End-to-End Alignment of Gold Nanorods on Topographically Enhanced, Cylinder Forming Diblock Copolymer Templates and Their Surface Enhanced Raman Scattering Properties

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ABSTRACT: We present a facile methodology for the end-to-end assembly of gold nanorods of various aspect ratios on corrugated, horizontal, cylinder-forming diblock copolymer templates. Although the depth of corrugation is significantly smaller than the diameter of the nanorods, they exhibit excellent selectivity (>98%) and alignment for placement in the polymer grooves due to capillary forces and the substrate’s topography. Enhanced corrugation of the diblock template is achieved by chemical swelling prior to deposition of the metallic nanorods. Graphoepitaxy of the diblock copolymer in nanoconfining channels is employed to achieve essentially perfect long-range orientation of the substrate, while subsequent deposition of nanorod arrays whose alignment maps onto that of the diblock template with high fidelity provides novel organic–inorganic hybrid surfaces whose surface enhanced Raman spectroscopy (SERS) properties are characterized. These arrays of aligned gold nanorods exhibit polarization-dependent spectra for adsorbed molecular species with a 24-fold enhancement in signal intensity when the trenches are aligned with parallel versus perpendicular orientation with respect to the incident polarization of the excitation laser. The simple construction of these systems and their unique SERS properties provide a new and efficacious platform for the construction of functional nanodevices.

INTRODUCTION

Thin films of nanoparticles (NPs) have attracted considerable attention due to their potential applications related to electronic devices,1,2 magnetic storage,3 and sensors.4,5 Investigations into the last category have focused on noble metal NPs due to their well-documented surface enhanced Raman spectroscopic (SERS) properties.6–7 Gold NP (AuNP) SERS systems are typically fabricated using either top-down or bottom-up techniques, where the regions of electric field enhancement, called hot spots, are made by electron beam lithography (EBL)8,9 or ion-beam sputtering10 or through the deposition of colloidal AuNPs. Controlling the deposition of colloidal AuNPs is attractive because the locations of the hot spots are determined by the order and alignment of the AuNPs on the substrate. This has been done by chemically functionalizing11–14 or patterning15–20 the substrates or by modifying the AuNP colloid.21–23

This paper presents a facile, bottom-up technique that produces highly ordered arrays of colloidal gold nanorods (AuNRs) aligned end-to-end with favorable and polarization-dependent SERS properties. AuNRs have received particular attention due to their controllable synthesis24–28 tunable plasmon resonances,29 and electromagnetic field enhancements,30 making these NPs6 and their assemblies7 of interest for SERS.20,23 Coupling between plasmonic NPs makes AuNR assemblies exhibit stronger hot spots than individual structures and increases the SERS response,7 as documented for AuNR assemblies31,32 and for various large-scale 2D and 3D AuNR aggregates.20,23,33

The AuNR arrays presented in this paper are made by depositing AuNR colloids onto silicon nitride substrates patterned with horizontal, cylinder-forming poly(styrene-block-poly(methyl methacrylate) (PS-b-PMMA) block copolymer (BCP) templates. BCP templates are attractive platforms because they self-assemble into spheres, lamellae, cylinders, and other well-ordered microdomains easily and cost effectively, and can achieve long-range, defect-free structures.34–37 BCP microdomains are also comparable in size to colloidal gold nanorods (5–50 nm).38

NP ordering and alignment when mixed in BCP systems have been demonstrated previously for AuNRs in PS–PMMA, where the NRs modified by poly(ethylene glycol) are fully embedded inside the PMMA domain.39 Semiconductor nanorods have also been successfully embedded into BCP designed with appropriate interactions.40 While bulk alignment is of interest, surface assembly has the advantage of giving chemical access to the particle surface. While the surface assembly of nanoparticles in specific domains has not yet been very successful when based solely on the surface’s chemical or wetting characteristics, it has been demonstrated that an enhanced corrugation helps. FePt NPs ordering at the surface...
of cylinder forming PS–PMMA domains was first demonstrated using UV enhanced corrugation. Plasma etching of a lamellar PMMA domain has also been examined, allowing alignment of gold nanorods with significant order. Solvent swelling of lamellar PMMA in acetic acid vapor has also been applied to several nanoparticle systems, including ZnO nanorods. This present work shows that a similar acetic acid swelling of PMMA in horizontal cylinder PS–PMMA microdomains can be used with great success to align gold nanorods even though the corrugation is less than half of the prior work involving lamellar PS–PMMA. Moreover, we demonstrate such hierarchical assembly for nanoconfined, highly aligned, and essentially defect-free cylindrical diblock substrates. Although the BCP corrugation is significantly smaller than the particle diameter, excellent alignment is readily achieved for single and individual chains of end-to-end aligned AuNRs. It is herein demonstrated that the combination of graphoepitaxy of the diblock substrate in nanoconfined channels to produce essentially perfect diblock orientation coupled with the subsequent deposition of nanorod arrays whose alignment maps onto that of the diblock template with high fidelity is a highly efficacious route to the formation of spatially anisotropic SERS platforms.

