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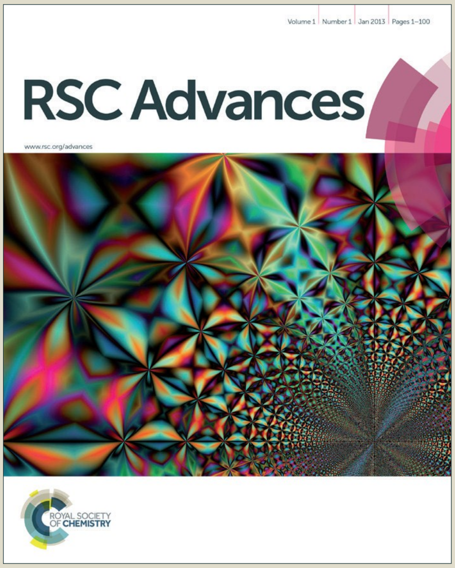

ROYAL SOCIETY OF CHEMISTRY

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Journal Name

ARTICLE

Tris Base Assisted Synthesis of Monodispersed Citrate-capped Gold Nanospheres with Tunable Size †

Received 00th May 2016,
Accepted 00th June 2016

DOI: 10.1039/x0xx00000x

www.rsc.org/

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We demonstrate a simple and effective method to obtain highly pure and monodispersed spherical gold nanoparticles (AuNPs) with a narrow size distribution (RSD ~ 4-7%) in aqueous medium. The synthetic strategy involves the addition of $HAuCl_4$ in preheated sodium citrate (SC) solution followed by addition of tris base (TB) which simultaneously acts as stabilizer, mild reducing agent and pH-mediator. A significant improvement in the uniformity and size tenability of the Au nanospheres has been observed by using subtle amounts of TB in contrast to the conventional way of using only SC. It is their synergistic effect that controls the amount of nuclei by heating SC, and then controlling the rate of nucleation and growth by introducing TB, which successfully produced particles with uniform morphology. Notably, $HAuCl_4$ solution was added in multiple steps to significantly improve the quality of the NPs in comparison to the addition of whole $HAuCl_4$ solution at one time. In this way, we have successfully developed spherical NPs with sizes ranging from 20 to 115 nm, which efficiently improve the classical Turkevich/Frens method with respect to the reproducibility and uniformity of the NP's size and shape. A representative set of NPs was controlled to spontaneously self-assemble into a monolayer assembly at a hexane/water interface. This will allow them to be used as a promising and outstanding candidate for application in the field of spectroscopy, catalysis, optoelectronic nanodevices and biosensors.

1. Introduction

Growth of monodispersed nanocrystals (NCs) with tunable sizes is highly important for both fundamental research and technological applications. From this perspective, gold nano-particles (AuNPs) are the most widely used and studied NCs because of their tunable surface plasmon resonance (SPR) peaks, which are precisely correlated with the NC's size and shape,[1-15] guide a wide range of applications including biological labeling, imaging, catalysis, electronic properties, and medical diagnostics. The optimization of these applications requires a high mono-dispersity both in shape and size together with the choice of the stabilizing agent. In this direction, several wet chemical routes have been established and out of these Turkevich method,[16] later slightly refined by Frens,[17] is believed to be the most popular because of its easy and reproducible protocol involving nontoxic citrate ions simultaneously used as reducing and stabilizing agent.[18] Despite the method allowing control of the NP's sizes ranging from 10 to 150 nm, uniformity in shape and size, especially for bigger (> 40 nm)[17] NPs, is poor. Several modification to this method have been put forward to improve their uniformity, however, it is still very difficult to achieve uniformity in shape and size. An alternative way to acquire monodispersed NPs has been evolved by using seeded growth approach.[19] However, this approach involves the usage of long chain polymer/surfactants, e.g. cetyltrimethyl-ammonium bromide (CTAB),[20-22] Pluronics L-31/F-68,[23] sodium acrylate[24] etc, which have strong affinity towards Au surfaces and thus restrict concomitant functionalization for biological applications. Quality of the NPs obtained in non-aqueous medium could be better than that in aqueous medium; nevertheless, non-aqueous medium stands far from the ideal green approach. To date, several other approaches have been adopted for synthesis of Au nanospheres, such as Brust-Schiffrin method,[25] growth and etching method,[26] laser irradiation method[27] etc. However, most of these nanospheres have limitations either in uniformity in size/shape or further modification for biological application. Therefore, it still keeps challenge to obtain aqueous dispersion of highly uniform Au nanospheres with suitable stabilizing agents for further surface modification.

