Dipole-dipole plasmon interactions in gold-on-polystyrene composites

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Red-shifting of the optical absorption spectra of aggregates of gold nanoparticles by dipole-dipole interactions is of considerable interest, both for theoretical reasons and because the phenomenon can be potentially exploited in various applications. A convenient and practical way to control the effect is to assemble the aggregated ensemble of *n* gold nanoparticles on the outer surface of larger dielectric spheres. Here we show by experiment and calculation how the spectra of these structures can be systematically morphed from that of isolated gold particles, through the regime of broad absorption dominated by particle-particle interactions and finally to the limiting case of a continuous nano-shell. The experimental data was produced using the process of deposition-precipitation, which provides a facile method to decorate polystyrene micro-spheres with gold nanoparticles. There is no need for prior functionalisation of the micro-sphere surface in our method of deposition-precipitation. Calculations were carried out using a code based on the discrete dipole approximation (DDA). The spectra were dominated by three effects. These were a peak absorption at about 540 nm produced by the conventional plasmon resonance of spherical gold nanoparticles, a broad absorption in the range 600 to 900 nm caused by diverse dipole-dipole interactions between particles which strengthened as the number of attached gold particles increased and finally, when *n* was large, an absorption peak due to the onset of nanoshell-like resonances. The experimental spectra could be successfully fitted by spectra calculated using combinations of these effects.

I. Introduction

There is an abundant literature covering the science and technology of gold nanoparticles, particularly in respect of their optical properties.[1] Much of the interest has been focused on the plasmon resonance of dilute suspensions of spherical particles, which have a red-purple color caused for the most part by an broad absorption peak centered on about 520 nm. However, when individual spherical gold particles come into close proximity to one another, their plasmon resonance is red-shifted by up to 300 nm causing the color in transmission to become blue.[2] This effect is negligible if $D>5r$, where D is the centre-to-centre distance and r the radius of the particles, but is increasingly important at less than that.[3] The wavelength at which absorption due to dipole-dipole interactions occurs may be varied from 520 nm (effectively isolated particles), through to ~750 nm (particles that are separated by only 0.5 nm) by this strategy,[4] Figure 1. The resulting spectra are a composite of the conventional plasmon resonance due to single, spherical particles and the new peak due to particle-particle interactions.

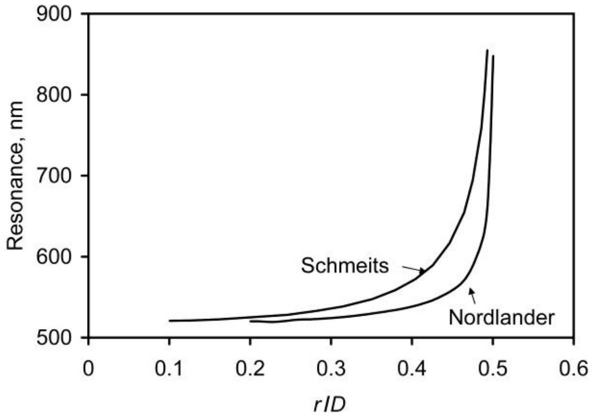


Figure 1. Plasmon resonance of gold nanoparticle dimers, showing values reported by two sources in the literature.[5]

The color change that follows from aggregation or densification of gold nanoparticles has been used commercially to provide sensitive biochemical assays,[6] and has been demonstrated in the form of coatings on glass.[4,7] The properties of regularly packed aggregates have been well explored.[4] However, randomly packed aggregates have different and rather variable, optical properties.[8] If these properties can be controlled then there might, for example, be applications for the clusters as the substrates in surface enhanced Raman spectroscopy,[8] as novel pigments, or in spectrally selective coatings for solar glazing.[7] Unfortunately, in general when gold nanoparticles in suspension are aggregated or densified, they precipitate out as mesoporous sponges, losing their plasmon resonance in the process. The present authors sought a method to prepare stable, strongly colored suspensions of randomly aggregated clusters of gold nanoparticles in order to investigate the change in optical absorption that accompanies a decrease in inter-particle distance. We suspected that agglomeration into mesoporous sponge precipitates could be prevented by confining the aggregation to the surfaces of dielectric micro-spheres in co-suspension with the gold. This geometry also has the advantage of increasing the available surface area for aggregation compared what is available from a single planar surface, a point possibly first noted by Westcott *et al.*[9]

