Solution-Phase Synthesis of Branched Metallic Nanoparticles for Plasmonic Applications

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Abstract: This review discusses wet processes to synthesize metallic nanoparticles with many surface projections. Such projections can be formed by the aggregation of seed nanoparticles or by anisotropic crystal growth from specific facets on a base nanoparticle. The aggregation process can be controlled by protecting agents, which also play a key role in determining the morphology of the projections and the size of the nanoparticles. The reducing agents used for this purpose are mostly moderate and therefore allow seed aggregation before crystal growth. Some reducing agents act catalytically on specific crystal facets to promote anisotropic crystal growth. Branched nanostructures with high symmetry can be prepared from monocristalline nanoparticles by site-selective growth and etching. The optical and plasmonic properties of the nanoparticles thus obtained can be used for various applications in surface-enhanced spectroscopy and in plasmon photocatalysts.

Key words: nanoparticle, surface plasmon, aggregation, particle growth, crystal facet

1 INTRODUCTION

In the 1970s, a unique enhancement in Raman scattering was found in association with the collective oscillation of free electrons on metallic nanostructures and was termed the localized surface plasmon (LSP)\(^1\)\(^-\)\(^3\). In 1997, single-molecule measurement using surface-enhanced Raman scattering (SERS) was achieved, and the importance of metallic nanostructures was recognized\(^4\), \(^5\). Today, surface enhancement using metallic nanostructures has been developed for the other spectroscopies, such as infrared absorption spectroscopy and fluorescence spectroscopy\(^6\), \(^7\). Accordingly, metallic nanostructures have been designed to improve the efficiency of the enhancement effects. Methods for the immobilization of nanoparticles on substrates have been developed, ranging from physical adsorption to chemical bond formation on the self-assembled monolayer\(^8\)-\(^10\). The Langmuir-Blodgett (LB) method was also used to control the density of nanoparticles\(^1\), \(^2\), \(^11\). While these methods were used for spherical nanoparticles, non-spherical nanoparticles were also designed to concentrate the LSP at the edges of nanoparticles and in the gaps between nanoparticles, called hot-spots\(^13\), \(^14\). Au nanorods have been studied for this purpose, and their preparation methods are now well established\(^15\), \(^16\). The immobilization methods mentioned above were applied to Au nanorods, and their superiority over spherical nanoparticles was demonstrated\(^17\), \(^18\). The nanorods can be arranged perpendicular to the substrate, and then their hot-spots are oriented toward the target molecules for effective SERS\(^17\). Although the particle density of nanorods in the LB film was lower than that of spherical nanoparticles, the highly concentrated LSP at the edges of the nanorods resulted in stronger SERS than that from the spherical nanoparticles\(^18\). Thus, the morphology of metallic nanostructures is crucial to the design of plasmonic materials. Metallic nanostructures on substrates are prepared not only by the arrangement of nanoparticles but also by lithography and vapor-deposition methods\(^19\)-\(^22\). These methods allow flexible nanostructure designs, such as spikes and cups, controlled by the templates. On the other hand, metallic nanostructures can be used as plasmonic materials in dispersions for unique applications that do not require substrates. For example, Au nanorods were examined for laser hyperthermia, and SERS measurement was reported from agglomerates of Ag and Au nanoparticles in living cells\(^23\), \(^24\). These nanostructures can be prepared in dispersions to be ready
for use; however, they require structures that effectively provide hot-spots by themselves because the agglomeration of nanoparticles to generate hot-spots can cause undesired precipitation in the dispersion. Therefore, the nanostructures are designed to have densely packed hot-spots in the individual particles. One of the structures that serves this purpose is the branched nanoparticle, and many studies synthesizing this structure have been reported in the past decade (Fig. 1A). The branched nanoparticles have been named by association with similar structures, such as flower-like (nano-flower)\(^{25-27}\), nano-star\(^{27-30}\), nano-urchin\(^{27,31}\), and confeito-like nanoparticles\(^{27,32}\). The authors also designed a series of branched Au nanoparticles and named them confeito-like Au nanoparticles (CAuNPs)\(^{33}\). The CAuNPs exhibit unique properties for surface-enhancement efficiency in spectroscopy, fluorescence quenching, and laser hyperthermia (Fig. 1B)\(^{33-38}\). However, these nanoparticle names do not originate from their scientific background, and their preparation methods were developed separately. A systematic approach for the further development of these nanomaterials should be considered based on the rationales in terms of crystallography and methodology. This review cites several strategies to prepare branched metallic nanoparticles for better plasmonic properties.

