Self Assembly of Colloidal Gold Nanoparticles on Diblock Copolymer Thin Film Templates

S.M. Adams and R. Ragan*

University of California, Irvine, CA, USA, rragan@uci.edu

ABSTRACT

Self-assembly of metallic nanoparticles were investigated for the development of field-enhanced chemical and biological detection devices with the capacity to achieve single-molecule level detection resulting from surface enhanced Raman scattering, associated with closely spaced noble metal nanostructures. Using chemical self-assembly, we attached monodisperse, colloidal gold nanoparticles on self-organized polymer templates, patterning arrays of nanoparticle clusters with sub-10 nanometer interparticle spacing in order to engineer enhanced optical fields. Poly(methyl methacrylate) domains in phase-separated polystyrene-b-poly(methyl methacrylate) diblock copolymer thin films were chemically modified with surface amination for varied arrangements. Chemically synthesized sub-20 nm diameter gold nanoparticles were attached to the amine-functionalized surfaces using EDC linking chemistry with thioctic acid ligand-bound to the nanoparticle surface.

Keywords: self assembly, nanoparticle, sensor, thin film

1 INTRODUCTION

Metallic nanoparticles exhibit a feature in which a surface plasmon resonance with wavelength approaching that of incident light is sustained through oscillation of the metal's conduction electrons. With closely spaced metal nanoparticles, the surface plasmon resonance is observed as a dipole due to the collective electronegative nature with respect to the positive ionic background [1]. These nanoparticle plasmonic resonance effects are desirable to enhance detection capabilities of molecular biosensors. The development of metal nanoparticle arrays with low interparticle spacing for use as field enhanced detection of chemical and biological components with high sensitivity has been a subject of great interest in the past several decades [2,3]. Comparison of state of the art biosensor technology design indicates significant benefit with nanoparticle array sensor technology. Current methods for optical sensor detection generally rely on fluorescent tagging, whereas the application of metal nanoparticle arrays have displayed a strong optical signal from plasmon scattering effects the equivalent of 500,000 fluorescein molecules, permitting detection of biomolecules up to near single-molecule detection [4-6].

Self-assembly techniques have been increasingly considered for their potential application in the development of nanoscale surface patterning as an alternative to conventional lithography techniques, enabling ordered patterning at scales previously unachievable with increased yield and cost-effectiveness using simple thermodynamic and chemical synthesis techniques [7,8]. In this study, metallic nanoparticles were investigated for the development of field-enhanced chemical and biological detection devices with the capacity to achieve single-molecule level detection resulting from surface enhanced Raman scattering (SERS) associated with closely spaced noble metal nanostructures [3]. Localized surface plasmon resonance (LSPR) sensors likewise benefit from ordered metal nanoparticles on surfaces, providing increased shift in minimum of reflectivity with biological binding event (figure 1). Furthermore, strong scattering from the interacting surface plasmons of metal nanoparticles in the patterned array is also applicable to enhancement of photovoltaic technology, in which the dipole interactions increase the optical path of incident light in the absorber layers of photovoltaic solar cells [9].

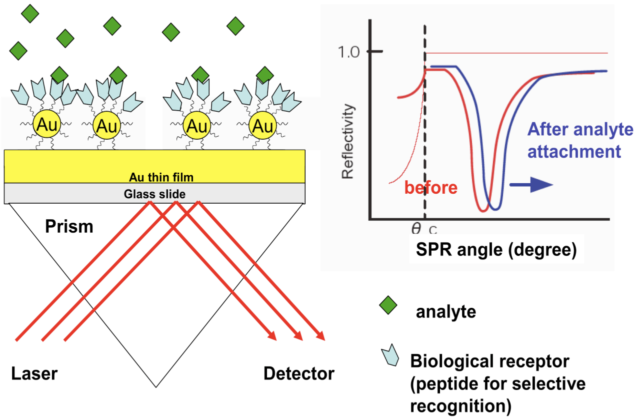

Figure 1: Refractive index of surface changes when analyte molecule binds to biological receptor on nanoparticle surface yielding a shift in SPR minimum reflectance angle.

