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Study of Light Extinction and Surface Plasmon Resonances of Metal Nanocluster: a Comparison Between Coated and Non-coated Nanogeometry

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Abstract We suggest a noble design of coated and non-coated nanospheroids to study the tunable behaviour of surface plasmon resonances with different physical environments. Incorporation of coated nanospheroids into the various dielectric media exhibits double dipole plasmonic resonance spectra, which are highly tunable in the visible to infrared regions of the electromagnetic spectrum. The tunability of double dipole peaks and its spectral width depend upon the shape anisotropy of the chosen nanogeometry (especially prolate- and oblate-shaped coated silver and gold nanospheroids). By changing the major and minor axes radii of the inner ellipsoid, there is gradual blue and red shifting in the surface plasmon resonance (SPR) peak position. It was accounted that for the prolate-shaped coated gold nanospheroid with inner radii a_1=10 nm and c_1=3.8 nm and outer radii a_2=16 nm and c_2=6.08 nm, two SPR peaks are found at wavelengths 615 and 826 nm. In addition, the tunability of SPR peaks and full width at half maximum (FWHM) value have also been discussed with surrounding media and it was found that the magnitude of the peak extinction is maximum for refractive index N=2. With the selection of various optical constants of embedding media, the wide tunability of plasmonic resonance spectra that lies in the range of 400–1100 nm has been observed. We have also discussed the advantage of coated nanospheroids over non-coated nanospheroids in the context of tunability of the SPR peak as well as the number of photons absorbed inside the thin-film wafer.

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Introduction

Plasmonics is an intriguing field of science and technology which focuses on plasmons, the collective oscillations of the free electron gas density [1–3]. Similar to photons and phonons which are the quanta of light and lattice waves, plasmons can be considered as quantized energy of a charge density wave or quanta of plasma oscillations. Plasmons crucially determine optical properties like scattering, absorption and extinction of metal nanoparticles (MNPs). For example, incident electromagnetic waves with a frequency below the bulk plasmon frequency are reflected because the electric field of the incident light is screened by the ensemble free electrons inside the metal [4–6]. The energy associated with the bulk plasmon is often considered as a constant, and it depends only on the electron density. Noble metals support the surface plasmonic mode which exhibits extraordinary optical properties in different regimes of the electromagnetic spectrum. When nanoparticles are excited by the electromagnetic radiation, they exhibit unique types of optical properties such as surface plasmon resonances (SPR) and local field enhancement. The SPR effects will be observed when the incident light frequency matches the frequency of collective oscillation of conduction electrons of MNPs. Under the SPR condition, maximum absorption of photons as well as local field enhancement surrounding the nanoparticle has been observed [7]. The SPR wavelength of MNPS can be controlled by controlling parameters such as particle size, shape and local dielectric environment. Hence, the MNPs with wide tunability of SPRs especially in the visible to near-infrared regions have been used in various applications such as optical filters, ultrafast optical

switching, surface enhanced Raman spectroscopy and sensing and solar photovoltaics [8–10]. Over the decades, several experimental and numerical studies have been showing the tunable SPR property of nanoparticles [11–13]. For the spheroidal topology, two distinct resonances appear and they possess amplitudes with different magnitudes. Clearly, a spheroid has axes of different lengths and so there are different oscillations along them which eventually give rise to resonance peaks of different magnitudes. This also gives an extra degree of freedom for tunability of the resonance. The frequency of two dipole modes has a wide tunability range from the visible to infrared regions of the electromagnetic spectrum. The first SPR peak (low wavelength domain) is small in amplitude in comparison to the second one.

Metallic nanoparticles strongly scatter and absorb light despite having subwavelength dimensions. Therefore, they can be used as a light-trapping agent in thin-film solar technology without introducing the surface roughness concept into the device. However, the metal nanoparticles must be correctly designed to optimise optical behaviour across the wavelength range of interest and to minimise losses. The optical properties (extinction, absorption, scattering) of nanoparticles are sensitive to a wide range of parameters, and so design optimisation is a complex task. Nowadays, various types of nanogeometries have been considered to enhance the absorption of photons inside the photoactive material, and various types of nanostructures are nanopillar, pyramid, rounded cubes, nanospheroid and coated geometries [1–5]. Recently, varieties of core/shell materials (in which the core is metal and the shell is a semiconductor and vice versa) have been used to trap solar light in different parts of the available spectrum. In a nutshell, by choosing the various parameters regarding size, shape and morphology of a nanostructure, we can tune plasmonic resonances and the magnitude of extinction.

Here, we have considered a coated nanospheroid embedded in various types of dielectric matrix. With this, a coated nanogeometry in which the core is a noble metal (silver or gold) and the shell is dielectric (silicon) has been taken to discuss the broadband tunability of SPRs. The advantage of choosing a coated nanoellipsoid is twofold: first, consideration of the metallic core which exhibits surface plasmonic modes that can offer a giant near electric field inside the semiconductor nanoshell which will greatly influence the magnitude of the extinction peak, and second, a nanospheroid geometry with prolate and oblate shapes can exhibit different types of optical resonances in different regimes of the electromagnetic spectrum. In addition, the choice of coated nanogeometry is beneficial for tuning the SPRs and the magnitude of extinction efficiency in the visible to infrared regions of the electromagnetic spectrum [14, 15]. The wavelength-dependent dielectric constant of core/shell (metals/Si) geometry has been taken from the literature [16]. Also, we have investigated how the prolate- and oblate-shaped coated nanoellipsoids play an important role in the tuning of SPRs of noble MNPs and its broadening in the desirable range of our available solar spectrum. We have also compared the SPRs and extinction magnitude for coated and non-coated nanospheroids separately and shown how the coated system is advantageous over the non-coated system.

The schematic diagram of a core/shell nanospheroid is shown in Fig. 1. In this core is noble MNP (used as a plasmonic material) and the shell is a semiconductor (silicon). The inner (core) radii are a_1, b_1 and c_1 and the outer radii are a_2, b_2 and c_2 along the x, y and z axes respectively.

