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# Conducting polymer–gold co-patterned surfaces via nanosphere lithography

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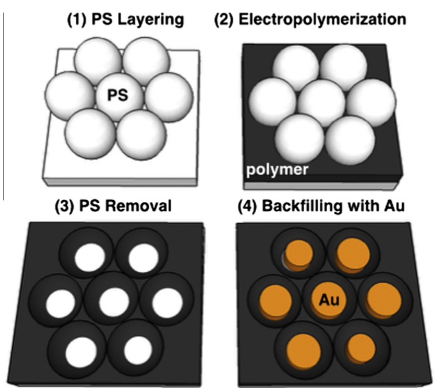
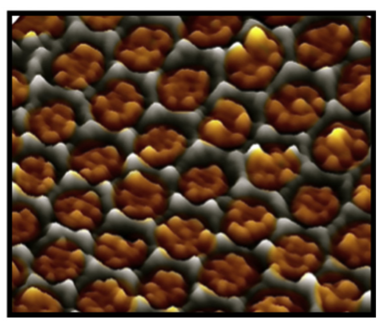
## GRAPHICAL ABSTRACT



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## ABSTRACT

*Hypothesis:* Co-patterned arrays comprised of conjugated polymers and nanostructured gold is an important matrix for sensing and stimuli-responsive plasmonic applications. Nanosphere lithography (NSL) is an easy-to-use patterning technique and viable method to fabricate inverse honeycomb structures with electrochemically deposited conjugated polymers. The cross-sectional height of the conducting polymer pattern can be tuned such that the macropores of the honeycomb structure expose electrochemically accessible areas for further gold deposition. Using time-dependent electrochemical reduction, $Au^{3+}$ is reduced to $Au^0$ and selectively deposit on the macropores thus forming a co-patterned surface.

*Experiments:* The Langmuir–Blodgett-like deposition was used to assemble polystyrene spheres on a conductive substrate. Then the carbazole-based monomer was electropolymerized within the interstices of the colloidal template, which was subsequently dissolved. A potentiostatic technique was used to deposit Au in the macropores.

*Findings:* Fabrication of the polycarbazole–Au co-patterned surface was characterized by atomic force microscopy (AFM), electrochemical quartz crystal microbalance (EC-QCM), and X-ray photoelectron spectroscopy (XPS). Surface plasmon resonance spectroscopy (SPS) data supported backfilling behavior and quantified the complex refractive index of the array. UV–Vis absorption spectroscopy shows overlapping polycarbazole and gold LSPR peaks useful for plasmonic sensing applications. The colloidal templating approach reported in this study was further used in the fabrication of highly ordered Au nanodisks.

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## 1. Introduction

Nanopatterns are the building blocks of numerous state-of-the-art surface-based technologies including corrosion-resistant and anti-reflection coatings [1–3], tissue engineering scaffolds [4], sensors [5], and nanoelectronics [6]. Among these surfaces, multi-component nanopatterned arrays, in particular, have tremendous potential in the development of compact high memory systems and spintronics useful in biomedical diagnostics and supercomputing. Interfacial junctions between components have their own set of properties, which should create new functions from the interactions of significantly different materials [7]. An interesting matrix should be composed of spatially arranged nanostructured gold and conducting polymers particularly for developing sensors and plasmonic devices [8].

Au is well-known for exhibiting localized surface plasmon resonance (LSPR), which occur whenever an electromagnetic wave interacts with nanometer-sized gold to cause free electrons oscillations in the same resonant frequency as the interacting radiation [9]. The energy of the incoming radiation either gets scattered and converted to radiation; or absorbed and converted to thermal energy, which can be observed as a strong peak in the visible or near-infrared spectral regions. The LSPR peak shifts depending on nanomaterial geometry, capping agent (if present), and surrounding environment, which makes the material useful for monitoring physico-chemical phenomena.

