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Noble metal nanoparticle arrays: control of size, shape and placement via chemical self-assembly

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ABSTRACT

Selective patterning of chemical functional groups on polymer surfaces is utilized for controlled placement of monodisperse noble metal nanoparticles. Self-assembled diblock copolymer films deposited on hydrophobic silicon substrates are used as a template for metal nanoparticle organization. By varying the processing conditions of polymer templates, micelle and cylindrical polystyrene-*b*-poly(methyl methacrylate) diblock copolymer templates were fabricated. Functional groups on the surface of poly(methyl methacrylate) domains in the diblock copolymer films were chemically modified from an ester group to a carboxylate using a base catalyzed hydrolysis step. Gold and silver nanoparticles were fabricated in solution in order to achieve size and shape control. After gold nanoparticle synthesis, a ligand exchange reaction was performed to produce nanoparticles with amine functional groups for chemical attachment on chemically modified poly(methyl methacrylate) surfaces. Atomic force microscopy and scanning electron microscopy images demonstrate that this fabrication route results in preferential attachment of metal nanoparticles on poly(methyl methacrylate) thin films and on poly(methyl methacrylate) domains in polystyrene-*b*-poly(methyl methacrylate) diblock copolymer thin films.

Keywords: self-assembly, noble metal nanoparticles, diblock copolymers, plasmon resonance, surface enhanced Raman spectroscopy

1. INTRODUCTION

Nanoparticle plasmon resonance biosensors allow for highly sensitive detection of biomolecular binding events without the need for complicated optical and mechanical systems.¹ The strong near field coupling between closely spaced particles leads to a surface enhanced Raman spectroscopy (SERS) signal with theoretically predicted enhancement factors of $10^6 - 10^{14}$, affording the possibility of single-molecule detection.^{2,3} In order to achieve strong enhancement to the electromagnetic signal, the nanoparticle spacing should be on the order of nanometers.⁴ Structure is important since in noble metal nanostructures, the plasmon resonance frequency is dependent on nanoparticle size,^{5,6} dielectric medium,⁷ shape⁸ and inter-particle spacing.⁹ Much theoretical work has been performed but experiments are slow to keep up with theory since throughput is often limited by fabrication techniques such as electron beam lithography. Only 0.1 to 1 % of nanostructures in arrays are predicted to have exhibited strong enhancement in experiments.¹⁰ In this paper, a fabrication process is presented that will allow the integration of metal nanoparticle-based biosensors having controlled nanoparticle size, shape, and inter-particle spacing with polymer lab-on-a-chip systems using self-assembly. The fabrication process allows for low-cost, high-throughput manufacturing of optimized structures for biomolecular sensing. The integration of a nanotechnology-based biosensor into the fabrication process for polymer microsystems will constitute a huge step forward in the knowledge of bio-nano-micro integrated systems on polymer and seems well-suited to the creation of multifunctional structures from a perspective of both performance and cost. The combination of high sensitivity and low cost is an unresolved issue and has thus far prevented capitalization on the huge scientific potential of plasmon sensors and their economic worth for the health care system. The challenge of integrating metal nanoparticles into an all-polymer microsystem is addressed through chemical assembly of ligand functionalized noble metal nanoparticles on phase-separated diblock copolymer templates with hexagonally ordered cylindrical morphology. The choice of a diblock copolymer template is motivated by the ability to vary the domain size and spacing in the template in order to vary the structure of nanoparticle arrays,¹¹⁻¹⁴ control number of particles in a cluster¹⁵ and the ability

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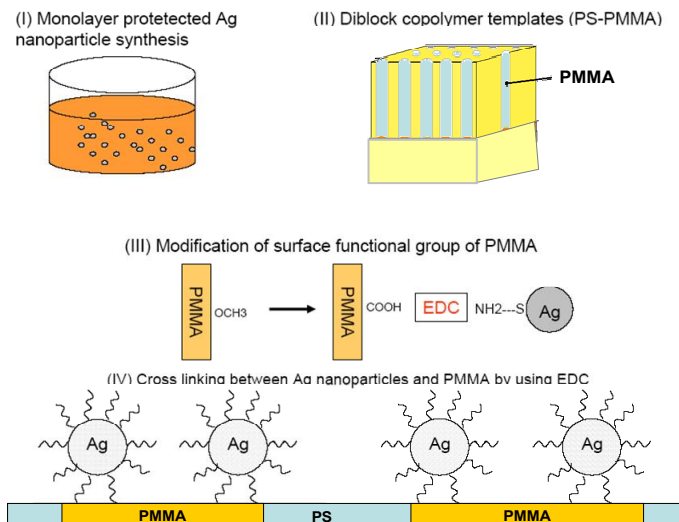