Theory

The interaction of light with the metallic nanospheroid will exhibit the SPR effects, and the tunability of this SPR peak position is highly dependent on size, shape (prolate and oblate spheroids) and dielectric environment [17, 18]. The optical properties of coated nanostructures can be understood by considering electrostatic approximation in which the dimensions of a nanoparticle are smaller than the wavelength of incident light. Under the electrostatic approximation, field scattered by nanoparticle can be found by solving Laplace equation with appropriate boundary condition [17]. Considering a nanospheroid-shaped particle placed in an arbitrary medium, if there exists a static electric field, then this field induces a lot of little dipoles which are pointing along the direction of the field and particles become polarised. A convenient measure of this effect is known as polarisation which is the dipole moment per unit volume expressed as [17, 19]

$$P = \varepsilon_m V_i \frac{(\varepsilon_1 - \varepsilon_m)}{3\varepsilon_m + 3L_{xyz}(\varepsilon_1 - \varepsilon_m)} E_0 \tag{1}$$

Therefore, the dipolar polarizability of a simple non-coated ellipsoid in a field parallel to one of its axes is given as

$$\alpha_{xx,yy,zz} = V_i \frac{(\varepsilon_1 - \varepsilon_m)}{3\,\varepsilon_m + 3\,L_{xyz}(\varepsilon_1 - \varepsilon_m)} \tag{2}$$

Here, we have considered a coated nanospheroid geometry in which the extinction spectra can be understood in terms of polarisability [19].

$$\alpha_{xx\,yy\,zz} = V \frac{\left((\varepsilon_2-\varepsilon_m)\left[\varepsilon_2 + (\varepsilon_1-\varepsilon_2)\left(L^1_{xyz} - f L^2_{xyz}\right)\right] + f\varepsilon_2\,(\varepsilon_1-\varepsilon_2)\right)}{\left[\varepsilon_2 + (\varepsilon_1-\varepsilon_2)\left(L^1_{xyz} - f L^2_{xyz}\right)\right]\left[\varepsilon_m + (\varepsilon_2-\varepsilon_m) L^2_{xyz}\right] + f L^2_{xyz}\varepsilon_2\left(\varepsilon_1-\varepsilon_2\right)} \tag{3}$$

$$V = \frac{4}{3}\pi a_2 b_2 c_2, \quad f = \frac{a_1\,b_1\,c_1}{a_2\,b_2\,c_2},$$

where V is the total volume of the ellipsoid and f is the volume ratio of the core to the whole of the ellipsoid. ε_1 and ε_2 are the dielectric constants of the core and shell of the nanoellipsoid, and ε_m is the dielectric constant of host media. $L^1{}_{x,\,y,\,z}$ and $L^2{}_{x,}$

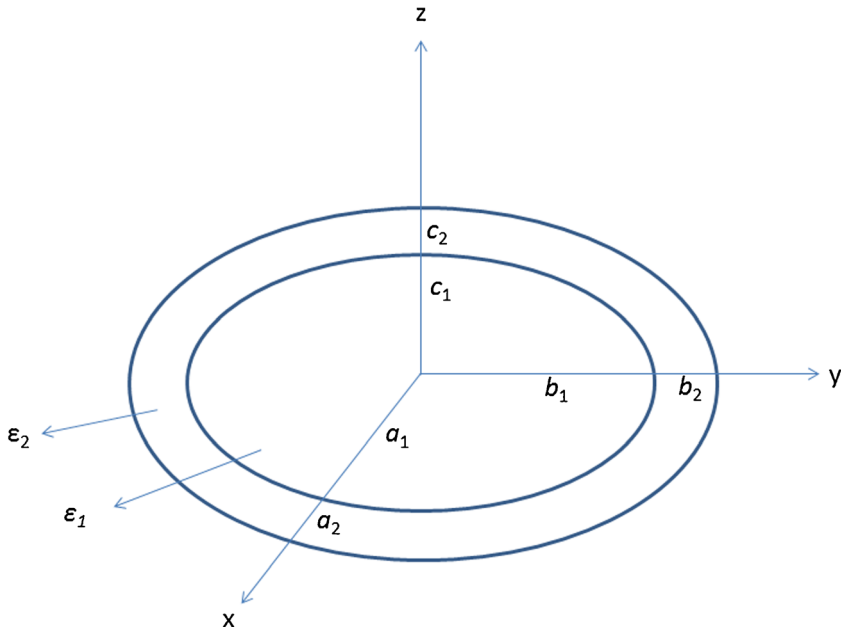

Fig. 1 Spheroidal particle with semiminor axes a_1, b_1 and c_1 and a_2, b_2 and c_2 of inner and outer ellipsoids along x, y and z axes respectively. ε_1 and ε_2 are the dielectric constants of core (Ag or Au) and shell (silicon)

$_{y,\,z}$ are the depolarization factors of the inner (core) and outer ellipsoid. $\alpha_{xx,\ yy,\ zz}$ is the polarizability of a coated ellipsoid when the applied field is parallel to the x, y and z axes respectively. A more general case of an ellipsoid is a spheroid in which two minor or major axes are equally known as prolate or oblate ellipsoid respectively. Only two of the three depolarization factors are independent because of the following relation:

$$L_x^i + L_y^i + L_z^i = 1$$

For the prolate-shaped spheroid, two minor axes ($a_i > b_i = c_i$) and depolarization factors L^i_y and L^i_z are equal, where $i=[1, 2]$, 1 for the inner ellipsoid and 2 for the outer ellipsoid. The polarisation factor (L^i_x) along the x direction is a function of eccentricity.

$$L_x^i = \frac{(1-e_i^2)}{e_i^2}\left(-1 + \frac{1}{2e_i} 2.303 \log \frac{1+e_i}{1-e_i}\right)$$
$$e_i^2 = 1 - \frac{a_i^2}{c_i^2}$$

