Self-Organization of Nanosized Gold Particles

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"Naked" colloidal gold solutions have been prepared in toluene using a two-phase system. The phase-transfer reagent used, a quaternary ammonium bromide salt ($R_4N^+Br^-$), is specifically adsorbed on the clusters through the formation of surface ion pairs, probably with the Br^- ion attached to the Au surface. The separation between clusters for two-dimensional structures is dependent on the chain length in R_4N^+. When more than one layer is present, the nanosized particles show unusual self-organization properties: the occupancy of 2-fold saddle sites is preferred to that of 3-fold hollow sites, leading to linear and circular arrangements. It is proposed that this is due to the balance between local electrostatic repulsion and dispersion forces between the particles.

Introduction

There have been strong efforts in the past few years to synthesize superlattices using nanosized clusters of metals[1–4] as building blocks, with appropriate organic ligands to complete the structure. This interest stems from the possibility of controlling the properties of the superlattice in two ways, by the size of the nanocrystalline particles and by the chemical nature of the ligands employed to join them in a 3-D structure. This flexibility allows the synthesis of a very wide range of new materials with controlled properties. One of the problems and goals that many research groups are currently addressing is how to achieve regular formation of domains so as to ensure periodicity and consequently long-range organization.

Colloidal gold has been the material of choice due to its well-established chemistry with organic ligands containing the –SH group. In particular, thiol-derivatized Au nanoclusters can be prepared in a one-step, two-phase reaction.[5–7] The stability conferred by the attachment of thiols in self-assembled structures is remarkable, and materials prepared with this ligand (in solid form and in solution) show no sign of decomposition or loss of solubility even after several months storage at room temperature.[5] These materials can be manipulated like simple organic compounds, precipi-

tated and isolated in solid form, redissolved, and made to participate in chemical reactions if the thiol employed has a reactive functionality,[8] and most importantly, as shown by Murray and co-workers,[9] they undergo ligand-exchange reactions with other thiols carrying a reactive group. These new synthetic advances have led to intensified efforts in the design of linking strategies based on classical organic chemistry methodologies.[2] Recently, Whetten et al. have described simple separation protocols for obtaining monodisperse preparations, based on a solvent precipitation technique.[3] Moreover, the crystallization of thiol-functionalized clusters to give ordered superlattices was observed. Other methods of self-organization of colloidal metallic particles have also been described using a variety of techniques, such as Langmuir–Blodgett films,[10a] electrophoretic deposition,[10b] ordered micellar block copolymer films,[10c] templating using lipid tubules,[10d] and methods from molecular biology.[10e,f] In the last case, oligodeoxyribonucleotides terminated with thiol groups have been used to organize Au colloids regularly and reversibly into ordered configurations.

The preparation of *stable* underivatized gold particles in toluene has been recently achieved using the two-phase method described in ref 5, but without the addition of thiol. By analogy with previous proposals,[11]

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stabilization is thought to be due to the presence of the quaternary ammonium salt (tetraoctylammonium bromide) used as the phase-transfer reagent in the preparation of the colloid. These colloidal preparations are important since it is most likely that the stabilization of the particles in solution does not involve the formation of strong metal−ligand bonds as is the case with the thiols, but rather results from electrostatic (image forces) and dispersion interactions involving the chains of the quaternary ammonium cation in the organic solvent. Thus, although these colloids remain in solution for periods of at least 1 year without appreciable deterioration, they are reactive enough to allow them to be used in the construction of 3-D structures by suitable chemical reactions.[2,4,12]

It has been shown that, in the presence of small amounts of dithiols acting as interparticle linking agents, the formation of locally ordered "superclusters" of nanoparticles occurs on evaporation of the solvent.[4] Unusual features of these aggregates were the presence of parallel rows of clusters separated by distances of the order of 1−2 nm and of hexagonal arrangements.

The purpose of the present work was to investigate further these unusual self-organized structures using underivatized colloidal gold as a starting material. An important question that needs to be understood is the role of the anion of the phase-transfer reagent: can the self-assembled structures observed be regarded either as a salt of stoichiometry $(R_4N^+)_mAu_n$ or is the anion adsorbed on the cluster surface?

