Au@SiO$_2$ colloids: effect of temperature on the surface plasmon absorption

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The effect of temperature on the surface plasmon absorption of Au@SiO$_2$ particles has been measured from 14 to 70 °C in aqueous solutions and from 16 to 50 °C in ethanolic solutions. The particles remain completely dispersed at elevated temperatures because of the silica shell. As the temperature is increased, there is pronounced damping of the surface plasmon absorption band. There are four effects contributing to the spectral changes. These are (*i*) changes in the metal plasma frequency due to metal volume expansion, (*ii*) changes in the solvent refractive index, (*iii*) changes in the solvent density and (*iv*) changes to the conduction electron scattering frequency with increasing temperature. We find that factors (*iii*) and (*iv*) dominate.

One of the most exciting properties of nanosized gold colloids is that they show a very intense plasmon absorption band in the visible (typically around 520 nm). The exact position and intensity of this plasmon band is extremely sensitive to both particle size and shape, and to the optical and electronic properties of the medium surrounding the particles.[1–4] In most cases, the temperature at which UV/VIS spectra are recorded is not reported because it is not considered of any importance. However, it is well-known that the refractive index of most solvents changes with temperature, which in turn affects the absorption spectra. In most solvents (like water) the effect of temperature on the refractive index[5] is small, but it becomes more noticeable in others (like ethanol).

The main problem associated with measurements at high temperature is the stability of standard gold sols, which are quite sensitive to almost any change in the dispersion medium. To overcome this stability problem, gold particles have been coated with a thin shell of silica, making use of a recently developed method[6,7]. Silica is electronically inert (it does not exchange charge with the gold particles), but the absorption spectrum is affected due to the different refractive index of the layer surrounding the particles.

This work shows the effect of temperature on the plasmon band of silica coated gold colloids in both water and ethanol. We analyse four effects contributing to the spectral changes. These are (*i*) changes in the metal plasma frequency due to metal volume expansion, (*ii*) changes in the solvent refractive index, (*iii*) changes in the solution volume and (*iv*) changes to the conduction electron scattering frequency with increasing temperature. We find that factors (*iii*) and (*iv*) dominate.

Experimental

3-Aminopropyltrimethoxysilane (APS) and sodium silicate solution [Na$_2$O(SiO$_2$)$_{3-5}$, 27 wt% SiO$_2$] were purchased from Aldrich. HAuCl$_4$ (Sigma), and trisodium citrate dihydrate (Panreac) were used as received. Technical grade ethanol (Panreac) and distilled water were used in all the preparations.

Transmission electron microscopy (TEM) was carried out with a Philips CM20 microscope operating at 200 kV, and particle size distributions were measured from several TEM negatives.

UV/VIS spectra were measured with a Hewlett Packard HP8453 spectrophotometer, equipped with a thermostatted cell holder. Each set of measurements was performed on the same sample by raising the temperature of both the blank and sample cells. A blank was measured before each measurement to account for any (unlikely) temperature effect on the solvent absorption.

The dispersions were prepared according to the procedures described in refs. 7 and 8, with slight modifications. Gold sols (5×10^{-4} M) were prepared according to the standard sodium citrate reduction method.[8] For silica coating, a freshly prepared aqueous solution of APS (0.25 mL, 1 mM) was added to 50 mL of gold sol under vigorous magnetic stirring. After 15 min, 2 mL of a 0.54 wt.% sodium silicate solution at pH = 10–11 was added to the surface-modified gold sol, again under vigorous magnetic stirring. The resulting dispersion (pH $\approx$ 8.5) was allowed to stand for 15 days, so that active silica polymerizes onto the gold particle surface. The excess dissolved silicate was then removed by repeated centrifugation at 4500 rpm and redispersion in distilled water. The resultant silica shell thickness was about 5 nm (see Fig. 1). Part of the dispersion was kept for UV/VIS measurements; the rest was transferred into ethanol and most of the water removed by a new centrifugation/redispersion (in pure ethanol) procedure.

Results

Shown in Fig. 1 is an electron micrograph where the morphology of the silica coated gold particles used for the present study can be easily observed. The *average* core diameter is 16 nm and the *average* silica shell thickness is 5 nm. The surface charge on silica is enough to confer a high stability, even in a less polar solvent like ethanol. This means that centrifugation can be performed without loss of stability. In fact, no change was observed in the particles after the solvent exchange process, as confirmed by the slight variation in the spectrum (measured at 20 °C), which almost quantitatively coincides with the calculated variation due to the increase in solvent refractive index from 1.33299 to 1.36048.