2 Controlled Aggregation of Seed Nanoparticles

2.1 Role of protecting agents

In the author’s studies, CAuNPs were synthesized by the reduction reaction of a Au complex ion \([\text{AuCl}_4]^{-}\) using \(\text{H}_2\text{O}_2\) as the reducing agent in an alkaline condition\(^{30}\). The plasmonic colors, which refer to the plasmon absorption bands of CAuNPs, can be controlled by the protecting agents and their concentrations. Then, the plasmonic effects can be optimized for applications (Fig. 2)\(^{33,34,37,38}\). With increasing concentration of the protecting agent, typically citrate, the nanoparticles decreased their sizes in inversely proportional to the concentration (Fig. 3)\(^{34,36-38}\). A higher amount of the protecting agent allows a larger specific surface area of the nanoparticles. On the other hand, the size of each tip was not significantly changed, while the number of tips on

![Fig. 1](image1.png)

Fig. 1 A schematic illustration of surface-enhancing effects at hot-spots on metallic nanostructures (A) and SERS spectra of rhodamine 6G in dispersions of CAuNPs (B). B is adapted from reference 37 with permission.

![Fig. 2](image2.png)

Fig. 2 Photos of CAuNP dispersions prepared under different conditions. A series of protecting agents: (A) conventional spherical AuNPs (as control) (B) polyvinylpyrrolidone, (C) Pluronic F-127, (D) sodium dodecyl sulfate, (E) citric acid, and (F) HTAB. Reproduced from reference 33 with permission.

![Fig. 3](image3.png)

Fig. 3 TEM images of CAuNPs synthesized in the presence of different concentrations of citrate. The concentrations of citrate were (A) 2 mM, (B) 4 mM, and (C) 8 mM. Reproduced from reference 34 with permission.
individual particles decreased. Therefore, the process controlling the size of CAuNPs was considered to be the aggregation of seed particles. The protecting agent regulated the aggregation of seeds to form polycrystalline nuclei in the early stage of the reaction, and the number of nanoparticles was thereby determined\cite{33, 36\textendash}38. The number of tips could also be determined by the number of nuclei that developed on the surface, which could not be precisely controlled in this method. Some studies added organic solvents to the aqueous reaction solutions to synthesize the branched nanoparticles, and the organic solvents can be assumed to loosen the protective layer on the metal surface and facilitate the aggregation of seed nanoparticles in the reaction solutions\cite{28, 29, 32, 39}.

2.2 Moderate reducing agents for slow reduction

The reducing agents are mostly moderate reductants, such as ascorbic acid, N,N-dimethylformamide, amines, phenols (catechol and L-dopa), and N$_2$H$_4$\cite{25\textendash}31, 39, 40. Due to their low reactivity, the reduction reaction takes a long time (from several minutes to a few hours). During this slow reaction, the seed nanoparticles can form aggregates in parallel with the crystal growth, and therefore, the particle structure is determined by this balance. The additional protection by polyvinylpyrrolidone could inhibit the growth of the branched nanostructures and result in spherical nanoparticles\cite{29}. Branched nanostructures are not obtained when the reducing agent is citric acid, which is also a weak reducing agent and is typically used to prepare spherical Au nanoparticles at high temperature. In this case, [AuCl$_4$]$^-$ is reduced to form seed nanoparticles in the early stage of the reaction, and the seeds can aggregate, resulting in a dark gray color that suggests the inter/intra-particle plasmonic interaction. However, the aggregates soon undergo “ripening” and are recrystallized into spherical nanoparticles\cite{31}. Although this ripening mechanism is not yet understood, the reaction of Au$^+$ on the Au surface can be assumed to redissolve the Au nanoparticles into the solution to allow recrystallization ($2$Au$^0$ + Au$^+$ $\rightarrow$ $3$Au$^+$). Therefore, the reducing agent should be strong enough to rapidly reduce Au$^{3+}$ to Au$^+$ to prevent the ripening process. Au$^+$ slowly changes to Au$^0$ and Au$^+$ by the disproportionation reaction ($3$Au$^-$ $\rightarrow$ $2$Au$^0$ + Au$^+$), and Au$^{3+}$ is again immediately reduced to Au$^+$. Notably, a slow reduction to metal with an induction period could allow homogeneous nucleation in the reaction solution, and then, the obtained nanoparticles have a relatively narrow size distribution\cite{25\textendash}31, 33, 39, 40).

