

# Metal Nano Networks by Potential-Controlled In Situ Assembling of Gold/Silver Nanoparticles

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Non-spherical Au/Ag nanoparticles can be generated by chemical reduction of silver ions in the presence of preformed gold nanoparticles. The process of particle formation can be controlled by concentrations of ligands and reducing agent. The formation of ellipsoidal, nanorod- and peanut-shaped nanoparticles as well as of more complex fractal nanoassemblies can be explained by changes in particle surface state,

electrochemical potential formation and particle-internal self-polarization effects. It is possible to create highly fractal nanoassemblies with sizes between the mid-nanometer and the lower micrometer range. The assemblies are marked by high optical absorption and complex nano-networks of very high surface-to-volume ratios and a granular base structure.

## 1. Introduction

The eminent importance of distributed metal nanoparticles is known since the fundamental pioneer work of Johann Wolfgang Döbereiner on platinum catalysis.<sup>[1]</sup> Metal particles and films with a high specific surface are crucial in industrial catalysis up to now. The black metallic nanostructures became further important for imaging,<sup>[2]</sup> for example in photography or as absorption layer in optical and infrared sensors.<sup>[3,4]</sup>

For an addressing of the chemical and optical properties of metal films, it is of importance to control the micro morphology. The investigations on so-called plasmonic nanoparticles as e.g. gold and silver nanoparticles in colloidal solutions have shown that the electronic and optical properties strongly depend on the composition, but also on the size<sup>[5]</sup> and the shape of metal nanoparticles.<sup>[6,7]</sup> In particular, metal nanoparticles with high aspect ratios are marked by long-wavelength electromagnetic resonances reaching from the visible up to the near infrared range.<sup>[8]</sup> This effect can be observed for one-dimensional particles as nanorods or nanoneedles<sup>[9,10]</sup> as well in case of two-dimensional metal nanoparticles as nanodisks and flat nanoprisms.<sup>[11,12]</sup> Pure colloidal solutions of one type of nanoparticles and narrow size distribution can be achieved, for example, by microfluidic syntheses and supplies sharp reso-

nance peaks in the optical spectrum.<sup>[13,14]</sup> Microfluidics can also be applied for a well-controlled generation of binary composed metal nanoparticles, for example in the thickness tuning of silver shells on gold cores or in the synthesis of double shell nanoparticles,<sup>[15]</sup> in which the optical properties strongly depend on the shell thicknesses.

In some cases, an assembling of two or several cores during the deposition of shells of metal core/shell particles can occur during their liquid phase synthesis. In result, the formation of flower- or star-shaped particles or of fractal aggregates can be observed.<sup>[16]</sup> Since the crucial investigations of J. Polte et al. on spontaneous aggregation of metal nuclei and colloidal restabilization during the liquid-phase formation of polynuclear gold nanoparticles<sup>[17,18]</sup> it is clear, that the morphology and the properties of nanoparticles can be strongly determined by in-situ assembling processes. Obviously, it is possible to generate very different nano-morphologies if it is possible to control the assembling behaviour of small nanoparticles and the in-situ assembling during the ongoing of metal deposition on forming metal cores during the liquid phase synthesis. These processes are controlled by the electric charge of the particles and by the electrochemical activity of metal ions, complexing ligands and reducing agents in the reaction mixture. The effect of ligands should also affect the formation of fractal structures of nanoparticle assemblies and highly absorbing networks with resonances covering the whole visible and parts of the UV and IR spectrum. Therefore, the here presented investigation focuses on the influence of chemical parameters on the formation of binary noble metal nano-networks.

## Experimental Section

All applied chemicals are pA grade. Following chemicals have been applied as received: Silver nitrate (purity 99%, Merck KGaA, Darmstadt, Germany), Ammonium thiosulfate (Merck), Tetrachloroauric acid trihydrate (purity 99.5%, Carl Roth GmbH, Karlsruhe, Germany), Ascorbic acid (purity 99.7%, Merck KGaA, Darmstadt, Germany)

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The particle morphology was characterized by scanning electron microscopy using a S4800 (Hitachi, Japan). The optical properties of colloidal solutions have been investigated by UV-Vis spectrophotometry using a Specord 200 (Analytik Jena, Germany).

