

The Third Order Nonlinear Optical Properties of Gold Nanoparticles in Glasses, Part II*

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Abstract: The optical properties of gold nanoparticles have been known for a number of years and recent advances in laser power have now allowed the non-linear optical properties to be studied. In this short review paper, the various theories that have been used to describe the optical properties of gold nanoparticles are presented. Methods of preparing gold nanoparticles in glasses are explained briefly, as well as characterization techniques. The optical properties of gold nanoparticles are reviewed, as well as the effects of particle size, shape, concentration and c.

Effects Of Nanoparticle Size

The relationship between optical properties and nanoparticle radius has been studied in glasses with dispersed colloid Au nanoparticles (111,112). The peak plasmon wavelength shifts continuously to longer wavelengths with increasing average particle radius. A similar dependence was seen in silica glasses dispersed with Au colloid particles (112,113). Foss *et al.* (68) found significant transparency in the near-IR region and strong extinction in the visible for particles with near-sphere like shape. The wavelength of maximum extinction increased with increasing particle radius, giving rise to colour variations (red-purple for 30 nm size and blue-green for 60 nm size). This is shown in Figure 1. This was consistent with the findings of Mie (17). Hosoya *et al.* (73) and Muto *et al.* (102) found in Au:Al₂O₃ thin films that the spectra broadened and the peak shifted to longer wavelengths as the particle size decreased. Muto *et al.* (102) explained it as due to charge transfer from the metal particles to the amorphous oxide by the aluminium-metal bonds used in adhesion. The decreased electron density of the metal particles gives rise to the blue-shift. This behaviour was opposite to that of Au:SiO₂, and indicates that the matrix has an effect on the blue- or red-shift of the plasmon peak with size.

As the wavelength of the surface plasmon resonance changes with particle size, the $\chi^{(3)}$ is also expected to change with size. Fukumi *et al.* (60), found $\chi^{(3)}$ to be approximately proportional to the fourth power of the particle radius. They also found that $\chi_m^{(3)}$ (of the metal particles on their own) had negligible dependence on the particle radius. The value of $\chi_m^{(3)} = 2.5 \times 10^{-8}$ esu agreed with that of Hache *et al.* (32) and Bloemer *et al.* (114).

Hornyak *et al.* (69) prepared Au nanoparticles in nanoporous alumina membranes, and absorption properties for nanoparticles of size 52 nm down to 16 nm, and with various aspect ratios. They used a modified form of MG theory, called the dynamic MG (DMG) theory (68), to model the optical properties. They found that as the nanoparticle size decreased, the wavelength of the maximum absorption intensity λ_{max} approached the value predicted by DMG theory. For the smallest diameter particles, (16 nm), the values were identical with DMG theory, and they suggested that there was a quasi-static DMG limit (λ_{max} does not change from ~508 nm) for nanoparticles of diameter 16 nm.

Alvarez *et al.* (115) prepared passivated gold particles with sizes 1.4-3.2 nm. They found that with decreasing size, the SPR band broadened until it became unidentifiable for sizes less than 2 nm. They also found a distinct onset for strong absorption near the energy (~1.7 eV) of the interbandgap (5d→6sp). Above this onset, a weak steplike structure was found. The experimental results were compared with Mie

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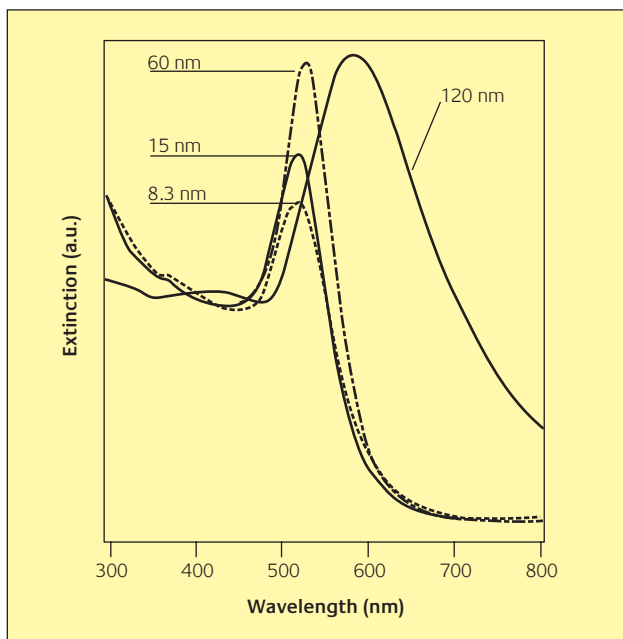


