The first system is wet chemical synthesis of gold nanoparticles using fast reduction. The second one is photodeposition of metal nanoparticles on TiO_2. The X-ray absorption fine structure (XAFS) study revealed their unique formation mechanisms different from the conventional mechanisms. Furthermore, we designed and synthesized new multidentate protecting ligand having sulfur functional groups to synthesize small gold nanoparticles efficiently.

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1. Introduction

1.1. Wet chemical synthesis of metal nanoparticles

There has been considerable interest in the unique properties of metal nanoparticles, such as catalytic activity, optical, and magnetic properties [1–4]. Their unique properties depend on their size, therefore, the size control synthesis of metal nanoparticles is demanded. Among the synthesis methods, wet chemical synthesis is one of the most useful methods for metal nanoparticles having well-defined size.

Metal nanoparticles can be easily synthesized by reduction of metal salts in solution (wet chemical synthesis). As reducing agents, for example, citric acid, ascorbic acid, borohydride, diborane, hydrogen, and alcohol are utilized. When citric acid or ascorbic acid are used, the resulting metal nanoparticles are stabilized by electrostatic repulsion due to the adsorbed citric or ascorbic acid ions on the surface of metal [5]. On the other hand, when the reducing agents which do not prevent aggregation of particles are used, protecting ligands are applied to hinder particle aggregation sterically. Polymers such as polyvinylpyrroldone, polyvinylalcohol, and polyvinylether are often utilized as protecting ligands, particularly in alcohol reduction process which is one of the most widely used methods in the wet chemical synthesis [6–9]. In this process, metal ions are reduced by heated alcohols in the presence of protecting ligands. Polyols (e.g. ethylene glycol) are also applied in the same manner as alcohol [10]. When surfactants (e.g. alkyl ammonium compounds) are utilized as protecting ligands, they form micelle or inverse micelle in a solution, which provide not only reaction field for formation of metal nanoparticles but also protecting layer for metal nanoparticles [11]. Schiffrin and Brust developed the inverse micelle method by using an alkanethiol as a protecting ligand which strongly binds to a surface of metal nanoparticles and self-assembles into monolayer on metal surface to prevent the coalescence of metal nanoparticles (Schiffrin–Brust method) [12]. It is also worth noting that they used sodium borohydride as a reducing agent. As a result, monodisperse small gold nanoparticles covered with thiolates were synthesized. There are other wet chemical synthesis methods, for example, heat and photolytic degradation of organic metallic compounds [13,14], reduction of ligands of metallo-organic complexes [15], and so on. In addition, various protecting agents are applied to each synthesis method of metal nanoparticles. Owing to these efforts, very recently, a number of atomically monodisperse nanoparticles have been available [16,17]. For synthesis of a series of precisely size-controlled metal particles, the studies on preparation methods are now underway.

1.2. Formation mechanism and size control synthesis of metal nanoparticles

The formation mechanism of metal nanoparticles has been studied to elucidate the effect of the preparation conditions on the size

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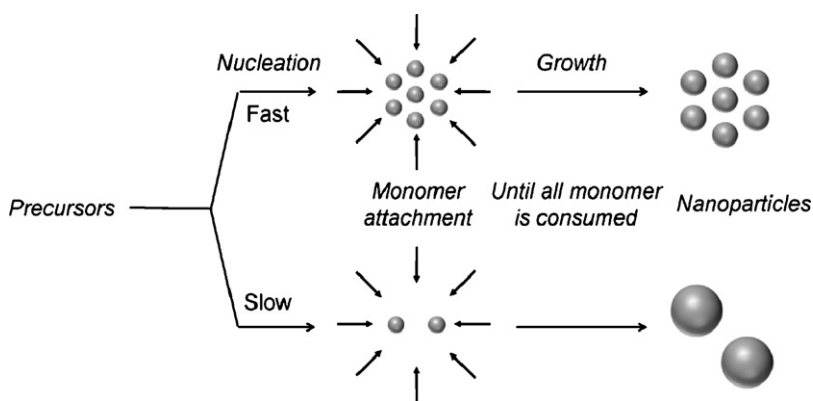
Scheme 1. Brief formation mechanism of metal nanoparticles.