From previous studies, it is believed that citrate-capped NPs will be the ideal particle for biological application if we could modify the method to obtain higher mono-dispersity. Moreover, negatively charged surface of citrate-capped particles will give better privilege to restrict the cell toxicity over the positively charged capping agents. This motivated us to develop citrate-stabilized AuNPs with high uniformity in size and shape. Key role to obtain AuNPs in a citrate-reduction method has been thought to be the moderately fast nucleation process followed by diffusive growth. Several experimental conditions may induce the nucleation/growth process; for example, the concentration of Au-precursor, sodium citrate, other stabilizing or co-reducing agents, temperature, heating time and pH of the solution. Therefore, an optimized condition is needed

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through a balance between the nucleation and growth process to obtain highly monodispersed particles.

In this work, we report a very simple method to prepare mono-dispersed citrate-capped spherical AuNPs with sizes ranging from 20 to 115 nm in presence of tris base (TB). TB used in the reaction served as stabilizer, reducing agent and pH-mediator for the synthesis of AuNPs. This approach not only optimized the traditional Turkevich/Frens method acquiring more uniformity of the NPs with very narrow size distribution but also improved the seeded growth method possessing better quality with very uniform morphology. Conspicuously, the NPs own better stability with tunable quantity of negative ions and pH value, which have promising applications in the fields of spectroscopy, catalysis, and biology. Moreover, these citrate-stabilized AuNPs can be spontaneously assembled into a well-defined monolayer at the interface, which holds great prospect for optoelectronic nano-devices and biosensors.

2. Experimental Section

2.1. Materials and instruments

Chloroauric acid ($HAuCl_4·3H_2O$, 99.9%), sodium citrate (trisodium citrate dihydrate), tris base were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai). Ultrapure water was used in all experiments. All other reagents were used as purchased without further purification.

The morphologies of AuNPs were observed by an S-4800 (Hitachi, Japan) field emission scanning electron microscope (SEM) at an acceleration voltage of 8 kV. Transmission electron microscope (TEM) was performed on a JEOL JEM 2100 electron microscope operating at 2.0 kV. UV-vis absorption spectra were recorded by virtue of TU-1810 UV-vis spectrophotometer provided by Purkinje General Instrument Co. Ltd. Zeta potential measurements were made by Malvern Instruments Co. Ltd.

2.2. Synthesis of AuNPs

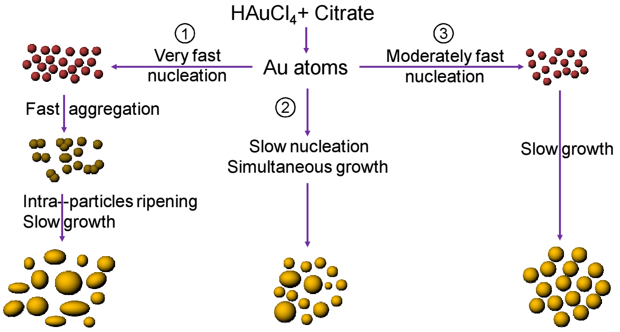
The SC (10 mL, 33 mM) solution was added into 140 mL of deionized water with continuous boiling and vigorous stirring. Then, $HAuCl_4$ (1 mL, 25 mM) and TB (5 mL, 0.1 M) were sequentially added (time delay 1 min) keeping the oil bath at a certain temperature (further details see Table S1 and S2). The representative color of the solution changed from colorless to light pink, rose-red, and fuchsine within just a few minutes. After 30 min of continuous heating, the temperature of the oil bath was maintained at 120 ^{o}C. Then, 1 mL of $HAuCl_4$ (25 mM) was injected for additional two times (interval of 30 min) to improve the shape and size uniformity of the particles (further details in Fig. S4B; Supporting Information). By changing the time or temperature of heating SC (further details in Table S1 and S2; Supporting Information), it becomes possible to acquire different particle sizes.

