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Light absorption efficiencies of gold nanoellipsoid at different resonance frequency

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Abstract Light absorption efficiencies (defined as the ratio of the absorption cross section to the total extinction cross section at each resonance wavelength) of gold nanodisk and nanorod were calculated based on quasi-static approximation. The absorption efficiency solely depends on the frequency of surface plasmon resonance. With increasing resonance wavelength, the absorption efficiencies change in the same fashion for both nanodisk and nanorod. However, the resonance absorption at short wavelength is easy to be obtained by gold nanodisk, whereas the resonance absorption at longer wavelength is easy to be obtained by gold nanorod. High absorption efficiency (>98%) can be obtained in the visible region by increasing the aspect ratio of gold nanodisk. Although the longitudinal absorption efficiency of gold nanorod is relative lower by increasing the aspect ratio, the absorption efficiency is also tunable in the near infrared region, which makes it potentially useful in silicon solar cells and vivo applications.

Introduction

Optical responses of gold and silver nanometer-sized particles with anisotropic shape have attracted a large number of theoretical and experimental investigations in recent years, because of their excellent potential in the fabrication of nanostructure with tunable optoelectronic properties [1–5]. The optical characters of small metal particles are dominated by the collective oscillation of the conduction electrons as a result of the interaction with incident electromagnetic field. So, gold nanoparticles strongly absorb and scatter light at the surface plasmon resonance (SPR) frequency, which results in their vivid color [6]. Stoleru and Towe [6] have found that the ratio of the scattering cross section to absorption cross section changes dramatically with the size of the nanoparticles. Then large particles scatter light very efficiently, whereas the color of small particles is mainly caused by absorption.

The optical radiation efficiency is defined as the ratio of the scattering cross section to the total extinction cross section [7]. Recently, Tanabe [7] reported the optical radiation efficiencies of 11 kinds of metal nanospheres for optoelectronic applications. Ag, Al, Au, and Cu were found to have much higher optical radiation efficiencies than the other metals at most range of wavelengths. This relative contribution of scattering to the extinction is strongly depending on the nanoparticle size, and the increase in the size results in an increase in the extinction as well as the relative contribution of scattering [8]. When the volumes of particles are fixed, the shape and aspect ratio become important factor. The ratio of scattered efficiency to the total extinction at each resonance maximum has also been named as scattering quantum yield [9]. In the report of Lee and El-Sayed [9], the radiative quantum yield for the longitudinal mode has been found to be significantly dependent on the aspect ratio of the nanorod in a somewhat complex manner, which is different from a typical linear relationship for the resonance wavelength. Langhammer et al. [10] have experimentally and theoretically explored

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the branching ratio of the radiative and nonradiative localized surface plasmon decay channels for nanodisks of Ag, Au, Pt, and Pd, with diameters ranging from 38 to 530 nm and height 20 nm. They have shown that the material choice for metal nanodisks strongly influences the branching ratio between scattering and absorption decay processes of a localized SPR.

Many researches focus on the optical radiation efficiencies, because high relative contribution of scattering to the extinction can be used for many applications such as sensing or plasmon mediated chemistry. For example, the superior scattering properties of gold nanospheres have already been exploited for the selective imaging of cancer cells [8, 11]. However, high relative contribution of absorption to the extinction also has many potential applications [8, 12], especially in the field of bio-thermo-therapy and solar energy materials [13–16]. For example, effective photothermal therapy with minimal laser dosage requires a high nanoparticle absorption cross section with low scattering losses [8]. Light trapping is particularly critical in thin-film crystalline silicon solar cells in order to increase light absorption and hence cell efficiency [13]. Pillai et al. [13] have investigated the effect of surface plasmons on silver nanoparticles as a means of improving the efficiency of thin-film and wafer-based solar cells. Nishioka et al. [14] reported antireflection sub-wavelength structure (SWS) of silicon surface formed by wet process using catalysis of single nano-sized gold particle. The reflectivity of the Si substrate was reduced to below 5% throughout the entire spectrum from 300 to 800 nm owing to SWS. Effects of silver particles on the photovoltaic properties of dye-sensitized TiO_2 thin films have been studied by Wen et al. [15], and their researches suggest that enhancement of the optical absorption of the dye by the Ag plasmon resonance effect contributes to the photocurrent, and indicates the possibility of improving the energy conversion efficiency of photoelectrochemical cells with Ag-island films.

