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Surface plasmon resonance of metal nanostructures as a complementary technique for microscopic size measurement

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Abstract

Physical principals and the relations between Surface Plasmon Resonance (SPR) spectra and geometrical properties of metal nanostructures specially silver and gold were reported. Applying SPR technique enable us to investigate the accuracy of some simple equations for investigating geometrical properties of metal nanostructures based on their plasmonic spectrum. Geometrical properties, shape and size polydispersity of particles as well as particles' embedding medium refractive index are the crucial ignored parameters, effective in the accuracy of those equations. The restrictions of these relations in terms of shape, size distribution and refractive index of particles' embedding medium are also investigated and compared with other published reports. Furthermore, the equations of spherical particles have been extended to non-spherical ones and their accuracy has been investigated. It was found that the modified forms of the equations may lead to more exact results for non-spherical metal particles.

Keywords: Metal nanostructures; Surface plasmon resonance; Extinction spectra; Geometrical properties

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Background

The two key parameters of nanostructures are their size and shape which have a crucial rule in their properties and diverse applications [1]. These key parameters are usually determined after synthesis of nanostructures using electron microscopic techniques such as transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Although these techniques are very powerful in determination of size and shape of the nanostructures but the problem is that these techniques are not at hand anywhere and anytime. Moreover, microscopic techniques are too expensive compared with other measurement techniques such as optical spectroscopy. The optical properties of metallic nanostructures are determined by the collective oscillations of their conduction electrons with respect to the positive ion background, known as plasmon which relates the extinction coefficients to the size and geometrical properties of metallic nanostructures [2]. Therefore, optical spectroscopy is one of the simplest and easiest ways to determine

the geometrical properties of metal nanostructures including their size and shape [3]. The unique advantage of this property is the ability of determining the geometrical properties of nanostructures during the synthesis process which causes their controlled production.

The symmetry of nanostructures determines the ways that they are polarized, and the number of these ways correlates to the number of plasmonic peaks [4]. For example extinction spectra of small particles with the most symmetry shape i.e. sphere (Figure 1(a)) has just one peak because a small sphere could be polarized only in dipole mode, while cubic particles could be polarized both in dipole (in about 530 nm) and quadrupole modes (in about 470 nm (Figure 1(b))). Therefore, they have two plasmonic peaks and the polarization modes are shown in Figure 2(a) and (b), respectively [5].

The symmetry also changes intensity of the extinction spectra. If surface charges are polarized according to mirror symmetry (without reflection plane which is bisector of corners) as depicted in Figure 2(c), the total dipole moment will increase, because accumulation of electrons in sharp corners are more than the other parts and in this polarization mode (Figure 2(d)) there will be four sharp corners instead of the two corners in Figure 2(c).

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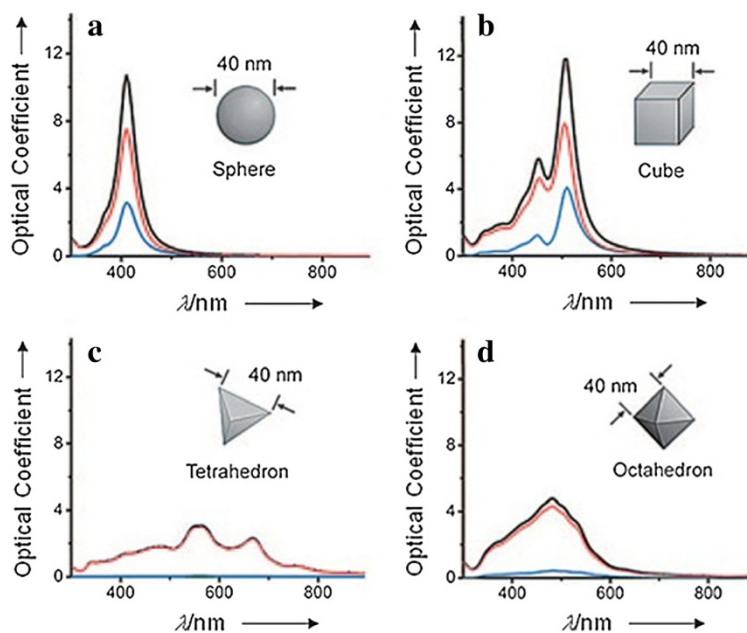


Figure 1 UV-Visible extinction (black), absorption (red), and scattering spectrum (blue) of Ag nanocrystals, illustrating the effect of shape on spectral characteristics: (a) sphere, (b) cube, (c) tetrahedron and (d) octahedron. Reprinted with permission from Xia *et al.* [4].