2.3. Preparation of AuNPs Self-Assembled into Monolayer

Self-assembly of AuNPs at a hexane/water interface was prepared according to traditional method, with small modifications.[28] In detail, 30 mL of an aqueous gold NP colloid was transferred to a culture dish (9 cm in diameter), and 10 mL of hexane was added to the top of the colloid solution surface to form an immiscible water/hexane interface. 0.25 µL of 1-dodecanethiol was then added to the hexane layer, and there was no observable change in the colloid solution. 30 mL of ethanol was then added to the surface of the water/hexane layers, which led to AuNPs trapping at the interface.

3. Results and Discussion.

The synthesis of citrate-stabilized AuNPs via the reduction of $HAuCl_4$ by sodium citrate was first developed by Turkevich et al. and later refined by Frens.[17] Although smaller particles (20-40 nm) obtained from this method are quite uniform, relatively larger particles (>40 nm) is virtually very poor in quality (size and size distribution) having nonuniform/irregular shaped particles, such as rod-like, triangles and hexagon, showing in Fig. 1A. This can be explained by fact that larger particles were formed in presence of lower citrate concentration maintaining a lower pH range (~4-6.5), which insists a very fast nucleation rate followed by a fast random attachment (aggregation) step and finally intra-particle ripening/growth process to form the final shape of the NPs (Scheme 1; path 1).[18] Extremely fast nucleation rate creates enormous number of nuclei in a very short time and those highly reactive nuclei encounter each-other to form random attachment, which is responsible for the appearance of non-uniform particles (Scheme 1; path 1). Again, very slow nucleation rate will simultaneously initiate the growth process and generate non-uniform particles (Scheme 1; path 2). In contrary, a moderately faster nucleation followed by the slower growth process may produce highly uniform particles (Scheme 1; path 3). This moderate nucleation rate was achieved by Ji et al[18] using higher pH range (~6.5-8) and successfully synthesized highly uniform particle up to 40 nm. However, they could not produce much larger particles with high uniformity. This might due to the fact that lower amounts of citrate, even at higher pH with moderate nucleation speed, was not able to stabilize the nuclei well and thus some aggregation occurred to produce non-uniform particles. To be freed from these problems, seeded growth method by the temporal separation of nucleation and growth processes was adopted to control the uniformity size and shape. However, this involves the use of CTAB or other strongly attached surfactants, which create difficulties for further application as described in the introduction section. Nevertheless, a small amount of other morphologies were still existed in the final products (Fig. 1B),[29] which strongly demands for a better approach. We aimed to solve



Scheme 1. Schematic representation of the reaction pathways for the synthesis of AuNPs.

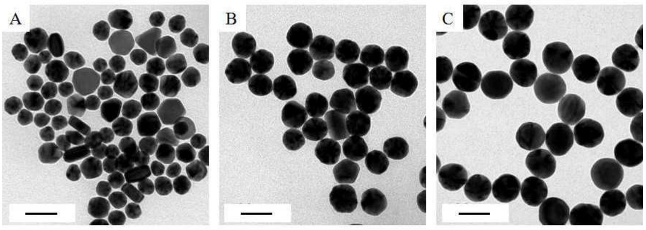


Fig. 1. Representative TEM images of AuNPs using different methods: Turkevich/Frens method (A) and seeded growth method (B) and TB assisted method (C). The scale bars represent 50 nm.

the difficulties by using additional stabilizing agent (TB) with citrate ion and guide to follow path 3 of Scheme 1. TB being a weak base also helped to increase the pH and retain the nucleation rate at moderately faster speed while maintaining the sufficient stabilizing capacity to be freed from the aggregation step. It is worth noting that TB has also mild reducing property due to the presence of ammine group which would further help in the growth process.