In the scheme of Westcott *et al.,*[9] and in most other published recipes, previously manufactured gold nanoparticles are attached to the functionalised surface of a somewhat larger sphere of a dielectric such as SiO_2 or polystyrene, and then grown by further reduction, [9-11] or by layer-by-layer attachment of metallic particles.[10,12] Functionalizing is performed with something like an ω-terminated trialkoxyorganosilane in the case of SiO_2[9] or 2-aminoethanethiol hydrochloride in the case of polystyrene spheres.[11] The purpose of this previous work was in general to make gold nanoshells, which have a significantly red-shifted absorption spectrum that can be 'tuned' deep into the infra-red if desired[13]. There has also recently been some interest in seedless schemes to coat SiO_2 and polystyrene to make gold nanoshells.[14,15]

In the present work we report a scheme to nucleate and grow gold particles *in situ* on the surface of latex micro-spheres. Like Shi *et al.*,[11] and Zhang *et al.,*[14] we chose polystyrene as a templating core because it can be readily removed later, if need be, unlike the case for cores of SiO_2 or AuS_2. Furthermore polystyrene micro-spheres are readily available in reasonably monodisperse latex suspensions from microscopy supply companies. We confirm the finding of Zhang *et al.* that it is practicable to decorate the polymer without pre-functionalizing its surface.

While the optical absorption of a nanoshell can be calculated by the exact methods pioneered by Mie, that of the aggregated particles cannot. One approach is to invoke the concept of an average or effective volume fraction of gold, and a consequent 'effective dielectric constant' such as that defined by Maxwell-Garnett.[4,7] However, this 'continuum approach' necessarily neglects the important effects of individual variations in cluster geometry, a factor well known to produce quite striking variations in optical spectra.[8] Therefore, we approached this problem by carrying out calculations based on the discrete dipole approximation (DDA). In this scheme the geometry of the particles is rendered onto a fine mesh as an array of dipoles, and the optical characteristics solved numerically.[16]

Here we show in detail how the optical spectra of random aggregations of gold nanoparticles on the surface of micro-spheres can be controlled. Suspensions of the resulting composite particles are increasingly blue in color, and we confirm that this is due to a corresponding increase in number and intensity of gold particle-particle interactions on the surface of the individual micro-sphere cores. However, once the surfaces of the polymer templates are substantially covered with gold particles, nucleation and growth of large, isolated particles in the surrounding liquid becomes significant. We support our proposed explanation by providing both high resolution images of the composite particles and calculations of the optical properties of simulated multi-sphere structures.

II . Experimental

The optical properties of model arrangements of 20 nm diameter gold spheres on polymer particles of 100 nm diameter were calculated using the DDSCAT code of Draine and Flatau ,[16] which is based on the discrete dipole approximation (DDA). We wrote a front-end program (nSpheres) to randomly nucleate a user-designated number of gold spheres on the surface of a 100 nm sphere, and then passed the simulated geometry to DDSCAT for further processing. DDSCAT works fastest and most accurately when $|m|$ is less than 2, where m is the complex refractive index of the material relative to the medium in which it is immersed. However, the imaginary part of m can be quite large in the case for metallic nanostructures. The solution to this problem is to refine the mesh used in DDSCAT by as much as computing resources allow.[17] We have used up to 15000 dipoles for these calculations. However, computation was very slow for λ>600 nm, a problem exacerbated by the need to present each model geometry to the incoming light in many different orientations in order to simulate a dispersion of randomly oriented particles. A typical spectrum, plotted from 300 to 900 nm, took of the order of 100 hours on a 2 GHz Windows machine.

Because the NSPHER target generation subroutine of DDSCAT can handle only two materials, we set the refractive index of the core to be the same as that of the surrounding medium (water) for the simulations of monodisperse gold spheres shown in Figure 4 in order to illustrate the broad trends. However, in the simulations of the actual structures produced from Au and polystyrene we used a medium that had the average refractive properties of water plus polystyrene, using the published optical properties of polystyrene.[18] Nevertheless, because the refractive index of gold is very much greater than that of water or polystyrene, the incorporation of the polystyrene core only produces a small amount of red shifting.

