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Linear aggregation of gold nanoparticles in ethanol

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Abstract

Gold colloidal particles were found to spontaneously organize into linear aggregates in ethanol. The morphology of these aggregates was characterized with transmission electron microscope (TEM) and atomic force microscope (AFM), which revealed the quasi one-dimensional (1D) chain-like shape. Immobilization of these chains from solution onto substrate surface as well as the measurement of UV–visible extinction spectrum was performed to investigate the aggregation mechanism. The results presented the evidence for the existence of the nanoparticle chains in solution. Moreover, the kinetic aspects of the chain-like aggregation were detailed studied using UV–visible spectroscopy. It is believed that dipole–dipole interaction is the driving force of nanoparticle linear aggregation. This finding provides a novel strategy for the construction of quasi 1D structures, which are suitable for the fabrication of solid-state devices based on single-electron tunneling.
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1. Introduction

During the last decade, metal and semiconductor particles within the nanometer size range have attracted much research attention due to their unique electric, catalytic, and optical properties originating from the quantum-scale dimensions [1–3]. Therefore, synthesis of colloidal nanoparticles has evolved into an important field in science and technology by now. It has also been demonstrated that colloidal particles offer a promising route to the simple assembly of complex structures and can be used to create a variety of electronic and sensorial components [4,5].

The device application of nanoparticles requires suitable methods to organize them into well-defined structures. A great deal of research effort has been devoted to the development of new methodologies for the construction of nanoparticle assemblies. Particularly, various approaches, including self-assembly, electrophoretic deposition, Langmuir–Blodgett (LB) technique, and DNA hybridization, have been presented towards ordered two-dimensional (2D) nanoparticles arrays

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[6–9]. However, relatively less work has been done on assembling colloidal particles into one-dimensional (1D) arrangements. Generally, chain-like molecules or 1D channels were required to serve as templates to fabricate 1D colloid particle arrays [10–12]. Therefore, development of novel methods to fabricate 1D arrangements of nanoparticles has great significance in both applied and fundamental researches.

In our previous work, a novel strategy was presented to assemble nanometer-sized gold particles into quasi 1D chains by taking advantage of linear aggregation of colloidal nanoparticles dispersed in organic solvents [13]. It has also been found that changing the concentration of the solutions could modulate the length of the nanoparticle chains. The present work reports a complementary study of the linear aggregation of gold colloidal particles in ethanol. Herein, we focus on presenting evidence for the nanoparticle chains formation due to the linear aggregation in solutions rather than the effect of the volatilization of the solvent on a substrate surface. Both immobilization of these chains from solution onto substrate surface and the measurement of UV–visible extinction spectrum were performed to investigate the aggregation mechanism. Moreover, the kinetic aspects of the chain-like aggregation were detailed studied using UV–visible spectroscopy. In addition, a dipole model was presented to understand the mechanism of linear aggregation.

2. Experimental

2.1. Preparation of aqueous gold colloidal particles

Aqueous gold colloidal particles were prepared according to the method of Slot and Tsutsui, who utilized the reduction of chloroauric acid by trisodium citrate and tannic acid [14,15]. Briefly, 20 ml solution containing 4 ml 1% (w/v) trisodium citrate and 0.08 ml 1% tannic acid was rapidly added into 80 ml solution containing 1 ml 1% (w/v) chloroautic acid after all of them were heated to 60 °C. Then the mixed solution was boiled for about 10 min. Simultaneously, it was stirred acutely and continuously until the end of the

operation. The solution was subsequently cooled down to room temperature with chilled water. The average size of the gold colloidal particles synthesized in this way was ca. 10 nm in diameter.

2.2. Phase transfer of aqueous gold colloidal particles into organic solutions

In order to transfer the aqueous nanoparticles into the organic solvent, i.e. ethanol, the gold colloidal particles were dropped to the bottom of a test tube by centrifugal force so that the clear supernatant could be removed carefully. The centrifugal force was $32\,000 \times g$ lasting for 60 min at 4 °C. Afterwards, new pure ethanol solvent was injected into the tube and an ultrasonic process was carried out for 20 min with the test tube surrounded by chilled water. Changing the amount of injected ethanol could control the particle concentration.