To identify the three roles of TB in the synthesis of mono-dispersed AuNPs, some experiments were designed. Firstly, for the role of reducing agent, TB was used as single reducing agent to synthesize AuNPs. Polydispersed AuNPs with the sizes from 200 to 550 nm are achieved (Fig. S5E). Kinetic data are provided to elucidate the mild reducing behavior of TB during the reaction. The reaction kinetic was studied by continuously recording absorption spectra of reactive solution (Fig. S5). It was found that the reactions using SC or TB as single reducing agent were completed after 30 min (Fig. S5A) or 60 min (Fig. S5B), respectively. The reducing ability of TB is lower than SC, exhibiting mild reducing behavior during the synthesis of AuNPs. On the other hand, using both of SC and TB as double reducing agent lead to a higher reaction rate, and the reaction was completed after 5 min (Fig. S5C). Secondly, for the role of stabilizer, Zeta potential was used to analyze the potential of AuNPs synthesized by only SC or SC/TB (Fig. S6). The additive amount of SC and the sizes of AuNPs are kept the same in the raction. It was found the surface potential of AuNPs synthesized by SC/TB is about -34.6 mV, which is higher obviously than that of AuNPs (-43.1 mV) produced by only SC. These results indicated the existence of positive-charged TB on the surface of AuNPs. Thirdly, for the role of pH-mediator, TB provided alkaline condition (pH>7.5) in our SC/TB-assisted reaction while single SC assistant reduction system had acidic surrounding (pH<6). The pH value in the SC/TB reaction of different sizes of AuNPs are detected and listed in Table S1 and Table S2.

Prior to addition of $HAuCl_4$ and TB, we first boiled SC solution to generate acetonedicarboxylate (ADC) species, which is actually considered to be the main active component for the reduction process.[30] Then $HAuCl_4$ and TB (time delay 1 min) was added into the reaction mixture and continued heating for another 30 min. After that, $HAuCl_4$ solution was injected into the reaction mixture in two consecutive steps (interval of 30 min), which significantly enhances the quality of the NPs with more uniform size and shape as shown in Fig. 1C. One-step addition of $HAuCl_4$ leads to the sudden increasing of Au^{3+} concentration, which results in the heterogeneous nucleation of Au atoms and further poly-dispersion of Au nuclei (path 1, Scheme 1). On the other hand, the addition of $HAuCl_4$ in consecutive steps allows Au atom form into uniform nuclei in a moderate rate and subsequent homogeneous growth of AuNPs, achieving monodispersed nanoparticles in the TB-assisted system (path 3, Scheme 1). The UV-vis spectra of AuNPs (Fig. 2) strongly support the above result based on correlation the integral area or peak width at a half height of curved lines.

