Facile shape control synthesis and optical properties of silver nanoparticles stabilized by Daxad 19 surfactant

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ABSTRACT
It is known that silver (Ag) nanoparticles are attractive due to their novel and mild chemical and physical properties. In this research, anisotropic mono-dispersed silver nanoparticles are synthesized via a simple chemical reduction method and assisted by Daxad 19 surfactant. The reactant temperatures and weight ratios of the chemical constituents play a key role in controlling the hybrid shaping mechanism. The results indicate that the reduction rate of Ag⁺ to Ag⁰ nanoparticles is enhanced significantly with increasing weight ratios of Daxad 19 and AgNO₃ under controlled reactant temperature. The results show that the as-prepared silver nanoparticles are well-dispersed and uniform in size and shape. The dimensions of the particles are easily controlled. A comparison between experimental absorbance UV–visible spectra and simulated spectra from Mie’s Scattering Theory is carried out. It is observed that the simulated spectrum confirms well with the optical behaviour of the experimental spectra.

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1. Introduction
In the past decades, metal nanoparticles are among the nanomaterials widely investigated because they exhibit unusual optical and electronic properties which are unavailable in their bulk counterparts [1,2]. Among these metal nanoparticles, silver has received considerable scientific and practical interest due to their potential use in academic and industrial applications [3,4]. The desirous for selected synthesis to form homogeneous and well dispersions of silver nanoparticles was clearly demonstrated by Feldmenn in 2003 [3]. Notwithstanding the fact that as compared with gold particles, silver nanoparticles stabilized inappropriately undergo fast oxidation and easily aggregate in a solution, which complicates their use in the development of sensors and optical instruments.

Silver is more reactive than gold. Hence, the methods for synthesis and effective stabilization of silver nanoparticles with narrow size distributions must be elaborated. This is intrinsically important in metastable thermodynamics, whereby the stability encountered with their high surface areas represents a positive contribution to the free enthalpy of the silver nanoparticles’ system. Nonetheless, if the activation energies are not sufficiently high, the disperse evolution of silver nanoparticles causes an increase in nanoparticles’ size. The highly dispersed silver nanoparticles can be kinetically stabilized and prepared under proper conditions via the most preferred technique, which is the chemical reduction technique [5]. In this technique, the well-known problem of coupling the synthesis of silver nanoparticles using an appropriate modifier on their surface is by no means an insurmountable obstacle for producing stable silver nanoparticles and for their applications.

Chemical reduction technique offers a systematic, efficient and simple procedure for synthesis of silver nanoparticles without decreasing the production rate. Among the first syntheses of silver nanoparticles performed in chemical reduction, inverse micelle techniques were carried out by reducing silver nitrate (AgNO₃) in the presence of cationic (cetyltrimethylammonium bromide) and non-ionic surfactants [6,7]. However, the resulting silver nanoparticles solutions (5–6 nm, λ = 414 nm) were stable for only several weeks. Most of the results described so far yield stable silver nanoparticles dispersion only at relatively low concentrations of metals and are therefore unsuitable for industrial applications. The characteristics and properties of silver nanoparticles obtained from reduction solutions are related to a number of critical process parameters, including reactant temperature, loading of chemical reagents and drying [8]. These factors significantly affect the rate of the chemical reduction process and growth reaction.

Fundamental studies carried out in the late 1980s and 1990s showed that silver nanoparticles possess an interesting interaction with light due to their dielectric constants, which enable the occurrence of light repines in the visible regime [9]. Silver is notably one of the metals which can be tailored to respond across the full visible spectrum. Their light interactions can be applied in various fields such as photonics, whereby new materials can be made to transport light to the optical cables with a higher yield [10]. These waveguides act as wires and can be made smaller and lighter than...
the present day wires; however, with the capability of carrying more light [10]. Silver nanoparticles exhibit pronounced resonance absorption of visible light due to the electron collective excitation known as surface plasmon resonance (SPR). Mie was the first to obtain the exact solution for light absorption by a sphere shape in terms of electrodynamics [10].

