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An Application of the Thermodynamic Approach to Explain the Shape Selection During Light-Induced Growth of Silver Nanoparticles

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Synthesis of silver nanoparticles of different shapes and sizes by the chemical reduction of Ag^+ may be strongly influenced by the light irradiation. A key question is understanding the mechanism underlying the transformation of initial spherical seeds into prisms and decahedra under visible light. In this study, we summarize existing theories of light-induced nanoparticle growth and apply a thermodynamic approach to shape selection during the synthesis of silver nanoparticles. We propose a universal thermodynamic model that explains both the influence of light on the synthesis and transformation of silver nanoparticles in the presence of H_2O_2. This model accounts for the shift of the chemical potential relative to interfacial energies and the monoatomic step energies on the {111} facets. Our results demonstrate that the morphology of silver nanoparticles is determined primarily by photon energy rather than by the chemical nature of the reagents.

Keywords: silver nanoparticles, light-induced synthesis, spectra, optical properties, photon energy, etching, surface energy, crystal growth, thermodynamics, solution.

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Introduction

Silver nanoparticles (NPs) are being extensively studied due to their remarkable chemical, physical, and biological properties [1, 2]. Decahedral and prismatic particles have a larger surface area than spheres for a given volume, which can enhance their interaction with bacterial cells [3, 4]. Silver prisms and decahedra can be used as catalytic converters and sensors [5, 6]. Surface plasmon resonance (SPR) arises when incident light induces coherent oscillations of conduction electrons in a metal nanoparticle, producing a dipole resonance. For silver and gold, the required energy typically lies in the visible range and depends on nanoparticle composition, size, shape, and surrounding environment [7, 8]. SPR not only determines the color of nanoparticles but also controls their functionality in surface-enhanced Raman scattering (SERS) detection and in their use as markers, contrast agents, or therapeutic agents for biomedical applications [8-10]. As reported in [11], plasmon-mediated synthesis is recognized as a controllable method for producing silver nanostructures with diverse morphologies. This process is driven by visible-light irradiation in the presence of trisodium citrate and plasmon-active seed nanoparticles ("plasmonic seeds"). Plasmon-mediated and photochemical reactions differ fundamentally in mechanism. In photochemistry, excitation produces a molecular excited state that acts as a stronger oxidant or reductant. In contrast, excitation of the SPR of a metal nanoparticle initiates several processes that facilitate metal ion reduction [8].

The key photophysical effects of SPR excitation for chemistry can be generally divided into three categories:

1) local heating of the nanoparticle and the surrounding environment;

2) the concentration of incident light near the particle surface leads to a stronger electromagnetic field and photon flux for nearby molecules;

3) the generation of energetic electron-hole pairs

that enable charge transfer reactions between the particle and surrounding molecules.

The predominant effect of Ag nanoparticle growth in plasmon-mediated synthetic methods is not yet clearly understood [11].

I. Synthesis and characterization of silver nanoparticles

The synthesis of silver nanoparticles was carried out in two stages. Firstly, the seed solution of silver nanoparticles was prepared by sequentially adding 2 mL of a 0.01 M $AgNO_3$ solution, 5 mL of a 0.05 M trisodium citrate ($Na_3C_6H_5O_7$) solution, 0.5 mL of a 1% polyvinylpyrrolidone solution, and 7 mL of distilled water to clean, dry test tubes. The solution was mixed for 5 minutes. Then, 8 mL of a 0.01 M $NaBH_4$ solution was added, and the test tubes were vortexed for 10 minutes to ensure homogeneous distribution of the reagents. The resulting solution was yellow, indicating the formation of silver nanoparticle seeds. Secondly, the seed solution was irradiated in a radial irradiator with 24 LEDs with different wavelengths of blue light: 450 nm and 462 nm for 4 hours to obtain decahedral silver nanoparticles.

Remarkable influence of wavelengths on NPs is illustrated below. Figures 1, 2 represent data that corresponds to the influence of different excitation wavelengths of light on the nanoparticle's diameter.