In our experiment, the synthesis of monodispersed AuNPs with average size ranging from 19 to 64 nm (Fig. 3) has been achieved by solely controlling the time of heating SC. Shorter heating time generates lesser amounts of ADC,[31] which is responsible for lesser number of nuclei to obtain larger sized particles. If continuously increasing the reaction time to 1h, the size of AuNPs was kept at 19 nm and did not change any more. In addition, polydispersed AuNPs with 64 nm were produced when the reaction was reduced to 1 min (Fig. S7A). TB provided alkaline condition (pH>7.5) in our SC/TB-assisted reaction while single SC assistant reduction system had acidic surrounding (pH<6), which might helped to produce uniform particles as suggested by Ji et al.[18] The pH value in the SC/TB reaction of different sizes of AuNPs are detected and listed in Table S1 and Table S2. Temperature also played an important role not only in initial formation of ADC that greatly determined the final sizes of NPs by formation of ADC-Au^{+}, but also in the reduction rate of Au^{3+} ions and the subsequent growth rates of AuNPs.[32] Lower temperature generate lesser amounts of ADC, which is responsible for lesser number of nuclei to obtain larger sized particles (Fig. 4 and Table S2; Supporting Information). By controlling the temperature of the bath, we successfully synthesized particles with size ranging from 70 to 115 nm (Fig. 4) keeping the pH ~8.2-8.3 which helped to maintain the uniformity of the particles. AuNPs showed improved mono-dispersity (RSD of 4~7%; Fig. S1) compared to the conventional methods. When the temperature is in the range <100 °C and >140 °C, polydispersed AuNPs with similar sizes were produced (Fig. S7B). In order to ensure uniformity of NPs, changing simultaneously the reaction time and temperature within some

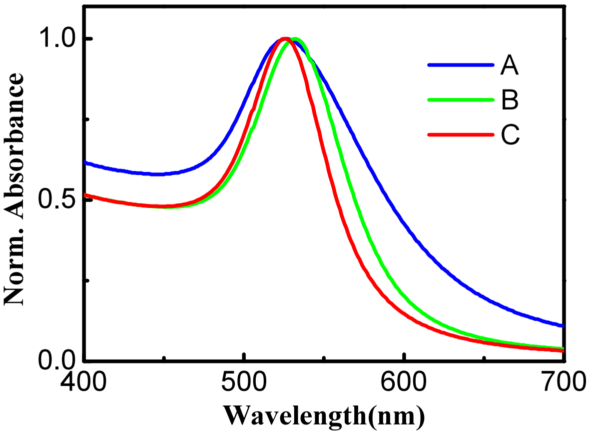


Fig. 2. UV-vis absorption spectra of AuNPs with different methods corresponding to the sample A-C in Fig. 1, respectively.

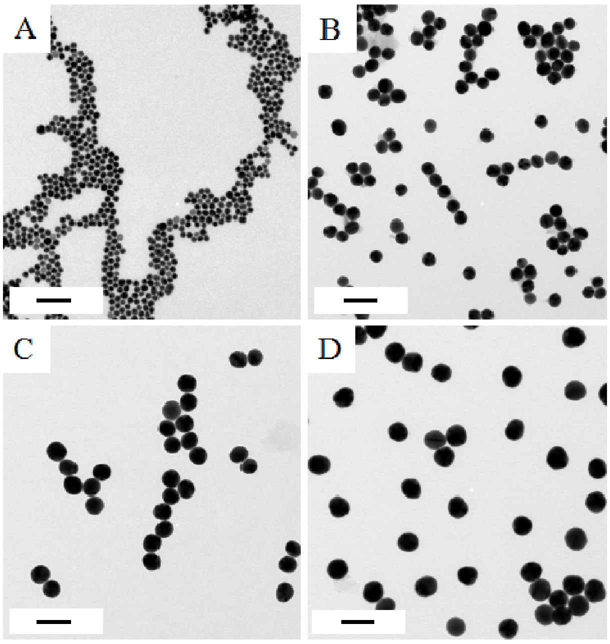


Fig. 3. Representative TEM images of AuNPs obtained by using TB assisted method with the time of heating SC for ~50, 40, 20, 10 min. The particle size increases from 19 to 39, 49, and 64 nm as shown in A-D, respectively. The scale bars represent 100 nm.

