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High yield shape control of monodispersed Au nanostructures with 3D self-assembly ordering

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ABSTRACT

High purity Au nanoparticles and nanorods have been synthesized using seed-mediated approach in aqueous solution with the presence of cetyltrimethylammonium bromide (CTAB) surfactant. The control of seed concentration and the addition of silver nitrate yield Au nanostructures of high monodispersivity. After obtaining high concentration dispersion of anisotropic monodispersed colloidal nanocrystals, evaporation induced self-assembly of Au nanostructures was carried out. The Au nanocrystals experience strong capillary forces through the surface of the drying solvent which forces them to self-assemble while CTAB assist in drawing the nanocrystals closer without aggregating them and finally homogeneity in the shapes and sizes of the as-synthesized Au nanocrystals facilitate the self-assembly of Au nanostructures into ordered 3D assemblies. Thus, in the preparation of a large-scale assembly, high concentration, surfactant capping and monodispersivity of the Au nanostructures are essential.

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1. Introduction

Nanoscale science is all about synthesis and assembly of nanostructures at multiple length (nano to macro) scales. The selfassembled ordered structures possess interesting new collective physical properties that are different from their bulk counterpart. Hence, it is crucial to control the spatial arrangement of these wellcontrolled nanostructured materials in 2D or 3D arrays for various optical and electronics applications such as surface enhanced optical grating [1], antireflective surface coating [2], selective solar absorbers [3], data storage devices [4] and single electron tunneling transistor [5]. In a conventional procedure, the synthesis process of nanoscale building blocks, such as nanocrystals, nanoparticles and nanorods is first finely tuned and eventually engineered to organize into higher-level functional assemblies and systems. The creation of uniformly size or monodispersivity nanostructures and then assembly into identical replication over a long-range proves to be an ultimate challenge.

Assembly of nanostructures by external forces or strong interactions such as electrophoretic [6], Langmuir Blodgett [7], electrostatic interaction [8] and DNA hybridization [9] have been reported. Other than the manipulation of external forces, spontaneous arrangement of nanostructures has also been reported using evaporative templating and capillary coating techniques [10,11].

Chen et al. assembled 2D periodic arrays of ring shaped CdSe semiconductor quantum dots [10]. The patterns were fabricated using an evaporative templating method which involves an aqueous solution containing both quantum dots and polystyrene microspheres. The quantum dots became confined to the meniscus of the microspheres during evaporation, which promotes the formation of ring assembly via capillary forces at the polystyrene sphere/glass substrate interface. Hu et al. fabricated monolayers of well-ordered close-packed silica nanoparticles Si substrates over a large area via a wet-coating process using a capillary coater [11]. Other than self-assembly of nanostructures, well-controlled synthesis of high monodispersivity in the shapes and sizes of nanostructures are also essential to study their shape dependent physical and chemical properties. However, shape control method which uses nanoporous template faces the challenge of scaling up in production and shape selectivity capability [12]. Thus a more reliable and simple method of producing high concentration of monodispersed Au nanostructures is needed.

In the present work, we study the shape control and the selfassembly of Au nanoparticles and nanorods capped by surfactant using colloid chemical method. Colloidal chemistry is relatively simple, economical and does not employ any external forces or nanoporous template, offering the possibility of large-scale synthesis. Herein, we report the control of Au seed concentration and additives to obtain high yield of monodispersed nanoparticles and nanorods and subsequently assembly them into ordered structures based on evaporation induced self-assembly approach. The evaporation induced self-assembly works on the basis of a

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Fig. 1. SEM images of Au nanostructures with centrifuge treatment of (a and b) 1000 rpm and (c and d) 3000 rpm.

high concentration dispersion of anisotropic monodispersed colloidal nanocrystals which lowers its free energy through Brownian motion of self-assembling into ordered liquid crystalline phase. The manipulation of surface properties and the strict control of the size distribution of the Au nanocrystals play an important role in the formation of ordered 3D assemblies.

