

STUDY OF THE KINETICS OF NUCLEATION AND GROWTH OF SILVER NANOPARTICLES: UV-VISIBLE SPECTROSCOPY VS. ATOMIC FORCE MICROSCOPY AND TRANSMISSION ELECTRON MICROSCOPY

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Abstract

Silver nanoparticles have been the subjects of research interest because of their unique properties and extensive use in modern-day applications. A variety of preparation techniques have been reported for their synthesis but among them mostly recognized is a modified version of the Turkevich citrate method. In this study, we also chose this method of silver nanoparticle synthesis. The synthesized nanoparticles were characterized first, traditionally with UV-Visible spectroscopy and then their sizes and shapes were identified employing Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM). From the UV-Vis data were extracted the rate constants for the nucleation (k_1) and growth (k_2) of the silver nanoparticles, and then these constants were further used to fit those obtained from AFM and TEM. Using the values of k_1 and k_2 independently in the two experimental methods validated and supported the well-acknowledged two-step mechanism of slow nucleation and fast autocatalytic surface growth.

Key words: silver nanoparticles, UV-Vis spectroscopy, atomic force microscopy (AFM), transmission electron microscopy (TEM), Finke–Watzky kinetic model

Introduction. Silver nanoparticles are of great interest for many applications in catalysis, electronics, bio-labelling surface-enhanced Raman scattering,

etc. [1]. One of the popular synthesis methods of silver nanoparticles is almost identical to the most cited Turkevich method for the synthesis of gold nanoparticles [2] but in it as a metallic precursor silver nitrate is used instead of tetrachloroauric acid together with sodium citrate as a reducing agent [3]. The obtained silver nanoparticles were reported to be with a diameter between 60 and 100 nm depending on the experimental conditions. The investigation of the size-dependent properties of small metal nanoparticles is highly motivated because many physical phenomena, e.g. the relative contribution from radiative damping through resonant scattering and absorption, are strongly dependent on the particle size [4]. As it was established if the particles are smaller than 30 nm in diameter then the absorption dominates over the light scattering which in turn becomes more prevalent as the particle size increases [5]. Hence, finding suitable experimental methods applicable for measuring transition-metal nanoparticles' sizes at the atomic and nanoscale levels with high accuracy is imperative for understanding the mechanism of their formation and growth [6]. The AFM proved to be a new and reliable method for studying the matter at the nano- and subnanometer level and broadly applicable for studying the mechanisms of metal-nanoparticle growth by applying convenient and easily executable experimental protocols [7].

There are two main aims of this work. First, AFM will be applied following one of the protocols for imaging silver nanoparticles. They will be deposited from the reaction solution on solid mica supports during their formation, at 6 and 8 min, respectively, from the beginning of the synthesis process. The AFM images will be analyzed, and some will be compared with the data obtained from TEM images.

Second, the obtained AFM data will be used to measure the nanoparticle size. Together with the UV-Vis absorption spectra detected at different reaction times, the data will be quantified and kinetically interpreted with the well-established Finke-Watzky (F-W) kinetic model [6, 8] – thus the nucleation (k_1) and growth rate (k_2) constants, respectively, will be evaluated.

Materials and methods. Chemicals and reagents. Silver nitrate (AgNO_3 , $M_W = 169.87$ g/mol) and Trisodium citrate dihydrate ($\text{Na}_3\text{C}_3\text{H}_5\text{O}(\text{COO})_3 \cdot 2\text{H}_2\text{O}$, $M_W = 294.1$ g/mol) were both of analytical grade and obtained from Merk (Germany). All the solutions were prepared with deionized water.

Synthesis procedure. The synthesis procedure, based on classical Lee and Meisel citrate method [2] was performed as follows: 10 ml of 47 mM silver nitrate (AgNO_3), was added to 88 ml deionized water. This mixture was stirred at 350 rpm and heated up to 90 °C, after that 2 ml 1% solution of trisodium citrate ($\text{Na}_3\text{C}_3\text{H}_5\text{O}(\text{COO})_3$, $MW = 258.06$ g/mol) was added as reducing and stabilizing agent. The colour of reaction mixture changed from colourless to yellow and at the end to green-gray for 60 min. These colour changes correspond to the nucleation and growth of spherical silver nanoparticles into the reaction mixture.