**Experimental Section**

The corrugated block copolymer thin films were fabricated on silicon nitride (Si$_3$N$_4$) substrates purchased from Virginia Semiconductor, Inc., which had been cut to ~1 cm × 1 cm, cleaned with toluene, acetone, and methanol using an ultrasonic cleaner, and then dried with nitrogen. The substrates were spin-coated with 77 kg/mol, 29 wt % PS-b-PMMA BCP, purchased from Polymer Source, Inc., and was used without further purification, in 0.9 wt % toluene solution at 4000–5500 rpm for 60 s, and then annealed at 523 K under an argon atmosphere for an hour. The phase separated BCP thin films were then exposed to saturated acetic acid vapor for 15 min to induce the selective swelling of the PMMA cylinder domains (Figure 1). For the substrates created by graphoepitaxy, the 500 nm wide, 20 μm long, and 50 nm deep trenches were patterned into the substrate with EBL using a Hitachi 2700 SEM operating at 300 μC/cm$^2$ before being coated with BCP. The polymer substrates were imaged by atomic force microscopy (AFM), using an Asylum Research’s MFP-3D AFM performed in ac (tapping) mode with an Olympus AC240TS cantilevers with a spring constant of 2 N/m.

![Figure 1](image_url)  
**Figure 1.** (a) Schematic representation of the corrugated, horizontal cylinder-forming PS-b-PMMA BCP template fabrication. The dark blue regions correspond to PMMA domains, while the light blue regions correspond to PS domains. (b–e) AFM images and topographic height profiles before (b, d) and after (c, e) the acetic acid vapor treatment. The film’s corrugation increases from ~1 nm (d) to ~4 nm (e) after the acetic acid treatment. The height profiles are taken along the arrows in (b) and (c), and the AFM images are 2 μm × 1 μm.

The AuNRs used in this study were synthesized using a scaled down and slightly modified version of the protocol developed by Ye et al. Hexadecyltrimethylammonium bromide (CTAB, ≥99%), gold(III) chloride trihydrate (HAuCl$_4$ ≥99.9% metals basis), and 5-bromosalicylic acid (5-BSA, ≥98.0%) were purchased from TCI and used without further purification. Silver nitrate (AgNO$_3$, 99.9999%), L-ascorbic acid (vitamin C, ≥99.0%), sodium borohydride (NaBH$_4$, ≥98.5%), and benzenethiol (BT, ≥98%) were purchased from Sigma-Aldrich and used without further purification. Hydrochloric acid (HCl, 1 N) was purchased from Fisher and used without further purification. In all cases, the AuNR seeds were synthesized by dissolving 364 mg of CTAB in 10 mL of NPH$_2$O at 30 °C and under vigorous stirring and then adding 250 μL of a 10 mM HAuCl$_4$ solution and 600 μL of a fresh, 10 mM NaBH$_4$ solution. The solution promptly turned yellow-brown and was vigorously stirred for 2 min before being set aside. Also, all AuNR colloids were made by dissolving 182 mg of CTAB and 21.9 mg of 5-BSA in 10 mL of nanopure water (NPH$_2$O) at 70 °C under vigorous stirring and were then cooled to 30 °C. For the AuNRs of aspect ratio (AR) 3.05 to 3.20, 96 μL of a 10 mM AgNO$_3$ solution, 500 μL of a 10 mM HAuCl$_4$, 51.2 μL of a fresh, 100 mM vitamin C solution, and 16 μL of the AuNR seed solution were added to the solution. For the AuNRs of AR 4.02, 384 μL of a 10 mM AgNO$_3$ solution, 500 μL of a 10 mM HAuCl$_4$, 500 μL of a 1 M HCl, 51.2 μL of a fresh, 100 mM vitamin C solution, and 16 μL of the AuNR seed solution were added to the solution. For the AuNRs of AR 6.33, 384 μL of a 10 mM AgNO$_3$ solution, 500 μL of a 10 mM HAuCl$_4$, 500 μL of 1 M HCl, 25.6 μL of a fresh, 100 mM vitamin C solution, and 16 μL of the AuNR seed solution were added to the solution. All of the colloids were vigorously stirred for 30 s and then left to age overnight (15–18 h). All were then hard centrifuged at 8500g and 30 °C for 15 min and had their supernatants decanted and pellets resuspended in 10 mL of NPH$_2$O before being centrifuged again under the same conditions. After the second centrifugation, the supernatant was decanted and the pellet resuspended with 250 μL of NPH$_2$O. Aliquots of these mixtures were removed for UV/vis and transmission electron microscopy (TEM) analysis (Figure 2). The UV/vis spectra were recorded using an Agilent HP 8453, and the TEM images were taken using a FEI Spirit TEM operating at 120 kV.