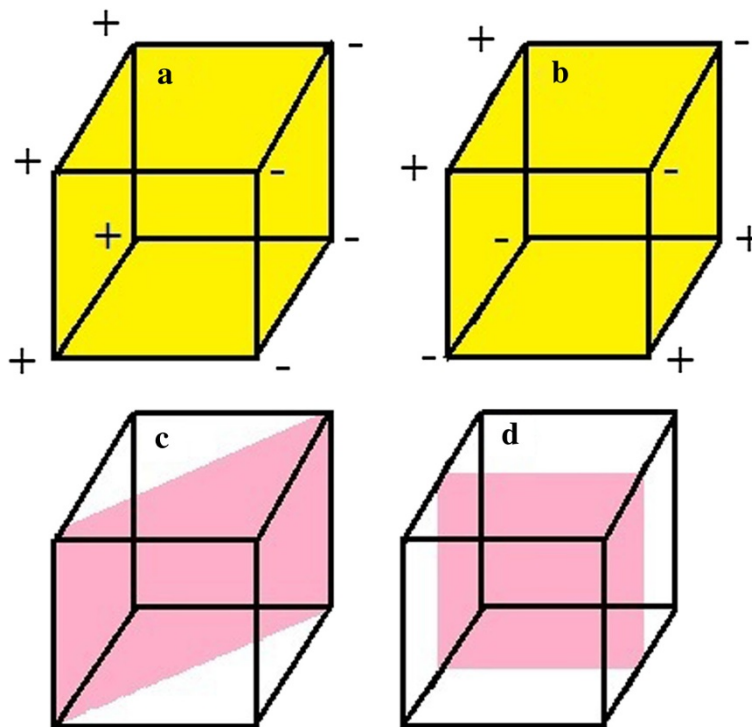


Figure 2 (a) Dipole, (b) quadrupole mode of a nanocube polarization, (c) and (d) the related symmetry planes of nanocubes in dipolar polarization. Reprinted with permission from Xia *et al.* and Zhang *et al.* [4,5].

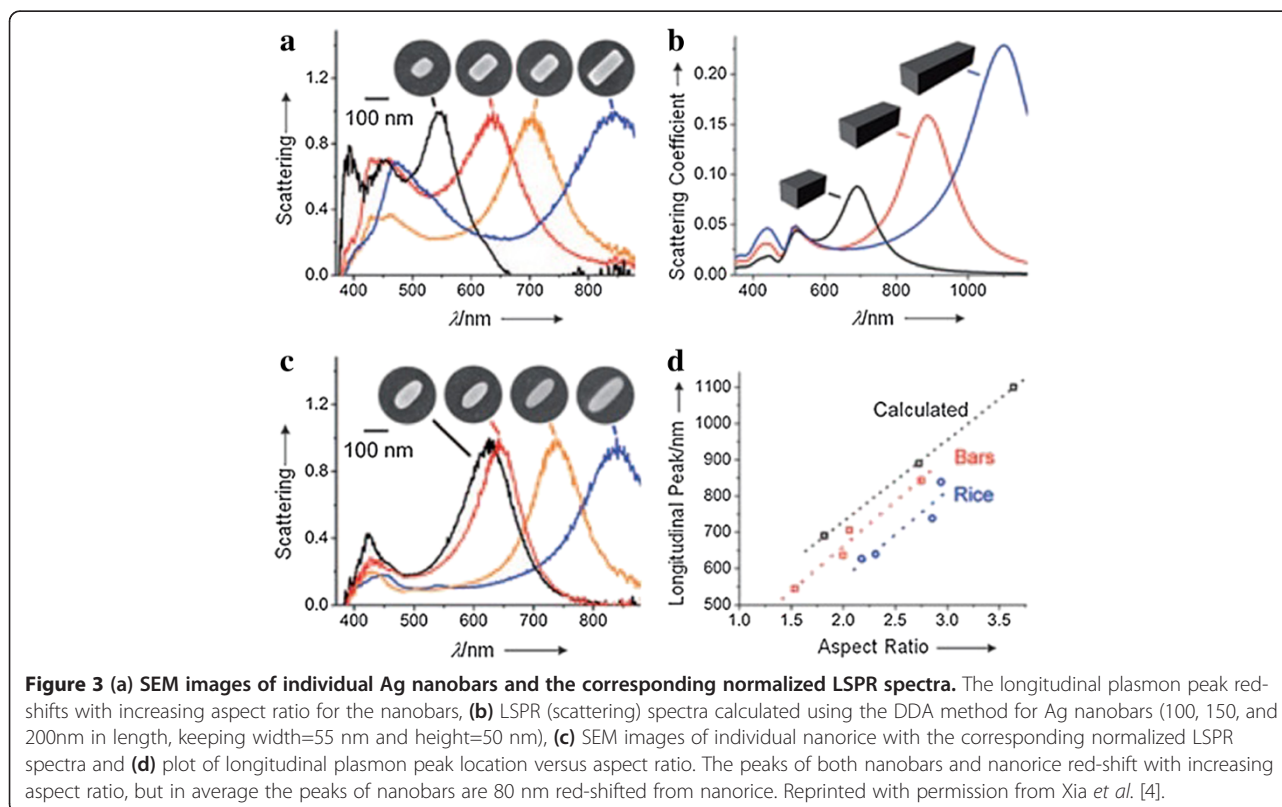
Therefore, the number of plasmons will increase which increases the intensity of extinction spectra [4]. Another reason for decreasing the intensity of the extinction spectra is that electrons in silver nanocubes accumulate in corners (the corners are face to face), but in silver tetrahedrons, each corner is in front of a plane, so the strength of the effective dipole moment decreases and as a result the intensity of extinction spectra decreases (Figure 1(c)). Consequently, the extinction spectrum of octahedron is blue shifted (maybe due to more distance of face-to-face corners in octahedron) and is more intensive than tetrahedron (Figure 1(d)) [4].