2.3. Morphology characterization with TEM

The morphology of nanoparticle aggregates was characterized with transmission electron microscope (TEM). A minute drop of solution was cast onto a microgrid covered with a very thin carbon film for TEM (JEM-200CX, JEOL Co., JP) observation.

2.4. Immobilization of nanoaprticle aggregates on substrate surface

A clean polished silicon (100) wafer with 2 nm thick native oxide served as a substrate, which was pretreated in a 3:1 H_2SO_4:H_2O_2 solution at 80 °C for 10 min, a deionized water rinse and then blown dry with nitrogen. Afterwards, the substrate was immediately immersed in a 1 mM distilled toluene solution of bifunctional molecules [i.e. (3-mercaptopropyl)-triethoxysilane, MPTS] for 5 h. Subsequently, the sample was successively rinsed in toluene and acetone to remove residuals and blown dry with nitrogen. The nanoparticle aggregates were immobilized on the substrate by immersing it into the ethanol solution of colloidal particles for ∼ 24 h. Then, the sample was rinsed with tow ethanol baths, and dried with nitrogen

for atomic force microscope (AFM) characterization.

2.5. AFM characterization of the immobilized nanoparticle aggregates

The AFM image of immobilized nanoparticle aggregates was obtained with AFM (Nanoscope IIIa, Digital Instruments, Santa Barbara, CA) in tapping mode under ambious at room temperature, using a 130×130 μm^2 scanner and a silicon nitride tip attached to a cantilever with a spring constant of 0.025 N m^{-1}.

2.6. UV–visible absorption of colloidal solutions

The UV–visible extinction spectrum of the colloidal solution was obtained with a spectrophotometer (U-3410 spectrophotometer, Hitachi).

3. Results and discussion

3.1. TEM characterization of nanoparticle aggregates

Fig. 1 shows a typical TEM photograph of the morphology of nanoparticle aggregates deposited on a microgrid covered with a very thin carbon film. Gold nanoparticles are found to spontaneously assemble into pearl-necklace assemblies. It should be noted that no separate nanoparticle has been found on the microgrid, which reveals that gold colloidal particles prefer linear aggregation with each other to staying alone. As shown in Fig. 1, every gold nanoparticle is closely linked with others and no gaps can be distinguished between neighboring particles. This finding provides a novel strategy for the construction of quasi 1D arrangements of nanoparticles, which have potential application in the fabrication of single electron devices.

However, the formation of nanoparticle chains has two possible distinct mechanisms. One is due to the linear aggregation because of the dipole–dipole interaction in the solution. The other is of the aggregation on drying the dispersions at the substrate surface. Therefore, immobilization of
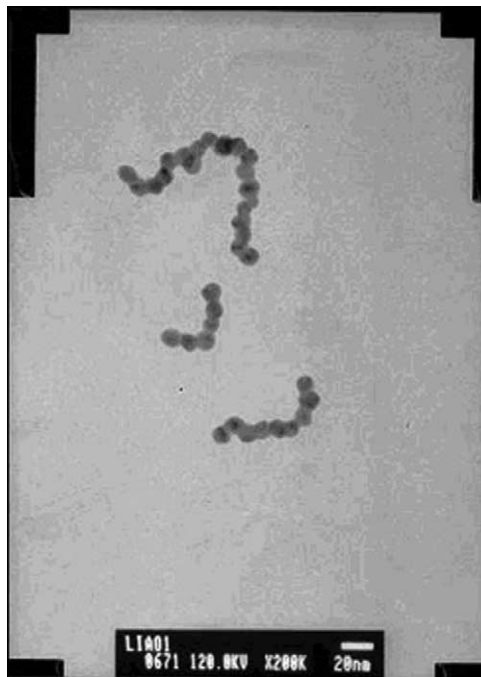

Fig. 1. A TEM photograph of chain-like nanoparticle aggregates deposited on a microgrid covered with a very thin carbon film.

nanoparticle aggregates from solution onto substrate surface and the measurement of the UV–visible extinction spectrum of the solution were performed in order to further explore the mechanism of the formation of nanoparticle chains.

