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## Self-assembly of silver nanoparticles into dendritic flowers from aqueous solution

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Similar to folding of proteins into three-dimensional (3D) structure, self-assembly of metallic nanoparticles (NPs) into dendritic or other supramolecular structures is of greater interest, yet less understood. We observed spontaneous, template-free organisation of silver NPs into 3D, dendritic, elegant, flower-like structures from an aqueous solution containing  $\text{AgNO}_3$  and L-cysteine (Cys). The resultant NPs and dendritic structures were characterised using UV–Vis spectroscopy and scanning and transmission electron microscopy. The process initiated most likely by diffusion-limited aggregation in the liquid phase, which were further grown into elegant, dendritic flowers probably by evaporation of residual wetting layer of larger NPs. Electrostatic attraction between  $-\text{COO}^-$  and  $-\text{NH}_3^+$  groups of L-Cys on the surface of silver NPs may also have a role in their growth.

**Keywords:** dendritic; silver nanoparticles; L(+) cysteine; nanoflowers

### 1. Introduction

There is a great deal of interest in self-assembly of molecules into supramolecular structure, as the final shapes or 3D structures, in many cases, define their function or use in electronic, photonic, catalytic or biological applications [1–3]. This is clearly evident in biological macromolecules, whose functions mostly depend on their final 3D structures. Often a minor distortion in a given structure caused by mutation is detrimental and gives rise to genetic diseases. Folding in biological macromolecules relies significantly on the interactions between the side-chains (R-groups) that can be several carbons long and usually carry polar atoms such as N or O. The interactions of these R-groups with the solvent also play a vital role in their acquired 3D architecture. These interactions may often involve hydrophobic, electrostatic and/or H-bonding. Dendritic structures of metallic origin formed by spontaneous spatial arrangements, to a certain extent, mimic the biological phenomena, in that assemblies define the properties that depend on size, spacing and higher order structure. The growth of well-defined supramolecular structures of metals is more interesting as they lack variety of R-groups to interact with selves as well as solvent, and are not yet fully understood.

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There has been much focused effort in devising methods that exhibit a large degree of shape control. Discrete cobalt discs, rods and cubes [4], platonic gold nanocrystals [5] and other shapes have been synthesised from solution phase reduction. Many methods have been described for preparation of dendritic silver nanoparticles (NPs) [6–16].

Silver dendritic nanostructures have been prepared by a template method [7]. Preparation of template-free silver dendritic structures were reported by ultraviolet photoreduction technique using poly(vinyl alcohol) [8], by reduction using ethanol in the presence of poly(vinyl pyrrolidone) [3] and tetrathiafulvalene [9], by sono-electrochemical method in the presence of nitrilotriacetate or DNA [10,11], by solvothermal technique [12] and *in situ* reduction with polyvinylacetone [13]. All these methods, however, used polymers as a protective/capping agent for controlling the sizes and shapes of the NPs [14]. In recent years, others such as surfactant and zeolite were also used for such purpose [15,16].

The thiol group present in L-Cysteine (Cys) acts as an electron donor to a variety of organic and inorganic acceptor molecules. In this report, we utilised this property of Cys to reduce silver ion into silver NPs in aqueous solution. These silver NPs aggregate to form highly organised dendritic flower-like structures.

## 2. Experimental details

### 2.1. Nanoparticles synthesis

AgNO<sub>3</sub>, and L(+) Cys solutions were mixed in a medium sized test tube, vortexed for a few seconds and incubated at room temperature for 0–3 h, with stirring. In some experiments, NPs were collected by centrifugation using an analytical centrifuge (Clay Adams, Cat. # 0151) and washed twice with an equal volume of water. Then dried for 30 min at 50°C and resuspended in the desired volume of water. Alternatively, various volumes of 25 mM AgNO<sub>3</sub> and 5 mM L(+) Cys solution were allowed to react directly on the surface of the stubs and dried completely at 50°C prior to viewing by SEM.

