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# NEMB2010-13126

## GOLD NANOPARTICLE SELF ASSEMBLY ON DIBLOCK COPOLYMERS FOR APPLICATION AS BIOMOLECULAR SENSORS

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### INTRODUCTION

Current efforts in medical diagnostic technology focus toward developing biological sensors with the capacity for detecting trace quantities of specified organic molecules. 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.[1, 2] Localized surface plasmon resonance (LSPR) sensors likewise benefit from the incorporation of ordered metal nanoparticles on surfaces, providing increased shift in minimum of reflectivity with biological binding event (figure 1).[3]

By integrating surface enhanced raman scattering and surface plasmon resonance sensors with microfluidic structures and optical waveguides (figure 2), metallic nanostructure devices may be used to yield high throughput fabrication of inexpensive lab-on-chip diagnostic biosensors.

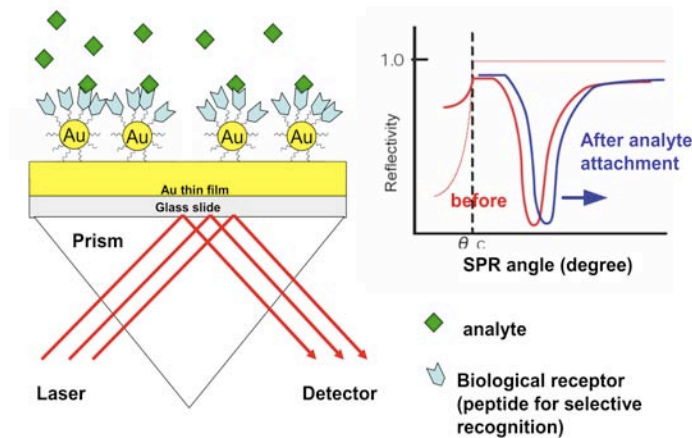
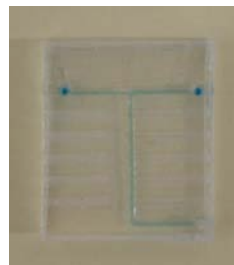


Figure 1. Refractive index of surface layer changes when analyte molecule binds to biological receptor on nanoparticle surface yielding a shift in the SPR minimum reflectance angle.

### Fluidic structure



### Waveguide

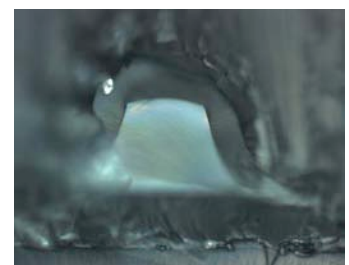
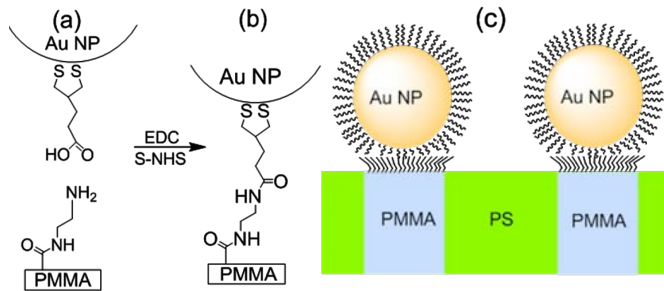


Figure 2. Microfluidic channels and waveguides for integration in micro-optic-fluidic biosensors.

### EXPERIMENTAL METHODS

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.[4] Poly(methyl methacrylate) domains in phase-separated polystyrene-b-poly(methyl methacrylate) diblock copolymer thin films [5] 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-

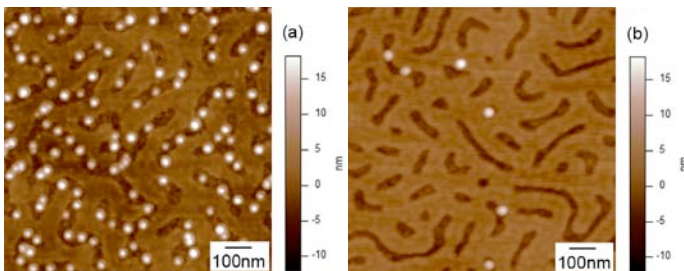
functionalized surfaces using EDC linking chemistry with thioctic acid ligand-bound to the nanoparticle surface (figure 3).



**Figure 3. 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 PS-b-PMMA template.[4]**

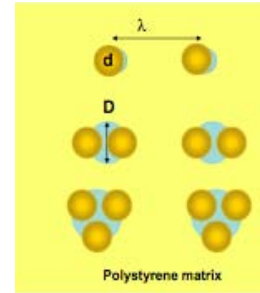
## RESULTS AND DISCUSSION

Atomic force and scanning electron microscopy was used to demonstrate that Au nanoparticles are 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 EDC and S-NHS (figure 4a) and without EDC and S-NHS (figure 4b). Gold nanoparticle distribution on the sample with EDC/S-NHS treatment exhibited high levels of selectivity for attachment on the dark regions where the PMMA has been selectively etched.



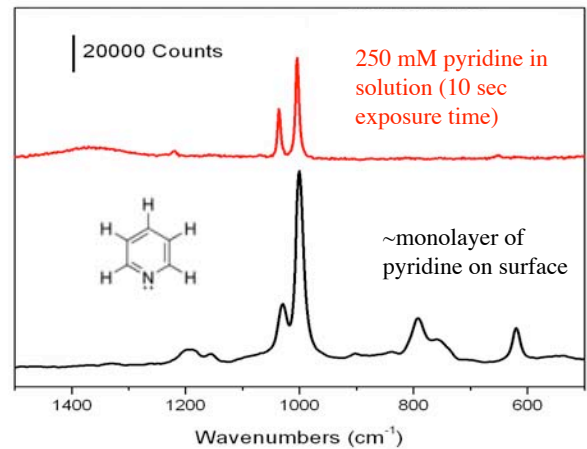
**Figure 4. Amine-treated polymer surface with attached nanoparticles with (a) and 3 without (b) EDC crosslinker treatment.[4]**

With chemical assembly techniques and colloids, arrays of gold nanostructures were developed with feature size and interparticle spacing unachievable using lithographic methods. By the size and spacing of the reactive polymer domains and the relative nanoparticle size, nanoparticle arrays are fabricated with controlled clustering arrangements (figure 5). This clustering technique is especially useful in arranging nanoparticles in dimer formations, which provide significant increase in detection limits for Raman enhanced molecules in SERS systems.



**Figure 5. Schematic of nanoparticle cluster array assembly for particles of diameter  $d$ , on polymer domain size  $D$ , and interdomain spacing  $\lambda$ .**

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 6).



**Figure 6. Preliminary SERS measurement of nanoparticle attached diblock copolymer surface.**

By incorporating chemical assembly techniques with fluidic colloids, inexpensive production of arrays of gold nanostructures suitable for bimolecular sensor with exceedingly low detection limits are shown to be achievable.

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