Figure 1
The Absorption Spectra of Different Sized Au Particles (99)

theory, and good agreement was found when the passivated layer was accounted for. They also suggested that there was a critical size of ~ 2 nm, below that the electronic structure changes dramatically. Palpant *et al.* (49) reported that the SPR blue-shifts with decreasing cluster size (2.0-3.7 nm). There was also increased damping and broadening of the absorption band, agreeing with Alvarez *et al.* (115). Palpant *et al.* (49) applied theoretical time-dependent local-density-approximation (TDLDA) calculations to their results, and found good agreement. In this theory, the conduction electrons are treated quantum-mechanically, whereas the optical properties of the matrix and ionic core background are treated classically through bulk-like dielectric functions. They explained the effects as follows: they considered the cluster to have two-regions, an inner medium and an outside shell. The blue-shift with decreasing size was due to the screening effects, due to the polarisable inner medium, that vanish in the shell of the particle.

Effects Of Nanoparticle Shape

For gold nanorods in an aqueous solution, the plasmon absorption splits into two bands (116,117), corresponding to the response along and perpendicular the long axis of the rods. The transverse mode (end on) corresponds to the simple case of spherical particles. The longitudinal mode (length-wise) is red-shifted, and depends strongly on the nanorod aspect ratio.

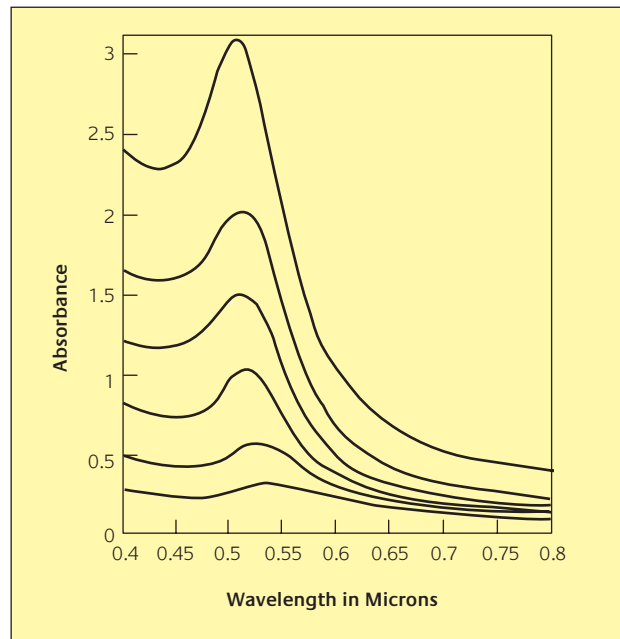


Figure 2
Absorption Spectra (due to the transverse plasmon resonance) for 32 nm Diameter particles with Different aspect Ratios. The Uppermost Curve is for the Highest Aspect Ratio, and the Lowermost Curve is for the Lowest Aspect Ratio Nanoparticle (69)

The colour of an Au:Al₂O₃ composite can be varied by changing the shape of the Au particles in the matrix (oriented gold nanorods). As the aspect ratio increases (with constant diameter), the extinction intensity increases and the extinction maxima wavelength is blue-shifted to shorter wavelengths (68). By varying the aspect ratio, systematic shifts in the extinction maxima can be attained. This is shown in Figure 2. When the cylinder radius is increased, the extinction maxima red-shifts to longer wavelengths. The effects of the aspect ratio follow qualitatively the predictions of MG theory.