## 2. Polarization-Based Mechanism Concept

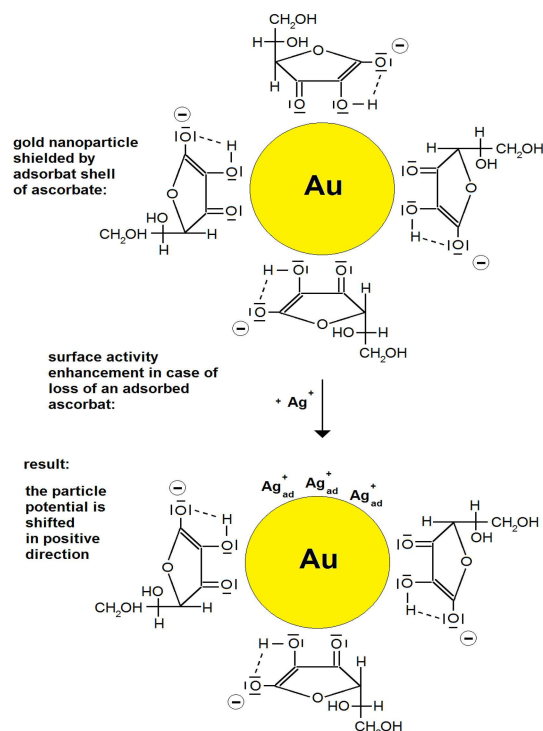
It is assumed that the concept of local self-polarization of charged particles in colloidal solution is applicable for the formation of binary metal particles, too. This concept was successfully applied for understanding the unexpected high stability of silver nanoprisms with high aspect ratios and for the explanation of the induction of spontaneous shape-transformation of flat triangular silver nanoprisms into compact silver particles.<sup>[19]</sup> And it was also useful for a strategy to control the shape of non-spherical polymer particles and tuning their geometry from spheres over ellipsoids, nano dumbbells to rods, astragal-like and branched structures.<sup>[20,21]</sup> In the first case, the polarizability of particles is due to the electric conductivity of the metal material. In the second case, the mobility of surface-attached highly charged polyionic macromolecules is responsible for a certain polarizability during the approach of particles in the assembling process.

The condition of electron density polarization is also fulfilled for spherical metal nanoparticles if a local interaction with ions occurs. Gold nanoparticles show a negative Zeta potential if they are produced by reduction of  $\text{HAuCl}_4$  in an aqueous solution with an excess of ascorbic acid. These colloidal solutions can be stabilized by organic ligands as citrate or ascorbate. Ascorbic acid, and in particular, the deprotonated species can form a protecting and stabilizing molecular film on the surface of gold nanoparticles.

The surface state of gold nanoparticles is very important, if a chemical process should deposit a second metal. This is the case with the generation of binary silver/gold nanoparticles. In principle, silver ions can be reduced by ascorbate, too. However, the nucleation rate of silver is comparatively slow. In contrast, silver can be quickly deposited on existing metal surfaces. Typically, gold/silver core/shell particles are formed in the presence of ascorbic acid.<sup>[15]</sup> Additional ligands such as thiosulfate, which adsorb on the particle surface can further modulate the electrical charge and the surface activity of metal nanoparticles.

In the following, a hypothetical mechanism for the formation of nanoparticle aggregates and networks is discussed. It is based on the SEM images and on the expectations about the electrochemical behaviour of the metal nanoparticles in colloidal solution during metal deposition and interaction with the reducing agent.

The film of molecular adsorbates on the gold particles can suppress the cathodic charge transfer and, therefore, a direct incorporation of silver atoms by de-charging at the metallic particle surface. The ascorbate-protected particles have probably also certain stability in the case of addition of silver ions. That means that they keep their negative particle potential.

