Optimisation of absorption efficiency for varying dielectric spherical nanoparticles

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Abstract—In this paper we compare the optical absorption for nanospheres made from a range of transition and alkali metals from Li (A=3) to Au (A=79). Numerical solutions to Mie theory were used to calculate the absorption efficiency, Q_{abs}, for nanospheres varying in radii between 5 nm and 100 nm in vacuum. We show that, although gold is the most commonly used nanoparticle material, its absorption efficiency at the plasmon resonance is not as strong as materials such as the alkali metals. Of all the materials tried, potassium spheres with a radius of 21 nm have an optimum absorption efficiency of 14.7. In addition we also show that, unlike gold, the wavelength of the plasmon peak in other materials is sensitive to the sphere radius. In potassium the peak position shifts by 100 nm for spheres ranging from 5 nm to 65 nm, the shift is less than 10 nm for gold spheres.

Keywords- nanoparticle; plasmon; absorption efficiency; Au; K

I. INTRODUCTION

Metallic nanoparticles have potential applications in thermal therapeutic techniques [1-4], nanolithography [5] and energy efficient window coatings [6]. Considerable progress has been made in recent years not only in synthesizing nanoparticles [7-9] with a variety of geometries, but also in modeling their optical properties [10-16]. The utility of nanoparticles with dimensions in the range of 5 nm to 50 nm lies in their ability to absorb incident light very efficiently with minimal scattering. Excitation of a surface mode, or plasmon resonance, is the underlying mechanism for such large absorption cross-sections [17]. Moreover, the wavelength of the plasmon resonance is sensitive to particle geometry and can therefore be tuned.

Predominately Au has been used to make spherical nanoparticles because the synthesis process is relatively simple [18], Au is inert, and absorption occurs within the visible spectrum. The peak absorption efficiency, Q_{abs}, for Au nanospheres with radius of 10 nm is 0.66 and occurs at a wavelength of 506 nm in vacuum. For gold the resonance position is relatively insensitive to sphere size over the size range of 5 nm to about 50 nm radius. For this reason Au nanoshells and nanorods have received considerable attention as they have much larger absorption efficiencies and the peak position can be tuned by varying the shell or rod aspect ratio [19]. For example a 25 nm radius, 0.9 aspect ratio nanoshell is capable of producing a Q_{abs} of 19 within the near-infrared spectrum [20]. However, synthesis of monodisperse nanorods, and nanoshells with uniform shell thickness is difficult.

In this paper Mie's analytical solution to Maxwell's equations is used to compare Q_{abs} for nanospheres composed of different metallic elements. For each element an optimum nanosphere diameter producing a maximum Q_{abs} is established and the shift in the plasmon resonance with increased sphere size is discussed. The results show that, in terms of absorption efficiencies alone, gold is far from the ideal material for nanoparticle plasmonic applications.

II. METHOD

The numerical implementation of Mie theory [21] in the program BHCOAT [22] was used to calculate the absorption and scattering efficiencies, Q_{abs} and Q_{sca} respectively. These quantities are the absorption and scattering per unit cross-sectional area of the particle. Hence a value greater than 1 implies absorption (or scattering) that is larger than the geometric area the particle presents to the incident radiation.

Particles were modeled with radii between 5 nm and 100 nm in 1 nm steps. A strong plasmon absorption occurs for particle sizes below about 50 nm. At larger radii scattering begins to dominate and higher order terms (beyond dipole) contribute. Tabulated values for the dielectric function in vacuum were taken from Weaver and Frederikse [23]. Calculations were performed between wavelengths of 100 nm and 1000 nm in 1 nm steps. This range encompasses the plasmon resonance and consequently the peak Q_{abs} for the various dielectric nanospheres.

The main numerical consideration is that calculated cross-section is sufficiently converged, that is, sufficient terms have been retained in the multipole expansion of Mie theory. For the particle size range and wavelengths considered here only the first few terms of the expansion are required to achieve this. Since Mie theory is the exact solution to the problem for any particle size and wavelength, we can have confidence in our numerical results.

