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A facile one-pot method to fabricate gold nanoparticle chains with dextran

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A biocompatible water-soluble dextran has been used for controllable one-dimensional assembly of gold nanoparticles via a one-pot method. Long gold nanoparticle chains with good dispersion in water could be easily obtained after adding dextran into the mixture of $HAuCl_4$ and sodium citrate. The measurements of scanning electron microscopy (SEM) and dynamic light scattering (DLS) confirmed the formation of gold nanoparticle chains. The morphology and dispersion properties of gold nanoparticle chains could be tuned by adjustment of the reagent ratio, stirring speed, and reaction time.

gold nanoparticle chains, self-assembly, dextran

1 Introduction

Nowadays, one-dimensional (1D) nanostructures such as wires, rods, belts, and tubes have received considerable concerns from both scientists and engineers because of their unusual opto-electronic and magnetic properties and their broaden applications in mesoscopic physics, nanoscale devices, medical diagnostics, sensors, biological imaging, and so on [1–8]. Except the direct synthesis of the 1D nanostructures, the controlled assembly of metallic nanoparticle into 1D nanostructure has also attracted more and more people's attentions because of its ability to tailor the surface plasmon properties [9–11]. However, reports on the assembly of nanoparticles into anisotropic 1D nanostructures are scarcely reported at the present time owing to the difficulties to prepare [12, 13].

Generally, the strategies for fabricating the 1D assembled nanostructures could be classified into two categories. One is template-free self-assembly method and the other one is linear-template method [2, 14, 15]. The template-free self-assembly method usually bases on the driving forces from magnetic dipole moments, electric-dipole moments, oriented aggregation, non-uniform stabilizer distributions and so on [2]. Alternatively, 1D nanostructures can be produced in presence of templates, including polyelectrolyte [16, 17], biomolecules (eg: phospholipids [18], DNA [19–22], peptide [13], proteins [23–25], polysaccharides [14, 26]), inorganic nanotubes [27, 28], nanoporous membrane [29] and so on. During these templates, biomolecules become more attractive because of their excellent biocompatibility. In addition, most of the reported methods need to modify the preformed nanoparticles with linker molecules before assembly procedures, which is time-consuming and complex. Therefore, it is desirable to develop simple methods to fabricate the biocompatible 1D assemblies of nanoparticles.

Recently, our group has successfully constructed one-pot green methods to fabricate 1D assemblies of gold nanoparticles in the presence of chitosan-ninhydrin conjugate and polyaldehyde dextran without involvement of any modification step [30, 31]. Herein, we further developed a new

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method for the preparation of gold nanoparticle chains in water using dextran, which is one-pot, simple, rapid and without the complex modification process or organic synthesis step. Moreover, because dextran has excellent biocompatability and it can be used as anticoagulation reagent, our prepared gold nanoparticle chains may have good promise in biomedical applications.

2 Experimental

2.1 Reagents

Dextran, with a molecular weight of 10000, was purchased from Amresco (America). Hydrogen tetrachloroaurate (III) tetrahydrate ($HAuCl_4 \cdot 3H_2O$) and sodium citrate was obtained from Sinopharm Group Chemical regent Co. Ltd. (Shanghai, China). Doubly deionized water (18.2 MΩ) was used throughout the experiment and all glasswares were cleaned using aqua fortis solution (HCl/HNO_3 in volume = 3:1) and subsequently rinsed with a copious amount of doubly deionized water.

2.2 Procedures

250 μL of 1% $HAuCl_4$ solution and 192 μL of 1.25×10^{-3} mol/L dextran were mixed with 30 mL of boiled nanopure water, and then 560 μL of 1% aqueous sodium citrate was added quickly into the mixture under vigorous magnetic stirring, this solution was boiled for 10 min under continual stirring before the next characterizations.

2.3 Characterization

The final products were examined by SEM, DLS and UV-vis spectroscopy. SEM was applied to investigate the size and morphology, and was carried out with an S-4800 scanning electron microscope (Hitachi, Tokyo, Japan) at an accelerating voltage of 20 kV. DLS was employed to measure the hydrodynamic diameter, and was completed on a Zetasizer Nano-ZS90 System (Malvern Inc.). UV-vis spectra were recorded on a Hitachi UV-3010 spectrophotometer (Hitachi, Tokyo, Japan) at room temperature. The images were made with a Nikon COOLPIX-4500 digital camera. The SZCL-3A magnetic stirrers (Henan, China) were used for the stirring and controlled the reaction temperature.