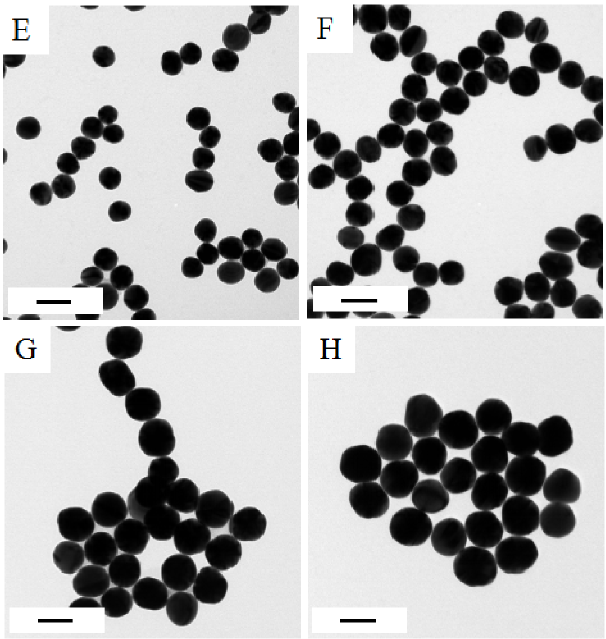


Fig. 4. Representative TEM images of AuNPs obtained by using TB assisted method with the temperature (at oil bath) of heating SC at ~140, 130, 120, 110 °C (actual temperature in the solution corresponding to 96, 91, 87, 80 °C, respectively). The particle size increases from 70 to 82, 105, and 115 nm as shown in E-H, respectively. The scale bars represent 100 nm.

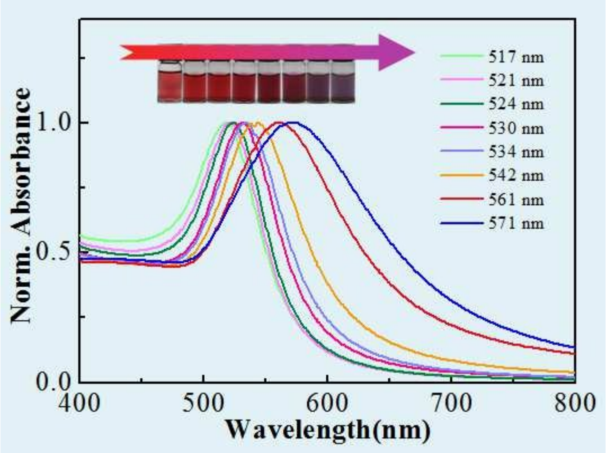


Fig. 5. UV-vis spectra of AuNPs with the diameters ranging from 19 to 115 nm corresponding to the sample A-H in Fig. 3 and Fig. 4. Representative colors of AuNPs with different sizes changed from red to purple as showing in the inset.

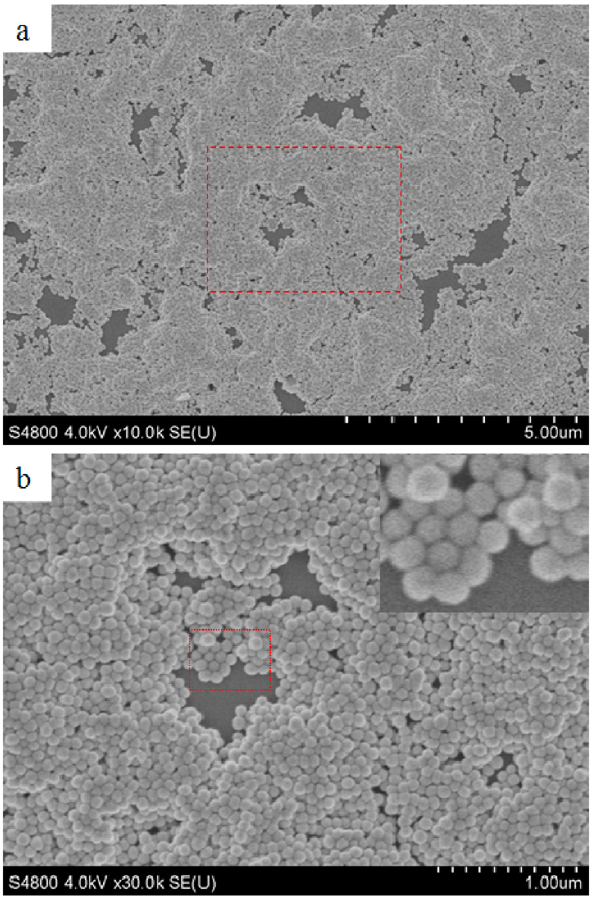


Fig. 6. SEM images of AuNPs using TB assisted method with diameters of 105 nm.