To achieve different surface densities of the same AR AuNRs on the thin, BCP fingerprint films, the AuNR colloid was spin-cast for 60 s at 3000 rpm, 2, or 10 times, dried in air, and then...
The topographically enhanced, horizontal cylinder-forming PS-b-PMMA BCP templates were fabricated by the selective swelling of the PMMA domains in a saturated vapor of acetic acid. Since the PMMA blocks are bound to the PS blocks, their microdomains cannot expand laterally. Instead, the PMMA chains swell and overflow onto the film surface, as shown in Figure 1a. When the substrates are removed from the solvent chamber, the acetic acid quickly evaporates, causing the PMMA chains to adopt a collapsed conformation and shrink, leaving behind a corrugated surface. Figures 1b,d are the atomic force microscopy (AFM) images and height profiles of the BCP films before the acetic acid treatment, and Figures 1c,e are the AFM images and height profiles of the films after the solvent treatment. As can be seen, the film’s height profile increases from ~1 to ~4 nm, with a periodicity of ~23 nm, after the acetic acid treatment (Figure 1e).

To investigate AuNR alignment on these BCP films, 20 nm by 61 nm AuNRs (aspect ratio (AR) 3.05, Figure 2b) were spin-cast onto the templates and imaged by AFM. Low surface density AuNR arrays were made by spin-casting the stock colloidal solution onto the BCP substrates to ensure the BT monolayer was deposited at this point. Also, none of the AuNRs exhibited obvious tilting or orientation defects arising from the solvent chamber, the acetic acid treatment. As can be seen, the fingerprint grooves, where they existed, were aligned along the contours. When the colloid was spin-cast 6 times onto the whole film, the surface density increased to 160 AuNRs/μm², and the AuNRs nearly covered the substrate as a fingerprint film (Figure 3b). The AuNRs were still aligned end-to-end along the contours of the fingerprints, resting within the grooves with over 97% selectivity. After 10 spin-coatings, the AuNRs formed 3D clusters with >300 AuNRs/μm² and lost the structure of the underlying substrate (Figure 3c). Increasing the AuNR aspect ratio did not change the alignment results. AuNRs of AR 3.20 (Figure 2c), 4.02 (Figure 2d), and 6.33 (Figure 2e), which varied from 11 to 18 nm in width and 59 to 71 nm in length, were spin-cast onto the BCP fingerprint templates. In all cases, the AuNRs deposited end-to-end in the fingerprint grooves with over 97% selectivity (Figure 4). Remarkably, the AuNRs of AR 6.33 did not exhibit any side-to-side packing, even though their diameters (11 nm) were a factor of 2 smaller than the width of the grooves (23 nm) (Figure 4c). Also, none of the AuNRs exhibited obvious tilting within the polymer grooves, and all were aligned with the pattern’s contours.
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These AuNR deposition results exhibit advantages over previous systems, attributed to our use of cylinder-forming and corrugation-enhanced BCP templates. First, the AuNRs only assemble end-to-end within the template grooves. Second, the AuNRs did not exhibit any obvious deviations from the contours of the grooves. Third, the AuNRs did this even though the BCP templates’ height profiles were far smaller than the deposited AuNRs’ diameters (ranging in ratio from 1:2.75 to 1:5). These observations are consistent with a simple model involving the capillary forces exerted on partially immersed rodlike viruses or colloidal particles and the topography of the BCP template (Figure 5). Because of the aspect ratio of the AuNRs, only the capillary force arising from the contact line along their length is considered. This force, \( F = \gamma L \cos(\alpha) \), is maximized when the particles are half-immersed, where \( \gamma \) is the surface tension of water (72.8 dyn/cm), \( L \) is the length of the rod, and \( \alpha \) is the contact angle of the water at the AuNR’s surface. The energy a AuNR gains by moving from a crest to a trough is calculated by integrating over the substrate’s corrugation \( h \), giving an energy of \( \gamma L h \cos(\alpha) \) (Figure 5a). For the AuNRs with 61 nm length, and \( \alpha = 30^\circ \), the crest to trough energy difference is \( 3.08 \times 10^{-17} \) J of energy, 4 orders of magnitude greater than their room temperature Brownian motion energy of \( 4.11 \times 10^{-21} \) J. The strength of the capillary force explains both the AuNRs’ extreme preference and the alignment in the grooves. Because the fingerprints are generated from the PMMA cylinder domains, their bottoms are curved (Figures 1a and 5a). Therefore, any misalignment in the grooves results in the AuNRs having a vertical displacement. From the equation of the tangent circle describing the curvature of the grooves (radius \( \sim 20 \) nm), the thermal energy could only induce a misalignment of \( \sim 0.5^\circ \).