From the statistics (fig. 1 (c), fig. 2 (c)), we can assume that even a slight change in the irradiating light (12 nm) leads to the formation of nanodecahedra from the same seed solution with different sizes. When the irradiation wavelength of light is 450 nm, the average diameter of the obtained nanodecahedra is 34 nm. When the wavelength of light is 462 nm, the average diameter of the obtained nanodecahedra is 50 nm. It has been established that using a photochemical synthesis, various types of silver nanoparticles can be formed from citrate-mildly stabilized silver nanoparticles through irradiation with inexpensive, narrow-band LEDs. Stamplecoskie et al. assume that it is rather the excitation wavelength and induced electromagnetic field that directs the growth [12]. However, this hypothesis does not account for the reduction stage of silver ions by sodium borohydride. It was experimentally proven that from the same initial "seeds" under irradiation of light with different energies, differently shaped particles are synthesized [13].

Three different theories of the transformation process from silver seeds into particles of different shape are discussed in the next section.

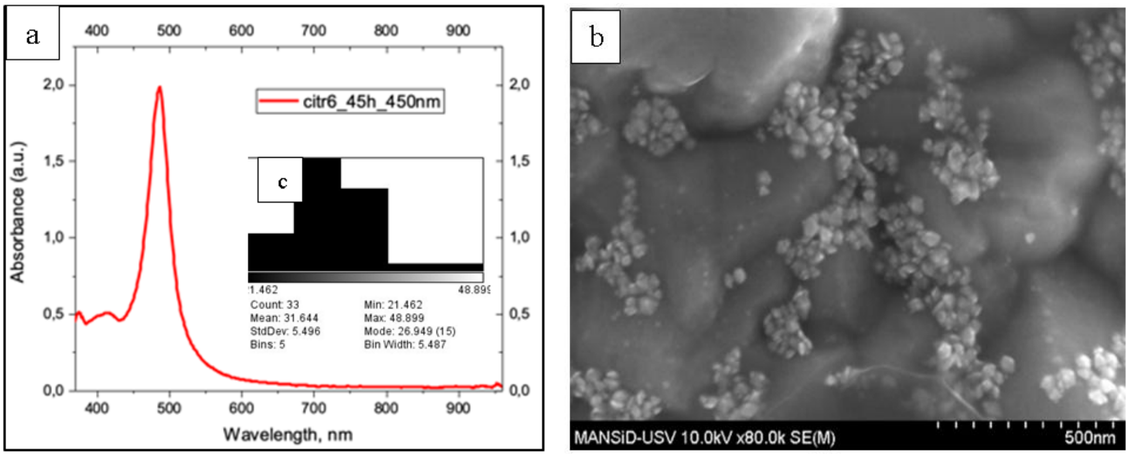

Fig. 1. Absorption spectrum (a), SEM image (b), and diameter distribution (c) of nanodecahedra samples, synthesized by irradiation with a wavelength of light 450 nm for 4 hours.