Deposits of gold on polystyrene particles in a latex suspension were achieved by first steeping the particles (95 nm diameter from ProSciTech, Australia) in 0.01 M aqueous solution of $HAuCl_4$ for at least 24 hours. The preparation of the $HAuCl_4$ has been described elsewhere.[7] Additional 0.01 M

$HAuCl_4$ was added to this solution to systematically increase the ratio of Au to polystyrene particles. The parameter we used to define the ratio of gold to polystyrene was the notional thickness of gold that would be achieved if all gold present had deposited onto the surface of the polymer micro-spheres. Mixtures designed to deposit between 40 and 160 nm Au onto the polystyrene were examined in this work. Between 50 and 700 μL of the mixture of $HAuCl_4$ and polystyrene latex was then added to 10 ml of 0.039 M sodium citrate solution held at between 98 and 100°C. This allowed for a variation in ratio of reductant to $HAuCl_4$ (samples C1 to C7) without changing the notional coverage of gold on the micro-sphere cores. Reduction of the gold occurred within a few seconds, and produced a liquid of blue color. When $HAuCl_4$ and reductant were mixed under clean conditions and without the presence of polystyrene micro spheres, the color of the suspension produced was the well-known red of free particles of gold. The two situations are compared in Figure 2. The optical properties of the suspensions in transmission were measured on a Carey 3E spectrophotometer. The baseline response of pure water has been subtracted from the data shown.

Figure 2. Comparison of the color of isolated gold nanospheres (left) and that of gold-on-polystyrene aggregates (right).

Droplets of the suspensions were allowed to evaporate on a holey carbon grid for examination under transmission electron microscopy (TEM). Three instruments were used in this work, a Phillips CM120 (used at 120kV), a Vacuum Generators VGSTEM HB601 scanning transmission electron microscope (used at 100 kV), and a JEOL 3000 field emission gun (FEG) TEM (used at 300 kV). In the case of the scanning electron microscope (SEM) images, the suspensions were centrifuged and washed twice, before droplets of them were dried out on a carbon stub and examined on a high-resolution LEO SEM using in-lens imaging.

III. Results

A. Transition from single particles through to nanoshell. The broad effects of geometry were tested by generating a random selection of three, ten, thirty five, one hundred, two hundred, three hundred and fifty, and one thousand particle aggregations of monodisperse gold spheres (Figure 3) and then simulating their corresponding optical absorption spectra. The onset of particle-to-particle dipole interactions is shown by the growth of the peak at 750 to 800 nm, Figure 4. This is negligible in the aggregate comprised of gold spheres of diameter, ϕ, of 20 nm when $n=3$, strong when $10<n<200$, and then becomes superseded when $n>200$ by the nano-shell resonance at ~660 nm as the individual particles fuse together into a continuous coating, Figure 4a. The absorption spectrum of the nearly continuous coating obtained for $\phi=20$ nm and $n=1000$ is compared in Figure 4b to the spectrum from a true nanoshell of similar dimensions. However, the absorption peak of the structure made by fusing 1000 spheres of gold is still significantly broader than that of the shell, due to the bumpy morphology of the surface of the latter compared to the smooth exterior of the latter. The situation for $\phi=10$ nm is shown in Figure 4c. Comparison of Figure 4a and Figure 4c shows that the use of the smaller diameter spheres has permitted the development of a stronger absorption in the near infra red.