### 2.2. UV–visible spectroscopy

Reaction mixtures were diluted to a final volume of 2.2 mL prior to a UV–Vis spectrum wavelength scan. The UV–visible spectra of each of the reaction mixtures were recorded between 300 nm and 700 nm using a Cary 300 Bio UV–Vis spectrometer with Varian UV Scan Application Version 3.00. A cuvette with 1 cm light path was used and dI H<sub>2</sub>O was used as blank.

### 2.3. Scanning electron microscopy

Nanoparticles collected from the reaction tubes by centrifugation were washed once with water, and again resuspended in 200 μL of H<sub>2</sub>O. Eighty microlitres of it was placed directly on a SEM stub and allowed to dry completely at 50°C. Alternatively, 50–100 μL of the reaction mixture was placed on the stub and was allowed to dry completely at 50°C.

The samples prepared on the stubs were observed under SEM at 15 kV using a Topcon SEM SM-510 (Robinson Detector, Orion version 6 software).

#### 2.4. Transmission electron microscopy

A sample reaction was used for transmission electron microscopic (TEM) analysis. TEM was performed on a sample mounted on a 300 Mesh Lacey carbon grid using a Philips EM430ST TEM with acceleration voltage of 300 kV.

#### 2.5. Measuring current between the SEM stub and NP solution

Direct current was measured by placing one electrode to the base of the stub, while the other in the solution containing either dI H<sub>2</sub>O, L(+) Cys, AgNO<sub>3</sub> or reaction mixture at T + 1 min.

#### 2.6. GC-MS analysis

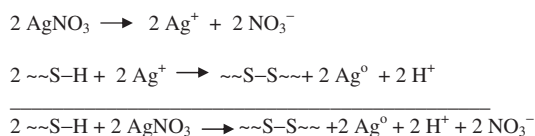
Reaction mixtures were injected into a GC column (Agilent 6890N) equipped with Mass Selection Detector (Model 5973). The inlet temperature was 170°C and increased to 350°C over a 15 min period.

### 3. Results and discussion

Aqueous solutions containing AgNO<sub>3</sub> and Cys were mixed and incubated at room temperature. The initially clear solution was turned into a reddish dispersion over time, possibly due to synthesis of silver NPs with assistance of electron transfer from Cys to silver ions in an aqueous solvent according to Scheme 1.

The presence of Cys-Cys (~~S-S~~) in the reaction mixture identified by the GC-MS analysis supports that the reduction of Ag<sup>+</sup> was proceeded through Scheme 1. However, the proton (H<sup>+</sup>) produced according to Scheme 1 should reduce pH of the reaction mixture, instead the pH was found to be constant throughout at 2.96. This is because the H<sup>+</sup> ion generated in the reaction was neutralised by the carboxylate (-COO<sup>-</sup>, pK<sub>a</sub> = 1.98) group present in the Cys.

The UV-Vis absorption spectrum taken immediately after mixing aqueous solutions of AgNO<sub>3</sub> and Cys showed a sharp and strong surface plasmon resonance absorption peak at



Scheme 1. Proposed reaction scheme for L(+) Cys induced reduction of AgNO<sub>3</sub>. Cys [H<sub>2</sub>N-CH(COOH)-CH<sub>2</sub>-SH] is shown by ~~S-H in the reaction.