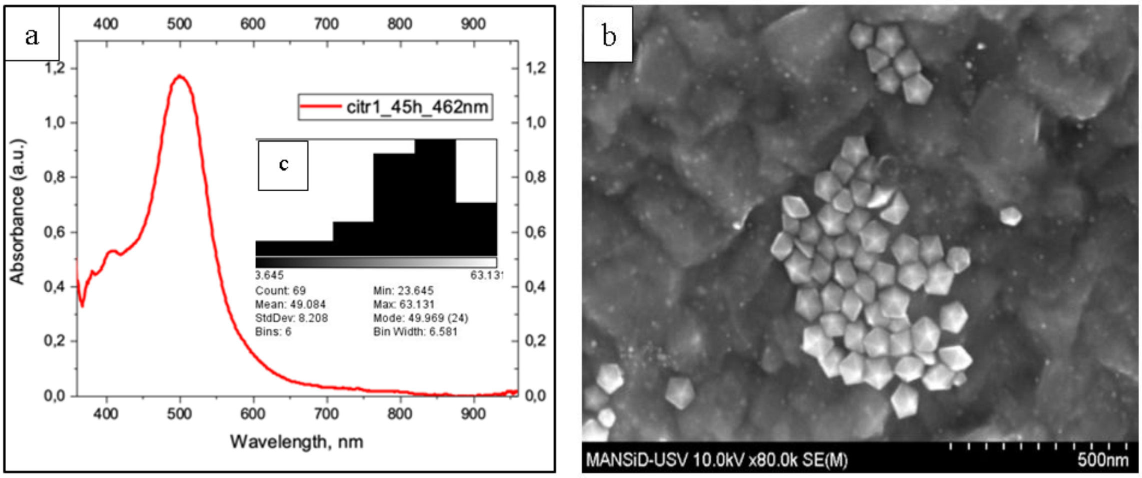

Fig. 2. Absorption spectrum (a), SEM image (b), and diameter distribution (c) of nanodecahedra samples, synthesized by irradiation with a wavelength of light 462 nm for 4 hours.

II. Thermodynamical model of nanoparticles' shape formation during light-induced synthesis

Most noble metals crystallize in the face-centered cubic (fcc) cell structure, in which atoms occupy the cube corners and the centers of all six faces [14]. According to Xia et al., fcc metals typically form icosahedral, decahedral, and Wulff polyhedral (truncated tetrahedron) seeds, and the corresponding nanocrystals are thermodynamically favored [15]. The main idea of Xia et al.'s theory is that the shape transformation of a metal nanocrystal can be considered a specific case of Ostwald ripening, guided by both thermodynamic and kinetic factors. As for the driving force, this transformation is driven by the minimization of the total interfacial free energy at constant volume. The kinetics are primarily determined by the surface atom diffusion, which is enhanced by heating, stirring, or oxidative etching. Additionally, Xia et al. proposed that the final shape of a nanocrystal is determined primarily by the crystallographic structure of the seed and the preferential adsorption of capping agents on specific crystal facets: polyvinylpyrrolidone on {100} facets and sodium citrate on {111} facets.

However, this concept mostly refers to the polyol synthesis of silver nanoparticles, where the reaction medium is heated to temperatures above 100°C. Xia et al.'s theory does not account for how different crystal facets develop from the same starting solution. In the case of light-induced synthesis at room temperature, the same initial spherically shaped silver seeds may have a mixture of {111}, {100}, and {110} facets, however, the selection of the final shape is due to the energy difference of light waves.

Another hypothesis formulated by Mirkin et al. [11] suggests that slower reduction rates of Ag^+ favor deposition onto {100} facets, resulting in nanoprisms, while faster reduction rates favor deposition onto {111} facets, resulting in bipyramids [16]. Red-shifted excitation wavelengths increase the reaction rate and yield nanorods with higher aspect ratios [17]. Kinetically controlled growth occurs under slow metal ion reduction rates, where Ag^+ is deposited at the highest-energy sites of the nanostructure, leading to growth at the edges of triangular nanoprisms or at the ends of nanorods, where twin defects are exposed and curvature is high. The same group suggested in [11] that the condition for obtaining nanoparticles of the desired shape is that nucleation of seeds must be the same crystallographic structure: planar-twinned seeds yield triangular prisms and bipyramids, while cyclic penta-twinned seeds form penta-twinned nanorods. Nonetheless, reaction conditions must also favor the growth of a single seed type. The oxidative dissolution process can selectively etch competing seed particles. For example, high-intensity, short-wavelength visible light has been shown to promote the growth of Ag penta-twinned nanostructures [18]. By the end of the reaction, only Ag decahedra remained due to the oxidative dissolution of planar-twinned plates, which were observed during growth.

Shape transformation also occurs through irradiation with light, whose energy is far from plasmon resonance (off-resonance), meaning that plasmons in particles do not play a leading role in the growth process of differently shaped particles. Finally, the influence of excitation wavelength on particle growth is not well established, particularly at the nucleation stage.

The most reasonable hypothesis of shape selection of metal nanoparticles, in our opinion, is represented by Viswanath et al. [19, 20]:

This theory applies an approach where different regimes of thermodynamic and kinetic control produce nanoparticles with different shapes. The metal's reduction driving force is quantified by calculating the free energy change for the reaction under specified conditions. It was established that plate-like structures form under low driving force conditions. In two-dimensional structures, kinetic control is related to a low driving force that enforces a layer-by-layer crystal growth, and facet selection (symmetry breaking). In chemical deposition, adatoms diffuse across the surface until they reach a step site, where they are incorporated onto the surface. The overall crystal growth is controlled by a balance between bulk energy reduction, which favors growth, and surface energy increase, which favors dissolution. This dynamic process drives the evolution of seeds into nanocrystals [14, 21].

