

Control of nanoparticle aggregation in aerogel hosts

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Abstract

Plasmonic aerogel containing 50 nm gold nanoparticles is made using a modified 2-step method that maintains control over the gel time while preventing nanoparticle aggregation. Strong narrow surface plasmon resonances verify that the nanoparticles are well dispersed within the silica matrix, and enable applications in sensing, SERS, nonlinear optics or plasmonic gain. Discrepancies between measured and simulated resonance wavelengths are attributed to the breakdown of the effective index approximation, due to the short-scale penetration of the resonance electric field into the host medium.

Highlights

- Formation of silica aerogel begins with the gelation of a sol
- Gold nanoparticles aggregate when added to a normally-prepared sol
- Aggregation is prevented by a new two-step method
- The resulting aerogel has close-to-ideal optical properties

1. Introduction

Gold nanoparticles (GNPs) exhibit several properties not found in the bulk material. A strong localised surface plasmon resonance (LSPR) resonantly scatters and absorbs green light, giving a vibrant red colour to low permittivity hosts such as glass [1, 2]. For example, the measured extinction spectrum of a cuvette filled with aqueous gold colloid (spherical gold particles suspended in water) is shown as curve (a) in figure 1, along with a photograph of the colloid and a transmission electron micrograph (TEM) of the nanoparticles. The extinction spectrum is peaked at 525 nm with a full width at half maximum (FWHM) of ~80 nm. The resonant wavelength varies with the size and shape of the GNPs and the refractive index of the surrounding medium. The diameters of our GNPs were quite uniform and were measured to be 51 ± 3 nm by TEM. The wavelength shift due to refractive index changes is well-defined and allows functionality as a refractive index sensor [3], particularly when non-spherical and core-shell NPs are used [4, 5]. GNPs are also reported to have a large, fast, optical non-linearity [6].

However, for such applications GNPs in water have several problems arising from the use of a liquid host. The GNPs are free to settle and need to be agitated before use. Liquids can evaporate, changing the concentration (and therefore altering the optical properties) if not

drying completely. Water introduces optical absorption at infrared wavelengths, restricting potential devices that exploit the nonlinear properties of GNPs. Finally, it is difficult to change the solvent (and thus the refractive index environment) without flushing the GNPs away or causing them to aggregate, since they are not fixed in place.

These drawbacks can be overcome by dispersing the GNPs in aerogels [7-14]. Silica aerogel, a highly porous form of fused silica glass with low refractive index and high optical transparency, potentially makes an ideal host medium for a volume distribution of GNPs. The silica structure physically traps nanoparticles that are comparable in size to the pores and prevents them being carried away by fluid flow, either during the aerogel fabrication process or afterwards. Such a nanoparticle-doped aerogel has myriad applications in optical sensors [7], catalysis [9], low-temperature glass-formation [10], and non-linear optics [6].

Some previous attempts to dope gels with metal nanoparticles suffered from apparent particle aggregation [9-12], leading to degraded optical properties. To illustrate the consequences of aggregation, curve (b) in Fig. 1 is the extinction spectrum of the colloid of curve (a) after mixing with methanol. The resulting fluid was purple rather than pink, and its spectrum shows a significantly reduced extinction peak and a broad new feature stretching into infrared wavelengths. The corresponding TEM confirms that the spectral changes are correlated with aggregation of the GNPs. Similar changes have been seen before when an alcohol is added to aqueous GNP colloids [15] and mirror those reported in GNP-doped gels [9-12].

Other accounts of GNP-doped aerogels [7,8,13,14] report that the nanoparticles were not aggregated. Nevertheless their spectra showed LSPR resonances that were nothing like as prominent (above the Rayleigh-like scattering spectrum of the host aerogel) as the resonances

seen in aqueous colloids like figure 1(a). It is not clear why but, assuming no aggregation, we speculate that the concentrations of the GNPs were too low for their optical extinction to dominate that of the aerogel host. Other drawbacks include a severe non-uniformity of GNP concentration ([13]; mitigated in [14]), or the need to add the GNPs as the sol is about to gel in order to keep the particle surface exposed for catalytic purposes [7, 8].

Here we report a modification of the fabrication procedure which overcomes these problems and enables the formation of aerogel doped with isolated nanoparticles. This pink GNP-doped aerogel has, for the first time, optical properties that are simple enough (and close enough to the ideal) to match simulations and enable applications based on optical responses. Such a comparison provides information about the environment around the nanoparticles and shows that the aerogel host does not behave optically like a uniform effective medium, with important consequences for the applications.