Foss *et al.* (118) compared the transmittance of Au microcylinders (0.26 μ m diameter) in Al₂O₃ membranes to that of Maxwell-Garnett and Bruggeman (33) theories. They found qualitative agreement between experimental and theory. It was considered that the particle separation in the matrix was not small relative to the wavelength, creating a phase lag between the incident and induced fields experienced by a given particle (called retarded polarisation (119)). By modifying the MG theory to take this particle separation into account, the theory followed the experimental data reasonably. They also systematically varied both aspect ratio and diameter, and compared the optical spectra with predictions of MG theory and Mie theory (68). They had qualitative agreement with the two theories, and proposed a modification of the MG theory using dynamical models for the depolarisation factor (120), to take into account size and shape effects in a unified calculation.

Effects Of Gold Concentration (Volume Fraction)

Liao *et al.* (48) reported that in Au:SiO₂, at 5% Au concentration, the wavelength of the surface plasmon resonance (SPR) was close to 520 nm. With increasing Au concentration, the SPR peak shifted to 530 nm at 21% Au, and 540 nm at 45% Au. Accompanying the shift was a sharpening of the SPR (due to the size increase of the Au clusters). However, at greater concentrations, the peak intensity decreased while the off-resonant absorption increased. The absorption spectra became completely different when the Au concentration reached the percolation threshold. At Au concentrations higher than the percolation threshold, there was a transmission window in the resonant region, consistent with theoretical predictions (121). Liao *et al.* (48) reported the susceptibility ($\chi^{(3)}$) as $\sim 2.5 \times 10^{-6}$ esu for co-sputtered Au:SiO₂ films. With increasing Au concentration, the susceptibility increased quickly and reached a maximum of $\sim 2.5 \times 10^{-6}$ esu at 40% Au. The effect of gold concentration is shown in Figure 3. This maximum value was three orders of magnitude larger than the value at 4% Au (3.5×10^{-9}) esu, and at least 10 times higher than that reported by Tanahashi *et al.* (105). The rapid increase of $\chi^{(3)}$ was due mainly to the enhancement of mutual interactions between the Au clusters, whereas at higher Au concentrations, the particle size becomes large so that only the outer layer of the Au particles contributes to the optical nonlinearity.

The laser pulse width will affect the values of $\chi^{(3)}$, as $\chi^{(3)}$ contains two components: a fast and slow component (19,122). Comparison of the results of Liao *et al.* (48) and Tanahashi *et al.* (105) show that there is a difference in measured values due to the difference in the laser pulses used. Bearing this in mind, values of $\chi^{(3)}$ near 40% Au could be as large as 5×10^{-5} esu for nanosecond pulses.

The effective $\chi_{\text{eff}}^{(3)}$ for low concentrations is linearly proportional to the metal concentration (19). The linear relationship is only valid up to 15% Au, and beyond that the relationship is no longer linear (48). Liao *et al.* (48) have found a power law dependence of the $\chi^{(3)}$ on Au concentration p ($\chi^{(3)} \sim p^r$) where t is approximately 3.

Liao *et al.* (48) suggested the enhancement of $\chi^{(3)}$ at high Au composition was the result of two effects: (1) the so-called local field enhancement due to the resonance of the probe beam within the cavities formed by the Au clusters, and (2) due to Mie resonance of the Au particles which would enhance the local field inside and outside the Au particles. When the first effect is considered at high Au concentrations (Au particles become connected), the large local field will be averaged out and the effect reduced, decreasing the $\chi^{(3)}$.