Crystal growth proceeds through nucleation and growth, driven by the associated change in volume free energy change. Cahn et al. [22, 23] provided a quantitative analysis of this driving force and its relation to the crystal growth mechanism. For the growth of crystals by solidification in one-component systems, the degree of undercooling quantifies the driving force. Two distinct growth regimes have been identified: continuous growth (3D) via normal interface motion at large driving forces and layer-by-layer (2D) growth through the formation of steps and their lateral motion on the surface at low driving forces [24].

The critical driving forces calculated by this theory for Ag are -46 kJ/mol for layer-by-layer growth on {111} planes ($-\Delta G_{2D}$) and -144 kJ/mol for continuous growth mechanism ($-\Delta G_{3D}$) (Fig. 3) [25].

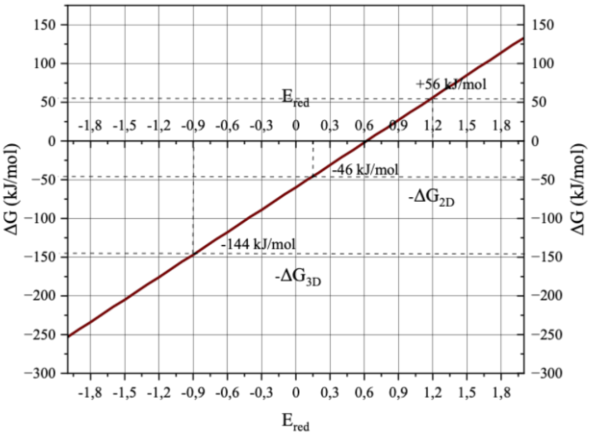

Fig. 3. Variation of chemical free energy change with the reduction potential of any arbitrary reductant at constant temperature T = 300 K, for Ag with 1 mM concentrations of the Ag^+ ion.

The critical driving force for any facet is proportional to its interfacial energy and is inversely proportional to the step height. Thus, the lowest energy facet with a large step height, such as {111} facets in fcc crystals, will advance when the available driving force is low. The authors [19, 20] assume that the critical values of driving forces are independent of the exact reaction leading to the crystal formation. The appropriate reaction conditions can be chosen to keep the driving force below the critical value for layer-by-layer growth, forming plate-shaped structures. The chemical driving force (free energy change) can be quantified using the Nernst equation for the reduction of noble metal salts by reducing agents. For a chemical reaction, the driving force can be widely tuned by adjusting the synthesis medium pH, reaction temperature, metal salt concentration, and the choice of reducing agent.

According to the data reported in [26, 27], primary chemical reactions involved in the plasmon-mediated generation of Ag nanostructures are as follows:

a) dissolution of Ag nanoparticles by oxygen to Ag^+ and hydroxide ions:

$$2Ag^0 + {}^1\!/_2\,O_2 + H_2O \rightarrow 2Ag^+ + 2OH^-$$

b) oxidation of citrate to 1,3-acetonedicarboxylate and carbon dioxide yielding two electrons:

$$C_6H_5O_7{}^{3-} + OH^- \rightarrow C_5H_4O_5{}^{2-} + CO_2 + H_2O + 2e^-$$

c) reduction of Ag^+ to Ag^0:

$$2Ag^+ + 2e \rightarrow 2Ag^0$$

It was confirmed by ^1H NMR spectroscopy, that the oxidation of sodium citrate leads to the formation of 1,3-acetonedicarboxylate and carbon dioxide, yielding two electrons that are used to reduce Ag^+ ions in the solution to Ag^0, and then further decomposes to acetoacetate [27].