2. Experimental

In the preparation of Au seed, 0.25 ml of the 0.01 M HAuCl₄·3H₂O was added to 7.5 ml of the 0.1 M CTAB. The mixture was gently shaked to give brownish yellow solution. Then 0.6 ml of the freshly prepared 0.01 M NaBH₄ was added into the solution followed by mixing for at least 2 min. The solution changed to pale brown colour after mixing. Typically a set of growth solutions were prepared by mixing 4.75 ml of 0.1 M CTAB, 0.2 ml of 0.01 M HAuCl₄·3H₂O, 0.03 ml of 0.01 M AgNO₃ and 0.032 ascorbic acid. The solution was brightly brownish yellow in colour before ascorbic acid was added and changed to colourless upon mixing with ascorbic acid. Finally, Au seed was added to the solution to initiate nanocrystals growth. Other synthesis parameters such as control of seed concentration (0.025-1 ml) and addition of silver nitrate (0.03 ml of 0.01 M AgNO₃) were carried out. The reaction mixture was shaked for 10 s and left in the water bath at 25 °C overnight to complete the reaction. The final solution contained a mixture of nanoparticles, nanorods and platelets structures. The solution was centrifuged at various speeds 1000-3000 rpm and time period 5 min. After the centrifuge, the solid was collected and dispersed with DI water. The nanostructures concentration can be adjusted with DI water to an optical density of 1.5–2.0. One drop of the collected colloidal nanostructure, approximately $5-10\,\mu$ L was dropped casted on the substrate and left to dry at a temperature of $16-20\,^{\circ}$ C and humidity of 50-60%.

SEM images were obtained from a JEOL JSM 6700 scanning electron microscope with operating voltage of 5.0 kV and operating current of 10 μ A. Energy dispersive X-ray (EDX) spectrum was obtained using Oxford Instrument and Inca software. The crystallography and structures of the as-synthesized nanostructures were analyzed using transmission electron microscope (TEM, Phillips FEG CM300) and X-ray diffractometer (XRD, Philip X-ray diffractometer equipped with a graphite monochromator Cu K α radiation λ = 1.541 Å). Absorption spectra of the sample were measured with a Shimadzu UV-1800 spectrophotometer.

3. Results and discussion

Various ways have been attempted to improve the yield of Au nanoparticles and nanorods which include controlling the centrifuge speed for size sieving, tailoring the seed concentration and adding of silver nitrate. We have tried a quick separation scheme by centrifuging the precipitated Au nanocrystals solution at various speed of 1000 and 3000 rpm. From the SEM images, it is observed that Au nanoparticles (~45 nm) are extracted at low centrifuge speed (Fig. 1a and b) while a combination of nanoparticles, nanorods and nanoplatelets (triangular and truncated triangular nanoplatelets) are extracted at higher centrifuge speed of 3000 rpm (Fig. 1c and d). This centrifuge sieving scheme is able to separate the smaller size Au nanoparticle from the

