

Two-dimensional self-organization of 1-nonanethiol-capped gold nanoparticles

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Abstract A two-dimensional (2D) ordered hexagonal close-packed structure, formed by 1-nonanethiol-capped gold nanoparticles, is reported. The structure was constructed only by dipping the gold nanoparticle colloidal solution on flat substrate. The gold nanoparticles were synthesized as follows: First, AuCl₄⁻ was transferred from aqueous solution to toluene by the phase-transfer reagent of tetraoctylammonium bromide. Then it was reduced with aqueous sodium borohydride in the presence of a given amount of 1-nonanethiol molecules which was used to control the nucleation and growth of the gold nanoparticles for the desired size. The experimental techniques, such as UV-Vis, FT-IR, and X-ray photoelectron spectroscopy (XPS), were employed to characterize the obtained product. Transmission electron microscopy (TEM) measurement demonstrated the size of the gold nanoparticle and the formation of two-dimensional ordered hexagonal close-packed gold nanoparticle structure.

Keywords: gold nanoparticle, characterization, self-organization.

According to some people's design in advance, using nanoparticles as building blocks to prepare under control two-dimensional and three-dimensional ordered structures has been among the most hot points in material chemistry today. Its realization will raise a new revolution in the fields such as optics, electronics, catalysis, chemical sensors, and nanometer-scaled information storage devices^[1-5]. In recent years, with the development of the techniques for preparing and characterizing metal and semiconductor nanoparticles, scientists have found some special ways to control the size and monodispersity of the nanoparticles. Among them, the wet chemistry approach proves quite effective. Brust et al. first performed the research work. Based on the ability of stable adsorption of thiol molecule monolayer on gold surface, they synthesized gold nanoparticles with the size varying from 1 to 3 nm in the presence of dodecanethiol by the chemical reduction method. After that, Leff et al. found that the gold particle size in a diameter range from 1.5 to 20 nm can be controlled by simply varying the initial gold-to-thiol ratio. At the same time, in their experiments, the X-ray powder

diffraction (XRD) technique was employed to roughly estimate the size of the nanoparticles. In this work, we selected 1-nonanethiol as the stabilizer to prepare expected gold nanoparticles in size of 5 nm through adjusting suitable Au/S ratio. The size selective precipitation technique was used to produce the nearly monodisperse gold nanoparticles. UV-Vis, FT-IR, X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) were employed to characterize the gold nanoparticles and gold colloidal-based ordered structure.

1 Experimental

(i) Reagents. HAuCl₄ · 3H₂O (Acros, 99.8%), tetra-*n*-octylammonium bromide (Acros, 98%), NaBH₄ (Acros, 99%), 1-nonanethiol (C₉H₁₉SH) (Aldrich, 99%) were used as received. AR grade solvents and deionized and subsequently distilled water (with the resistance more than 18 MΩ · cm) were used.

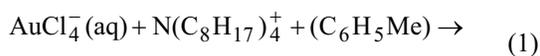
(ii) Preparation of sample. Colloidal gold nanoparticles were synthesized using the method suggested by Brust as follows: First, 10 mL tetraoctylammonium bromide toluene solution (0.1 mol/L) was added to a vigorously stirred 15 mL HAuCl₄ · 3H₂O aqueous solution (0.03 mol/L). Immediately, the upper layer became orange/red organic phase and the lower buff aqueous phase. The system was shaken repeatedly in order to remove the color from the aqueous phase. After the complete separation of the two phases, the organic phase was collected and 0.12 mmol 1-nonanethiol was injected into the organic phase, followed by the addition of 12.5 mL sodium borohydride aqueous solution (0.4 mol/L). After the reaction mixture was successively stirred under ambient condition for 24 h, the deep red organic phase was separated from the aqueous phase and concentrated to ~5 mL by evaporating in a rotary evaporator. Sequentially, 350 mL methanol was poured into the dispersion, and the mixture was kept in a refrigerator for 4 h to effectively precipitate the gold nanoparticles. The black precipitate was collected by filtering the mixture with 2.5 μm polypropylene filter paper and washed several times with ethanol. The size selective precipitation technique employing chloroform/methanol as the solvent was used to narrow the product. Finally, the nearly monodisperse 5 nm sized gold nanoparticles were thus prepared for various characterizations.

