

Effects of particle size and surrounding media on optical radiation efficiencies of spherical plasmonic metal nanoparticles

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Abstract. The optical radiation efficiency (η), the ratio of scattering cross-section to extinction cross-section, of spherical metal nanoparticles ($M = \text{Al, Ag, Au and Cu}$) surrounded by glass and water was calculated using classical electrostatics. The effect of varying particle diameter (~ 100 nm) on η was also studied for free space wavelengths in the range of 400–1200 nm. The variations in the value of η with the diameter (d) of the metal nanoparticles were calculated on the basis of quasi-static approximation. The η increases with the size of metal nanoparticles. Corresponding to a metal nanoparticle, η was found to exhibit a sharp dip (η_{dip}) at a characteristic wavelength $(\lambda_{\mu})_M$ in a particular medium ($\mu = \text{air, glass and water}$). $(\lambda_{\mu})_M$ was independent of particle size. The $(\lambda_{\text{medium}})_M$ was found to be slightly blue shifted for all metal nanoparticles surrounded by glass or water with respect to those in the air.

Keywords. Metal nanoparticles; optical radiation efficiency; surface plasmon resonance; scattering and absorption cross-section.

1. Introduction

Noble metals are known to exhibit diverse and complex optical properties in nanoscale regime (Wokaun *et al* 1981). The exotic optical behaviour of metal nanoparticles is a consequence of the large density of conducting electrons, quantum confinement and unique frequency dependence of the real and imaginary parts of the dielectric functions (ϵ). All these factors contribute to surface plasmon resonance (SPR) (Lakowicz 2005; Miller and Lazarides 2005; Zhu *et al* 2008). The localized SPR at the interface of metallic nanoparticles and surrounding dielectric media gives rise to enhanced electromagnetic field (Barnes *et al* 2003) and thus responsible for fascinating optical properties. The frequency and intensity of SPR are strongly dependent on the size and shape of the nanoparticle as well as the dielectric function of the surrounding medium. The metal nanoparticles find useful applications in the area of nanophotonics (Stuart and Hall 1998; Peyser *et al* 2001; Cao *et al* 2002; Fritzsche and Taton 2003; Andersen *et al* 2004; Prasad 2004).

The optical radiation efficiency (η) is the fraction of incident energy which is re-radiated from the metal nanoparticles. The tailored η values of metal nanoparticles would find useful applications in fabrication of mirrors,

waveguides, photodetectors (Stuart and Hall 1998) etc. In a waveguide, the metal nanoparticle coatings may efficiently trap the incident light and provide maximum energy at the other end.

Tanabe (2007) calculated η for 11 different spherical (symmetrical) metal nanoparticles for air medium only and reported $\sim 90\%$ of efficiency for Ag and Al metal nanoparticles having diameter ~ 150 nm. Zhu *et al* (2008) calculated light absorption efficiency (defined as ratio of absorption cross section to the total extinction cross section) for gold nanodisc and nanorods (asymmetrical) by using quasi-static approximation. He reported that how the light absorption efficiency of these asymmetric nanostructures of gold changes their intensity with varying aspect ratios.

In this paper, the optical radiation efficiency (η) was calculated for spherical metal nanoparticles ($M = \text{Al, Ag, Au and Cu}$) with varying diameters (~ 100 nm) surrounded by glass and water medium at the free space wavelengths of 400, 700 and 1200 nm. We have compared our theoretically calculated η values with the experimental data (Evanoff Jr and Chumanov 2004) for Ag metal nanoparticles surrounded by water medium at a wavelength of 400 nm. We have also compared our results of Au nanoparticles surrounded by water at free space wavelength of 400 nm with the Mie calculator (Mie Plot v4101). The results were matching with our calculation, which demonstrates the validity of the quasi-static approximation used in our calculations.

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The effect of surrounding medium (μ) on the optical radiation efficiency of the metal nanoparticles was studied with the objective of gaining insight into the optical phenomenon at nanoscale and generating useful data for the design and development of metal nanoparticles based electro-optical devices.

2. Theory

Interaction of light with metallic nanoparticles generates surface plasmon resonance (SPR) which is size, shape and surrounding medium dependant. The SPR produces two strong processes, namely, scattering and absorption. The extinction cross section (C_{ext}) consists of two components, viz. absorption cross section (C_{abs}) and scattering cross section (C_{scat}). The optical radiation efficiency, η , is expressed by the following equation (Bohren and Huffman 1983; Stuart and Hall 1998; Tanabe 2007):

$$\eta = \frac{C_{\text{scat}}}{C_{\text{scat}} + C_{\text{abs}}}. \quad (1)$$

The absorption and scattering cross sections depend on the polarizability, α , of the selected nanoparticle. If we assume a sub-wavelength size and spherical nanoparticle surrounded by a medium, then α is determined from the following electrostatics equation