3 Result and discussion

The preparation of gold nanoparticle chains was very facile by adding dextran into the reaction mixture of $HAuCl_4$ and sodium citrate. The typical SEM images of gold nanoparticle chains obtained when the concentration of dextran was 8.0×10^{-6} mol/L and the molar ratio of $HAuCl_4$ to sodium citrate ($Na_3C_6H_5O_7$) of 1:3 were recorded as shown in Figure 1. It was found that there were obvious high branched chain structures of gold nanoparticles in the whole field of vision, and the length of the chain could reach several mi-

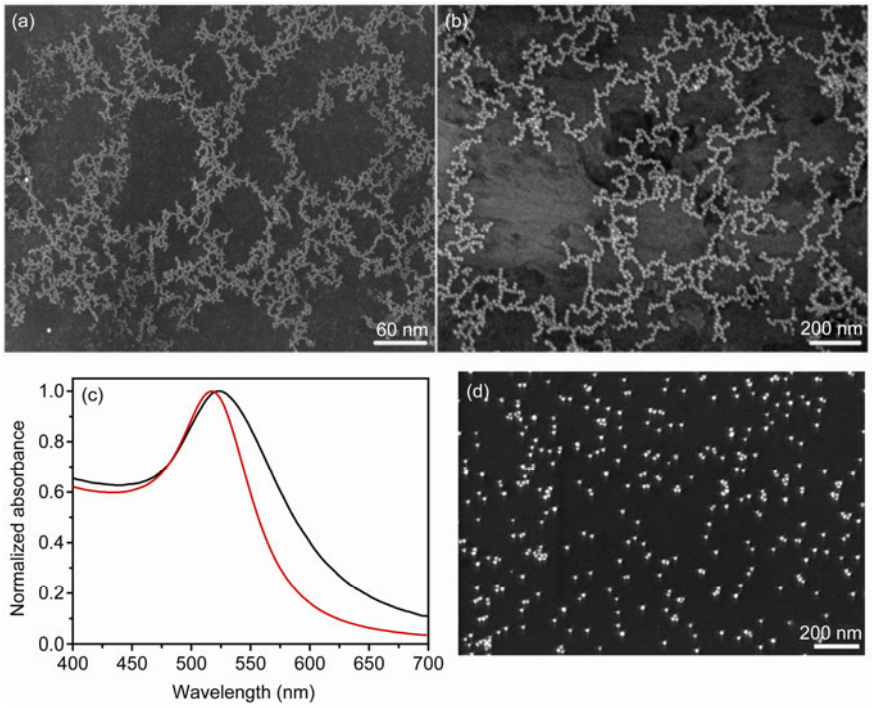

Figure 1 SEM images at low magnification (a) and high magnifications (b) of the gold nanoparticle chains. (c) the UV-vis spectra of the products in the absence (red) and presence (black) of dextran. (d) SEM image of gold nanoparticles in the absence of dextran. c_{HAuCl_4}, 2.0×10^{-4} mol/L; $c_{Na_3C_6H_5O_7}$, 6.0×10^{-4} mol/L; $c_{dextran}$, 8.0×10^{-6} mol/L.

crometers (Figure 1a), indicating that our one-pot method for the synthesis of gold nanoparticle chains was highly effective. In addition, the sizes of the gold nanoparticles on the chains were very uniform (Figure 1(b)). Control experiment showed that in the absence of dextran, most of the obtained products were monodispersed gold nanoparticles without any long chain structure (Figure 1(d)), confirming that it was dextran that induced the self-assembly of individual gold nanoparticles to chains. Moreover, the state of the 1D gold nanoparticle chains in solution was also compared with that of monodispersed gold nanoparticles by the UV-vis spectra, as shown in Figure 1(c). There was a distinct plasmon resonance absorption (PRA) peak at 518 nm in the absence of dextran, and it was red-shifted to 523 nm and significantly broadened in the presence of dextran, which was ascribed to the plasmon coupling of gold nanoparticles after the formation of 1D chains.

