



Modeling of the processing dynamics of aerogel/gold nanoparticle composites



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HIGHLIGHTS

- Colloidal gold nanoparticles encapsulated in silica aerogels were investigated.
- Gelling resulted in changes in the optical spectra.
- A modified Maxwell Garnett theory was used to model spectral changes.
- Acceptable agreement between theory and experiment was achieved.

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ABSTRACT

Colloidal gold nanoparticles were encapsulated in silica aerogels, and the dynamics of the gelling process in different solvents was investigated using visible spectroscopy. Modified Maxwell Garnett (MG) theory was used to model the behavior of aggregating gold nanoparticles in the silica network; our modifications incorporate additional filling factors with weighting components into the traditional MG equations to better fit experimental data. The introduction of 1-octanethiol protected Au nanoparticles to the aerogel matrix resulted in decreased aggregation of the particles and an unexpected blue shift in the surface plasmon resonance spectrum after solvent exchange from acetone to cyclohexane, with the plasmon peak moving from 558 nm to 529 nm. Such a shift did not occur in the non-thiol protected aerogel/nanoparticle composites. Our modeling indicates that modified MG theory is an effective means of tracking the physical/structural changes taking place during the solvent processing of porous silica gel/Au nanoparticle composites.

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1. Introduction

Aerogels have become highly useful materials due to their high optical transparency and porosity. These solid architectures are composed of a silica network that is up to 95% porous with large inner pores formed by sol–gel processing [1–3]. Aerogels can be used as chemical and physical sensors and for various other optical applications [4]. An interesting optical phenomenon results from embedding nanoparticles within the aerogel's porous solid network due to the preservation of the nanoparticles' intense surface plasmon resonance absorption [5]. This phenomenon could serve as an excellent basis for any number of different optical sensing devices.

Nanoparticles tend to aggregate towards the bulk metal which is thermodynamically favored unless they are encapsulated in a solid matrix (such as an aerogel network) or stabilized by molecules attached to their surface (such as a thiol) which prevent particles from coming into close proximity with each other [5]. Metallic nanoparticles display interesting optical and electronic properties that differ from those of the bulk metal and individual atoms [6]. Extensive studies have shown that nanoparticle size, inter-particle distance, and even particle shape affects such properties, and so understanding their influence on the expected experimental outcome becomes paramount with regard to formulating a practical sensor [7–10].

In a system incorporating isolated gold nanoparticles, Mie theory predicts and describes the metal's absorption spectrum by using the dielectric constant of the bulk metal [11]. This theory is essentially a solution to Maxwell's equations within the context of a truncated series where only the dipole oscillation is maintained, and was first reported for spherical nanoparticles by Mie in 1908

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[11]. For nanoparticles that are significantly smaller than the wavelength of light, the approximation is valid, and the extinction cross-section (directly related to the absorbance spectrum) can be calculated accurately. For gold, the theory begins to break down as nanoparticle sizes increase above 20 nm, as the plasmon resonance causing the absorbance can no longer be described within this dipole approximation [5,8,12]. Often, when gold nanoparticles are introduced to a host material (in our case, an aerogel matrix) [13], aggregation occurs, effectively increasing particle size. This results in a plasmon resonance red shift and band broadening, and Mie theory becomes an inadequate tool with respect to predicting spectra [5,8,12].

Aerogels infused with gold nanoparticle aggregates can be described with Maxwell Garnett (MG) theory which was developed by J. C. Maxwell Garnett in 1904 [14,15]. MG theory calculates an effective dielectric by combining properties of the particles and their surrounding media, and this is treated as the overall dielectric causing the extinction spectra of said particles. This theory, again, is a simplification and not a full solution to Maxwell's equations. However, it becomes attractive as a theoretical tool as it provides spectroscopic information over a wider range of particle sizes relative to Mie theory while avoiding the complexity involved in finding the explicit solutions to Maxwell's equations required by theories such as the discrete dipole approximation (DDA) or finite-difference time domain (FDTD) methods [8,12,16,17].

