

Formation and Adsorption of Clusters of Gold Nanoparticles onto Functionalized Silica Nanoparticle Surfaces

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This paper reports a systematic investigation of the growth and attachment of small gold nanoparticles to the functionalized surfaces of larger silica nanoparticles. Dilution of the gold nanoparticles in mixtures of water and ethanol led to the self-assembly of gold nanoparticles in aggregates of regular size and shape attached to the surfaces of the silica nanoparticles. Functionalization of the surfaces of silica nanoparticles with different terminal groups had a profound influence over the coverage of gold nanoparticles and clusters. While the hydrophilic functional groups NH_2 and SH bound the gold nanoparticles, hydrophobic functional groups such as CH_3 and PPh_2 did not. The coverage of the gold nanoparticles and clusters on the surfaces of the silica nanoparticles was evaluated using transmission electron microscopy.

Introduction

The self-assembly of nanoparticles into useful morphologies is a much-anticipated development in nanotechnology as it offers the promise of creating materials from well-characterized, nanometer-scale constituents with interesting properties. Such self-assembly of ligand-passivated, charge-neutral metallic nanoparticles has been observed in drops of solution dried on transmission electron microscopy (TEM) grids.¹ When nanoparticles of multiple sizes were present, ordered regions with larger nanoparticles in the center and smaller nanoparticles at the edges were formed. From more dilute solutions, silver nanoparticles produced 900-nm diameter rings ~ 10 nanoparticles thick.² Highly monodisperse charge-neutral nanoparticles formed close-packed two-dimensional arrays.³ With charged gold nanoparticles, however, electrophoretic deposition was necessary to overcome the mutual repulsion of the nanoparticles and permit the formation of close-packed two-dimensional arrays.⁴

Nanoparticles have also been assembled and bound to functionalized substrates.⁵ This procedure begins by attaching one terminal group of a bifunctional molecule to a surface. The chemical makeup of the remaining terminal group is chosen so that it binds to the nanoparticles. Two common systems are dithiols on gold substrates⁶ and aminoalkylalkoxysilanes on silica substrates.^{7,8} When an appropriately functionalized substrate

is exposed to a solution of nanoparticles, the terminal groups bind the nanoparticles onto the surface of the substrate.

Charged metallic nanoparticles electrostatically repel each other and are typically well-separated on the substrate.^{7,9} Ligand-stabilized, charge-neutral nanoparticles form close-packed arrays on the substrate.⁶ Charged nanoparticles on a substrate can react with molecules from solution to reduce their charge, allowing higher coverage¹⁰ and more ordered packing.⁸ Nanoparticles on substrates have been used for surface-enhanced Raman spectroscopy (SERS),^{7,9} the construction of electrochemically active surfaces,¹¹ and the assembly of single nanoparticles,¹² chains of nanoparticles,¹³ or arrays of nanoparticles⁶ between metallic leads for measurements of tunneling or electrical conduction through the nanoparticle assemblies.

By using a solution of larger (but still sub-micrometer) nanoparticles as substrates, the available surface area upon which smaller nanoparticles may be bound and assembled can be increased to hundreds of cm^2/mL of solution compared to the limited surface area of planar substrates. This dense concentration of assemblies may enhance optical signal sensitivity for analytical or device applications such as SERS or nonlinear optics and may facilitate higher reaction rates in electrochemistry or catalysis applications.¹⁴ This type of geometry also expands the realm of practical analytical probes with which to study the properties of nanoparticle assemblies.

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(1) Ohara, P. C.; Leff, D. V.; Heath, J. R.; Gelbart, W. M. *Phys. Rev. Lett.* **1995**, *75*, 3466.

(2) Ohara, P. C.; Heath, J. R.; Gelbart, W. M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1078.

(3) Harfenist, S. A.; Wang, Z. L.; Alvarez, M. M.; Vezmar, I.; Whetten, R. L. *J. Phys. Chem.* **1996**, *100*, 13904.

(4) Giersig, M.; Mulvaney, P. *J. Phys. Chem.* **1993**, *97*, 6334.

(5) Colvin, V. L.; Goldstein, A. N.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1992**, *114*, 5221.

(6) Andres, R. P.; Bielefeld, J. D.; Henderson, J. I.; Janes, D. B.; Kolagunta, V. R.; Kubiak, C. P.; Mahoney, W. J.; Osifchin, R. G. *Science* **1996**, *273*, 1690.