For an oblate spheroid ($c_i < a_i = b_i$), the depolarisation factor $L^i_x = L^i_y$ in terms of eccentricity is

$$L_x^i = \frac{g(e)}{2e_i^2}\left[\frac{\pi}{2} + \tan^{-1} g(e)\right] - \frac{g(e)}{2}$$
$$g(e_i) = \left(\frac{1-e_i^2}{e_i^2}\right)^{\frac{1}{2}},\ e_i^2 = 1 - \frac{c_i^2}{a_i^2}$$

The dielectric constants which are used in the polarizability expression are the key parameters for the computation of optical parameters such as scattering, absorption and extinction efficiency. Since the dielectric property of bulk MNPs is entirely different from the nanolevel properties, at the nanolevel, the dielectric constants of MNPs are highly dependent on the size and shape of the nanoparticles. Hence, the size-dependent dielectric constant of nanoparticles can found by solving the Drude Lorentz model [20–22].

$$\varepsilon(\omega) = \varepsilon_{\text{bulk}}(\omega) + \frac{\omega_p^2}{\omega^2 + j\,\varepsilon_{\text{bulk}}\,\omega} - \frac{\omega_p^2}{\omega^2 - j\gamma\omega} \tag{4a}$$

where ω_p is the bulk plasma frequency (1.36×10^{16} Hz, 1.37×10^{16} Hz for silver and gold respectively), ω is the frequency of incident electromagnetic waves and γ_{bulk} is the damping constant of bulk MNPs. When the size of a particle is smaller than the mean free path, there is an interaction taking place between the free electrons with the particle boundary. Due to this interaction, the spectral width and SPRs of MNPs are affected. Hence, there is a strong need of the correction of the bulk damping rate of the nanoparticle, which can be expressed as

$$\gamma = \gamma_{\text{bulk}} + A\frac{\nu_f}{R}$$
$$\tau = \frac{1}{\gamma},\ \ \tau_{\text{bulk}} = \frac{1}{\gamma_{\text{bulk}}} \tag{4b}$$

where τ is the effective relaxation time, τ_{bulk} is the bulk metal free electron scattering time, ν_f (=1.39×10^6 m/s, 1.38×10^6 m/s for silver and gold) is the Fermi velocity of an electron in noble MNP, A is the geometrical parameter and its value lies between 2 and 1 (in our case, we have chosen $A=1$ for isotropic scattering) [22] and l is the effective radius of the metallic core which depends on the shape.

$$R = [(a_2 - a_1)(b_2 - b_1)(c_2 - c_1)]^{1/3} \tag{4c}$$

Here, we have used the coated nanoellipsoid geometry in which the core radius is smaller than the mean free path of bulk metallic materials, so that the surface interaction term must play a significant role in spectral broadening and SPR peak positions [23–25]. The dielectric constants of MNPs are highly dependent on the shape parameter. Hence, by changing the major and minor axes' distance of the chosen nanogeometry, we can change the SPR peak positions and its broadening. There are two types of spectral broadening, (1) extrinsic, which occurs in large-sized nanoparticles, and (2) intrinsic, which occurs in smaller sized nanoparticles, and it arises due to the interaction of electrons near the surface or boundary of nanoparticles.

The general expression of absorption, scattering and extinction cross section of a coated nanoellipsoid under quasi-static approximation (the particle size is much smaller than the wavelength of light) can be expressed as [22, 24]

$$C_{\text{abs}} = k\text{Im}\left\{\frac{1}{3}\alpha_{xx} + \frac{1}{3}\alpha_{yy} + \frac{1}{3}\alpha_{zz}\right\} \tag{5a}$$

$$C_{\text{scat}} = \frac{k^4}{6\pi}\left\{\frac{1}{3}|\alpha_{xx}|^2 + \frac{1}{3}|\alpha_{yy}|^2 + \frac{1}{3}|\alpha_{zz}|^2\right\} \tag{5b}$$

$$\begin{aligned} C_{\text{extn}} &= C_{\text{abs}} + C_{\text{scat}} \\ k &= \frac{2\pi(a_2 b_2 c_2)^{1/3}}{\lambda} \end{aligned} \tag{6}$$

where k is the size parameter and strongly depends upon the shape of the nanostructure. The efficiency parameter can be calculated by taking the ratio of the optical cross section to its geometrical cross section, and the geometrical cross section also depends on the shape of the nanoparticle. Our aim is to find the extinction spectrum of a coated nanospheroid (specifically prolate and oblate shaped) with different core/shell radii. The wavelength-dependent extinction efficiency can be expressed as

$$Q_{m\,\text{prolate}} = \frac{C_{m\,\text{prolate}}}{\pi a_2 c_2} \tag{7}$$

$$Q_{m\ \text{oblate}} = \frac{C_{m\ \text{oblate}}}{\pi a_2 c_2} \tag{8}$$

for a prolate spheroid ($c_2 > a_2 = b_2$), for an oblate spheroid ($c_2 < a_2 = b_2$) and m=[abs, scat, extn].

In order to study the plasmonic effects in a silicon wafer, we must calculate the overall absorption of photons in the thin-film silicon wafer in the presence and absence of the chosen nanogeometry under the influence of AM1.5 solar spectrum [25], and metallic nanoparticles are incorporated up to the band edge of silicon. The efficiency of the solar device in the presence of coated and non-coated nanoparticles is given by [26]

$$\eta = \frac{\int_0^{\lambda_g} I(\lambda)\, Q_{\text{scat}}(\lambda)\, \frac{\lambda}{\lambda_g}\, d\lambda}{\int_0^{\infty} I(\lambda)\, d\lambda} \tag{9}$$

where $I(\lambda)$ is the intensity of incident light photons according to the AM1.5 solar spectrum available, Q_{scat} is the scattering cross section of the nanoparticle which is normalised by its geometrical cross section and λ_g is the band edge for the silicon cell. The total number of photons absorbed (under the influence of coated and non-coated nanogeometries) inside the thin silicon cell is given as

$$N_{\text{ab}} = \left[I(\lambda) \times N_{\text{p}} \times C_{\text{scat}} + I(\lambda) \times \left(1 - N_{\text{p}} \times C_{\text{ext}}\right) \times A\right] \tag{10}$$

where N_{p} is the nanoparticle concentration (here, we have done the calculation for 10 % particle concentration) and A is the fraction of photon absorbed by a 1-μm-thick silicon film which is given as

$$A = 1 - \left[R + \frac{T^2 R Q^2}{1 - R^2 Q^2} + \frac{T^2 Q}{1 - R^2 Q^2}\right] \tag{11}$$

where $Q = e^{-\alpha x}$ (α is the absorption coefficient and x=1 μm is the thickness of the silicon wafer), and R and T are reflection and transmission coefficients of the silicon wafer respectively (http://www.pveducation.org/pvcdrom/appendicies/optical-properties-of-silicon) [27].