Our goal in this paper is to obtain high light absorption efficiency at different resonance frequencies by modulate the shape of gold particles. To the best of our knowledge, the effect of the shape and aspect ratio changing on the light absorption efficiency of gold nanoparticle has not yet been carefully studied. So, we report how the light absorption efficiency of the gold nanodisk and nanorod changes their intensity with different aspect ratios and polarized direction of the incident field.

The model

Figure 1a schematically shows the nanometer dimensions of gold disk. We use an oblate (pancake-shaped) spheroid with rotation symmetry to model the gold disk. This oblate spheroid is generated by rotating an ellipse about its minor axis, which has semi-major axis $a = b$ and semi-minor axis c. Figure 1b schematically shows the nanometer dimensions of gold rod. We use a prolate (cigar-shaped) spheroid with rotation symmetry to model the gold rod. This prolate spheroid is generated by rotating an ellipse about its major axis, which has semi-major axis c and semi-minor axis $a = b$. The gold spheroids (disk or rod) have a dielectric function $\varepsilon_1 = \varepsilon_{1r} + i\varepsilon_{1i}$ [17], and the surrounding medium has a dielectric function ε_2. In our studies, the gold spheroids (disk or rod) are illuminated by polarized light of wavelength λ, which travels in the direction with an included angle θ makes with z-axis (for disk) or makes with x-axis (for rod). In the calculation, the size of gold spheroids is much smaller than the wavelength of the incident light. So, the gold spheroids are subjected to a uniform static electric field $\vec{E}_0$.

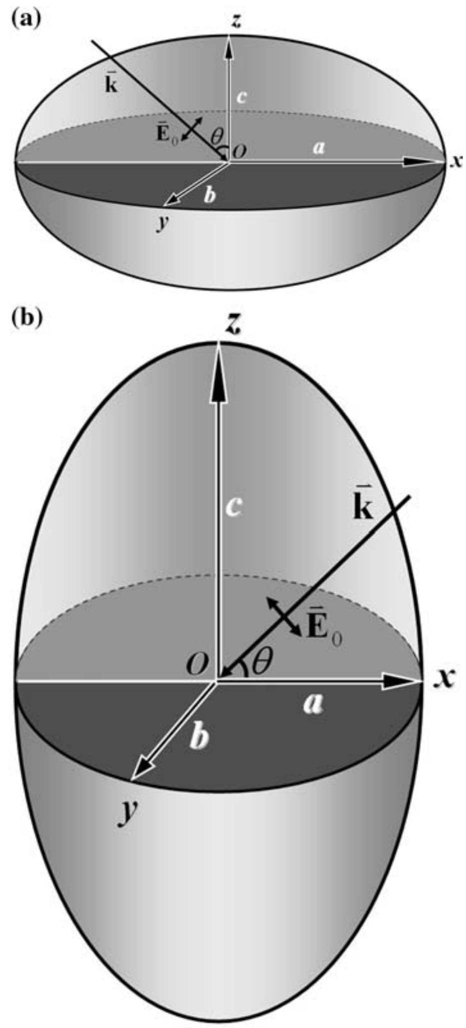

Fig. 1 Schematic picture of (a) gold nanodisk and (b) gold nanorod

In the quasi-static approximation, the polarizabilities along the semi-major axis (x-, y-axis) and semi-minor axis (z-axis) of the oblate spheroids are different [18]. When the incident light travels along the z-axis, the applied electric field is polarized parallel to the disk (x–y plane). So, the corresponding polarizability is given by [18]

$$\alpha_{\parallel} = \frac{4\pi abc}{3} \cdot \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_2 + L_{\parallel}(\varepsilon_1 - \varepsilon_2)}. \tag{1}$$

