Self-Assembly of TOPO-Derivatized Silver Nanoparticles into Multilayered Film

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A novel method for transferring silver nanoparticles from aqueous solution into organic solvents such as toluene or hexane was developed. Phase-transfer reagent, tri-*n*-octylphosphine oxide, TOPO, provides a capping shell around Ag particles that enables concentrating nanoparticle dispersion in toluene, which is a prerequisite for successful 3D self-assembly. The dispersed particles are stable for a long period of time (at least six months). Self-assembly of high concentrations of TOPO-capped Ag particles results in a multilayered mirrorlike film formed onto glass substrates. SEM images reveal a fine-grained film consisting of 10-nm close-packed particles. The surface plasmon absorption of the 3D structure is 100 nm red-shifted compared to that of isolated particles in toluene solution, and is a result of interparticle coupling of dielectric functions of particles in near proximity. Redispersing of particles from the 3D film into toluene solution revealed a spectrum of silver particles virtually identical to that of the original solution used for the formation of the multilayered film. This confirms that the shift of surface plasmon absorption of 3D film is a result of interparticle communication/coupling.

Introduction

The self-assembly of metallic nanoparticles into macroscopic structures offers a pathway for the creation of macrocrystallites with tunable, designer-specified optical, electronic, and catalytic properties.[1,2] Small metal particles and their ensembles exhibit unusual optical and electronic properties that are between those of bulk and molecules, such as charging steps due to Coulomb blockade,[3,4] thermally activated conductivity by electron hopping,[5−7] and nonlinear optical effects observed in the generation of second-order harmonics.[8] In past years, there has been a great interest in developing two- (2D) and three-dimensional (3D) metallic macroscopic structures, such that the particles are closely packed, and at the same time not allowing the onset of uncontrolled aggregation. The key issue in the creation of ordered close-packed structures is the ability to preserve isolated particles as the volume fraction of particles increases, and as the particles begin to interact with each other. The prerequisite for a self-assembly route in macrostructure preparation is (i) availability of stable building blocks of metallic nanoparticles with well-characterized uniform particle sizes and shapes, and (ii) the presence of suitable capping material (ligand or linker), that at the same time allows interparticle assembly, and preserves domination of repulsive forces between building-block nanoparticles over interparticle irreversible aggregation. The capping material should provide uniform protection of the surface without modification of essential structural and electronic properties of the particle. The uniformity of sizes is necessary in obtaining ordered assemblies. If unprotected colloidal particles are used, the resulting aggregate exhibits properties of bulk metal. To date, there have been two approaches in capping and successful assembling of mainly gold, and to a lesser extent silver, nanoparticles. It has been shown that the use of organic alkanethiol-funcionalized ligands[7−11] or quaternary amines[12] as surface capping materials results in self-assembly of metallic particles analogous to “soft sphere” crystallites. The dithiol or amino groups act as linker molecules on the surface of

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colloidal metallic particles, while interaction among the long ordered alkane chains favors spontaneous assembly, and controls interparticle spacing.[7,9] Another approach is to use metal core–optically transparent inorganic shell particles, such as Au@SiO_2,[13,14] as building-blocks for ordered "hard sphere" tin films. The shell material acts as a physical barrier preventing aggregation of metallic nanoparticles.

Alkanethiols are widely used to stabilize gold and silver particles, to chemically deposit them on various substrates, and in the process of their self-assembly. The high stability of thiol-capped gold particles is a result of the formation of covalent metal–sulfur bonds,[15,16] that give surface-derivatized metallic particles. However, the presence of a semiconducting (AuS_2 or AgS_2) layer on a surface of particles influences electronic properties of metallic nanoparticles. To study electronic properties of an ensemble of metal particles, such as conductivity, it is desirable to avoid formation of chemically bound sulfur. This has prompted interest in using different capping agents for stabilization, and as linkers in the self-assembly of silver particles.[12–14] In this paper we report the use of tri-*n*-octylphosphine oxide (TOPO) as a capping agent in the formation of stable colloidal silver particles in toluene. TOPO as a stabilizer was previously used in the preparation of quantum dots (InP, CdSe, and ZnO) in organic solvents.[17–20] In our approach, we synthesized colloidal Ag particles in aqueous solution, and used TOPO for their transfer and simultaneous concentration in organics, prior to self-assembly. The 3D structure consists of 10-nm silver particles with TOPO linkers between particles.

