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NANOCRYSTAL SUPERLATTICES OF THIOLATED GOLD

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Abstract

We present two methods for a reproducible preparation of monodisperse gold colloids stabilized by alkanethiol molecules. The first method is based on the widely employed inverse micelle technique. The second one uses the solvated metal atom dispersion (SMAD) method that is very suitable for the synthesis of large amounts of colloids. An important feature of the SMAD technique is the purity of the colloids from reducing agents, surfactants, etc. Thus, no purification of the as-prepared systems is necessary before further procedures are conducted with them. In both methods, the colloids are subjected to a heated reflux for a certain amount of time (digestive ripening) resulting in a dramatic narrowing of the particle size distribution. Because of the uniformity of the shape and size of the final gold nanoparticles, they self-assemble into large (up to several micrometers in length) 2D- and 3D-superlattices when deposited on a support. Among several alkanethiols with different chain length, it was found that dodecanethiol gives the best results in terms of monodispersity of gold particles and quality of superlattices. The organization of the gold nanoparticles in superlattices is investigated by transmission electron microscopy (TEM) and UV-VIS spectroscopy.

Introduction

Crystals in Nature are built from atoms or molecules arranged in a specific order. Particles with the same size in the nanometer region dispersed in a colloidal solution can behave as 'atoms' and construct their own crystal lattice, usually called a nanocrystal superlattice (NCS). This idea has recently attracted significant interest, which stems from both scientific and practical points of view.[1-3] Nanomaterials due to their unique properties find numerous applications as information storage devices, sensors, catalysts, destructive adsorbents, therapeutic drugs, etc.[4] One of the most appealing characteristics of NCSs is that their structure and properties are different from those of the separate nanoparticles. They are mainly dependent upon the mutual interactions between the particles forming the crystal. Since many properties of the material are strongly contingent on the sizes of the constituting particles, its characteristics can be tailored by changing the particles' sizes or interparticle spacing.[5] The key step in realizing this idea is the ability to synthesize colloids with a very narrow size distribution. In such a way, nanoparticles could reach the perfection and uniformity of atoms and molecules in Nature. It is indispensable to have synthetic methods that allow reproducible preparation of large amounts of monodisperse colloids before they are applied for specific purposes.

Here, we present two methods for the reproducible preparation of thiol-stabilized gold colloids characterized with uniformity of the shape and sizes of the nanoparticles. Gold as a noble metal has been chosen as a standard system for investigation mainly because of ease of preparation, since no special precautions against oxidation are necessary. In addition, it has been found that gold nanoparticles organized into superlattices possess a lot of interesting properties like correlated single-electron tunneling, which is potentially applicable in nanoelectric digital circuits.[6]

The first method is based on the widely employed inverse micelle technique.[7] The second one uses the solvated metal atom dispersion method (SMAD).[8-10] The SMAD method has been extensively studied in our laboratory and it has the great advantage of producing large amounts of the desired colloidal solutions. In all experiments we have utilized the amazing 'digestive ripening' procedure for obtaining monodisperse colloids from polydisperse ones.[11] This method includes a heated reflux of a polydisperse colloid for a certain amount of time resulting in a colloid containing highly uniform particles. Because of the high degree of uniformity, gold particles prepared by both techniques have the tendency to organize into long-range ordered NCSs when deposited on different supports.

However, the preparation of a monodisperse colloid is not sufficient for insuring the formation of a well ordered crystal built from particles. In this respect, the task is similar to the case of crystallization of

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macromolecules like proteins and viruses. A crystal composed of nanoparticles is characterized by a relatively low mechanical hardness due to the weak collective van der Waals interactions.[14] This means that the role of gravity in this case is of a considerable importance. The most prominent undesirable consequences of gravity upon growth of crystals are sedimentation, convective flows and necessity of performing the crystal growth process in some vessel, of which the inherent structure can strongly influence the processes of nucleation and/or growth.[14, 15] Therefore, it is to be expected that environments with reduced gravity will improve crystal quality. In fact, numerous space shuttle missions have demonstrated that crystallization in the microgravity environment of space greatly improve crystal quality.[16] For example, proteins crystallized in microgravity are usually with a higher degree of perfection and an extended resolution of the diffraction patterns.[15-18]

