Simple morphological control over functional diversity of SERS materials

A A Semenova\textsuperscript{1} and E A Goodilin\textsuperscript{1,4}

\textsuperscript{1}Department of Materials Science, Lomonosov Moscow State University, 1 Leninskie gory, building 73, Moscow 119991, Russian Federation
\textsuperscript{2}Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, 31 Leninsky prospect, Moscow 119991, Russian Federation
\textsuperscript{3}Department of Chemistry, Lomonosov Moscow State University, 1 Leninskie gory, building 3, Moscow 119991, Russian Federation
\textsuperscript{4}Author to whom any correspondence should be addressed: goodilin@yandex.ru

Abstract. Nowadays, surface-enhanced Raman spectroscopy (SERS) becomes a promising universal low-cost and real-time tool in biomedical applications, medical screening or forensic analysis allowing for detection of different molecules below nanomolar concentrations. Silver nanoparticles and nanostructures have proven to be a common choice for SERS measurements due to a tunable plasmon resonance, high stability and facile fabrication methods. However, a proper design of silver-based nanomaterials for highly sensitive SERS applications still remains a challenge. In this work, effective and simple preparation methods of various silver nanostructures are proposed and systematically developed using aqueous diamminesilver (I) hydroxide as a precursor.

1. Introduction
The great number of effective and diverse ways of nanoparticle design is known nowadays [1, 2] thus allowing various practical applications from catalysis to the development of new innovative analytical methods based on the Surface-enhanced Raman spectroscopy (SERS). In the latter, a major part of all the studies is biomedically oriented and demands for a high chemical purity of the prepared nanoparticles with no residuals of reagents, surfactants and other byproducts which can be cell toxic or could harm analytically representative measurements because of worsening of a signal-to-noise ratio, a signal background shape, reproducibility and sensitivity of the SERS analysis. A possible solution of this important problem is based on the application of aqueous diamminesilver (I) hydroxide as the only reagent containing volatile components favouring reduction of silver ions into pure metallic silver nanoparticles under gentle conditions [3–5]. In this paper, we present our experimental results demonstrating a flexibility of this approach leading to a number of SERS-active nanostructured materials as predetermined by processing conditions.

2. Materials and methods
Silver nanoparticles and nanostructures were prepared using several novel routes based on transformation of diamminesilver (I) hydroxide via formation of silver (I) oxide and pure silver under different conditions such as hydrolytic heating [3], aerosol pyrolysis [4,5] or reduction by H$_2$O$_2$ [6].
Silver nitrate (AgNO₃), sodium hydroxide (NaOH), ammonium hydroxide (NH₄OH, 30%), polyvinylpyrrolidone (PVP), hydrogen peroxide (H₂O₂, 10%), Rhodamine 6G (Rh6G), cyclohexanethiol were of high purity grade. In all the experiments, ultra-pure water with resistivity ca. 18 MΩ·cm (Milli-Q, Millipore) was used.

2.1. Hydrolytic heating
In a typical preparation route [3], 0.5 M aqueous NaOH solution was added dropwise to 20 ml of freshly prepared 0.1 M aqueous AgNO₃ solution until complete precipitation of black-brown silver (I) oxide. Then this as-prepared precipitate was washed with water and dissolved in 5 ml of 10% aqueous ammonia solution. The obtained transparent silver complex solution was filtered through Millex-LCR syringe driven filter units (Millipore, 0.45 μm pores). The aliquot of the resulting solution (0.1, 0.5 or 2.5 ml) was added to 50 ml portions of boiling water. After 20, 30 and 60 min of the decomposition reaction the aliquots of pure silver sols were collected and immediately cooled down and stored in a refrigerator at about 5°C overnight.