2.3 Aggregation on templates

Another method to prepare polycrystalline nanoparticles before particle growth is also available. The aggregates can be formed not only by the coagulation of identical nanoparticles but also by aggregation on base nanoparticles such as polymer nanoparticles\cite{42}. In this case, the seed nanoparticles were formed by the adsorption of Ag$^+$ ions on the polymer surface via the electrostatic interaction, and then, the Ag nanoparticles were prepared as seeds by a reducing reaction. The Au spikes then grew radially from the Ag seeds on the surface of the polymer nanoparticles in the growth solution. This strategy seems suitable for designing the particle size independently of the aggregation of the seed nanoparticles. The base nanoparticle is not limited to polymer nanoparticles; large metallic nanoparticles can also be used\cite{43\textendash}45. However, the spikes formed randomly on the surface, and their number was hardly controlled. Recently, monocrystalline Au nanoparticles were used as the base, and a periodic growth of Au crystals at the intersections of crystal plane was reported\cite{46}.

3 Low-Dimensional Crystal Growth in Projections

3.1 Selective protection on crystal facets

The surface morphology of the CAuNPs differed with the protecting agents (Fig. 4)\cite{33}. This change can be explained by the adsorption behaviors of the protecting agents. The weak protection by citrate leads to crystal growth in the close-packed $\{111\}$ plane, whereas hexadecyltrimethylammonium bromide (HTAB) preferentially caps the $\{100\}$ and $\{110\}$ facets of gold nanoparticles\cite{45}. Citrate cannot protect the crystal facets well because of its small molecular structure, and the resulting rapid crystal growth led to non-faceted growth, forming fernlike dendrites (Fig. 4A and C)\cite{46}.

![Fig. 4](image-url)  
SEM images (A and B) and TEM images (C and D) of CAuNPs synthesized with the protecting agents citrate (A and C) and HTAB (B and D). Adapted from reference 33 with permission.
HTAB can form a thicker adsorbed layer than citrate, and this effective capping led to smooth crystal surfaces (Fig. 4D)\(^{33}\). HTAB not only protects the crystal facets with its long alkyl chain but also regulates the reducing reaction because of the bromide ion\(^{27,32}\). The bromide ion can lower the redox potential of Au\(^{+}\), which decreases the reaction rate to allow anisotropic crystal growth. Without HTAB, the bromide ion could be supplied by KBr, and the resulting nanoparticles were large polyhedra, which suggested slow crystallization\(^{29}\). At a high concentration of HTAB (typically, 100 mM), Au nanorods formed with high aspect ratio in high yield\(^{15,16}\); however, the tips of branched Au nanoparticles synthesized at the same concentration of HTAB in the presence of organic solvents were not clear\(^{29}\). This poor structure selectivity can be explained by the weakened protection. At a low concentration of HTAB (3 mM), the morphology of the tips on the CAuNPs was not uniform (Fig. 4B). Therefore, a trade-off exists between the control of crystallization and aggregation.

On the other hand, effective protection can lead to irregularly branched edges on nanoparticles. Au nanoparticles were sandwiched by the protecting agent and then grew into a network structure\(^{47,48}\). This edge formation can be explained by the limited supply of the precursor only at the edges. A similar structure was also observed in CAuNPs protected with sodium dodecyl sulfate, which took the longest induction period (several min) to exhibit the plasmonic color\(^{30}\). The crystal growth of Au nanoparticles in the presence of Ag\(^+\) ion results in tapered structures, which are suitable for concentrating the LSP at the tips\(^{31,33,34,43,44}\). Therefore, various spiky Au nanostructures are formed by this method, and strong SERS efficiencies are reported\(^{31,43,45}\). The tapered tips are formed by the crystal growth of bipyramids in the\([110]\) direction\(^{49-51}\). The Ag\(^+\) ions adsorb on the\((111)\) plane by underpotential deposition and stabilize the\((110)\) plane with steps to sharpen the tips. The Ag also provides a reductive condition on the tips of Au crystals caused by the galvanic current, and the Ag on the tips can be nearly replaced with Au. However, this method results in significant contamination of Ag in the core of Au nanostructures\(^{43,44}\). The remaining Ag and Ag\(^+\) can produce side effects in applications (especially in biomedical use).