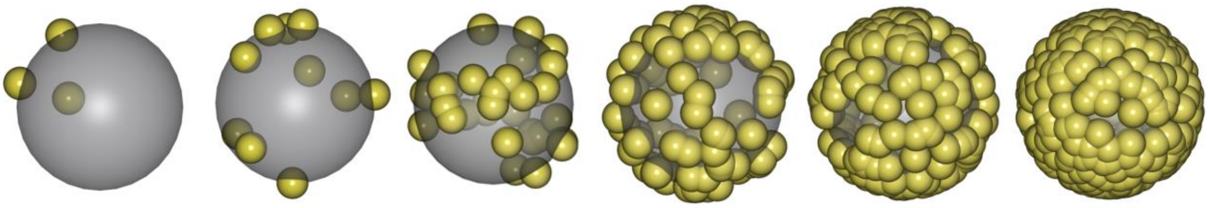
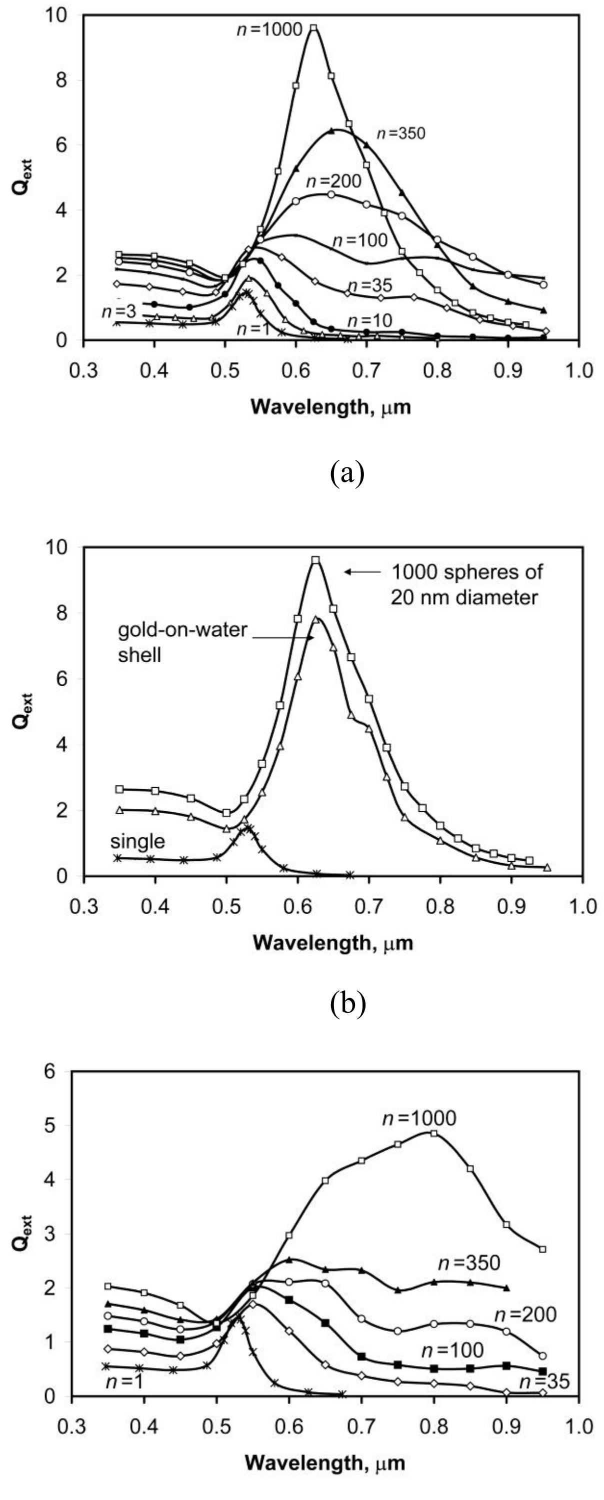


Figure 3. Randomly generated gold-on-polystyrene nanostructures with monodisperse gold particles, showing a range of particle-particle separations and configurations, from left, *n*=3, 10, 35, 100, 200, 350 gold particles of 20 nm diameter.



(a)

(b)

(c)

Figure 4. Calculated extinction coefficients of simulated nanostructures, showing results for selected nanostructures with one, three, ten, thirty five, one hundred, two hundred, and three hundred and fifty gold nanoparticles. Each curve shown is the average of 27 orientations, (a) gold spheres of 20 nm diameter, (b) comparison of case where *n*=1000 and *ϕ*=20 nm to case for true nanoshell of similar dimensions (c) gold spheres of 10 nm diameter. These calculations are performed for gold in water, ignoring the small effect of the polystyrene core.

B. Real particles. The optical extinction spectra of dispersions of gold-on-polystyrene particles are shown in Figure 5. Also shown in Figure 5 is the spectrum expected for discrete gold nanoparticles. It is apparent that the gold-on-latex particles are very different.