Despite these expectations, we still need to understand as completely as possible the best conditions leading to the formation of a good quality crystal composed of nanoparticles. Below we discuss some of our findings about arrangement in 2D- and 3D-structures of monodisperse gold particles prepared by the inverse micelle and SMAD techniques. The shape and sizes of free particles and particles organized in 2D- and 3D- superlattices are investigated by transmission electron microscopy (TEM) and UV-VIS spectroscopy.

Inverse Micelle Method

Inverse micelles are formed in systems containing both hydrophobic and hydrophilic solvents and a surfactant when the hydrophobic phase is the much greater fraction. The surfactant forms structures in which its hydrophilic heads surround hydrophilic solvent droplets, while the hydrophobic parts point towards the continuous hydrophobic solvent. These structures are called inverse micelles. In fact, the inverse micelles act as cavities in which the processes of particle formation and growth take place.[7] Figure 1 schematically illustrates the inverse micelles and their role as microreactors.

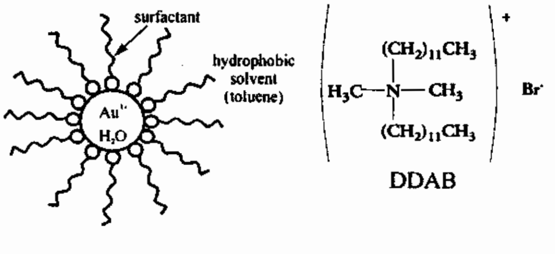

Fig.1 Schematic representation of inverse micelles.

We use didocelyldimethylammonium bromide (DDAB) as a surfactant, toluene and water are the hydrophobic and hydrophilic solvents, respectively. All synthetic steps are conducted in an inert box to prevent any influence of air. The first step is the synthesis of the so-called as-prepared gold colloid. It is synthesized by a reduction of gold chloride ($AuCl_3$) dissolved in DDAB/toluene solution with an aqueous solution of sodium borohydride ($NaBH_4$). It is believed that the reduction of Au^{3+} ions to Au atoms and their further growth into particles take place inside the inverse micelles (Figure 1). This ensures that the particles are not agglomerated and they remain with finite sizes in the nanometer region after the reaction if completed. The as-prepared colloid is polydisperse and characterized by particles with various shapes (rod-like, hexagonal, spherical) and sizes varying from 10 to 100 nm as visible from the TEM micrograph shown in Figure 2.

Fig.2 TEM micrograph of an as-prepared gold colloid by the inverse micelle method.

The next step in the synthetic procedure is the addition of an alkanethiol (saturated hydrocarbon with a terminal –SH group) to the as-prepared colloid. The alkanethiol acts as a stabilizing agent that strongly adsorbs on particles' surface via strong gold-sulfur interactions.

Thiol-derivatized gold nanoparticles have been prepared by Brust and coworkers[19] and it was shown that they can be handled just like normal compounds in the sense that they can be precipitated, washed, redisolved without any significant change in properties. The addition of dodecanethiol to the initial polydisperse colloid has an amazing effect in our case. The shape and sizes of the particles are drastically changed in only a few minutes (Figure 3).