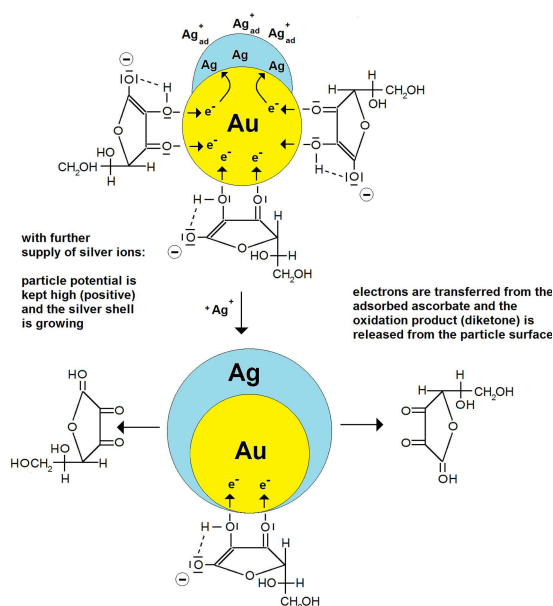


**Figure 1.** Scheme of the hypothesis on formation of Au/Ag nanoparticles from ascorbate-stabilized gold nanoparticles by a mixed potential model including the cathodic partial process of de-charging of adsorbing silver ions and the anodic partial process of ascorbate oxidation

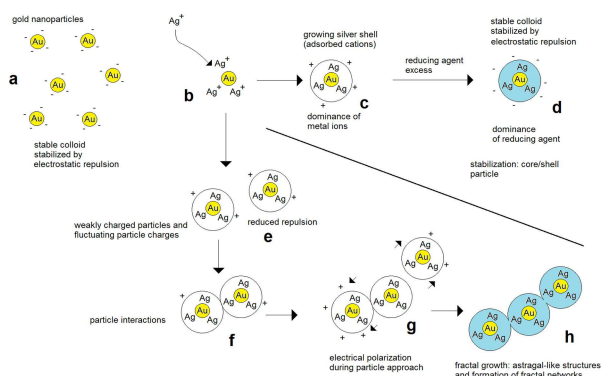
In case of a loss of ascorbate molecules from the surface of such a gold particle, silver ions can directly adsorb at the gold surface (Figure 1). This leads to an increase of particle potential, local deposition of silver and further increase of particle potential (Figure 2). Probably, the switching from negative to positive particle potential results into a fast oxidation of the remaining adsorbed ascorbate molecules and the oxidation products, the product diketones are released from the particle surface.

The change in the electrical particle state is very important for the further fate of the particles because the electric charge is mainly responsible for the stability of the colloidal system. The gold colloid, which is formed in excess of ascorbate, is stabilized by the electrostatic repulsion of the negatively charged particles (Figure 3a). The addition of silver ions can cause a fast increase in electrical potential (Figure 3b). If the mixing is going on fast enough, this switching in the electrical potential can be realized without a flocculation of the colloid, due to an intermediate co-existence of negatively and positively charged particles. Therefore, fast microfluidic mixing processes are very useful for the initiation of the formation of gold/silver core/shell particles in order to avoid uncontrolled particle agglomeration due to mixed electrical charges.<sup>[14]</sup> In result, a colloidal solution of core/shell particles is forming (Figure 3c), which can be finally stabilized after a fast re-switching from positive to negative potential due to the exhaustion of silver ions in case of an excess of ascorbic acid (Figure 3d).

The situation can be changed if the reduction of electric charge during the silver deposition leads to a slower decharging (Figure 3e). In this case, particles are no longer repulsing each other, but can interact directly (Figure 3f). The attachment of one spherical particle to another represents a break of the spherical symmetry. Small aggregates of two particles represent non-linear objects, in which the remaining charge is pushed towards the poles due to the metal conductivity. The electrically charged non-linear metallic nano-objects show a polarization between their central and their periphery parts (Figure 3g). The attachment of a third particle of the same total charge will have higher probability in the central region, which leads to more compact particles. But, oppositely charged particles will preferentially join the poles resulting in a



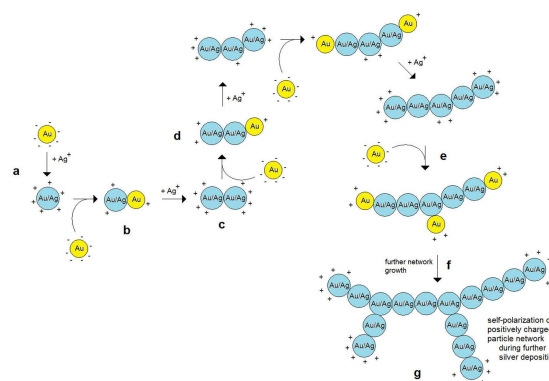
**Figure 2.** Schematic graph for the proposed positive feedback mechanism for the switching from negatively charged ascorbate-stabilized gold nanoparticles to positively charged growing Au/Ag core/shell particles during the chemical silver deposition