(7) Freeman, R. G.; Grabar, K. C.; Allison, K. J.; Bright, R. M.; Davis, J. A.; Guthrie, A. P.; Hommer, M. B.; Jackson, M. A.; Smith, P. C.; Walter, D. G.; Natan, M. J. *Science* **1995**, *267*, 1629.

(8) Sato, T.; Brown, D.; Johnson, B. F. G. *Chem. Commun.* **1997**, 1007.

(9) Chumanov, G.; Sokolov, K.; Gregory, B. W.; Cotton, T. M. *J. Phys. Chem.* **1995**, *99*, 9466.

(10) Grabar, K. C.; Smith, P. C.; Musick, M. D.; Davis, J. A.; Walter, D. G.; Jackson, M. A.; Guthrie, A. P.; Natan, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 1148.

(11) Doron, A.; Katz, E.; Willner, I. *Langmuir* **1995**, *11*, 1313.

(12) Klein, D. L.; McEuen, P. L.; Katari, J. E. B.; Roth, R.; Alivisatos, A. P. *Appl. Phys. Lett.* **1996**, *68*, 2574.

(13) Sato, T.; Ahmed, H.; Brown, D.; Johnson, B. F. G. *J. Appl. Phys.* **1997**, *82*, 696.

(14) Haruta, M. *Catal. Today* **1997**, *36*, 153.

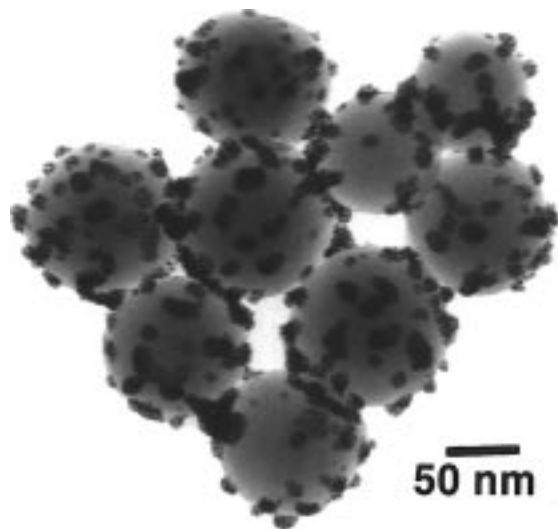


Figure 1. TEM image showing clusters of small gold nanoparticles assembled on the surfaces of larger silica nanoparticles. The silica nanoparticles were functionalized with a mixture of 5% APTMS and 95% PTMS. The assembly was generated in a mixture of 33% water and 67% ethanol.

The small size of the substrate nanoparticles permits TEM imaging of the immobilized smaller nanoparticles on the silica nanoparticles. We have previously demonstrated that gold nanoparticles can be immobilized on functionalized silica nanoparticles and used as nucleation sites for the growth of a thin gold shell.¹⁵

In this paper, we demonstrate the formation of clusters of gold nanoparticles that adsorb onto the functionalized surfaces of silica nanoparticles. Figure 1 shows a typical TEM image of the conglomerate nanostructures generated by this process. The cluster size and shape are highly regular, and clusters occur throughout the solution. We explore the role of solvent composition and the chemical makeup of the terminal group used to functionalize the surface of the silica nanoparticles as a means of understanding and controlling the growth of these nanostructures.

Experimental Section

Reagents. Tetrakis(hydroxymethyl)phosphonium chloride (THPC), 3-aminopropyltrimethoxysilane (APTMS), 3-mercaptopropyltrimethoxysilane (MPTMS), *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPTMS), tetraethyl orthosilicate (TEOS), and hydrogen tetrachloroaurate trihydrate were obtained from Aldrich. 2-(Diphenylphosphino)ethyltriethoxysilane (DPPETES) was purchased from Gelest, Inc., and propyltrimethoxysilane (PTMS) was purchased from United Chemical Technologies. Absolute ethanol was purchased from Pharmco Products. NH_4OH and NaOH were purchased from Fisher Scientific. All chemicals were used as received. Highly pure water (having a measured resistivity of $18.2 \text{ M}\Omega \text{ cm}$) was obtained from a Millipore Milli-Q UV system.