Use of chemical self-assembly techniques for developing nanoparticle arrays also provide significant benefits. As enhanced optical [10] and catalytic [11] properties have been observed with sub-10 nm inter-particle spacing, adaptation of bottom-up chemical assembly techniques for template design would likewise be optimal for development for its capacity for such low inter- particle dimensions. Nanoparticles prepared from colloidal solution can be produced with diverse size [12], shape [13], and interfacial features [14]. By using surface chemistry techniques to instigate nanoparticle attachment from colloidal solution, metal nanoparticles with desired physical characteristics can be implemented in template design. Using chemical self-assembly, the surface template can likewise be varied by simple changes in the chemical design to optimize for particle spacing and alignment. Moreover, the method of processing relies on a simple batch of chemical reactions, which would be both reproducible when optimized as well as provide a relatively low cost fabrication technique in comparison to traditional lithographic methods. These design characteristics provide generous motivation for development of self-assembled nanoparticle templates.

2 EXPERIMENTAL MODEL

With chemical self-assembly, we have attached monodisperse, colloidal gold nanoparticles on self-organized polymer templates, patterning arrays of nanoparticle clusters with sub-10 nanometer interparticle spacing in order to engineer enhanced optical fields. Poly (methyl methacrylate) (PMMA) domains in phase-separated polystyrene-b-poly(methyl methacrylate) (PS-*b*-PMMA) diblock copolymer thin films were chemically modified with surface amination for both lamellar and hexagonal arrangements. Chemically synthesized sub-20 nm diameter gold nanoparticles were attached to the amine-functionalized surfaces using EDC linking chemistry with thioctic acid ligand-bound to the nanoparticle surface (figure 2) [7].

2.1 Surface Functionalization

Sodium citrate stabilized Au nanoparticle colloids with particle size of 20 and 10 nm in diameter were prepared from reduction of $HAuCl_4$. The surface of the Au nanoparticles was chemically functionalized with carboxylic acid surface functional groups by ligand attachment of DL-6,8-thioctic acid (Sigma- Aldrich) as depicted in figure 2a [7]. This method of functionalizing the nanoparticle from a colloidal solution permits the attachment of particles of various sizes and shapes, as long as carboxyl ligand can be attached.

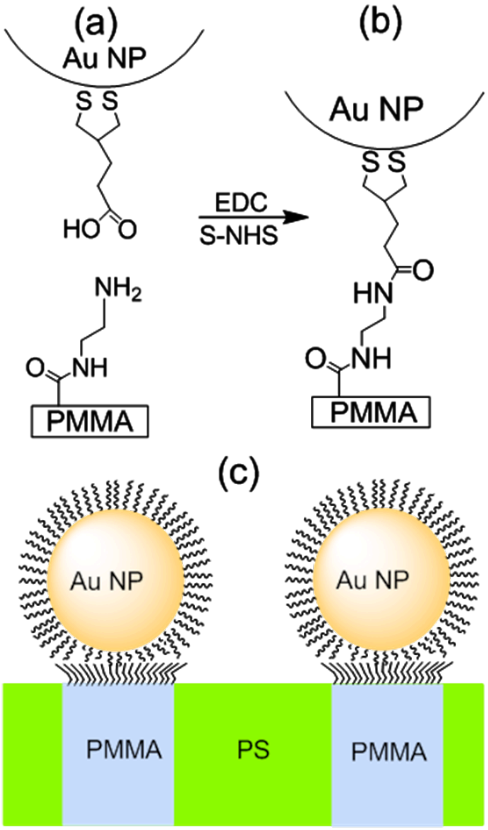

Figure 2: Schematic representation of assembly method: (a) Nanoparticles functionalized with thioctic acid and PMMA with primary amine; (b) Crosslinking chemistry of nanoparticles to amine-treated surfaces; and (c) Au nanoparticles selectively assembled on PMMA regions of the PS-b-PMMA template [7].

The surface of the PMMA regions of the PS-*b*-PMMA thin film diblock copolymer, prepared by spin coating on a Si substrate followed by thermal annealing, were functionalized with primary amine functional groups by reacting with dilute ethylenediamine [7]. Controlled surface patterning of the aminated regions is accomplished by thin film self-assembly relative to copolymer fractional molecular weight and degree of polymerization [15].

2.2 Nanoparticle Self-Assembly

The carboxyl-functionalized Au nanoparticles were selectively attached to the amine-functionalized PMMA regions of the diblock copolymer (figure 2c) by the use of a chemical crosslinker, designed to join carboxylic acids with primary amines. In this case, 1- ethyl-3-[3-dimethylaminopropyl] carbodiimide hydrochloride (EDC) linking chemistry with N-hydroxy sulfosuccinimide (S-NHS) [16] is used to form a covalent bond is formed between the metallic nanoparticles and patterned copolymer surface (figure 2b), yielding a self-assembled patterned array of nanoparticles on the polymer thin film [7].