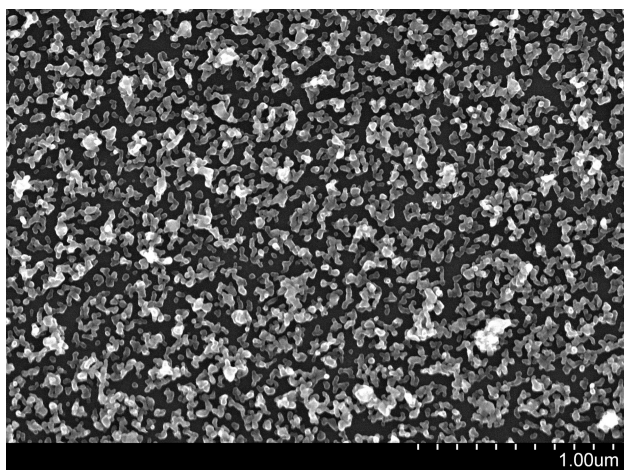
**Figure 3.** Hypothesis for the different possible fates of gold cores (a) with growing silver shell (b): 1. fast switching between anodically and cathodically dominated particle potential leads to the formation of a stable colloidal solution of dispersed spherical core/shell particles (c and d); 2. Aggregation caused by reduced electrostatic repulsion due to different potential states or slow transitions between the positive and the negative state of particles (e-h)

more stretched arrangement and astragal-like geometries of aggregates. This above drawn concept is in agreement with the phenomena observed in the case interaction of charged submicron polymer particles and the control of the interaction by the composition and ratios of surface-attached polyionic macromolecules. In addition, branched structures could be achieved at certain concentrations and compositions of these aggregated polymer submicron particles.<sup>[21,22]</sup>

It was assumed that structures that are more complex can also be formed by metal nanoparticles if an interaction between antagonistically charged particles occurs. This situation could appear during the deposition of silver on colloid gold nuclei. It could be caused by the comparatively good stabilization of negatively charged small gold nanoparticles by ascorbic acid on the one hand and the intermediate formation of positively charged particles due to the fast switching of electrical potential to positive values by starting silver deposition on the other hand. In a first step, a positively charged growing core/shell particle joins a negatively charged gold nanoparticle by the attractive electrostatic force (Figure 4a). The positive charge of the electrochemical active growing shell dominates the total charge of the small particle aggregate and causes a switching of the formerly non-active surface of the gold core into an active surface (Figure 4b), at which further silver can be deposited. This join particle has a growing silver shell. Its positive charge is pushed towards the poles by the self-polarization effect (Figure 4c). The positive charged poles attract other negatively charged gold particles resulting into a preferential assembling into linear (rod-like) or – at least – other non-compact shapes (Figure 4d). The further silver deposition and electrostatic attachment of gold nanoparticles can cause positively charged growing aggregate particles with a multipolar polarization structure (Figure 4e). This can be the reason for the formation of branches (Figure 4f) and a further growth of complex branched fractal metal nanostructures (Figure 4g). Probably, the increasing size of aggregate particles can cause an avalanche effect by which a moderate deposition rate of silver is accompanied by an exploding attraction of the remaining small negatively charged gold nanoparticles by the



**Figure 4.** Proposed mechanism of formation of fractal nanoparticles with granular base structure by successive attachment of small – mainly spherical – negatively charged nanoparticles at the charge-focussing poles of a growing positively charged assembly particles



**Figure 5.** Nanoparticles obtained by chemical deposition of silver on gold nanoparticles in a colloidal solution containing ATS

electrochemically active positively charged aggregates. In this process, also a certain integration of weakly charged preformed aggregate particles is thinkable.