Au nanorods and nanoplatelets. However, this separation method is not successful for similar size/weight nanospheres, nanorods and nanoplatelets. Shape selective of similar size/weight nanostructures was proven not to be successful with this separation method. In addition, the success of size selective separation is only limited to small size nanoparticle with a mixture of large size nanorods and nanoplatelets. Next, the effect of seed concentration in the growth precursor solution on the synthesis of Au nanostructures is investigated. It is observed that a seed concentration of 0.025 ml produces end-product of a mixture of faceted of nanoparticles, nanorods and nanoplatelets (Fig. 2a). The aspect ratio of the produced nanorods is 7-14 while the nanoparticles have an average diameter of 30-45 nm. By increasing the seed concentration to two times (0.05 ml), nanorods and nanoparticles with hardly any nanoplatelets are observed (Fig. 2b). The aspect ratio of the nanorods produced with the increased of seed concentration has decreased to 5–7 while the diameter of the nanoparticle has decreased to 15-30 nm. Further increase of the seed concentration to 0.1 ml, produces high yield of Au nanoparticles with diameters of 10-20 nm (Fig. 2c). There are only small amount of nanorods by-products. This observation can be attributed to the fact that for an increase in Au seed concentration, there are less Au ions per seed available for nucleation and growth with the growth precursor kept constant. Thus, high seed concentration produces better monodispersivity of nanoparticles while low seed concentration yields polydispersivity of varying shape and sizes of nanocrystals. Furthermore, the control of seed concentration in the growth solution is observed to control the size (diameter) and the aspect ratio of the Au nanoparticles and nanorods, respectively. Visible-NIR absorption spectra (Fig. 2d) show a sequence of extinction spectrum taken with various Au seed concentration. The spectra display two absorbance peaks at \sim 525 nm and \sim 650–1100 nm which corresponds to plasmon resonance in transverse direction and longitudinal direction, respectively. The longitudinal surface plasmon resonance peak blue shifts with increasing Au seed concentrations which indicate a decrease in the aspect ratio of the nanorods. It eventually becomes predominantly single peak with increase in Au seed concentration which suggests transformation from a mixture of various Au nanostructures to mainly nanoparticle. We have also attempted to increase the monodispersivity and uniformity of Au nanoparticles via the addition of silver ions. The addition of small amount of silver ions (0.03 ml of 0.01 M AgNO₃) into high Au seed concentration solution (0.1 ml) are observed to dramatically improve the yield of the nanoparticles with diameter of 15 ± 2 nm (Fig. 3a). Subsequently, another experiment was carried out with the same amount of silver ions with a decrease in Au seed concentration (0.05 ml). Relatively high yield of short and uniform length Au nanorods, aspect ratio of 3-5 and small amount of other Au nanostructures (nanoplatelets) are produced (Fig. 3b and inset). The Au nanorods are fairly well-assembled and are arranged side-by-side. There is a higher tendency of nanorods to align parallel to each other which may be due to higher lateral capillary forces along the length of a nanorod as compare to its width. The strong anisotropy interaction between the nanorods can be the driving force for side-by-side rather than end-to-end alignment.

In the synthesis of the gold nanostructures system, $HAuCl_4 \cdot 3H_2O$, ascorbic acid and $NaBH_4$ are the primary reactants. Both ascorbic acid and $NaBH_4$ take part in the reduction of Au(III) to Au(0), whereby $NaBH_4$ is a strong reducing agent, while ascorbic acid is significantly weaker. The formation of various shapes is likely the interplay between the crystal faceting of the stabilizing agent and the growth kinetics which involves the supply of Au(0) to the crystallographic planes [13]. High seed concentration favors the initial formation of a large number of nuclei. For a given concentration of growth precursor, the presence of a



Fig. 2. SEM images of Au nanostructures synthesized with seed concentration of (a) 0.025 ml, (b) 0.05 ml and (c) 0.1 ml and (d) UV-vis absorbance spectra of the respective seed concentrations.



Fig. 3. SEM images of Au nanostructures synthesized with addition of silver nitrate at a seed concentration of (a) 0.1 ml and (b) 0.05 ml (inset image shows higher magnification of the Au nanorods).

large number of initial nuclei would results in the formation of a large number of spherical nanoparticles with smaller diameter and narrower size distribution. As for the formation of the nanorods, it is postulated that an initial low seed concentration enables prolong nucleation which follows gold ion interparticle diffusional coupling within the soft templates made of the surfactant molecules [14]. This trend is expected because high quantity of gold ions per seed particle was available for the growth of nanorods given that there are less nuclei to begin with [15]. As for other shapes, it is possible that seed particle aggregation can occur which often leads to multiple twinning forming various shapes of gold nanocrystals [14]. It would be very interesting and important to establish a relationship between the kinetics of the reaction and the shape and size of the gold nanocrystals formed. However it is noted that the reaction does not follow simple kinetics. The general trend is that higher concentration of seed solution (more starting nuclei) leads to quick growth termination to form spherical nanocrystals while slower growth is more favorable for formation of other shapes. In fact, nanocrystal growth is likely the outcome of two major processes: the volume transport of Au ions to the seed nanoparticle and the incorporation of growth units onto specific facet. The kinetics of these competitive parameters yields the final shape formation of the nanocrystals.