Results and Discussion

The plasmonic response of coated metal nanostructures depends upon size, shape and type of coating materials. Figure 2 shows the wavelength-dependent extinction efficiency of a coated nanospheroid. To discuss the SPR peak position, full width at half maxima (FWHM) and extinction efficiency, we have taken a prolate-shaped ($c_1 > a_1 = b_1$, $c_2 > a_2 = b_2$) core/shell nanoellipsoid. In the core/shell nanoellipsoid, the core is noble MNP (silver or gold) and the shell is a semiconductor (Si). The coated MNPs are embedded in silica matrix. By choosing different radii along the semiminor axis of an inner ellipsoid with fixed outer ellipsoid radii, we observe the double plasmonic resonance peak that can be tuned in the desired region of the electromagnetic spectrum. Figure 2a indicates the extinction spectra of a prolate-shaped core/shell (Ag/Si) nanospheroid embedded in silica matrix. The observation shows that with an increase in size of the silver core keeping

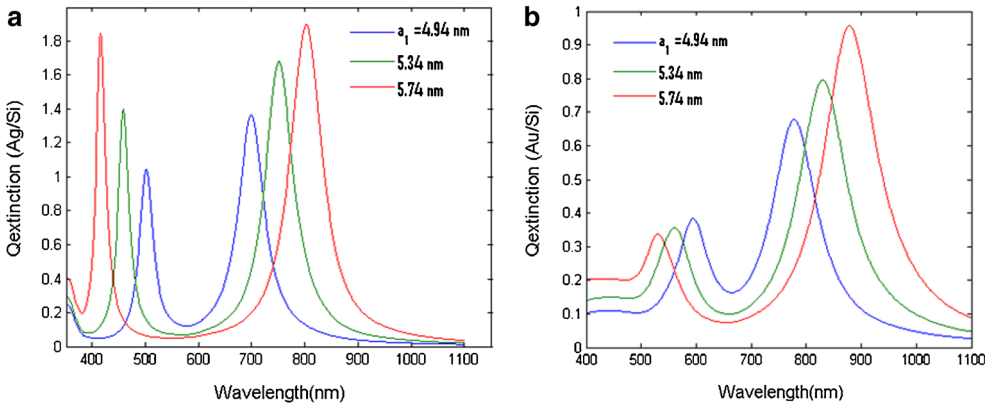

Fig. 2 **a** and **b** show the extinction spectra of prolate shape ($c_1>a_1=b_1$, $c_2>a_2=b_2$) core/shell (MNP/Si) nanoellipsoid with inner radii a_1=4.94, 5.34 and 5.74 nm and c_1=13 nm and fixed outer radii a_2=6.08 nm, b_2= 6.08 nm and c_2=16 nm

constant the shell size, the first dipole peak is blue shifted while the second dipole peak is red shifted and the magnitude of the extinction peak is also enhanced. The same trend has been confirmed with a system having gold as a core material where the magnitude of the extinction peak is in decreasing order for the first dipole peak and increasing order for the second dipole peak. In order to discuss the extinction spectrum for the case of silver, we have taken the inner ellipsoid radii (a_1=4.94 nm, $b_1=a_1$, c_1=13 nm) and the outer ellipsoid radii (a_2=6.08 nm, $b_2=a_2$, c_2=16 nm) along the x, y and z axes. For the present case, the first and second dipole peaks are obtained at SPR wavelengths 503 and 701 nm respectively. To increase radii along the minor axis of the prolate ellipsoid, keeping the other sensitive parameters such as aspect ratio (asr=0.38), outer ellipsoid radii, etc. constant, the resonance is observed to be blue shifted for the first dipole peak and red shifted for the second dipole [28, 29]. With the gold nanoparticle used as core and silicon as a shell embedded in a silica matrix having the same inner and outer radii (a_1= 4.94 nm, $b_1=a_1$, c_1=13 nm) as discussed for the silver case, we have found the SPR wavelength of the first and second dipole peaks are at 595 and 778 nm respectively, as shown in Fig. 2b. We have also discussed the spectral broadening of the core/shell system in terms of full width half maxima (FWHM). Next, we increase the core size with fixed shell size, and the spectral broadening for the first dipole peak decreases, whereas for the second dipole, it increases. We consider a case of Ag/Si (core/shell) geometry with minor axes radii (a_1= 4.94 nm, $b_1=a_1$, c_1=13 nm). The FWHM values for the first and second dipole peaks are obtained at 35 and 60 nm respectively. Table 1 summarises the SPR wavelength of double plasmonic peaks and FWHM of core/shell (Ag or Au/Si) nanogeometry with three different minor axes radii.