Experimentally, it is difficult to avoid gold nanoparticle aggregation during the gelling process of aerogels due to the rearrangement of the aerogel architecture as cross-linking occurs. Assuming that all particle sizes and separation distances are infinitely smaller than the wavelength of incident light, the effective medium predicted by MG theory stems from an assumed homogeneous composite of surrounding media and nanoparticle [5,8]. The Maxwell Garnett equation [8,14] describes this effective dielectric, ϵ_{eff} as

$$\epsilon_{\text{eff}} = \epsilon_m \frac{1 + 2fA}{1 - fA} \quad (1)$$

with

$$A = \frac{1}{\epsilon_m} \frac{\epsilon(\omega) - \epsilon_m}{\epsilon(\omega) + 2\epsilon_m} \quad (2)$$

where ϵ_m is the dielectric of the surrounding media, f is the filling factor/volume fraction of aggregated gold nanoparticles in the surrounding sample (directly relating to aggregate size), and $\epsilon(\omega)$ is the dielectric of the bulk metal for incident frequency ω . The effective dielectric of the system is then treated as any other complex dielectric function, and an absorption coefficient can be calculated with the formula

$$\alpha(\omega) = \frac{\text{Im}[\epsilon_{\text{eff}}]}{n} \frac{\omega}{c} \quad (3)$$

where n is the refractive index and c is the speed of light [18]. For a system with a single population of particles where one f describes the space occupied by each aggregate, the theory works well. For the processing of gold nanoparticles embedded in aerogels, however, it becomes evident that multiple populations of aggregates (and thus multiple f values) may exist in the complex silica framework, which needs to be addressed for proper application of this theory [19].

This manuscript reports on our efforts in not only the production of such aerogel/gold nanoparticle composites, but also on the use of MG theory as a tool allowing for a qualitative understanding

of processes occurring on the nano/micro level during the aging and curing of such systems. A modified MG theory is proposed, and experimental spectra are compared to predicted theoretical spectra, thus allowing for a discussion of the processing dynamics relating to the composite formation.

2. Experimental

2.1. Materials

Tetramethoxysilane (TMOS; 98% purity) and gold nanoparticles (10 nm diameter; suspended in citrate buffer) were obtained from Sigma–Aldrich. Methanol (99.9% purity) and ammonium hydroxide was purchased from Fisher. Ethanol (95.01% purity; 190 proof) and acetone (99.9% purity) were purchased from Pharmco-Aaper. Cyclohexane (100.0% purity) was obtained from J.T. Baker. 1-Octanethiol (97% purity) was obtained from Acros Organics. All purchased chemicals were used in these experiments without further purification.

Water was purified on-site with a Barnstead Nanopure Diamond water purification system to 18.2 M Ω -cm.

2.2. Methods

2.2.1. Basic (standard) aerogel preparation

Basic (standard) aerogels were prepared using the procedure of Anderson et al. [13] with a base catalyzed reaction. More specifically, exactly 3.940 mL of tetramethoxysilane and 4.520 mL of methanol were combined in a plastic beaker (1) with a magnetic stir bar. In a glass beaker (2), 4.515 mL of methanol and 1.525 mL of water were mixed. To yield a base catalyzed reaction, 5.5 μ L of ammonia was added to 2. 2 was poured into 1, and the mixture was stirred for three minutes on a medium setting. Then, exactly 1.000 mL of the stirred mixture was pipetted into a 3 mL glass cuvette and sealed with Parafilm.

2.2.2. Colloidal gold aerogel preparation

Aerogels with encapsulated colloidal gold were prepared the same way as basic aerogels, except after stirring the mixture for three minutes, the mixture was left to sit for one hour. Then 1.000 mL of stock colloidal gold sol was added with minimal additional stirring to prevent aggregation. A separate 3 mL cuvette was used as a mold for 1.000 mL of the colloidal gold/aerogel mixture, which was added before sealing with Parafilm.

2.2.3. Thiol-protected colloidal gold aerogel preparation

Aerogel composites comprised of thiolated colloidal Au were prepared identically to the basic aerogel preparation above except for the following changes. To surround the gold particles in a more nonpolar environment, 1.000 mL of ethanol was added to 1.000 mL of colloidal gold sol. Then 6.5 μ L of 1-octanethiol were added to the gold/ethanol mixture, which was then left to sit for 45 min prior to adding the entire gold sol, ethanol, and thiol mixture to the basic aerogel prep. Exactly 1.000 mL of this mixture was added to a 3 mL cuvette as before.

2.2.4. Solvent exchanges

The aerogels mixtures were left to sit for one day to polymerize after preparation while covered with Parafilm. The resulting gels (in their cuvettes) were submerged in an acetone bath to allow for solvent exchange. The acetone was replaced two to three times per day for three days total. Subsequent solvent exchanges were made with cyclohexane which was replaced two to three times a day for thirteen days total.

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