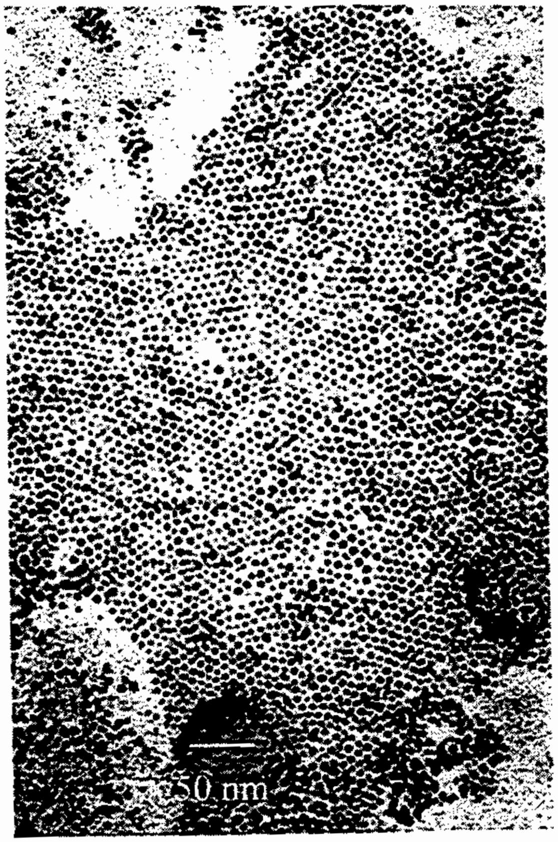

Fig. 3 TEM micrograph of an as-prepared gold colloid after addition of dodecanethiol.

The shapes become predominantly spherical and sizes are reduced to the range of 2 to 6 nm. Further, the size distribution can be narrowed by a remarkable *digestive ripening procedure* recently discovered in our group.[11] It is based on a reflux (usually 90 min) at the boiling point of toluene of the polydisperse colloid in the presence of an alkanethiol resulting in a dramatic narrowing of the size distribution of the particles. The uniformly sized and shaped particles have a tendency to self-organize (without any external forces) in 2D- and 3D- superlattices when deposited on a support (the most common for TEM study is a carbon coated formvar copper grid).

We have tested the effect of the alkane chain length of the saturated thiols upon the size of the particles and superlattice formation after digestive ripening. The most thoroughly investigated system is with dodecanethiol ($C_{12}SH$) and we have found that it gives the best results in terms of monodispersity of particles and quality of the superlattices. The TEM images of the digestively ripened gold colloids with $C_{12}SH$ show uniform spherical particles with an average size of 5 nm. Figures 4, 5 and 6 show highly ordered 3D-superlattices formed by the gold particles.

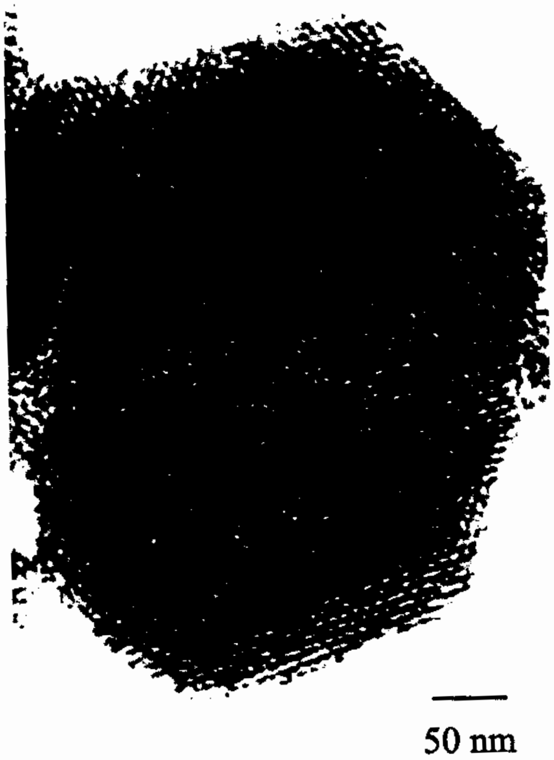

Fig. 4 TEM micrograph of a digestively ripened gold colloid in the presence of dodecanethiol prepared by the inverse micelle method (sampling is done after the colloid is cooled down to room temperature).