Experimental Section

Stable solutions of Au nanoparticles in toluene were prepared following a method similar to that described by Brust et al.,[5] using as phase-transfer reagents a series of tetraalkyl-ammonium bromides, $NR_4^+Br^-$ with R ranging from C_6 to C_{18}. An aqueous solution of hydrogen tetrachloroaurate (Aldrich, 30 mL of 30 mM) was mixed with tetraoctylammonium bromide (Fluka) in toluene (80 mL of 50 mM). The two-phase mixture was vigorously stirred until all the tetrachloroaurate was transferred into the organic phase, which turned deep orange in color while the aqueous phase became colorless. While continuing to stir, aqueous sodium borohydride (Fisons, 25 mL of freshly prepared 0.4 M) was slowly added. Within a few seconds the orange color of the organic phase changed to ruby red. After further stirring for 20 min the organic phase was extracted and washed once with dilute sulfuric acid for neutralization and five times with distilled water and then dried with anhydrous sodium sulfate. The resulting ruby-colored dispersions were stored in the dark at room temperature and showed no significant precipitation for over a year.

For electron microscopy, a drop of the colloidal gold solution was placed on a carbon-coated Cu grid, and the toluene allowed to evaporate. Specimens were examined in a 200 kV JEOL 2000FX transmission electron microscope equipped with a LINK energy-dispersive X-ray analysis system.

Results and Discussion

The colloidal particles observed by TEM showed a remarkable degree of self-ordering into regular arrays. This is rather surprising since the colloids were *not*
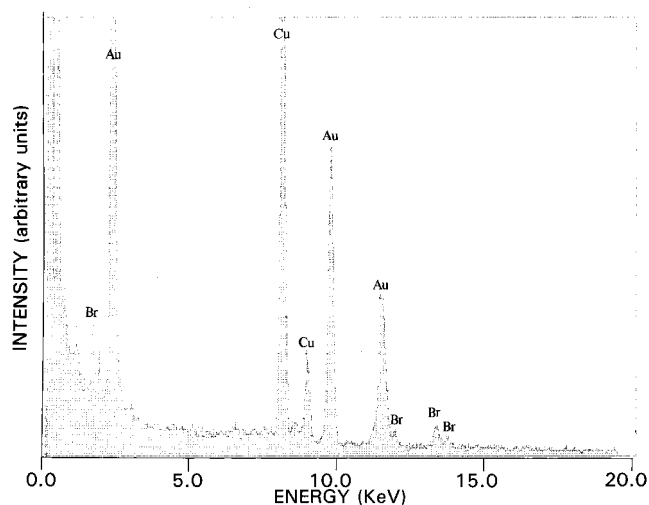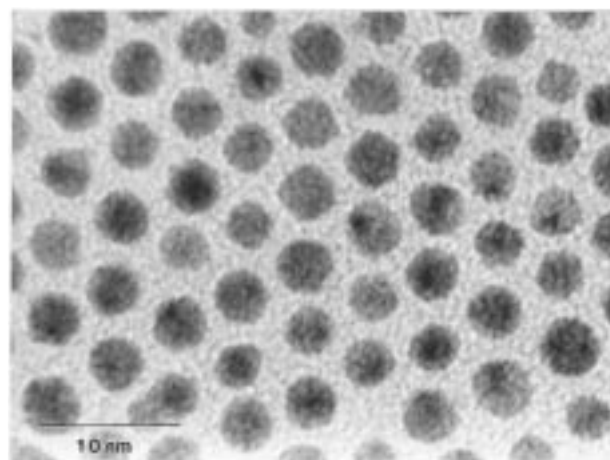
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Figure 1. (a) Bright-field micrograph showing Au nanoparticles obtained with $(C_8H_{17})_4N^+Br^-$ as the phase-transfer reagent, agglomerated into pseudohexagonal rafts. (b) An EDX spectrum obtained from the region imaged in Figure 1a showing characteristic Au and Br peaks. The Cu peaks arise from X-ray emission from the supporting grid bars.

