Large-area and Free-standing 3D Superlattices
Induced by Droplet Evaporation

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Keywords: Gold nanorods, Self-assembly, Superstructure, Surface-enhanced raman spectroscopy.

Abstract. In this article, we make our effort to scale up the synthesis of gold nanorods (GNRs) using the modified strategy. The prepared GNRs are self-assembled vertically to the substrate over an large micrometer-size area without external fields. We also demonstrate that this complex superstructure is an excellent surface-enhanced Raman scattering (SERS) substrate with uniform electric field enhancement, high intensity of hot spots and reproducible enhancement factors (EFs) in the desirable spectral range. For practical perspective, the substrate shows great promise for fluorescence and luminescence.

Introduction

The preparation of rod-like nanoparticles such as CdSe, CdS nanorods\textsuperscript{[1]} and Ag\textsubscript{2}S\textsuperscript{[2]} have been extensively pursued over the past decades due to their potential applications in catalysts, biosensors and electronics. But more recently, nanoscience and nanotechnology have taken much attention to solving ruly revolutionary solutions for drug delivery\textsuperscript{[3]} and sensors\textsuperscript{[4]} etc., while many of these applications are based not on individual nanoparticles but on assemblies on which these nanoparticles interact with one another and organize in purposeful ways\textsuperscript{[5]}. Thus, facing nanoscience and nanotechnology, the challenge is to develop efficient and simple ways to assemble nano-components onto large higher-ordered nanostructure whose shape symmetry and unique collective properties are different from those individual nanoparticles.

Numerous reports have shown the techniques for directing the assembly of nano-objects in one, two or three dimensions, such as Langmuir-Blodgett\textsuperscript{[6]}, Droplet-Evaporation\textsuperscript{[2, 7]}, Lithographic Method and DC Electric-Field-Assisted\textsuperscript{[8]} But the principles, such as the interactions, drying kinetics, coarsening mechanism, hydrodynamic effects and the diffusion of particles underlying the formation of the ordered nanostructure, have not yet been studied systematically. For instance, though the various types of interactions\textsuperscript{[5]}, including van der Waals forces, electrostatic forces, magnetic interactions, molecular surface forces and entropic effects are well-understood, little literature has justified and proved/disproved their applicability in the assembly process.

The surface-enhanced Raman scattering (SERS) spectroscopy is not only a new powerful analytical technique with ultrahigh sensitivity but also can be used for the biological samples analysis\textsuperscript{[9]}. Unfortunately, there are still two additional serious challenges\textsuperscript{[10]}: One is the quantitative detection by SERS, the other is the necessity of reproducible geometry of “hot spots”. Moreover, the way to solve these problems is to design and fabricate a
highly-organized photonic structure which provides a high electromagnetic field enhancement in reproducible geometry. Furthermore, the nanorods (NRs) can cause the nano-antenna effect which has paved the way for the development of ultra-sensitive SERS substrates, which allows the acquisition of ultrahigh enhancement factors (EFs).

In this article, we make our effort to scale up the synthesis of GNRs using the modified strategy and report a simple technique for fabricating perpendicular GNRs over an large micrometer-size area without external fields. For practical perspective, the substrate shows great promise for fluorescence and luminescence.

**Experimental Section**

**Material and reagents.** cetyltrimethylammonium-bromide (CTAB), ascorbic acid, silver nitrate (AgNO₃), hydrochloric acid (HCl), chloroauric acid terahydrate (HAuCl₄·4H₂O), and Sodium borohydride (NaBH₄) were bought from Nanjing Sunshine Biotechnology Ltd., China. All of the chemical reagents were analytical grade and used without further purification. Aqueous solution used in the experiments was prepared by Milli-Q water from Milli-Q system (resistivity >18 MΩ).