Liao *et al.* (48) reported the figure of merit (without the time factor $-\chi^{(3)}/\alpha$) increased as the Au concentration in SiO₂ increased, and reached a maximum value of 1.1×10^{-11}

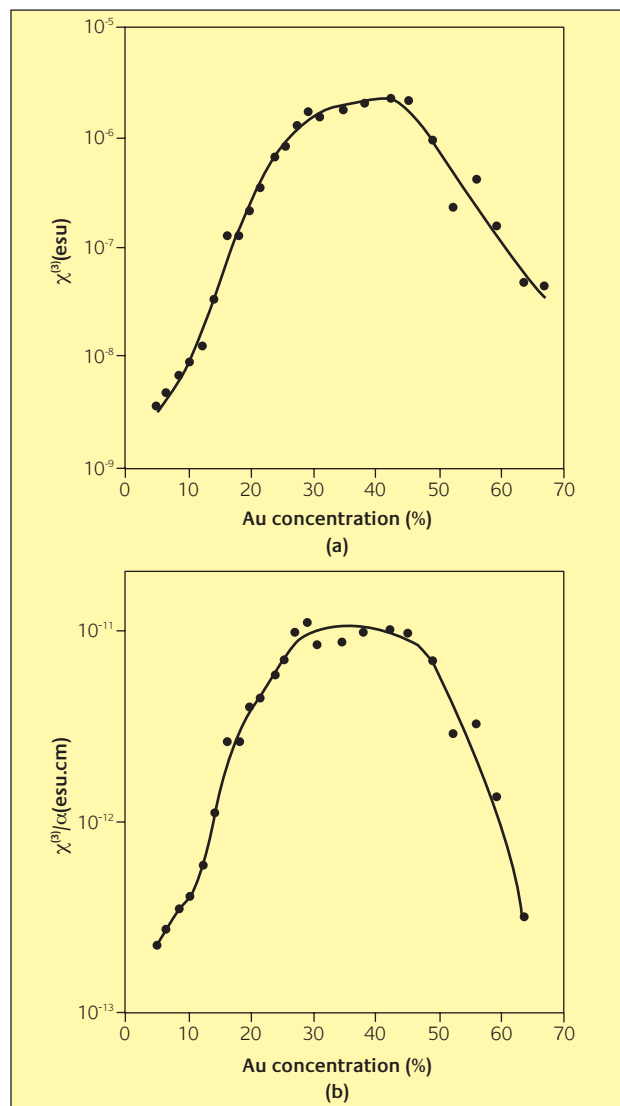


Figure 3
(a) Au-Composition Dependence of $\chi^{(3)}$ and (b) Au-Composition Dependence of $\chi^{(3)}/\alpha$ (α Absorption Coefficient) in a Au:SiO₂ Composite (48)

(esu.cm) at $\sim 40\%$ Au, larger than previously reported values (105). They also found that the dependence of the figure of merit $\chi^{(3)}/\alpha$ to the Au concentration also followed a power law, with an exponent of ~ 2.7 .

Liao *et al.* (92) reported results for Au:TiO₂ composites, shown in Figure 4. They found that at 17% Au concentration, the wavelength of the SPR was near 665 nm. With increasing Au concentration, the SPR red-shifted, accompanied by a sharpening of the absorption peak. With further Au concentration, the absorption peak started to decrease, and at 60% Au, the absorption peak disappeared. Liao *et al.* (92) also measured the $\chi^{(3)}$ and found that at 630 nm, with increasing Au concentration, $\chi^{(3)}$ increased and reached a maximum of 2.5×10^{-7} esu at 38% Au, and then decreased. At 670 nm (close to the SPR), the same trend was observed, but $\chi^{(3)}$ was larger