In Fig. 3, we consider the extinction spectra of the oblate-shaped core/shell nanospheroid embedded in silica matrix. For the oblate-shaped ($c_1<a_1=b_1$, $c_2<a_2=b_2$, where c_1 and c_2 are minor axes and a_1 and a_2 are major axes radii of the inner and outer ellipsoids respectively) core/shell (meta/silicon) nanostructures, we have found the double plasmonic peaks with different SPR wavelengths and peak extinction value. From the extinction spectrum, it is evident that when we increase the semimajor axis of the inner ellipsoid with fixed radii of the outer ellipsoid, both dipole peaks are blue shifted. Taking the particular case of the oblate-shaped

Table 1 Represents the SPR wavelength and FWHM value of the first and second dipole peaks with different minor and major axes radii

Inner radii		Outer radii		SPR wavelength				FWHM of first and second dipole peaks			
				Silver		Gold		Silver		Gold	
a_1	c_1	a_2	c_2	λ_{1Ag}	λ_{2Ag}	λ_{1Au}	λ_{2Au}	W_1	W_2	W_1	W_2
Prolate ellipsoid ($c_1>a_1=b_1$, $c_2>a_2=b_2$), asr=0.38, $a_1=c_1\times$asr											
4.94	13	6.08	16	503	701	595	778	35	60	133	109
5.34	13	6.08	16	458	750	561	830	27	67	145	119
5.74	13	6.08	16	418	803	532	880	23	74	156	132
For oblate-shaped ellipsoid ($c_1<a_1=b_1$, $c_2<a_2=b_2$)											
10	3.8	16	6.08	521	750	615	826	34	61	93	107
10.5	3.99			514	727	604	802	32	56	91	97
11.5	4.37			495	685	587	763	30	50	90	84

λ_1 and λ_2 stand for the first and second SPR wavelengths respectively. W_1 and W_2 are the spectral widths of the first and second peaks

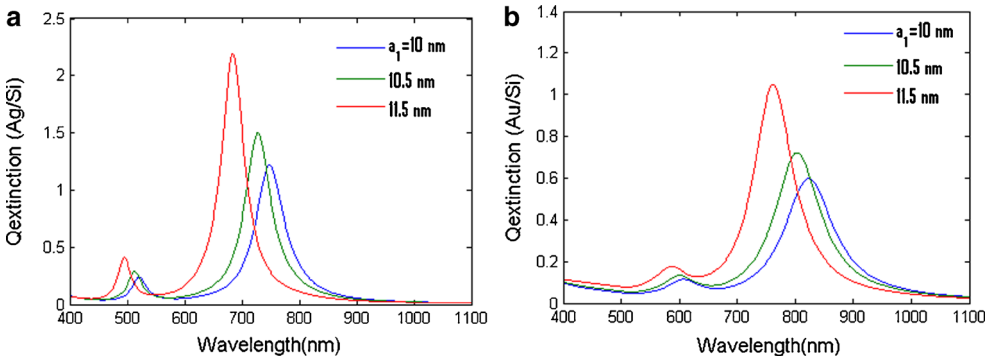

Fig. 3 **a** and **b** show the extinction spectra of oblate shape ($c_1<a_1=b_1$, $c_2<a_2=b_2$) core/shell (MNP/Si) nanoellipsoid with major axes radii a_1=10, 10.5 and 11.5 nm and c_1=asr×a_1, where aspect ratio (asr)=0.38

core/shell (Ag/Si) nanospheroid having inner radii a_1=10 nm, $b_1=a_1$ and c_1=3.8 nm and outer radii a_2=16 nm, $b_2=a_2$ and c_2=6.08 nm, the SPR wavelength and FWHM value are observed at 521 and 750 nm and 34 and 61 nm respectively as shown in Fig. 3a. In the case of Au/Si (core/shell), with an increase in the inner radii of the oblate-shaped nanospheroid, there is a consistent decrease in spectral broadening as well as blue shifting of the SPR peak position. With the same minor and major axes radii as we have taken in silver, the first and second SPR wavelengths of Au/Si are at 615 and 826 nm respectively. It is due to the higher plasma frequency of conduction electron of gold nanoparticle as compared to silver.

Now we have discussed the optical behaviour of a coated nanospheroid with three different physical environments as shown in Fig. 4. The optical property of a coated nanogeometry is highly dependent on the surrounding dielectric environment, so that the refractive index of embedding media is one of the key parameters in our discussion. For the solar cell purpose, the smallest refractive index is nearly 1.5, corresponding to SiO_2 or glass, and the largest refractive index material (which is used as an embedding medium) is a semiconductor. For the analysis of the extinction spectrum, first, we have embedded a prolate-shape coated nanoellipsoid into three different dielectric matrices having constant refractive indices 1.5, 2.0 and 2.5. To discuss the wavelength-dependent extinction spectra as indicated in Fig. 4a, we have taken a silver-coated silicon nanoellipsoid having fixed inner radii (a_1=4.94 nm, $b_1=a_1$, c_1=13 nm) and outer radii (a_2=6.08 nm, $b_2=a_2$, c_2=16 nm) that are embedded in three different embedding media. As we increase the refractive index of the embedding media, there is gradual red shifting of both the dipole peaks and an increment in the FWHM value. The reason for spectral broadening (FWHM) is the special behaviour of electrons near the MNP surface. These surface effects come into the picture via size-dependent permittivity of nanoparticles represented by Eqs. (4a), (4b) and (4c). The expression of size-dependent permittivity has been derived by solving the equation of motion for a bunch of electrons interacting with the external optical field. The same trends are followed by Au/Si (core/shell) nanogeometry. With the same outer and inner radii (as mentioned for the Ag/Si), the value of the first and second SPR peak positions are found at 594 and 781 nm and their spectral widths are nearly at 88 and 105 nm respectively. The higher the refractive index of host media, the more will be the polarisation of charges which reduces the frequency of oscillation of electrons. Due to the reduction in frequency oscillation of electrons, the resonance peak shifted to a longer wavelength. The width of the resonance peaks (FWHM) is due to the shape anisotropy where the effective shell thickness is smaller than the mean free path of electrons. The FWHM value also depends on both choice of host media and type of noble metal nanoparticles. Different types of metal nanoparticles (Ag, Au) exhibit different spectral widths as shown in Tables 1 and 2. Table 2 represents the SPR peak