$$\alpha = 3V \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}, \quad (2)$$

where ε is the relative permittivity of the metal nanoparticles of diameter d and ε_m the relative permittivity of the surrounding medium. The ε is expressed as the sum of real and imaginary parts, i.e., $\varepsilon = \text{Re}(\varepsilon) + \text{Im}(\varepsilon)$. The optical properties of metal nanoparticles were described within the framework of quasi-static (dipole) approximation. This approximation was valid for first-order Mie calculation. The introduction of geometrical factor within the quasi-static approximation enables us to determine the optical properties of non-spherical (prolate and oblate ellipsoidal) metal nanoparticles (Kooij and Poelsema 2006). It should be noted that this is quasi-static approximation and, therefore, the calculations presented in this paper are valid for particles sufficiently smaller than the free space wavelengths where the phase retardation is negligible throughout the objects (Tanabe 2008). Therefore, we limited our calculations of η for particle diameters smaller than 100 nm similar to those in Maier (2007) and Tanabe (2008). For the calculations presented in this paper, we used the dielectric function data as given in Palik (1985) for metals. We assumed $\varepsilon = 3.7$ for all the considered wavelengths of the glass. Although this dielectric constant value is relatively high for the glass material and may correspond to a highly-doped one, we adopted this value to clarify the contrast from the case of air medium. We assumed $\varepsilon = 1.7$ for all the free space wavelengths of water.

The absorption and scattering cross sections for nanoparticles were written in terms of wave number (K) and polarizability (α) as;

$$C_{\text{abs}} = K \text{Im}(\alpha), \quad (3)$$

$$C_{\text{scat}} = \frac{K^4}{6\pi} |\alpha|^2. \quad (4)$$

It is evident from (3) and (4) that C_{abs} increases as d^3 whereas C_{sca} increases as d^6 .

3. Results and discussion

3.1 Effects of particle diameter (d) on optical radiation efficiency (η)

3.1a Metal nanoparticles in glass: Figure 1 shows (η - d) curves for Al, Ag, Au and Cu nanoparticles surrounded by glass ($\varepsilon = 3.7$) for free space wavelengths of 400, 700 and 1200 nm. It is seen that Ag and Al nanoparticles of 100 nm diameter, exhibit higher values of η (\sim above 70%) as compared to Au and Cu nanoparticles, and thus are less lossy. The rate of increase of η in case of Ag and Al is higher than Au and Cu at 400 nm. It can be inferred from figure 1 that the optical radiation efficiency increases with the particle diameter for all the metal nanoparticles surrounded by glass. This may be attributed to higher polarizability (α) of large size nanoparticles and thus resulting into larger radiative rates. At 700 nm, Au and Cu show remarkable improvement in η and attain efficiency of $\sim 60\%$, whereas in the case of Al, the optical efficiency decreases to $\sim 50\%$ when the particle diameter is 100 nm. All the metal nanoparticles at 1200 nm show an identical behaviour and efficiencies lying between 40 and 60%. It is to be noted again that the size of metal nanoparticles should be kept smaller (< 100 nm) than the optical wavelength to maintain the validity of the quasi-static approximation.

The optical radiation efficiencies (η) of Al, Ag, Au and Cu nanoparticles, typically of 40, 60, 80 and 100 nm diameter were calculated for wavelengths of 400, 700 and 1200 nm and are summarized in table 1.

3.1b Metal nanoparticles in water: Similar calculations were carried out for Ag, Al, Au and Cu nanoparticles surrounded by water ($\varepsilon = 1.7$) for free space wavelengths of 400, 700 and 1200 nm. The corresponding (η - d) curves are shown in figure 2. At an optical free space wavelength of 400 nm, the η for Al nanoparticles, increases rapidly with the particle size to attain the saturated value of 85% at $d \sim 80$ nm. All other metal nanoparticles with same diameter showed efficiency below 60%. At an optical wavelength of 700 nm, the η increases at slower rate as compared to that at $\lambda = 400$ nm for all metal nanoparticles. As compared to Al, other three metals show relatively higher efficiency. The Ag nanoparticles of a 100 nm diameter show a very high η of $\sim 82\%$ at a free space wavelength of 700 nm. All metal