On the other hand, when the incident light travels along the x-axis, the applied electric field is perpendicular to the disk (x–y plane). So, the corresponding polarizability is given by

$$\alpha_{\perp} = \frac{4\pi abc}{3} \cdot \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_2 + L_{\perp}(\varepsilon_1 - \varepsilon_2)}, \tag{2}$$

where

$$L_{\parallel} = \frac{g}{2e^2}\left(\frac{\pi}{2} - \tan^{-1} g\right) - \frac{g^2}{2}, \tag{3}$$

$$g = \left(\frac{1-e^2}{e^2}\right)^{\frac{1}{2}}, \tag{4}$$

$$e^2 = 1 - \frac{c^2}{a^2}, \tag{5}$$

$$L_{\perp} = 1 - 2L_{\parallel}. \tag{6}$$

Similarly, the polarizabilities along the semi-major axis (z-axis) and semi-minor axis (x-, y-axis) of the prolate spheroids are different too. When the incident light travels along the z-axis, the applied electric field is polarized perpendicular to the rod (z-axis). So, the corresponding polarizability is given by [18]

$$\alpha_{\perp} = \frac{4\pi abc}{3} \cdot \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_2 + L_{\perp}(\varepsilon_1 - \varepsilon_2)}. \tag{7}$$

On the other hand, when the incident light travels along the x-axis, the applied electric field is parallel to the rod (z-axis). So, the corresponding polarizability is given by

$$\alpha_{\parallel} = \frac{4\pi abc}{3} \cdot \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_2 + L_{\parallel}(\varepsilon_1 - \varepsilon_2)}, \tag{8}$$

where

$$L_{\parallel} = \frac{1-e^2}{e^2}\left(-1 + \frac{1}{2e}\ln\frac{1+e}{1-e}\right), \tag{9}$$

$$e^2 = 1 - \frac{a^2}{c^2}, \tag{10}$$

$$L_{\perp} = \frac{1}{2}\left(1 - L_{\parallel}\right). \tag{11}$$

The concept of light absorption efficiency has been used in many fields [19–21]. In general terms, the light absorption efficiency of a homogenous material is defined as the fraction of the total irradiance absorbed by this material [19]. The optical properties of gold nanoparticles are dominated by the collective oscillation of the conduction electrons resulting from the interaction with incident electromagnetic field. So, gold nanoparticles strongly absorb and scatter light at SPR frequency. The competition between scattering and absorption could be described with light absorption efficiency. Outside the plasmon resonance, the cross section of both absorption and scattering is very low. However, our real goal is to obtain a high (resonant) absorption cross section while also have a high efficiency. Therefore, we calculate the relative contribution of absorption to the extinction at resonance frequency,

$$\eta(\omega) = \left.\frac{C_{\mathrm{abs}}}{C_{\mathrm{sca}} + C_{\mathrm{abs}}}\right|_{\mathrm{resonance}}, \tag{12}$$

where the absorption and scattering cross sections of the gold nanoparticles are evaluated by the optical theorem [7],

$$C_{\mathrm{abs}} = k\,\mathrm{Im}(\alpha), \tag{13}$$

$$C_{\mathrm{sca}} = \frac{k^4}{6\pi}|\alpha|^2, \tag{14}$$

where $k = 2\pi/\lambda$ is the wavenumber of the light.

Results and discussion

The absorption and scattering cross sections of gold nanodisk and nanorod at different frequency are shown in Fig. 2. In this calculation, the semi-major and semi-minor axis of gold spheroid are 24 and 12 nm, respectively, and the dielectric constant of the matrix is 1.5. It is well known that, when the spherical particle is flattened into an oblate spheroid or elongated into a prolate spheroid, the particle shape become anisotropic and the SPR will depends on the orientation of the nanoparticle with respect to the incident light, as well as the polarization of the incident light [9]. In Fig. 2a, the longer wavelength peaks are attributed to the parallel resonance of gold disk, whereas the shorter wavelength peaks are attributed to the perpendicular resonance. In Fig. 2b, the longer wavelength peaks are attributed to the longitudinal resonance of gold rod, whereas the shorter wavelength peaks are attributed to the transverse resonance. Although the scattering and absorption have the similar resonance wavelength, the intensities of absorption are much greater than that of scattering.