2. Base method: 1-step aerogel

We made aerogel by forming an alcogel with the desired glass structure but the pores filled with methanol, followed by solvent extraction with supercritical carbon dioxide to prevent collapse of the pores by the action of capillary forces [16]. Here we describe the initial unmodified procedure for making undoped aerogel, and the problems that arise when GNPs are introduced.

2.1. Alcogel formation

The alcogel was formed by the base-catalysed "1-step" hydrolysis of tetramethoxysilane (TMOS, Acros Organics >99%) with methanol as the solvent. This can produce very

transparent aerogel [17] which is crucial for optical applications. The molar ratio of TMOS, methanol (Fisher, 99%), water (Fisher, 99%) and ammonia (2.0M in methanol, Sigma Aldrich) was 1 : 4.6 : 10.3 : 4×10^{-3} . The sol, cast in PMMA cuvettes, became a rigid alcogel after 10 minutes at room temperature and was then placed under pure methanol to prevent evaporative drying at its exposed top surface.

2.2. Aging and silylation

The alcogel was aged for two weeks to allow the gelation reaction to complete without evaporative drying or concentration gradients within the fluid. For the first 5 days the alcogel-containing cuvettes were immersed in a mixture of methanol, water and ammonia roughly equivalent to the pore fluid. They were then transferred into pure methanol for 2 days. We found this softened the cuvettes and so allowed us to easily remove the blocks of alcogel from them. The alcogels were left for a further 3 days in fresh methanol before the internal surface was partially silylated [18] to make the resulting aerogel hydrophobic. Silylation was carried out by immersing the gels in 15 vol-% hexamethyldisilazane (HMDS, Sigma Aldrich 98%) in methanol for 2 days. Excess HMDS and the reaction by-products were then diffusively removed by replacing the solution with pure methanol for 2 days. In each of the above steps, the volume of the aging solution was 10× that of the alcogel.

2.3. Supercritical drying

The methanol in the alcogel blocks was diffusively exchanged with supercritical CO₂ at 100 bar and 40 °C by immersion in an autoclave for 4 hours, before depressurising to 1 bar over 2.5 hours. The solvent exchange time was long enough for crack-free transparent aerogel to be successfully formed, although the process was not optimised and we believe the exchange time could be shortened.

The resulting $1 \times 1 \times 2.5 \text{ cm}^3$ blocks of aerogel typically shrunk by $< 2\%$ linearly compared to the alcogel, and were hydrophobic enough for drops of water to be supported on the surface without causing damage. To protect the aerogels (both internally and externally) they were carefully put back into fresh PMMA cuvettes with a small amount of silica-indicator desiccant gel and sealed with Parafilm.

2.4. Doping with GNPs

To make doped aerogel, we substituted the pure water used to make the alcogel for an aqueous colloid of 50 nm diameter GNPs (British Biocell International). The initially-pink sol invariably turned a uniform purple colour quite quickly and remained a similar colour after gellation, indicating that the GNPs had aggregated. Indeed, TEMs of the aerogel show GNPs in clusters of 2-3 and rarely singly. Even by significantly decreasing the reaction time in the hope of trapping the particles in the gel before they could aggregate, it was not possible to prevent aggregation and produce a pink alcogel. After supercritical drying, the nanoparticles remained aggregated and the resulting aerogel was a grey-purple colour. There did not appear to be any additional aggregation or removal of particles during aging, silylation or supercritical drying.

2.5. Optical extinction measurements

We measured the spectral transmission of the 1 cm thick aerogel samples using an incandescent lamp, monochromator (Bentham TMc300F) and large-area photodetector. The aerogels were inserted between the output slit of the monochromator and the photodetector, and the photodetector signal was recorded over a range of wavelengths. The monochromator was calibrated against a fibre-optic spectrum analyser (Yokogawa AQ6370) which is itself

internally calibrated with an acetylene gas cell, and the (systematic) wavelength setting error was found to be 0.2 nm at 1000 nm. The 3 dB bandwidth of the monochromator output was 2 nm at visible wavelengths.

The normalised optical extinction (in decibels) was calculated via

$$\text{extinction (dB)} = -10 \log_{10} \left(\frac{P_s}{P_0} \right) \quad (1)$$

where P_s and P_0 are the photodetector signals when the sample is present and absent respectively. (Few previous reports quantify optical extinction measurements in this way, with absolute units - or even just a zero - on the vertical axes of optical spectra, which we think would have helped in their interpretation.)