deliberately functionalized in order to link them chemically. For instance, Figure 1a shows a typical two-dimensional raft in which the individual nanoparticles have adopted a pseudohexagonal close-packed arrangement. Electron diffraction patterns from such regions reveal only the characteristic 111, 200, 220, 331, 222, and 400 reflections of fcc gold. Since the diameter of the particles varies between 3 and 5 nm (i.e., between ca. 750 and 3500 Au atoms) the hexagonal packing is imperfect in places. Furthermore, slight variations of the shape of individual particles are apparent, with most appearing roughly spherical while a few show distinct evidence of faceting. A characteristic feature of the pseudohexagonal array is that the Au nanoparticles are not in direct contact with each other; they are in fact separated by a region that does not exhibit any diffraction contrast, typically about 1.2 nm across for the preparation using the tetraoctylammonium salt. Similar observations have been recently made by Reetz et al. for giant palladium clusters.[13]

We propose that the separation of the particles in Figure 1a is due to the presence of a layer of tetraoctylammonium bromide $(C_8H_{17})_4N^+Br^-$ adsorbed on the Au surface. Figure 1b shows an energy-dispersive
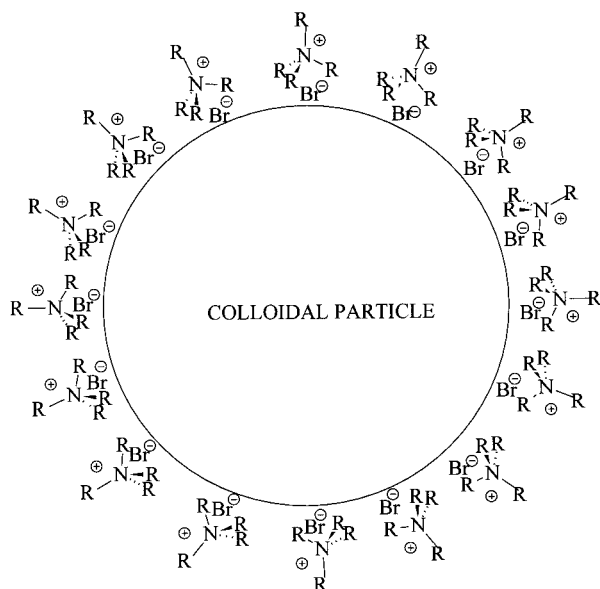
Figure 2. Schematic diagram showing the proposed arrangement of R_4N^+ and Br^- species adsorbed on the surface of Au particles. Note that the positive ends of the molecular dipoles created always point away from the Au surface.

X-ray (EDX) spectrum obtained from the same two-dimensional raft of colloidal particles. This shows Au peaks at 2.16, 9.71, and 11.43 keV and additional weak peaks at 1.48, 11.36, and 11.90 keV which are characteristic of bromine. Control spectra obtained from the carbon grid about 30 nm away from the raft region showed no Au or Br peaks, demonstrating that the Br^- ion is directly associated with the raft and not dispersed uniformly over the grid. This confirms that the bromide ion is associated with the Au particles and suggests the presence of quaternary ammonium ions as required to preserve electroneutrality in the structure as a whole. In addition, Br^- is known to be strongly adsorbed on Au surfaces. For instance, a surface charge density of 90 μC cm^{-2}, independent of bulk Br^- concentration, has been measured on Au(111) in aqueous electrolytes.[14] The washing stages of the preparation do not eliminate the residual bromide, as shown by exhaustive washing of the toluene solution.

A schematic diagram of the proposed adsorbed layer present on Au is shown in Figure 2. Such an arrangement would provide the necessary barrier to particle coalescence since electrostatic interactions are likely to provide the necessary stability to the surface ion pairs. These effects have been known in solution equilibria; for instance, the interaction between R_4N^+ and BF_4^- ions in solvents of low dielectric permittivity leads to strong ion pairing.[15] An interesting characteristic of these electrolytes is that the distance of closest approach of the paired ions is almost independent of the chain length of the R_4N^+ cation, which indicates that the separation between the anion and the N^+ center is determined only by steric hindrance to the approach of the two charges due to the methylene groups in the hydrocarbon chains of the cation closest to the nitrogen.
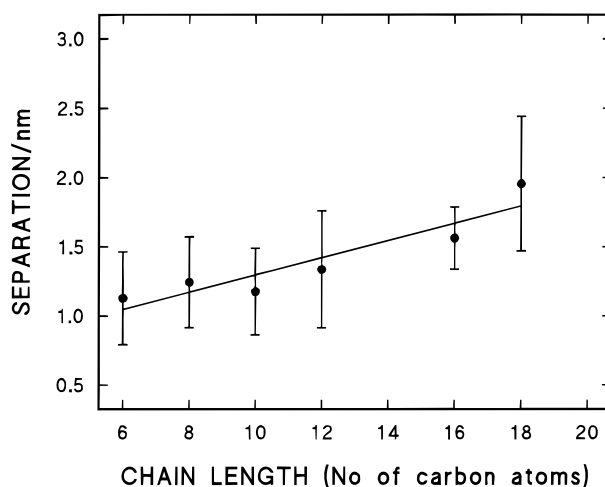