The initially formed Small Silver Nanoparticle (SSNPs) nuclei grow from sizes of $5 \div 10$ nm to 100 nm in diameter at the end of reaction.

Characterization methods. *UV-Vis absorption spectroscopy.* The UV-Visible absorption spectra of silver nanoparticle dispersions were determined by Spectrophotometer Thermo Scientific Evolution 300 (USA). The samples of nanoparticle solutions were taken at different reaction time intervals. Deionized water was used as a reference sample.

Transmission Electron Microscopy (TEM). The morphology and the size of silver nanoparticles and Small Silver Nanoparticle (SSNPs) nuclei prepared by citrate synthesis were determined by JEM-2100 LaB6 Transmission Electron Microscope (JEOL Ltd., Japan). The sample preparation for TEM was made as silver nanoparticles solution was deposited on a copper grid and after evaporation of the liquid the samples were analyzed.

Deposition of silver nanoparticles. Deposition procedure involved dropping solution of silver nanoparticles with different size taken during the synthesis on mica solid supports. Freshly cleaved quadratic mica sheets (Structure Probe Inc./SPI Supplies, West Chester, PA, USA) with sizes 10×10 mm glued to the metal pads were used for silver nanoparticles and Small Silver Nanoparticle (SSNPs) nuclei deposition. From the dilute nanoparticle's solution about 100 μ L were deposited on the mica support and spin-coating method was used. The spin coating Precision Spin Coater Model KW-4A (West Chester, PA, USA) was used. The timer I was adjusted for 10 s at 0.4 rpm and the timer II for 60 s at 2000 rpm. After the spin-coating procedure the samples were dried out with nitrogen gas and then transferred for AFM measurement.

Atomic Force Microscopy (AFM). AFM imaging was performed on the NanoScope V system (Bruker Ltd, Germany) operating in tapping mode in air at room temperature. The silicon cantilevers (Tap300Al-G, Budget Sensors, Innovative solutions Ltd, Bulgaria) with 30 nm thick aluminium reflex coating were used. The cantilever spring constant was 40 N/m and the resonance frequency was 300 kHz. The tip radius was less than 10 nm. The scan rate was 1 Hz and the images were captured in the height mode with 512×512 pixels in a JPEG format. The Nanoscope software was used to flatten the images, for section analysis and particle size determination.

Results and discussion. The optical properties of small metal nanoparticles with diameters less than 20 nm are dominated by the collective oscillation of the valence electrons that interact with the electric field of the incident radiation which in turn induces the formation of a dipole in the nanoparticles [9]. As a result, the UV-Vis spectra of the silver nanoparticle dispersion due to surface plasmon resonance have an absorption maximum at about 430 nm whose intensity depends on the nanoparticles' size. Figure 1 presents a typical kinetic curve obtained during the process of silver nanoparticles' nucleation and growth.

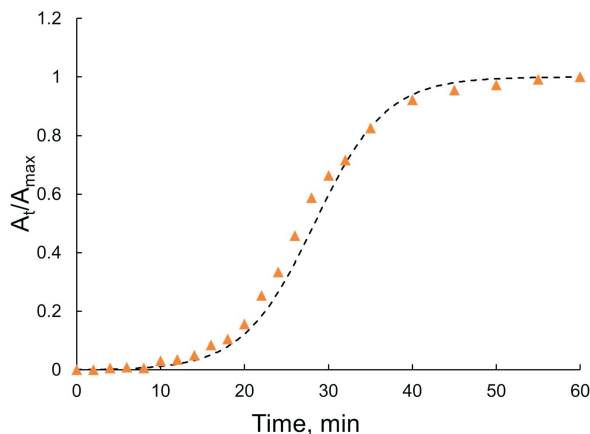


Fig. 1. Typical kinetics curve obtained from the UV-Vis data within the time course of the reaction that spans from the occurrence of silver nuclei until their growth to nanometer-sized particles. The fit line follows the F-W kinetic model. The inset: Data points were collected from the change of the absorbance spectra maxima versus time