Thus, the capillary force explains the AuNRs’ order, but it does not explain the lack of lateral packing. For the AuNRs with larger diameters (20, 18.41, and 14.87 nm), which are close to the grooves’ widths (23 nm), the absence of side-to-side packing could be explained due to geometric confinement. However, this does not address the case of the AR 6.33 AuNRs, whose diameters are about half the channel width. The dearth of horizontal packing is attributed to the electrostatic repulsion between the AuNRs. The colloidaly synthesized AuNRs are coated in a hexadecyltrimethylammonium bromide (CTAB) and 5-bromosalicylic acid (5-BSA) bilayer, so each rod can be approximated as having a positive charge, \( q \), roughly equal to the number of CTA\(^+\) molecules in its outer layer, as determined by calculating the AuNR surface area and multiplying by the optimum CTA\(^+\) packing density of 2.44 CTA\(^+\)/nm\(^2\). The Debye length of the colloid is given by \( \kappa^{-1} = \left( \frac{e_i e_F q_0^2}{2 N A^2 \varepsilon_0 k_B T}\right)^{1/2} \), where \( e_i \) is the relative permittivity of water at room temperature, \( e_0 \) is the permittivity of vacuum, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, \( N_A \) is Avogadro’s number, \( \varepsilon \) is the fundamental unit of charge, and \( l \) is the colloid’s ionic strength in mol/m\(^3\). Using a \( e_i \) of 78.54 and a CTAB concentration of 1 mM, the Debye length is 9.62 nm. The electrostatic repulsion for two AR 6.33 AuNRs separated by their Debye length, \( (1/4 \pi e_0 e_F) \left[ q_1^2/(\kappa^{-2}) \right] \), yields a very large repulsive force of \( 1.36 \times 10^{-6} \) N, consistent with the long-term stability of the colloidal suspension. Moreover, as long as the particles are fully submerged in solution, they will be separated by at least their Debye length, irrespective of the substrate. As the solvent evaporates, the AuNRs will still be fully immersed, with their interparticle interactions governed by electrostatics. This will keep them well spaced as they come closer to the substrate surface. When enough of the solvent has evaporated such that AuNRs are partially immersed, the capillary forces are strong enough to induce the final assembly on the substrate (Figure 5b). We believe that end-to-end assembly is favored because of the orientation’s reduced electrostatic repulsion in solution, as compared to lateral assembly. We note that if the deposition is formed at higher concentration of the AuNRs, side-to-side and random aggregates appear which we attribute to an increase of the ionic strength as the water evaporates, drastically shrinking the Debye length. Attractive capillary forces can facilitate further the end-to-end assembly of the AuNRs in the channels.