III. RESULTS AND DISCUSSION

Table 1 gives the calculated Q_{abs} for each metal at the maximum of the plasmon resonance, together with sphere radius and wavelength corresponding to this maximum.

TABLE I. COMPARISON OF CALCUALTED OPTIMUM ABSORPTION EFFICENCES FOR VARIOUS METALLIC SPHERES

Atomic Number	Element	Q_{abs}	Sphere Radius (nm)	Wavelength (nm)
3	Li	4.8	30	401
11	Na	12.4	16	387
13	Al	13.0	6	143
19	K	14.7	21	555
22	Ti	2.4	36	315
23	V	2.8	32	309
24	Cr	2.7	18	183
25	Mn	1.9	28	203
26	Fe	2.3	22	194
27	Co	2.4	22	200
28	Ni	2.4	23	208
29	Cu	2.3	23	204
41	Nb	2.4	17	153
42	Mo	3.0	14	150
44	Ru	2.9	16	169
45	Rh	3.0	18	187
46	Pd	2.7	22	217
47	Ag	5.8	23	361
72	Hf	2.1	32	256
73	Ta	2.3	19	162
74	W	2.5	17	151
75	Re	2.4	17	152
76	Os	2.6	18	164
77	Ir	2.5	22	202
78	Pt	2.1	31	247
79	Au	3.3	49	516

This data has been extracted from complete calculations of the optical spectrum for each metallic nanoparticle over the range of 100 nm to 1000 nm wavelengths. A representative subset of the optical spectra is shown in Fig. 2. In the visible spectrum K and Na are excellent absorbers, while Al has the best absorption in the UV. Cu is a poor absorber while Ag, Li and Au are average. Fig. 2 shows that the plasmon resonance in K, Na and Al is very sharp, while in Cu it is broad and ill-defined. Au falls somewhere between these two extremes. Comparing K and Au nanospheres, the optimum particle sizes from table 1 are 21 nm and 49 nm, respectively. The difference in optimum size influences the proportion of absorption to scattering. Larger particles as a general rule tend to scatter more. This can be seen in Fig. 2 with the K particle absorbing around 5 times the amount it scatters, whereas the Au particle absorbs around 1.7 times the amount it scatters.

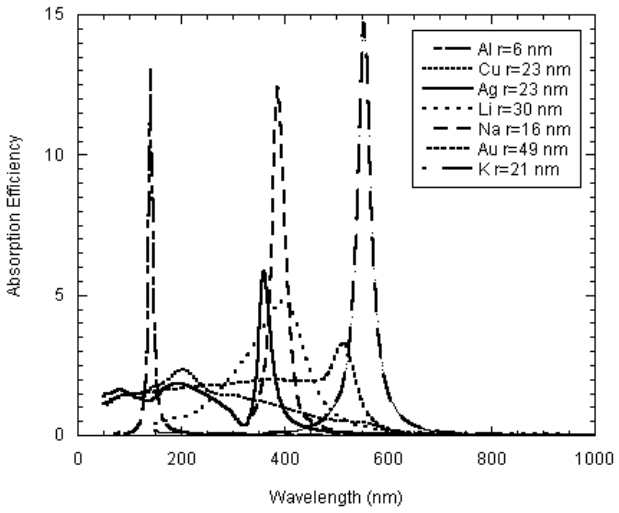

Figure 1. Complete absorption spectra for a small number of nanoparticles in table 1.