Fig. 1. Schematic for chemical assembly of metal nanoparticles on diblock copolymer films on polymer substrates: (I) synthesis of Ag or Au nanoparticles in solution; (II) diblock copolymer thin films are deposited on silicon or polymer substrates in order to use as a template for nanoparticle attachment; (III) modification of surface functional groups of PMMA from an ester group to a carboxylic acids; and (IV) attachment of Ag or Au nanoparticles onto the PMMA phase using EDC and sulfor-NHS chemistry.

to deposit copolymer thin films on polymer substrates in order to integrate polymer microsystems and biological sensing arrays. In this paper we report selective binding of ligand functionalized Au and Ag nanoparticles onto poly(methyl methacrylate) (PMMA) thin films and on PMMA domains in polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) diblock copolymer films. The fabrication process is divided into three steps: (Sec. 2.1) Au and Ag nanoparticle synthesis in solution with cysteamine functional groups; (Sec. 2.2) diblock copolymer fabrication (Sec. 2.3) modification of PMMA surface functional group on the polymer templates. The surface function group of PMMA was changed from ester to carboxylate; and (Sec. 2.4) cross linking between Au and Ag nanoparticles and PMMA surfaces. A schematic of the fabrication process as described is shown in Fig. 1.

2. EXPERIMENT

2.1 Nanocrystal Synthesis

Monolayer protected Ag and Au nanoparticles having diameters ranging from 15 nm to 40 nm were synthesized in solution.¹⁶ This synthetic technique allows for control of particle size and shape.¹⁷⁻¹⁹ Furthermore surface ligands attached in solution can be used for functionalization of nanoparticles with biomolecules and are also used to prevent aggregation of metal nanoparticles into clusters having uncontrolled and non-uniform particle number. Metal nanoparticles were synthesized using a previously reported procedure¹⁶ and this procedure is summarized below.

Ag nanoparticles were synthesized from 0.025 g of silver nitrate (AgNO_3 99.8%) dissolved in 10mL of distilled water and 2g of tetraoctylammonium bromide ($(\text{C}_8\text{H}_{17})_4\text{NBr}$, 98%) phase transfer reagent dissolved in 20 mL of CHCl_3 . The two solutions were mixed and stirred for 30 min. Following stirring, 0.15 g of cysteamine ($\text{C}_2\text{H}_7\text{NS}$, 95%) was added. After stirring for 5 additional min, 0.400 g of NaBH_4 (99%) dissolved in 25mL of water was added to the Ag mixture and was stirred for 3 more hours. CHCl_3 was then evaporated using a rotary evaporator until the volume of solution was approximately 5 mL. The 5 mL solution was added to 250 mL of isopropyl alcohol, and was stored at -18°C for 12 hours in order to effectively precipitate metal nanoparticles. The resulting black Ag precipitate was dissolved in 2 mL of chloroform in an ultrasonicator and 30 ml of isopropyl alcohol was added. A filtering step was then performed to remove phase transfer catalyst and unbound capping materials from the solution.

Au nanoparticles were synthesized from 0.59 g of hydrogen tetrachloroaurate (III) (HAuCl_4 99.9%) dissolved in 10 mL of distilled water and 2 g of $(\text{C}_8\text{H}_{17})_4\text{NBr}$ (98%) phase transfer reagent dissolved in 20 mL of CHCl_3 . The two solutions were also mixed and stirred for 30min. After this step, 0.8 ml of octanethiol ($\text{C}_8\text{H}_{18}\text{SH}$, 99%) was added. The solutions were stirred for 5 min. followed by the addition of 0.400 g of NaBH_4 (99%) dissolved in 25 mL of water. The mixture