In our previous study [28], cyclic voltammetry of sodium citrate in aqueous solution was performed. It was established that this compound oxidizes at a potential close to 1.0 V against the Ag/AgCl electrode, which corresponds to 1.197 V against the standard hydrogen electrode. This value is close to the oxidation potential associated with the conversion of sodium citrate to 1,3-acetonedicarboxylate. If the chemical driving force for the reduction of Ag^+ by trisodium citrate is calculated, where $E^0_{ox}(Cit^{3-}) = +1.2$ V, $E^0_{red}(Ag^+) = +0.62$ V, $[Ag^+] = 1$ mM, $[C_6H_5O_7{}^{3-}] = 2.5$ mM, $E^0_{cell} = -\ 0.58$ V, the following equation is obtained:

$$\Delta G_r\ (\text{kJ/mol}) = +55.6 + 0.019(\text{pH})T - 0.082T$$

The Gibbs free energy change is positive, indicating that the reaction is not spontaneous. This explains why seed solutions remain stable in the absence of irradiation over extended periods. Sodium citrate has too low a reduction potential to reduce Ag from seeds, but it is sufficient to stabilize the particle surface in the presence of light. Exposure to light of different energies induces the transformation of spherical seed particles into 2D structures (prisms), an intermediate region comprising a mixture of 2D and 3D structures, and 3D structures (decahedra) as the photon energies increase. Long-term storage of the seed solution (over 2 years) shows that Ostwald ripening of seeds and the formation of more thermodynamically stable particles (i.e., prisms) occur even without irradiation. The effect of the H_2O_2 produces more stable particles through oxidative etching. To accelerate the transformation of thermodynamically stable seeds, light appears to enhance either photoreduction or oxidative etching simultaneously [29-31].

Irradiation accelerates the reduction of Ag^+ ions to such an extent that not only two-dimensional structures (prisms) but also three-dimensional ones (decahedra) are obtained. Seeds dissolve faster, producing more Ag^+ ions that subsequently form nanoparticles. Additional energy, in the form of photons, allows the reactants to overcome the barrier for the initiation of silver reduction and the formation of nanoparticles of various shapes. Photons of different energies change the chemical potential in different ways, thereby influencing the driving force in proportion to the Gibbs free energy change (ΔG). Accordingly, irradiation with red and green photons shifts the reactants' chemical potential into a two-dimensional region ($0 < \Delta G < -\ 46$ kJ/mol), whereas irradiation with blue photons shifts it into a three-dimensional region ($\Delta G > -\ 144$ kJ/mol) (Fig. 4). Excitation wavelength plays a crucial role in determining particle morphology. The main reason for shape diversity is the photon energy of visible light (kJ/mol), which is comparable to the energy required for the transition from flat to three-dimensional Ag structures.

The decahedral morphology represents an alternative structure that forms when ten {111} facets grow simultaneously, instead of just two, because there is enough energy for the formation of new facets, but not enough for the growth of disordered ones. The initial reduction of almost all silver into seeds decreases the concentration of silver ions so much that it shifts ΔG to higher energies.

Theoretically, the energy of red light is sufficient for spontaneous reduction. In an ideal case, this energy could be fully utilized to overcome the free energy barrier of a reaction. A red photon can have an energy up to 2 eV, corresponding to $\Delta G \approx -193$ kJ/mol, while for a blue photon, ΔG can reach -260 kJ/mol, a difference of about 70 kJ/mol. Lower energies promote a larger surface area of the {111} facets. For this reason, prisms vary broadly in size, while decahedra show size variations only within a narrower range. The energy difference between the larger (50 nm) and smaller (35 nm) decahedra is estimated to be 10 kJ/mol (Fig. 1, 2).