The mechanism by which Ag⁺ assists in controlling particle shape is not well-understood at the present stage. However, it has been reported that the addition of silver ion into the reaction mixture for the gold nanoparticle growth changed the ionic strength of the solution, which alters the shape of the growth template. More specifically, the authors support the notion of AgBr formation on the Au surface and proposed that AgBr decreases the charge density and, hence, repulsion between the neighboring headgroups resulting in changes the shape of the soft template [16]. Similarly, it has been proposed that AgNO₃ forms AgBr in the presence of CTAB and AgBr adsorbs differentially to the facets of Au particles, thereby restricting their growth accordingly [15]. In the reported experiments, the final Au nanostructures samples contained at most \sim 4% silver based on energy dispersive X-ray analysis. However, it was not experimentally distinguished whether the silver is alloyed within gold nanostructures or merely adsorbed on their surfaces in elemental or compound form [15].

Ordered assemblies of the as-synthesized Au nanoparticles are observed on most of the support substrates, where an ordered monolayer to multilayers of Au nanocrystals resulted spontaneously after the evaporation of solvent. Au nanocrystals aggregation induced by solvent evaporation has also been reported by others [17-19]. It is noted that inhomogeneity in the as-synthesized Au nanocrystals shape and size can affect the self-assembly architecture. The presence of the non-uniform structures and sizes has been observed to cause irregularity of spacing between arrays of a specific structure and consequently distort the orderly assemblies. To improve the self-assembly mechanism, it is ensure that minimum by-products are present before the dispersion of the Au nanostructures are carried out. Thus, in our preparation of a well-ordered assemblies or superlattices, prior synthesis of high concentration and monodispersivity of the Au nanostructures are ensured. In general, a monolayer or chain of nanoparticles assemblies is usually observed at the periphery/edge of the evaporated Au nanoparticles solution droplet (Fig. 4a). The resulting nanoparticles are individually isolated, and no coagulation of the nanostructures is observed (Fig. 4b), indicating a stable dispersion. Further inwards towards the centre of the evaporated Au nanoparticles solution droplet, region containing aggregates of nanoparticles from a monolayer to multilayers assemblies are observed (Fig. 4c and d). A typical 3D ordering of nanoparticles has ~10-20 monolayers of nanoparticles. In general, there is an extensive hexagonal close-packed assembly and at higher magnification image of Fig. 4e, it is observed that the nanoparticles are not perfectly arranged, there are missing nanoparticles with some voids and misalignments. On the other hand, for polydispersed samples containing a mixture of nanoparticles, nanorods and nanoplatelets, the assembly often takes place into regions of exclusively shaped oriented type (Fig. 4f). Same shapes are attracted to each other and spontaneous shape separation occurs. The phenomenon of such shape separation assembly is termed "depletion attraction" [20].

This simple evaporation induced self-assembly approach exploits the physical, chemical, and shape affinities of the nanoparticles. In principle, a high concentration dispersion of anisotropic monodispersed colloidal nanocrystals can lower its free energy through Brownian motion by self-assemble into ordered liquid crystalline phase [20,21]. Nanocrystals can experience strong capillary forces through the surface tension of the drying solvent and are forced to self-organize. Furthermore, it is well-known that the CTAB molecules bounded on the Au nanocrystals can assist in drawing the nanocrystals closer, to share a common layer of counterions, or through the interdigitated CTAB tails from neighboring nanocrystals upon solvent evaporation [20]. As the density of nanocrystals increased, the CTAB molecules provide both steric and electrostatic repulsion between nanocrystals to ensure no aggregation of nanocrystals. Such concentration dependent liquid crystalline ordering is also highly influenced by shape dispersivity. With good particle anisotropy, spontaneous ordering via an isotropic-smectic