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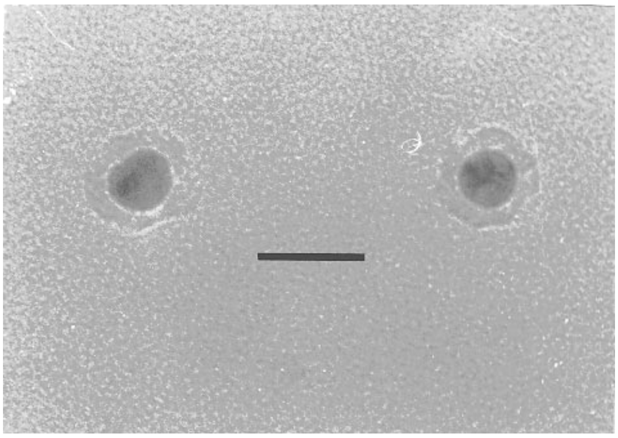

Fig. 1 TEM micrographs of 15 nm gold particles coated with 5 nm thick silica layers. Scale bar is 25 nm

The extinction coefficients for dispersions of spherical particles can be calculated by using the equations derived by Mie.[9a] These equations can also be used for the case of core–shell particles following the modifications made by Aden and Kerker.[9b] Whole spectra were calculated using the algorithm described by Bohren and Huffmann.[2] Two different sets of optical constants were used for gold. The first set was taken from values for evaporated thin films,[10] while the second corresponds to a single crystal.[11] Values at intermediate wavelengths were calculated by interpolation and were corrected for the effect of the small particle size on the dielectric constants for gold.[12] These data have been shown to give a good agreement for a variety of solvents[13] but there can be a slight mismatch (the single crystal data yield band positions at higher wavelengths) because the position of the surface plasmon band depends weakly on the particle size; experimental maxima between 514 and 520 nm have been reported.[14–16] The uncoated gold sols used had a maximum at 518.5 nm in water, whereas the data of Johnson and Christy[10] lead to a predicted peak at 521.5 nm and those of Weaver *et al.*[11] at 527 nm, differences of 3.0 and 9.5 nm, respectively. For silica, a dispersionless dielectric constant was used, taken as the square of the refractive index (1.456),[17] whilst for both water and ethanol the values at 589 nm were adopted since experimental values[5] were obtained at this wavelength, which is also close to the plasmon absorption band.

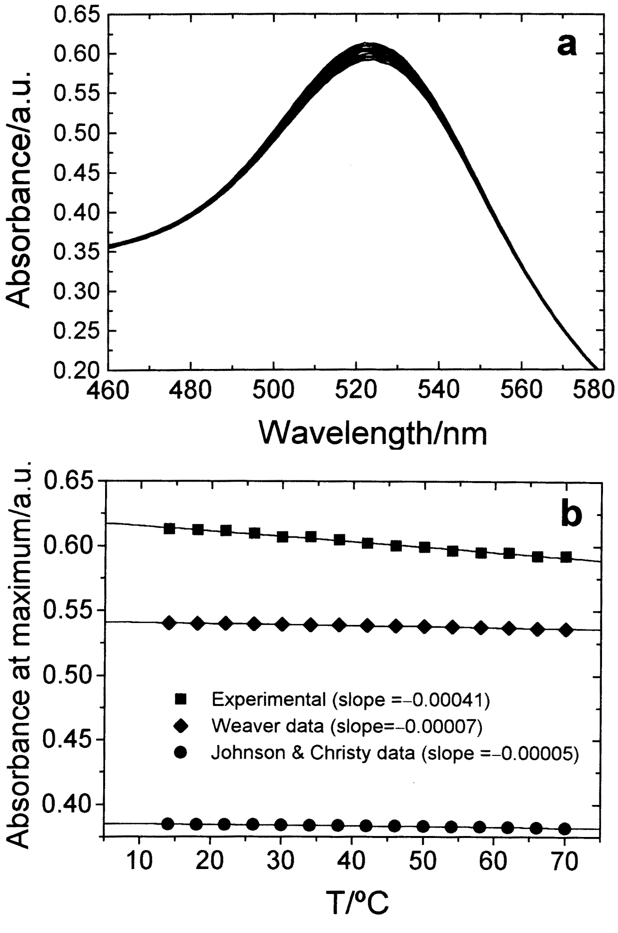

Fig. 2 Influence of temperature on the UV/VIS spectra of Au@SiO$_2$ hydrosols. (*a*) Experimental spectra. (*b*) Intensity variation at maximum position for the experimental and calculated spectra. In the calculations only the change in solvent refractive index was considered