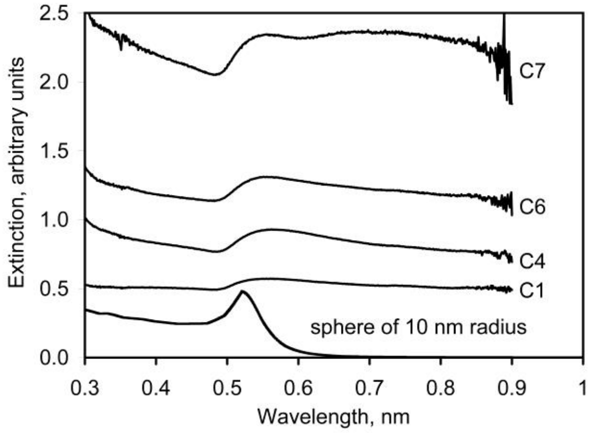


Figure 5. Optical extinction spectra of selected gold-on-latex composites with calculated spectrum of a 10 nm radius gold sphere in water shown for comparison. Note, the spectra C1 to C7 have not been vertically offset, and their vertical position therefore reflects the increase in optical density of the series.

Close examination of the particles using transmission and scanning electron microscopy showed that small nanoparticles of gold, with an average size of 16 nm and a standard deviation (*n*=50) of 9 nm, were attached to the surface of the polystyrene spheres (Figure 6(a) and (b). Furthermore, the coverage of these particles on the polymer was proportional to the quantity of gold used in the reaction, with increased quantities of the gold aggregating in semi-continuous (Figure 6(c) and, in the limit, continuous (Figure 6(d), zones. It can be seen that there is a tendency of the gold particles to stick to one another, and in this respect there is a similarity between the present structures, and those reported by Westcott et al for Au on SiO_2.[9]

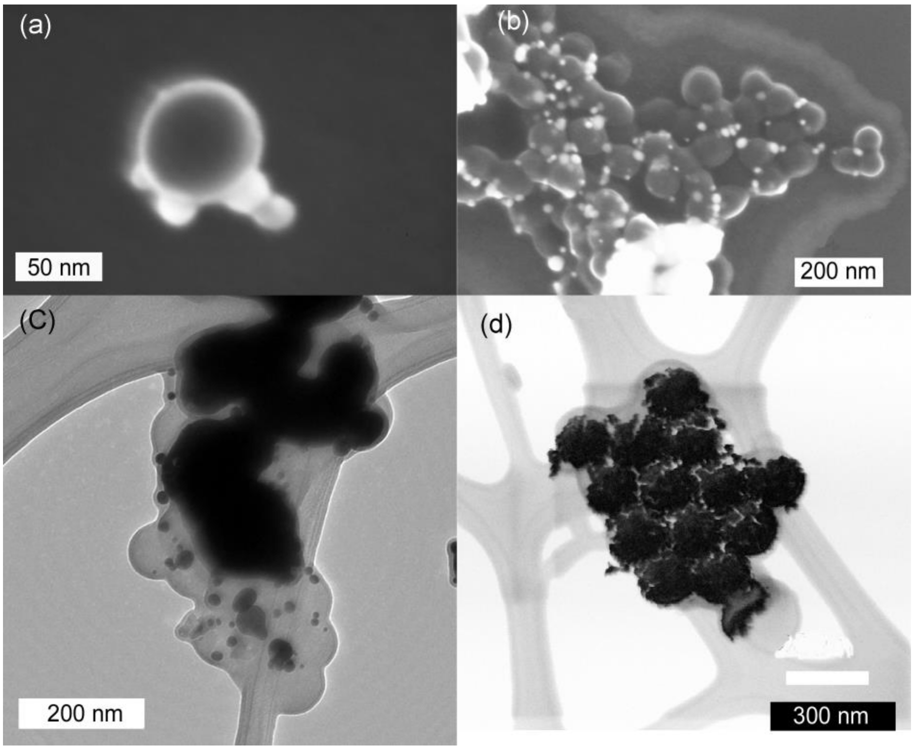


Figure 6. Nucleation of gold nanoparticles on surface of latex particles. (a, b) Particles showing attached single and dimerized gold nanoparticles, (scanning electron microscope), (c) aggregated polystyrene spheres showing semi-continuous coating of gold (transmission electron microscope) (d) spheres of polystyrene coated with continuous shells of gold nanoparticles (transmission electron microscope)