Experimental Section

Chemicals. Silver nitrate was obtained from B&A. Sodium borohydride, tri-*n*-octylphosphine oxide, TOPO, magnesium sulfate heptahydrate, and toluene were purchased from Aldrich. All the reagents were analytical grade and used as received, without further purification. Milli-Q deionized water (resistivity 18.2 MΩ cm^{-1}) was used for synthesis.

Nanocrystal Synthesis. Preparation of silver hydrosols, using $NaBH_4$ as a reducing agent, is described in the literature.[21] In 100 mL of Ar-saturated aqueous solution of 2×10^{-4} M $AgNO_3$, 10 mg of $NaBH_4$ was added under vigorous stirring, resulting in formation of a transparent yellow colloidal silver solution. Dispersed silver nanoparticles were transferred into organic solvents with low dielectric constants such as toluene and *n*-hexane using TOPO and magnesium salt. Typically, 100 mL of aqueous colloidal solution of silver nanoparticles (2×10^{-4} M), was mixed with 15 mL of 5.1×10^{-3} M TOPO in toluene. The TOPO stabilizer therefore served two functions: it brought the silver sol into contact with the immiscible solvent phase by emulsification and also engulfed the particles, allowing them to transfer. The mixture was emulsified by strong mixing in a funnel for 30 min. During that period silver nanoparticles inside the water droplets started to transfer spontaneously to the organic phase. After 30 min of mixing, 22 mg of magnesium sulfate heptahydrate was added to obtain a quantitative transfer of silver particles into the organic phase.[22] The emulsion was mixed for an additional 20 min to achieve complete dilution of magnesium salt and transformation of the emulsion into two liquid phases. This fast transformation of emulsion into two liquid phases is a necessary condition for silver particles' film preparation on glass. At the end of this process, the organic phase exhibits a dark yellow color and contains silver nanoparticles, whereas the residual aqueous phase is clear and colorless.

Multilayered Film Synthesis. The self-assembly of silver particles into a multilayer film starts during the process of phase separation. Particularly, after 20 min of mixing, the emulsion was quickly transferred from a funnel into a vial in which a microscopy glass slide was immersed at a top position. The self-assembly onto glass slides, as well as onto the vial's glass walls, started immediately. About 30 s is usually enough for a typical multilayered Ag film to be deposited. The obtained mirrorlike film appears purple when viewed through a glass. For efficient binding of derivatized silver nanoparticles on the glass slides, their surfaces were cleaned by dipping the slides in different solutions. First, slides were dipped in an acetone–ethanol mixture (50:50 %) in an ultrasound bath for 30 min. After the slides were dipped in detergent for the next 30 min and then rinsed with water, they were dipped in a 25% solution of sulfuric acid for 30 min, and then thoroughly washed with water. Finally, the slides were dipped in an ethanol solution of 20% NaOH for 30 min, washed with water, and dried with N_2.

Techniques. UV–visible absorption spectra of silver nanoparticles in water and toluene, and silver particle films were measured with a Beckman DU 640 spectrophotometer. A field emission scanning electron microscope (Hitachi S-4700-II) was used for imaging silver thin films on the glass substrate. The size and distribution of sizes for silver nanoparticles in solution were determined using a JEOL 100CX transmission electron microscope (TEM). Transmission electron micrographs were obtained at room temperature, operating at 100 kV. Samples for TEM measurements were prepared by placing a drop of silver nanoparticle dispersion onto a holey carbon-coated standard copper grid (400 mesh) and evaporating the solvent.

Results and Disccussion

Optical Properties of TOPO-Coated Silver Particles in Solution. The absorption spectrum of TOPO-coated silver particles in toluene, obtained by transferring silver hydrosols into organic solvent, shows a strong surface plasmon resonance band with maximum at 410 nm (see Figure 1). The absorption maximum is 20 nm red-shifted compared to the plasmon band of the initial silver particles in aqueous solution synthesized by the reduction of silver ions with borohydride. The concentration of particles transferred into toluene is 10 times higher than that in the "starting" aqueous solution. The red shift of the maximum absorption wavelength to lower energies is a consequence of the increased refractive index of the surrounding medium,[23] in the first approximation from water ($n^{20}_{\text{water}} = 1.33$) to toluene ($n^{20}_{\text{toluene}} = 1.49$). As can be seen from Figure 1, the intensity of plasmon absorption decreases, while slight broadening of the plasmon band occurs. The full width at half-maximum (fwhm) value of a symmetric plasmon