Extinction spectra of typical undoped and doped aerogels are shown in figure 2, (1) and (2). The undoped aerogel shows Rayleigh-like scattering with extinction proportional to λ^{-4} . The doped aerogel has additional extinction at all wavelengths, with a broad peak around 800 nm and only a remnant of the single-particle LSPR peak at ~520 nm. As shown in figure 1 and inferred from previous reports [10, 12, 15], the long wavelength feature is characteristic of GNP aggregation.

3. Modified method: 2-step aerogel

A modification of the base procedure allowed the formation of alcogels (and hence aerogels) doped with well-dispersed gold nanoparticles, by limiting the opportunities for the particles to aggregate.

3.1. Alcogel formation

The modified method is similar (though not identical) to previous 2-step procedures where TMOS initially reacts with a substoichiometric amount of water to form a partially hydrolysed sol [8,19]. The two key principles of our method are simple: the mixing time between methanol and gold colloid should be reduced, since methanol induces aggregation (figure 1); and the gel should be partially formed before the colloid is added, to restrict the mobility of the GNPs.

In the first step, a sol was formed by mixing TMOS, pure water, methanol and ammonia catalyst in the molar ratio 1 : 1.8 : 1.03 : 1.5×10^{-3} . In the second step, the remaining methanol and water containing GNPs were added after 15 minutes so that the final molar ratio was the same as in the base 1-step process. Varying the amount of ammonia in the second step allowed control of the gel time up to 35 minutes. Once the alcogel had formed the GNPs were completely trapped in the glass matrix, preventing aggregation at later stages. The method then proceeds as for the base method, with aging, silylation and supercritical drying to form doped aerogels. These subsequent steps do not appear to affect the state of the GNPs in the gel.

A photograph and spectrum of the pink aerogel made using the modified method are shown in figure 2, labelled as (3). The long wavelength peak has disappeared and the LRSP peak is restored, leaving a spectrum that clearly looks like that of the original aqueous colloid (figure 1a) superimposed on the Rayleigh-like response of undoped aerogel. The peak is distinct, being over twice as high as the Rayleigh background. Also shown are TEM images of crushed fragments of doped aerogel made by the base and modified methods, with a single isolated GNP in view in the latter case. Although GNPs were hard to find using TEM, given

their low concentration and 3-dimensional distribution in the aerogel, the respective images are entirely typical.

3.2. Characterisation

The first-step time (the interval allowed to elapse before starting the second step) controlled the subsequent aggregation of the GNPs during the second step. Figure 3a shows the effect of the first-step time on the spectrum of the resulting alcogel, keeping the second-step time fixed at 7 minutes. The long wavelength peak that indicates aggregation disappeared for first-step times of 15 to 20 minutes, resulting in pink gels with a narrow LSPR peak. Enough time should be allowed to pass for the gel network to partially form, as expected. However the final gel lost transparency and became milky-looking for first-step times exceeding 25 minutes, though the pink colour was still visible. Excessive first-step times therefore cause a general degradation of the aerogel's optical properties rather than GNP aggregation.

The second-step time (when gelation was observed after starting the second step) was controlled by varying the ammonia concentration in the final sol. For a fixed first-step time of 15 minutes the second-step time had almost no effect on the optical properties of the gel, figure 3b. Thus our method retains the gellation times before and after GNP introduction as valuable degrees of freedom for optimising the properties of aerogels.

The measured BET surface area [20] of 2-step aerogels was $1000 \pm 20 \text{ m}^2/\text{g}$, compared with $700 \pm 10 \text{ m}^2/\text{g}$ for the corresponding 1-step aerogels. BJH pore-size analysis [20] suggests that this difference is due to a large mesoporous regime in the 2-step aerogel. The 2-step aerogel also had slightly more optical extinction at 800 nm, $0.14 \pm 0.04 \text{ dB}$ compared with $0.09 \pm 0.04 \text{ dB}$. This is consistent with a larger number of bigger pores, which causes stronger light

scattering. For visible light both aerogels exhibit the $\propto \lambda^{-4}$ response characteristic of Rayleigh-like scattering.

Using different mixtures of water and gold colloid in the second step allows control of the GNP concentration. Figure 4 shows spectra for doped alcogels and aerogels, with the magnitude of peak extinction shown in the inset. The spectra of the corresponding undoped materials have been subtracted to isolate the effect of the GNPs. The height of the LSPR peak is proportional to the particle concentration in both, as expected.