The relative contribution of absorption to the extinction are strongly dependent on the nanoparticle volume, this may be explained by carefully looking at the formulas 1 and 2, 7 and 8, 13 and 14, which describe the optical scattering, absorption, and polarizability for gold disk and rod. The scattering cross sections are proportional to the

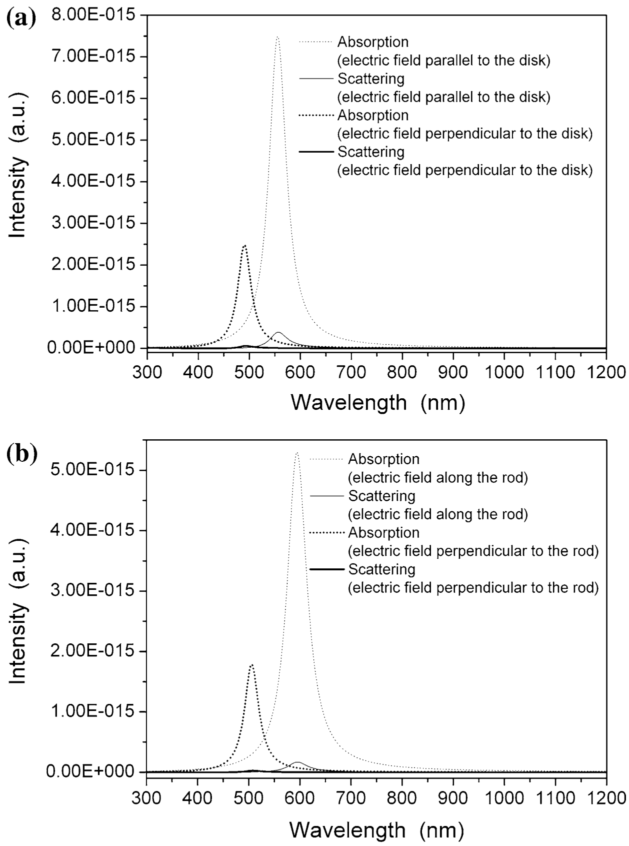

Fig. 2 Calculated optical absorption and scattering of gold (**a**) nanodisk (with a aspect ratio 2.0; $a = b = 24$ nm and $c = 12$ nm; $\varepsilon_2 = 1.5$) and nanorod (with a aspect ratio 2.0; $a = b = 12$ nm and $c = 24$ nm; $\varepsilon_2 = 1.5$)

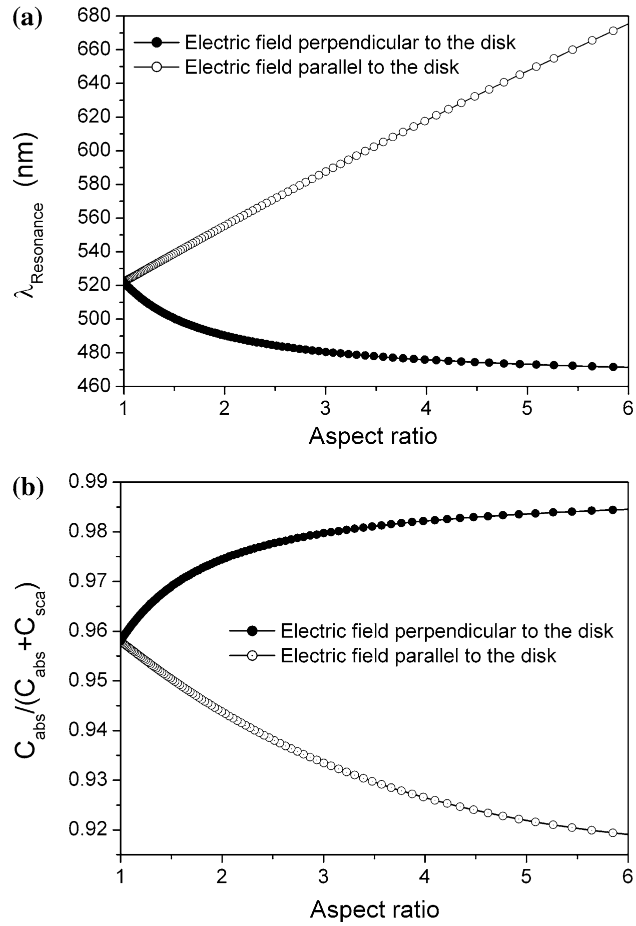

Fig. 3 Calculated (**a**) SPR wavelength and (**b**) light absorption efficiencies of gold nanodisk with different aspect ratio when the volume are fixed at $4\pi/3 \cdot 20^3$ nm^3

square of the particle volume, so the scattering is more sensitive to the volume than absorption. In order to find the dependence of the light absorption efficiency on the particle's shape, we calculated the absorption efficiency as a function of aspect ratio by fixing the particle volume at a constant. The changing fashion of the absorption efficiency is different from the incident polarization due to the anisotropy of the particle shape.