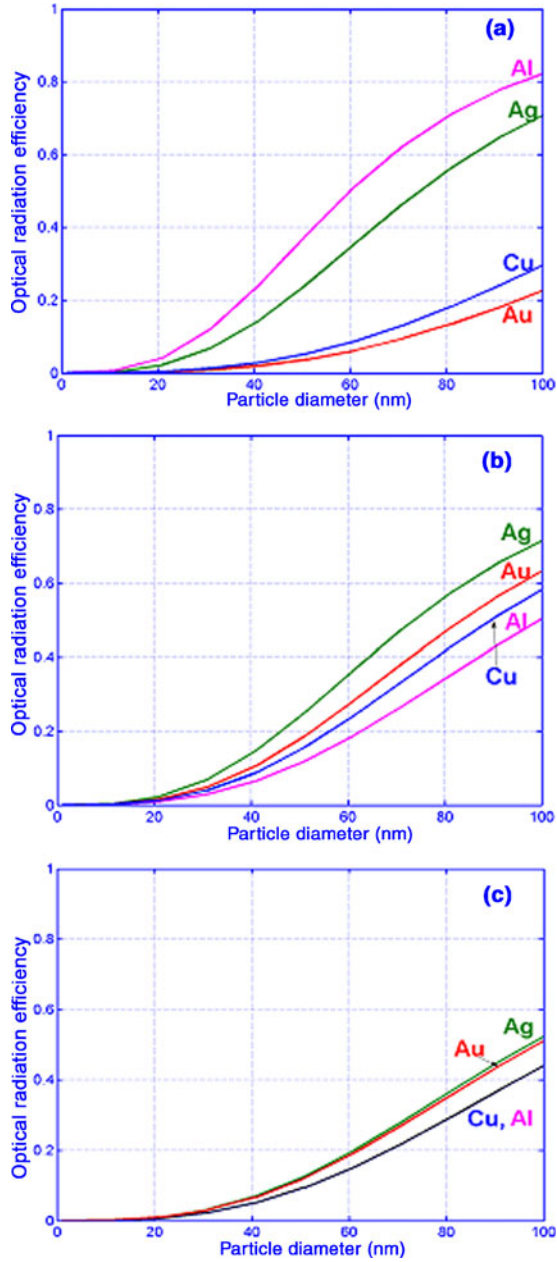


Figure 1. $(\eta-d)$ curves for the metal nanoparticles surrounded by glass, at various free space wavelengths: (a) 400 nm, (b) 700 nm and (c) 1200 nm.

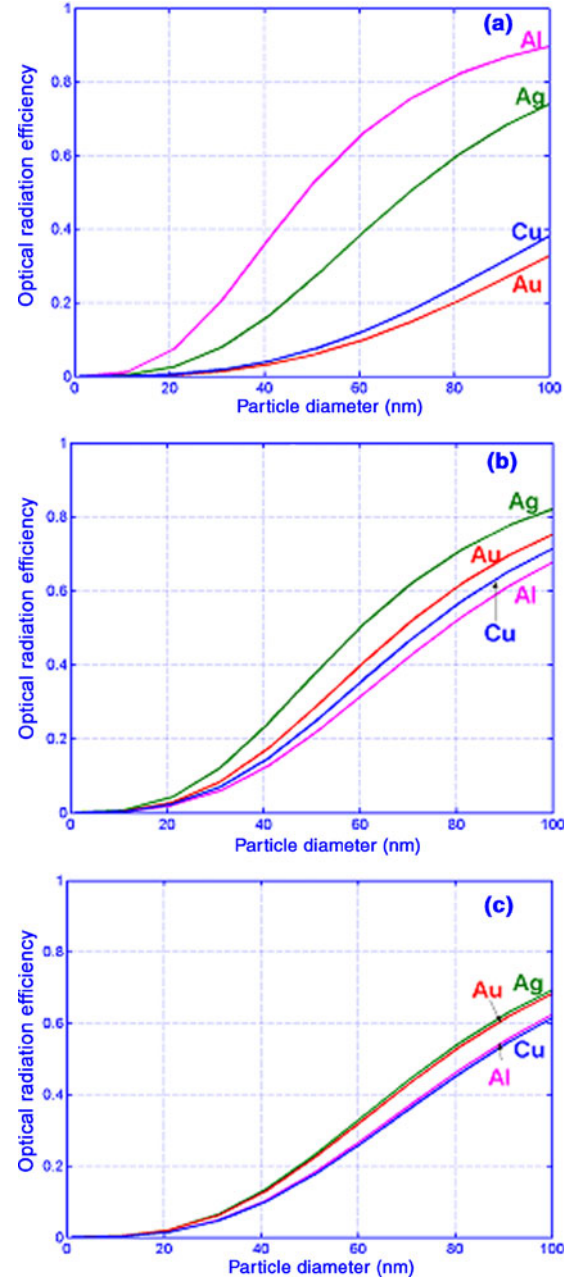


Figure 2. $(\eta-d)$ curves for the metal nanoparticles surrounded by water, at various free space wavelengths: (a) 400 nm, (b) 700 nm and (c) 1200 nm.

Table 1. Optical radiation efficiency (η) of metal nanoparticles of different diameter (d) surrounded by glass at various wavelengths.