**Synthesis of gold nanorods.** Gold nanorods (GNRs) were synthesized by a seed-mediated method. The seed solution was prepared by adding HAuCl₄ (0.5 mM, 5 mL) to CTAB (0.2 M, 5 mL) under stirring. Then, freshly prepared ice-cold NaBH₄ (0.01 M, 0.6 mL) was added under stirring. This solution was stored at 25°C for 2 h to yield small nanoparticles as the seed solution. After that, the growth solution was prepared by adding AgNO₃ (4 mM, 2.5 mL) and HAuCl₄ (1 mM, 50 mL) to CTAB (0.2 M, 50 mL) followed by thorough mixing, then 800 µL of 0.0788M ascorbic acid was added to this solution, of which the color changed from yellow to colorless after this process. Then, 280 µL of the seed solution was added into the growth solution, and was kept at 30°C for overnight. Thus high yields of nanorods were obtained. At last, UV-vis-NIR extinction spectra of GNRs samples were measured using a Shimadzu UV3150 UV-vis-NIR spectrophotometer, and a Zeiss ULTRA-plus scanning electron microscope (SEM) was used to characterize the morphology of GNRs on different conditions at 15 kV.

**Self-assembly of gold nanorods.** To remove excess CTAB from the as-prepared sample, the GNR solution was purified at least twice by centrifuging at 8000 rpm for 30 min and was redispersed in ultrapure water. In this manner, one can adjust the concentration of GNR and reduce the amount of excess surfactant in the solution.

All silicon substrate were washed with Aqua Regia (HCl:HNO₃ in a 3:1 ratio by volume) and rinsed with ultrapure water for at least five times. The substrate were further cleaned in ethanol by sonication for three times and dried at 70 °C for 2 h in an air oven.

For the preparation of GNRs assembly, a drop of processed dispersion of GNRs solution of certain concentration was cast onto a clean silicon substrate. The sessile droplet was kept at room temperature under approximately 60% humidity over several hours for evaporation of water. After evaporation, 3D- or 2D-supercrystals of GNRs were observed at the edge or middle of the substrate. A Zeiss ULTRA-plus scanning electron microscope (SEM) was used to image the morphology of the assembled GNRs on different conditions at 15 kV.

**SERS measurements.** In order to determine the SERS efficiency of the assembled GNRs substrate, the GNRs were mixed with previous-prepared 10⁻⁶ M NBA solution for 8 h, then the above self-assembled experiment was repeated. The Raman signals were collected using a
Renishaw Invia Reflex system equipped with Peltier-cooled charge-coupled device (CCD) detectors and a Leica confocal microscope. Samples were excited by a 785 nm diode laser under linefocus mode and a grating of 1200 mm\(^{-1}\) was used. The corresponding laser was focused onto the sample surface using a 50× long working distance objective. Spectra were collected in continuous mode with 10 s exposure time and accumulated twice, the laser power was adjusted to 0.05%, which was about 0.06 mW. Every SERS spectrum was averaged from 5 measurements. All experiments were performed in triplicate and the values were averaged. Results were given as means ± the standard deviation (SD). The microscope should be refocused after each measurement and all Raman experiments were carried out at room temperature.

**Results and Discussion**

Various ways have been attempted to improve the yield of GNRs which include adding silver nitrate, tailoring the concentration of reactants\[11\], and controlling the crystallinity of seed particle\[12\]. However, we just regulate the factor, especially the pH of the incubate solution to enhance the synthesis of monodisperse GNRs. In this case, the level of shape impurities such as nanoplates and nanoparticles in as-synthesized samples is obviously lower than those of previous GNRs prepared without using hydrochloric acid in the incubate solution, which is also demonstrated by the strong and sharp longitudinal surface plasmon resonance (LSPR) peaks in the ensemble extinction spectra (Fig. 1c). SEM images (Fig. 1a, b) also show the same result. As is known\[10\], when the prepared GNRs meet the conditions that are (1) 1,000-fold increase in the amount of gold nanorods synthesized in one batch, and (2) very narrow size distribution\[10\], GNRs can spontaneously and reproducibly crystallize into 3D superstructure. In consideration of this fact, we make our effort to scale up the synthesis of GNRs using the above modified strategy, as demonstrated by GNRs sample (Fig. 1d).