Fig. 4. SEM images of self-assembly of monodispersed Au nanoparticles from (a and b) monolayer to (c-e) multi-layers. (f) SEM image of polydispersed Au nanocrystals with exclusively shaped oriented assembly.

phase transition will occur [19]. It is noted that the formation of the organized assembly with a stable structure is possible only when the collective interaction energy associated to the nanocrystals is sufficient to overcome the effect of the entropy loss due to ordering [22]. Thus, the organization of such self-assembled structures is determined by a balance of van der Waals forces, capillary forces, surface tension and collective interaction energy of nanocrystals.

The crystallographic structures of the Au nanocrystals are characterized by TEM and XRD. Fig. 5a shows the nanoparticles synthesized using a high Au seed concentration. The as-synthesized nanoparticles are rather uniform in size with diameter of \sim 20–30 nm. High resolution image (Fig. 5b) shows that the nanoparticles are well-crystallized with *d*-spacing of 0.25 nm corresponding to (1 1 1) lattice plane while Fig. 5b inset shows a high magnification image of a nanoparticle [23]. The interparticle distance between adjacent nanoparticles is typically \sim 2.2–2.4 nm. Fig. 5c shows Au nanorods with fairly uniform diameter of \sim 10–15 nm and has a typical inter-nanorods distance of 2.2–4.2 nm. Fig. 5c inset shows indexed selected area electron diffraction (SAED) pattern of typical Au nanostructures. Since the

interparticle spacings are observed to be fairly regular among the arrays of nanoparticles and nanorods regardless of their shapes and sizes, this may suggest that the CTAB may act as the "glue" that holds the nanocrystals in a tight and regular configuration. It is reported that the length of a fully stretched CTAB ion is ~2.2 nm [24]. From the TEM observations, it is likely that a single or bilayer of interdigitated CTAB alkyl chains binds the adjacent nanoparticles/nanorods to each other. The phase purity and the crystallinity of the Au nanoparticles are analyzed using XRD (Fig. 5d). EDX spectrum of the nanoparticles dispersed on Si substrate was obtained and confirmed the presence of Au element (Fig. 5d inset). Two major peaks and two minor peak can be observed, and the peaks are assigned to the diffraction from the $\{111\}, \{200\}$ and $\{220\}$ {311} planes of face-centred cubic (fcc) Au, respectively [25]. No diffraction peaks due to possible impurities are observed. The intensity of {111} is the highest which indicate that the asprepared Au nanoparticles has a predominant {111} plane. This is due to the fact that $\{1 \ 1 \ 1\}$ facet of fcc metal has the lowest surface energy compared to the other facets, thus the Au nanoparticle confers its tendency to nucleate and grow with their surfaces bounded by {111} facets.



Fig. 5. TEM images of (a and b) Au nanoparticles at different magnifications (inset image shows an individual Au nanoparticle) and (c) Au nanorods (inset image shows the SAED pattern). (d) XRD spectrum of Au face-centred cubic structure (inset image shows the EDS spectrum).

4. Conclusions

High purity Au nanoparticles and nanorods have been synthesized using seed-mediated approach in aqueous solution with the presence of CTAB surfactant. The control of seed concentration and the addition of silver nitrate yield Au nanostructures of high monodispersivity. High seed concentration produces better monodispersivity of nanocrystals while low seed concentration yields polydispersivity of varying shape and sizes nanocrystals. The addition of AgNO₃ effectively promotes differentially adsorption on the specific facets of Au nanocrystals, thereby confining the growth and depending on the amount of Au seed concentration used; the resulting nanocrystals can be of a high yield of nanoparticles or nanorods. The formation of ordered assemblies of the as-synthesized Au nanoparticles is successfully demonstrated via evaporation induced self-assembly approach. This organization of self-assembled structures is determined by a balance of van der Waals forces, capillary forces, surface tension and the collective interaction energy associated to the Au nanocrystals.

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