Metal nanoparticles	Optical radiation efficiency, $\eta(\%)$											
	$\lambda = 400$ nm				$\lambda = 700$ nm				$\lambda = 1200$ nm			
	$d = 40$	$d = 60$	$d = 80$	$d = 100$	$d = 40$	$d = 60$	$d = 80$	$d = 100$	$d = 40$	$d = 60$	$d = 80$	$d = 100$
Al	23	50	70	82	07	18	34	50	05	14	28	44
Ag	14	34	55	70	14	35	56	71	07	19	36	52
Cu	03	09	17	29	09	23	42	58	05	14	28	44
Au	02	06	13	22	10	27	47	63	06	18	35	51

Table 2. Optical radiation efficiency (η) of metal nanoparticles of different diameter (d) surrounded by water at various wavelengths.

Metal nanoparticles	Optical radiation efficiency, η (%)											
	$\lambda = 400$ nm				$\lambda = 700$ nm				$\lambda = 1200$ nm			
	$d = 40$	$d = 60$	$d = 80$	$d = 100$	$d = 40$	$d = 60$	$d = 80$	$d = 100$	$d = 40$	$d = 60$	$d = 80$	$d = 100$
Al	35	65	85	89	12	31	52	67	10	27	46	62
Ag	15	38	59	74	23	50	70	82	13	33	53	69
Au	03	09	20	32	16	39	61	75	12	31	52	68
Cu	04	12	24	38	14	35	56	71	09	25	44	61

nanoparticles at 1200 nm show optical radiation efficiency 60–70%. The values of η in different cases are summarized in table 2.

Figure 3 compares our theoretically calculated η to corresponding experimental results for Ag nanoparticles of various sizes in water at a wavelength of 400 nm (Evanoff Jr and Chumanov 2004). It is seen that our calculation is quite consistent and well reproduces the experimental results. The slight discrepancy in η between our calculation and the experimental results could be attributed to the non-spherical shape of the Ag nanoparticles prepared in (Evanoff Jr and Chumanov 2004).

Figure 4 shows comparison of our results of Au nanoparticles surrounded by water at free space wavelength of 400 nm with a Mie calculator (MiePlot v4101). The results are matching with our calculation, which demonstrates the validity of the quasi-static approximation used in our calculations of this work.

3.2 Effects of surrounding medium

The variations in the optical radiation efficiency (η) with the free space wavelength of the incident radiations (λ) for Ag nanoparticles of varied diameters of 20, 40, 60, 80 and

100 nm surrounded by air, glass and water are shown in figure 5. The $(\eta-\lambda)$ graphs were also plotted for Al, Au and Cu nanoparticles and are shown in figures 6, 7 and 8. Interestingly the η curve for each metal nanoparticle shows a sharp dip, η_{dip} , at a characteristic wavelength $(\lambda_{\mu})_{\text{M}}$, where μ and M represent the surrounding medium (air, glass and water) and the metal nanoparticle, respectively. It was observed from these graphs that the $(\lambda_{\mu})_{\text{M}}$ is independent of the nanoparticle diameter, d . This behaviour is attributed to the surface plasmon resonance (SPR) associated only with the shape of the nanoparticles and not with their size, as is well known. When a light is incident on metal nanoparticles, the oscillating electric field of a light produce a force on the conduction electrons in the metal, which induces a dipole moment (polarizability, α) in the particle. The relative permittivity of metal is not a fixed quantity but it varies with wavelength. The resonance condition in the optical spectra of the particle becomes dominant when the denominator of equation (2) is closest to zero and occurs when the relative permittivity of the metal satisfies $\epsilon = -2\epsilon_{\text{m}}$.

It is evident from all the graphs (figures 5–8) that as the particle size increases, η increases overall for the optical wavelengths in the range 250–2000 nm. However, the existence of η_{dip} remains unchanged at $(\lambda_{\mu})_{\text{M}}$ for all sizes of the nanoparticles. The η_{dip} is changing with the

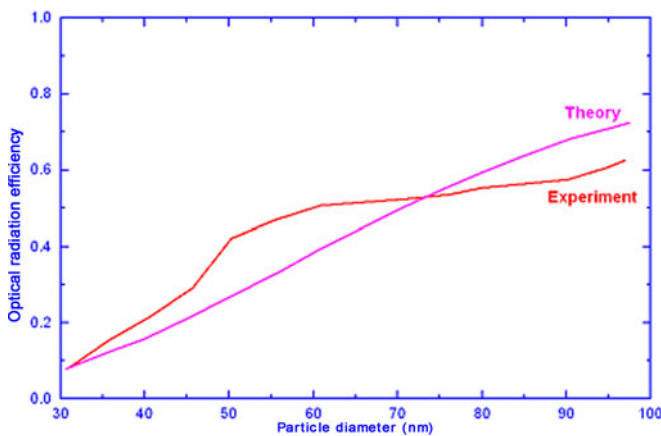


Figure 3. Comparison of theoretically calculated values with the experimental data in (Evanoff and Chumanov 2004) for the $(\eta-d)$ curves for Ag metal nanoparticles surrounded by water medium at a wavelength of 400 nm.