To confirm the gold nanoparticle chains were indeed formed in solution but not in the SEM sample preparation process by solvent drying, the dynamic light scattering measurements were carried out. It revealed that the hydrodynamic diameter of product obtained in the absence of dextran was 26.0 nm. However, in the presence of dextran, there were two size distribution regions. One was 21.1 nm, which is about 49%, and the other was 105.5 nm, about 51%, which could be attributed to the large assembled structure of gold nanoparticles (Figure 2). Although the actual sizes of gold nanoparticle chains can't be revealed by DLS data, these results unambiguously confirmed that the self-assembly of gold nanoparticles to chains was actually occurred in solution by dextran [30–32].

In order to study the mechanism of the formation of gold nanoparticle chains, the influences of various reaction conditions on the self-assembly of gold nanoparticle chains were investigated by optical spectroscopy and SEM. Firstly, considering the concentration of dextran might influence the assembly fashion of the reduced gold nanoparticles significantly, a series of experiments in which the molar ratio of the dextran to $HAuCl_4$ was systematically varied from 2.00:1 to 0.01:1 were carried out. As shown in Figure 3, with the decrease of molar ratio (dextran/$HAuCl_4$), the PRA peaks were gradually blue shifted from 530 nm to 520 nm and the half-widths of the peaks were became narrower, and accompanied with the color of the solution of the nanoparticle chains changed from dark blue to red. The different PRA and color of products should be attributed to the different degree of nanoparticle aggregation in solution (see the SEM images in Figure 3). Only when the molar ratio (dextran/$HAuCl_4$) was about 0.04:1, we could obtain the homogeneous size distribution of gold nanoparticles chains. If the molar ratio (dextran/$HAuCl_4$) is too high, the increased number of the hydroxyl of dextran could promote the quick connection of gold nanoparticles and cause random aggregation. Contrarily, when the molar ratio is too low, there are not enough hydroxyls to link the gold nanoparticles and induce the formation of many dissociative gold nanoparticles [12].

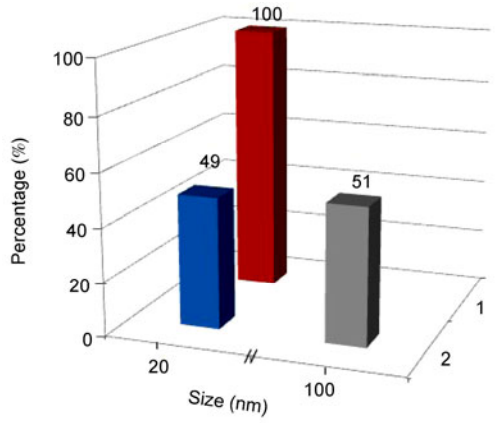

Figure 2 The size distributions and their corresponding percentages of the as-prepared gold nanoparticles in the absence (1) and presence (2) of dextran as measured by dynamic light scattering. c_{HAuCl_4}, 2.0×10^{-4} mol/L; $c_{Na_3C_6H_5O_7}$, 6.0×10^{-4} mol/L; $c_{dextran}$, 8.0×10^{-6} mol/L.

In addition, we also investigated the influence of the molar ratio of the $HAuCl_4$ to sodium citrate. It was found that the PRA peak shifted from 538 to 520 nm and the color changed from mauve to red with increasing the concentration of $Na_3C_6H_5O_7$. From the SEM images, we found that the morphology of the products was ideal when the molar ratio ($HAuCl_4$/$Na_3C_6H_5O_7$) was about 1:3 (Figure 4). When the ratio was lower than 1:3, big aggregates could be observed. However, when the ratio was higher than 1:3, there were a lot of dissociative gold nanoparticles. In our experiment, sodium citrate was used as reducing agent. It was hypothesized that when the concentration of sodium citrate was not enough, it couldn't reduce $HAuCl_4$ totally. Thus, the insufficient binding of gold nanoparticles with the hydroxyl of dextran might induce the aggregation of the gold nanopartcles chains. And if the concentration of sodium citrate was too high, the gold nanoparticles couldn't assemble on dextran owing to too many nanoparticles, leading to the existence of the dissociative gold nanoparticles.