was then stirred for 3 hours. CHCl_3 was evaporated using a rotary evaporator until solution's volume was approximately 5 mL. The resulting 5 mL solution was added to 250 mL of isopropyl alcohol, and was stored at -18°C for 12 hours to effectively precipitate metal nanoparticles. After Au nanoparticle fabrication, a ligand exchange reaction²⁰ was performed for selective chemical attachment of Au nanoparticles to PMMA thin films and the PMMA phase of PS-*b*-PMMA diblock copolymer templates. The black Au precipitate was dissolved in 2 ml of chloroform in an ultrasonicator and then 0.045 g of cysteamine was added in order to exchange octanethiol functional groups with cysteamine functional groups on Au nanoparticles. After, 30 ml of isopropyl alcohol was added and a filtering step was performed to remove phase transfer catalyst and unbound capping materials from the solution.

After the previous filtering step, 1 mg of the black precipitate was added to a 20 mL chloroform and isopropyl alcohol solution. This step is performed to reduce the size distribution of the nanocrystals in the solution for both Ag and Au nanoparticles, using chloroform and isopropyl alcohol as a solvent and non-solvent pair.²¹ Three different solutions were prepared and mixed with 1 mg of Ag nanoparticle precipitate having a chloroform/isopropanol ratio of 1:4, 1:8, and 1:12. The solution was then vacuum filtered using 1.6 micron, 0.45 micron, and 0.1 micron membrane sheets. In Fig 2, SEM images are shown of Ag nanoparticles that were size selected using this procedure and that have solvent/nonsolvent (chloroform/isopropanol) ratios of: (a) 1:4, (b) 1:8, and (c) 1:12. The measured size of Ag nanoparticles is approximately (a) 25-40 nm, (b) 20-30 nm, and (c) 18-23 nm in the SEM images.

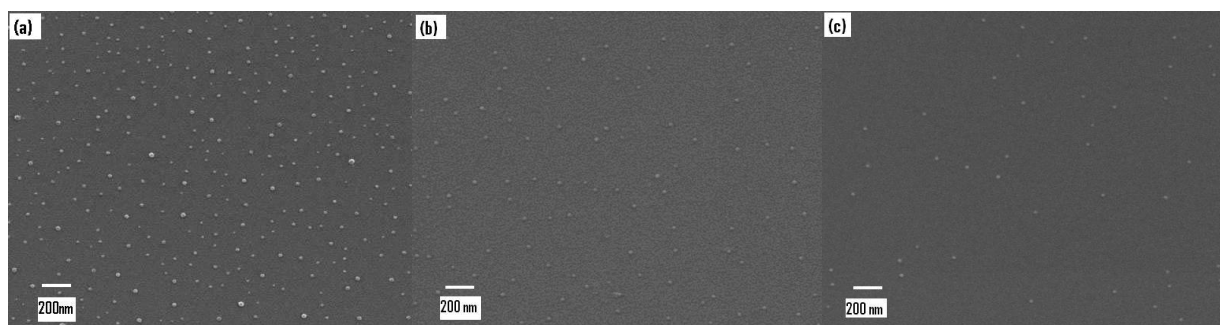


Fig. 2 SEM images of monodisperse Ag nanoparticles with mean size selected via chloroform/ isopropanol ratio: (a) 1:4, (b) 1:8, and (c) 1:12. The size of Ag nanoparticles in the SEM images is measured as approximately (a) 25-40 nm, (b) 20-30 nm, and (c) 18-23 nm.