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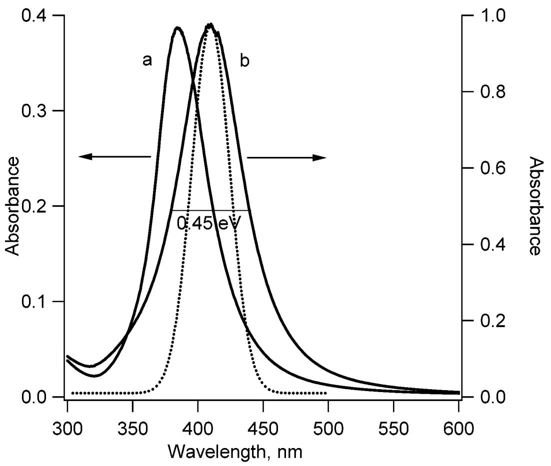

Figure 1. Absorption spectra of 10-nm silver particles in (a) aqueous solution (0.2 mM) and (b) toluene (2 mM). Optical path length is 0.2 cm. Dotted line represents calculated spectra for TOPO-capped silver particles in toluene (shell layer is 1.5 nm thick).

band of passivated silver nanoparticles in toluene is 0.45 eV, compared to 0.39 eV for hydrosols. The intense and relatively narrow absorption band of TOPO-capped silver particles indicates rather narrow distribution of particle sizes,[16,24] and at the same time interaction of metal particles with TOPO layers. TOPO is known to function as a relatively strong monodentate ligand in metal ion complexation.[25]

The diameter and size distribution of the silver nanoparticles dispersed in toluene were examined by TEM. Bright field transmission electron micrograph and histogram of the size distribution are shown in Figure 2. From TEM measurements we obtained the average diameter of spherical silver particles of (10.0 ± 1.95) nm. The histogram of the size distribution (Figure 2, inset) was obtained by measuring the diameter of 200 particles from the four photographs made from different parts of the grid. The micrographs show areas of spontaneous organization of silver nanoparticles in close-packed structures. This is a consequence of high concentration of silver particles in toluene. There are places (as indicated in Figure 2) where particles are organized in hexagonal structures, which are favored by the low polydispersity (19.5%) of the system.[26]

The optical absorption of small isolated metallic particles, such as silver particles in toluene, is described by the Mie theory,[27] which regards spherical particles and surrounding medium as they are each homogeneous and describable by their optical dielectric functions:

$$\mathrm{OD} = \frac{18\pi V N l \epsilon_m^{3/2}}{2.303\lambda}\frac{\epsilon_2}{(\epsilon_1 + 2\epsilon_m)^2 + \epsilon_2^2} \qquad (1)$$

where V is the volume of the particles, N is the number of particles per unit volume, l is the optical path, λ is the wavelength of incident light in a vacuum, ϵ_m is the dielectric constant of the matrix or solvent, ϵ_1 and ϵ_2 are the real and imaginary parts of the frequency dependent dielectric constant of the metal, $\epsilon(\omega) = \epsilon_1 + i\epsilon_2$. However, when particles are coated, the surfactant additionally affects the electronic density of core metallic particles.[28,29] The influence of a coating layer to the position of absorption maximum (λ_{max}) is described by[29]

$$\frac{\lambda^2_{max}}{\lambda^2_p} = \epsilon^\infty + 2\epsilon_m + \frac{2g(\epsilon_s - \epsilon_m)}{3} \qquad (2)$$

where ϵ_s is the optical dielectric function and g is a volume fraction of the shell layer; $\lambda_p = 2\pi c/\omega_p$ is the bulk plasmon wavelength, and ϵ^∞ is the frequency-independent part of a dielectric constant of metal. The third term on the right side of eq 2 describes the changes in a dielectric coating on the surface of a sphere. The dielectric constant of external medium (solvent, surfactant, support) is related to the refractive index by $\epsilon = n^2$.