3.3. Effect of host medium

For a given particle concentration, the height and wavelength of the LSPR peak are different in the aerogel compared to the alcogel (and indeed the original colloid). The peak wavelength was 535 nm in the colloid suspension, 540 nm in the alcogel and 520 nm in the aerogel. This is a consequence of the different refractive indices around the particles [1, 2].

We used the finite element method (FEM) to numerically simulate the optical extinction properties of an isolated gold sphere with a diameter of 51 nm in external media of uniform refractive index n [21]. It was possible to choose external indices so that the calculated extinction spectra matched the measurements for GNP-doped alcogel and aerogel (see figure 4 in [21]), confirming that the doped gels behaved optically as if the GNPs were not aggregated. There were however large discrepancies between the index values required to achieve the match and the expected effective indices of the gels. For example, the simulated index ($n=1.20$) needed to match the response of the aerogel is far from the measured index ($n=1.05$) of our aerogel. As discussed in more detail in [21], these discrepancies arise from the nm-scale localisation of the LSPR's electric field distribution, which does not sample a

macroscopic average of the host gel. Effective index approximations should therefore only be used with great care when modelling LSPRs of nanoparticles in inhomogeneous materials. However, encapsulation of the GNPs by thin silica layers was found not to greatly reduce its electromagnetic sensitivity to its environment.

4. Discussion and Conclusion

We have developed a method for making nanoparticle-doped silica aerogel. Using this method, based on a simple modification of a well-known procedure, we were able to ensure that the nanoparticles were well-dispersed and not aggregated. This gives the aerogel the strong colour and narrow extinction spectrum associated with the localised surface plasmon resonance of isolated gold nanoparticles. Such plasmonic aerogels are natural candidates for exploring active plasmonic systems, as they offer access to well-separated single Au nanoparticles in an air-like matrix. Indeed, co-doping with emissive species (for example quantum dots, ions and dye molecules) would allow studies of plasmonic gain and new laser media. Due to the reported high nonlinearity of Au nanoparticles, plasmonic aerogels might also find applications for enhancing intrinsic nonlinearities of co-doped species. Lastly, the prospect of infiltrating holey fibre systems, as recently demonstrated for undoped aerogels [22], should lead to a new class of plasmonic integrated sensing devices.

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References

1. S.A. Maier, *Plasmonics: Fundamentals and Applications*, Springer, New York, 2007.
2. V. Giannini, A. I. Fernandez-Dominguez, S. C. Heck, S. A. Maier, *Chem. Rev.* 111 (2011) 3888-3912
3. S.K. Eah, H.M. Jaeger, N.F. Scherer, G.P. Wiederrecht, X.M. Lin, *Appl. Phys. Lett.* 86, 3 (2005) 031902
4. F. Tam, C. Moran, N. Halas, *J. Phys. Chem. B* 108 (2004) 17290-17294
5. C.L. Nehl, H. Liao, J.H. Hafner, *Nano Lett.* 6, 4 (2006) 683-688
6. R.F. Souza, M.A.R.C. Alencar, E.C. da Silva, M.R. Meneghetti, J.M. Hickmann, *Appl. Phys. Lett.* 92, 20 (2008) 201902
7. M.L. Anderson, C.A. Morris, R.M. Stroud, C.I. Merzbacher, D.R. Rolison, *Langmuir* 15, 3 (1999) 674-681
8. D.D. Smith, L. Sibille, E. Ignont, R.J. Cronise, D.A. Noever, *J. Porous Mat.* 7, 4 (2000) 499-508
9. T. Yazawa, K. Kadono, H. Tanaka, T. Sakaguchi, S. Tsubota, K. Kuraoka, M. Miya, D.X. Wang, *J. Non-Cryst. Solids* 170, 1 (1994) 105-108
10. D.D. Smith, L. Sibille, R.J. Cronise, D.A. Noever, *J. Non-Cryst. Solids* 225, 1-3 (1998) 330-334
11. D.D. Smith, L.A. Snow, L. Sibille, E. Ignont, *J. Non-Cryst. Solids* 285, 1-3 (2001) 256-263
12. C.A. Morris, M.L. Anderson, R.M. Stroud, C.I. Merzbacher, D.R. Rolison, *Science* 284, 5414 (1999) 622-624