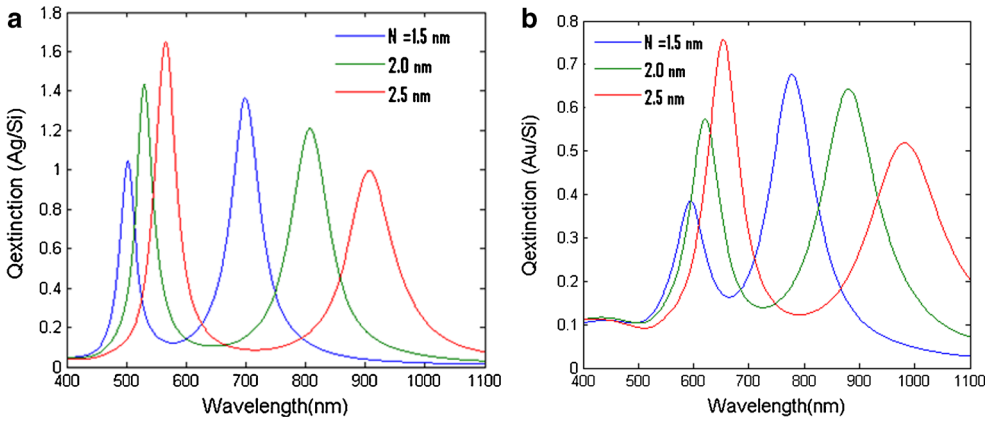

Fig. 4 **a** and **b** show the extinction spectra of prolate shape core/shell (MNPs/Si) nanoellipsoid with different embedding media N=1.5, 2.0 and 2.5 and fixed minor axes radius a_1=4.94 nm

Table 2 Represents the SPR wavelength and FWHM value of the first and second dipole peaks with three different refractive indices and fixed minor and major axes radii of inner and outer ellipsoids

Refractive index	Inner radii		Outer radii		SPR wavelength				FWHM of first and second peaks			
					Silver		Gold		Silver		Gold	
N	a_1	c_1	a_2	c_2	λ_1	λ_2	λ_1	λ_2	W_1	W_2	W_1	W_2
For prolate ellipsoid ($c_1>a_1=b_1$, $c_2>a_2=b_2$)												
1.5	4.94	13	6.08	16	500	698	594	781	33	59	88	105
2.0					530	809	621	878	34	78	78	131
2.5					566	908	655	983	44	96	74	176
For oblate-shaped ellipsoid ($c_1<a_1=b_1$, $c_2<a_2=b_2$)												
1.5	10	3.80	16	6.08	528	742	612	812	35	60	97	105
2.0					535	795	622	865	37	70	95	120
2.5					545	837	630	907	39	73	83	128

λ_1 and λ_2 stand for the first and second SPR wavelengths, and W_1 and W_2 are the spectral widths of the first and second peaks

wavelength and spectral broadening (FWHM) for the first and second dipole peaks with fixed outer and inner radii and various embedding media. All extinction calculations of coated nanospheroids have been done by using Eqs. (7), (8) and (3), where Eq. (3) represents the polarizability of a coated sphere.

Figure 5 provides an illustration of an oblate-shaped coated nanoellipsoid embedded in various types of embedding media. The SP modes of the spheroid show different plasmon resonances along its different axes. In our case, we have considered prolate and oblate spheroids where two of the minor and major axes are equal respectively. So, we have found the two plasmon resonances corresponding to the oscillation of electrons along the two axes of nanoparticles. By embedding an oblate-shaped core/shell (Ag, Au/Si) nanoellipsoid into three different types of embedding matrices, there is broad tunability of SPR peaks. For both the cases where silver and gold are used as core materials, the value of FWHM increases for the first plasmonic peak and SPR peak positions are red shifted as shown in Fig. 5a, b. But in both the cases, we have seen that the peak extinction value for the first dipole peak is smaller than that of the second dipole peak. It can also be seen that the spectral width for both dipole peaks in the case of silver is smaller than that of gold, considering the oblate-shaped nanospheroids with inner radii a_1=10 nm, $b_1=a_1$ and c_1=3.8 nm and outer radii a_2=16 nm, $b_2=a_2$ and c_2=6.08 nm are embedded into the dielectric matrix of refractive index N=2.5. With this parameter, it is found that the first and second SPR wavelengths for silver are at 545 and 837 nm while for gold they lie at 630 and 907 nm respectively. We can also conclude that the tunability of the SPR wavelength and its spectral width depend both on shape anisotropy and the embedding environment.

The magnitude of $Q_{\text{extinction}}$ is the sum of absorption and scattering cross section normalised by its geometrical cross section. Usually it is found that the optical cross section is larger than its geometrical cross section. The physical significance of extinction is the attenuation of electromagnetic waves by scattering and absorption when it travels into dielectric media [30]. Figure 6 shows the variation of the peak extinction value of oblate-shaped silver- and gold-coated nanospheroids at resonance wavelength with a medium refractive index. The maximum extinction value increase

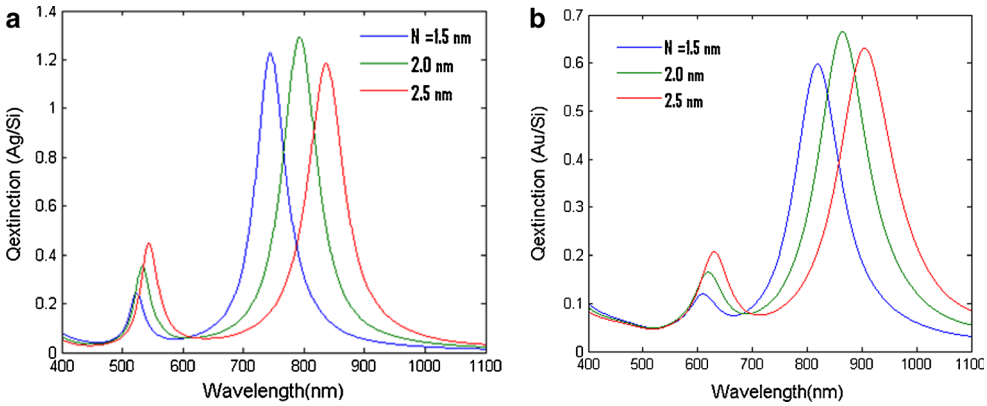

Fig. 5 **a** and **b** show the extinction spectra of oblate shape core/shell (MNPs/Si) nanoellipsoid with different embedding media N=1.5, 2.0, and 2.5 and fixed minor axes radius a_1=11 nm