Stirring could promote the uniform of reaction solution and prevent nanoparticles from part aggregation. In order to get uniform and steady products, keeping the experimental conditions and the other components fixed, we studied the influence of different stirring speed on the morphology of gold nanoparticle chains. As shown in Figure 5, when the stirring speed was moderate (1080 r/min), the newly admitted reaction reagent could quickly disperse in solution and obtain homogeneous size distribution of gold nanoparticle chains. Contrarily, if the stirring speed was too low, the products were nonuniform and had certain aggregations. In addition, if the stirring speed was increased to 1800 r/min, we couldn't get the gold nanoparticle chains but round shapes. Maybe the stirring force is too high to form the long gold nanoparticle chains. And the short gold nanoparticle chains may self-assembly to form the round structure of

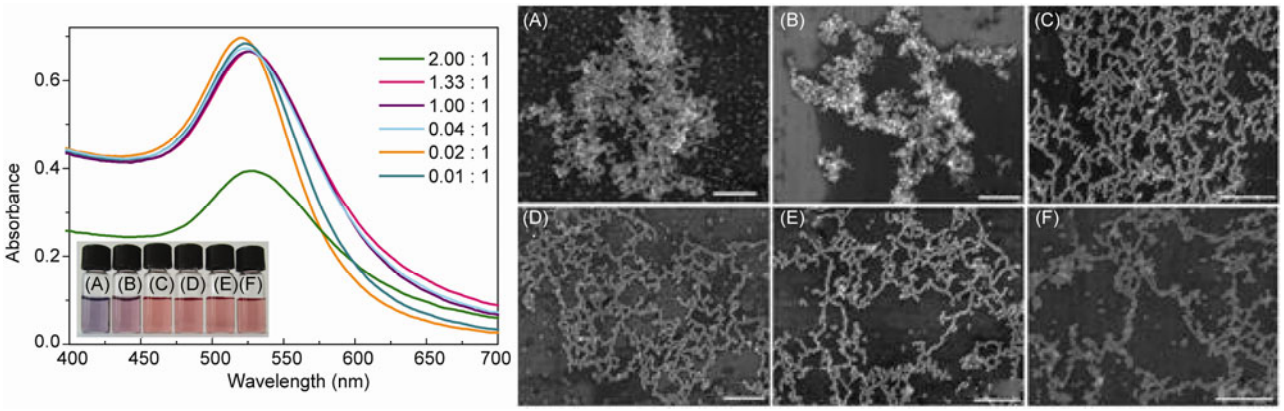

Figure 3 UV-vis spectra (tleft) and SEM images (right) of samples prepared with various dextran to $HAuCl_4$ molar ratios. The inset photograph in left picture shows the color change of the samples. From A to F in the inset photograph in UV-vis spectra and SEM images, the molar ratio (dextran to $HAuCl_4$) is: 2.00:1; 1.33:1; 1.00:1; 0.04:1; 0.02:1; 0.01:1. c_{HAuCl_4}, 2.0×10^{-4} mol/L; $c_{Na_3C_6H_5O_7}$, 6.0×10^{-4} mol/L.