2.2. Aerosol pyrolysis
In a typical experiment, 0.1 M aqueous NaOH was added dropwise to freshly prepared 0.01 M aqueous AgNO₃ until complete precipitation of the black-brown silver (I) oxide. The as-prepared oxide was thoroughly washed with water and dissolved in 10% aqueous NH₄OH to have 0.01 M solution of the diamminesilver (I) hydroxide. The obtained silver complex solution was filtered through Millex-LCR syringe driven filter units with 0.45 μm pores. In the ultrasonic silver rain (USR) deposition process, this initial ammonia solution of silver (I) oxide was nebulized into mist and 1–5 micron droplets were streamed either onto hot glass substrates heated up to 250–300 °C without preheating the mist and resulted in formation of silver rings [4] or into a hot zone (550–950 °C) of a tubular furnace followed by the condensation of the decomposition products at about 60 °C and formation of more complex shapes of silver nanoparticles [5]. The entire run of nanostructured substrate preparation demanded typically 30–60 min only.

2.3. Silver octahedral particles
The synthesis of silver octahedral particles was based on the protocol proposed originally by J.Fang, et al. [6] and customized to provide porous octahedra with a morphologically predetermined large number of hot spots. The first stage included the formation of silver (I) oxide octahedral particles by adding 0.5 M NH₄OH solution dropwise into 50 ml 100 mM aqueous solution of AgNO₃ in the presence of 0.1 mM of PVP solution as a specific face-selective surfactant until the mixture became transparent. After that, 0.3 ml of 2M NaOH aqueous solution was added to the colorless solution under vigorous stirring. The brownish-black precipitate immediately formed. The obtained silver (I) oxide was washed with distilled water and ethanol several times using centrifugation (4000 rpm, 10 min, Sartorius Sigma 3-30 K) and finally redispersed in ethanol. The second stage allowed the synthesis of porous faceted silver octahedral pseudomorphs by the reduction of silver (I) oxide solution by H₂O₂ and, unlike the initial protocol, by additional etching with ammonia solution. For this purpose, 10 ml of 10% H₂O₂ was added to the obtained silver (I) oxide under stirring followed by the injection of 10 ml of 0.5 M ammonia solution. The synthesized silver particles were collected by centrifugation (4000 rpm, 10 min) and washed with distilled water and ethanol.

2.4. Characterization
The obtained nanomaterials were comprehensively characterized by a transmission electron microscopy (TEM) and electron diffraction (ED) using LE0912 AB OMEGA (Carl Zeiss) electron microscope. The pristine sample microstructure was studied using a scanning electron microscope (Carl Zeiss NVision 40) at 0.5–5 kV accelerating voltage. UV-vis absorption spectra were recorded using the UV-vis spectrophotometer Lambda 35 (Perkin-Elmer) with an attached diffuse reflectance accessory. The obtained substrates were examined using Rigaku D/MAX 2500 (Japan) with a rotating copper anode (CuKa irradiation, 5–80° 2Q range, 0.02° step). Diffraction maxima were indexed using the PDF-2 database. Raman and SERS experiments were performed using an InVia Raman
microscope (Renishaw, UK) equipped with a 20 mW 514 nm argon laser and power neutral density filter (10%). All the spectra were collected using a 50x objective lens and 10–120 s of acquisition time. A silicon wafer was used for calibration.

3. Results
Decomposition of aqueous diamminesilver (I) hydroxide (figure 1) allows a wide variation of given morphologies of thus prepared materials controlled by simple changes of concentrations and thermal treatment procedures (figure 2). Mild heating of bulk or dispersed aqueous solutions in the form of aerosol drops as well as shape-preserving preparation of pseudomorphs results in pure silver nanoparticles or hierarchic silver nanostructures with following morphologies: spheres, rings, porous spheroids, cuboids, octahedra and more complex structures with multiple hot spots. All the prepared nanostructures demonstrate their high efficiency in SERS measurements with enhancement factors of about $10^5$ – $10^8$ and were used in a form of SERS-active substrates for a study of different biomolecules and pollutants (figure 3).

Figure 1. Calculated potentials for the reaction $\text{Ag} + 1/4 \text{O}_2 + 2\text{NH}_3 + 1/2\text{H}_2\text{O} = [\text{Ag(NH}_3)_2]=-\text{OH}^-$ as a function of ammonia concentration in boiling water, the lower curve is equal to 0.1 M concentrations of $[\text{Ag(NH}_3)_2]^-$, the upper one is diluted, $10^{-4}$ M, solution of the complex.