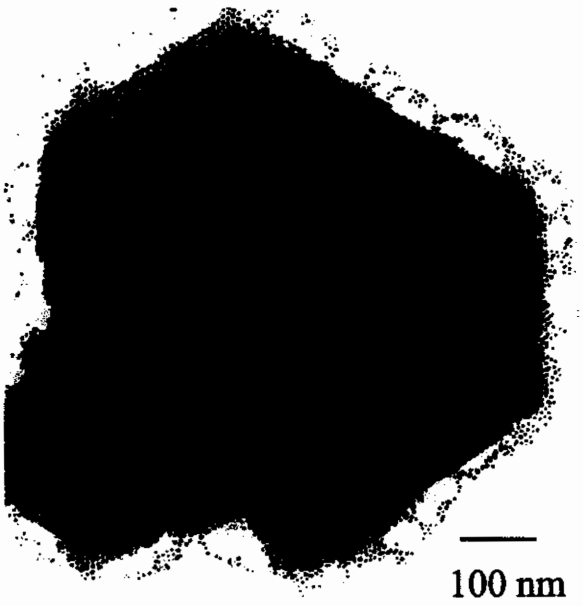

Fig. 5 TEM micrograph of a digestively ripened gold colloid in the presence of dodecanethiol prepared by the inverse micelle method (sampling is done after the colloid is cooled down to room temperature).

In most of the cases, the superlattices formed by particles coated with $C_{12}SH$ are in equilibrium with separate particles in solution at room temperature. This is clearly seen in Figures 5 and 6 where free particles surround the superlattices. The free particles-superlattice equilibrium is supported by the UV-VIS spectrum at room temperature of the digestively ripened $C_{12}SH$-derivatized gold colloid (Figure 7). It is characterized by a broad plasmon peak with a shoulder. Such shape of the plasmon peak could be attributed to absorption by both single particles and superlattices due to strong electromagnetic coupling between gold particles in the lattices leading to a shift of the plasmon peak towards higher wavelengths.[20-22] At elevated temperatures (above 60°C), only separate particles are available in the system independent of the length of the alkanethiol chain. This is consistent with the UV-VIS spectrum at 80°C for octanethiol (C_8SH)-, $C_{12}SH$- and hexadecanethiol ($C_{16}SH$)-covered particles where only one plasmon peak appears at 525 nm (Figure 8). The position of the peak is in agreement with the sizes of the particles (5-6 nm).

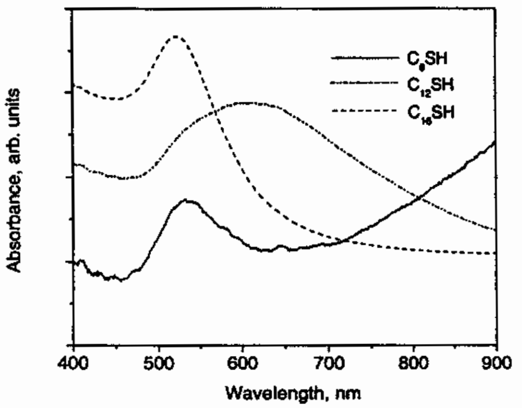

Fig. 7 UV-VIS spectra at room temperature of gold colloids prepared by the inverse micelle method and digestively ripened in the presence of different chain length alkanethiols.

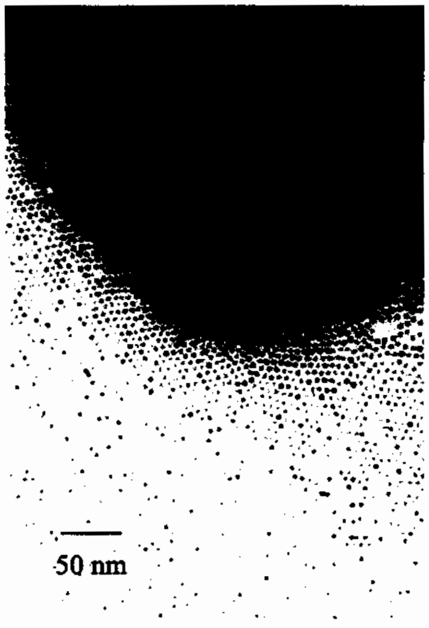

Fig. 6 TEM micrograph of a digestively ripened gold colloid in the presence of dodecanethiol prepared by the inverse micelle method (sampling is done after the colloid is cooled down to room temperature).