Nanoparticle Assembly. Silica nanoparticles were prepared using a variation of the method developed by Stöber et al.¹⁶ A solution of 3 mL of 30% ammonia was mixed with 50 mL of dry ethanol. After 1.5 mL of TEOS was added, the solution was stirred overnight. These reactant concentrations produced silica nanoparticles having a diameter of approximately 100 nm. Assuming that all of the TEOS reacted and that these silica nanoparticles have a density of 2 g/cm^3 ,¹⁷ the typical concentration of these solutions was 7×10^{12} silica nanoparticles/mL.

The functional groups at the surface of these unmodified silica nanoparticles are predominantly silanol ($\text{Si}-\text{OH}$) or ethoxy ($\text{Si}-\text{OCH}_2\text{CH}_3$) groups.¹⁸ These groups were treated with an ω -terminated trialkoxyorganosilane to modify the surface such that the ω -terminal functional group was exposed.^{17,18} Treatment with APTMS or AEAPTMS produced a surface terminated with amine groups; MPTMS produced a surface terminated with thiols; DPPETES produced a surface terminated with diphenylphosphine groups; PTMS produced a surface terminated with methyl groups. Silica nanoparticles were also treated with mixtures of APTMS and PTMS to generate mixtures of amine and methyl groups, respectively, on the surface.

The functionalizations were carried out by mixing the solution of silica nanoparticles with approximately 5 equiv of organosilane (sufficient to provide five monolayer coatings of the silica nanoparticles). The area on the nanoparticle surface covered by each organosilane molecule was assumed to be nominally 0.6 nm^2 .¹⁹ Typical reactant quantities were $\sim 50 \mu\text{L}$ of organosilane with 100 mL of silica nanoparticle solution. After it was left to react overnight, the solution was held at a low boil for 1 h to promote covalent bonding of the organosilane to the surface of the silica nanoparticles.^{17,19} Aliquots of ethanol were periodically added to maintain a constant volume. The solution was then centrifuged and redispersed in ethanol at least five times to remove excess reactants.

Aqueous solutions of small gold nanoparticles (2–3 nm in diameter) were prepared by the reduction of chloroauric acid with THPC as detailed in the literature.^{20,21} Using the bulk density of gold and assuming that all chloroauric acid was reduced, typical solutions of 3-nm diameter gold nanoparticles had concentrations of 7×10^{14} nanoparticles/mL. As solutions of THPC gold nanoparticles have aged, changes in pH and UV/visible absorption have been observed.²⁰ For the studies reported here, the solutions were stored in the refrigerator after preparation and used within 1 week.

Simple addition of an undiluted solution of the amine-coated silica nanoparticles to a solution of undiluted gold nanoparticles led to the ready attachment of the gold nanoparticles to the silica nanoparticles. To explore the effects of the solvent on this process, we systematically diluted the solutions of the nanoparticles. Typically, we started with 2 mL of the gold nanoparticle solution and diluted it in the following manner: with 6 mL of water, 4 mL of water and 2 mL of ethanol, 2 mL of water and 4 mL of ethanol, or 6 mL of ethanol to a total volume of 8 mL. We then estimated the volume of silica nanoparticle solution required to provide a surface area of silica equal to the total cross-sectional area of the gold nanoparticles. This volume of silica nanoparticle solution (typically 20–100 μL) was diluted with ethanol to 2 mL. The diluted gold nanoparticle solution was added to the diluted silane-coated silica nanoparticle solution in 1-mL aliquots over about 5 min. These final solutions had approximately 20% the concentration of gold nanoparticles as the initial gold nanoparticle solution and relative water:ethanol ratios of 80:20, 60:40, 40:60, and 20:80. The solutions were stirred for 30–90 min.

Characterization. The ultraviolet/visible (UV/visible) extinction spectra of the nanoparticles and nanoparticle assemblies were measured in solution using a Hitachi U-2001 UV/visible spectrophotometer with the appropriate mixture of ethanol and water as a reference. A JEOL JEM-2010 electron microscope operating at an accelerating bias voltage of 200 kV was used to collect the TEM images. Samples for TEM were prepared on copper grids (size 200 mesh) coated with a carbon support film (Electron Microscopy Sciences). Samples were prepared by placing a drop of a solution of the nanoparticles on a grid placed on filter paper and allowing the solvent to evaporate.

Results and Discussion

When an aqueous solution of gold nanoparticles is mixed with an ethanolic solution of APTMS-functionalized silica

(15) Oldenburg, S. J.; Averitt, R. D.; Westcott, S. L.; Halas, N. J. *Chem. Phys. Lett.* **1998**, *288*, 243.