(iii) Characterizations. The UV-Vis absorption spectrum of the colloidal gold nanoparticles dispersed in cyclohexane was measured using a Shimadzu UV-1601 PC double beam spectrophotometer in the range of 200—800 nm with 2 nm resolution. FT-IR spectra were recorded on a Bio-Rad FT-IR spectrophotometer using a 150 mg KBr disk dispersed with the colloidal gold cyclohexane solution or a drop of 1-nonanethiol liquid. The background correction was performed using a reference blank KBr pellet. The XPS spectrum of gold nanoparticles

was obtained on a VG ESCALAB 5 multi-technique electron spectrum meter that focused monochromatic Mg K_{α} X-rays onto the sample, the main C(1s) peak was set to 284.8 eV as the final calibration of the energy scale. The sample for TEM experiment was prepared by depositing a drop of the toluene solution of the colloidal gold nanoparticles onto a carbon-coated copper grid and letting it dry completely under ambient condition. TEM images were obtained from a Jeol 2000EX TEM system operated at 200 kV.

2 Results and discussion

(i) Synthesis and properties of thiol-capped gold nanoparticles. The synthesis of the gold nanoparticles was completed in toluene solution in the presence of a given amount of 1-nonanethiol molecules. The overall process from aqueous phase to organic phase can be summarized by equations as follows:



The size of the gold nanoparticles can be adjusted by an initial Au/S (m/n) ratio. In this experiment, we selected the ratio of 4/1(Au/S). Many other experiments have shown that thiol molecules can form stable, self-assembled monolayer on gold surface due to the strong interaction between gold and sulfur. In the process of formation and growth of gold nuclei, if thiol molecules exist in the system, the growth of gold nuclei will be restricted quickly due to the interaction between gold and sulfur. As a result, small thiol-capped gold nanoparticles are produced. In general, the product thus-obtained is with dark waxy texture, which is soluble very easily in nonpolar solvents such as benzene, cyclohexane, hexane but insoluble in polar solvents, including water and alcohol, suggesting that the gold particles have been indeed surrounded by the hydrophobic organic molecules.

(ii) UV-Vis, FT-IR and XPS spectral studies. UV-Vis characterization of the gold nanoparticles was conducted using a Shimadzu UV-1601 PC double beam spectrophotometer. In the experiment, 1 mg sample was first dissolved in cyclohexane, then adjusted to a suitable concentration for the measurement; meanwhile, cyclohexane was selected as a correction. Fig. 1 gives the typical UV-Vis spectrum of the system. It can be seen that a clear peak maximum, corresponding to the plasmon excitation, occurs at around 518 nm. In addition, a continuous rising background toward shorter wavelength can also be observed, which might result from the Mie scattering of the nanoparticle suspension. The FT-IR spectrum can provide us the knowledge about the presence of thiol molecules on the nanoparticles. FT-IR spectra of pure 1-nonanethiol

molecules and the thiol-capped gold nanoparticles are shown in fig. 2. The comparison of the FT-IR spectra reveals extremely similar feature. The only difference between them is that the intensities of peaks at various frequencies increase to some extent while widths of them become narrow in the case of gold nanoparticles. A possible qualitative explanation is originated from the special orientation and state of the alkanethiol molecules adsorbed on the gold nanoparticle surfaces. The FT-IR experimental evidence strongly suggests that 1-nonanethiol has been an essential component of the composite nanoparticles. The XPS spectrum can present the information on the existence of Au and S elements in the nanoparticles. Fig. 3 shows the scanning range of binding energy of the particle sample from 80 to 95 eV, in which a double-peak occurs at 83.7 and 87.3 eV, corresponding to $\text{Au}_{4f_{7/2}}$ and $\text{Au}_{4f_{5/2}}$, respectively, a typical character of the presence of Au^0 state. It is worth noting that we do not find the obvious peak of Au oxidation state at 84.9 eV for Au(I) octanethiolate complex, which presumably suggests that the gold atoms must be present largely as Au^0 . In addition, the sulfur region (not shown here) exhibits weaker broad double peaks at 163.1 and 162.1 eV, showing the existence of S element on the surfaces of the gold nanoparticles.

