ANISOMETRIC GOLD NANOPARTICLE SELF-ASSEMBLY AT WATER/AIR INTERFACE

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Abstract

We present gold nanorods (AuNRs) self-assembly at liquid/gas interface. Gold nanoparticles of various shapes (spheres, rods, cubes) forms 2D packed arrays at water/air interface during controlled drying from aqueous colloidal solution. The formed AuNR arrays are deposited on optically transparent substrate and identified by white-light transmission optical microscopy and scanning electron microscopy. The two methods are used to correlate the differing rod orientation/assembly to the far-field optical response of formed 2D arrays. AuNRs are synthesized by modification of seeded growth method and used in the form of colloidal solution with cetyltrimethylammonium bromide (CTAB) as stabilizing surfactant. We utilize self-assembly of AuNRs in aqueous environment using simple system of AuNR/CTAB/water.

Keywords: Gold nanorods, colloids, self-assembly, localized surface plasmon resonance, plasmon-coupling

1. INTRODUCTION

Self-assembly of nanoparticles is contemporary topic both in fundamental science and technological applications [1,2]. A great potential of the self-assembly approaches favors a traditional sol-gel methods. This techniques offer sufficient flexibility, and they are also a cost-effective [3]. Especially the self-assembly of noble metal nanoparticles attracts interest because of the coupling effects of the localized surface plasmon resonance (LSPR) at close interparticle spacing [4]. Gold nanorods (AuNRs) presents excellent model system for their great tunability and polarization dependent effect deriving from their spatial anisometry [5]. The technological applications of the self-assembly of such anisometric particles still holds many obstacles [2]. However, the potential advantages of such composite materials are many [5] and several groups already proposed approaches for preparation of self-assembled AuNR superstructures [6–8]. Recently Xei et al. demonstrated their method for preparation of vertically stacked monolayers of cetyltrimethylammonium bromide (CTAB) capped AuNRs [9] on various substrates.

In present work we demonstrate AuNR self-assembly into vertically stacked arrays using similar setup of rapidly drying colloidal droplet. We concentrate on the use of strong convective flows towards the water/air boundary to create homogeneously distributed packs of vertically stacked AuNR arrays on transparent substrates. The area size of the individual AuNR assembly is viable for examination by transmission optical microscope. By correlating the optical microscope and scanning electron microscope micrographs we show strong dependence of color behavior of the vertically stacked AuNR arrays on offset of the AuNRs from the vertical axis.

2. METHODS & MATERIALS

Gold(III) chloride trihydrate and silver nitrate were purchased from Sigma-Aldrich, CTAB was purchased from Fluka, ascorbic acid from Penta and hydrochloric acid from lachner. 18.2 MΩ Milli-Q purified water was used throughout the experiments.

2.1 Instrumentation

Wide-field white-light transmission optical microscope images were acquired with Nikon Eclipse LV-100 microscope using 60X 0.7NA plan-fluar objective and Nikon D300s DSLR camera. Scanning electron
microscope (SEM) images were acquired by JEOL JSM-7500f FE-SEM utilizing upper secondary electron detector with 2 kV probe energy and lower in-chamber back-scattered electron detector with 10 kV probe energy. Absorbance spectra of colloidal solutions of AuNRs were measured by Shimadzu UV-1601 spectrophotometer.

2.2 Gold nanorod synthesis & Characterization

Nanorods samples were synthesized by seeded-growth method in the presence of silver nitrate [10]. By varying the amount of silver(I), one can fine tune the aspect ratio of the grown rods. The usual synthesis process involves preparation of monocrystalline gold seeds (2-4 nm) by fast reduction of gold(III) salt in the presence of CTAB and adding them into the growth solution of gold(I) complexed to CTAB in the presence of silver(I) in aqueous solution (pH 2-3). This starts the growth process where the amount of seeds added and the starting concentration of silver(I) influences the size and aspect ratio of rods produced.