We have examined the effect of the TOPO layer on the shift of plasmon absorption of silver particles in toluene, and compared it with observed experimental spectrum. The λ_{max} was calculated for both cases: bare silver particles in toluene (equation 1), and TOPO-coated particles in toluene (equation 2). In calculations, the values for frequency-dependent real and imaginary parts of dielectric constant for bulk silver were taken from Johnston and Christy,[30] and corrected for the particle size effect that controls the mean free path of the conduction electrons, according to Kreibeg's method:[31]

$$\epsilon(r)_2 = \epsilon(\mathrm{bulk})_2 + {\omega_p}^2 \nu_F/\omega^3 r \qquad (3)$$

where $r = 5$ nm is the particle radius, $\omega = 2\pi c/\lambda$ is the frequency of light, $\omega_p = 1.35 \times 10^{16}\ \mathrm{s}^{-1}$ is the plasmon frequency for the bulk silver, and ν_F is a Fermi velocity of the electrons in bulk material ($1.4 \times 10^6\ \mathrm{m\ s}^{-1}$). The shell layer thickness of 1.5 nm was estimated from TEM images of close-packed parts of a monolayer, yielding a volume fraction of the TOPO layer, $g = 0.54$. For calculation of a dielectric constant of surfactant, $\epsilon_s = n_s^2$, in eq 2, we took a refractive index of tri-*n*-octylphosphine, TOP, ($n^{20} = 1.468$). The actual value for a refractive index of TOPO might be slightly different due to the existence of an additional =O bond.[32] The value $\lambda_{max} = 410$ nm was obtained for the position of plasmon absorption maximum of TOPO-capped silver nanoparticles dispersed in toluene. Despite assumptions, this value agrees exceptionally well with experimental data. The calculated spectrum is presented in Figure 1 with dotted line. However, the position of the plasmon peak calculated for bare silver nanoparticles dispersed in toluene, $\lambda_{max} = 407$ nm, is also very close (within 3 nm) to the experimental value. The small difference in calculated values for bare and TOPO-coated particles

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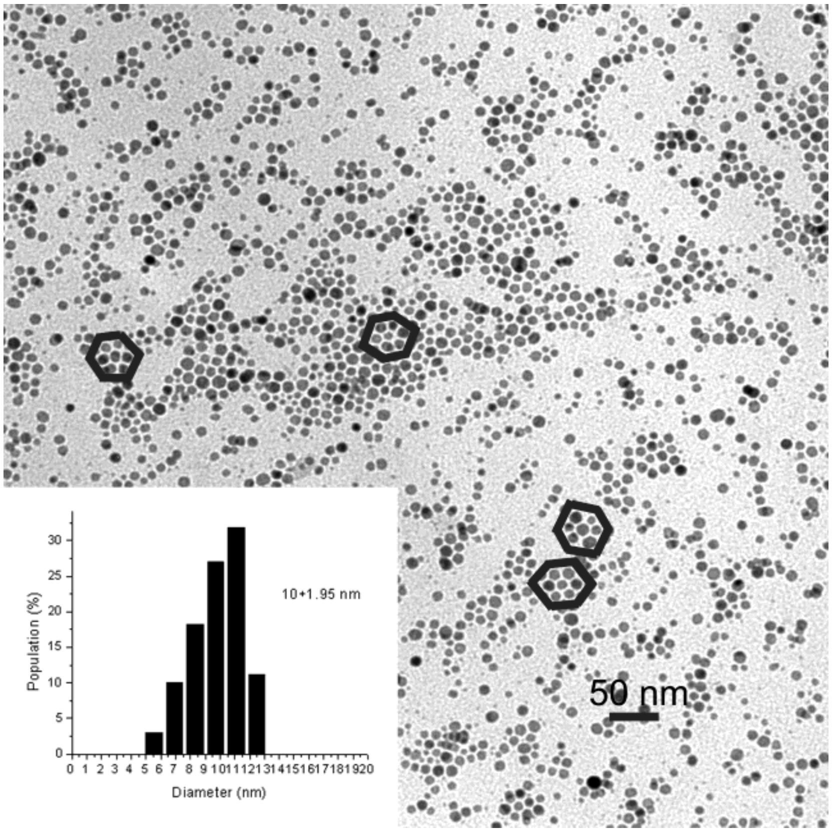

Figure 2. TEM image of Ag particles from toluene solution. Inset: histogram of particle size distribution.

in toluene is a result of small variations in the dielectric constants of the solvent and the capping agent, as well as the thickness of the TOPO layer.