For the last phase of particle growth, two scenarios are possible: In the first case, the availability of the remaining original ascorbate-protected gold nanoparticles decreases faster than the availability of silver ions. In this case, the aggregates “fishes” all small particles and only or – at least mostly larger aggregates are formed, finally. In the second case, the silver availability decreases faster than the concentration of original small gold nanoparticles. In this case, all positively charged particles – also the larger aggregates – switch their potential from positive to negative charge due to the excess of ascorbic acid. This potential switching can also take place by an excess of other reducing agents and ligands. In result, both larger aggregates and small particles are stabilized and conserved.

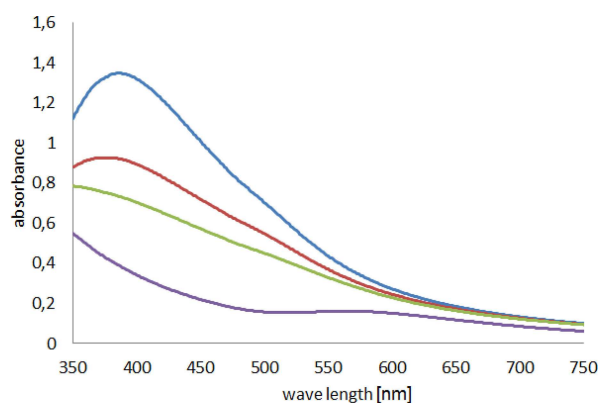
### 3. Results and Discussion

Experiments for the in situ formation of Au/Ag nanoparticle aggregates have been performed by a two-step process. In the first step, spherical gold nanoparticles are generated by reduction of tetrachloroaurate in an excess of ascorbic acid at room temperature (20 °C). Typically, the gold nanoparticles are formed within about two seconds after mixing of equal volumes 20 mM Ascorbic acid with 1 mM  $\text{HAuCl}_4$  solution. The nanoparticle formation becomes immediately visible by the appearance of the typical pink colour of the colloidal solution. In deviation to earlier studies for the generation of gold/silver nanoparticles,<sup>[23]</sup> here an addition of ammoniumthiosulfate (ATS) was applied. This reagent can act as reducing agent, too. In addition, it modulates the activity of free silver ions by complex formation, as it is known from its traditional application for fixation in silver halogenide photography. The formation of star-like fractal structures of Au/Ag nanoparticles was observed in case of a temporal destabilization of colloids

by the fast addition of silver salt solution during the completion of Au nanoparticle growth.<sup>[16]</sup> In TEM images, dark core structures connected by brighter junctions support the idea that preformed gold nanoparticles can be connected by the subsequent chemical deposition of silver (Figure 3b in [24]).

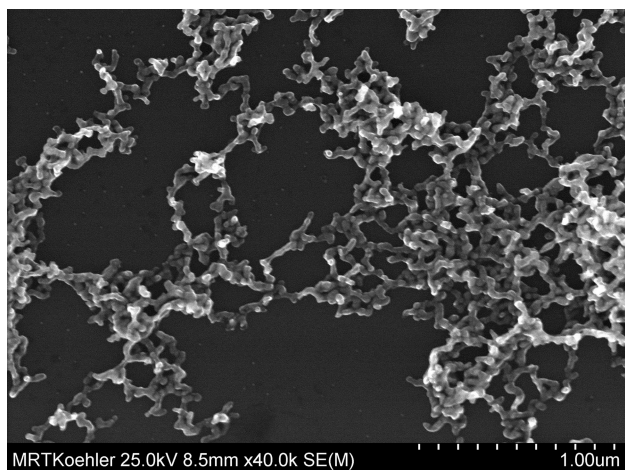
ATS was added to the colloidal solution of gold containing the excess of ascorbic acid. After addition of a silver nitrate solution (final concentrations: 5 mM ascorbic acid, 0.1 mM ATS; 1 mM silver nitrate) the colour of the reaction mixture turned to black within about ten seconds. The colour change during the reaction corresponds to the well-known so-called “sun-set reaction”.<sup>[25]</sup> The fresh prepared colloidal liquid was transferred on a silicon chip in order to investigate the morphology of the formed particles by scanning electron microscopy (SEM). After the drop of the colloidal solution has dried on the Si-chip and the noble metal particles were attached to the surface, the chip was rinsed with deionized water in order to remove any kind of soluble crystals which might interfere with the SEM measurements. In the SEM image, a hierarchical particle structure was observed (Figure 5). The basic element is a granular structure with a diameter of about 20 nm. These grains are a little larger than the diameter of the original gold nanoparticles. It is assumed that these grains represent a binary material consisting of gold cores and silver shells. These grains are connected to aggregates with sizes between about 30 nm and 0.5  $\mu\text{m}$ , which are composed of a few or several dozen of the elementary grains.