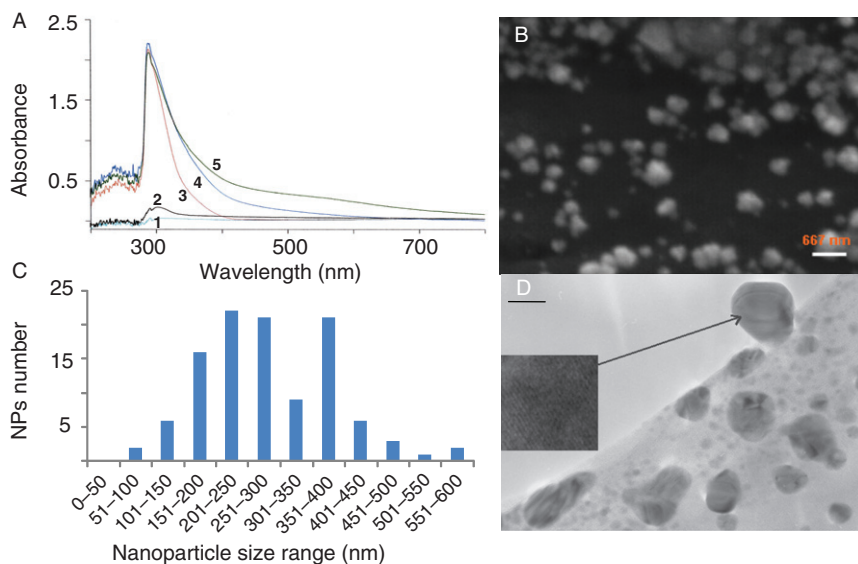


Figure 1. UV-visible absorption spectra of 5 mM Cys (1), 12 mM  $\text{AgNO}_3$  (2), colloidal mixtures containing Ag NPs produced by mixing  $\text{AgNO}_3$  (12 mM) and Cys (5 mM) read immediately (3), after incubation at room temperature for 5 h (4) or heating at  $50^\circ\text{C}$  for 3.5 h (5) against  $\text{H}_2\text{O}$ . The  $\lambda_{\text{max}}$  is observed at 300 nm. (B) SEM images (15,000x, bar = 667 nm) of the NP formation from a reaction mixture prepared with  $\text{AgNO}_3$  (12 mM) and Cys (5 mM) showing non-aggregated, isolated silver NPs, (C) histogram showing the size distribution of the NPs in (B). The particles have clear outline with an average size range 50–300 nm and (D) in good agreement with the result from the TEM image (bar = 50 nm). Inset D: HRTEM resolved single Ag particle showing the prominent fringes with regular spacing of 0.20 nm due to Moiré interference.

302 nm (Figure 1), due to the formation of small  $\text{Ag}_n$  clusters of 30–60 nm [13], compared with the theoretical calculated value of 380 nm in aqueous system [9]. A second broader absorption band appeared between 400 and 500 nm (Figure 1A), which may be attributed to the classical surface plasmon resonance of larger silver NPs [9]. The intensity of this broader band increased gradually over time, indicating formation of NPs aggregate. This notion was supported by SEM analysis. On the basis of SEM (Figure 1B) and TEM (Figure 1D) data, size of the isolated NPs ranged from below 50 to well above 300 nm (Figure 1C). The high resolution (HR) TEM image (Figure 1D inset) showed a well-resolved lattice spacing of 0.2 nm, corresponding to the (111) plane of Ag phase.

Viewing at lower magnification (Figure 2A) revealed, in addition to isolated NPs, numerous larger aggregate particles, most of which were 3D, dendritic and elegant flower-like (Figure 2B and C) structures, in which one particle is formed on another and adhered to the growing structure in all directions (Figure 2D).

In general, non-equilibrium growth and molecular anisotropy are the prerequisites for dendritic fractal formation [17,18] in liquid phase. In this study, although the growth mechanism of the dendritic silver is not fully understood, some insights have been obtained from the SEM images and UV-Vis spectra. Increase in intensity of the broader absorption