13. Y. Tai, M. Watanabe, K. Kaneko, S. Tanemura, T. Miki, J. Murakami, K. Tajiri, *Adv. Mater.* 13, 21 (2001) 1611-1614
14. Y. Tai, M. Watanabe, J. Murakami, K. Tajiri, *J. Mater. Sci.* 42, 4 (2007) 1285-1292
15. J. Liao, Y. Zhang, W. Yu, L. Xu, C. Ge, J. Liu, N. Gu, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 223 (2003) 177-183
16. M.J. van Bommel, A.B. de Haan, *J. Mater. Sci.* 29, 4 (1994) 943-948
17. G.M. Pajonk, *J. Non-Cryst. Solids* 225, 1 (1998) 307-314
18. H. Yokogawa, M. Yokoyama, *J. Non-Cryst. Solids* 186 (1995) 23-29
19. T.M. Tillotson, L.W. Hrubesh, *J. Non-Cryst. Solids* 145, 1-3 (1992) 44-50
20. G. Reichenauer, G.W. Scherer, *J. Non-Cryst. Solids* 285, 1-3 (2001) 167-174
21. M.D.W. Grogan, S.C. Heck, K.M. Hood, S.A. Maier, T.A. Birks, *Opt. Lett.* 36, 3 (2011) 358-360.
22. M.D.W. Grogan, S.G. Leon-Saval, R. England, T.A. Birks, *Opt. Express* 18, 21 (2010) 22497-22502.

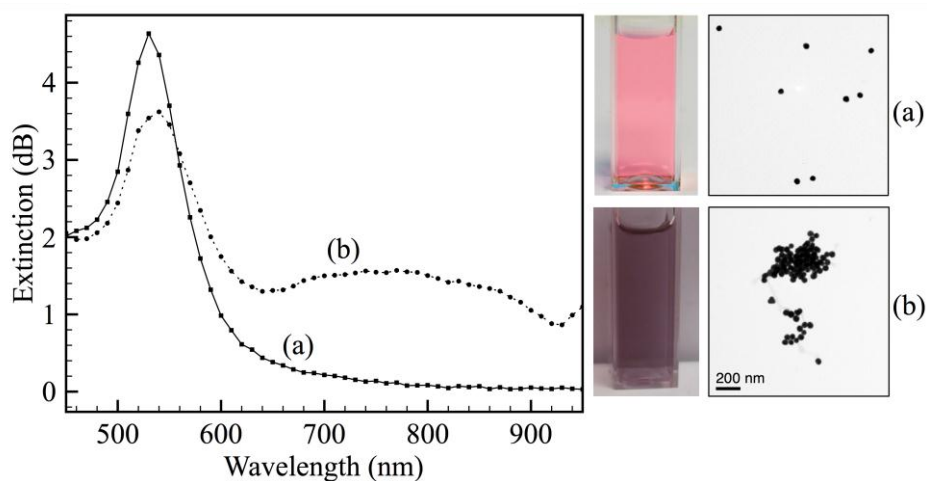


Figure 1: Measured extinction spectra, photographs and TEM images of an aqueous colloid of gold nanoparticles before (a) and after (b) mixing with methanol. The spectra are relative to the measured transmission of pure water through the same 1 cm path.