extent is beneficial to gain uniform NPs with large size.

Optical properties of these NPs were studied and given in Fig. 5. UV-visible spectra and corresponding colors of AuNPs provide a convictive description to the consequence as shown in the Fig. 5, where we observed a gradual red shifting of SPR peaks with increasing size of the NPs (Table S1 and S2; Supporting Information). The relationship between the size of AuNPs and their SPR peaks are shown in Fig. S2 in Supporting Information. When the SPR peak shifts from 517 nm to 571 nm, the sizes of AuNPs increase from 19 nm to 115 nm, which agrees with the variation tendency in previous work. There are some deviations in the specific calculated sizes compared with reported work. It is considered that the differences arise from the inconsistent dielectric constant resulting from different ligands on surface of AuNPs.[33, 34] To visualize the uniformity, a representative lower magnified SEM images from the samples with average size 105 nm (corresponding to Fig. 4G) is shown in Fig. 6, which hardly shows any non-spherical byproducts. pH of the solution was slightly higher for larger particles. This can be explained by the fact that, for lager particles, lesser amounts of SC/TB will be utilized for stabilization compared to smaller particles due to the lower specific surface area for bigger particles. This will provide more number of free SC/TB to be dissociated in the aqueous medium to increase the pH in the solution. Zeta potential of the particles was varied with the size of the particles (Fig. S3; Supporting Information).

The frequency of $HAuCl_4$ injected into the growth solution is another important factor influencing the final size and shape distribution. We found that the uniformity in shape obtained by adding the requisite $HAuCl_4$ solution in three consecutive steps was significantly improved in comparison to the addition of whole $HAuCl_4$ solution once (Fig. S4; Supporting Information). The NPs obtained by the addition of $HAuCl_4$ in a single step (Fig. S4A; Supporting Information) are relatively non-uniform and agglomerated compared to the particles obtained by the addition of $HAuCl_4$ in three consecutive steps (Fig. S4B; Supporting Information). This is also revealed in their corresponding UV-vis spectra (Fig. S4C; Supporting Information), which shows that the peak for the particles obtained by single step addition of $HAuCl_4$ arrives at higher wavelength with wider distribution. However the spectra of NPs obtained through three times $HAuCl_4$ addition was relatively narrowed and the peak arrived at slightly lower wavelength. This can be explained by the fact that the NPs obtained in a single step addition method produced some aggregated particles as observed in their corresponding TEM image (Fig. S4A; Supporting Information). For better understanding, a temporal evolution of UV-vis spectra is shown in Fig. S4D, where we observed that the peak, in a three-step process, was gradually blue shifted and narrowed during the progress of the reaction, resembling the formation of uniform particles and/or disappearance of the aggregation behavior.

The self-assembly of the AuNPs in controlled architectures or patterns[20, 35, 36] is a subject of great importance in nanoscience as the assembled architectures exhibiting different collective properties from their counterparts in the case of both individual and bulk ones. In this direction, a representative set of NPs with average size of 49 nm was forced to self-assemble into a monolayer assembly as shown in Fig. 7, which could show great prospect for optoelectronic nanodevices and biosensors.