The wavelength of plasmon resonance is affected by both particle size and refractive index of embedding medium [4,6-10]. In large particles surfaces are far enough from each other and electrons need less energy to shift from their equilibrium positions and consequently the effective restoring force applying to electrons by the ions decreases, compared with smaller particles. In contrast with nanocubes, one dimensional nanostructures have two dipole plasmonic peaks, one belongs to oscillating charges along longitudinal axis, and another belongs to oscillating charges along latitudinal axis [4]. Increasing the aspect ratio of these nanostructures not only causes a red shift in dipolar longitudinal plasmonic peak, but also increases intensity of the plasmonic peak.

Consequently, more plasmons will be excited and the intensity of their dipolar longitudinal plasmonic peaks will increase, too. This phenomena is illustrated both experimentally and theoretically (using discrete dipole approximation) for silver nanobars in Figure 3(a) and Figure 3(b), respectively.

As was mentioned earlier, sharp corners causes red shift in plasmonic peak due to accumulation of electrons in the corners and large distance among the electrons and positive ions. In very small nanostructures, extinction cross section is determined mainly by absorption cross section, in contrast with larger structures in which is determined mainly by scattering cross section, as is proofed by calculating absorption and scattering coefficients using Mie's theory [11]. Comparison of scattering coefficients in large enough nanobars and nanorices illustrates that sharp corners of nanostructures causes red shift of their extinction spectra (Figure 3(a) and (c)). The linear relation between aspect ratio of one dimensional nanostructures and their longitudinal dipolar plasmonic peak is illustrated both theoretically and experimentally in Figure 3(d).

In this work, only very useful relations for this purpose for metal nanostructures with different shapes have been collected, but also some of those relations from spherical to non-spherical particles are expanded using Coronado and Schatz's equation [10,12-17].



Methods

In this section, simple empirical equations are presented which are used for determining geometrical properties of free-electron metal nanostructures. These relations are listed in Tables 1 and 2.

Khlebtsov derived an equation which relates average equivolume diameter (\bar{d}_{ev}) of gold nanospheres to moderate inversion of spherical shape and their dipolar surface plasmon resonance wavelength (λ_{SPR}) using several experimental data, as following [16]:

$$d_{ev} = \begin{cases} 3 + 7.5 \times 10^{-5} X^4, & X < 23 \\ \frac{(\sqrt{X-17}-1)}{0.06}, & X \geq 23 \end{cases}, \quad X = \lambda_{SPR} - 500 \quad (1)$$

He has also used linearity of $\frac{A_{max}}{A_{min}}$ V.S. $\ln(\bar{d}_{ev})$ and A_{450} V.S. $\ln(\bar{d}_{ev})$ graphs for determining \bar{d}_{ev} nanoparticles with other properties (Table 1). In addition, Hoonacker and co-workers found that the graph of FWHM of extinction spectra of silver nanospheres with smaller diameter than 20 nm versus the inverse of their diameter is linear and one may use this method for size determination of Ag NPs [14].

e and σ in Table 1 are the aspect ratio of spheroids and s-cylinders (cylinders with semi sphere ends) and standard normal distribution parameter that determines size distribution of nanoparticles, respectively. In a spheroid and s-cylinder \bar{d}_{ev} may be calculated as:

$$\bar{d}_{ev} = 2b \left[1 + \frac{3(e_{av}-1)}{2} \right]^{1/3} \quad (2)$$

Where

$$e_{av} = \frac{a_{av}}{b_{av}} \quad (3)$$

Also A_{max} and A_{min} in Table 1 are the maximum and minimum of extinction coefficient in extinction spectra.

Manikandan and co-workers [12,13] and Hoonacker et al. [14] have derived useful equations which relates diameter of nanospheres to their λ_{SPR} for all kind of metallic particles and silver particles respectively, as follows:

$$R = \frac{v_F \lambda_{SPR}^2}{2\pi c \Delta\lambda} \beta \quad (4)$$

$$\lambda_{SPR} = 382.6 + 1.18d_{av} \quad (5)$$

Where $\Delta\lambda$ is full width at half maximum of extinction spectra (FWHM), R is particle radius, C is light velocity in vacuum ($c = 3 \times 10^8$ m/s), β is proportionality constant, v_F is Fermi velocity of electron gas in the particle which is equal to 1.4×10^6 m/s for gold and silver particles and d_{av} in Eq. 5 is the average diameter of particles [18].