The wavelength position, size and width of the plasmon absorption peak is often described by (1) [17],

$$\sigma_{ext}(\lambda) = 12\frac{\pi r^3 \varepsilon_m^{3/2}}{\lambda}\frac{\varepsilon_2(\lambda)}{[\varepsilon_1(\lambda)+2\varepsilon_m]^2+\varepsilon_2(\lambda)^2} \qquad (1)$$

where σ_{ext} is the extinction cross section resulting for dipole absorption only, ε_m is the dielectric function of the surrounding medium (assumed constant and non-absorbing), r is the nanosphere radius, and $\varepsilon(\lambda)$ is the dielectric function of the nanosphere. In vacuum, according to (1) the peak occurs approximately where the real part of the dielectric function of the sphere is –2 and is independent of size. Strictly, (1) is true only in the quasistatic limit, i.e. as the size factor (particle radius divided by wavelength) approaches zero. As we shall show this is only a reasonable approximation in some cases. Materials with a small imaginary component at the plasmon resonance will have a large, narrow absorption peak, for example K (ε = -2.14 + 0.147i), Al (ε = -2.20 + 0.179i) and Na (ε = -2.15 + 0.191i). Conversely materials with large imaginary components at the plasmon resonance will have small, broad absorption peaks, for example Cu (ε = -1.37 + 3.17i).

The plasmon peak position as a function of particle size for K and Au spheres from 5 nm to 65 nm is shown in Fig. 3. For Au particles the plasmon position, as described by (1) is quite size independent and occurs where $\varepsilon' = -2$. However, for K the peak shifts about 100 nm over the same range of particle sizes. Closer inspection of our calculations shows that contributions from higher order terms in the multipole expansion are not the cause of this shift, the dipole term dominates across this size range. Furthermore, this phenomenon is not unique to K with the position of the plasmon resonances of most other metallic nanospheres experiencing a significantly greater dependence on sphere radius than Au.

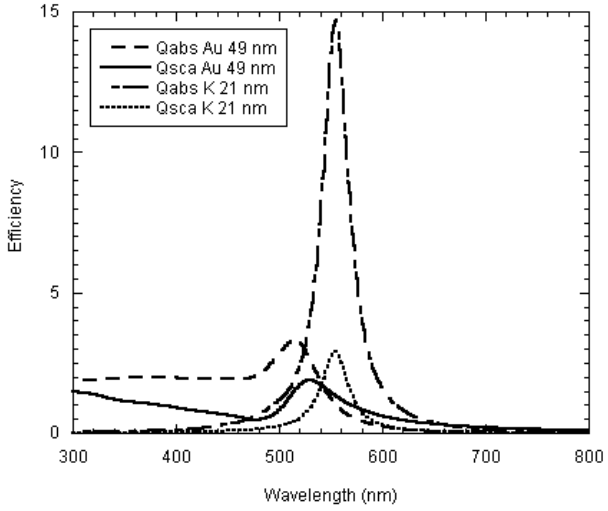

Figure 2. Q_{abs} and Q_{sca} for a 21 nm K and 49 nm Au nanoparticle.

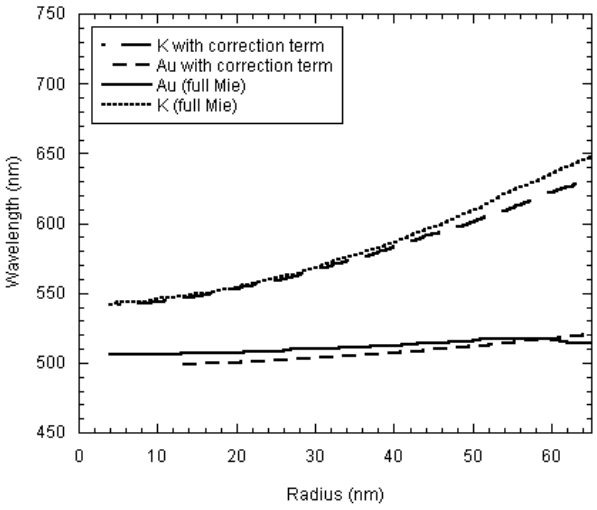

Figure 3. Plasmon peak shift for Au and K with increasing radius

The result that the plasmon resonance occurs at $\varepsilon = -2$ (relative to vacuum) clearly does apply to K, and indeed to many of the other metallic nanoparticles investigated here. This is not surprising given that almost all metallic nanoparticles have a plasmon resonance at a wavelength of order 100 nm with particles sizes of order 10 nm. Hence, it is questionable, even for gold, whether the quasistatic limit, and (1), can be applied to real metallic nanoparticles.