Figure 4. AFM images of AuNRs with different ARs on the topographically enhanced, horizontal cylinder-forming PS-b-PMMA BCP thin films. (a) AuNRs of Figure 2c, length 58.95 ± 3.63 nm and width 18.41 ± 1.95 nm, AR = 3.20. (b) AuNRs of Figure 2d, length 59.76 ± 7.26 nm and width 14.87 ± 2.00 nm, AR = 4.02. (c) AuNRs of Figure 2e, length 70.50 ± 7.59 nm and width 11.14 ± 1.62 nm, AR = 6.33. All of the AuNRs align in grooves with over 97% selectivity. The images are 2 \( \mu \)m \times 2 \( \mu \)m.

Figure 5. Schematic representation of the AuNRs drying on the substrates. (a) Partially immersed AuNR being drawn into a polymer trench. The \( \vec{F} \) indicates the direction of the capillary force. All variables are the same as defined in the text. (b) Schematic representation of the AuNR deposition process, from the fully immersed AuNRs, to the partially immersed AuNRs, to the aligned product.
AuNRs/μm² (Figure 7a) and 160 AuNRs/μm² (Figure 7b), the AuNRs aligned along the straight BCP contours, while trenches with over 250 AuNRs/μm² (Figure 7c) exhibited large 3D clusters that lost the structure of the underlying film, similar to Figure 3c.

The nearly monolayer coverage of linearly aligned AuNRs in the trenches of Figure 7b present a combination of surface density and alignment that should have the most interesting and useful SERS properties. Explicitly, we wished to investigate how the AuNR localization affected the Raman signal across the substrate and whether the nanowire AuNR arrays exhibited polarization dependent SERS.34−38 Because the graphoepitaxy trenches are optically identifiable, local regions on the substrates can be closely matched with corresponding AFM images (Figures 8 and 9). Thus, samples were functionalized with a monolayer of BT,44 mounted on a rotation stage, and the images are 0.75 μm × 1.5 μm.

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spot diameter was ~1064 nm, ~50% larger than the spacing between the trenches. When the trench was aligned perpendicular to the laser polarization (Figures 8c and 9b), the Raman signal intensities were severely reduced and showed no correlation with the substrate’s surface (Figures 8d and 9b). The in-trench signal intensities of the parallel orientation exhibited a 24-fold enhancement over the same regions in the perpendicular orientation, demonstrating that these large, ordered, macroscopic arrays of anisotropic NPs maintain the polarization dependence of single structures (Figure 9). These SERS results show that macroscopic systems of closely spaced, colloidal AuNRs will still have strong, directionally dependent electromagnetic enhancement properties when their alignment is carefully controlled.

## SUMMARY AND CONCLUSIONS

In summary, we investigated the alignment of gold nanorods on topographically enhanced, horizontal cylinder-forming PS-b-PMMA BCP templates, whose corrugation was much smaller than the widths of the gold nanorods. We demonstrated precise control over the ordering and orientation of gold nanorods of multiple aspect ratios for surface densities at and below 160 AuNR/μm² and presented a simple model that demonstrated that the topography of the substrate, while shallow, drives the gold nanorod alignment. Enhanced corrugation of the diblock template was achieved by chemical swelling prior to deposition of the metallic nanorods. Graphoepitaxy of the diblock copolymer in nanoconfining channels was employed to achieve essentially perfect long-range orientation of the templating substrate, while subsequent deposition of nanorods whose alignment map onto that of the diblock template with high fidelity provides novel organic–inorganic hybrid surfaces exhibiting highly aligned arrays of nanorods. We characterized the SERS properties of these structures and found that they exhibit extreme signal localization and polarization dependent spectra, with a 24-fold signal enhancement due to nanorod orientation with respect to laser polarization. This method for producing aligned AuNR assemblies with strong, directional electromagnetic enhancements offers great potential for the fabrication of reproducible, macroscopic, colloidal AuNR based plasmonic waveguides, optoelectronic, and sensing chips.

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### Notes

The authors declare no competing financial interest.

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