One day after the synthesis AuNRs were washed of the excess reactants and concentrated by two subsequent centrifugation runs (8000 RPM for 10 minutes) to the equivalent of 10mM [Au] concentration in approx. 1mM CTAB/water solution (20-fold increase the concentration of gold in the solution, 100-fold decrease of CTAB concentration). The concentration was further changed to [Au] = 5 mM and [CTAB] = 0.5mM by diluting in Milli-Q water. The AuNR solution was characterized by absorption spectroscopy and SEM imaging (Figure 1 a,c). Dimensions of nanorods used in this work were estimated as 59 nm ± 5 nm in length and 24 ± 3 nm in width. The corresponding aspect ratio is 2.5 ± 0.3 which agrees well with the longitudinal LSPR position at 640 nm.

2.3 Gold nanorod self-assembly by rapid droplet evaporation

Our AuNR deposition setup consist of continuously pumped desiccator vessel filled with distilled water and equilibrated at 30 °C. The continuous evacuation creates high-humidity environment close to the point of saturated vapors and low pressure approximately 4000 Pa. Typical deposition experiment consists of placing droplet of AuNR solution on desired substrate and letting it equilibrate for 2 minutes inside the vented desiccator vessel above the water level. Subsequently the vessel is pumped down to 4000 Pa which starts the rapid evaporation of the colloidal droplet.
3. RESULTS & DISCUSSION

We obtained self-assembled domains of vertically stacked AuNRs. The domains were acquired by rapid colloidal droplet evaporation and subsequently allowing the formed small (< 1 um) (Fig. X) domains to grow by migration in hydrated film in high humidity environment. The initial forming of small ensembles of vertically oriented AuNR was checked by drying the sample immediately after the droplet collapse and imaging in SEM. Figure 2 (b,c) depicts an area within the initial footprint of the drop with clearly formed homogeneous distribution of vertically stacked AuNR islands.

![Fig. 1. Preparation of vertically stacked AuNR domains by rapid colloidal droplet evaporation. (a) The schematic drawing illustrates the basics of the self-assembly process – the colloidal droplet undergo rapid evaporation in high-humidity environment, the convective flow drive the nanoparticle to the surface. The formation of vertically stacked AuNR arrays is governed by the dynamic processes between the AuNR, CTAB surfactant, and solvent. The described presumption was checked by the SEM imaging: (b) SEM micrograph of the area within the dried droplet footprint showing continuous coverage of vertically stacked AuNR arrays. (c) The detailed view also reveals assemblies with second AuNR layer stacked on top.](image_url)

After the aging of the initial viscous AuNR/CTAB/water film for approximately 5 hours we acquired vertically stacked AuNR domains with area over tens of micrometer squared which can be easily identified in wide field transmission optical microscope (Fig. 3 a,e). The vertically stacked domains exhibited deep violet color in transmission mode when observed with 60X 0.7NA objective, an effect which is not trivial to discuss as it was shown the LSPR of individual AuNRs form collective resonant fields at such close spacing [11]. The apparent color of the individual AuNR islands is dependent on the rod orientation, number of stacked layers and also on interparticle distances. Recently Xie et. al. [9] shown under similar condition to ours the finally drying of the format AuNR/CTAB/water film produces cracks in the formed AuNR assemblies. Here we want to demonstrate also collective angling of the individual AuNR within the formed array in intricate pattern which greatly influence the apparent color under the transmission optical microscope. The optical information can be coupled with SEM observation to connect the change in optical behavior to the deviation of AuNRs from vertical axis (Fig. 3). The vertically stacked AuNR arrays has recently induced interest as spectroscopy enhancers [12] and has been shown to by prospective candidates as a vectorial material [7,13].
Fig. 3 Correlated optical microscope/scanning electron microscope study of the self-assembled vertically stacked AuNRs. (a - d) The apparent violet color of the AuNR assembly and its SEM micrograph showing the rods are mainly in upright position. (e - f) Similar imaging on other AuNR domains which exhibits greenish appearance under optical microscope. The rods conformation in this case is changed significantly as the rods are angling from the vertical axis with different directions. Interesting circular patterns can be identified in the collective AuNR orientation.

4. CONCLUSION

We used the convective flows within rapidly drying colloidal droplet to drive the AuNR to the liquid air boundary and allow them to self-assemble into vertically stacked domains. We show our method produce AuNR arrays big enough to allow examination of their optical behavior under transmission optical microscope. We demonstrated the strong and interesting color behavior dependence on the AuNR alignment inside the stacked AuNR array.

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LITERATURE