We assume that this thermodynamic model is versatile and should not depend on the nature of the reagents used. This is confirmed by numerous studies on the transformation of silver nanoparticles with different shapes into prisms under the influence of H_2O_2 [32, 33]. In such a process, a competing redox process can occur. The shape-defining reaction is the reduction of Ag^0 by H_2O_2. Using this approach, the free energy change for the reaction between Ag^+ and H_2O_2 can be calculated:

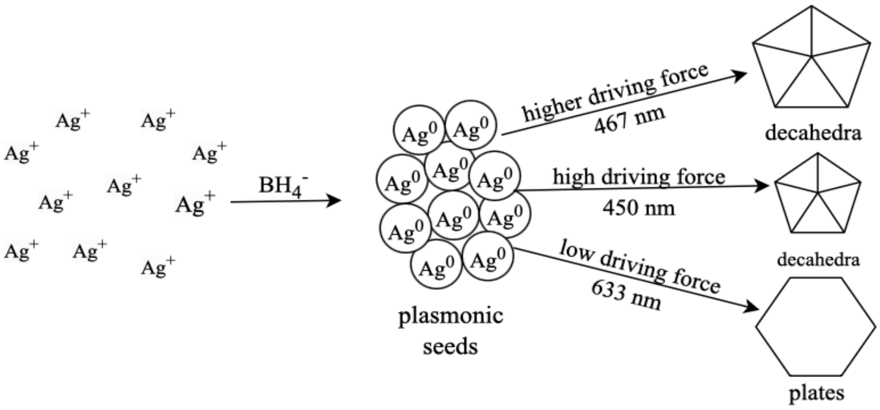

Fig. 4. Scheme explaining light influence on the shape selection of nanoparticles.

a) reduction of Ag^+ to Ag^0:

$$2Ag^+ + 2e \rightarrow 2Ag^0 \qquad [Ag^+] = 1\text{ mM}, E_0 = +0.62\text{ V}$$

b) oxidation of H_2O_2:

$$H_2O_2 - 2e \rightarrow O_2 + 2H^+ \qquad [H_2O_2] = 1\text{ M}, E_0 = -0.68\text{ V}$$

c) Full reaction is:

$$2Ag^+ + H_2O_2 = 2Ag^0 + O_2 + 2H^+, \qquad E_{cell} = +0.12\text{ V}$$

The Gibbs free energy change of Ag for the reaction is $\Delta G \approx -23$ kJ/mol, which, according to the diagram in Fig. 4, corresponds to the two-dimensional growth regime and the formation of prisms, as described in all relevant experiments in the literature [34, 35].

We believe that the low concentration of polyvinylpyrrolidone and its weak binding affinity to the silver nanoparticle facets [36] allow us to disregard its effect. Furthermore, the fact that different products are obtained from the same initial solutions confirms that the addition of polyvinylpyrrolidone does not play a significant role in photostimulated synthesis.

Conclusion

This study proposes a universal model to explain the influence of light irradiation on the synthesis of isomeric silver nanoparticles of various shapes, as well as the transformation of differently shaped silver nanoparticles into prisms in the presence of H_2O_2. The model is based on the idea that the energy of photons with different wavelengths shifts the chemical potential of the initial reactants relative to the interfacial energies and monoatomic step energies on the Ag {111} facet. As the excitation changes from red to green and then from green to blue light, the growth mode of the nanoparticles also changes - from two-dimensional, to mixed 2D/3D area, and finally to three-dimensional.

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Застосування термодинамічного підходу для пояснення визначення форми наночастинок срібла під час фотостимульованого синтезу

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Синтез наночастинок срібла різної форми та розмірів шляхом хімічного відновлення Ag^+ може суттєво залежати від опромінення світлом. Ключове питання полягає у розумінні механізму, що лежить в основі перетворення початкових сферичних зародків у призми та декаедри під дією видимого світла. У цьому дослідженні ми узагальнюємо наявні теорії фотостимульованого синтезу наночастинок і застосовуємо термодинамічний підхід до вибору форми під час синтезу срібних наночастинок. Ми пропонуємо універсальну термодинамічну модель, яка пояснює як вплив світла на синтез, так і перетворення наночастинок срібла у присутності H_2O_2. Ця модель враховує зміщення хімічного потенціалу відносно енергій міжфазової взаємодії та енергій моноатомних сходинок на гранях {111}. Наші результати демонструють, що морфологія наночастинок срібла визначається насамперед енергією фотонів, а не хімічною природою реагентів.

Ключові слова: наночастинки срібла, фотостимульований синтез, спектри, оптичні властивості, енергія фотонів, травлення, поверхнева енергія, ріст кристалів, термодинаміка, розчин.