2.2 Diblock Copolymer Fabrication

Diblock copolymer films are chosen as a template for metal nanoparticle assembly since previous work has demonstrated the ability to fabricate ordered arrays over areas hundreds of microns in length.²² Phase-separated diblock copolymer films can have various morphologies that depend on molecular weight, block ratio,²³ and processing conditions. For this study, diblock copolymers thin films with hexagonally close packed PMMA cylinders oriented parallel with the surface normal and those having a micelle morphology were fabricated. In the case of diblock copolymer thin films having a cylindrical morphology, the domain spacing can be as low as 30 nm, the domain size on the order of 10 nm, and an achievable area density of $10^{11}/\text{cm}^2$.²⁴ The size of the cylindrical domains as well as domain periodicity can be tuned with the relative volume fraction of the two different polymers in the diblock copolymer film.²³ Several material combinations have been demonstrated to form these cylindrical structures, e.g., PMMA-*b*-PS,²⁴ PS-*b*-poly(ethylene oxide),²² polyisoprene-*b*-poly(ethylene oxide).²³ In this study, PS-*b*-PMMA diblock copolymer films were deposited on hydrophobic Si substrates. Si substrates were etched in 20 wt% hydrofluoric acid for 2 min and then rinsed thoroughly with methanol to hydrogen passivate the surface. After preparation of the silicon substrate, a random copolymer P(S-*r*-MMA) (PS fraction: 59.4 mol%, Mn: 8900, Mw: 13100, Mw/Mn: 1.47) thin film was spin coated from a 2 wt% toluene solution at 3000 rpm for 60 sec and annealed at 172°C for 72 hr under vacuum. Random copolymer material that was not attached to the Si substrate was removed with toluene rinsing step leaving about 5-6 nm film of anchored P(S-*r*-MMA). Spin coating was performed using a model P-6000 spin coater (Specialty Coating System, Inc., IN). After, 1 wt% PS-*b*-PMMA diblock copolymer (Mn: PS (55000)-PMMA (22000), Mw/Mn: 1.09) in toluene was spin coated at 3000 rpm for 60 sec onto silicon substrates with a P(S-*r*-MMA) thin film. The resulting films were then annealed at 172°C (well above the glass transition temperature of 105°C) in vacuum to facilitate micro-phase separation of the two polymer domains and provide polymer mobility. In Fig. 3, SEM images of PS-*b*-PMMA diblock copolymer films are shown. In order to accentuate the two different phases in the SEM image, the film was exposed to

ultraviolet radiation for 10 min and etched in acetic acid for 10 min. As seen in Fig. 3, PS-*b*-PMMA diblock copolymer thin films were obtained with hexagonally close packed PMMA cylinders oriented normal to the surface. The image of Fig. 3(a) spans a region of approximately $6.5 \mu\text{m} \times 5 \mu\text{m}$ yet the film had the same surface structure over an $11 \mu\text{m} \times 7 \mu\text{m}$ region. The inset of Fig. 3(b) is a fast Fourier transform that shows a preferred spacing between PMMA domains in the thin film as well as the imperfect hexagonal symmetry of the PMMA domains.

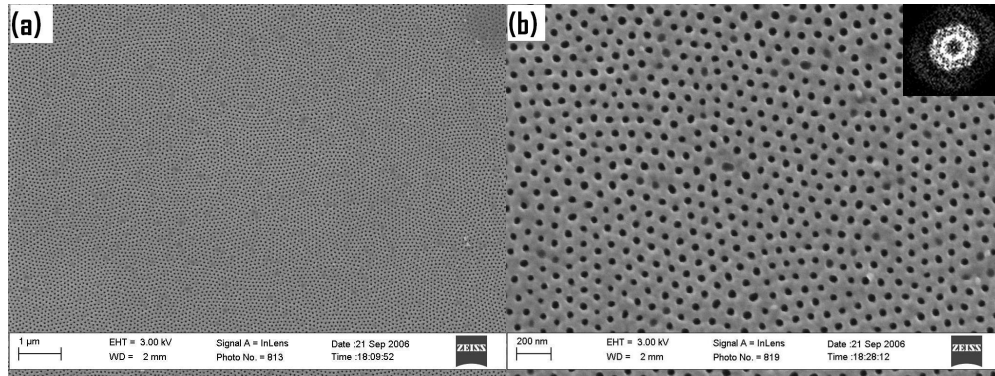


Fig. 3. SEM images of a PS-*b*-PMMA diblock copolymer thin film obtained by spin coating at 3000 rpm a 1 wt% PS-*b*-PMMA diblock copolymer solution in toluene for 60 sec onto a silicon substrate with a P(S-*r*-MMA) thin film.. In order to enhance contrast in the SEM images the films was UV cured for 10 min and etched in acetic acid for 10 min. The magnification is (a) x 10,000 and (b) x 40,000. The inset is a fast Fourier transform of the SEM image shown in (b) in order to examine the periodicity of the PMMA domains in the thin film.