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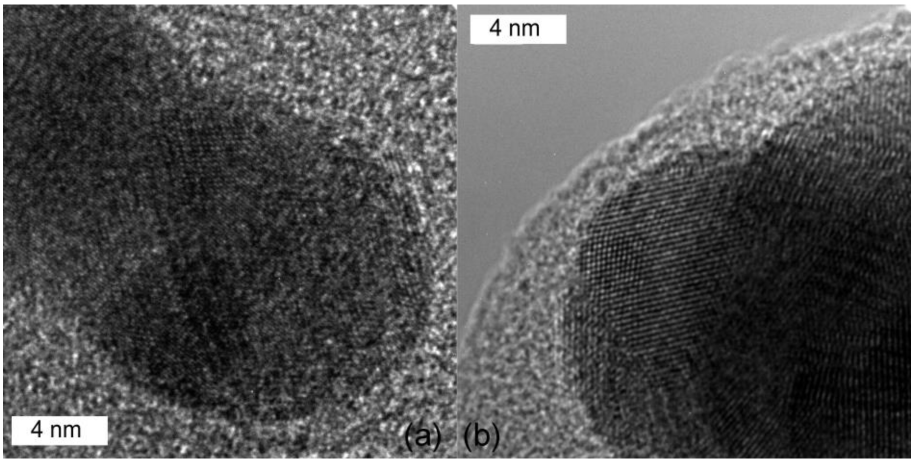


Figure 7. High magnification views of the gold nanoparticles nucleated on latex, showing crystalline nature and presence of twinning-style defects (transmission electron microscope)

A close-up examination of the gold nanoparticles revealed that they contained a high proportion of twinning-type defects, Figure 7, but were otherwise face centered cubic. Since the founding nuclei in this citrate-based system are likely to be icosohedral,[19] twinning in the gold nanoparticles analyzed in the TEM is likely to be the result of recrystallization into the fcc phase.

C. Random aggregates. It is evident from a comparison of Figures 4 and 5 that the measured optical spectra are likely to derive from the aggregated result of diverse individual spectra from nanostructures containing some 100 to 800 gold spheres per polystyrene particle. Furthermore, it was shown in Figures 6 and 7 that the actual diameter, ϕ_{Au}, of the gold spheres varied between 5 and 40 nm, whereas the spectra shown in Figure 4 were calculated for monodisperse gold spheres. We surmised that the very broad absorption spectra of the experimental particles could be simulated by generating random nanostructures with a variable number and size of gold spheres. The results of such simulations are shown in Figure 8 for randomly generated structures with mean ϕ=15 nm and a standard deviation of 10 nm. A medium with the average refractive index of water and polystyrene was used for the calculations of the optical properties of such structures. Examples of calculated and measured spectra are shown in Figure 9. All have been rescaled and offset along the vertical axis for ease of comparison of their shape. It is evident that the shape of the measured spectra in the early stages of the aggregation (Figure 9a) can be explained as being the result of the averaged average of various individual gold-on-polystyrene particles of varying geometry. However, no single Gaussian distribution of particle sizes and numbers could be found to account the spectrum of sample C7, which has peak absorptions at about 550 and 700 nm. The only way found to reproduce that spectrum was to allow for a bimodal distribution of gold spheres-on-latex mixed with a quantity of discrete gold spheres of ~60 nm diameter. This possibility is feasible, since as the concentration of gold relative to latex was increased over samples C1 through to C7, there could be a concentration at which all nucleation sites on the polymer sphere become occupied. Further nucleation of gold would then necessarily have to occur in the bulk solution, leading to the development of a second population of gold spheres.