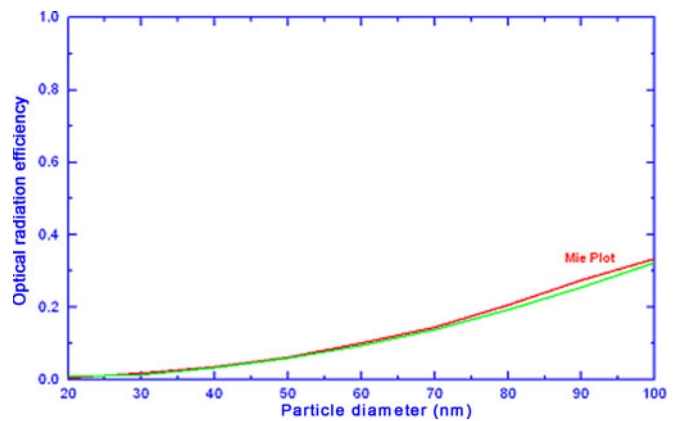


Figure 4. Comparison of our results of Au nanoparticles surrounded by water at free space wavelength of 400 nm with the Mie calculator (MiePlot v4101).

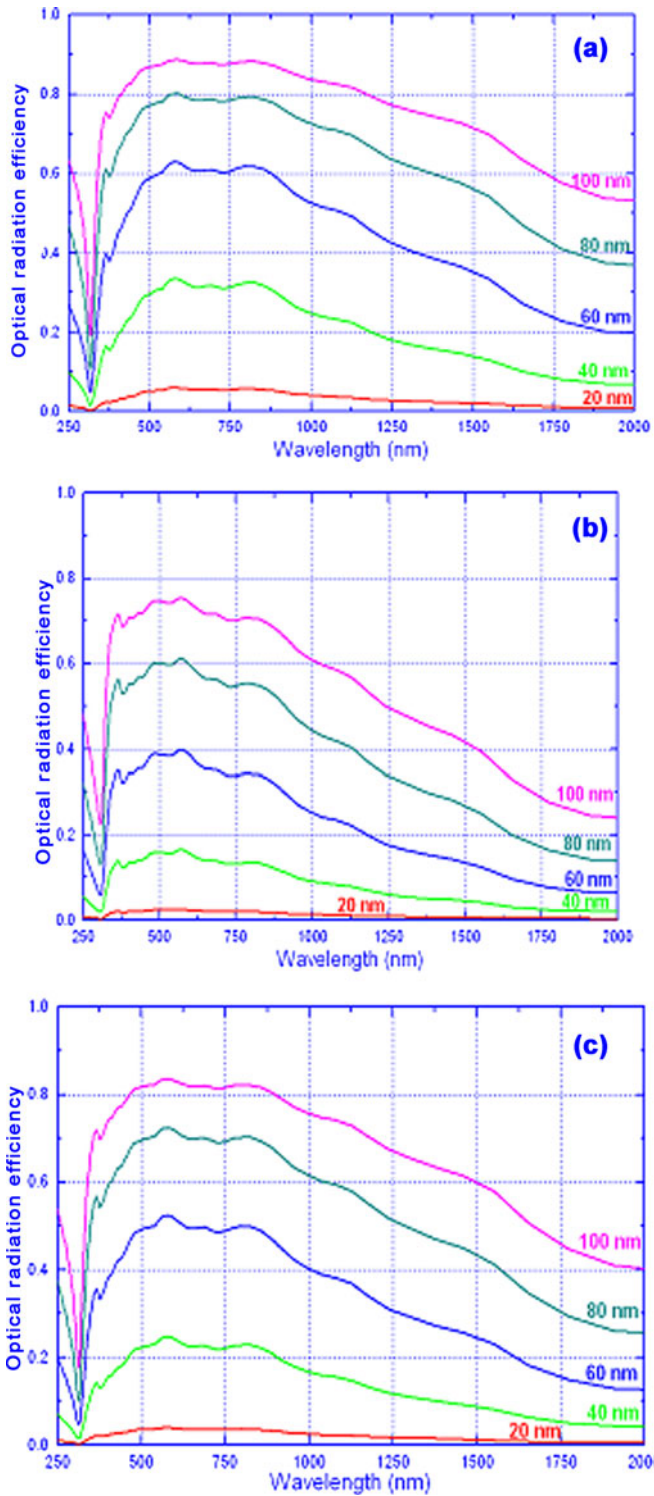


Figure 5. $(\eta-\lambda)$ curves for Ag nanoparticles with various diameters in (a) air, (b) glass and (c) water.

medium because the dielectric constant is different for different medium. The positioning of η_{dip} at a characteristic wavelength may be attributed to surface plasmon resonance of the metal nanoparticles. The occurrence of sharp absorption dip, for the metal nanoparticles surrounded by different dielectric media, is an interesting behaviour which may find