3 RESULTS AND DISCUSSION

Atomic force and scanning electron microscopy was used to demonstrate that Au nanoparticles were preferentially immobilized on poly(methyl methacrylate) (PMMA) domains of the copolymer templates. AFM topography images are shown of templates exposed to TA-Au colloids with (figure 3a) and without (figure 3b) EDC and S-NHS presence to promote chemical crosslinking. Gold nanoparticle distribution on the sample with EDC/S-NHS treatment exhibited high levels of selectivity for attachment on regions where the PMMA has been selectively etched [7].

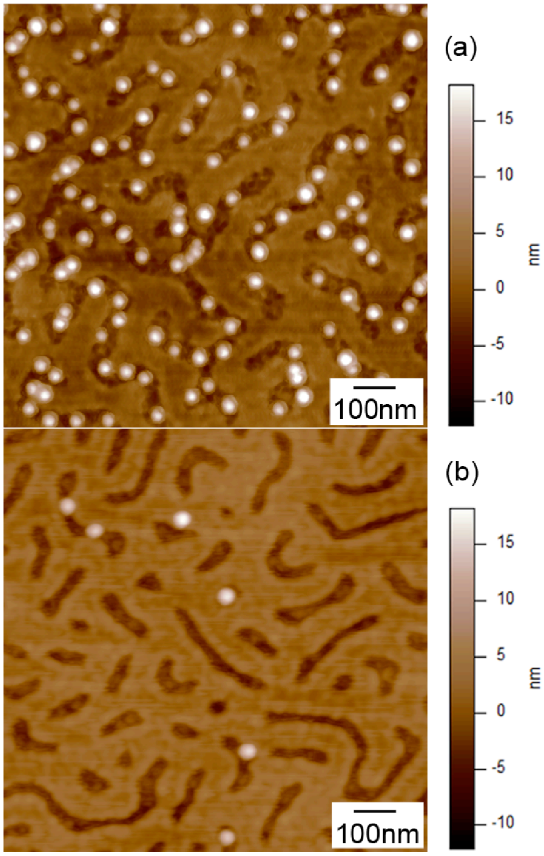

Figure 3. Amine-treated polymer surface with attached nanoparticles with (a) and without (b) EDC crosslinker treatment [7].

By controlling the size and spacing of the reactive polymer domains and the relative nanoparticle size, nanoparticle arrays are fabricated with controlled clustering arrangements (figure 4). The spacing between nanoparticle clusters is directly affected by the interdomain spacing (λ) of the copolymer matrix. While the number of particles in the nanoparticle cluster is a function of the difference between nanoparticle size (d) and PMMA domain size (D). Interparticle distances within nanoparticle clusters arranged on the patterned surface are controlled by the relative ionic strength of the nanoparticle colloid used for attachment. This clustering technique is especially useful for arranging nanoparticles in dimer formations, which provide significant increase in detection limits for Raman enhanced molecules in SERS systems.

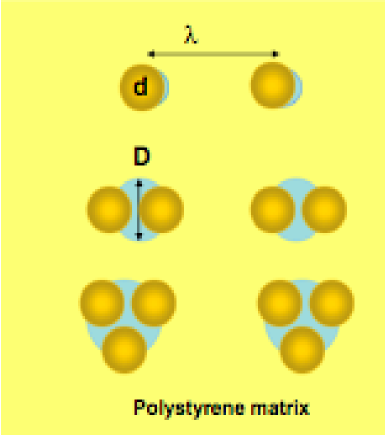

Figure 4. Schematic of metal nanoparticle cluster array assembly for nanoparticles of diameter d, on polymer domain size D, and interdomain spacing λ.

Analysis of the preliminary SERS enhancement measurement on the gold nanoparticle array showed an enhancement factor of the order of 10^7 for the detection of molecular pyridine (figure 5). As there would be 10^4 more pyradine molecules per cubic cm of solution than square cm of a closely packed monolayer of pyradine on the surface, this indicates that far fewer molecules need be present for detection. This is beneficial for developing sensitive signal enhancement and supports further efforts to analyze and optimize this self-assembly-based sensor design.

with primary amines. In this case, 1- ethyl-3-[3-dimethylaminopropyl] carbodiimide hydrochloride (EDC) linking chemistry with N-hydroxy sulfosuccinimide (S-NHS) [16] is used to form a covalent bond is formed between the metallic nanoparticles and patterned copolymer surface (figure 2b), yielding a self-assembled patterned array of nanoparticles on the polymer thin film [7].