The S-shaped dependence of experimental data is well-fitted to the two-step F-W model [6] with kinetics constants $k_1 = 3 \times 10^{-4} \text{ min}^{-1}$ and $k_2 = 235 \text{ mM}^{-1} \text{ min}^{-1}$. These constants were similar to reported elsewhere constants of the F-W model, applied for the synthesis of silver nanoparticles, $k_1 = 4 \div 6 \times 10^{-4} \text{ min}^{-1}$ and $k_2 = \sim 145 \text{ mM}^{-1} \text{ min}^{-1}$, obtained, though, in slightly different experimental conditions, e.g. smaller concentrations of the sodium citrate [8].

Further, we will exploit the spectroscopy data and the extracted from them F-W constants and correlate them with measurements for the nanoparticles' size obtained from TEM and AFM, namely with the equation derived from F-W two-step mechanism [7],

$$(1) \quad \frac{d_t}{d_{\max}} = \left(1 - \frac{k_1 + k_2 [A]_0}{k_2 [A]_0 + k_1 e^{(k_1 + k_2 [A]_0)t}} \right)^{\frac{1}{3}},$$

where d_t and $d_{\max}$ are the diameters of the silver nanoparticles in the time of their synthesis t and at the end of the synthesis process, respectively, while $[A]_0$ is the initial concentration of the precursor. Figure 2 presents TEM images of silver nanoparticles extracted from the reaction solution and dropped on the copper grid at the 6th min (Fig. 2A), and at the 30th min of the synthesis (Fig. 2B).

The TEM image of the Ag nanoparticles and the histogram of their size distribution in Fig. 2A show that they are spherical and relatively monodisperse

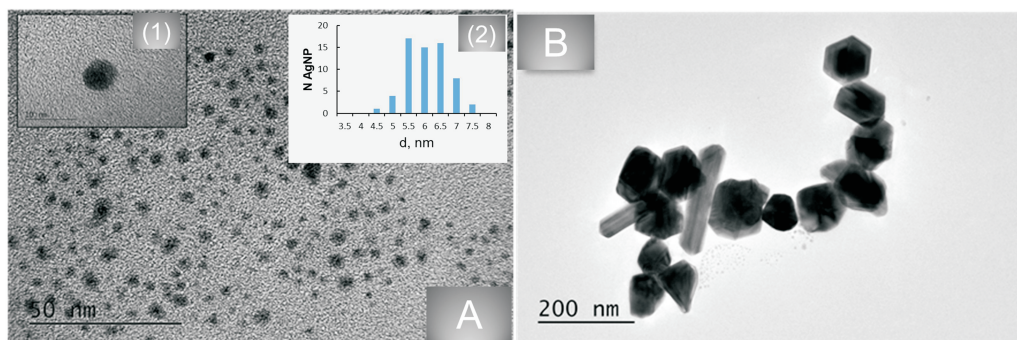


Fig. 2. TEM micrographs of the synthesis silver nanoparticles at (A) the initial (6th min), scale bar is 50 nm, and (B) at the 30th min of the reaction, scale bar is 200 nm. The insets in (A): (1) Image of an individual AgNP, scale bar is 10 nm; (2) The histogram of the Ag nanoparticles' size distribution

with diameters around 6 nm. In comparison, during their synthesis at the 30th min (Fig. 2B), but especially at the end of the reaction process, they have various shapes (e.g., spherical, hexagonal, and cylindrical). For example, as seen in Fig. 2B, 200 nm long rod-shaped particles can also be observed, however, their number was less than 2% of the total number of Ag nanoparticles and substantial at the end of the synthesis. Hence, for the analysis, we used only the data at the 30th min and we measured only the spherical particles with sizes within the range of 35 nm ÷ 75 nm and average about 55 nm. Analyzing TEM micrographs of such Ag colloids it was reported elsewhere that these particles have an average diameter of between 40 ÷ 100 nm [2]. Our result is not a surprise, though, because it is well known that the shape and size-controlled synthesis of silver nanoparticles is tedious and challenging [1, 2].