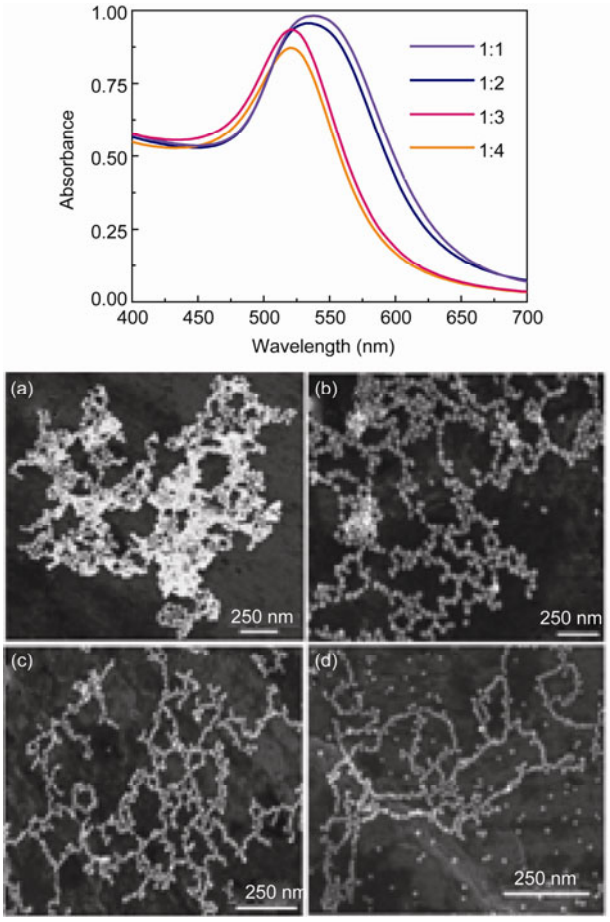

Figure 4 UV-vis spectra (top) and SEM images (bottom) of samples prepared with various $HAuCl_4$ to $Na_3C_6H_5O_7$ molar ratios. The inset photograph in left picture shows the color change of the samples. From (a) to (d) in the inset photograph in UV-vis spectra and SEM images: the molar ratio ($HAuCl_4$ to $Na_3C_6H_5O_7$) is: 1:1; 1:2; 1:3; 1:4. c_{HAuCl_4}, 2.0×10^{-4} mol/L; $c_{dextran}$, 8.0×10^{-6} mol/L.

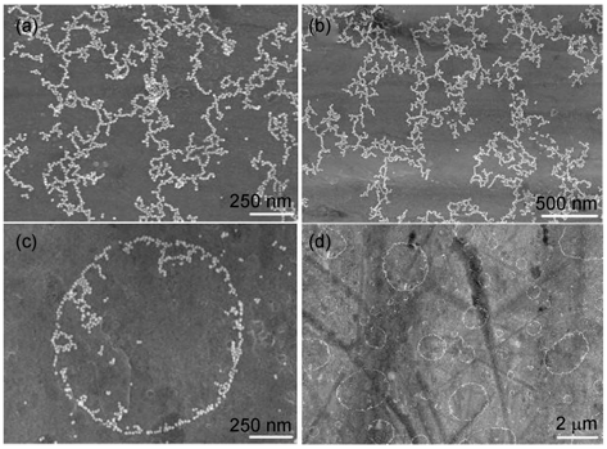

Figure 5 The influence of different stirring speed on the morphology of gold nanoparticle chains. Speed: (a) and (b), 1080 r/min; (c) and (d), 1800 r/min. c_{HAuCl_4}, 2.0×10^{-4} mol/L; $c_{Na_3C_6H_5O_7}$, 6.0×10^{-4} mol/L; $c_{dextran}$, 8.0×10^{-6} mol/L.

gold nanoparticles by strong centripetal force.

In order to elucidate the mechanism of gold nanoparticle chains formation, we further studied the time-dependent optical spectra and SEM images of samples at the optimum conditions. From the PRA in Figure 6, we can see that the PRA shifted to shorter wavelength and the absorbance gradually increased with the increased reaction time, which didn't change any more until 10 min later. At the same time, the SEM images also revealed the cause for the change of the PRA properties. At the first 2 min, gold nanoparticles were produced and they started to aggregate within a few of particles; in the second 2 min, the degree of aggregation increased; between 6 and 8 min, nascent chain-like nanoparticles appeared, and the length of chains further increased and dispersed; after 10 min, a great deal of gold nanoparticle chains were obviously observed, and remained almost unchanged.

Dextran as a reductive polysaccharide, is composed of D-glucose with alpha-1, 6-linkages in backbone chain and alpha-1, 3-linkages in branched chain. It has abundant hydroxyl and ether groups that could complex with metal ions, which makes the metal ions concentrate round the dextran