It should be mentioned that one may use Mie theory for simulation of extinction spectra of monodisperse metal and insulator spherical particles, and for extinction spectra of particles with non-spherical shapes T-Matrix simulation (linear transformation between coefficients of scattered and incident fields [19]) is the only exact solution [16,20-23].

Not only particle size, but also some other parameters possibly would be determined using surface plasmon resonance during production process. In quasi-static approximation, which the particles' dimensions are much less than incident wavelength, electromagnetic fields in the particle only depends on the time and standing plasmonic waves will be produced. In such a case the dependence of longitudinal resonance wavelength (λ_n) to the resonance order (n) and aspect ratio (e) is given by this Equation [15]:

$$\lambda_n \approx A_0 + A \frac{e}{n} \quad (6)$$

Where $n=1, 2, 3$, etc. corresponds to dipolar, quadrupolar, octapolar and etc. plasmon resonances.

Table 1 Different methods of determining \bar{d}_{ev} for metal nanostructures

Nanostructure shape	Nanostructure material	\bar{d}_{ev} limit (nm)	σ limit	e limit	Method	Ref.
Spherical	Any material	Any size	$\sigma \approx 0$	$e \approx 0$	Mie Theory	[16]
Spherical and quasi-spherical	Any material	$1 \leq \bar{d}_{ev} \leq 10$	Not Determined	$1 \leq e \leq 1.2$	Using linear graph $\frac{A_{max}}{A_{min}}$ V.S. $\ln(\bar{d}_{ev})$	[16]
quasi-spherical	Any material	$3 \leq \bar{d}_{ev} \leq 70$	Not Determined	$1.2 \leq e \leq 1.4$	Using linear graph A_{450} V.S. $\ln(\bar{d}_{ev})$	[16]
Spherical	Silver	Less than 20	Not determined	Not determined	FWHM V.S. $\frac{1}{\bar{d}}$	[14]
Spherical	Gold	$5 \leq \bar{d}_{ev} \leq 100$	Not determined	Moderate invert of sphere	Equation 1	[16]
Spherical	Silver	$5 \leq \bar{d}_{ev} \leq 118$	$\sigma < 0.0001$	Not determined	Equation 5	[14]
Spherical	Any material	Not determined	Not determined	Not determined	Equation 4	[12,13]

Table 2 Methods of determining different geometrical parameters of nanostructures

Unknown parameter	Nanostructure shape	Nanostructure material	Nanostructure size	σ limit	e limit	Method	Ref.
e (aspect ratio)	Spheroid and nanorod	Any material	Not determined	Not determined	Not determined	Equation 6	[15]
h (shell thickness)	spherical	Any material	Quasi-Static approximation, $h_{\max} \approx d_{ev}$	Not determined	Not determined	Equation 8	[10]
Δn_m^*	Not determined	Any material	Not determined	Not determined	Not determined	Equation 7	[15]

* Changes of embedding medium refractive index.

The constants A_0 and A are independent of n factor which depend on the size and morphology of the particle. Surface plasmon resonances are very sensitive to changes of refractive index of their embedding medium upon thickness of their size [6-9]. Consequently this phenomenon makes free-electron metal nanoparticles excellent candidate for nanoscale sensors. Dependence of longitudinal dipolar and multipolar plasmon resonances to the changes of refractive index of embedding medium (Δn_m) is given by [15]:

$$\frac{\Delta \lambda_{SPR}}{\lambda_{SPR}} \approx B \frac{\Delta n_m}{n_m} \quad (7)$$

Where n_m initial medium refractive index and B is a weak function of particle shape and order of multipole resonances which reduces by increase in the order.

Muskens and co-workers [10] derived a simple equation for measuring thickness of dielectric shell (h) around metal core with weakly dispersed imaginary part of dielectric function in core-shell systems embedded in dielectric medium in a quasi-static regime, which for usual dielectric shells like water and glass is expressed as:

$$1-a \approx \frac{\Delta \lambda_{SPR}(h)}{\Delta \lambda_{SPR}^{\max}} \quad (8)$$

Where "a" is the core volume fraction:

$$a = \frac{D^3}{(D+h)^3} \quad (9)$$

and

$$\Delta \lambda_{SPR}(h) = \lambda_{SPR}(h) - \lambda_{SPR}(h=0) \quad (10)$$

$$\Delta \lambda_{SPR}^{\max} = \lambda_{SPR}(h=0) - \lambda_{SPR}(h \rightarrow \infty) \quad (11)$$

$\lambda_{SPR}(h=0)$ and $\lambda_{SPR}(h \rightarrow \infty)$ define as surface plasmon resonance wavelength when there is not any shell around the core ($h=0$) and when the shell is too thick ($h \rightarrow \infty$) which the core does not sense embedding medium.

The parameters, which are describe by equations (6–11), and their applications are listed in Table 2. Tables 1 and 2 are very helpful for researches who are interested in controlling the production process of free-electron metal nanostructures.