2.3 Surface Chemistry Modification

In order to demonstrate the proposed mechanism allows for selective attachment of nanoparticles to PMMA versus PS surfaces, a surface chemistry modification procedure was performed on two separate PMMA and PS thin films deposited on Si substrates. The initial chemical reaction on the surface was designed to change the functional group of PMMA domains to a carboxylic acid. This was done using a base catalyzed hydrolysis. Both PMMA and PS thin films on silicon substrates were submerged into a mixture of 10:10:80 (vol%) (1 M NaOH:MeOH:H₂O) for 60 min. Following this procedure, both thin films were rinsed for 5 sec in 0.5 M HCl solution and rinsed again with distilled water. Immediately the substrates were submerged in 2 mM 1-Ethyl-3-[3-dimethylaminopropyl] carbodiimide Hydrochloride (EDC) solution in BupH[™] phosphate buffered saline pack (PBS) and 5 mM of N-hydroxysulfosuccinimide (sulfo-NHS) in 2-(N-mopholino)ethanesulfonic acid (MES) for 60 min. Metal nanoparticles with cysteamine functional groups were exposed onto PMMA and PS thin films on Si. EDC and sulfo-NHS were utilized for attaching metal nanoparticles with amine surface group onto polymer thin films with carboxyl groups (e.g. methyl methacrylate). EDC is a zero-length cross-linking agent used to couple carboxyl groups to primary amines.²⁵ In Fig. 4, AFM images that were acquired in tapping mode are shown of both a (a) PMMA thin film and a (b) PS thin film that have undergone the above chemical modification. Both films were rinsed isopropanol after spotting with a Au nanoparticle solution. The AFM images of Fig. 4 show Au particles attached to the PMMA film of Fig. 4(a) but there is no evidence of nanoparticles on the PS film shown in Fig. 4(b) after a similar procedure. These images indicate that our described chemical modification procedure of functional groups on PMMA surface can be utilized for selective nanoparticle placement into ordered arrays on diblock copolymer surfaces.

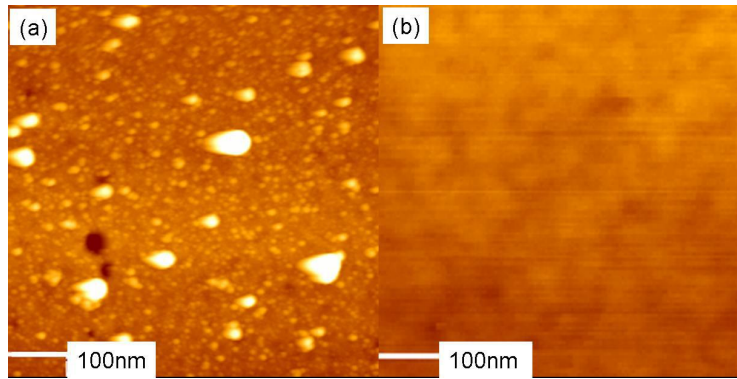


Fig. 4. AFM images of (a) PMMA and (b) PS thin films on Si substrates acquired in tapping mode. Both surfaces underwent a base catalyzed hydrolysis that was performed for 60 min followed by submerging the surfaces in 2 mM EDC solution in PBS and 5 mM of sulfo-NHS in MES for 60 min. After modification of the polymer surface chemistry, both surfaces were exposed to Au nanoparticles that underwent a ligand exchange reaction to obtain Au nanoparticles with cysteamine functional groups. Only the PMMA surface in (a) has particles on the surface after rinsing in isopropanol.