4. Discussion
We consider a group of robust and effective processing methods of silver nanostructures supported by our previous works [3–5] which is based on gradual self-reduction of one of the most useful and well-known ammonia complex of silver, $[\text{Ag(NH}_3)_2]^-$, due to the lost of its stability upon the ammonia ligand elimination. This route plays with drastic stabilization of silver ions within the complex ($K_{\text{stab}}([\text{Ag(NH}_3)_2]^-) = 1.3 \cdot 10^7$, $\text{Ag}^+ + 2\text{NH}_3 = [\text{Ag(NH}_3)_2]^-$) and a huge variation of the redox potential of silver $E_{\text{Ag}/\text{Ag}^+} = 0.8$ V in the presence of ammonia of different concentrations and also a possibility to precipitate the Ag$_2$O solid phase or dissolve it by ammonia $(\text{Ag}_2\text{O} + \text{H}_2\text{O} + 4\text{NH}_3 = 2[\text{Ag(NH}_3)_2]^+ + 2\text{OH}^-)$. This method is characterized by the absence of side-anions in the redox system except $\text{OH}^-$, which is a natural part of all the aqueous solutions. Another part of the system is oxygen which can be dissolved in the solution as an oxidizing agent or evolved from the solution as a product of silver oxide decomposition, the standard potential of the pair $\text{O}_2/\text{OH}^-$ is $E_0(\text{O}_2/\text{OH}^-) = 0.401$ V. That is why the shift of the equilibrium in the overall process $\text{Ag} + 1/4 \text{O}_2 + 2\text{NH}_3 + 1/2\text{H}_2\text{O} = [\text{Ag(NH}_3)_2]^+ + \text{OH}^-$ serves as a good control tool for generation of silver nanoparticles simply by changing the concentration of ammonia which could generate enough $\text{Ag}^+$ ions and cause their reduction to metallic silver otherwise $\text{Ag}^+$ is stabilized as $[\text{Ag(NH}_3)_2]^+$ and can not be reduced. The calculated data of the potentials are presented in figure 1. It is evident that even very small concentrations of ammonia makes the reaction to shift to the right side forming $[\text{Ag(NH}_3)_2]^+$, no silver nanoparticles could be formed, they will be dissolved due to stabilization of silver ions within the stable ammonia complex. However if the NH$_3$ ligand is lost for some reasons (heating and evolving from the solution), there is an area of negative potentials where diamminesilver (I) hydroxide is not stable thermodynamically and decomposes forming metallic silver which deposits as nanoparticles. The ABC pathway means a starting point of a high concentration of separately prepared $[\text{Ag(NH}_3)_2]^+$ in an excess of ammonia, then a sharp drop of the concentration of ammonia should happen, for example, due to the ligand
evaporation with partial decomposition of the complex, and, afterwards, the process ends up at a very small concentration of $[\text{Ag(NH}_3\text{)}_2]^+$ and a higher concentration of bare silver ions.

The use of the aqueous diamminesilver (I) hydroxide to prepare silver nanostructures gives a large benefit owing to the simplicity, promptness and low temperature conditions of the production process (typically lower than 250 °C). In the case of pure silver hydrosols (figure 2, left – top), their formation occurs in bulk solutions and they represent 2–30 nm, mostly spherical, nanoparticles with a broad size distribution which is evidently connected with nearly equilibrium conditions of their nucleation and growth under supersaturation generated by the above described redox reactions due to a drop of ammonia concentration in hot water and its step-by-step lost.

Evaporation of water from aerosol droplets as microreactors together with ammonia ligands lost gives polyhedral silver nanoparticles in a cooling zone of a hot reactor at 50–70 °C (figure 2, right – top). Their etching with ammonia and water vapors results in shape-preserving transformation of silver (I) oxide single crystalline nanoparticles into aggregates of smaller silver nanoparticles of the same shapes. However, the difference in molar volumes of metallic silver and its oxide leads to shrinkage and also pore formation. As a result, porous polyhedral nanoparticles, pseudomorphs, are formed due to such topochemical transformations.