Figure 3. Dependence of the average separation between particles on the chain length of the quaternary ammonium salt employed.

From the above it is proposed that the stabilization of the Au particles, both in solution and in the structures observed, is due to the attachment of $R_4N^+Br^-$ ion pairs to the Au surface. In these structures, not only does anion adsorption give an anchoring point to the quaternary ammonium ions but also the hydrocarbon chains provide further stabilization by dispersion forces. In fact, anion-induced cation adsorption on metals has been known for a long time.[16,17] For example, Devanathan and Fernando[16] studied these effects at the mercury–solution interface for the coadsorption of I^- and $(C_4H_9)_4N^+$.

The four (C_8H_{17}) chains of the quaternary ammonium ion are arranged tetrahedrally around the central nitrogen atom and assuming that the alkyl chains are fully extended in an all-trans conformation, the distance between the nitrogen atom and the end of the alkyl chain is approximately 1.2 nm. This value has been calculated from simple geometry taking the contribution of each $-CH_2-$ unit as 0.127 nm[18] and indicates that the interparticle separation observed is consistent with the presence of adsorbed $[(C_8H_{17})_4N^+]$ ions on the surface of each particle, probably with Br^- adsorbed on the Au surface and the N^+ center some distance away from it (see below).

To confirm the presence of quaternary ammonium ions on the gold surface, the preparation of colloidal gold described above was repeated using tetraalkylammonium bromides with alkyl groups ranging from C_6 to C_{18}. TEM images showed that although there was some variation in the particle size distribution as the chain length was increased, the mean interparticle separation (s) systematically increased with the number of carbon atoms (n) in the alkyl chains, as shown in Figure 3. The average separation was calculated from measurements on at least 60 particles using a calibrated eyepiece graticule. A linear regression analysis yields the expression $s/nm = 0.062n + 0.67$, which can be understood in terms of the structure proposed in Figure 2. How-

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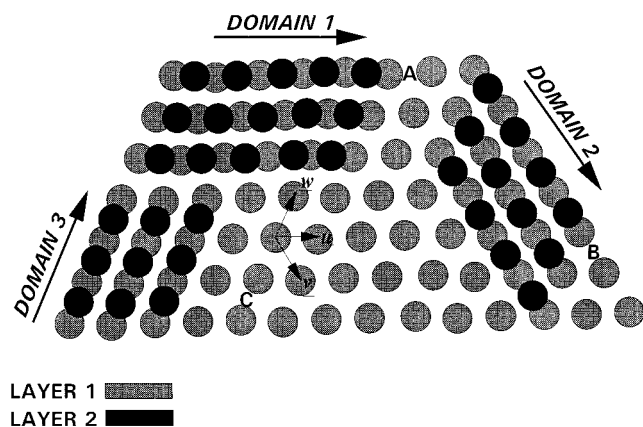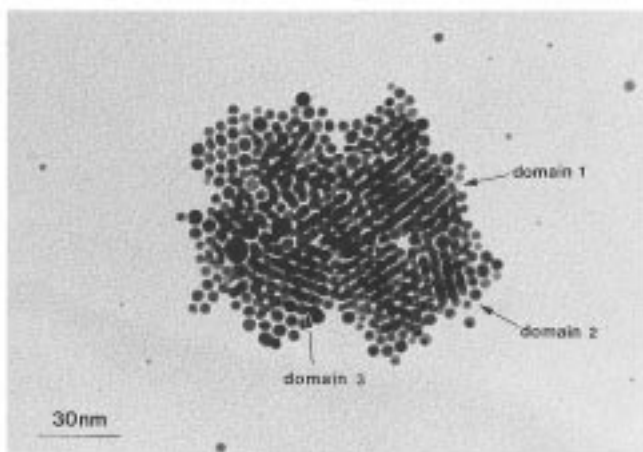
Figure 4. (a) Bright field micrograph of a bilayer structure showing ordered straight chains of Au clusters (in projection). (b) Schematic diagram illustrating how three equivalent domains of projected chains can be generated by second layer clusters occupying the 2-fold saddle sites (labeled A, B, and C) on the basal raft of particles.