In the synthesis of CAuNPs using H\(_2\)O\(_2\), tapered structures were also observed, although no Ag source was used in the reaction (marked by arrows in Fig. 4B). These projections can be formed by the effective protection of HTAB and by the autocatalytic decomposition of H\(_2\)O\(_2\) on the tips\(^{52}\). The sharp edges can decompose more H\(_2\)O\(_2\) than the flat plane, and crystal growth is thereby facilitated at the intersections of facets. The growth of Au nanosheets from the edges of CAuNPs protected by HTAB also supports this autocatalytic mechanism (Fig. 5)\(^{33}\). This result suggests that a monometallic Au system can be used to design sharp edges on branched nanostructures.

### 4 Dendritic Structures from Single Crystals

#### 4.1 Stellate-shaped nanoparticles

Anisotropic growth can lead to branched nanostructures even in a single crystal. As mentioned above, CAuNPs prepared with citrate had fernlike dendrites on projections as a result of non-faceted growth, and these projections could be monocrystalline (Fig. 4C)\(^{33,46}\). On the other hand, diffusion-controlled growth in monocrystalline nanoparticles can result in the star polygons in the plane and stellate-shaped nanoparticles (also called “multipods”)\(^{51-56}\). These nanoparticles were synthesized under diluted conditions with large excess amounts of moderate reducing agents (H\(_2\)O\(_2\) and ascorbic acid), which led to anisotropic crystal growth before aggregation. From this viewpoint, CAuNPs synthesized with an adequate amount of protecting agent are expected to develop a branched monocrystalline nanostructure without aggregation. In fact, some CAuNPs synthesized with 8 mM of citrate formed stellate polyhedra (Fig. 6)\(^{36,37}\). This structure seems to have eight tips grown from the corners of cubic nanostructures, and its formation process may be crystal growth in the\((110)\) directions from\([100]\) facets in a truncated cube or cuboctahedron (Scheme 1)\(^{55}\). This structure is not yet confirmed to be monocrystalline, and further study is needed for the selective synthesis of this structure. This method would be preferred for the precise design of branched nanoparticles because their morphologies can be geometrically defined. In terms of applications, several parameters such as the number of tips per particle are controlled, and then, the
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Plasmonic behavior can be theoretically calculated by simulation. Moreover, a recent study reported that differences in crystal facets affected the surface-enhancement factor in SERS by different charge-transfer mechanisms, which were not yet solved in detail. Therefore, the development of preparation methods for monocrystalline branched nanoparticles is highly desired.

4.2 Anisotropic etching for symmetric nanostructures

The other method to prepare monocrystalline branched nanoparticles is selective oxidation on the edges. The base nanoparticle was prepared as a single crystal and then treated under oxidative conditions. Because of their chemical reactivity, this method was performed on Ag nanoparticles. Using a mixture of NH₄OH and H₂O₂, octahedral Ag nanoparticles were symmetrically etched to form 8-armed nanoparticles. The morphology of the arms was changed by the degree of etching, and the plasmon absorption bands shifted toward longer wavelengths at higher etching ratios. Ag nanoparticles are preferentially used for surface enhancement in spectroscopy due to their excellent plasmonic properties; however, their low chemical stability constrains their applications. Typically, Ag nanostructures are etched by TiO₂ under light irradiation via plasmon-induced electron transfer. Therefore, Ag nanostructures cannot be used as plasmon-induced photocatalysts, which have attracted attention over the years for use in artificial photosynthesis systems. A core-shell structure of Ag and Au could support the plasmonic property of Ag and the chemical stability of Au. Then, the preparation method for obtaining highly symmetric branched structures from monocrystalline Ag might be applied to Au nanostructures to develop robust plasmonic devices.

5 Conclusion

This short review has highlighted solution-phase methods to synthesize branched metallic nanostructures for plasmonic applications. Protecting agents can control aggregation and the subsequent crystal growth by selective adsorption on facets. Moderate reducing agents allow the nuclei of nanoparticles to aggregate for multicore nanoparticle formation. Ag facilitates anisotropic growth of Au nanoparticle on specific crystal axes to form sharp edges, which are preferable for their plasmonic properties. According to these concepts, CAuNPs were prepared as the effective branched nanoparticles by a reducing reaction with H₂O₂ under various protecting agents.

On the other hand, branched single crystals with highly symmetric nanostructures can be obtained under diluted and well-protected conditions. An oxidation reaction was also useful to synthesize branched monocrystalline Ag nanoparticles. These strategies and mechanisms should be developed to define nanostructures for advanced plasmonic devices.

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Fig. 6 SEM (A) and TEM (B) images of CAuNPs synthesized in the presence of 8 mM of citrate. Adapted from ref. 35 and 37 with permission.

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