For gold nanodisk, parallel electric field leads the SPR red shifts distinctly with the increasing aspect ratio, as shown in Fig. 3a. At the same time, the optical absorption efficiency at each resonance wavelength decreases, as shown in Fig. 3b. On the contrary, perpendicular electric field leads to the SPR blue shifts slightly with the increasing aspect ratio. At the same time, the absorption efficiency at each resonance wavelength gets intense. For gold nanorod, longitudinal electric field leads to the SPR red shifts greatly from visible to near infrared band with the increasing aspect ratio, as shown in Fig. 4a. At the same time, the optical absorption efficiency at each resonance wavelength decreases firstly and then increases, as shown in Fig. 4b. On the contrary, transverse electric field leads to the SPR blue shifts very slightly. At the same time, the absorption efficiency at each resonance wavelength gets intense.

Light absorption efficiencies of gold nanodisk and nanorod at different SPR wavelengths are compared in Fig. 5. The resonance wavelength spans nearly full visible region and part of near infrared region. Furthermore, the absorption efficiency solely depends on this SPR wavelength. With the increasing resonance wavelength, the absorption efficiencies change in the same fashion for both nanodisk and nanorod. However, resonance absorption at short wavelength is easy to be obtained by gold nanodisk, whereas resonance absorption at longer wavelength is easy to be obtained by gold nanorod. These calculated results also show that high absorption efficiency (>98%) can be obtained in the visible region (450–500 nm) of gold nanodisk by increasing the aspect ratio, when the incident field is perpendicular to the disk. For nanorod, the high absorption efficiency is also resulted from transverse field, whereas the efficiency is lower than that of gold disk. However, in the near infrared region, the absorption

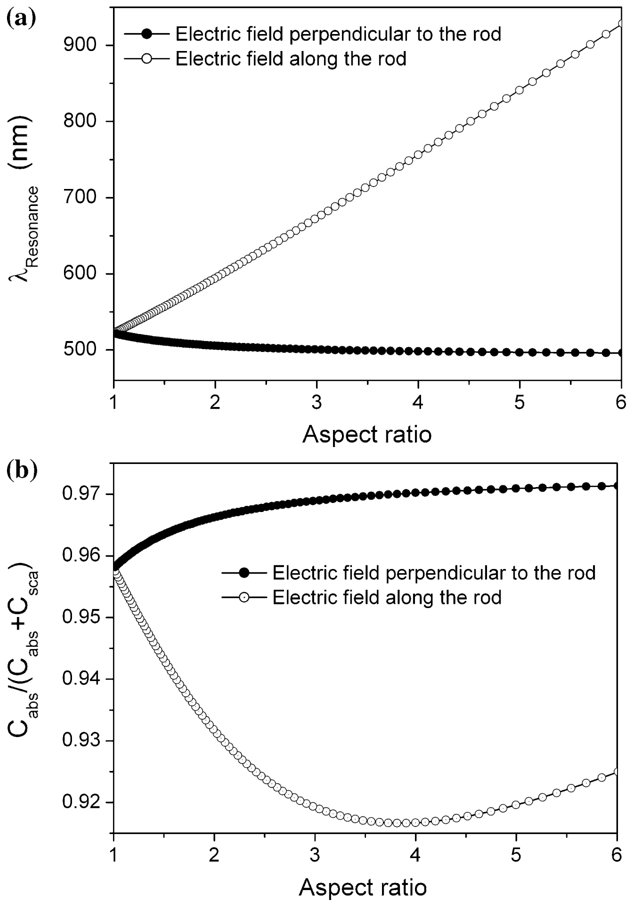

Fig. 4 Calculated (**a**) SPR wavelength and (**b**) light absorption efficiencies of gold nanorod with different aspect ratio when the volume are fixed at $4\pi/3 \cdot 20^3$ nm^3