The exact solution exists only for simple particle shapes, such as sphere and ellipse. Based on the main assumption from Mie’s theory on optical absorption of small particles, the particle and its surrounding medium are homogeneous and describable by their own bulk optical dielectric functions [10]. However, the absorption calculated from Mie’s theory uses a size-dependent damping term. Consequently, the width of the plasmon resonance is underestimated, indicating the presence of additional damping mechanisms in such particles. The optical constants of metal particles follow the Drude’s model, whereby the damping term depends on the particle size. This forthright framework has been applied in colloidal solutions of metal particles, but also in not-highly diluted systems [11–14].

In this study, the analysis is performed by numerical computations of randomly distributed spherical metal particles embedded in a dielectric matrix. The theoretical aspects concerning the implementation of Mie’s theory to determine the size of silver nanoparticles as well as numerical scheme are employed in order to compute the effective dielectric function of the simulated system. The modified Mie’s theory describes well the pattern of the extinction spectra with respect to variations in particle size [15–18]. It was assumed that only the dipole absorption in Mie’s scattering theory contributes to the extinction of the nanoparticle’s cross-section whose size is very much smaller than the wavelength of the exciting light source [19]. The extinction of the cross-section is given by:

$$\sigma_{\text{ext}}(\lambda) = 18\pi f \varepsilon_0^{3/2} \frac{\varepsilon_2}{\lambda [(2\varepsilon_0 + \varepsilon_1(\omega))^2 + \varepsilon_2^2]}$$  \hspace{1cm} (1)$$

where $\varepsilon_0$ and $f$ represents the medium dielectric constant and particle concentration, respectively. A frequency-dependent dielectric function of the metal spherical particle is given by:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i \varepsilon_2(\omega)$$  \hspace{1cm} (2)$$

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ represents the real and imaginary part of the metal dielectric constant, respectively. From Eq. (1), it is obvious that the extinction would be maximum when $\varepsilon_1(\omega) + 2\varepsilon_0 = 0$ and when $\varepsilon_2(\omega)$ is small. This gives rise to a strong resonance band. According to Drude’s model [20], the real ($\varepsilon_1(\omega)$) and imaginary ($\varepsilon_2(\omega)$) parts of the metal dielectric constant can be represented by:

$$\varepsilon_1(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \omega_c^2}$$  \hspace{1cm} (3)$$

and

$$\varepsilon_2(\omega) = \frac{\omega_p^2 \omega_c}{\omega(\omega^2 + \omega_c^2)}$$  \hspace{1cm} (4)$$

whereby

$$\omega_c = \frac{v_f}{L} + \frac{2V_f}{d}$$  \hspace{1cm} (5)$$

and

$$\omega = \frac{2\pi c}{\lambda}$$  \hspace{1cm} (6)$$

In Eqs. (5) and (6), $\omega_p$ is the bulk plasmon frequency, $L$ is the electron mean free path in bulk silver, $c$ is the velocity of light in vacuum ($3 \times 10^8$ m/s), and $v_f$ is the velocity of conduction electron at the Fermi level.

2. Theoretical framework

The growth of silver nanoparticles was investigated using theoretical models based on the extinction of the nanoparticles cross-section. A number of theoretical models were proposed to justify the observed peak shift and its broadening in the optical spectra with respect to variations in particle size [15–18]. It was assumed that only the dipole absorption in Mie’s scattering theory contributes to the extinction of the nanoparticle’s cross-section whose size is very much smaller than the wavelength of the exciting light source [19]. The extinction of the cross-section is given by:

$$\sigma_{\text{ext}}(\lambda) = 18\pi f \varepsilon_0^{3/2} \frac{\varepsilon_2}{\lambda [(2\varepsilon_0 + \varepsilon_1(\omega))^2 + \varepsilon_2^2]}$$  \hspace{1cm} (1)$$

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3. Experimental

3.1. Preparation

The chemicals used were of analytical reagent grade without further purification. Daxad 19 (sodium salt of polyvinylpyrrolidone formaldehyde condensate, MW 8000) (Canamed United Supply Company) was used as stabilizer. Silver nitrate (AgNO3) (Fisher Scientific) was selected as the source of silver. Polyethylene glycol (PEG) (MW 8000 in monomer units) (Acros Organic) was used as an initial reducing agent before Daxad 19. Double-distilled water was used in the preparation of aqueous solutions.