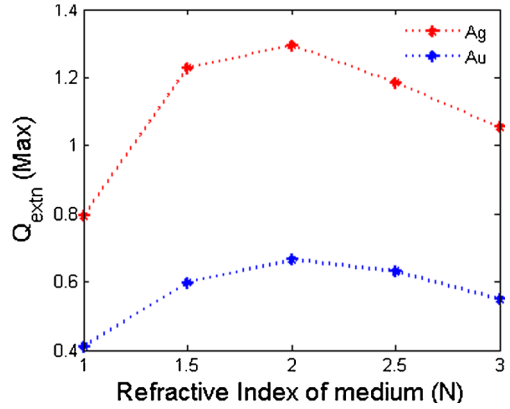

Fig. 6 Variation of peak value of $Q_{extinction}$ with refractive index of embedding media for oblate-shaped silver- and gold-coated nanospheroids having inner radii a_1=10 nm and c_1=3.8 nm and outer radii a_2=16 nm and c_2=6.08 nm respectively

consistently until a peak at N=2.0 and then decreases gradually with the refractive index of the surrounding medium. We have seen that the magnitude of the peak extinction is larger for silver as compared to a gold nanospheroid.

Let us now discuss the effects of a non-coated metal nanospheroid (prolate and oblate) on the extinction spectra and SPR peaks which are embedded in dielectric media having a refractive index N=2 as shown in Fig. 7. We calculate wavelength-dependent absorption, scattering and extinction expression by using Eqs. (5a), (5b) and (6), and the polarizability expression which we have used in the extinction calculation has been taken from Eq. (2). The first and second rows of Fig. 7 show the extinction spectra of oblate- and prolate-shaped silver and gold metal nanospheroids respectively. From Fig. 7a, we have observed the double dipole peak of the oblate-shaped silver nanospheroid with three different major axes radii 8, 9 and 11 nm and the first SPR peaks are at

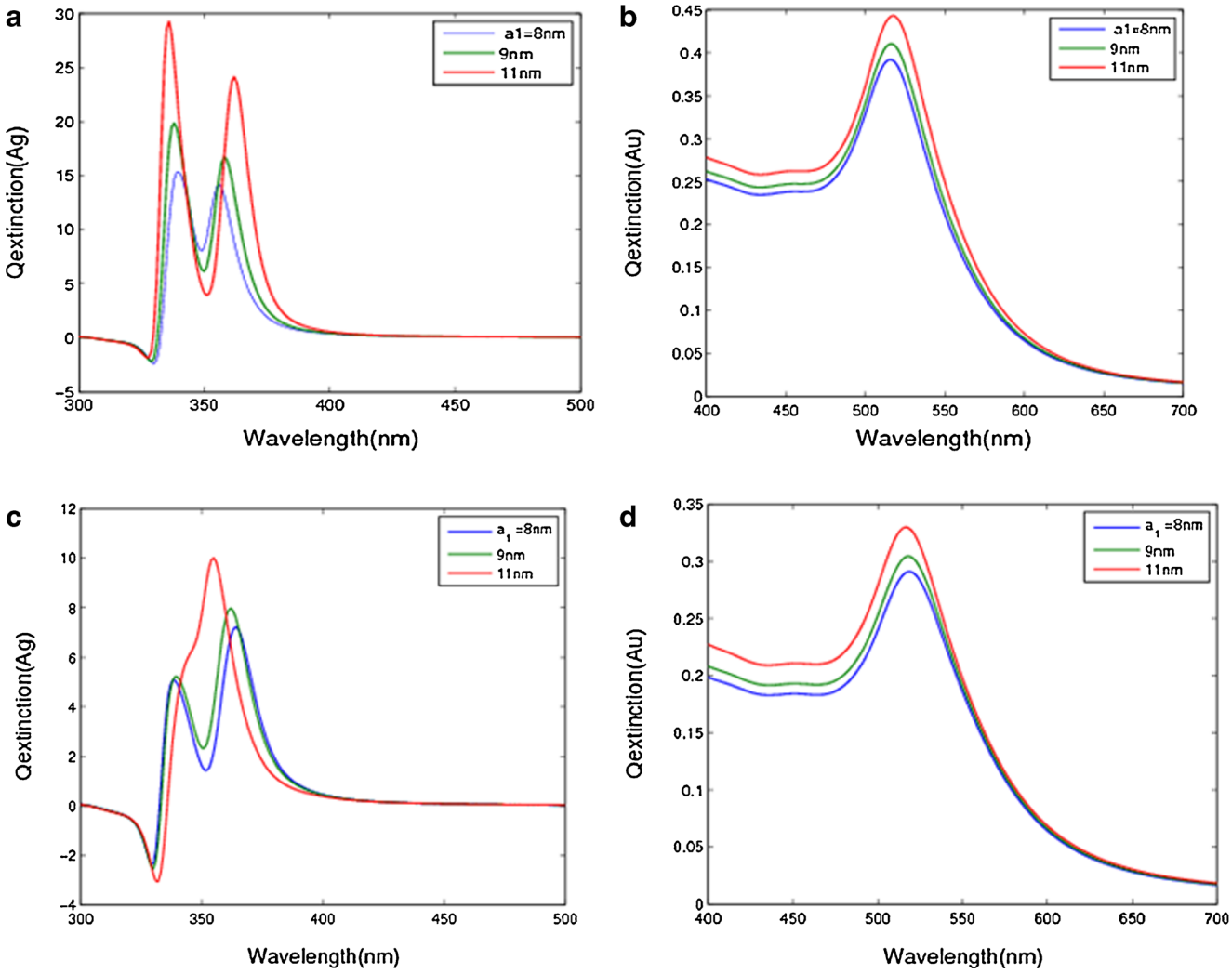

Fig. 7 Wavelength-dependent extinction spectra of oblate-shaped **a** silver and **b** gold nanospheroids with three different major axes radii a_1=8, 9 and 11 nm and **c** for prolate-shaped silver and **d** for prolate gold nanospheroid having three different minor axes radii 4.04, 5.22 and 6.38 nm which are embedded in dielectric media having N=2