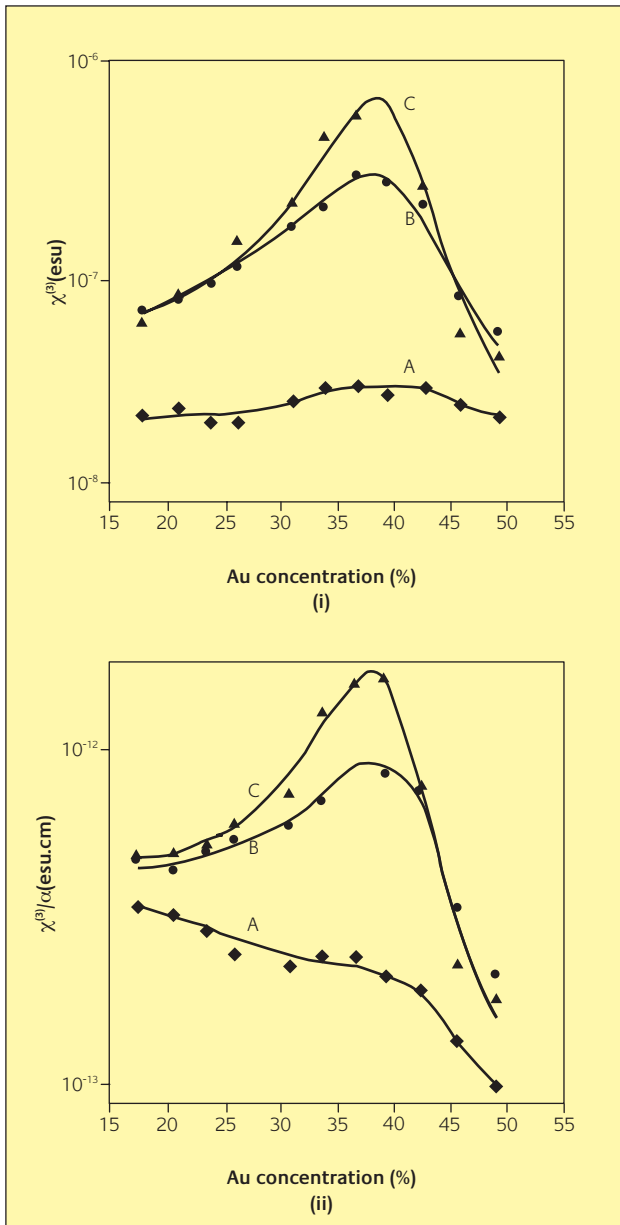


Figure 4
 (i) Au-Composition Dependence of $\chi^{(3)}$ and (ii) Au-Composition Dependence of $\chi^{(3)}/\alpha$ (α Absorption Coefficient) in a Au:TiO₂ Composite (92) at Wavelengths: (A) 532 Nm, (B) 630 Nm and (C) 670 Nm

between 26% Au and 44% Au. The maximum $\chi^{(3)}$ was 6×10^{-7} esu at 38% Au. They also found the figure of merit (close to the SPR - 670 nm) increased with Au concentration, reached a maximum of 2×10^{-12} esu.cm at 38% Au, then decreased with a further increase in concentration.

Third-order non-linear susceptibility ($\chi^{(3)}$) values of $\sim 10^{-8}$ esu have been found for Au in Al₂O₃, for low Au concentrations (123,124). Liao *et al.* (125) reported the wavelength of SPR of Au in Al₂O₃ at 550 nm for Au concentration of 17% Au (Figure 5). As the Au concentration increased, the resonance peak shifted to 575 nm at 36% Au and 585 nm at 42% Au. Beyond 50% Au concentration, the peak absorption decreased. In comparison with Au:SiO₂ (48), the SPR in the Au:Al₂O₃ are shifted to longer wavelengths because of the larger dielectric constant of Al₂O₃. With an increase in Au concentration, $\chi^{(3)}$ increased and reached a maximum value at 1.2×10^{-6} esu at 45% Au, and then decreased in value (125). Theoretical calculations (126) deviated significantly from the trend of change of $\chi^{(3)}$, although it gave the correct order of magnitude. Liao *et al.* (125) suggested the enhancement of $\chi^{(3)}$ near the percolation threshold may not be due to the SPR