4 g of silver nitrate were dissolved in a mixture comprising of 200 mL distilled water, 4.5 g of PEG and 5 g of Daxad 19 at 80 °C. The solution was stirred for 1 h at this temperature. It was observed that the light brown solution transformed into a grey-black colour, which indicates the formation of silver nanoparticles. The solution was then centrifuged at a maximum speed of 15,000 rpm, and
Fig. 1. High-resolution TEM images of silver nanoparticles at various reactant temperatures. TEM images are shown in the inset by directing the electron beam perpendicular to the flat surface at (a) 80 °C (b) 100 °C and (c) 120 °C.
washed with distilled water several times before being dried in a vacuum oven at 65 °C. The resulting product was used for characterization. The details of the experimental procedure and conditions are summarized in Table 1.

3.2. Characterization

Characterization studies were carried out via High-Resolution Transmission Electron Microscopy (HRTEM) using LEO LIBRA electron microscope operated at 120 kV. UV–vis spectroscopic measurements (320–630 nm) were performed using UVIKON 923 Double Beam spectrophotometer at room temperature.

4. Results and discussion

Fig. 1 shows the TEM results of the samples obtained at various reaction temperatures. At the lowest temperature (80 °C), the particles are spherical and fairly dispersed, with an average diameter of 4.5 nm. The HRTEM image shown in the inset of Fig. 1(a) indicates that the silver nanoparticles are present in the crystalline state. The atoms are arranged in an orderly manner, indicating that the aggregation process at this temperature may be in an equilibrium condition, with a slow reaction rate. It shall be noted that the nullified boundaries assist the nucleation process by releasing the free energy, which reduces the activation energy barrier for nucleation [21,22]. Meanwhile, a weak interparticle aggregation of oblate polygonal nanoprisms with triple grain boundary point is clearly observed at 100 °C. The average particle size is 7.5 nm. The HRTEM image in the inset of Fig. 1(b) shows that the individual nanoprisms are perpendicular to its flat surface. The activation energy for the nucleation process is reduced for this morphology. The reduction in free energy is due to the nullified grain boundary areas, which are larger than the boundaries with two grains. The subunits of the silver nanoparticles at the grain boundaries are preferentially adsorbed and grown to nuclei due to the lowered free energy. Consequently, big particles (56 nm) appeared concurrently with regular-sized particles due to dispersion at 120 °C.

The HRTEM image shown in the inset of Fig. 1(c) represents a different common lattice when the nanoparticles coalesce. This indicates that the individual nanoparticles rearrange their crystal structures when they coalesce. Consequently, silver nanoparticles having the same crystalline orientation creates free energy situation. The relative standard deviation (R.S.D.), which is obtained by dividing the standard deviation, \( \sigma \) by the average particle size, increases from 2.9 to 5.2 with increasing temperature. From the observations, it can be concluded that temperature affects the morphology of silver nanoparticles.

The absorption spectra of silver nanoparticles were simulated from Eq. (1) using the typical properties of silver, and are shown in Figs. 3 and 4. It can be observed that the plasmon-derived resonance of silver nanoparticles become distinct and stronger for silver nanoparticles at lower reactant temperatures, but smudges out with aggregation of silver nanoparticles at higher reactant temperatures. It shall be noted that Mie’s scattering theory describes the experimental observation more or less faithfully, with a slight departure in the higher wavelength region. In this, the simulations exhibit a similar trend; however, the simulations are invalid for non-spherical nanoparticles. The fitted values of the particle size agree well with the peak values of the particle size distribution. It is note worthy that Mie’s theory accounts well with the size of isolated metal particles in the optical spectra, but is restricted only for spherical shapes.

![Graph](image)

Fig. 2. Experimental and Mie simulated optical absorbance spectra at 80 °C. Fitting parameters are: \( f = 0.2, d = 4.5 \text{ nm} \) and \( \varepsilon_0 = 4.5 \).