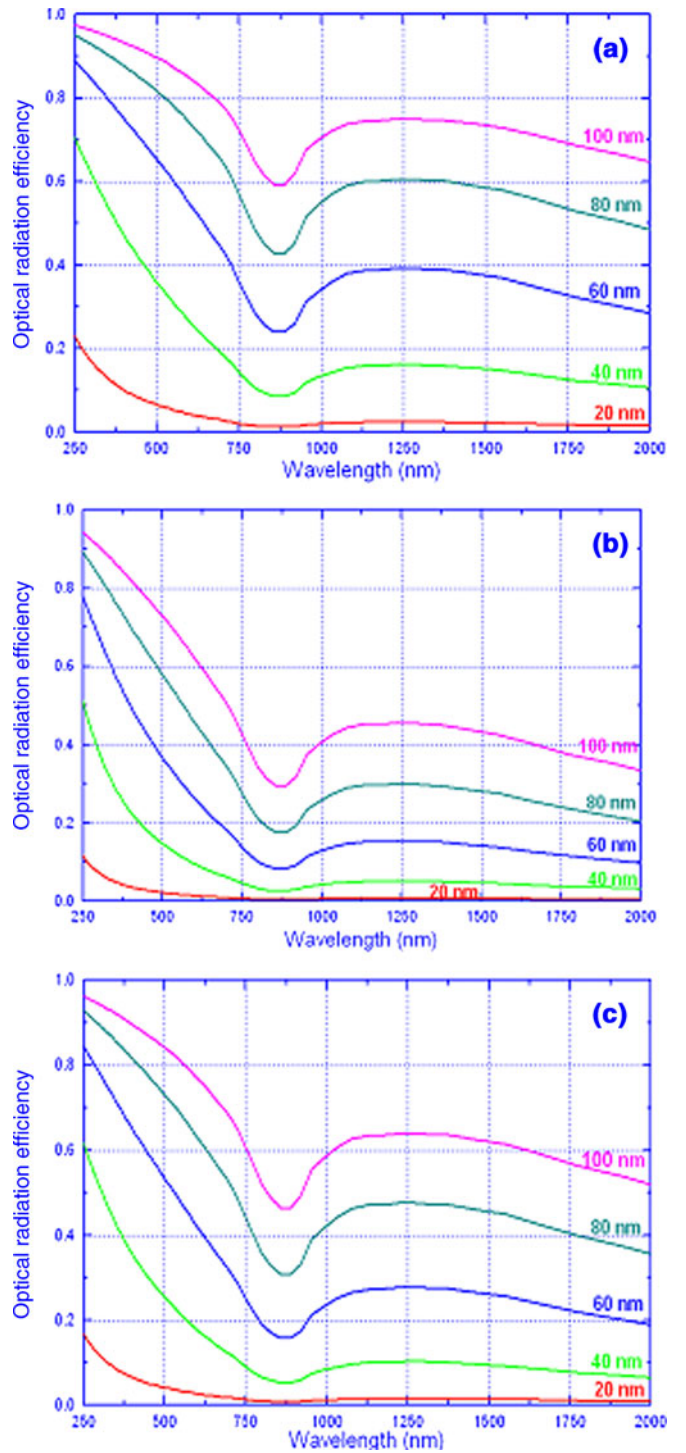


Figure 6. $(\eta-\lambda)$ curves for Al nanoparticles with various diameters in (a) air, (b) glass and (c) water.

useful applications in the fabrication of devices like resonant absorbers (anti-lasers), tunable optical detectors, waveguides etc.

The η reduces to a value of $\sim 20\%$ for Ag nanoparticles, surrounded by air, for a particle diameter of ~ 100 nm the corresponding η_{dip} , at a characteristic optical wavelength $(\lambda_{\text{air}})_{\text{Ag}}$ is 316 nm (figure 5a). The Ag