3.2. AFM characterization of immobilized nanoparticle aggregates

Characterizing the morphology of nanoparticle aggregates immobilized directly from solution onto substrate surface should be a credible approach to demonstrate the state of nanoparticles in solution, because the morphology of nanoparticle aggregates can be preserved during the process. Fig. 2 shows the AFM image of nanoparticle chains immobilized on a silicon substrate with bifunctional molecules (MPTES). It clearly reveals the chain-like morphology of nanoparticle aggregates, which implies that the nanoparticle chains have formed in solution before deposition on the substrate surface.
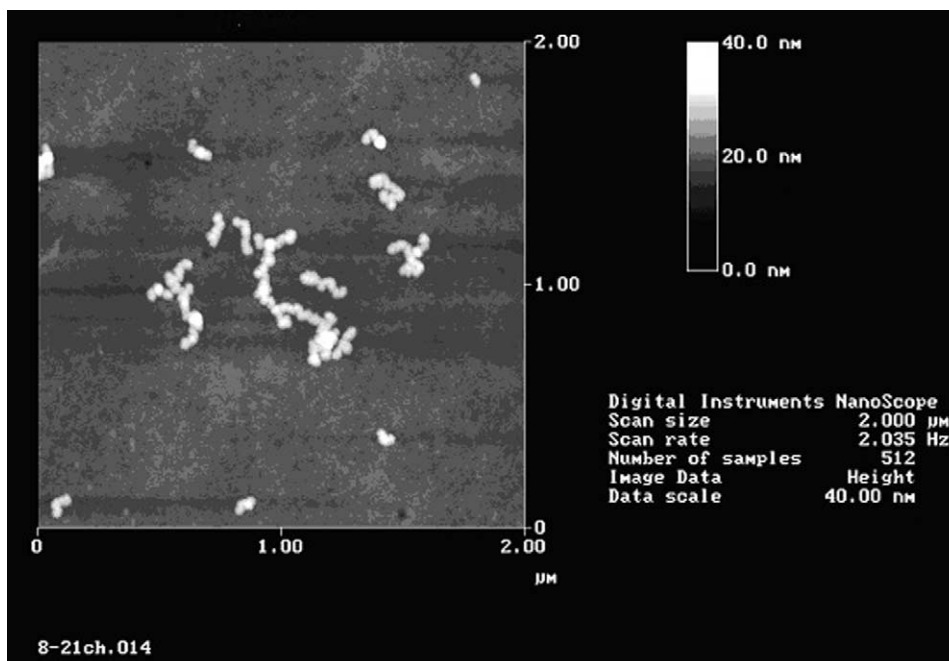
Fig. 2. An AFM image of the gold nanoparticle chains immobilized on oxide silicon surface with APTES molecules.

In addition, the morphology of immobilized nanoparticles from aqueous colloidal solution, in which the nanoparticles are well dispersed as known, was characterized by AFM after the same process. The results suggested that the nanoparticles were separated from each other and no nanoparticle chains were found on the substrates. Therefore, it can be concluded that the formation of the nanoparticle chains are indeed due to the linear aggregation in solutions rather than the effect of the volatilization of the solvent on a substrate surface.