ever, the value of the slope is smaller than the contribution of each $-CH_2-$ group to the length of a fully extended alkyl chain in an all-trans conformation, of 0.127 nm.[18] The observed value implies that the chains are randomly organized and that interpenetration occurs between adsorbed species on adjacent particles. Such interpenetration has previously been proposed by Whetten et al.[3] and Lennox et al.[19] for thiol-capped gold nanoparticles.

Figure 4a shows self-ordered structures commonly observed when the rafts contain more than one layer. Chain arrangements of nanoparticles, which appear as straight lines in projection, are visible. Furthermore, three discrete domains (labeled 1, 2, and 3) in which lines of clusters are rotated by 60° with respect to each other are clearly discernible, further indicating that the underlayer and overlayer have the same hexagonal symmetry. A schematic representation of these structures is shown in Figure 4b.

Interestingly, these chainlike arrangements can be generated only if the second layer of particles occupy the 2-fold saddle site between two particles in the first layer rather than 3-fold hollow sites created where three basal plane particles meet. The three domains of chains that can be observed are then just a consequence of
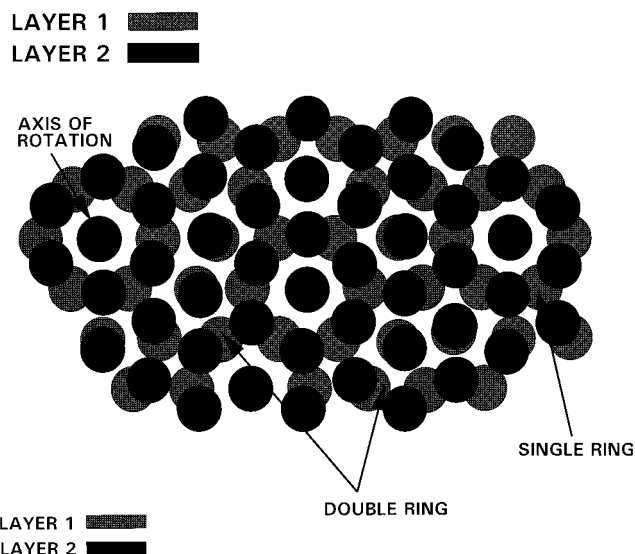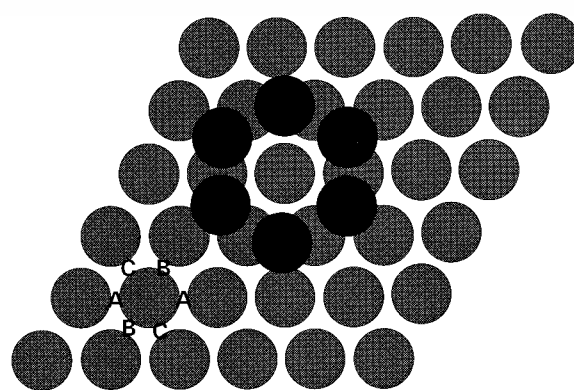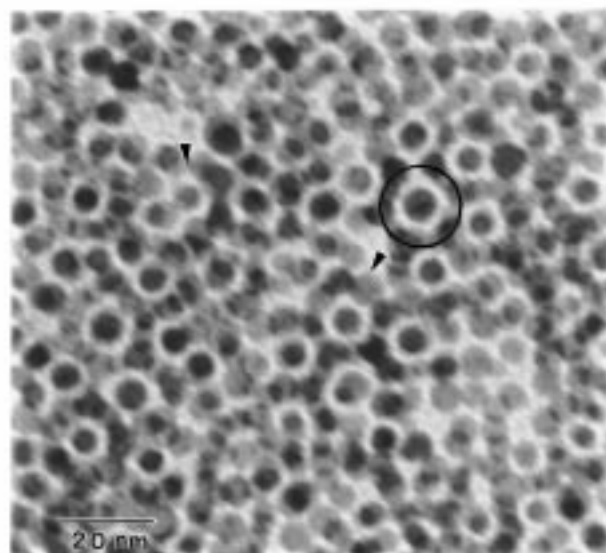