The application of the AFM for characterization of small metal nanoparticles is an experimental approach, that proved to have some advantages over TEM [7]. Figure 3 presents 2D- and 3D-AFM images together with cross-section analysis of small silver nanoparticles obtained after solution deposition of silver suspension on the mica solid supports in the course of their citrate synthesis. Figure 3 presents AFM images with two different magnifications of the scanned area, 5 μm (Fig. 3A) and 1.5 μm (Fig. 3B), respectively. In the AFM image in Fig. 3A when the scanning XY area was 5 $\mu\text{m} \times 5 \mu\text{m}$ the silver nuclei at the mica surface were visible and easily detectable while when XY area was 1.5 $\mu\text{m} \times 1.5 \mu\text{m}$, some details showing their clustering were also visible (Fig. 3B). From the 3D-AFM images in Fig. 3 and cross-section analysis, it is seen that the silver nuclei are spherical. We also determined the size distribution of the silver nanoparticles from a histogram that gave us the number of silver nanoparticles versus their size as measured from the AFM images.

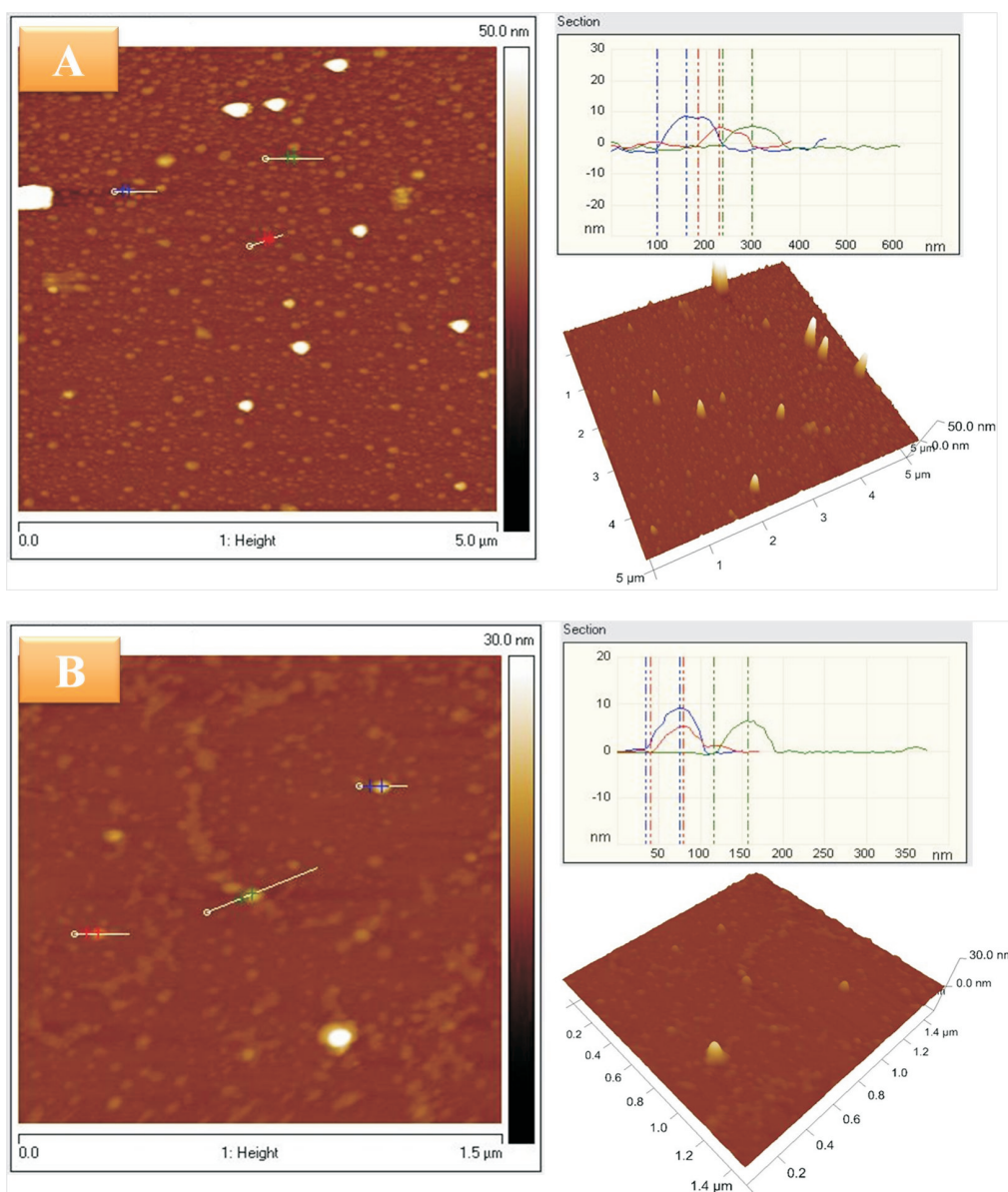


Fig. 3. 2D- and 3D-AFM images and section analysis obtained after depositing of silver nanoparticles suspension on mica support the classical citrate synthesis, with magnification (A) 5 μm and z-range $z = 50$ nm and (B) 1.5 μm and z-range $z = 30$ nm. The inset in the 2D image: The histogram of the Ag nanoparticles' size distribution

As an example of the procedure for measuring their size in Fig. 3B, in the inset of the 2D image is presented a histogram for the size distribution of the SSNPs measured from the sample extracted at the 6th min. From the section analysis of about 100 nanoparticles at different sample locations the mean diameter of

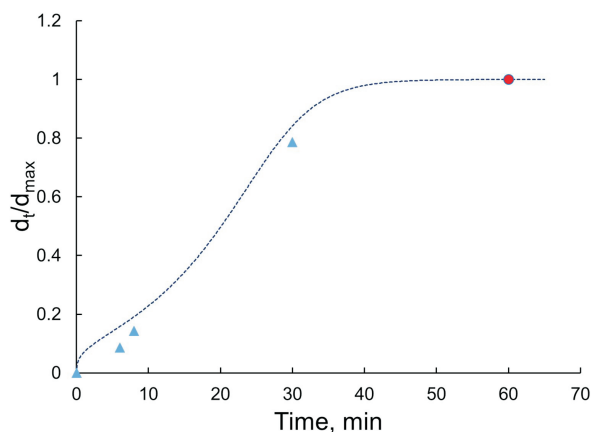


Fig. 4. The kinetics curve of silver nanoparticles' growth obtained from AFM image data at the 6th, 10th, and 30th min, and the data from [2] for the ultimate nanoparticle size at the end of their synthesis (red circle dot on the graph). On the graph is presented the F-W fit according to Eq. (1) (dotted line)