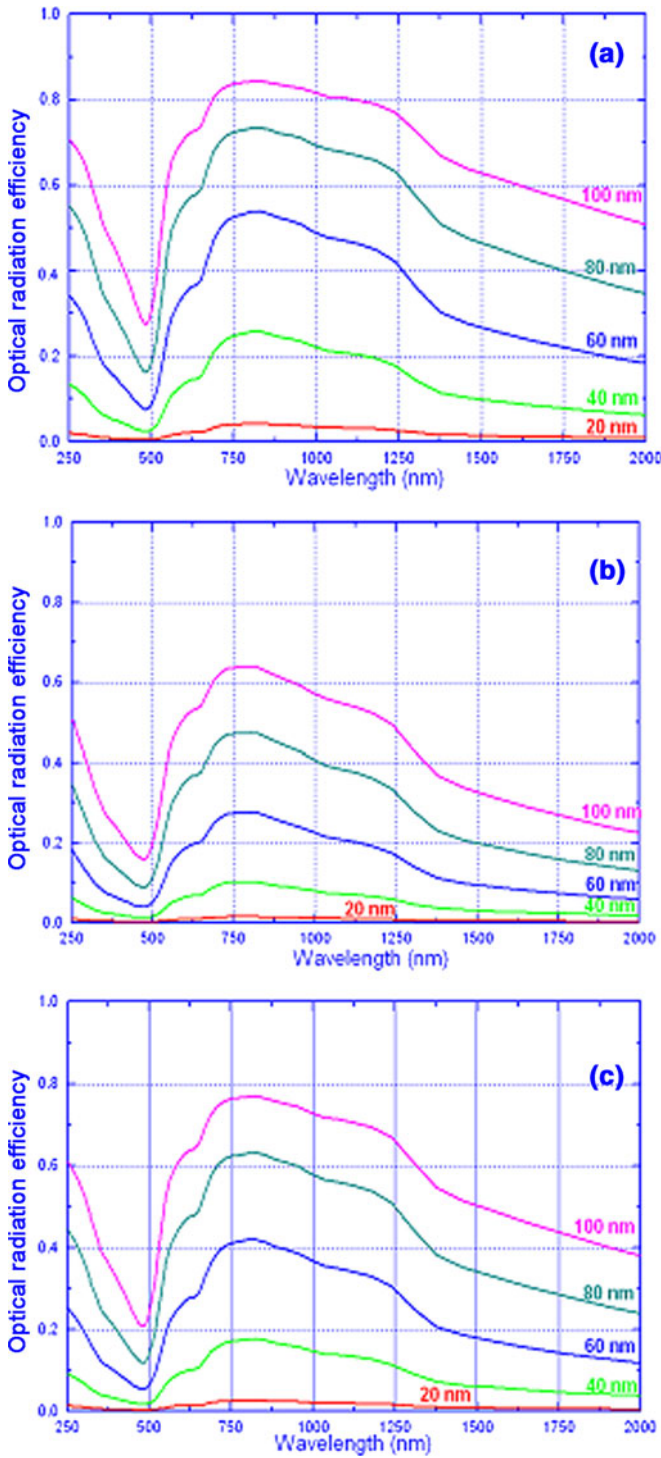


Figure 7. $(\eta-\lambda)$ curves for Au nanoparticles with various diameters in (a) air, (b) glass and (c) water.

nanoparticles show η_{dip} at the characteristic wavelength, $(\lambda_{\text{glass}})_{\text{Ag}}$ of 306 nm (figure 5b) and $(\lambda_{\text{water}})_{\text{Ag}}$ of 314 nm (figure 5c). For Al, Au and Cu nanoparticles in air, the optical radiation efficiency, η_{dip} , was found to occur at optical wavelengths of 871, 484 and 547 nm, respectively. It may be understood that Ag nanoparticles of 100 nm size are efficient absorbers in UV region whereas Al is a better candidate for