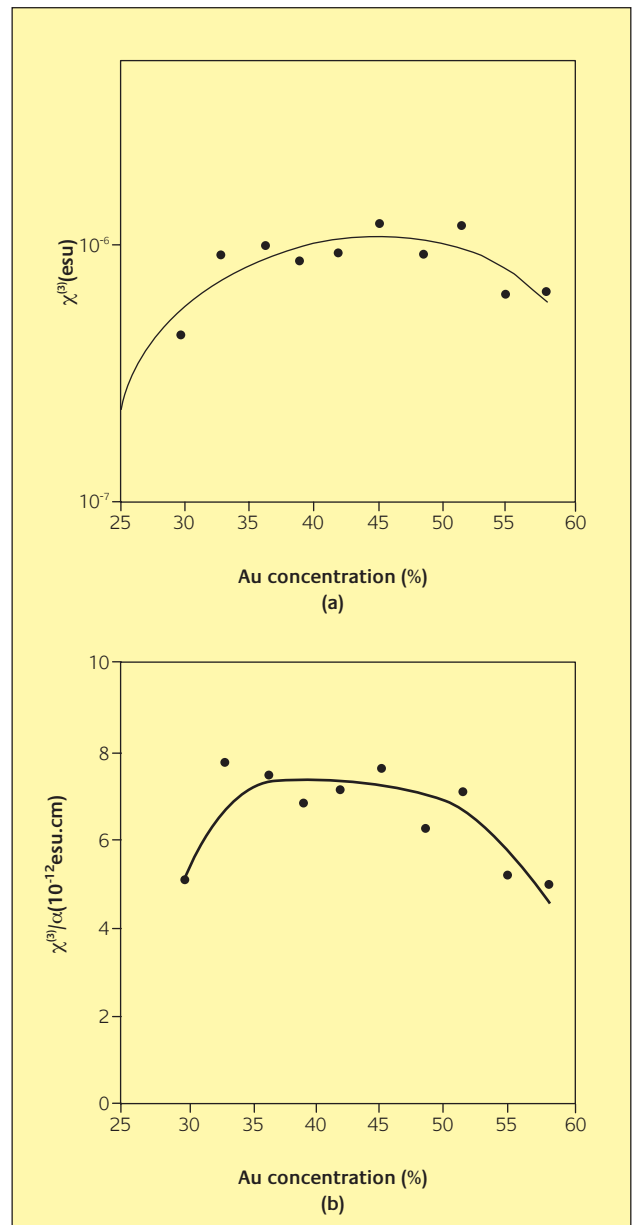


Figure 5
 (a) Au-Composition Dependence of $\chi^{(3)}$ and (b) Au-Composition Dependence of $\chi^{(3)}/\alpha$ (α Absorption Coefficient) in a Au:Al₂O₃ Composite (125)

575 nm at 36% Au and 585 nm at 42% Au. Beyond 50% Au concentration, the peak absorption decreased. In comparison with Au:SiO₂ (48), the SPR in the Au:Al₂O₃ are shifted to longer wavelengths because of the larger dielectric constant of Al₂O₃. With an increase in Au concentration, $\chi^{(3)}$ increased and reached a maximum value at 1.2×10^{-6} esu at 45% Au, and then decreased in value (125). Theoretical calculations (126) deviated significantly from the trend of change of $\chi^{(3)}$, although it gave the correct order of magnitude. Liao *et al.* (125) suggested the enhancement of $\chi^{(3)}$ near the percolation threshold may not be due to the SPR

of Au, but more likely from the strong interaction between the Au particles. They also suggested that the matrix contribution (Al_2O_3 or SiO_2) to $\chi^{(3)}$ was negligible in the composite, as it was seven orders of magnitude smaller than that of gold. Liao *et al.* (125) found that the figure of merit for the Au: Al_2O_3 films increased with Au concentration and remained constant at a value of 7×10^{-12} esu.cm in the range 35-50% Au.

Directions for further study

A logical question would be how to increase the non-linear properties further. Magruder *et al.* (127) doped Ag and Cu together into glass, and found that the Ag enhanced the response of the Cu near resonance. This would suggest that incorporating another element may increase the non-linear properties further, and give more control of the properties.