In the case of C_8SH-coated particles, only superlattices are found at room temperature (Figure 9). The UV-VIS spectrum at room temperature in Figure 7 of a colloid ripened in the presence of C_8SH show plasmon peak at 525 nm and a long tail at wavelengths above 700 nm consistent with the predominant superlattices in the system observed by TEM (Figure 9). The formation of mainly superlattices and the lack of free particles at room temperature could be related to the short chain length of C_8SH molecules, which allows the particles to be driven very closely together.

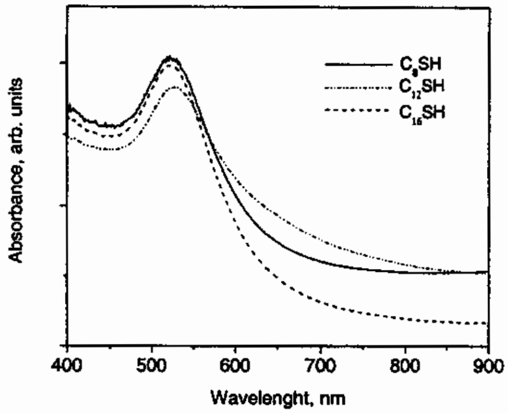

Fig. 8 UV-VIS spectra at 80°C of gold colloids prepared by the inverse micelle method and digestively ripened in the presence of different chain length alkanethiols.

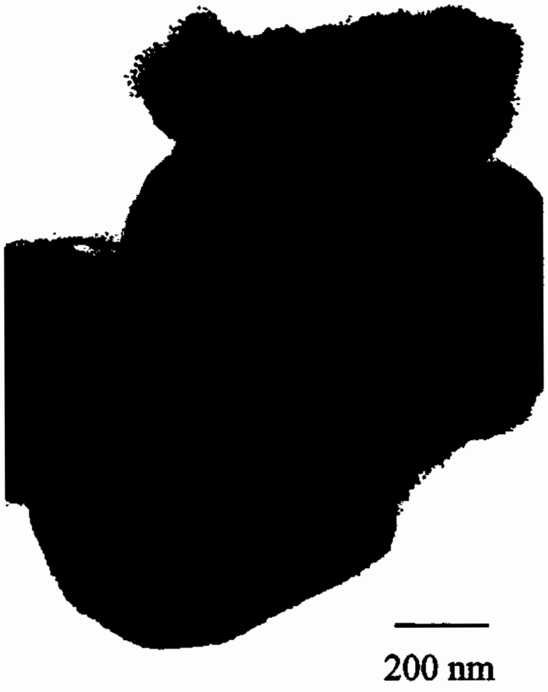

Fig. 9 TEM micrograph of a digestively ripened gold colloid in the presence of octanethiol (C_8SH) prepared by the inverse micelle method (sampling is done after the colloid is cooled down to room temperature).

On the other hand, in the case of digestively ripened $C_{16}SH$-derivatized particles no superlattice formation is observed at room temperature. A representative TEM picture is shown in Figure 10. The particles are with an average size of 5.3 nm and they are less monodisperse compared to $C_{12}SH$-coated particles.