Silver octahedra preparation could be also performed in a more controllable manner (figure 2, left – bottom) although two conditions have to be obeyed: surfactants (PVP) should be added to confine crystallization of silver (I) oxide in alkaline media, also an appropriate reducing agent like ascorbic acid has to be used to provide fast redox transformation of silver (I) oxide into metallic silver since no elevated temperatures are used in such a procedure as compared to aerosol pyrolysis.

![Figure 2](image)

**Figure 2.** The diversity of silver nanostructures prepared from diamminesilver (I) hydroxide as an universal precursor of metallic silver.

The most nonequilibrium process among the depicted in figure 2 is aerosol spray deposition of hierarchic ring nanostructures onto substrates preheated up to 250 – 300 °C (figure 2, right – bottom). Such substrates after processing consist of overlapping pure silver rings of a complex morphology originating from decomposition of micron-sized droplets of ultrasonic mist of diamminesilver (I) hydroxide solution. Indeed, if a droplet of liquid dries on a solid surface, forming nanoparticles, the latter would be deposited in a ring-like fashion. During the drying process, droplet edges become pinned to the substrate, and capillary flow outward from the centre of the droplet brings suspended
particles to the edge as evaporation proceeds. The particles are left highly concentrated along the original droplet edge. As soon as the formed nanoparticles are moved to the rim by the outward flow, their local attractions lead to the formation of loosely packed structures near the rim. The complexity of this “coffee ring” phenomenon yields unusual silver ring structures observed for the substrates. In our experiments, silver deposition gives intersecting circles of 30–100 microns in diameter. This value is several times larger than the expected size of 1–10 microns of the falling mist droplets therefore the liquid from the droplets spreads laterally over the substrate. Solvent evaporation increases the concentration of the silver complex and then metallic silver resides on rims of the spreading circles, producing walls of silver craters according to the reactions mentioned above. The thickness of walls typically lies in a range of 1–3 microns while the residual part is covered with silver nanoclusters gradually increasing in their sizes from 10–20 nm in the centers of circles to about 100 nm in the wall vicinities. The nanoclusters increase the role of capillary forces and, afterwards, more droplets stack onto the surface and boil; an increase of sputtering time leads to rough and porous layers. Most of the circles form groups or long chains until the surface becomes rather uniformly covered with stochastically intersecting silver rings. “Coffee ring” formation onto the substrates is accompanied by nanostructuring. When silver forms, large and smaller gaps appear in the region of rims and this gives random blocks (“bricks of the wall”) of 200–500 nm. The bricks and the walls are composed of nanometer-sized interconnected silver particles because every act of droplet transformation on the substrate gives newborn silver nanoparticles of a very small size of several nanometers. Later, these nanoparticles grow, join each other and form channels, making the rims highly porous. Instant capillary transport of nutrient solution to the top of walls through the channels leads to the growth of 10–50 nm “sesame seed” grains of silver covering the bricks.

Formation of various nanoparticle morphologies is a highly suitable way to optimize materials for different desired SERS measurements. The analysis of enhancement coefficients among the nanomaterials demonstrated in figure 2 prove that the best SERS functions are revealed for silver rings and octahedral silver skeleton porous particles (figure 3).

![Figure 3. SERS spectra of a model dye rhodamine 6G and cyclohexanethiol recorded using silver ring substrates (right) and porous octahedral pseudomorphs (left), respectively.](image)

This finding is not surprising since both the materials possess hierarchic structures allowing the development of numerous “hot spots” [1, 2] greatly enhancing the Raman spectral signal from molecular analytes. The spectra in figure 3 revealed the most important vibration modes of the analytes at submicromolar concentrations, such bright spectra with distinct and intense peaks make a strong proof that the suggested preparation method of SERS-active materials is effective and can be highly recommended for a practical use.
5. References

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