Prével *et al.* (128) have embedded gold, silver and bimetallic silver-gold clusters in a porous alumina matrix, with particle sizes 2-6.7 nm. They suggested the two metals alloyed in the matrix. The two metals were deposited in the ratio 50% Ag and 50% Au. The optical absorption band was almost halfway between that of the Au and the Ag. It must be noted that no other ratios were considered, so no conclusion could be drawn about the relationship between the absorption and composition ratio. With decreasing particle size, the Au absorption peak blue-shifts, as well as the Ag:Au absorption peak. They observed that the observed blue-shift trend in the case of the Ag:Au was intermediate between the size evolution obtained in pure Ag or Au nanoparticles. TDLDA could theoretically describe the experimental results very well. The SPR position varies strongly as a function of the composition of Ag-Au alloy nanoparticles (129,130). The position varies linearly with gold composition, blue-shifting with decreasing Au mole fraction. This makes the system easily tunable. However, the optical properties should not be viewed as a linear combination of those of pure Ag and Au, as seen by the inability of the theory to predict the experimental results.

AuCu and Au₄Cu nanoparticles were produced in silica thin films using a sol-gel method (131). Absorption peaks were found at 555 nm for AuCu and at 562 nm for Au₄Cu, and these absorption peaks are attributed the intermetallic phases.

Henglein and Giersig (132) reported a study of Au/Hg nanoparticles in aqueous solution. The optical spectra obtained was not a superpositioning of the individual constituents. This suggested the deposition of Hg on the gold particles. With increasing Hg deposition, the plasmon peak blue-shifted and became weaker, and a second broad absorption band builds up in the 300-400 nm range, without shifting with increasing Hg content.

Sequential ion implantation has been used to form multi-component nanometer dimension metal particles in glasses (133,134), which alters the electronic structure of the colloids by changing the composition of the metal particles. This results in changes in the optical properties (both linear and non-linear) that are not possible with single element colloids (135,136).

Zuhr *et al.* (137) used sequential ion implantation to create intermetallic nanoclusters of Cd/Ag and Sb/Ag in silica. Changes in both the linear and non-linear optical properties of the composites could be attained that were not possible with single element colloids alone. The surface plasmon resonance showed significant changes in the wavelength and the magnitude.

From the discussion, it is noted that when incorporating two nanoparticle sized elements in a matrix, either intermetallic nanoparticles form (with their own optical properties) or the one species ends up coating the other (or some other interaction where no intermetallics form). With the above in mind, an interesting investigation would be to embed two elements (which do not form any intermetallic compounds) together in SiO_2 . The result would be a matrix with two discrete nanoparticle elements. Each element would affect the other species (the effective properties of the composite would change), giving rise to further control of the optical properties. It has been observed that Ag and Cu particles prepared by the sol-gel process exist as independent particles without forming alloys (138). A logical question that could be asked is: is there a gold analogy, and how would the two nanoparticle species affect each other? Considering the relative simplicity of the sol-gel process, the challenge would be to find a sol-gel process (for producing nanoparticles of Ag, Pt or another element) that is compatible with the sol-gel processes used to produce Au nanoparticles in a glass.

Conclusions

In this brief review of the non-linear optical properties of Au nanoparticles, the theory and experimental data of Au nanoparticles in various substrates have been presented. In the theory section, the basic theories used to model the nanocomposites have been introduced together and the various geometries and the related theory. The methods used to fabricate nanoparticles were discussed in light of mechanical methods (ion-implantation) and chemical methods (sol-gel). The techniques that are used to characterise the nanocomposites were briefly discussed.

The results that have thus far been obtained for Au in various matrices were presented. The effects of response time, particle size and shape, and concentration were discussed. The effects of adding another element to the nanocomposites were investigated, and it appears that further enhancements in the non-linear properties may occur with multicomponent nanocomposites.

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