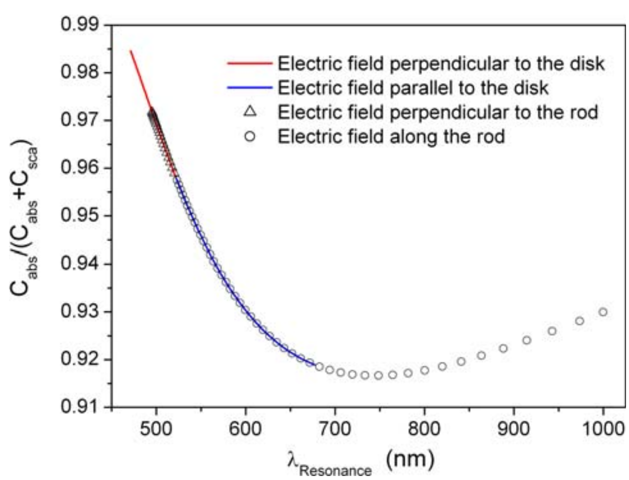

Fig. 5 Calculated light absorption efficiencies of gold nanodisk and nanorod with different SPR wavelength when the volume are fixed at $4\pi/3 \cdot 20^3$ nm^3

efficiency can also be enhanced by increasing the aspect ratio, which makes gold nanorods potentially useful in silicon solar cells and vivo applications.

Further, we shall be interested in how the incident polarized direction influences the optical absorption efficiency of the gold nanodisk and nanorod. For both oblate nanodisk and prolate nanorod, the SPR depends on the orientation of the electric field. As a consequence, the existence of the two distinct plasmon bands related to parallel and perpendicular electron oscillations are possible. We calculated the absorption and scattering spectra for gold nanodisk and nanorod with varying incident angle θ (the aspect ratio is fixed at 2.5), as shown in Fig. 6. For gold disk, with increasing θ from 0 to $\pi/2$, both the absorption and scattering maximum of the parallel modes decrease, but the perpendicular modes get intense, as shown in Fig. 6a, b. Similarly, gold rod has the same changing fashions, as shown in Fig. 6c, d. However, both the parallel and perpendicular electron oscillations contribute the optical absorption efficiency. The maximum scattering of the perpendicular mode is much weaker than that of parallel mode. Therefore, the absorption efficiency of both gold disk and rod gets intense as θ is increases from 0 to $\pi/2$, as shown in Fig. 7. The optical absorption efficiency represents the fraction of the energy absorbed by the gold nanoparticles out of the energy of the incident light. So, these tunable characters of optical absorption efficiency are effective guide for the design and fabrication of gold nanostructure for optoelectronic devices in plasmon-mediated chemistry.

Conclusion

The influence of aspect ratio on the light absorption efficiency of gold nanodisk is demonstrated by theoretical calculation. Intense absorption efficiencies have been obtained in nearly full visible region and part of near infrared region. When the volume of gold particle is fixed, the effect is greatly dependent on their shape and aspect ratio. Gold nanodisk has higher absorption efficiency than that of nanorod. When the incident field is polarized parallel to the disk, the absorption efficiency decreases as the aspect ratio is increased. On the contrary, increasing the aspect ratio results in an enhancement of absorption efficiency when the incident field is perpendicular to the disk. Similarly, increasing the aspect ratio also results in an enhancement of absorption efficiency when the incident field is perpendicular to the rod. However, when the incident field is polarized along the rod, the absorption efficiency decreases firstly and then increases as the aspect ratio is increased. When the incident polarization changes from parallel direction to perpendicular direction, the absorption efficiencies of both gold disk and rod get intense. These tunable optical absorption efficiencies of gold disk and rod may help us to optimize the properties of solar energy materials and fabricate the nanometer solar cells.