3.3. UV–visible extinction spectrum of colloidal solution

Another efficient method to investigate the state of nanoparticles in solution is the measurement of UV–visible extinction spectrum because of the in situ property. For comparison, two different samples were prepared. Sample I was an aqueous solution of gold nanoparticles, which was demonstrated to be without aggregation. Sample II was a solution of gold nanoparticles dispersed in etha-

nol. The particle concentration of these two samples was controlled to be equal, i.e. 4.95×10^{15} ml^{-1}. The inserted AFM images in Fig. 3 show the states of nanoparticles deposited on silicon substrates from the two different solutions. It can be demonstrated that nanoparticles are isolated in sample I (in Fig. 3(a)) but chain-like aggregated in sample II (in Fig. 3(b)), which is consistent with the results of UV–visible extinction spectrum as following.

The UV–visible extinction spectrum of sample I, displayed in Fig. 3(a), presents a strong extinction band with a maximum at 520 nm, characteristic of the collective excitation of the free conduction band electrons of the particles know as the surface plasmon resonance. However, for sample II, a significant difference in extinction spectra was observed as shown in Fig. 3(b). A second absorption band appeared on the red side of the spectrum. Established theoretical descriptions of Mie scattering from similar small aggregate clusters suggested that the plasmon resonance absorption of the aggregates would have an additional long wavelength component in the
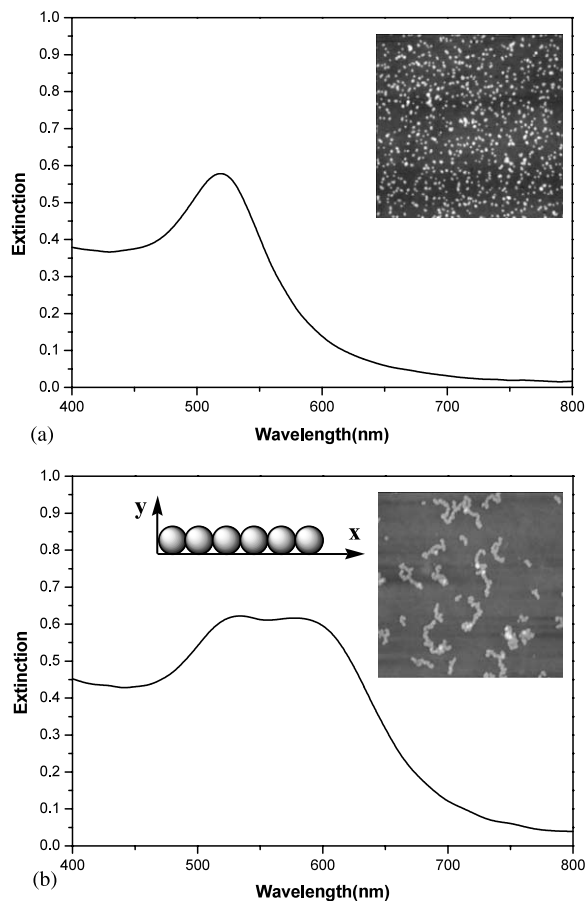
Fig. 3. Experimental extinction spectra of gold colloidal solutions for different states of dispersion: (a) well dispersed solution of aqueous gold colloidal particles; (b) linearly aggregated solution of gold colloidal particles dispersed in ethanol. The inserted AFM images (2 μm × 2 μm) correspond to the morphologies of nanoparticles deposited on silicon substrates from two different solutions, respectively. The up left insert in (b) showed the two resonant modes of a chain of gold nanoparticles.

optical absorption spectrum relative to the absorption from isolated nanoparticles dispersed in solutions [16]. According to this theory, this new long wavelength band is then associated with the longitudinal mode of the electronic plasma oscillation along the long axis of the gold nanoparticle chains. The two resonant modes are illustrated at the top left corner of Fig. 3(b), in which x direction represents the longitudinal mode and y direction represents the transverse mode. This result is consistent with the TEM photograph as shown

in Fig. 1, which recognizes the morphology of the aggregates to be a chain-like shape rather than a compact cluster of particles. In a word, the UV–visible extinction spectrum provides direct evidence for the formation of nanoparticle chains in solution through in situ measurement.