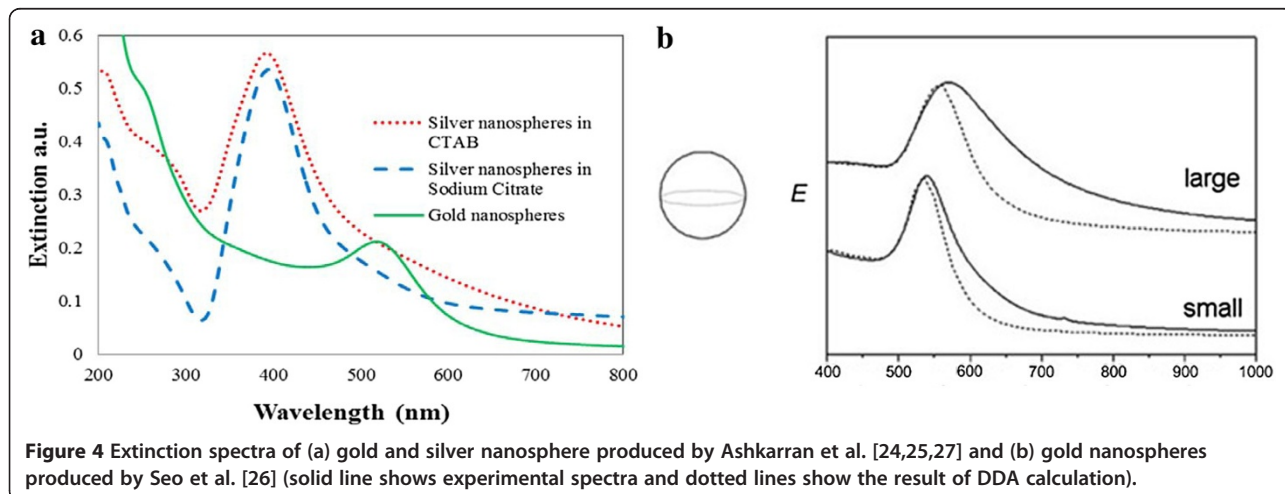


Figure 4 Extinction spectra of (a) gold and silver nanosphere produced by Ashkarran et al. [24,25,27] and (b) gold nanospheres produced by Seo et al. [26] (solid line shows experimental spectra and dotted lines show the result of DDA calculation).

Table 3 Data of Figure 4 and calculated amounts of \bar{d}_{ev} and β for nanospheres

Material	λ_{SPR} (nm)	FWHM (nm)	\bar{d}_{ev} (nm)	Calculated \bar{d}_{ev} (nm)	β	Ref.
Silver in CTAB	393	142	14	8.81	8.66	[25,27]
Silver in sodium citrate	394	101	30	9.66	13.14	[25,27]
Gold	519	118	8	12.77	2.36	[24,25]
Gold	542.1	126.3	49±5	66.83	14.17	[26]
Gold (calculated by DDA)	535	80.7	49	54.04	9.30	[26]
Gold	573.7	Incalculable	81±8	108.83	Incalculable	[26]
Gold (calculated by DDA)	559.6	Incalculable	81	92.11	Incalculable	[26]

In classical mechanics point of view, the mean free path (MFP) of electrons decreases by scattering from clusters' or particles' surface [11], Coronado and Schatz used a geometrical method to derive a practical equation for calculation of MFP in nanostructures [17]:

$$L_{eff} = \frac{4V}{s} \quad (12)$$

This equation has been used to expand Equations (1, 4, 5) to non-spherical shaped nanostructures to investigate the applicability of these equations about them.

$$L_{eff} = \begin{cases} 2 + 5 \times 10^{-5} X^4, & X < 23 \\ \frac{(\sqrt{X-17}-1)}{0.09}, & X \geq 23 \end{cases}, X = \lambda_{SPR} - 500 \quad (13)$$

$$L_{eff} = \frac{2 V_F \lambda_{SPR}^2}{3 \pi C \Delta \lambda} \beta \quad (14)$$

$$\lambda_{SPR} = 382.6 + 1.77 L_{eff} \quad (15)$$

Although, these equations have some strength points but they also have some weaknesses, which will be illustrated in the next section. In fact, some of those results

possibly may not be exact due to the effects of shape, size distribution of particles and refractive index of embedding medium on extinction spectra, which are not considered in those equations.

Result and discussion

In this section, the applicability of Equations (1, 4, 5, 13–15) for gold and silver nanoparticles with different shapes is investigated. At first, the reliability of Equations (1, 4, 5) about spherical particles is investigated and then the equations are expanded to particles with non-spherical shapes. Extinction spectra of spherical gold nanoparticles produced by Ashkarran and co-workers [24,25] and Seo et al. [26] are shown in Figure 4. The data of these spectra, calculated values of \bar{d}_{ev} and β are shown in Table 3. Note that it was doubled the half of FWHM whenever it was impossible to be measured exactly.