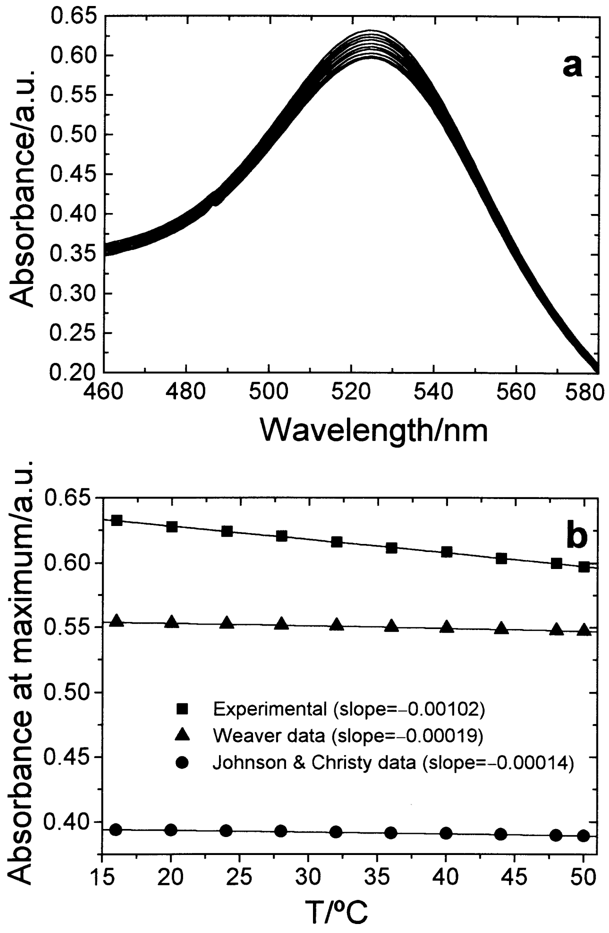

Fig. 3 Influence of temperature on the UV/VIS spectra of Au@SiO$_2$ alcosols. (*a*) Experimental spectra. (*b*) Intensity variation at maximum position for the experimental and calculated spectra. In the calculations only the change in solvent refractive index was considered

The influence of the silica layer on the optical properties of the suspension was shown in ref. 7 for silica shells of several thicknesses in water and ethanol. The general tendency is an increase in the intensity of the plasmon absorption band, as well as a redshift in the position of the absorption maximum, due to the increase in the local refractive index around the particles. This effect is accounted for by Mie theory calculations.[7] For the coated particles used here, the maxima of the experimental spectra were 523.5 nm in water and 524.5 nm in ethanol, while the calculations yielded 527.5 and 528.5 nm respectively using data for thin films, and 531.5 and 532 nm using single crystal dielectric constants. We can see that the shift between measured and calculated peak positions is the same (within experimental error) for uncoated and coated particles.

We first attempted to measure the effect of temperature on the absorption of citrate stabilized gold sols. However, at temperatures above about 40 °C the stability of the dispersions was decreased, as observed by oscillations in the intensity of the measured spectra. This effect was not observed when silica coated particles were used.

Fig. 2 shows the changes in the spectrum of an aqueous dispersion of the 16 nm gold particles with 5 nm silica shells, when increasing temperature from 14 to 70 °C. It should be mentioned that when the temperature is decreased back to 14 °C the same spectra are measured for each temperature. It can clearly be observed that only the part of the spectra around the plasmon band (500–550 nm) varies with temperature, while no significant changes occurred at higher or lower wavelengths. As shown in the figure, the intensity around the maximum steadily decreases with increasing temperature. No significant variation in the position of the maximum is observed. Extinction coefficients calculated using the two mentioned sets of dielectric data show the same tendency, as shown in the lower part of Fig. 2, where the intensity at the maximum is plotted *versus* temperature. For both sets, the experimental variation is noticeably faster than the calculated one, by a factor of ≈ 6. As is clear from the comparison in Fig. 2 and 3, simple refractive index changes do not account for the plasmon damping at higher temperatures. Other factors need to be taken into account, which will be discussed below.

Precisely the same trend was observed when the temperature was changed from 16 to 50 °C in an alcosol of 'the same particles' (see Experimental Section for details on the solvent exchange procedure). However, as shown in Fig. 3, the decrease in intensity with increasing temperature is noticeably faster, both in the experimental and in the calculated data. Again, the experimental spectra decrease *ca.* 6 times faster than the calculated ones.