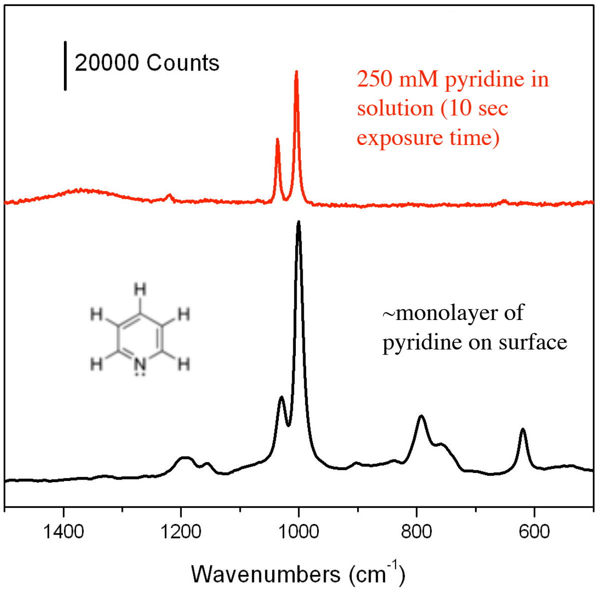

Figure 5. Preliminary SERS measurement of nanoparticle attached diblock copolymer surface.

4 CONCLUSIONS

By altering the surface chemistry of colloidal nanoparticles with carboxylic acid functional groups and a nanoscale patterned chemical templates with primary amine functional groups, we have selectively attached the nanoparticles as an array structure using crosslinking chemistry techniques. Through incorporating chemical assembly techniques with fluidic colloids, inexpensive production of arrays of gold nanostructures suitable for biomolecular sensors with exceedingly low detection limits and enhanced photovoltaics are shown to be achievable.

REFERENCES

[1] T. Jensen, L. Kelly, A. Lazarides, and G. C. Schatz, J. Clust. Sci., 10, 295-317, 1999.
[2] S. Nie and S. R. Emory, Science, 275, 1102-1106, 1997.
[3] K. Kneipp, Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. R. Dasari, and M. S. Feld, Phys. Rev. Lett., 78, 1667-1670, 1997.
[4] M. Bally, M. Halter, J. Vörös, and H. M. Grandin, Surf. Interface Anal., 38, 1442-1458, 2006.
[5] P. Bao, A. G. Frutos, C. Greef, J. Lahiri, U. Muller, T. C. Peterson, L. Warden, and X. Xie, Anal. Chem., 74, 1792-1797, 2002.
[6] G. Raschke, S. Kowarik, T. Franzl, C. Sonnichsen, T. A. Klar, J. Feldmann, A. Nichtl, and K. Kurzinger, Nano Lett., 3, 935-938, 2003.
[7] J. H. Choi, S. M. Adams, and R. Ragan, Nanotechnology, 20, 065301-065306, 2009.
[8] W. A. Lopes and H. M. Jaeger, Nature, 414, 735-738, 2001.
[9] K. Nakayama, K. Tanabe, and H. A. Atwater, Appl. Phys. Lett., 93, 121904, 2008.
[10] P. J. Schuck, D. P. Fromm, A. Sundaramurthy, G. S. Kino, and W. E. Moerner, Phys. Rev. Lett., 94, 017402, 2005.
[11] M. Valden, X. Lai, and D. W. Goodman, Science, 281, 1647-1650, 1998.
[12] T. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein, and M. A. Elsayed, Science, 272, 1924-1926, 1996.
[13] S. E. Skrabalak, L. Au, X. Li, and Y. Xia, Nat. Protoc., 2, 2182-2190, 2007.
[14] H. Chen, X. Kou, Z. Yang, W. Ni, and J. Wang, Langmuir, 24, 5233-5237, 2008.
[15] U. Y. Jeong, H. C. Kim, R. L. Rodriguez, I. Y. Tsai, C. M. Stafford, J. K. Kim, C. J. Hawker, and T. P. Russell, Adv. Mater., 14, 274-276, 2002.
[16] Z. Grabarek and J. Gergely, Anal. Biochem., 185, 131-135, 1990.