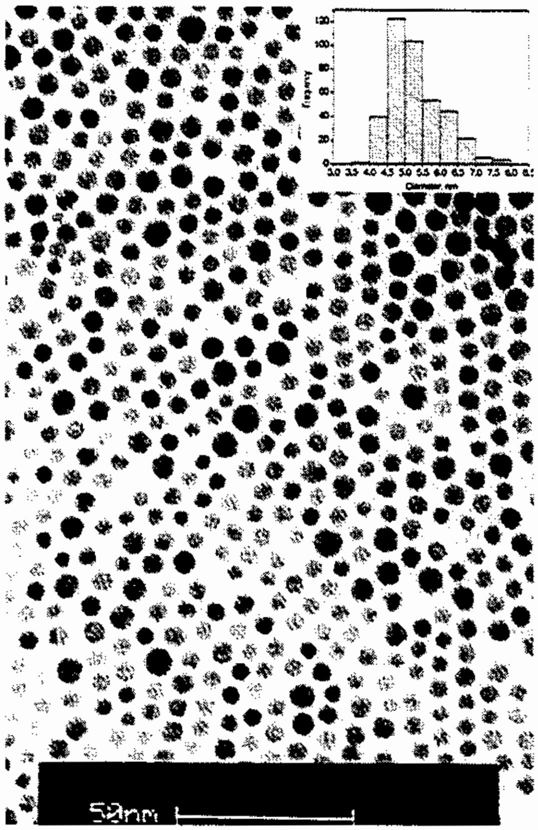

Fig. 10 TEM micrograph of a digestively ripened gold colloid in the presence of hexadecanethiol ($C_{16}SH$) prepared by the inverse micelle method (sampling is done after the colloid is cooled down to room temperature).

The UV-VIS spectrum at room temperature shows only one plasmon absorption maximum at 525 nm as expected for a colloid containing free, not organized particles.

In summary, the application of the inverse micelle method for the synthesis of gold nanoparticles has led to several important discoveries: a) possibility to improve the monodispersity of a given colloid by refluxing it for a certain amount of time (digestive ripening); b) ability to break large nanometer sized (~10-150nm) gold particles to sizes under 10 nm by an alkanethiol addition, and c) among the saturated alkanethiols, dodecanethiol ($C_{12}SH$) acts as the best stabilizing ligand for gold particles in terms of monodispersity and perfection of particles organization.

The inverse micelle method, however, is difficult to be scaled up and purification of the as-prepared particles from the excess reducing agent and surfactant is necessary before further procedures are conducted. These disadvantages are overcome by the SMAD method.

SMAD Method

The SMAD technique is based on a co-deposition of the vapors of a metal and an organic solvent on the walls of a reactor cooled to the temperature of liquid nitrogen (77K).[8] In such a way a frozen metal/ organic solvent matrix is formed. At the end of the vaporization process, this matrix is allowed to melt down for a certain amount of time. Particle growth and stabilization take place during the warm-up stage. Therefore, it is the most critical step in the whole process. The more slowly the matrix warm up is carried out, the smaller the particles at the end of the process are. In addition to metal colloids, the SMAD method is also suitable for the preparation of colloids of different compounds like metal oxides, fluorides, sulfides, etc.

The SMAD technique has two very important advantages: a) the colloids are free from impurities, i.e. they contain only the dispersed compound and the solvent (other stabilizing agents can be present in some cases), and b) large amounts of the desired colloids can be reproducibly synthesized.

Particle stabilization is achieved by two major ways. The first one is a strong solvation by the organic solvent molecules. The second mechanism is believed to be the electrostatic stabilization by electron scavenging from the reactor electrodes, walls and solvent. Therefore, gold particles prepared by the SMAD method are negatively charged. Since solvation plays a crucial role for the stability of the colloid, it is to be expected that more polar solvents will achieve better stabilization.

In fact, one of the most stable (several months and even more than a year) gold colloids is in acetone, a polar solvent. Stable gold colloids in acetone were first introduced and characterized by Klabunde and coworkers[9] in 1986 and since then, they have been extensively studied in our laboratory. Figure 11 shows a representative TEM micrograph of Au colloid prepared in acetone. It is characterized by particles with sizes from 10 to 50 nm and no definite shapes.

Fig. 11 TEM micrograph of gold-acetone colloid prepared by the SMAD method.

By applying a combination between acetone and toluene as solvents and dodecanethiol as a stabilizing agent we have been able to obtain highly monodisperse gold colloids by the SMAD method with an average particle size of 4.5 nm. The high degree of uniformity of the particles was achieved after removal of acetone from the system and digestive ripening of the gold-toluene colloid in the presence of dodecanethiol ($C_{12}SH$). The thiol-stabilized gold particles are self-organized in large NCSs of several micrometers when deposited on a TEM grid. Figure 12 illustrates a perfect 3D-array of gold particles and the corresponding electron diffraction with a well-defined first-order pattern. According to it, the plane spacing is 6.6 nm that is consistent with the particle diameter and the size of the alkanethiol chains. Another highly ordered 3D-array of gold particles prepared by the SMAD method is shown in Figure 13.