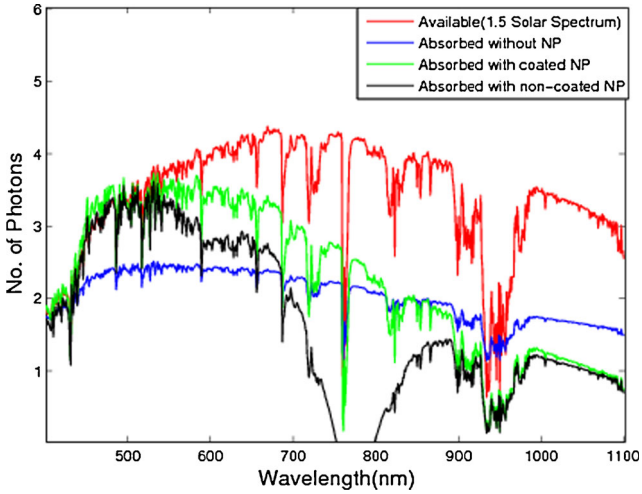

Fig. 8 Absorption of photons in a thin silicon wafer by integrating oblate-shaped coated and non-coated nanoparticles. The coated parameters a_1=10.5 nm, c_1=3.99 nm, a_2=16 nm and c_2=6.08 and non-coated oblate-shaped parameter a_1=11 nm and c_1=6.38

340, 338 and 336 nm (blue shifted as we increase radii) while the second SPR peaks are found at 356, 358 and 362 nm (gradually red shifted with increase of major axes radii) respectively. In the case of the oblate-shaped gold nanospheroid, there is a single SPR peak observed. As we increase major axes radii, the magnitude of $Q_{\text{extinction}}$ increases while the plasmonic peaks are fixed at wavelength 516 nm for all radii as shown in Fig. 7b. An interesting observation has been made in Fig. 7c, d, which reveals the extinction behaviour of prolate-shaped silver and gold nanoellipsoids. As we increase the minor axes radii, two dipole peaks are converted into a single dipole peak. Take the particular case of a_1=4.68 nm; here, two dipole peaks are found at 340 and 364 nm while for a_1=6.38 nm, we have only one SPR peak at 355 nm as shown in Fig. 7c. In Fig. 7d, the extinction behaviour of the prolate-shaped gold nanospheroid is the same as shown in Fig. 7b but the magnitude of extinction and SPR peak position are slightly different and are found at wavelength 520 nm. From Fig. 7, it can be concluded that the SPR peaks and magnitude of $Q_{\text{extinction}}$ are the function aspect ratio (ratio of minor to major axes radii). As we increase the major and minor axes radii of oblate- and prolate-shaped nanospheroids, corresponding depolarisation factors are changed which influences the SPR peaks and $Q_{\text{extinction}}$ magnitude.

Finally, we have found that for the case of silver, tunability in the SPR peak lies in the range of 300 to 400 nm while in the case of gold, it is almost fixed at a particular wavelength. But in the case of the coated nanospheroid, there is wide tunability of the SPR peak from 400 to 1100 nm for both metal nanoparticles, so that coated nanogeometries are more preferential as compared to non-coated.

Generally, the photovoltaic absorbers are optically thick to enhance the absorption of photons inside the active layer of the device, but the thicker active layer creates a problem in transportation of the charge carrier due to a short diffusion length; hence, a thicker layer degrades the solar cell efficiency. To take care of the physical parameter regarding cell efficiency, we need to use a thin silicon wafer but it still absorbs a lesser number of photons. In order to increase the photon absorption, we integrate coated and non-coated oblate-shaped gold nanospheroids on a thin silicon wafer as shown in the inset of Fig. 8. The number of photons absorbed by protruding coated and non-coated nanoparticles on a bare silicon wafer with standard AM 1.5 solar spectrum is illustrated in Fig. 8. Non-coated gold nanoparticles have a_1=11 nm and c_1=6.38 nm while coated case radii of inner and outer spheroids along major and minor axes are a_1=10.5 nm and c_1=3.99 nm and a_2=16 nm and c_2=6.08 nm respectively. The absorption of photons inside a solar cell including the effects of coated and non-coated nanoparticles is calculated by using Eq. (10), and in the case of a bare silicon cell, we have considered the multiple absorption that can be calculated by using Eq. (11). From the photon absorption spectrum, we conclude that an oblate-shaped coated gold nanospheroid enhances the photon number absorption over the non-coated and bare silicon in the visible to infrared regions of the electromagnetic spectrum. Hence, the benefits of coated nanogeometries on a thin-film wafer are more than that of non-coated.

Conclusion

In this work, we have discussed the extinction spectra of prolate- and oblate-shaped coated and non-coated nanospheroids in the domain where particle size is less than the incident wavelength. The electrostatic interaction of incident light with a silicon nanoshell surrounded by the silver and gold nanoparticles gives a highly tuneable and broadband response. For prolate- and oblate-shaped nanospheroids, the dipolar peaks can be tuned from 300 to 1100 nm and their corresponding spectral width from 23 to 132 nm with different minor and major axes. The tunability of SPR peaks and spectral width can be controlled by controlling major and minor axes radii as well as the surrounding dielectric environment. We want to mention that we have done the extinction calculation of isolated coated and non-coated metal nanoparticles. This proposed model can provide a very useful general platform for plasmonic researchers to study the various types of nanogeometries and their interaction with the surrounding environment.

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