Discussion

In order to account for the plasmon damping at elevated temperatures, we need to consider four possible contributions: metal expansion, solvent refractive index changes, solvent expansion and resistivity changes in the metal as a function of temperature. To quantify these effects we first present the relevant equations used to model the optical properties of dilute colloid spheres in a non-absorbing medium of refractive index n_o.

The extinction coefficient of the gold particles is accurately given by the dipole absorption formula to within 2%, provided that the enhanced surface scattering of conduction electrons is included.[4] Thus

$$C_{\text{ext}} = \frac{18\pi M V \varepsilon_m^{3/2}}{\lambda} \frac{\varepsilon''}{(\varepsilon' + 2\varepsilon_m)^2 + \varepsilon''^2} \tag{1}$$

where M is the particle concentration, V the particle volume, $\varepsilon_m = n_o^2$, and

$$\varepsilon = \varepsilon' + i\varepsilon'' \tag{2}$$

is the particle dielectric function. Doremus[18] has shown previously that the dielectric function is accurately fitted by the Drude model:[2]

$$\varepsilon = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + \omega_d^2} + i\,\frac{\omega_p^2\,\omega_d}{\omega(\omega^2 + \omega_d^2)} \tag{3}$$

Here ω_p is the bulk metal plasma frequency and ω_d the scattering frequency, which for the bulk metal is given by

$$\omega_d = \frac{v_F}{R_{\text{bulk}}} \tag{4}$$

where v_F is the velocity of conduction electrons at the Fermi level and R_{bulk} is the mean free path for conduction electrons in the bulk metal. The scattering of free electrons is directly related to the metal conductivity in the Drude formalism by

$$\sigma = \frac{Ne^2 R_{\text{bulk}}}{m v_F} = \frac{Ne^2}{m\omega_d} \tag{5}$$

Finally, because the particle radius is considerably smaller than the mean free path in the bulk, the electrons are scattered by the surface as well as by impurities or phonons in the bulk. Doremus[18] and later Kreibig[12] both demonstrated that this can be well accounted for by assuming an effective mean free path

$$\frac{1}{R} = \frac{1}{R_{\text{bulk}}} + \frac{1}{R_{\text{part}}} \tag{6}$$

that is,

$$\sigma(R) = \frac{Ne^2 R}{m v_F} \tag{7}$$

We now consider each of the four parameters mentioned above on the absorption coefficient through eqn. (1)–(7).

Metal expansion

The bulk plasma frequency is:

$$\omega_p^2 = \frac{Ne^2}{m\varepsilon_o} \tag{8}$$

where N is the conduction electron concentration, e the electronic charge, m the electron mass in the conduction band and ε_o the vacuum permittivity. Assuming one electron per atom and the free electron mass for m gives $\omega_p = 1.44 \times 10^{16}\ \text{s}^{-1}$, in agreement with experiment. Expansion of the metal at higher temperatures will cause a decrease in electron concentration of approximately

$$\frac{N}{\Delta N} = \frac{\Delta V}{V} = \alpha \Delta T \tag{9}$$

Using the bulk expansion coefficient for gold[5] of $\alpha = 1.42 \times 10^{-5}\ {}^\circ\text{C}^{-1}$, we get a fractional decrease in N of about 0.07% over the 50 °C range of the experiments. This decrease in N will decrease ω_p, and since the peak occurs when

$$\varepsilon_\infty + 2\varepsilon_m = \frac{\omega_p^2}{\omega_{\text{peak}}^2} \tag{10}$$

if $\omega_{\text{peak}}^2 \gg \omega_d^2$, it is clear that volume expansion of the metal will shift the band to longer wavelengths, away from interband transitions. Since these transitions act as a source of damping, this redshift actually leads to a slight increase in the intensity of the surface plasmon band; consequently, the observed decreases in peak intensity are not due to dilation of the metal lattice.

Solvent refractive index changes

The refractive index of the solvent decreases with increasing temperature. Assuming that it is dispersionless, then we see from eqn. (10) that a decrease in ε_m will shift the peak to higher frequencies. Due to interband transitions, which in gold begin at energies above 2.4 eV, the blue shift will also cause some damping. The variations in n_o with increasing temperature for water and ethanol are $-1.58 \times 10^{-4}\ {}^\circ\text{C}^{-1}$ and $-4.27 \times 10^{-4}\ {}^\circ\text{C}^{-1}$ respectively,[5] and reasonably linear from 20 to 70 °C. As can be seen from the data in Fig. 2 and 3, whilst these changes do lead to damping, the observed decreases are much larger. We obtain, from simulated spectra using eqn. (1) with this variation in refractive index, a predicted damping of the absorption, $\mathrm{d}A/A\mathrm{d}T$, equal to $-7 \times 10^{-5}\,°\mathrm{C}^{-1}$ in water and $-1.9 \times 10^{-4}\,°\mathrm{C}^{-1}$ in ethanol. Thus the solvent effects account for about 10–15% of the observed change.