The stability of TOPO-protected silver nanoparticles in toluene was tested over a period of a few months by measuring their absorption spectra. No change in intensity or broadening of the surface plasmon peak was observed, confirming that the particles in solution were stable over a long period of time.

Collective Optical Properties of Particles in Multilayered Film. The scanning electron micrograph (SEM) of the top layer of mirrorlike multilayer silver particles film chemically deposited on glass, and the histogram of size distribution of silver particles is shown in Figure 3. As can be seen from Figure 3, silver nanoparticles are closely assembled, but well separated. The distance between particles is very uniform (2.5−3.5 nm). The separation of the silver nanoparticles is due to the presence of a tri-*n*-octylphosphine oxide layer adsorbed on the silver surface. The three fully extended alkyl chains provide the barrier for particle agglomeration through their electrostatic interactions. The measured distance between particles is slightly larger than that predicted by the number of carbon atoms in the alkyl chain taking into account the contribution of the length of each CH_2 unit as 0.127 nm.[33] Schiffrin[12] calculated the dependence of the average separation between particles from the chain length of the quaternary ammonium salt adsorbed on the surface of gold nanoparticles. He concluded that a measured lesser value for the interparticle distance than predicted by alkyl chain lengths implies that chains are randomly organized in space and interpenetrate each other. In our case with slightly larger interparticle distance than predicted, we propose that alkyl chains in TOPO molecules are fully extended and interpenetration between ligand chains on adjacent particles does not occur. From a histogram of the size distribution we calculated a mean diameter of silver particles in the surface layer of the film. The obtained result, $2r_{\mathrm{Ag}} = (11.7 \pm 2.5)$ nm, is evidence that there is no change in diameter of the silver nanoparticles in film as compared to that in the solution, which also means that particles preserved original polydispersity of sizes within one standard deviation.

Optical absorption spectra of continuous silver particles film, measured in air, are shown in Figure 4. The intensity of the plasmon absorption band increases with the time of self-assembly deposition. The linear increase in absorbance with film thickness clearly suggests that the 3D film, as well as particle coverage, is homogeneous.[13,34,35] The UV/vis spectrum of 3D assembly shows the maximum of absorption at $\lambda_{\max} = 515$ nm, which is c.a. 0.6 eV shifted toward lower energies compared to the plasmon absorption band of isolated TOPO-capped silver naoparticles in toluene.

Redispersion of deposited silver particles from 3D film in toluene resulted in their separation and the generation of well-defined individual particles in solution. The dotted line in Figure 4 represents normalized absorption spectrum of silver nanoparticles in toluene after dis-

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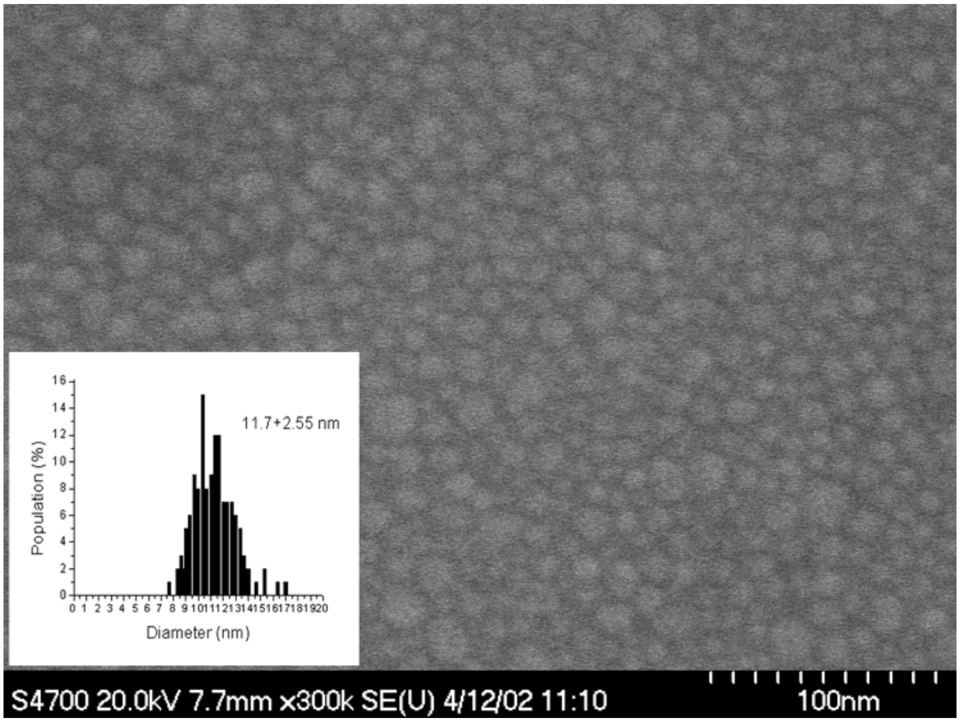

Figure 3. SEM image of multilayer mirrorlike film of Ag particles. Inset: histogram of particle size distribution.