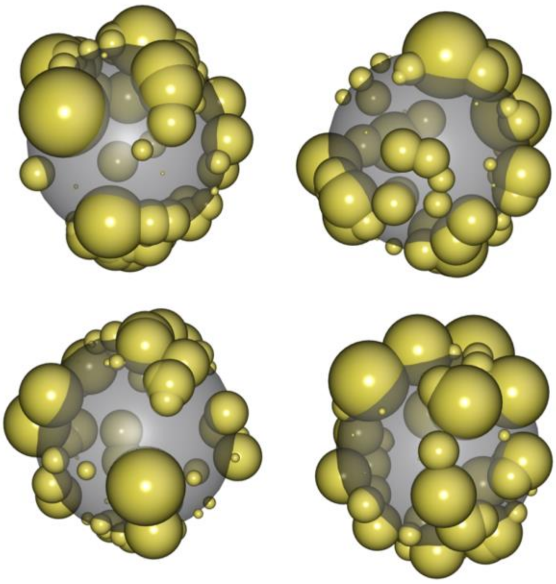
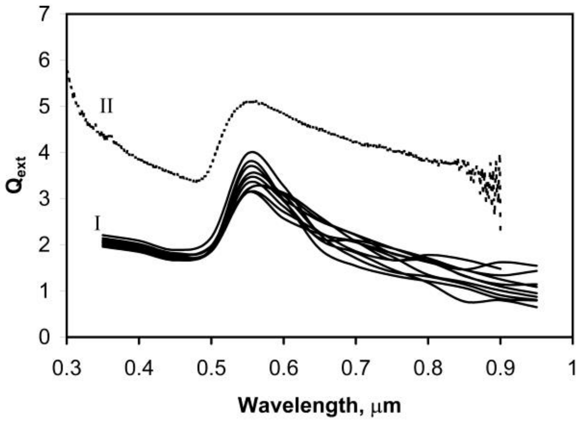
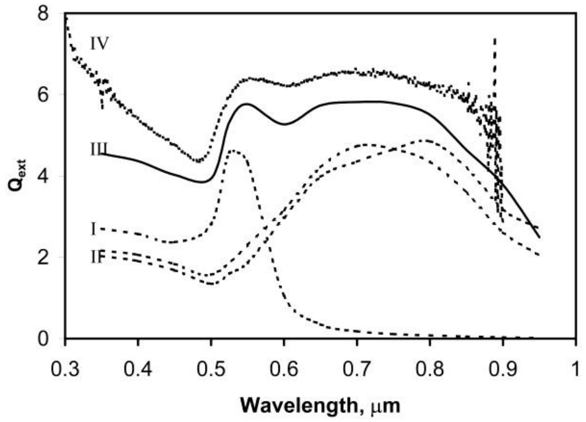


Figure 8. Examples of randomly generated gold-on-polystyrene nanostructures, showing a range of particle-particle separations and configurations. The structures shown were using averages and standard deviations for *n* and ϕ_{Au} of 80 ± 20, and 15 ± 10 nm, respectively,



(a)



(b)

Figure 9. Comparison of the measured spectra, and spectra calculated for random aggregations such as shown in Figure 8. The measured data have been rescaled and offset along vertical axis to facilitate comparison to the calculated curves. Each curve shown is calculated for a single orientation with respect to the light. (a) Spectra (I) of structures randomly generated from a population in which the average and standard deviation of n and ϕ_{Au} are 80 ± 20, and 15 ± 10 nm respectively are compared to a measured early-stage spectrum (II). (b) A composite spectrum (III) produced by summing contributions of isolated nanoparticles (I) and composites of 700 and 1000 particles of 10 ± 5 nm diameter (II), are compared to a late stage measured spectrum (IV).

III. Conclusions

Controlled aggregation of gold nanoparticles on polystyrene templates can be used to produce a system with a plasmon resonance that can be smoothly tuned from that of an isolated spheres, through a region of broad, red-shifted resonance, to end in the limiting case of a nanoshell. The absorption spectrum in the mid-region is particularly controlled by the distribution of interparticle spacings in the nanoparticle ensemble. However, once all nucleation sites on the surface of the polymer sphere have been occupied, it is likely that further precipitation of gold will take place in the bulk solution. This leads to the development of a bimodal distribution of gold spheres, with associated twin absorption maxima. The method of *in situ* nucleation and growth described here appears to offer a convenient new protocol, particularly if applied to a latex suspension of polymer micro-spheres. In this manner a continuous range of composites, with optical properties varying from those of single, isolated gold nanoparticles through to those of core-shell particles, may be obtained.

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Supporting information available: Source and executable of program nSPHERES (Windows platform); sample input files for DDSCAT.

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