It is expected that the plasmonic peak of silver nanoparticles in sodium citrate have more red shift than in CTAB because their average diameter is larger, but there is blue shift in their spectra compared with spectra of silver nanoparticles in CTAB. Because refractive index of CTAB (1.4 [28]) is larger than of sodium citrate (1.3 [29]), there is not any remarkable red shift in resonance wavelength of particles in sodium citrate. This is one of

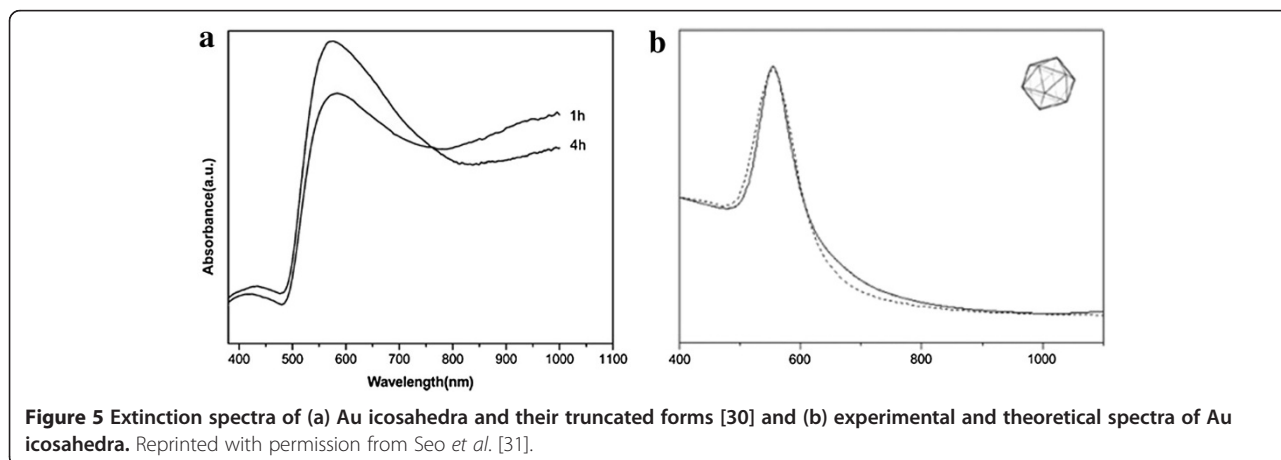


Figure 5 Extinction spectra of (a) Au icosahedra and their truncated forms [30] and (b) experimental and theoretical spectra of Au icosahedra. Reprinted with permission from Seo *et al.* [31].

Table 4 Calculated amounts of $\overline{d_{ev}}$, L_{eff} and β for Au icosahedra and their truncated forms

Shape	Average size (nm)	λ_{SPR} (nm)	FWHM (nm)	Calculated size (nm)	β	Ref.
Truncated icosahedral	222.48	574.7	120.3	109.93	54.55	[30]
icosahedral	253.45	583	135	118.73	67.77	[30]
Icosahedral (experimental)	94±10	561.96	101.96	95.08	20.43	[31]
Icosahedral (teoritical)	94	560	105.88	92.62	21.36	[31]

the weaknesses of Eq. 5 which in spite of high sensitivity of silver nanoparticles to the changes of refractive index of their embedding medium, the equation does not have any dependence to this important parameter. It seems that the difference between calculated $\overline{d_{ev}}$ for particles in CTAB and the measured one is mainly due to this weakness. Another weakness is that Hoonacker and co-workers did not considered the required limits of σ in their equation.

Similarly, Eq. 4 does not depend on refractive index of particles' embedding medium nor size distribution. It was expected that β values to be same for different silver

samples but they were not, due to different values of these parameters.

Equation 1, which was obtained by Khlebtsov and co-workers, does not depend on refractive index of embedding media, shape and size distribution of particles, too. So, in spite of approximate results, for exact results the constants in this equation should be replaced with functions of above parameters. Considering these points in Equations 4 and 5 the accuracy and generality of these equations would increase. Note that particles with same shape have the approximately same β values.

Now the validity of Equations 1 and 4 for truncated icosahedrons [30] and icosahedrons [30,31] gold nanoparticles are investigated. The extinction spectra of these structures are shown in Figure 5. In Table 4, experimental and calculated values of \overline{d} and β are presented. The average size of particles has been considered as their equivolume diameter for samples of Ref. [30] and [31].

Equation 1 leads to exact results for both theoretical and experimental data of Ref. [31]. So, one could expect validity of this equation for dipolar resonance of other regular polyhedral nanoparticles. Note that the results of gold nanospheres in Table 1 were not exact probably because the effect of refractive index of embedding