3.4. The kinetics of the chain-like aggregation

UV–visible extinction spectrum was also used to study the kinetics of the chain-like aggregation in order to investigate the evolvement of the nanoparticle chains in solution. After centrifugation, ethanol was infused into the tubes and an ultrasonic treatment was performed, subsequently. And then, the UV–visible extinction spectrum was recorded at appropriate intervals. We prepared two samples with different particle number concentrations, i.e. 1.98×10^{15} and 4.95×10^{15} ml^{-1}, respectively. Fig. 4 shows the UV–visible extinction spectrums of two samples recorded at different time. Litter difference can be distinguished from the UV–visible extinction spectrum curves recorded at 3 h, 1, 3 and 5 days for the sample with the particle number concentration of 1.98×10^{15} ml^{-1}, as shown in Fig. 4(a). The single extinction band in Fig. 4(a) indicates that the gold colloidal particles are well dispersed in this solution. Moreover, it is demonstrated that gold particles will not aggregate when the particle concentration of the solution is smaller than 1.98×10^{15} ml^{-1} in ethanol. This result was demonstrated by Huang et al. [15,17], who studied the dispersibility of gold nanoparticles in different solvents. On the contrary, gold colloidal particles will spontaneously reorganize into chain-like aggregates at the particle number concentration of 4.95×10^{15} ml^{-1}, which can be indeed reflected from Fig. 4(b). In detail, there is an additional extinction peak in each curve as shown in Fig. 4(b), which corresponds with the surface plasmon resonance along the long axis of the linear colloidal aggregates. During the time period from 3 h to 5 days, the second absorption band on the red side of the spectrum gets clearer and clearer. In addition, it is obvious that the right peak shifts to the red side, which indicates that the nanoparticle chains get longer and longer with the elapsing of the time.
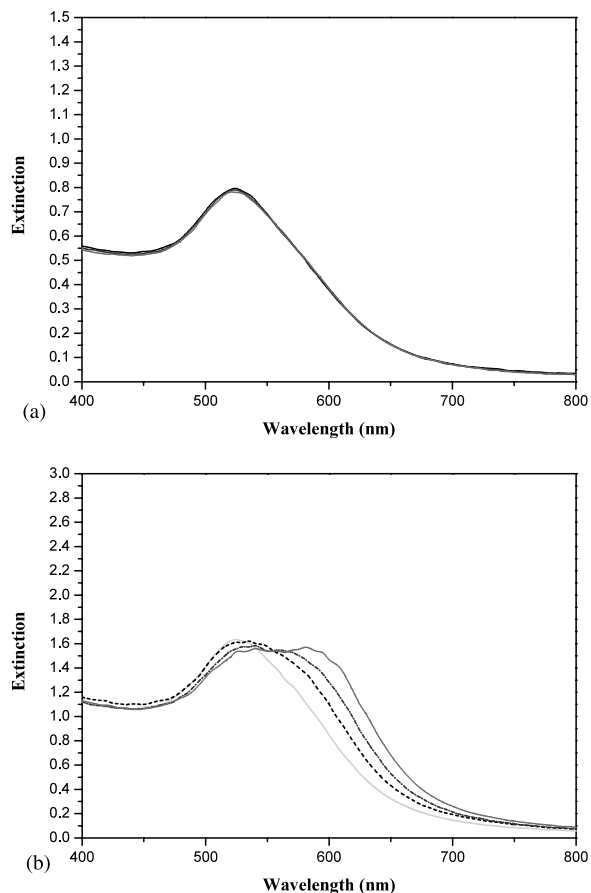
Fig. 4. Kinetics of chain-like aggregation of gold nanoparticles in ethanol with the particle concentration of 1.98×10^{15} ml^{-1} (a) and 4.95×10^{15} ml^{-1} (b). The recorded times corresponding with the solid lines, dashed lines, dash dot lines and short dot lines are 3 h, 1, 3 and 5 days, respectively.