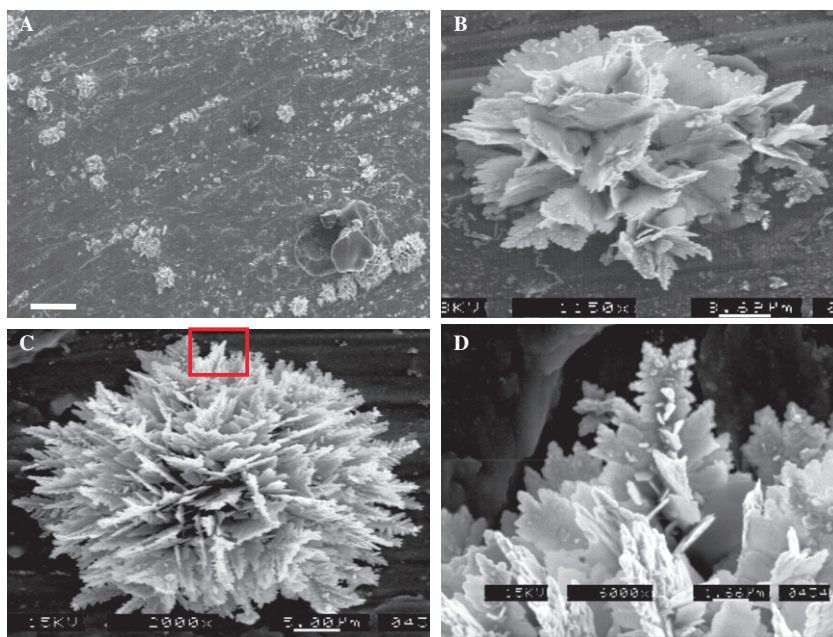


Figure 2. (A) SEM image (105x, bar = 35.2  $\mu\text{m}$ ) the reaction mixture prepared from aqueous solution of  $\text{AgNO}_3$  (15 mM) and Cys (1 mM) dried on an aluminium stub, showing numerous self-assembled structures, (B) SEM image (1050x, bar = 3.6  $\mu\text{m}$ ) of a self-organised structure into flower, (C) SEM image (960x, bar = 5.0  $\mu\text{m}$ ) of another self-assembled flower, (D) expanded SEM image (4100x, bar = 1.16  $\mu\text{m}$ ) of the region marked by the red box in (C), showing wafer-shaped, dendritic structures in the nanoflower.

band around 450 clearly indicated larger NPs formation, most likely by diffusion-limited aggregation (DLA), in which rapidly forming reduced silver atoms aggregated on top of each other and adhered before diffusing away as proposed in an earlier report [16]. The requirement of 10-fold higher concentration of the reductant Cys for the dendritic growth supports such hypothesis. Other conditions such as rapidly evaporating films of dispersed NPs, dipole-directed self-assembly and electrostatic interaction, in combination, may also have played a role [15]. It is shown earlier that Ag in the particles readily forms a complex and distributes uniformly with S, if present enough in the reaction and exhibits an absorption band of  $\sim 300$  nm [9]. The instantaneous exhibition of the absorption peak at 302 nm, which virtually remained unchanged over time, although the band became broad with a long tail due to aggregation of NPs, suggests that this peak is entirely due to complex formation between  $\text{Ag}^+$  and Cys and that reduction of  $\text{Ag}^+$  to  $\text{Ag}^0$  has taken place slowly in the complex. There is a report that says some surface modified nanocolloids do not produce the characteristics plasmon absorption band [9,19]. Both Cys and Cys–Cys contain a negatively charged carboxylate ( $-\text{COO}^-$ ) ion and a positively charged amino ( $-\text{NH}_3^+$ ) ion, which on the surface of the silver NPs may well provide another platform for aggregation by electrostatic attraction. Voltage measurements showed a value of  $-350$  mV

for the reaction mixture, which was significantly different from  $-420\text{ mV}$  for  $\text{AgNO}_3$  solution,  $+1200\text{ mV}$  for Cys solution and  $+700\text{ mV}$  for water when placed on the aluminium stub and may well support such notion that electrostatic force may well be involved. Although the mechanisms proposed here are disparate, they may prove to be synergetic in the assembly of well-organised dendritic structures. Further studies are required to fully understand the growth mechanisms of these beautiful, dendritic flowers.

#### 4. Conclusions

Spontaneous, template-free organisation of silver NPs into dendritic, flower-like structures from an aqueous solution containing  $\text{AgNO}_3$  and L-Cys was observed. Aggregation of the NPs initiated in the liquid phase by DLA and developed into dendritic structures, most likely by evaporation of residual wetting layer. By providing electrostatic attraction, charges on Cys on the surface of the NPs may also have played a role in their formation.

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