

Electrostatic-Assembly-Driven Formation of Micrometer-Scale Supramolecular Sheets of (3-Aminopropyl)triethoxysilane(APTES)-HAuCl₄ and Their Subsequent Transformation into Stable APTES Bilayer-Capped Gold Nanoparticles through a Thermal Process

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In this letter, we demonstrate for the first time the electrostatically driven assembly of (3-aminopropyl)triethoxysilane (APTES) and HAuCl₄ in aqueous media into novel micrometer-scale supramolecular sheets and their subsequent transformation into small, stable APTES bilayer-capped gold nanoparticles through a thermal process. The nanoparticle formation mechanism is also discussed.

During the past few years, metal nanoparticles have been the focus of much scientific research because of their size-dependent physical and chemical properties, and considerable attention has been paid to their synthesis and characterization.¹ Among them, gold nanoparticles are the most stable noble nanoparticles, and as key materials and building blocks for the 21st century,² they represent one of the most widely studied nanomaterials.³ Although the use of soluble gold dates back to the fifth to fourth century B.C.,² the first report of the formation of stable gold colloids appeared as recently as 1857.⁴ After that, a wealth of preparative methods were developed;^{1,2} however, the chemical reduction of gold salt solution by a reducing agent such as sodium borohydride, sodium citrate, and carbon monoxide is the most convenient and most widely used method. Unfortunately, such nanoparticles tend to aggregate in solution because of their small particle size and therefore a suitable protective agent such as thiol, surfactant, or polymer is often involved in the synthesis to control nucleation and prevent the coagulation of nanoparticles.⁵

Self-assembly refers to the spontaneous organization of molecules, molecular clusters, and aggregate structures on planar solid substrates or in solution into two-dimensional arrays, three-dimensional networks, and larger components such as colloids and micrometer-scale objects.⁶ This technique is also largely used to assembly monolayer films or multilayer ultrathin films on colloids.⁷ (3-Aminopropyl)triethoxysilane (APTES) is a kind of aminated silane and currently is widely used as a coupling agent

for the modification of silica or glass surfaces by self-assembly to increase the adhesion of fiberglass–epoxy composites, polymer films, protein, DNA, and cells,⁸ and the resulting amine-derived surface can also serve as a platform on which to assemble metal nanoparticles into arrays.⁹ However, to the best of our knowledge, no attention has been paid to the assembly of APTES into supramolecular structures in solution. In this letter, we demonstrate for the first time the electrostatically driven assembly of APTES and HAuCl₄ in aqueous media into novel micrometer-scale supramolecular sheets and their subsequent transformation into small, stable APTES bilayer-capped gold nanoparticles through a thermal process. The formation mechanism involved is also discussed.

APTES and HAuCl₄ were purchased from Aldrich and used as received without further purification. The APTES–HAuCl₄ supramolecular microstructures were obtained by adding 400 μ L of APTES to 3.5 mL of a 0.024 M HAuCl₄ aqueous solution under vigorous stirring at room temperature. The gold nanoparticles were prepared by heating as-formed microstructures in aqueous media at 100 °C for 15 min, followed by dialysis of the colloidal solution against water to remove free APTES and other byproducts. For scanning electron microscopy (SEM) characterization, 20 μ L of the dispersion was placed on an indium tin oxide (ITO) glass slide and air dried at room temperature. SEM measurements were made on a Zeiss CrossBeam 1540XB microscope at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) measurements were made on a Zeiss LIBRA 120 microscope operated at an accelerating voltage of 120 kV. The sample for TEM characterization was prepared by placing a 100-fold dilution of colloidal solution on a carbon-coated copper grid and drying at room temperature. The UV–vis spectrum was collected on a Perkin-Elmer Lambda 18 spectrophotometer. Zeta potential measurements and dynamic light scattering (DLS) experiments were carried out on a Nano ZS model ZEN3600 (Malvern Instruments Ltd.). IR spectra were acquired on a Perkin-Elmer 2000 FT-IR spectrometer.

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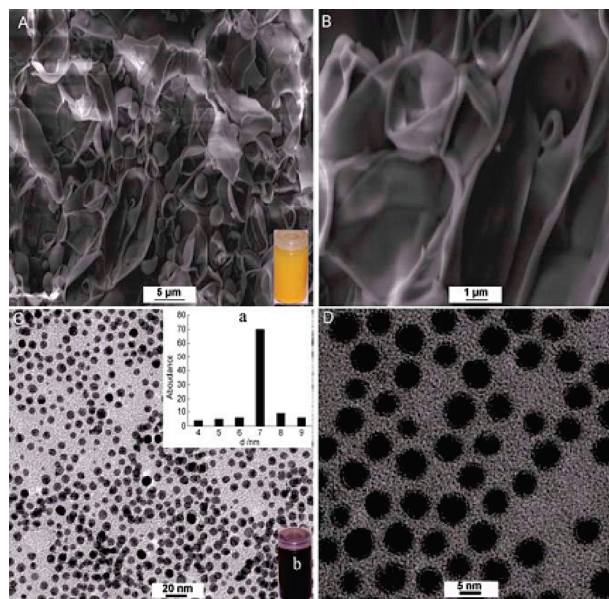


Figure 1. (A) Low-magnification SEM image of the supramolecular structures of APTES-HAuCl₄ thus formed (inset: photograph of the supramolecular structures dispersed in water) and (B) high-magnification SEM image of the supramolecular structures of APTES-HAuCl₄ thus formed. (C) Low-magnification TEM image of gold nanoparticles (inset a: particle size distribution histogram; inset b: photograph of the resulting colloidal gold dispersion) and (D) high-magnification TEM image of gold nanoparticles.

