

Wet Preparation of Metal Nanoparticles and Their Two-Dimensional Arrangement

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This review article describes about wet preparation of metal nanoparticles, especially, noble metal nanoparticles and preparation of their ordered two-dimensional arrangement. Wet preparation is relatively easy and useful for high volume preparation. After the breakthrough of Brust's thiol stabilizing system, small and monodispersed nanoparticles have been demonstrated frequently. By using such thiol-stabilizing nanoparticles, their ordered two-dimensional arrangement has been prepared with tuned stabilizing molecules. In this manuscript, such techniques of 2-D arrangement preparation will be also discussed in detail.

Key words: nanoparticle, gold, silver, arrangement, self-assembly

1. Introduction

Nanoparticle research has been focused intensively as a new class of materials with special chemical and physical properties different from conventional bulk materials or from atoms.¹ Size-controlled metal nanoparticles can be excellent candidates for bio-sensing materials,² materials for molecular electronics,³ catalysts,⁴ as well as magnetic materials.⁵ Since the pioneering work by Brust *et al.*,⁶ metal nanoparticles stabilized by organic monolayers (e. g., thiolates) have gained widespread attention as promising materials.^{7,8}

Preparation method of metal nanoparticles can be largely divided into two categories, that is, the physical process and the chemical process.⁹ The physical process includes the subdivision of bulk metals into metal nanoparticles and the atomize process. The chemical process includes the wet process, that is, chemical reduction of metal ions and thermal decomposition of metal complexes, and the dry process, that is, evaporation of metal atoms and their controlled aggregation. For economical mass production of uniformly sized metal nanoparticles, the chemical process, especially, chemical reduction of the corresponding metal ions in the presence of the stabilizing reagents, are much more favorable than dry processes. Recently, therefore, wet preparation of metal nanoparticles becomes more and more important in modern nanotechnology.

Various methods have been proposed in order to construct ordered 2-D arrangement of metal nanoparticles. Langmuir-Brodgett process may be one of the best ways to construct ordered 2-D arrangement of nanoparticles in large area.¹⁰ Electrostatic interaction between nanoparticles and substrates can also be used for 2-D arrangement.¹¹ In that case, highly charged substrate surface is indispensable to obtained closely packed structure.¹² By using such size-controlled metal nanoparticles, two-dimensional arrays can be obtained readily by simple casting homogeneous nanoparticle dispersions onto flat surfaces. The smaller size

distribution of metal nanoparticles gives the more ordered arrays.

In this review article, wet preparation of metal nanoparticles and formation of their ordered 2-D arrangement will be surveyed.

2. Wet preparation of metal nanoparticles

Various preparative processes have been already introduced. Reduction of noble metal ions by citrates gives very stable gold nanoparticles showing wine-red color as well as very stable nanoparticles of platinum group metals and their alloys. Alcohols can be good reducing reagents and disperse media for noble metals and poly-ols are very good for preparation of transition metal nanoparticles.¹⁴ Photo-reduction processes are quite useful for micelle-stabilized noble metal nanoparticles.¹⁵

Sodium borohydride (NaBH_4) is a strong reducing reagent to produce various metal nanoparticles. Cu nanoparticles stabilized by PVP have been already proposed.¹⁶ In 1994, Brust combined NaBH_4 -reduction and formation of self-assemble monolayer of thiols on metal surfaces to produce highly stable thiol-stabilized metal nanoparticles, especially gold ones (Fig. 1).⁶ After then, various functionalized metal nanoparticles have been produced by using this method. This method is quite simple and gives stable nanoparticle dispersions

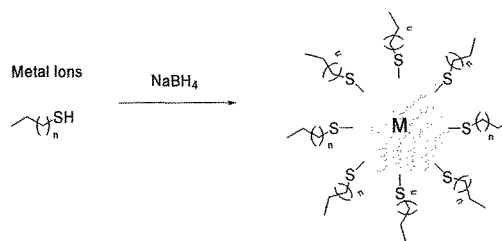


Fig. 1 Preparation scheme of metal nanoparticles by NaBH_4 -reduction of metal ions in the presence of thiol compounds.

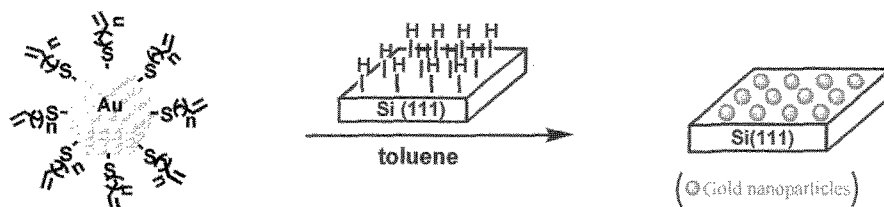


Fig. 3 Schematic illustration of covalently immobilization of gold nanoparticles onto hydrogen-terminated silicon surface by hydrosilylation.²²

with a small size distribution. The surface of these metal nanoparticles is covered by thiol self-assembled monolayer. Of course, therefore, the stabilizing layer has a unique thickness. This process may be very useful for ordered 2-D arrangement formation.