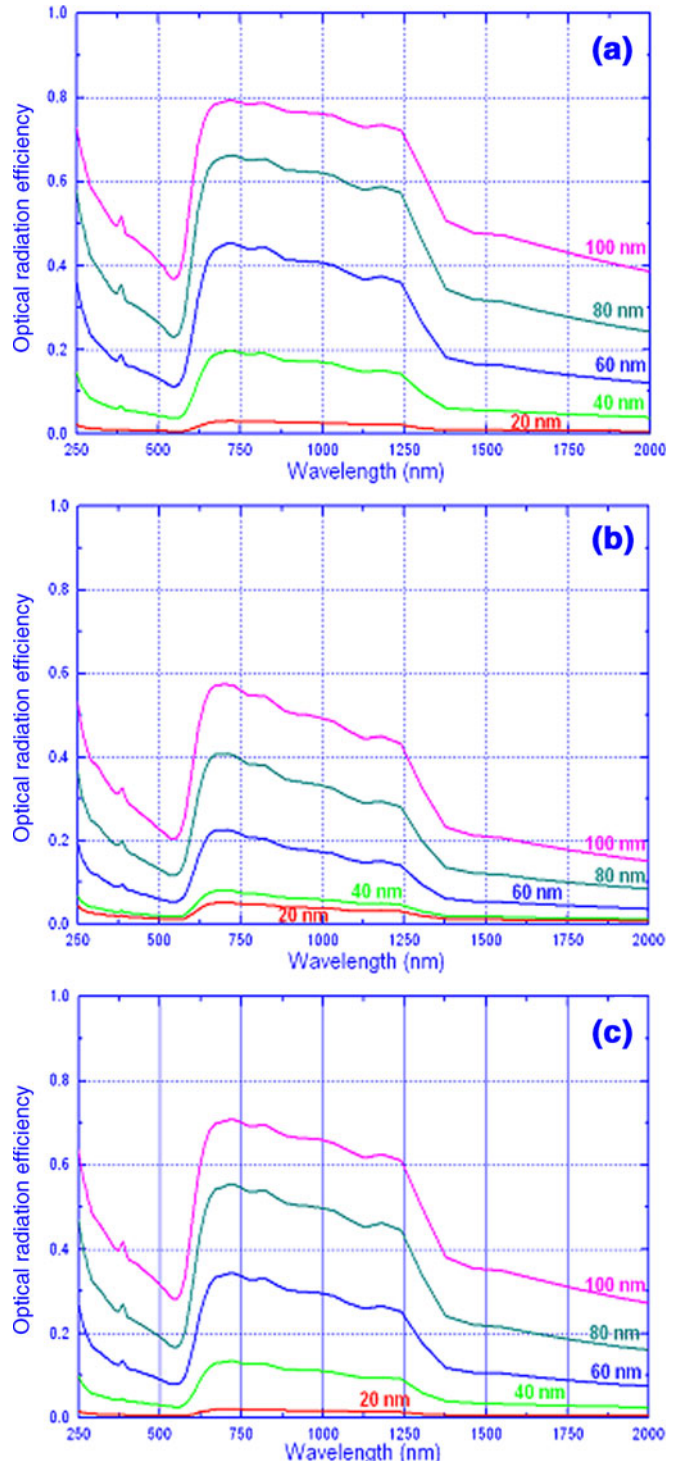


Figure 8. $(\eta-\lambda)$ curves for Cu nanoparticles with various diameters in (a) air, (b) glass and (c) water.

applications in infra-red region. The Au and Cu nanoparticles are efficient absorbers in visible region. All the metal nanoparticles considered above have the potential for useful applications in electro-optical devices by adjusting their η accordingly for each application.

The shift in the characteristic wavelength when surrounded by a medium (glass or water), with respect to the

Table 3. The wavelength position of η_{dip} and the $\Delta\lambda$ for metal nanoparticles surrounded by glass and water relative to air.

Metal nanoparticles	$(\lambda_{\mu})_{\text{M}}$ (nm)			$(\Delta\lambda)_{\text{water}}^{\text{air}} = \lambda_{\text{air}} - \lambda_{\text{water}}$ (nm)	$(\Delta\lambda)_{\text{glass}}^{\text{air}} = \lambda_{\text{air}} - \lambda_{\text{glass}}$ (nm)
	Air	Water	Glass		
Ag	316	314	306	02	10
Au	484	478	471	06	13
Al	871	869	868	02	03
Cu	547	545	542	02	05

cases in the air, exhibited by a metal nanoparticle, is denoted by

$$(\Delta\lambda)_{\text{medium}}^{\text{air}} = \lambda_{\text{air}} - \lambda_{\text{medium}}. \quad (5)$$

For Ag nanoparticles, $(\Delta\lambda)_{\text{glass}}^{\text{air}}$ was calculated to be 10 nm whereas $(\Delta\lambda)_{\text{water}}^{\text{air}}$ was found to be 2 nm. Similarly, the values of $(\Delta\lambda)_{\text{medium}}^{\text{air}}$ were calculated for Al, Au and Cu nanoparticles and are summarized in table 3.

4. Conclusions

The optical radiation efficiencies defined as the ratio of scattering cross-section to extinction cross-section, as a function of particle size and free space wavelength, of Al, Ag, Au and Cu nanoparticles, surrounded by air, glass and water, were calculated in the quasi-static limit. It was found that the optical radiation efficiency of metal nanoparticles increases with increase in the particle size.

Al and Ag nanoparticles showed optical radiation efficiency above 70% at the optical wavelength of 400 nm in glass and water medium. The optical radiation efficiency for Al, Ag, Au and Cu nanoparticles initially decreases sharply with wavelength and exhibited a dip (η_{dip}) corresponding to surface plasmon resonance at a characteristic wavelength, $(\lambda_{\mu})_{\text{M}}$, then rises fast to reach a saturation level and decreases gradually thereafter. The position of η_{dip} , i.e. $(\lambda_{\mu})_{\text{M}}$ was independent of particle size. The $(\lambda_{\text{medium}})_{\text{M}}$ was found to be blue shifted with respect to air for Al, Ag, Au and Cu nanoparticles when surrounded by glass or water.

The knowledge of η for metal nanoparticles is essential for fabrication of mirrors, selective absorbers, waveguides etc. In a waveguide these coatings of metal nanoparticles efficiently trap incident light and provide maximum energy transport. The Al/Ag nanoparticle (size ~ 100 nm) films

(Stuart and Hall 1998), owing to their higher optical radiation efficiency, as compared to Au/Cu nanoparticles, are better candidates for the fabrication of waveguides, photodetectors or any optical device at a wavelength of 400 nm.

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