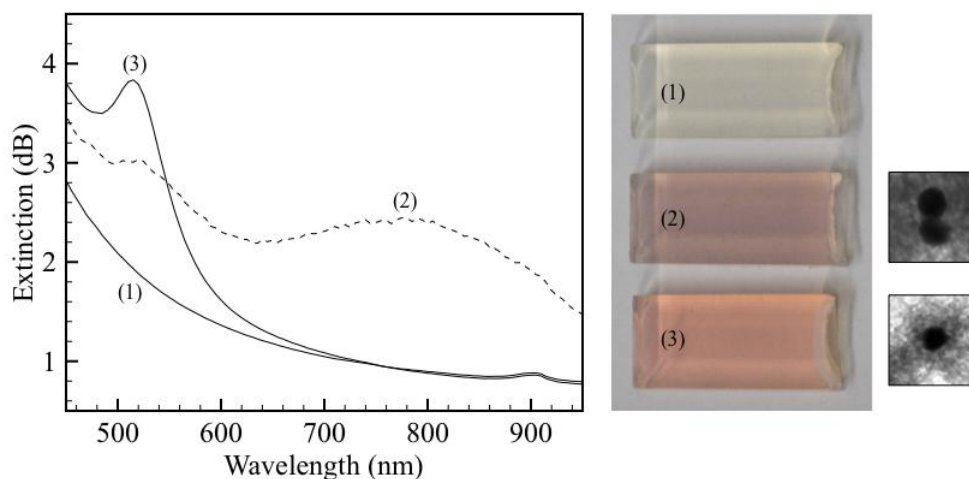


Figure 2: (left) Measured extinction spectra, (middle) photographs and (right) typical TEM images of 50 nm diameter GNPs in (1) undoped aerogel, (2) doped aerogel using the base 1-step procedure where GNPs have aggregated, and (3) doped aerogel made using the modified 2-step procedure so the GNPs remain dispersed in the matrix. (2) and (3) can be compared with (b) and (a) respectively in figure 1. The spectra are relative to the measured transmission of free space through the same 1 cm path.

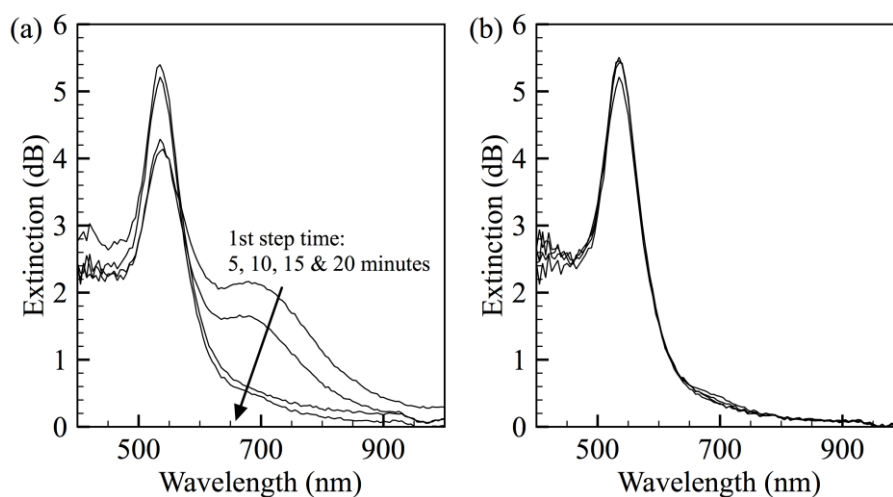


Figure 3: Measured extinction spectra of 2-step GNP-doped alcogels while (a) varying first-step time for a fixed second-step time of 7 minutes, and (b) and varying second-step time (from 5 to 35 minutes) for a fixed first-step time of 15 minutes. The spectra are relative to the measured transmission of an undoped alcogel through the same 1 cm path.

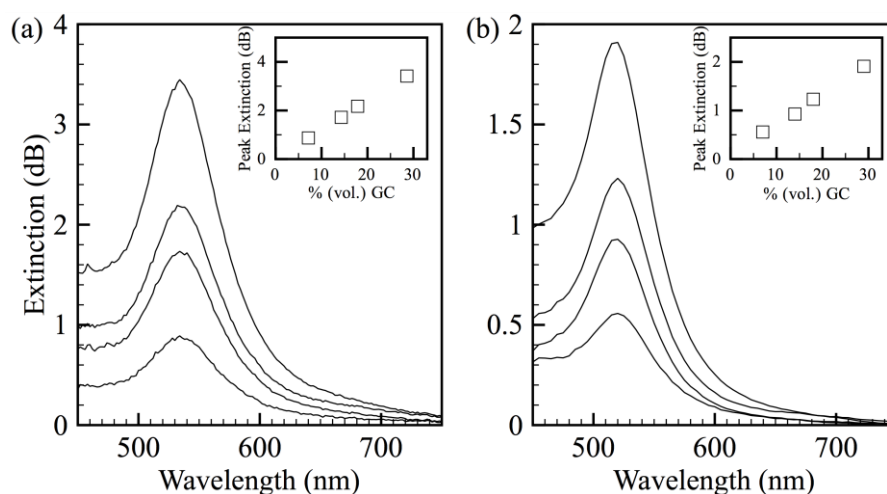


Figure 4: Measured extinction spectra for different concentrations of GNPs in (a) alcogel and (b) aerogel, higher peaks corresponding to greater concentrations. The wavelength shift of the peak between (a) and (b) is due to the difference in refractive index. The peak extinction due to the LSPR as a function of colloid concentration is inset in each graph. The spectra are relative to the measured transmission of undoped alcogel and aerogel (respectively) through the same 1 cm path.