(16) Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.

(17) van Blaaderen, A.; Vrij, A. *J. Colloid Interface Sci.* **1993**, *156*, 1.

(18) Badley, R. D.; Ford, W. T.; McEnroe, F. J.; Assink, R. A. *Langmuir* **1990**, *6*, 792.

(19) Waddell, T. G.; Leyden, D. E.; DeBello, M. T. *J. Am. Chem. Soc.* **1981**, *103*, 5303.

(20) Duff, D. G.; Baiker, A.; Edwards, P. P. *Langmuir* **1993**, *9*, 2301.

(21) Duff, D. G.; Baiker, A.; Gameson, I.; Edwards, P. P. *Langmuir* **1993**, *9*, 2310.

Table 1. Summary of How the Composition of the Organosilane Layer and the Mixture of Solvents Affects the Clustering and Attachment of the Gold Nanoparticles (Terminology Illustrated in Figure 2)

silica nanoparticle termination (amine:propyl)	solvent of 80% water/20% ethanol	solvent of 60% water/40% ethanol	solvent of 40% water/60% ethanol	solvent of 20% water/80% ethanol
100:0	single	single	mixed	cluster
50:50	single	single	mixed	cluster
33:67	single	single	mixed	cluster
5:95	single	mixed	cluster	cluster

nanoparticles, the gold nanoparticles become immobilized on the surfaces of the silica nanoparticles.¹⁵ The coverage of gold nanoparticles is $\leq 30\%$, consistent with the reported coverage of charged gold nanoparticles on planar amine-functionalized surfaces.²² The gold nanoparticles are well-separated from each other on the surface. The attachment is sufficiently strong so that the gold nanoparticles remain attached to the silica nanoparticles when the silica nanoparticles are centrifuged out of solution and redispersed using an ultrasonic probe.

By diluting the gold nanoparticle solution with mixtures of water and ethanol before addition to the silica nanoparticle solution, we observe the attachment of clusters of gold nanoparticles to the surface of the silica nanoparticles (Figure 1). These self-assembled aggregates each consist of tens of gold nanoparticles. With very few exceptions,¹ most previously observed self-assembled structures involve hundreds or thousands of nanoparticles and long-range ordering.^{2,3,4,6} The assembly we observe is also intriguing because these THPC gold nanoparticles are negatively charged²³ and thus should be mutually repulsive.

We explored two strategies for controlling the growth of these assemblies of gold nanoparticles. The first strategy was to vary the nature of the functionalization of the silica nanoparticle surfaces; the second was to vary the relative concentrations of ethanol and water for dilution of the gold nanoparticles. The silica nanoparticles were systematically functionalized with mixtures of APTMS and PTMS in the following ratios: 100:0, 50:50, 33:67, and 5:95. Because APTMS exposes an amine group with an available electron lone pair that should bind to the gold nanoparticles and PTMS exposes a nonpolar methyl group that should not bind to gold, the functionalized silica nanoparticles examined in this particular study should exhibit varying affinities for the gold nanoparticles. Silica nanoparticles functionalized with 100% PTMS were also examined to confirm that their surfaces were inert to nanoparticle attachment.

During the systematic variation of these parameters, several types of assemblies were observed by TEM. Figure 2a shows "single" attachment, where individual gold nanoparticles are well-separated from their neighbors. Figure 2b shows "cluster" attachment, where clusters of gold nanoparticles are attached to the silica nanoparticle surface. Figure 2c shows an example of "mixed" attachment: many of the gold nanoparticles are attached singly, but some are attached close together in a densely packed arrangement or in clusters. Figure 2d shows the extremely sparse coverage that resulted with silica nanoparticles coated with 100% PTMS.