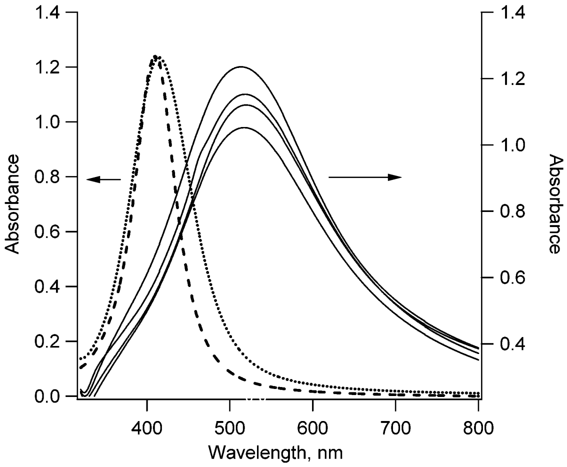

Figure 4. Absorption spectra of mirrorlike silver film as a function of film thickness (full lines). Dashed line: spectrum of silver particles in toluene before self-assembly. Dotted line: spectrum of silver particles after dissolution of film in toluene.

solution from film, while the dashed line shows the spectrum of original TOPO-capped silver nanoparticles in toluene before their self-assembly. The obtained spectra agree within 2−3 nm on the position of plasmon absorption band maximum, which indicates that redissolved particles are well-isolated, noninteracting spheres. The shift of the plasmon absorption band back to its original position upon dissolution is firm evidence that the film is indeed nanostructured, containing well-protected silver nanoparticles. Thus, a large red shift of plasmon absorption of silver particles in film is not a consequence of some physical or chemical changes associated with coagulation or Ostwald ripening of particles, rather it is a result of interparticle coupling due to their close packing, and is expected to influence electronic properties of the organized assembly. For particles organized in multilayers, each silver particle is surrounded by 12 other particles. When particles are brought into close proximity to each other, the dielectric surrounding a single particle is strongly modified by the presence of adjacent (conducting) particles, resulting in an increase in the dielectric constant of the medium, and causing the plasmon resonance maximum to shift to lower energies. The main factors that control interparticle coupling are interparticle separation, and the size of the particles, which can be quantitatively expressed as $D/2r$, where D is a distance between the centers of adjacent particles, and $2r$ is the diameter of a core silver particle.[8] It has been demonstrated that for values of $D/2r > 1.25$, the classical approximations, such as the Maxwell−Garnett (MG) effective medium theory, can be used for treating dipole coupling between nanocrystals in 2D superlattices. The classical, dipole, interpretation of silver particle monolayers reproduces well its linear optical properties, including the position of plasmon resonance.[8] We estimated the $D/2r = 1.26$ value from the mean diameter and measured distances between particles from SEM images of silver film, and applied the MG theory for calculating the position of a plasmon band of multilayered film. The original theory is applicable to isolated spheres isotropically dispersed in nonabsorbing medium, i.e., for relatively diluted systems with a low volume filling factor.[36] In general, the MG theory provides a relationship between the collective dielectric constant of a “composite” and the number density of spheres (eq 4):

$$\frac{\epsilon_c - \epsilon_m}{\epsilon_c + 2\epsilon_m} = Q\left(\frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m}\right) \tag{4}$$

where $\epsilon_c = \epsilon_{1c} + i\epsilon_{2c}$ is the dielectric constant of composite, $\epsilon = \epsilon_1 + i\epsilon_2$ is the complex dielectric constant

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of metal, and ϵ_m is the dielectric constant of surrounding medium. Both ϵ_c and ϵ are frequency dependent. Q is the volume fraction of metal particles in film. The MG theory defines the conditions for appearance of absorption maximum at $\epsilon_{1c} = [(2 + Q)/(1 - Q)]\epsilon_m$. The consequence is that the surface plasmon maximum shifts to longer wavelengths as the packing, and thus volume fraction Q, of the particles increases.