Solvent volume expansion

At constant pressure, the heating of colloid solutions will also cause the solvent to expand. The change in volume is simply

$$V_S(T) = V_S(20\,°\mathrm{C})(1 + \alpha_S \Delta T) \tag{11}$$

where α_S is the expansion coefficient. Then it is apparent that

$$\frac{\mathrm{d}A}{A\,\mathrm{d}T} = -\alpha_S \tag{12}$$

The value of α_S is not quite linear over the range 20–70 °C, but the average values calculated from data in the CRC Handbook[5] are $\alpha_S = 4.14 \times 10^{-4}\,°\mathrm{C}^{-1}$ for water and $\alpha_S = 1.034 \times 10^{-3}\,°\mathrm{C}^{-1}$ for ethanol, which amount to 98% of the observed change.

Resistivity changes

From the results in the previous sections we see that the absorption of colloidal metals in solution is affected by both solvent refractive index and solvent volume changes as the temperature is increased. In addition, heating of the metal increases the metal resistivity, because the electrons are more readily scattered by lattice vibrations. Within the Drude model this implies a decrease in the mean free path or alternatively a higher scattering rate, ω_d. This increases ε'' through eqn. (3) and ultimately results in surface plasmon broadening. The peak intensity decrease is directly proportional to the increase in resistivity or $\varepsilon''_{\mathrm{peak}}$, as given by

$$A_{\max} = \frac{18\pi N V \varepsilon_m^{3/2}}{\lambda \varepsilon''_{\mathrm{peak}}} \tag{13}$$

Scattering reduces R_{bulk}, so that the effective mean free path in small particles as a function of temperature will be given by

$$\frac{1}{R(T)} = \frac{1}{R_{\mathrm{part}}} + \frac{1}{R_{\mathrm{bulk}}(T)} \tag{14}$$

The temperature coefficient of the electrical resistance of gold is linear over the range 0–80 °C[19] and has the value $\beta = 0.0034\,°\mathrm{C}^{-1}$. The bulk resistivity is 2.44 μΩ cm, which corresponds to a mean free path of $R_{\mathrm{bulk}} = 370$ Å if $v_F = 1.4 \times 10^6\ \mathrm{ms}^{-1}$ from eqn. (5). The actual change in band intensity depends on the particle size through eqn. (14). Larger particles show a substantially stronger effect than smaller particles. Substituting into eqn. (14), we find that

$$\frac{\mathrm{d}A}{A\,dT} = \frac{-\beta}{1 + R_{\mathrm{bulk}}/R_{\mathrm{part}}} = -6.04 \times 10^{-4}\,°\mathrm{C}^{-1} \tag{15}$$

This is actually slightly larger than the measured value of $-4 \times 10^{-4}\,°\mathrm{C}^{-1}$ and probably reflects errors in R_{part} and R_{bulk}. Values for R_{bulk} vary from 370 Å down to 108 Å. The latter value would yield a slope of $-1.45 \times 10^{-3}\,°\mathrm{C}^{-1}$. Conversely, a value of $R_{\mathrm{part}} = 51$ Å would account exactly for the surface plasmon bleaching.

In summary, we see that the temperature dependence is contributed to substantially by three different processes. Both resistance changes and solvent expansion appear to be the most important factors in ethanol and aqueous solution. Solvent refractive index effects are perceptible but a factor of 5–6 smaller. The measurement of the temperature dependence of the metal spectra is probably not a good way to examine the behaviour of the conduction electron population, unless care is taken to subtract these other factors. We have in addition assumed that there are no important changes to the silica shell as a function of temperature. Whilst shell volume increases would not play an important role, reversible refractive index changes to the shell could play a minor role in determining the extinction coefficient of Au@$\mathrm{SiO_2}$ colloids at elevated temperatures. Doremus[18] and later Kreibig[12] examined the temperature dependence of the plasmon absorption band in glasses. The shifts reported here are substantially larger. The reason for this is simple. In glasses, the glass expansion coefficient is smaller, which makes the changes in intensity much smaller. The change in resistivity is the dominant factor for metal particles in glasses.

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