Using this terminology, Table 1 summarizes the results of varying the surface amine concentration and the solvent mixture. For all mixtures of APTMS and PTMS, the gold nanoparticles were associated in larger numbers at higher

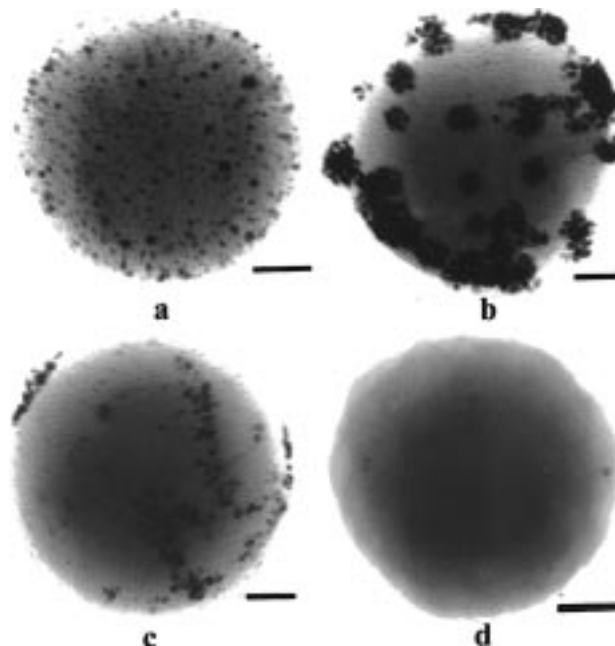


Figure 2. TEM images showing different ways that gold nanoparticles can adsorb to silica nanoparticles, depending on the composition of the organosilane coating and the mixture of solvents used: (a) shows "single" attachment; (b) shows "cluster" attachment; (c) shows "mixed" attachment; (d) shows that silica nanoparticles functionalized with 100% PTMS have sparse coverage. All scale bars are 20 nm.

concentrations of ethanol. In general, the behaviors of the silica nanoparticles terminated with 100%, 50%, and 33% APTMS were indistinguishable both in total number of gold nanoparticles attached and the morphology of the attachment. In contrast, the silica nanoparticles terminated with a mixture containing 5% APTMS had a lower coverage of gold nanoparticles.

In addition to APTMS, other organosilanes including AEAPTMS, MPTMS, and DPPETES have been used to functionalize planar silica substrates for the immobilization of negatively charged gold nanoparticles.^{8,22} While amines, phosphines, and thiols all have lone electron pairs that can coordinate to the surface of gold, alkylamines exist predominantly as positively charged $R-NH_3^+$ groups at values of pH < 10 . Gold nanoparticles were exposed to the silica nanoparticles at pH 6–8 in mixtures of water and ethanol. Consequently, the interaction between the amines and the negatively charged THPC gold nanoparticle clusters might be electrostatic rather than coordinative in nature. Interactions between gold nanoparticles and thiol or phosphine groups, however, would be more likely coordinative than electrostatic.

To investigate whether different functional groups influence the formation or adsorption of clusters of nanoparticles, we examined the attachment of clusters to silica nanoparticles functionalized with APTMS, AEAPTMS, MPTMS, and DPPETES as well as unfunction-

(22) Grabar, K. C.; Allison, K. J.; Baker, B. E.; Bright, R. M.; Brown, K. R.; Freeman, R. G.; Fox, A. P.; Keating, C. D.; Musick, M. D.; Natan, M. J. *Langmuir* **1996**, *12*, 2353.

(23) Vogel, W.; Duff, D. G.; Baiker, A. *Langmuir* **1995**, *11*, 401.

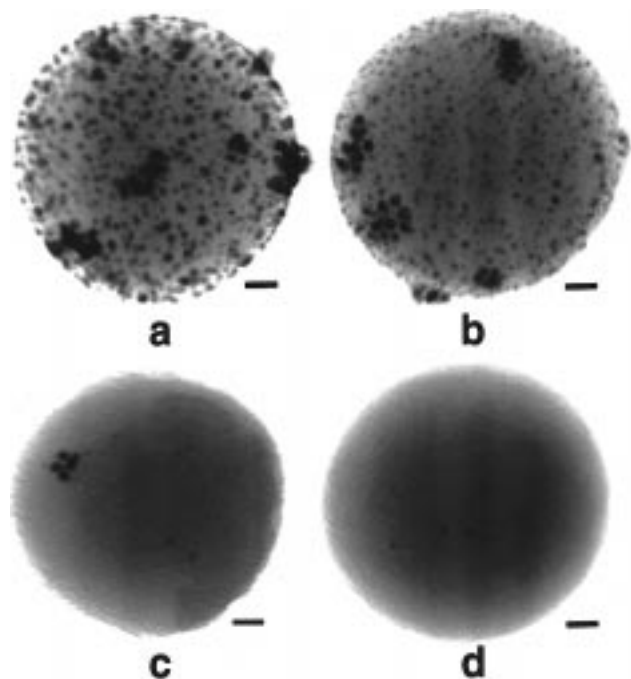


Figure 3. TEM images of silica nanoparticles after reaction with gold nanoparticles. The silica nanoparticles were functionalized with (a) 100% AEAPTMS, (b) 100% MPTMS, (c) 100% DPPETES, and (d) unfunctionalized. The assemblies were generated in a mixture of 40% water and 60% ethanol. All scale bars are 10 nm.