The effect of lower ATS concentrations on the formation of aggregates was studied by variation of the final ATS concentration between 0.063 and 0.25 mM and concentration of ascorbic acid of 1.2 mM and silver nitrate of 0.1 mM. The optical spectra reflect a nearly constant state of the obtained colloidal solutions after about two minutes. It was found that the absorption of product liquids increased with decreasing ATS content (Figure 6). This behaviour corresponds to the assumption of a masking effect of silver ions by ATS. In case of 0.25 mM ATS, nearly no reaction took place, which is indicated by the absorbance spectrum of the original colloidal gold solution. Reaction mixtures with lower ATS concentrations



**Figure 6.** Optical spectra of colloidal product solutions of Au/Ag nano-assemblies obtained at different ATS concentration with start concentrations of 1.2 mM ascorbic acid and 0.1 mM silver nitrate (spectrophotometry in a 1-cm cuvette)

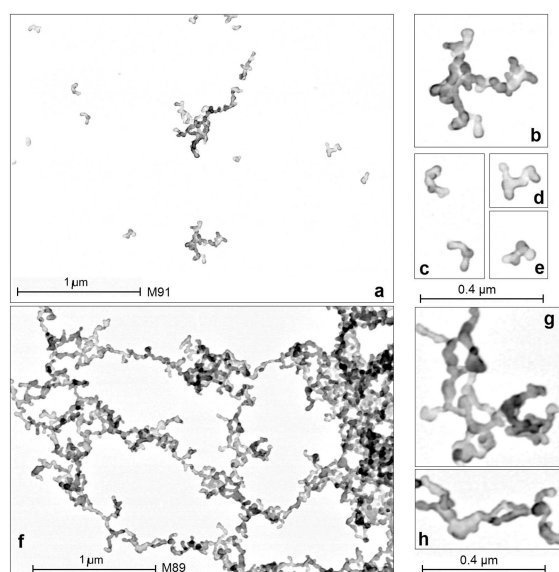




**Figure 7.** Nano-network of Au/Ag assembly particle obtained at comparatively low ATS concentration (SEM image)

supplied final spectra with absorption over the whole visible range up to the near infrared.

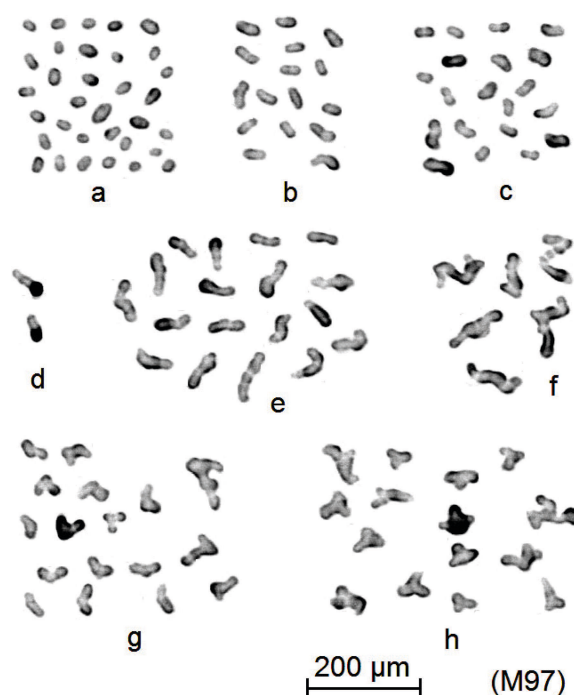
In case of low ATS content (50 μM), larger aggregates with sizes of several microns have been found. They consist of larger nano-network structures (Figure 7) which are based on the same elementary granular structure as in the experiment with higher silver and ascorbic acid content. No single grains or small aggregate particles were observed in this case. The appearance of these nano-network aggregates corresponds to the model, in which the remaining gold nanoparticles are more or less completely consumed by integration into the nano-network before the silver ions are completely consumed. Similar networks (Figure 8f–h) had also been observed in the case of a very low ATS content (25 μM), whereas smaller and smallest