about 6 nm was determined, which is close to the nanoparticle size determined by TEM. The size of the nanoparticles measured at the 8th min of their synthesis was found to be about 10 nm. Finally, we used the values for k_1 and k_2 extracted from *UV-Vis* data, to fit with Eq. (1) the experimental from AFM image analysis for the nanoparticle sizes. The kinetic curve in Fig. 4 shows the normalized diameters of Ag nanoparticles versus time. We used only our data for the 6th, 10th, and 30th min but for the ultimate size, we prefer to use to fit the data from the literature [2].

The diameter values d_t at corresponding time t , normalized to the maximal diameter at the end of the synthesis, $d_{\max}$ were acquired from the maxima of the size distributions data obtained from the AFM images within the time course of their synthesis. It confirms that the F-W model applies to the kinetics of the synthesis of Ag nanoparticles similarly to the citrate synthesis of gold nanoparticles [7].

Conclusions. The future and potential use of silver nanoparticles in many areas of pharmacy and medicine, especially for cancer diagnosis and treatment are immense, hence finding reliable methods and understanding the mechanisms of their synthesis will likely establish a standard platform for the prevention of some diseases, especially those caused by infection with pathogens [10,11]. In this article, first, we applied *UV-Vis* spectroscopy and then, AFM and TEM to study the kinetics of silver nanoparticles synthesized by the popular citrate method. From the first method, we obtained the values for the rate constants k_1 and k_2 corresponding to the nanoparticle nucleation and growth, respectively. Then using

their values, we fitted the experimental data for the nanoparticle size from AFM and TEM with the F–W model thus confirming the validity of the F–W 2-step mechanism of nucleation and growth of metal nanoclusters.

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