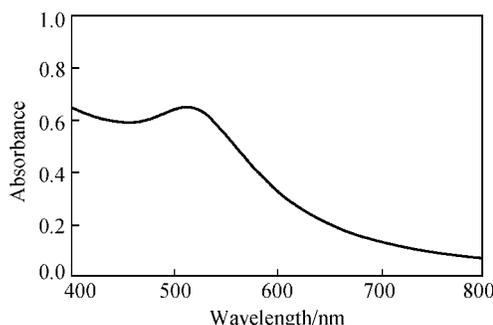


Fig. 1. UV-Vis spectrum of 1-nonanethiol gold colloidal in cyclohexane.

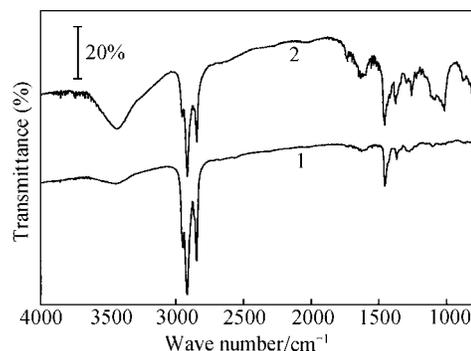


Fig. 2. FT-IR spectra of free 1-nonanethiol (1) and thiol-capped gold nanoparticles (2).

(iii) TEM characterization. A TEM image of the gold nanoparticles is shown in fig. 4, in which near spherical gold nanoparticles with the average size of $5.0 \pm$

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0.5 nm are clearly observed. From a further observation of fig. 4, it is found that the nanoparticles do not fuse into larger particles, but in the way of the lowest energy, forming the hexagonal close-packed structure, in which some defects have also been found. The average distance between nanoparticles is about 1 nm, corresponding to the length of one 1-nonanethiol molecule. This implies that the thiol molecules attached to the adjacent nanoparticles likely interpenetrate with each other due to the intermolecular interaction. Moreover, in TEM measurement, we found that the ordered array could be destroyed by higher operating voltage (>200 kV) and some nanoparticles even fused with each other. The smaller the nanoparticle, the faster the rate of fusion. The experimental result showed that higher electron irradiation would evaporate the attached organic ligands, leading to the development of bigger particles.

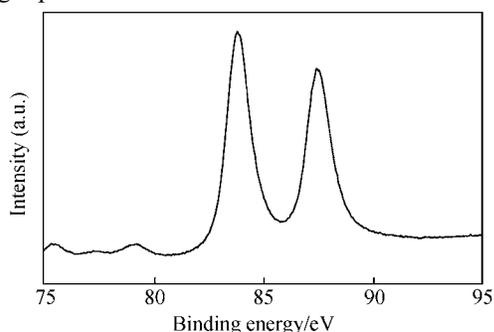


Fig. 3. XPS spectrum of gold nanoparticles in the region of Au4f.

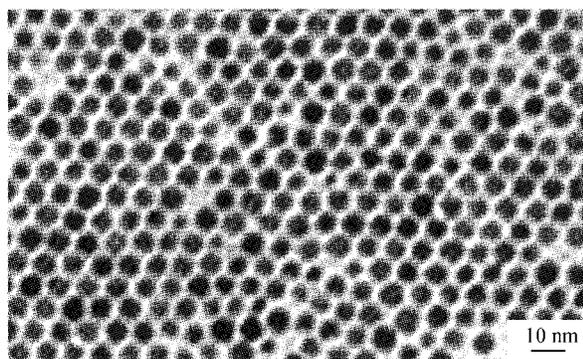


Fig. 4. A TEM image of gold nanoparticles.

3 Conclusions

In conclusion, we have used the method of liquid-liquid extraction to successfully synthesize the gold nanoparticles with the size of 5.0 ± 0.5 nm in the presence of a given amount of 1-nonanethiol molecules. After that, the step-by-step precipitation technique has been employed to narrow the distribution of obtained nanoparticles. At the same time, the techniques including UV-Vis, FT-IR, XPS have also been utilized to characterize the product. The results provide the direct evidence of the formation of the thiol-capped gold nanoparticles. Furthermore, after dissolving the particles into toluene and depositing the colloidal solution on carbon-coated copper grid, we found the formation of ordered hexagonal close-packed structure by TEM. We conclude that the gold nanoparticles can self-organize into ordered two-dimensional close-packed structure on the flat substrate after solvent evaporates under suitable concentration. The formation of the ordered structure is closely related to the thiol molecules attached on gold surfaces.

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