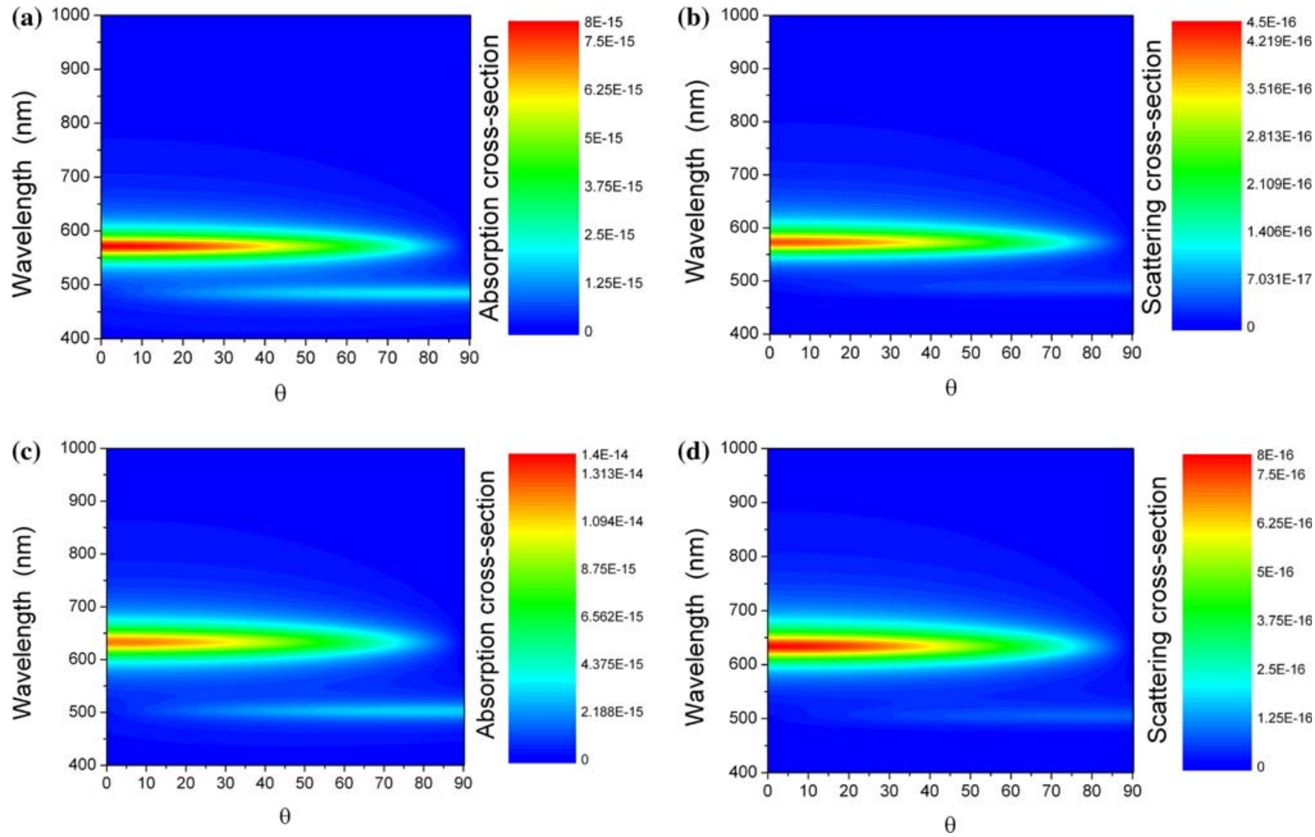

Fig. 6 Calculated absorption and scattering cross sections of (**a**, **b**) gold nanodisk and (**c**, **d**) nanorod with different incident angle θ when the aspect ratio are fixed at 2.5

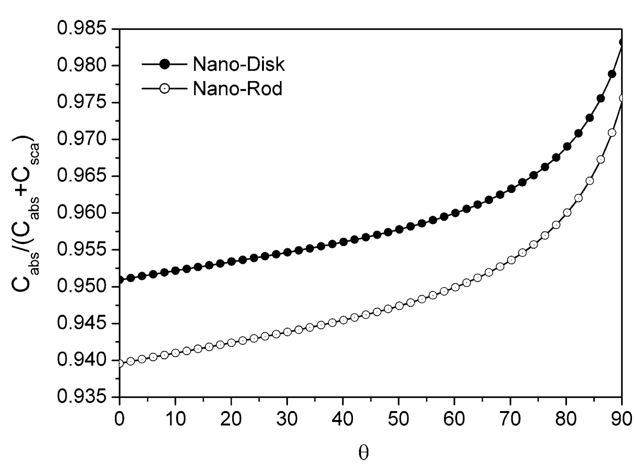

Fig. 7 Calculated optical absorption efficiencies of gold nanodisk and nanorod with different incident angle θ when the aspect ratio are fixed at 2.5

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