Currently we are working on the isolation of particles organized in macrosuperlattices in a dry state.

Acknowledgments

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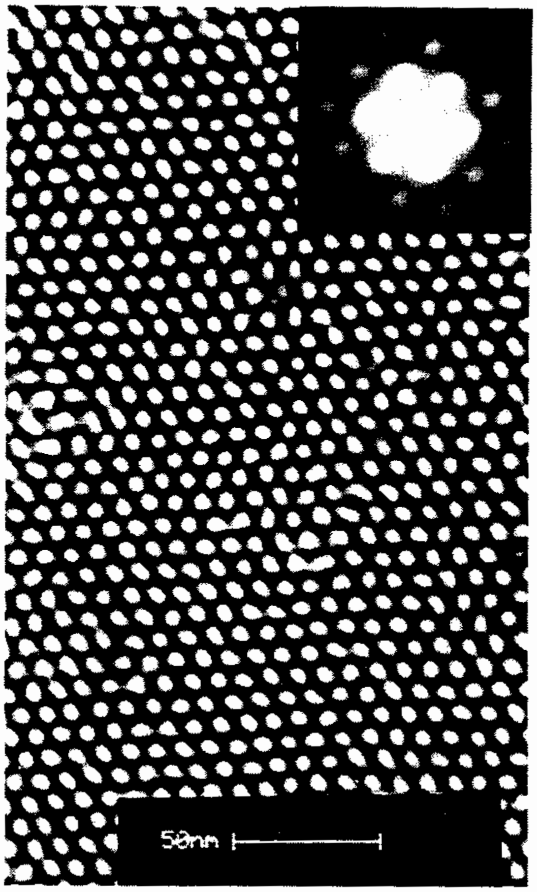

Fig. 12 TEM micrograph of gold-toluene colloid prepared by the SMAD method and digestively ripened in the presence of dodecanethiol (sampling is done after cooling down to room temperature).

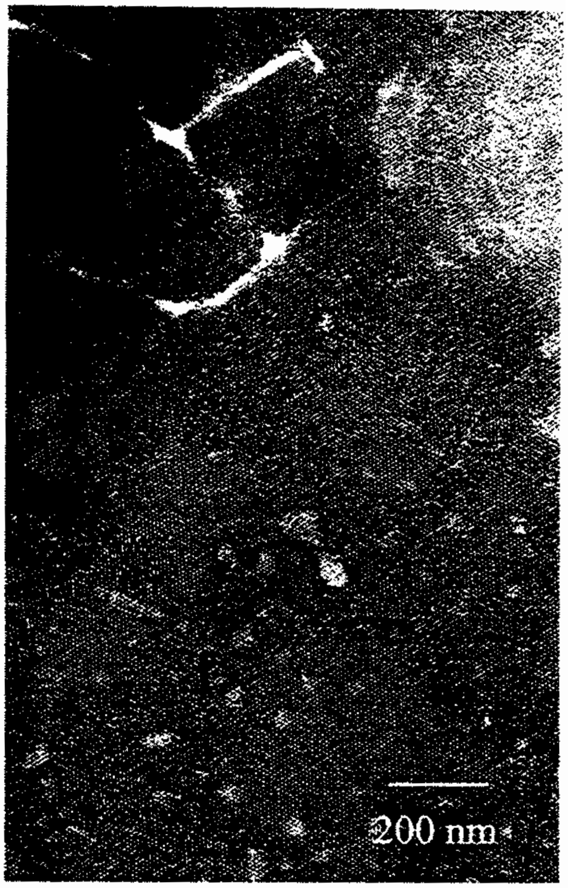

Fig. 13 TEM micrograph of gold-toluene colloid prepared by the SMAD method and digestively ripened in the presence of dodecanethiol (sampling is done after cooling down to room temperature).

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