alized silica nanoparticles. To our knowledge, no previous studies have explored the attachment of gold nanoparticles to uncoated silica surfaces. However, because the silanol groups of the uncoated silica nanoparticles generate a negatively charged surface,¹⁷ we would not expect the adsorption of negatively charged gold nanoparticles to these surfaces. For these experiments, the gold nanoparticles and functionalized silica nanoparticles were diluted and mixed to an overall ethanol concentration of 60% as in column 3 of Table 1. Amine-functionalized silica nanoparticles (treated with either APTMS or AEAPTMS) exhibited heavy coverage of gold nanoparticles as shown in Figure 3a. Although some clusters were present, single gold nanoparticles predominated. For thiol-functionalized silica nanoparticles (treated with MPTMS), the total coverage was sparser, but some clusters were also immobilized as shown in Figure 3b. In these attachments, the interaction of the gold nanoparticles with the silica nanoparticles cannot be purely electrostatic. For silica nanoparticles treated with DPPETES (Figure 3c) and unfunctionalized silica nanoparticles (Figure 3d), only a few gold nanoparticles were attached to any silica nanoparticle; many silica nanoparticles were bare.

Given that silica surfaces functionalized with DPPETES are known to bind other negatively charged gold nanoparticles,²² we were surprised to observe the negligible attachment of gold nanoparticles and clusters to the DPPETES-functionalized surfaces studied here. The THPC gold nanoparticles used in our studies may have a higher negative surface charge density and, consequently, might not be able to penetrate the hydrophobic environment of the phenyl groups and bind to the phosphine of DPPETES. In addition, gold nanoparticles used in previous studies were prepared with different reductants, leading to different surface properties that might influence binding. It is known, for example, that phosphorus is present on the surfaces of THPC gold

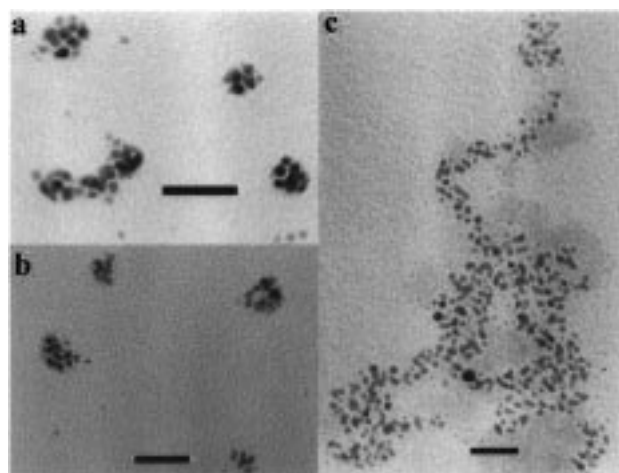


Figure 4. (a) Gold nanoparticles diluted to a concentration of 40% water and 60% ethanol aggregated in groups of up to ~10 nanoparticles. (b) Excess gold nanoparticle aggregates from an attachment experiment with 100% APTMS-coated silica nanoparticles in a mixture of 40% water and 60% ethanol. (c) Gold nanoparticles diluted to a concentration of 20% water and 80% ethanol solution aggregated in larger structures than in (a) or (b). All scale bars are 20 nm.

nanoparticles^{20,24} and that the phosphorus can be displaced by a thiol group.²⁴