**Figure 8.** Examples of particle assembling and nano network formation (SEM images): a–e) 0.2 mM ATS, f–h) 0.05 mM ATS; a–h) 1.2 mM ascorbic acid, 0.1 mM AgNO<sub>3</sub>

aggregate particles (Figure 8a–e) had been found beside larger aggregates at higher ATS concentration.

A further enhancement of ATS concentration (0.3 mM) resulted into a prevalence of these smaller and smallest aggregate particles. It is assumed that the lower chemical activity of the silver ions and the resulting lower electrochemical potential of the growing particles during the silver deposition are responsible for the lower aggregation tendency and the dominance of the small non-spherical aggregates. Several types of aggregate particles can be distinguished in the ensemble of formed non-spherical assemblies. All forms can be explained by the superposition of a particle assembling and the silver deposition. The simplest geometry is shown by ellipsoidal particles (Figure 9a), which are



**Figure 9.** Different types of small particles formed by superposition of silver deposition and in-situ assembling (0.3 mM ATS, 1.2 mM ascorbic acid, 0.1 mM AgNO<sub>3</sub>, SEM images): a) ellipsoidal particles, b) short nano rods, c) peanut-shaped nanoassemblies, d–f) longer and distorted rods, g) kinked assemblies, h) branched assemblies

obviously formed by an early pairing of two nearly spherical particles. Short rods (Figure 9b) and beam- or peanut-like particles (Figure 9c) seem to have been formed by a nearly linear assembling of two or three spherical grains. More asymmetric and distorted rods are integrating three or more grains (Figure 9d–f). Kinked structures of different angles (Figure 9g) are formed comparatively frequently. In several cases, also small branched particle aggregates are observed (Figure 9h), which seem to represent an early (starting) stage of network-like nanostructures. The different absorbances (total oscillator strength) in the optical spectra are neither caused by different original silver ion content nor by limitation due to reducing agents. An explanation could be given by an increase of the oscillator strength of the larger

assemblies in comparison with the smaller ones. The highest absorbance was found for the large network aggregates.

It can be summarized, that in all investigated cases, an in-situ assembling of small spherical nanoparticles takes place, which results into the formation of non-spherical nanoparticles with a granular base structure. The spectrum of aggregate particles reaches from simple binary and ternary assemblies over midsize fractal nanoparticles up to larger nano-network assemblies depending on the reactant and ligand concentrations. The formation of these different nanoassemblies can be well interpreted by the mechanistic concepts drawn above (Figure 1–4).

## 4. Conclusions

The formation of non-spherical, rod-like and branched gold/silver nanoparticles can be explained by the superposition of chemical silver deposition and electrostatically controlled particle assembling when silver ions are reduced by an excess of ascorbic acid in the presence of spherical gold nanoparticles. The proposed key mechanism is the switching of electrochemical particle potentials in dependence on the intensity of anodic and cathodic partial processes on particle surface due to changes in particle surface state and the availability of electrochemical active species. The electrical conductivity of primary formed small non-spherical binary particle assemblies cause a symmetry break in the charge distribution and, therefore, an electrical self-polarization pushing the excess charges into the pole directions. This mechanism supports the preferential further attachment of particles in the pole regions resulting into the formation of non-compact fractal and net-work-like nanostructures.

The larger nanometallic assemblies with a granular base structure are marked by high oscillator strength from the UV to the near infrared range. This absorption can be understood as a superposition of different of so-called plasmonic resonances in the complex metal nano-network. Such a type of Au/Ag nano-networks with very high surface-to-volume ratio and a high variety of surface planes is of interest, for example, for heterogeneous catalysis, for analytics and sensing as for application in surface-enhanced Raman spectroscopy (SERS).

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** bimetallic nanostructures · nonspherical nanoparticles · metal nano-networks · self-polarization effects · silver

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