After APTES was added to the HAuCl₄ aqueous solution, the solution immediately became turbid and a large quantity of yellowish precipitate occurred. Figure 1A shows the low-magnification SEM image of the precipitate, indicating the formation of micrometer-scale sheets that are further evidenced by a close view of the precipitate as shown in Figure 1B. During the heat treatment, the yellowish turbid dispersion (inset in Figure 1A) gradually changed into a dark-purple/red solution (inset b in Figure 1C) without the observation of any precipitate. When the solution thus obtained is diluted 100-fold with water, we obtain a red dispersion exhibiting a plasmon resonance band centered at 520 nm characteristic of the colloidal gold surface plasmon resonance band,¹⁰ providing one piece of evidence to support that gold nanoparticles are generated after the thermal process.⁵ It should be pointed out that both the color and the UV-vis spectrum of the red-gold solution do not show any change upon the addition of NaBH₄, indicating the complete depletion of HAuCl₄ contained in this system. Figure 1C shows a typical TEM image and the corresponding particle size distribution histogram (inset a) of the diluted colloidal gold dispersion. The photograph shows that all of the particles are almost spherical. The size distribution histogram reveals that the resulting gold nanoparticles range from 4 to 9 (± 0.3) nm with an average particle size of 7 nm. A close view of the nanoparticles further reveals that they consist of a dark core in the central part and a relatively light thin shell with a thickness of about 1.3 (± 0.2) nm on the edge (Figure 1D). Also, it can be clearly seen that all of these particles are well separated from each other. The zeta potential of the gold nanoparticles measured by DLS experiment is +24 mV, indicating that such nanoparticles are positively charged in nature.

After APTES is mixed with HAuCl₄, protonated APTES is formed. Considering the negative charge of AuCl₄⁻ and the positive charge of protonated APTES, we can suggest that the

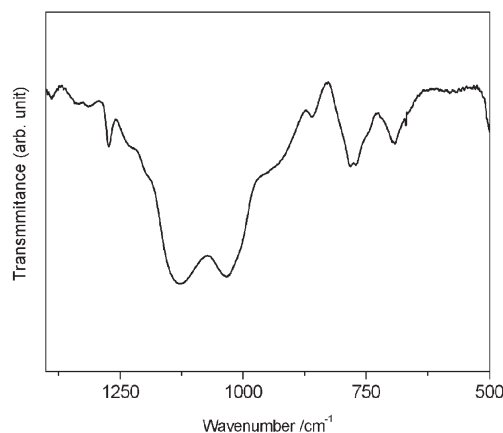


Figure 2. IR spectrum of the APTES-capped gold nanoparticles.

electrostatic attractions between these two components drive them to assemble into micrometer-scale supramolecular structures.¹¹ Indeed, mixing these two components under basic conditions with a pH of 11 gave a clear solution without the observation of any precipitate, which can be attributed to the fact that APTES fails to protonate under such basic conditions and thus no electrostatic assembly occurs. It is also possible that a competing process, such as the hydrolysis of the silane to the silanol and their subsequent condensation into the siloxane, may also be involved in the formation of the sheets under aqueous conditions. This possibility is excluded by the fact that, first, the sheets were formed immediately after mixing APTES and HAuCl₄ aqueous solutions and second, that such a competing process was not expected to occur on such a short timescale at room temperature. However, the mechanism for the formation of such sheet morphology is not clear so far and requires further investigation.

It is documented that an amine-containing compound can serve as a kind of mild reducing agent for noble metal salts and the redox reaction rate can be dramatically accelerated by increasing the reaction temperature.^{5,12} The spontaneous transformation of microsheets of APTES-HAuCl₄ into gold nanoparticles in our present study can also be attributed to the direct redox between APTES and AuCl₄⁻, and the heat-treatment is induced and accelerated markedly by the reduction of AuCl₄⁻ by APTES. During the heating process, the microsheets are gradually broken down and depleted with the co-occurrence of free APTES and AuCl₄⁻ counterparts and at the same time gold atoms are generated and nucleate and further grow into nanoparticles coated with one monolayer of APTES because of the large complexation constant for gold amines¹³ with the silanol groups pointing into solution. Indeed, we have found that the amine groups can bind strongly to gold nanoparticle surfaces and hence effectively stabilize the gold nanoparticles.^{5,14} Considering the presence of excessive APTES in this system and the hydrolysis nature of APTES in water, some free APTES will be expected to condense further with the APTES monolayer coated on the particle surface after their hydrolysis to form a siloxane backbone on the particle surface. The IR spectra of APTES-coated gold nanoparticles (Figure 2) shows two bands at 1140 and 1036 cm⁻¹ that are assigned to Si-O-Si,¹⁵ indicating the formation of the