Therefore, Fig. 4(b) in situ describes the growth of nanoparticle chains, which begin from a single gold nanoparticle and get to be chain-like aggregates.

3.5. A dipole model for the linear aggregation of gold colloidal particles dispersed in ethanol

As known to all, gold colloidal particles consist of an elemental gold core surrounded by a negative ionic double layer of charges, which prevent them from aggregating in solutions [18]. Account for this, strong dipole–dipole interaction is believed to be the driving force of the nanoparticle self-organization. Previous research suggested that linear assembly of colloidal particles might take place in the presence of an intrinsic or induced dipole moment once the dipole–dipole interaction was strong enough to overcome the thermal energy and the electrostatic repulsion between the colloidal particles [19–23].

In our experiments, the effect of transferring gold colloidal particles from water to ethanol was two-fold. First, the excess stabilizer, i.e. citrate ions, was removed from the solution. As the excess stabilizer would not precipitated by centrifugal force, they were removed with the get rid of the clear supernatant. Secondly, solvent molecules were changed from water to ethanol. It is known that the polarity of water molecules is stronger than that of ethanol molecules. Theoretically, the asymmetrical distribution of the charges on the particle surface can take place due to the coulomb interaction in both water and ethanol solutions. However, the strong polarity of the solvent molecules or the existence of excess stabilizer will counteract the effect of the asymmetrical distribution of the charges on the particle surfaces so that linear coagulation would be suppressed. Shipway et al. suggested that string-like aggregates would form in the case of low charge, which was deemed to be associated with the neutralization of the ζ potential and the creation of local cationic regions [24]. Similarly, we found that high concentration and low charge caused chain-like aggregation for gold nanoparticles in ethanol.

Fig. 5 shows the schematic illustration of the self-assembly process of gold nanoparticle chains. In ethanol, there exists coulombic repelling force between gold nanopartilces, which may lead the adsorbed charges to asymmetrically distribute on the surface of the particles. The asymmetrically distributed charges will generate the dipole moment. Because of the dipole–dipole interaction, two individual gold nanoparticles will assemble to be a dimer once the thermal energy and the columbic repulsion are suppressed. As the dimer comes into being, the integrative dipole moment will increase and then level off. The integrative dipole moment of a dimer will exert a stronger attractive force than an individual particle to another particle, therefore causing chain growth.
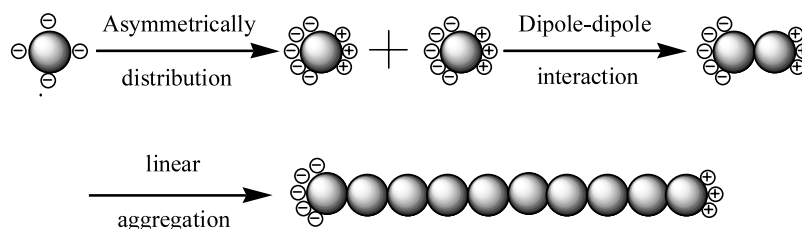
Fig. 5. The schematic illustration of the self-assembly process of gold nanoparticle chains based on the dipole assembly model.

Thus, pre-formed chains may serve as a template and facilitate the addition of free colloidal particles to the end of the chains via the dipole–dipole attraction.

4. Conclusions

In summary, linear aggregation of gold colloidal particles dispersed in ethanol was investigated by TEM, AFM and UV–visible extinction spectrum. The immobilization of nanoparticle aggregates and UV–visible extinction spectrum provide evidences for the formation of the nanoparticle chains in solution. The kinetics of linear aggregation was also studied with optical absorption spectrum. Moreover, a dipole model was presented to interpret the causation of the linear aggregation of gold colloidal particles in ethanol. This finding presents a novel strategy for the construction of quasi 1D nanoparticle arrangements, which have potential application for the fabrication of solid-state devices based on single-electron tunneling.

Acknowledgements

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