![Graph](image)

Fig. 3. Mie simulated optical absorbance spectra at (a) 80 °C (b) 100 °C and (c) 120 °C. Fitting parameters are: (1) \( f = 0.2, d = 4.5 \text{ nm}, \varepsilon_0 = 4.5 \); (2) \( f = 0.2, d = 7.5 \text{ nm}, \varepsilon_0 = 8.5 \); and (3) \( f = 0.2, d = 15 \text{ nm}, \varepsilon_0 = 12.5 \).

![Graph](image)

Fig. 4. UV–visible absorption spectra of silver nanoparticles at various reactant temperatures: (a) 80 °C (b) 100 °C and (c) 120 °C.

The particle size obtained from curve fitting is 4.5, 7.5 and 15 nm at a temperature of 80, 100 and 120 °C, respectively. The results agree well with the TEM observations, as shown in Fig. 2. The changes in the SPR curve in Fig. 3 can be related to the size effect. Strong absorption centred at 420 nm becomes red-shifted and broadened with increasing particle size. Fig. 3 also shows that the intensities of the SPR band and their full width at half maximum (FWHM) increase with temperature, as tabulated in Table 2. The characteristics of the absorption spectra vary accordingly with increasing particle size. Pal et al. [22] showed that Mie’s scattering theory describes the experimental observation more or less faithfully with a slight departure in the higher wavelength region. In this, the simulations exhibit a similar trend; however, the simulations are invalid for non-spherical nanoparticles. The fitted values of the particle size agree well with the peak values of the particle size distribution. It is note worthy that Mie’s theory accounts well with the size of isolated metal particles in the optical spectra, but is restricted only for spherical shapes.
Table 2
Aspect parameters in the formation of silver nanoparticles.

<table>
<thead>
<tr>
<th>Shape</th>
<th>Reactant temperature of sample (°C)</th>
<th>Mie's Scattering peak, $\lambda_{\text{max}}$ (nm)</th>
<th>FWHM, $\lambda_{\text{FWHM}}$ (nm)</th>
<th>Absorbance (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spherical</td>
<td>80</td>
<td>430</td>
<td>67</td>
<td>1.7</td>
</tr>
<tr>
<td>Truncated prism</td>
<td>100</td>
<td>477</td>
<td>78</td>
<td>3.5</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>120</td>
<td>496</td>
<td>85</td>
<td>4.7</td>
</tr>
</tbody>
</table>

Fig. 4 shows the SPR bands of silver nanoparticles at various reactant temperatures. A single clear peak at 392 nm indicates the presence of uniform, spherical-shaped nanoparticles at the lowest temperature (80 °C) [10]. The peak centre shifts to 409 nm at a higher reaction temperature (100 °C). At this temperature, the SPR bands are broad and exhibit two maxima at 409 and 348 nm, respectively. This indicates the formation of spherically shaped silver nanoparticles and the presence of truncated edges in the anisotropic structures, respectively. The most prominent SPR peaks for oblate polygonal silver nanoparticles appear at 436 and 322 nm, at the highest reaction temperature (120 °C). The UV–vis results clearly support the TEM images in Fig. 2. The increase in maximum absorbance at each temperature is due to the particle density, which is strongly dependent on the amount of silver reduction at the surface of the medium [23–25].

Fig. 5 shows the UV–visible spectra of silver nanoparticles with and without Daxad 19 at various reactant temperatures. A light grey transparent solution was formed (without Daxad 19), indicating that the reduction of Ag$^+$ to Ag$^0$ nanoparticles did not occur (Fig. 5(d–f)). The magnitudes of the absorbance peaks are significant when the medium was mixed with Daxad 19 (Fig. 5(a–c)). The disappearance of peaks in Fig. 5(d–f) indicates that the silver nanoparticles would not develop without Daxad 19 as a stabilizer. PEG no longer played a role, or contributed the least as a reducing agent when compared to Daxad 19.

Table 2 depicts the variations in SPR dependence, full width at half maximum (FWHM) and the average particle size at 80, 100 and 120 °C. An initial increase in reactant temperature leads to a peak shift towards a longer wavelength. The increase in FWHM at increasing reactant temperature indicates an increase in particle size [26]. The observations compare well with the TEM results (Fig. 2).
Figs. 6–8 display the effects of various concentration ratios of AgNO₃ and Daxad 19 at 80, 100 and 120 °C. Generally, it is clear that the FWHM is broader with a low absorbance intensity at the lowest concentration ratio. The FWHM becomes narrower and the intensity is augmented with an increase in AgNO₃. Daxad 19 concentration ratio (2:3 to 4:5). The SPR maximum is slightly blue-shifted, which correlates to a reduction in particle size. This indicates that the particle size indeed influences the position of the SPR band, whereby an increase in particle size is related to a red-shift of the SPR maximum [10].