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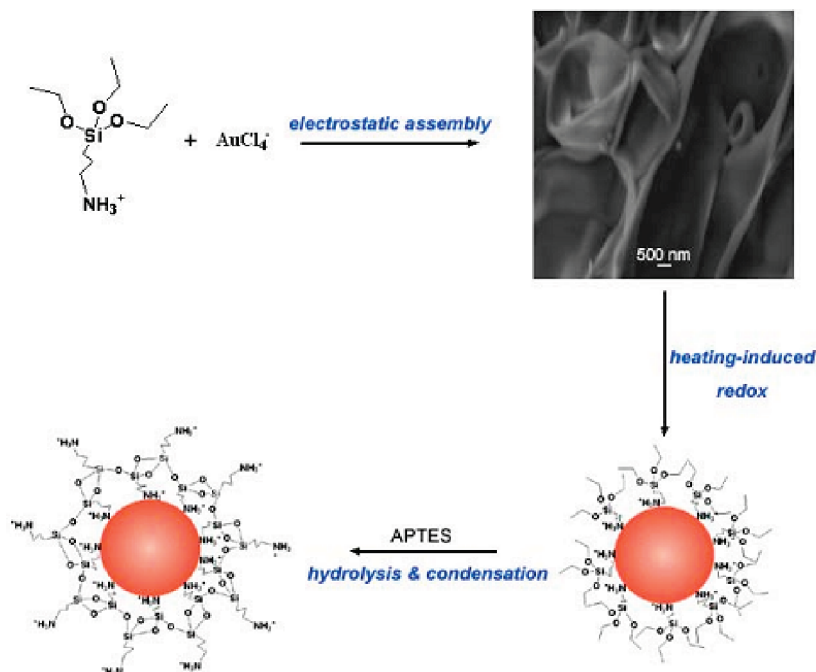
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Scheme 1. Diagram Illustrating the Formation of Supramolecular Microstructures of APTES-HAuCl₄ and Their Subsequent Transformation into APTES Bilayer-Capped Gold Nanoparticles



polymeric phase of APTES.¹⁶ It has reported that stand-alone APTES generally shows a doublet 1100 and 1075 cm^{-1} and two bands at 1175–1160 and 970–940 cm^{-1} for the Si–O–C stretching mode. In our present study, these characteristic bands of APTES disappear after the formation of APTES-capped gold nanoparticles but with the occurrence of the characteristic band of the Si–O–Si backbone, clearly confirming the condensation of APTES into the polymeric phase.¹⁶ Furthermore, because the electron density of Au is greater than that of APTES, the dark central region and relatively light shell of the nanoparticles revealed by TEM can correspond to the gold and APTES phases, respectively. It is documented that the APTES monolayer is about 0.7 nm in thickness.¹⁷ On the basis of our TEM observation that the APTES shell is about 1.3 (± 0.2) nm in thickness, it is reasonable to conclude that the shell corresponds to an APTES bilayered structure.

It is worthwhile to mention that such a gold dispersion is quite stable for several months without any observable aggregation, indicating that APTES bilayers effectively protect gold nanoparticles against aggregation partially because of the electrostatic repulsion between positively charged shells. Please note the following two experimental observations: (1) the zeta potential of the particles is low (< 30 mV), and (2) such nanoparticles remained stable even if the pH of the colloidal solution was increased up to 9.0 or higher, at which point some of the amine

groups of the shell were deprotonated and hence the positive charge density of the nanoparticle surface was decreased and even a neutral particle surface was developed. Such observations indicate that the steric hindrance of the APTES shell also contributes greatly to the formation of stable nanoparticles. We also performed quantitative elemental analysis of the gold nanoparticles after using centrifugation to separate them from the dispersion and drying them under vacuum overnight at 50 °C. It suggests that the atom number ratio of Au/Si/O/C/N/Cl is 91.71:1.78:3.10:1.52:0.94:0.92 (total: 99.97). Our failure to observe H in the elemental analysis may be attributed to the fact that the content of the H element itself is too low to be detected by the SEM-EDS system. The presence of the Cl element can be due to the fact that it functions as a counterion to the positively charged amine groups at the particle surface. Scheme 1 shows a schematic diagram to illustrate the electrostatically driven formation of supramolecular microstructures and their subsequent transformation into APTES bilayer-capped gold nanoparticles induced by heat treatment.

In conclusion, electrostatic assembly in aqueous solution has been proven to be an effective route to obtaining micrometer-scale supramolecular sheets of APTES-HAuCl₄, which can be subsequently transformed into small, stable APTES bilayer-capped gold nanoparticles through a thermal process. It not only extends the use of APTES as a supramolecular assembly agent from a solid substrate⁸ to solution but also provides us a new method for the preparation of stable gold nanoparticles from supramolecular microstructures of APTES-HAuCl₄ using APTES as both a mild reducing agent and an effective protecting agent for applications.²

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