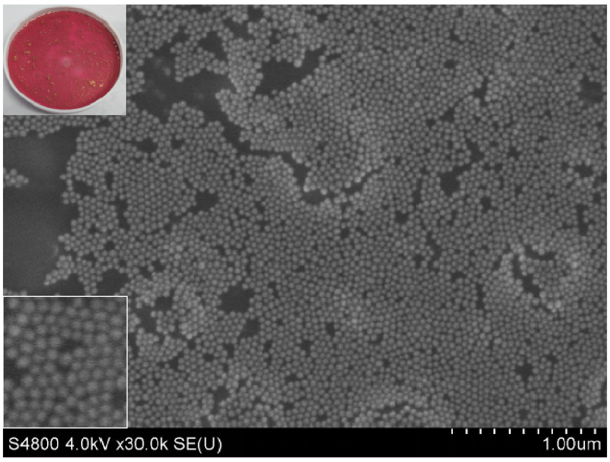


Fig. 7. SEM images of AuNPs (the diameters of 49 nm) self-assembled into monolayer at a hexane/water interface. The color of the solution shows in the inset.

4. Conclusions

We report a simple route to synthesize monodispersed citrate-stabilized Au NPs in using TB as secondary stabilizing agent, which simultaneously acts as mild reducing agent and pH-mediator, too. Three different aspects are of crucial importance to obtain highly monodispersed AuNPs. Firstly, preheating of SC solution prior to the addition of precursor salt generates the ADC to control the nucleation and subsequent growth process. Time and temperature of preheating are also important to control the size/shape of the final NPs. Secondly, addition of TB in place of extra SC restricts the secondary nucleation and maintains the reaction pH to secure the moderate rate of nucleation, which has been proven to be an important point in improving the monodispersity of the resultant particles. Finally, we established that the addition of precursor salt ($HAuCl_4$) in few consecutive steps allowed the shifting of the system towards the optimized condition, which increased the uniformity in contrast to a single step addition of the precursor. As a consequence, highly monodispersed AuNPs with diameters ranging from 20 to 115 nm have been synthesized. Monolayer self-assemblies of the developed NPs have also been achieved. Therefore, the ability to synthesize monodispersed citrate-capped Au NP and their controlled self-assemblies allows the expansion of the well-known applicability of the AuNPs to biological, biomedical and optoelectronic applications.

Acknowledgements

We thank the Natural Science Foundation of China (51303195, 51573203, 21404110, 51473179), Excellent Youth Foundation of Zhejiang Province of China (LR14B040001), Ningbo Science and Technology Bureau (2014B82010, 2015C110031), Chinese Academy of Science for Hundred Talents Program, and Chinese Central Government for Thousand Young Talents Program, Youth Innovation Promotion Association of Chinese Academy of Sciences (2016268), the Technology Foundation for Selected Overseas Chinese Scholar, Ministry of Personnel of China (2015).

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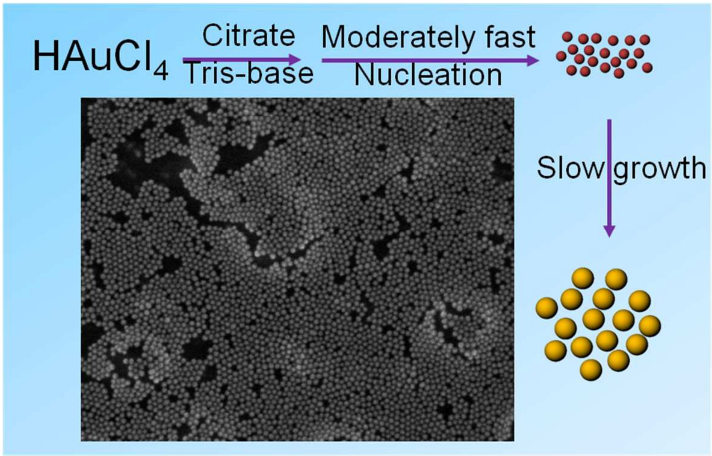
Table of Content Entry



Tris base assisted synthesis of highly uniform citrate-capped gold nanospheres was achieved by controlling the mode of moderately fast nucleation.