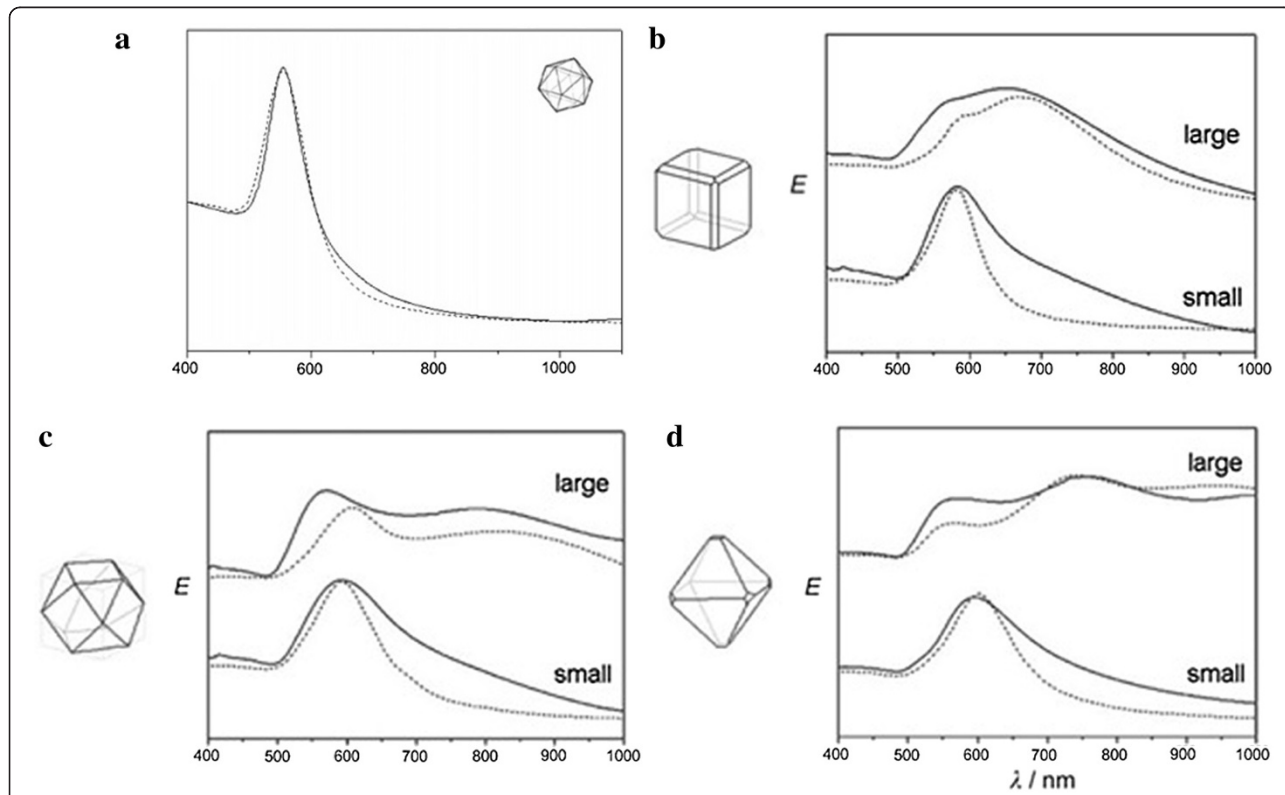


Figure 6 (a) Extinction spectra of the Ag and Au nanocubes [32], Extinction spectra (solid lines) and results of DDA calculations (dotted lines) of (b) large (edge length 116 nm) and small (67 nm) cubes, (c) large (edge length 122 nm) and small (54 nm) cuboctahedra and (d) large (edge length 236 nm) and small (88 nm) octahedral. Reprinted with permission from Seo *et al.* [26].

Table 5 Calculated values of edge size, \bar{d}_{ev} , L_{eff} and β for Au nanoparticles with different shapes

Ref.	[26]	[26]	[26]	[26]	[32]	[32]	[26]	[26]	[26]	[26]	[26]	[26]	[26]	[26]
β using L_{eff}	22.89	38.16	Incalculable	Incalculable	17.26	60.28	14.31	26.35	Incalculable	Incalculable	20.26	32.77	Incalculable	Incalculable
β using \bar{d}_{ev}	25.29	42.17	Incalculable	Incalculable	21.42	74.79	17.75	32.69	Incalculable	Incalculable	23.96	38.75	Incalculable	Incalculable
Calculated L_{eff} (nm)	84.59	84.59	182.61	172.87	64.24	85.53	77.56	78.74	129.52	118.27	90.11	84.59	218.91	233.08
Calculated \bar{d}_{ev} (nm)	126.89	126.89	273.92	259.31	96.37	128.30	116.35	118.11	194.28	177.41	135.17	126.89	328.37	349.62
Calculated edge (nm)	76.84	76.84	165.89	157.04	77.67	103.41	93.77	95.19	156.58	142.99	139.98	131.41	340.06	362.07
FWHM (nm)	147.3	245.6	Incalculable	Incalculable	105.6	304	107	198.2	Incalculable	Incalculable	150.8	236.8	Incalculable	Incalculable
λ_{SPR} (nm)	591.2	591.2	821.0	791.2	563	534	580.7	582.4	677.2	652.6	600	591.2	945.6	1000
Kind	Theoretical	Experimental	Theoretical	Experimental	Experimental	Experimental	Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental
L_{eff} (nm)	53.79	53.79	121.53	121.53	51.33	56	44.66	44.66	77.33	77.33	47.90	47.90	128.46	128.46
\bar{d}_{ev} (nm)	89.16	89.16	201.44	201.44	95.53	104.21	83.126	83.126	143.92	143.92	84.97	84.97	227.88	227.88
Edge (nm)	54	54±8	122	122±13	77±6	84±6	67	67±6	116	116±11	88	88±10	236	236±19
Shape	Cuboctagonal	Cuboctagonal	Cuboctagonal	Cuboctagonal	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Octahedral	Octahedral	Octahedral	Octahedral
Material	Gold	Gold	Gold	Gold	Gold	Silver	Gold	Gold	Gold	Gold	Gold	Gold	Gold	Gold