Having established that the attachment of THPC gold nanoparticles (and their clusters) to silica nanoparticles is strongly influenced by the nature of the functionalization of the silica nanoparticles, we examined in greater detail the dependence of the formation of the clusters on the composition of the solvent. We compared the behavior of gold nanoparticles in diluted solutions without silica nanoparticles to that of excess, nonimmobilized gold nanoparticles in solutions containing silica nanoparticles. Gold nanoparticles deposited on a TEM grid from an undiluted aqueous solution (in the absence of silica nanoparticles) did not form clusters. Similarly, for solutions diluted to concentrations of 20% or 40% ethanol, no clusters were observed. However, when the gold nanoparticles were diluted to 60% ethanol in the absence of silica nanoparticles, some of the gold nanoparticles on the TEM grid were associated in groups of 5–10 as shown in Figure 4a. Similar clustering was observed for the excess nonimmobilized gold nanoparticles in the presence of APTMS-treated silica nanoparticles upon dilution to 60% ethanol (see Figure 4b). Figure 4c shows that, in solutions diluted to a concentration of 80% ethanol in the absence of silica nanoparticles, the gold nanoparticles associated into large, stringlike structures. In the presence of APTMS-treated silica nanoparticles at the same concentration of ethanol, the excess, nonimmobilized gold nanoparticles were observed as both stringlike structures and smaller groupings of gold nanoparticles. Different batches of gold nanoparticles had some variation in the number of associated gold nanoparticles but followed these trends.

One possible explanation for the variation in clustering as a function of relative ethanol concentration involves screening of the repulsive forces between the negatively charged gold nanoparticles. In solution, the negative charges are screened by positive ions. The magnitude of the screening can be related to the Debye decay length,²⁵ which describes the distance from the particle over which

(24) Sarathy, K. V.; Raina, G.; Yadav, R. T.; Kulkarni, G. U.; Rao, C. N. R. *J. Phys. Chem. B* **1997**, *101*, 9876.

(25) Hunter, R. J. *Foundations of Colloid Science*; Oxford University Press: Oxford, 1987; Vol. 1.

the electrostatic potential decreases. For higher relative concentrations of ethanol in the solutions, there is a lower dielectric constant of the solvent. The lower dielectric constant decreases the Debye decay length and nanoparticles can approach each other more closely. Since, however, the initial, undiluted aqueous solutions of gold nanoparticles contain an average of 5 times higher ion concentrations than the solutions diluted to 80% ethanol, the Debye decay length should be even shorter in the undiluted samples. Nevertheless, we observe no association of the gold nanoparticles in the undiluted samples.

Analysis using only the Debye decay length fails to consider the surface properties of the gold nanoparticles. For example, the surface charge of the gold nanoparticles likely develops from adsorbed ions or ionizable molecules and thus could be influenced by the concentration of ions in the solution. However, the exact ions or molecules are unknown, as are their ionization constants, so only general trends can be considered. The Derjaguin–Landau–Verwey–Overbeek (DLVO) theory considers the total potential energy between two colloidal particles as the sum of a repulsive electrostatic energy and a van der Waals-like dispersion attraction.^{26,27} We considered a simple DLVO model (as presented in colloid texts such as ref 25) with ionizable molecules determining surface charge. The lower dielectric constant of ethanol led to lower potential energy barriers, but the higher ion concentrations of the undiluted aqueous solutions resulted in an equally low potential energy barrier. While it is possible that the surface properties of the gold nanoparticles tend more toward a solution-independent surface potential, we suggest that the solvent not only simply acts as a dielectric medium but also affects the gold nanoparticles via solvation, hydrogen bonding, or other local-scale effects.

As noted above, the self-assembly of gold nanoparticles has previously been documented using analysis by TEM.¹ In that study, the particles were proposed to assemble as the solvent evaporated from the TEM grid. At ethanol concentrations of 80%, however, we find that the gold nanoparticles aggregate to a visible size and precipitate from solution after 1 day. Consequently, we believe that clustering of the gold nanoparticles (at least at some level) occurs in solution. From these studies alone, however, we cannot rule out the possibility that the clustering seen in TEM images is affected by evaporative loss.

Further evidence that the clustering of gold nanoparticles on the silica nanoparticles occurs in solution is available from UV/visible extinction measurements. THPC gold nanoparticles are too small to have the striking plasmon absorption peak at 520 nm that typically characterizes larger gold nanoparticles.^{28,29} The extinction spectrum of a solution of THPC gold nanoparticles (dotted line in Figure 5c) shows a shoulder near 500 nm from the suppressed, broadened plasmon resonance absorption as well as absorption at wavelengths below 520 nm due to d-band to conduction band transitions in gold and scattering from the nanoparticles. When multiple nanoparticles are closely associated, however, interactions between the nanoparticles are expected to occur that can modify their absorption spectrum.³⁰