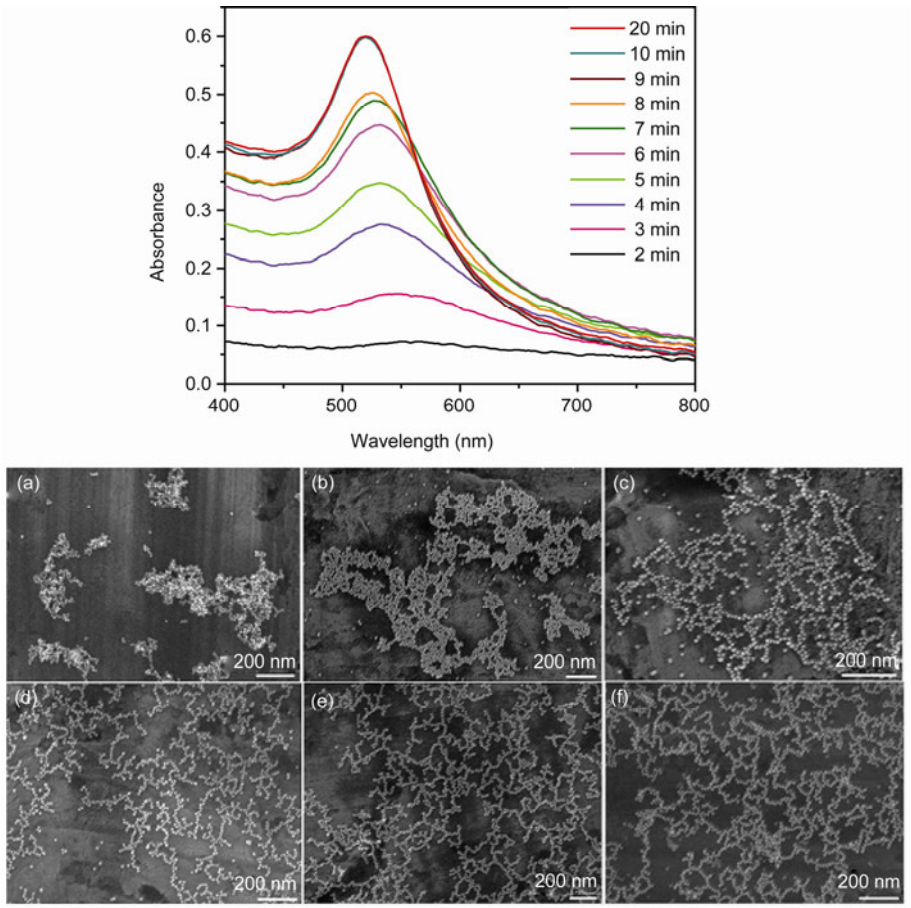

Figure 6 UV-vis spectra (top) and SEM images (bottom) of gold nanoparticle chains at different reaction time. In the SEM images, the reaction time from (a) to (f) is 2 min, 4 min, 6 min, 8 min, 10 min and 20 min, respectively. c_{HAuCl_4}, 2.0×10^{-4} mol/L; $c_{Na_3C_6H_5O_7}$, 6.0×10^{-4} mol/L; $c_{dextran}$, 8.0×10^{-6} mol/L.

and could control the growth of nanoparticles in the micro-space of dextran [26]. Therefore, we suppose the formation of the gold nanoparticle chains in our method involves in three main processes: first, $HAuCl_4$ interacts with the hydroxyl groups of dextran by complexation to form Au/dextran complex [33, 34]. Then, $HAuCl_4$ is reduced by sodium citrate to produce gold nanoparticles. Third, because gold nanoparticles have polyhedral nanocrystal structure [35, 36], dextran might cap different crystal faces of gold nanoparticles, and thus gold nanoparticles can assemble to the chain-like structure through dipole-dipole interaction between the uncovered faces [30, 31].

4 Conclusion

We have successfully utilized dextran to quickly prepare high dispersion gold nanoparticle chains. UV-vis spectra, SEM images and dynamic light scattering study allowed us to identify the existence of gold nanoparticle chains in solution. Importantly, through such a preparation procedure, we found that the morphology and the dispersion property of the gold nanoparticle chains were affected by the reagent ratio, stirring speed and reaction time. The new self-assembly method is one-pot, simple, rapid, and without any modification step. Based on the different binding capacity of dextran to glucose or concanavalin A, these gold nanoparticle chains could be potentially applied for colorimetric detection of glucose without any coupling process. In addition, the assembled gold nanoparticle chains might be very useful in the biochemical study and imaging because of the good biocompatibility of dextran and the strong plasmon coupled by the assembled gold nanoparticles.

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