Figure 5. (a) Bright-field micrograph showing isolated and connected rings in a bilayer structure. The circle drawn is only included to aid the eye. (b) Schematic diagram illustrating how a single ring feature can be formed by filling 2-fold saddle sites in an ABCABC sequence. (c) Generation of single and double ring structures, such as those in Figure 3a, by rotating an upper hexagonal raft of clusters by 30° with respect to the lower raft.

filling the energetically equivalent saddle sites labeled A, B, and C in Figure 4b. For example, filling saddle

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sites in an A–A–A sequence leads to domain 1. These chain structures can be considered as a simple rigid body shift of an upper hexagonal raft of clusters with respect to a basal raft. Translation vectors of $U/2$, $V/2$, and $W/2$ will create domains 1, 2, and 3, respectively, illustrated in Figure 4b.

The preferred stabilization of the 2-fold saddle over the 3-fold hollow site is surprising. In fact, it would be expected that occupancy of the 2-fold saddle positions should be less energetically favorable than that of a 3-fold hollow position if the stabilization energy of the lattice depended *only* on a balance between polarizability interactions of particles and short-range repulsive interactions. The proposed particle model (Figure 2) requires the presence of a strong surface dipole moment, which suggests that the origin of the 2-fold site occupancy is the short-range dipole–dipole repulsion between the adsorbed ion pairs. In the presence of a strong short-range electrostatic dipolar repulsive component to the energy, the 3-fold sites will be unfavorable compared with 2-fold sites due to the reduced number of surface dipoles present in the latter case on the surfaces of the nearest neighbor clusters.

Ring structures, such as those shown in Figure 5a, are a second commonly observed feature in bilayer agglomerates. Single ring structures of about 20 nm external diameter, as well as paired structures of adjacent rings, are observed. Examples of both these features are indicated by arrows in Figure 5a for a C_8 preparation. Figure 5b shows schematically how these features can arise. The rings are simply closed chain structures where once more, the second layer particles preferentially occupy 2-fold hollow sites, but this time in an ABCABC sequence. These features can be reproduced by a notional 30° rigid-body rotation of a second layer of clusters with respect to a basal plane, as shown in Figure 5c. This leads not only to isolated ring structures of the correct dimensions but also to the formation of an occasional pair of adjacent rings. Thus, the ring structures observed are probably again a consequence of the balance between electrostatic repulsion of the surface dipoles present on the Au clusters and dispersion interactions. However, the electronic

properties of these nanostructured arrays are still under investigation, and the possibility of overlap of electronic levels between clusters cannot be entirely ruled out as a stabilizing mechanism of the observed structures. The structures shown in Figures 4 and 5 for bilayers are always observed and are specially prevalent for preparations using quaternary ammonium salts having alkyl chain lengths in the range 6–12.

Ring structures can also be observed with thiol-capped gold clusters obtained by reaction of the C_8 quaternary ammonium preparation with excess C_{10} thiol. In view of the large surface dipole of gold alkanethiolates,[20] this behavior can be understood on the basis of the electrostatic arguments presented above.

A final point worthy of note is that in the solid state, the structures generated are unstable with time. If a TEM sample is reexamined after being stored at ambient temperature for several weeks, the original Au colloids begin to sinter to form larger (10–20 nm diameter) particles which tend to exhibit {111}- and {100}-type facets. Many of the crystallites are in fact multiply twinned, but it is interesting to note that the separation of the individual particles is unchanged.

In summary, it has been demonstrated that $R_4N^+Br^-$-stabilized colloidal Au particles self-assemble into characteristic structures when allowed to deposit on an amorphous carbon film. The characteristic line and ring features clearly observed in bilayer structures are due to particle stacking in the 2-fold saddle sites rather than in the 3-fold hollow sites. It is proposed that the growth of superstructures results from the presence of surface ionic dipoles on the Au particles. This, in combination with interchain dispersion forces leads to preferential occupancy of the 2-fold sites.

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