From Mie theory it is possible to derive a correction term that gives the shift of the plasmon resonance with particle size. The value of the real part of the dielectric function, ε', at which the plasmon peak now occurs is given by (2).

$$\varepsilon' = -2\varepsilon_m - \frac{12}{5}\frac{4\pi^2 r^2 \varepsilon_m^2}{\lambda^2} \qquad (2)$$

where λ is the wavelength, r the sphere radius, and ε_m is dielectric of the surrounding medium (assumed constant and non-absorbing). The results of (2) for Au and K are also plotted in figure 3. They agree well with the full Mie calculation. Taking the derivative of (2) and removing constants gives the following proportionality between the shift in the plasmon resonance position, λ_p, with particle size, r, and gradient of the dielectric function,

$$\frac{\delta\lambda_p}{\delta r} \propto -\frac{\delta\lambda_p}{\delta\varepsilon'} = -1/\frac{\delta\varepsilon'}{\delta\lambda_p} \qquad (3)$$

In other words (3) demonstrates that the amount the resonance wavelength shifts for a given change in particle size is inversely proportional to the gradient of the real part of dielectric function around the value –2. Moreover, if the gradient is negative, as it invariably is for Drude-type metals, the resonance shifts to longer wavelengths as the particle size increases.

Note, that gold is not very Drude-like below about 550 nm due to interband transitions and the plasmon resonance actually shifts, albeit slightly, in both directions as particle size increases.

The real part of the dielectric function for gold is quite steep around the value –2, and has a gradient of about –65 μm^{-1} in this region, whereas potassium is relatively flat with a gradient of only –10 μm^{-1}. It is for this reason that the plasmon peak is relatively size insensitive in gold spheres of about 5 nm to 50 nm radius, and not because the quasistatic approximation is valid in this size region. This is quite fortuitous, and for most other metals the gradient is sufficiently small that the peak shifts considerably over the same size range, deviations from the quasistatic limit are then more apparent.

IV. CONCLUSION

We have used Mie theory to calculate the optical response of nanosphere of varying radii and composed of a range of metallic elements. The results show that for the different metals there is an optimum radius that maximizes the absorption efficiency, Q_{abs}. Potassium and sodium nanospheres produce the greatest Q_{abs} within the visible spectrum, achieving magnitudes of 14.7 and 12.4, respectively. These results far exceed those for Au particles, where the maximum value of Q_{abs} is only 3.3.

In addition, if a large Q_{abs} and minimal Q_{sca} within the visible region are desired then we have shown that K and other metallic nanospheres offer better optical responses than Au nanospheres. For example, potassium particles absorb five times the amount they scatter at their optimum size of 21 nm. Because the optimum Au particle size is larger, 49 nm, they scatter relatively more, the ratio of Q_{abs} to Q_{sca} in this case is 1.7.

The calculations also demonstrate that gold nanospheres are rather unique in having a plasmon resonance that is relatively size independent in the size range of 5 nm to about 50 nm. The

reason for this is not so much that the quasistatic approximation applies across this range of particle sizes, but that the shift in peak position is small. For K nanospheres, by contrast the peak shift is about 50 nm and the quasistatic approximation is clearly not valid. We have shown that the underlying reason for this behaviour is the gradient of the dielectric function, with larger gradients as for example in gold giving smaller peak shifts.

While the synthesis of Au nanoparticles is relatively simple, the synthesis of K nanoparticles is more problematic due to their extreme instability. However, work has already begun in this direction with a report by Beitia *et al* [24]. These authors have investigated the effect of the substrate on the polarisability of 18 nm radius K particles. The particles were, however, produced by evaporation in ultra-high vacuum onto a silicon substrate at -80^{o}C. Whether it is feasible to synthesize K particles by capping in some protective barrier remains to be seen. However, the computational work reported here provides motivation for pursuing such a course.

V. ACKNOWLEDGEMENT

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VI. REFERENCES

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