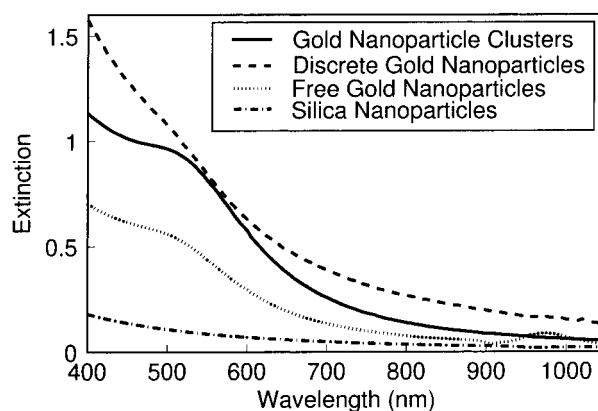


Figure 5. UV/visible spectrum of gold nanoparticle clusters attached to silica nanoparticles (—) compared to the UV/visible spectrum of discrete gold nanoparticles attached to silica nanoparticles (---). The spectra of silica nanoparticles (- · -) and free gold nanoparticles (···) are shown for reference.

Before the extinction spectra of gold nanoparticles immobilized on silica nanoparticles were recorded, the samples were centrifuged and redispersed in water to remove any free gold nanoparticles from the solutions. The concentration of free gold nanoparticles in the supernatants was determined from the absorption using Beer's Law. By subtracting the concentration of the supernatant gold nanoparticles from the original concentration of gold nanoparticles, the concentration of immobilized gold nanoparticles was determined. Figure 5 shows the UV/visible extinction spectra of gold nanoparticles immobilized either singly or in clusters on the silica nanoparticles. A higher concentration of gold nanoparticles is immobilized in clusters; these spectra have been scaled to similar concentrations. The spectra of free THPC gold nanoparticles and silica nanoparticles are also shown. The singly attached gold nanoparticle spectrum has a similar shape to the sum of the silica nanoparticle and free gold nanoparticle spectra (at appropriate concentrations) and, like that of the free gold nanoparticles, is flat in the plasmon resonance region. In contrast, the extinction spectrum for gold nanoparticles attached in clusters to silica nanoparticles shows an enhanced absorption in the plasmon resonance region. We interpret this result as a collective effect of the gold nanoparticles in the cluster³¹ which would indicate that the gold nanoparticle clusters are present on the silica nanoparticles both in solution and when deposited on TEM grids.

Conclusions

We have demonstrated a variety of parameters that influence the self-assembly of gold nanoparticles into clusters attached to the surfaces of functionalized silica nanoparticles. Dilution of the gold nanoparticles in solutions that contained a progressive increase in the concentration of ethanol showed a corresponding progressive increase in the degree of cluster formation and

(26) Derjaguin, B. V.; Landau, L. *Acta Physicochim. USSR* **1941**, *14*, 633.

(27) Verwey, E. J. W.; Overbeek, J. T. G. *Theory of the Stability of Lyophobic Colloids*; Elsevier: Amsterdam, 1948.

(28) Kreibitz, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer-Verlag: New York, 1995.

(29) Duff, D. G.; Baiker, A.; Edwards, P. P. *J. Chem. Soc., Chem. Commun.* **1993**, 96.

(30) Quinten, M.; Kreibitz, U. *Surf. Sci.* **1986**, *172*, 557.

(31) For larger nanoparticles (≥ 5 nm) with a well-developed plasmon absorption, the effect of plasmon–plasmon interactions on the absorption of a group of nanoparticles has been calculated (see refs 28 and 30). For example, with four 10-nm diameter particles arranged in a tetrahedron, a splitting of the peak or broadening between 510 and 530 nm is predicted. Since the theoretical picture of plasmon–plasmon interactions does not strictly apply to small nanoparticles (≤ 5 nm) for which the plasmon absorption is suppressed, a direct comparison with our experiment is not possible. However, the enhancement that we observe upon nanoparticle aggregate formation does lie in the expected spectral region near 520 nm.

attachment. We propose that the lower dielectric constant of ethanol is largely responsible for the observed phenomenon. The coverage was also strongly influenced by the chemical makeup of the functional groups used to modify the surfaces of the silica nanoparticles. Hydrophilic functional groups such as NH_2 and SH led to the attachment of gold nanoparticles; hydrophobic functional groups such as CH_3 and PPh_2 led to minimal attachment.

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