of metal nanoparticles. In 1950, LaMer et al. studied the formation mechanism of sulfur sol, and proposed that the sol is formed by fast nucleation from supersaturated solution of monomer and growth by attachment of monomers to the resulting nuclei [18]. The LaMer mechanism has been applied to formation mechanism of the metal nanoparticles by wet chemical synthesis [19]. On the other hand, Finke et al. have studied the formation kinetics and mechanism of Ir nanoparticles from the precursors by H_2 reduction [19]. They proposed a different mechanism from LaMer one; nuclei are formed slowly but constantly and the nanoparticles grow mainly by autocatalytic reduction of metal precursors on the particle surface. Although both of the mechanisms are different in kinetics of nucleation and growth, particles mainly grow by the addition of monomer (precursor) on the particle surface in the both mechanisms. In contrast, Baiker et al. proposed that combination/coalescence of particles is the dominant growth mechanism for the gold particles prepared by using strongly reducing and protecting agent [20]. Furthermore, other mechanisms such as thermodynamic factors and Ostwald ripening have been also proposed [21–23]. Thus, particle formation mechanism is still unclear. This is due to the difficulties of observation of the formation process, more specifically the nucleation process. Since the formation mechanisms can be utilized as a guide line for design of morphology of metal nanoparticles, it is necessary to investigate particle formation mechanism more closely.

Here, we would like to consider how the size of metal nanoparticles can be controlled on the basis of a simple particle formation mechanism shown in Scheme 1 [24]. When particles grow by addition of metal atoms on a surface of particle without Ostwald ripening and aggregation between particles, the size should vary with the number of nuclei, in other words, relative rate of nucleation to growth. The high relative rate increases the number of particles and leads the small particles. On the contrary, the low relative rate results in the low concentration of particles and thus formation of large metal particles. Therefore, understanding and manipulation of the relative rate of nucleation to growth is critical for the size control of metal nanoparticles. The relative rate can be controlled by reduction rate of metal precursors, the initial molar ratio of a passivant to a metal precursor, and the affinity of passivants for metal species and the structure of passivants.

The reduction rate of metal precursors has an effect on the particle size. Teranishi et al. reported the dependence of the size of gold nanoparticles protected by PVP on the kinds of reducing agents, alcohols and potassium borohydride [25]. The reduction with alcohols provided polydispersed gold nanoparticles having 2–14 nm diameter. But, potassium borohydride, which reduce gold ions faster than alcohols, afforded monodispersed particles with ca. 2 nm diameter. They also investigated the variation of the particle size with the amount of potassium borohydride, and showed that the particle size increases as a decrease in the concentration of potassium borohydrides. This result indicates that the fast reduction of gold ions causes the formation of large number of nuclei and provides small particles. In the case of the preparation of platinum and palladium nanoparticles using alcohol reduction method, the easily oxidized alcohol gave the small metal nanoparticles [26,27]. Therefore, the rapid reduction of metal ions would cause fast nucleation, resulting in formation of many nuclei and thus small metal nanoparticles.

Small metal nanoparticles are generally formed at high molar ratio of protecting agents to precursors. The large amount of protecting agents will suppress the growth of metal nanoparticles, which makes the relative rate of nucleation to growth fast and provides small metal nanoparticles [21,26,27,25,28]. However, there is an exception; Weller et al. reported that the size of $CoPt_3$ increased with an increase in the ratio of 1-adamantanecarboxylic acid to metal precursors [24]. They proposed that the protecting agents strongly stabilize the metal precursors, and the large amount of the protecting agents decreases the nucleation rate. As for the preparation of gold nanoparticles covered with alkanethiol, the particle size decreases from 5 to 2 nm with an increase in the ratio of alkanethiol to gold ion [21]. This variation of particle size can be explained by the kinetic control mechanism. But, Leff et al. proposed that the size of gold nanoparticles with alkanethiol is determined by the thermodynamic factors for surface stabilization rather than the relative rate of nucleation to particle growth [21]. Although size control by a ratio of protecting agents to metal precursors is easy and useful, it is necessary to understand the role of protecting agents in a particle formation process in more detail.

As described above, the affinity of protecting agents for metal precursors influence the size control behavior. The interaction of protecting agents to the surface of metal can also affect the size of metal nanoparticles. For example, the protecting ligands with thiol and cyano groups, which are known to have a high affinity for gold, give smaller and narrower size-distributed gold nanoparticles than the protecting ligands with carbonyl and alcohol groups having a low affinity for gold [25]. On the other hand, the use of multidentate ligands has been employed by several groups in effort to stabilize metal nanoparticles. For example, multidentate ligands inhibit the aggregation of metal nanoparticles in organic solvents [29,30]. Multidentate ligands also increase the monodispersity of the resultant metal nanoparticles with an increase in the number of coordinate position of ligands [30]. Recently, such ligands have been attracted the attention for the synthesis of size-specific metal