3. Formation of ordered 2-D arrangements of thiol-stabilized metal nanoparticles by electrostatic interaction

The other merits of thiol-stabilized metal nanoparticles for preparation of their ordered arrangements are listed below: (1) nanoparticles can be readily purified by e.g. re-precipitation, (2) the obtained nanoparticles can be often treated as a powder form and re-dispersed readily into an appropriate disperse medium, (3) various functions can be added to the particle, and (4) stabilizer molecules can control the disperse media. Various kinds of thiol-stabilized metal nanoparticles have been already synthesized and we first proposed to use quaternary ammonium-stabilized metal nanoparticles which can be adsorbed onto anionic surface.^{16,17} Other groups have also introduced such positively charged nanoparticles.¹⁸⁻²¹

Quaternary ammonium halides are positively charged at any pH conditions. Therefore, the particles which are surrounded by quaternary ammonium-thiol molecules

are highly positively charged and well dispersed into water at any pH.

Thiocholine bromide ($\text{HS}-(\text{CH}_2)_2-\text{N}(\text{CH}_3)_3^+ \text{Br}^-$, TCB) is one of the smallest quaternary ammonium-thiol ligands.^{17,21} TCB-stabilized gold nanoparticles have been adsorbed onto the bundles of DNA molecules or other anionic biomolecules. Some reports described that electrostatic interaction cannot assemble nanoparticles densely because the electrostatic repulsion between the particles prevents the closed packed structure formation on the substrates. However, even though TCB-stabilized nanoparticles were highly positively charged, they could assemble densely on λ -DNA bundles. By mixing the aqueous solutions of DNA and TCB-stabilized nanoparticles, the gold nanoparticles adsorbed densely as shown in Fig. 2.¹⁷ Most of the gold nanoparticles assembled with the width of ca. 25 nm. As TCB contains short ethylene spacer units between the thiol and ammonium groups, its molecular length is only 0.8 nm. The hydrophobic interaction between TCB molecules is very weak and this situation is reflected in the observed larger occupied area of one TCB molecule on the particles surface (22.9 \AA^2). Therefore, when these gold nanoparticles accumulated on DNA bundles, gold nanoparticles fused automatically.

4. Immobilization of metal nanoparticles onto silicon surface by covalent Si-C bonds

Arrangement of nanoparticles is of great importance, but immobilization of nanoparticles onto solid substrates is another important issue. Strong ionic interactions between nanoparticles and surfaces are highly useful for such ordered immobilization. For example, on highly positively charged surface, negatively charged nanoparticles can be adsorbed densely to form 2-D nanoparticle monolayers.¹²

We would like to propose covalent immobilization of metal nanoparticles onto flat silicon substrates by using hydrosilylation reaction. Hydrogen-terminated silicon surfaces could be obtained by HF and NH_4F treatment of commercially available silicon wafers. Several approaches have been taken to deposit organic moieties covalently bonded on Si. Terminally double bonded alkythiol-stabilized gold nanoparticles could be attached onto hydrogen-terminated Si surface by thermal hydrosilylation (Fig. 3).^{22,23}

HR-SEM images of nanoparticle attached silicon surfaces are collected in Fig. 4. Allylthiol-stabilized gold nanoparticles were fused on silicon surface at even as low as $50 \text{ }^\circ\text{C}$,^{22,23} at such temperature, they did not form precipitates in liquid form. Another study revealed that gold nanoparticles can be readily fused on substrates

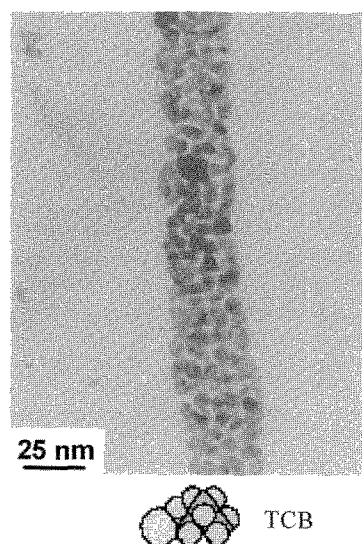


Fig. 2 TEM of TCB-stabilized gold nanoparticles and λ -DNA mixture. The particles are assembled densely and fuse automatically on DNA molecules.¹⁷

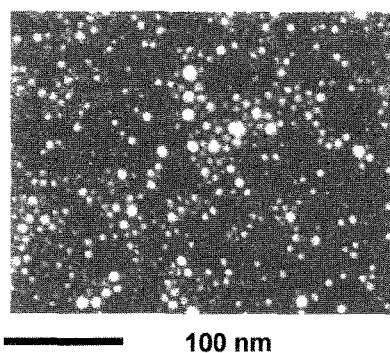


Fig. 4 HR-SEM image of silicon surface after immobilization of 5-hexene-1-thiol-stabilized gold nanoparticles.²²

when the particles are very closely packed with an inter-particle distances ca. 1.6 nm. 5-hexene-1-thiol- or 11-undecene-1-thiol-stabilized gold nanoparticles could be attached independently onto silicon surface. This process can be suitable to observe electronic properties of nanoparticles.

5. Conclusion

In this manuscript, wet preparation processes of metal nanoparticles and their assembly formation have been surveyed. Monolayer-stabilized metal nanoparticles with unique size distributions are very suitable for ordered assembly formation. Purification of such nanoparticles may be an important key to produce wide ordered area. Such self-assembling process should be investigated more profoundly.

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