2.4 Nanoparticle attachment on PS-b-PMMA templates

A PS-b-PMMA thin film underwent a similar chemical modification procedure as the PMMA and PS thin films shown in Fig. 4. After spotting a Au nanoparticle solution onto this treated PS-b-PMMA template for 15 min, the surfaces were characterized by SEM and AFM in tapping mode. As seen in the images of Fig. 5, most of the spherical Au nanoparticles are distributed on the bright regions in both the SEM and the AFM images. Analysis of AFM line profiles from Fig. 5(b) yielded a height difference of 15-20 nm between the bright and dark regions on the diblock copolymer thin film. The inset of Fig. 5 (b) is an AFM image of a PS-b-PMMA diblock copolymer thin film before exposure to Au nanoparticles in solution. Close inspection of the image of the inset of Fig. 5 (b) shows cylindrical domains on both the bright and dark features. Yet the cylindrical features are observed in higher density on the raised features; thus we conclude the bright regions are predominantly PMMA. Ideally diblock copolymer should be flat but many factors affecting surface morphology such as high annealing temperature and surface treatment may cause height differences. As seen in Fig. 3, it is possible to fabricate PS-b-PMMA thin films with hexagonally close packed cylinders. Phase contrast AFM images of surfaces with a micelle structure proved better surface to examine the preferential attachment of Au nanoparticles to PMMA domains due to the larger PMMA domain size. As seen in Fig. 4, SEM and phase contrast AFM images both indicate preferential attachment of Au nanoparticles to PMMA phases on PS-b-PMMA diblock copolymer thin films.

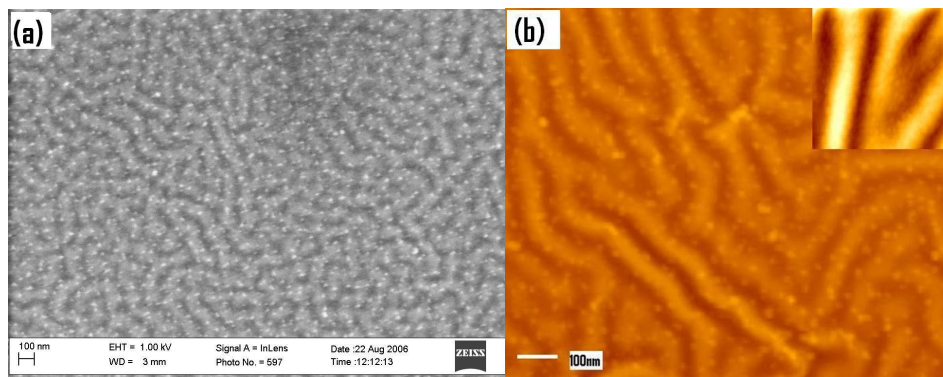


Fig. 5. (a) SEM and (b) AFM images of Ag nanoparticles selectively attached on PMMA domain in PS-b-PMMA diblock copolymer. The inset is the AFM image of PS-b-PMMA diblock copolymer before attaching Ag nanoparticles

3. CONCLUSIONS

Here we have outlined a process for fabricating ordered arrays of metal nanoparticles on polymer surfaces. The processing steps are: (1) synthesis of size controlled and ligand functionalized noble metal nanoparticles in solution; (2) diblock copolymer thin film fabrication on silicon substrates; (3) modification of surface functional group in the PMMA domains of PS-*b*-PMMA diblock copolymer templates to obtain stable adhesion of metal nanoparticles onto the PMMA domains; and (4) deposition of metal nanoparticles from solution onto diblock copolymer templates. AFM images acquired in tapping mode demonstrated preferential attachment of Au nanoparticles onto chemically modified PMMA surfaces versus PS surfaces that have undergone the same surface treatment. Furthermore, phase contrast AFM and SEM images have also indicated Ag nanoparticle attachment to PMMA phases on PS-*b*-PMMA diblock copolymer thin films. Diblock copolymer thin films have tremendous versatility in the types of periodic structures that can be obtained on surfaces. Thus, these thin films have great potential for patterning noble metal nanoparticles in order to engineer desired optical properties. By using this parallel process for nanostructure array fabrication we can explore the phase-space of the effects on signal enhancement on structure and inter-particle spacing much more efficiently than nanostructures fabricated by electron beam lithography. Furthermore, we can make nanostructure arrays that are not attainable with even state of the art e-beam lithography. Fabrication of these nanostructure arrays via chemical self-assembly allows one to cover large areas using a low cost and non-time prohibitive technique that is compatible with polymer microsystem processing. Future work will involve the integration of this assembly technique with polymer substrates as well as measurement of optical properties of periodic metal nanoparticle arrays.

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