The SPR peaks for the lowest to the highest AgNO₃: Daxad 19 concentration ratios are 423, 419, 418, 395 and 392 nm, respectively, as shown in Fig. 6. This induces the formation of mono-dispersed silver nanoparticles small particle size. On the contrary, low concentration ratios favourable to form larger particle size since the reactants would be rapidly transferred from one core to another. Thus, the resultant particle size is relatively big and the size distribution becomes relatively wide. When the temperature increases to 100 °C, the SPR peaks in Fig. 7 also show a blue-shift pattern, which corresponds to 424, 413, 412, 410 and 409 nm for the lowest, medium and highest concentration ratio, respectively.

Fig. 8 shows similar characteristics. A symmetrical SPR band appears at 417 nm for the lowest concentration ratio and becomes narrower at higher concentration ratios, whereby the SPR peak shifts to 412, 411, 403 and 401 nm, indicating blue – shift. A minor peak appears at 322 nm for each spectrum and becomes clearly visible as the reactant temperature increases (Figs. 6–8). The origin of the peak refers to a change in prolate anistropic shapes of the silver nanoparticles. A minor SPR peak occurs when the shapes of the silver nanoparticles enable electrons in the attached particles to begin interactions with each other [26]. This, in turn results in the emergence of a new SPR peak.

In addition, the FWHM of the SPR band has a linear relationship with respect to the particle diameter. For a small particle, the maximum absorbance intensity and bandwidth of the SPR peak rely on the surroundings of the medium. When the silver nanoparticles strongly dominate the matrices’ condition, a large broadening of the SPR occurs. This would result in blue-shift characteristics. A red-shift with small broadening would take place when low interactions occur between the silver nanoparticles and matrices. From Figs. 7 and 8, it is clear that the FWHM for smaller particles is narrower with higher absorbance intensity. The FWHM value decreases with an increase in AgNO₃: Daxad 19 concentration, as shown in Figs. 6–8. There is an increase in FWHM when the concentration ratio decreases. The deduction is summarized in Table 1, and is supported by the TEM micrographs.

The nucleation and formation growth rate of silver nanoparticles increase with AgNO₃ concentration. As shown in Figs. 6–8, the absorbance intensity increases with AgNO₃ concentration. This reflects that a higher amount of silver nanoparticles form in the solution. This proves that the maximum absorption is dependent on the initial silver ion concentration. For instance, in Fig. 7, the SPR peak shifts towards shorter wavelengths from 424 to 409 nm when the AgNO₃ concentration is altered, showing a decrease in particle size [27]. The size of the silver nanoparticles decreases with an increase in AgNO₃ concentration (Figs. 6–8). The size increases when the temperature increases from 80 °C (Fig. 4). At higher concentration ratios and temperatures, the silver nanoparticles begin to aggregate and form larger particles [28].

5. Conclusion

In this research, silver nanoparticles have been synthesized via chemical reduction technique using Daxad 19 as stabilizer. The use of Daxad 19 provides a suitable environment for silver nanoparticles’ formation and also prevents the aggregation of particles. The results of the numerical simulations show that the surface plasmon broadening is affected by the size and interparticle interactions, even for particle volume filling fractions as small as a few percent. It is evident that Daxad 19 clearly stabilizes silver nanoparticles and effectively produces large amounts of silver due to the inhibition of reduction reaction. Additionally, it is noteworthy that the reaction of Daxad 19 increases rapidly with an increase in weight ratio and reactant temperature, which shows the ease and novelty of the synthesis method. A comparison of the shift and broadening of the SPR bands between experiment and simulated spectra from Mie’s theory has been carried out. Both the experimental and simulated spectra show that an increase in particle size is accompanied by a red-shift and broadening of the SPR band.

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References