medium is not considered in Eq. 1. Different values obtained for β considering the data of Ref. [31] show the effect of size distribution in validity of Eq. 4. Also different calculated β values for Ref. [30] and [31] are probably due to effect of refractive index on this equation, since small changes in refractive index lead to changes in λ_{SPR} . It is important to note that embedding mediums of nanoparticles of Ref. [30] are the same and the large difference between calculated β values is probably due to shape effects of NPs on their extinction spectra. So, for overgeneralizing Eq. 4 one should consider shape and size distribution effects, as well as the effects of refractive index of embedding medium on extinction spectra.

Now the validity of Equations 1, 4, 5, 13, 14 and 15 about cuboctahedral, octahedral and cubic gold and silver nanoparticles are investigated using data in Ref. [26] and [32]. Their extinction spectra are depicted in Figure 6 (theoretical spectra obtained using DDA calculation), and the calculated values of \bar{d}_{ev} , L_{eff} and β using both \bar{d}_{ev} and L_{eff} are listed in Table 5.

Differences between theoretical and experimental values of β for cuboctahedra, cubes and octahedra may be due to size distribution and in this regard dispersity should be considered in Eq. 4 and 14. Although refractive index of the embedding medium of the cuboctahedral particles affects the final results but, for larger particles Eq. 1 and 13 are not applicable since their equivalent diameters are larger than that Khlebtsov determined.

Exact calculated value of edge size of cubic gold particles prepared by Lee and co-workers [32] show the applicability of Eq. 1 and 13 for non-spherical particles if the effects of shape, size distribution and medium were considered [32]. Moreover, the results obtained for silver nanostructures confirm this expression and reveal that β depends on particles' matter. It seems that for particles with sharp corners like octahedra, these equations are not applicable. Because sharp corners affect extinction spectra and cause such a high red shift in extinction spectra which modifications of Eq. 1 and 4 would not lead to exact results. Therefore, Eq. 13, 14 and 15 are more exact for non-spherical particles since they deal with MFP of electrons which is determining in electrical and optical properties of nanoparticles, independent of their shapes.

Conclusion

The applicability of size determination equations based on extinction spectra of spherical and non-spherical silver and gold nanoparticles have been investigated. It has been found that modified forms of those equations may give more exact results and they should be modified as a function of shape, size distribution and refractive index of particles' embedding medium in order to be overgeneralized

to non-spherical particles instead of sphere only. Furthermore, equations of spherical particles should depend on these parameters to rise to more exact results. Moreover, it has been found that modified forms of those equations do not lead to exact results for particles which have corners with spatial angles less than $\pi/2$ sr such as octahedral particles. Such sharp corners cause additional redshift in the extinction spectra which has not been considered in those equations.

Abbreviations

SPR: Surface Plasmon Resonance; \bar{d}_{ev} : Average equivalent diameter; λ_{SPR} : Surface plasmon resonance wavelength; e : The aspect ratio of spheroids and s-cylinders; σ : Standard normal distribution parameter; A_{max} : Maximum of extinction coefficient in extinction spectra; A_{min} : Minimum of extinction coefficient in extinction spectra; A_{450} : Extinction coefficient in 450 nm in extinction spectra; a_{av} : The average major semi-axis; b_{av} : The average minor semi-axis; $\Delta\lambda$: Full width at half maximum of extinction spectra (FWHM); R : Particle radius; C : Light velocity in vacuum; β : Proportionality constant; v_{F} : Fermi velocity of electron gas in the particle; d_{av} : The average diameter of particles; λ_{r_n} : Longitudinal resonance wavelength where $n=1, 2, 3$, etc. corresponds to dipolar, quadrupolar, octapolar and etc. plasmon resonances; A_0 : Constant; A : Constant; n_{m} : Initial medium refractive index; B : A weak function of particle shape and order of multipole resonances; Δn_{m} : Changes of refractive index of the embedding medium; h : Thickness of dielectric shell around metal core with diameter D ; a : The core volume fraction; L_{eff} : The mean free path in nanostructures; V : The volume of particles; S : The surface area of particles.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

AAA carried out the absorption spectroscopy studies, participated in the derivation of equations and prepared the manuscript. AB carried out the derivation of equations and drafted the manuscript. All authors read and approved the final manuscript.

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