Various approaches to mathematically quantifying multibody interactions between metallic particles in dense systems have been discussed in the literature.[9,13] We used methods and equations described by Heath,[9] Mulvaney,[13,14] and Doremus[37] for predicting the position of the maximum of surface plasmon of silver particles film, λ_{max}. For monolayer film, or isolated metal islands, the influence of the substrate refractive index dominates the position of λ_{max},[38] which increases linearly as the refractive index of surrounding medium increases.[39] By increasing the thickness of film the influence of a substrate becomes less important until it diminishes completely.[40] For relatively thin and close-packed film in air, such as that presented here, we first assumed the environment of a TOPO layer, and then introduced the effect of support, taking into account the refractive index of a glass slide ($n^{20} = 1.52$ [38]). The obtained values for maximum absorption are 501 and 513 nm, respectively. The volume fraction, assuming a hexagonal close packed structure, was calculated according to the following:[13]

$$Q = \frac{0.74 r_{Ag}^3}{(r_{Ag} + r_{chain})^3} \tag{5}$$

where $r_{Ag} = 5.8$ nm is the radius of the particle, and $r_{chain} = 1.5$ nm was taken from an average distance between particles. The calculated values predict a red shift of λ_{max} of c.a. 100 nm for multilayered film of TOPO-capped Ag particles in air relative to the isolated particles in solution, which is in agreement with experimental observations.

The sensitivity of λ_{max} to the external medium was tested by placing the film in different solvents: water ($n^{20} = 1.33$), 2-propanol ($n^{20} = 1.38$), and benzene ($n^{20} = 1.50$). The measured absorption spectra are presented in Figure 5, together with the spectrum of film measured in air ($n^{20} = 1.00$). Except for the benzene, no changes in λ_{max} with different solvents were observed. Similar, unspecific changes were previously observed for alkanethiolate-covered Au films, and nonlinear dependence of λ_{max} on a refractive index was proposed.[11] We propose that the nature of octyl chains of the TOPO layer plays a dominant role in solvent penetration into the film. In general, the position of the plasmon band upon immersion of the film into various solvents will change according to their refractive indices if particles in the film can sense changes in the surrounding environment, i.e., if the solvent infiltrates around the grains of film.[39−42] Because of the nonpolar nature of tri-*n*-octyl chains, only benzene can penetrate into the film and influence the medium around silver particles. Polar solvents, such as water and alcohol, are prevented from wetting the film and particle surface, and the dielectric environment around silver particles does not change significantly upon immersion of film in these solvents.

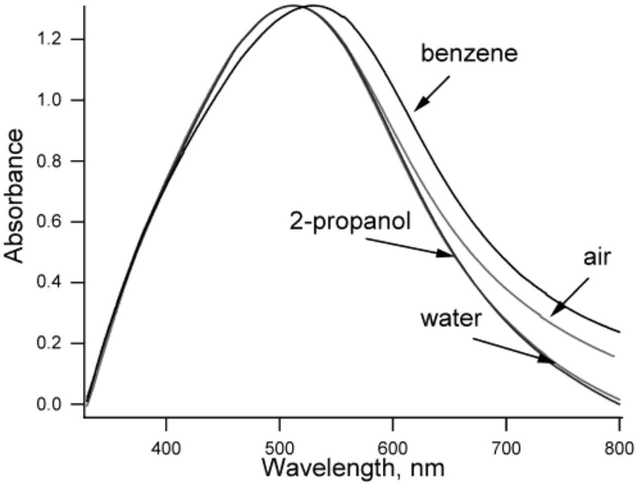

Figure 5. Absorption spectra of film suspended in air ($n^{20} = 1.00$), water ($n^{20} = 1.33$), 2-propanol ($n^{20} = 1.38$), and benzene ($n^{20} = 1.50$).

Conclusion

TOPO-capped silver nanoparticles preserve their original individual properties, and exhibit the ability to be isolated as solids and redissolved in organic solvent without aggregation, like ordinary molecules. The self-assembly of these particles results in a nanostructured mirrorlike film. The 3D structure exhibits optical properties that are characteristic for dipole coupling of particles in close proximity.

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