![Figure 1. SEM images of the gold nanorods synthesized under (a) 0 M HCl (b) 1 M HCl (c) UV-vis-NIR spectra of the corresponding prepared gold nanorods (d) Photograph of the 2000 mL beaker used for the scale-up synthesis.](image)

Self-assembly is the most promising candidate for "next technological revolution", at least in principle, the evolution of monodisperse nanoscale building block to ordered arrays\[5\]. In particular, beautiful liquid-crystalline superstructure or superlattices have been reported such as TiO\(_2\)\[13\] and \(\beta\)-FeOOH\[14\]. Here, we explore the superstructure of ordered GNRs assembled by slow evaporation of condensed GNRs aqueous solution at room temperature. As been
investigated, GNRs, whose length is 100 ± 3 nm, diameter is 20 ± 0.5 nm, aspect ratio (AR) is 3.88, LSPR wavelength is 750, assembled free-standing and vertically aligned on the substrate, which are shown in Fig. 2 at different magnifications. As we can see, this superstructure covers at least 30 µm² and is 3D lamellar accumulation with multilayer, making this axial alignment perpendicular to the substrate, which is the desired geometry of most interest in nanoelectronic, nanomagnetic and nanophotonic applications.

It is well known that the lateral capillary force is caused by the perturbation of the shape of the liquid meniscus around a given particle at the presence of a second particle\textsuperscript{[15]}. The larger the interfacial deformation created by the particle, the stronger the capillary interaction between them. So to explain the observed tendency, the lateral immersion or capillary forces along the length of the gold nanorod is higher than that of its width, which may be one of the main reasons. In addition, in the experiment performed by C. J. Murphy and N. R. Jana’s groups\textsuperscript{[16]}, van der Waals forces can cause the highly directional interaction between anisotropic particles such as nanorods and rectangular nanoparticles.

The SERS enhancing efficiency of the gold nanorods superstructure is demonstrated by NBA whose concentration is 10\textsuperscript{-6} M. Extensive comparative testing revealed that the superstructure as SERS substrate is superior to the previously used individual gold nanorod and the EF of the former(10\textsuperscript{5}) is 10-fold to the latter(10\textsuperscript{4}) (unlikely as it seems, but is enough to microanalysis). This superstructure possess additional advantages such as highly homogeneous distribution, chemical stability and reproducibility, allowing the quantitative SERS detection of complex biomolecules\textsuperscript{[10]}. 

Figure 2. SEM images of self-assembled gold nanorods synthesized under the same conditions at different magnification.

Figure 3. Left: SERS spectra of 10\textsuperscript{-6} M NBA on five different 3D substrates; Right: SERS spectra of 10\textsuperscript{-6} M NBA on individually isolated gold nanorods substrate (black) and on the self-assembled 3D-superlattice substrate (red).
Our group also find other amazing superstructures formed by GNRs (in Fig. 4), such as 3D lamellar accumulation of hexagonal array (Fig. 4a), schlieren (Fig. 4b), lays of waves (Fig. 4c) and side-by-side lying on the substrate (Fig. 4d). Detailed description about these superstructures is under way.

Figure 4. SEM images of other structures self-assembled by GNRs (a) 3D lamellar accumulation of hexagonal array (b) schlieren (c) lays of waves (d) side-by-side lying on the substrate.

Conclusion

In conclusion, we have reported a simple technique for fabricating perpendicular gold nanorods self-assembly from monodisperse sample over large micrometer-size area without external fields. We also demonstrate that this complex superstructure is an excellent SERS substrate with uniform electric field enhancement, high intensity of the hot spots, and reproducible EFs in the desirable spectral range. For practical perspective, these substrates show great promise for fluorescence and luminescence. But further and detailed study on this superstructure is still on the way.

References