Conducting polymers are highly interesting materials due to its electrical conductivity, flexible synthetic methods and optical properties [10]. Among its characteristics, its capability to electrochemically switch from an oxidized to a reduced state (or conductive state to an insulating state) is arguably the most vital since a complete change in properties can be observed. Recently, reports have investigated synergistic properties of hybrid polyaniline–Au materials and demonstrated modulation and damping of the LSPR peak as controlled by the potential-dependent doping state of the conducting polymer [11–13]. With these properties, nanostructured arrays comprising of Au and conducting polymers have great potential as materials for active plasmonic devices and electrochemical sensors [14]. In this study, the conducting polymer selected is a polycarbazole that has been electrochemically synthesized from a first generation carbazole monomer with tetraethylene glycol functional group. As compared to other conducting polymers, polycarbazoles have a much better stability due to the fully aromatic carbazole moiety [15] as indicated by a higher oxidation potential [16,17]. Carbazole-based conjugated polymer systems are widely known for its photoconductive, hole transport properties and high charge mobility which are essential in developing polymeric light emitting diodes (PLED), organic photorefractive materials, electrochromic displays and other electronic devices [16]. Furthermore, the carbazole moiety is highly reactive at various points: C-2, C-3, C-6, C-7 and the N positions, which allow flexible modification schemes. In the past decade, our group has demonstrated fluorescence quenching applications and energy transfer behavior by synthesizing novel colloidal and thin film polycarbazole–gold nanoparticle assemblies [17–19]. Meanwhile, other groups are employing polycarbazole–gold thin films in engineering sensitive and highly selective sensors [14,20]. Combining these energy transfer properties and detection application of the polycarbazole–gold matrix can potentially lead to more functional sensing arrays and nanoelectronics. In addition, the tetraethylene glycol attached to the polycarbazole has protein-repellant properties [21,22], hence co-patterning the conjugated polymer and Au can potentially be used in biological patterning and sensing arrays.

In a step toward developing plasmonic applications for hybrid conducting polymer–Au matrices, the study proposes a more rapid, inexpensive, and robust co-patterning method using template-assisted electrochemical polymerization of a conducting polymer followed by electro-reduction of Au. Monolayer colloidal crystal (MCC) templates produced by nanosphere lithography is an array typically composed of silica or polystyrene (PS) latex microbeads in a hexagonally close-packed arrangement [23,24]. The resulting assembly will act as masks for the electropolymerization of a conducting polymer and will be dissolved as an inverse honeycomb pattern is revealed. Since the macropores of the inverse colloidal pattern exposes conductive substrate surface, Au is expected to preferentially deposit on these areas thus forming a co-patterned conducting polymer–Au array. Previously, the Van Duyne group has demonstrated various metallic nanoscale architectures using nanoscale lithography and investigated their plasmonic behavior [25–27]. By combining nanosphere lithography and electrodeposition, our study aims to fabricate a highly defined co-pattern of a conjugated polymer with gold nanostructures and investigate its properties, which may be used for potential sensing, electronic and biological patterning applications. Moreover, the proposed protocol presents more control the periodicity and amount of material without the need of highly sophisticated equipment and complicated lithographic techniques such as scanning probe lithography [28], microcontact printing [29], electron-beam lithography [30], among others.

## 2. Materials and methods

### *2.1. Materials*

The Polybead® polystyrene (PS) microspheres (500 nm in diameter, 2.59 wt.% latex in water) were purchased from Polysciences, Inc. (Warrington, PA) and were used without further purification. The monomer 2-(2-(2-(2-hydroxy)ethoxy)ethoxy)ethyl-3(4-(9H-carbazol-9-yl)butoxy)-5-(4-(9H-carbazol-9-yl)butoxy))benzoate ($G_1$cbz-TEG), a generation 1 carbazole monomer with pre-grafted tetraethylene glycol denoted as ($G_1$cbz-TEG), was synthesized in our group [14] and used for polymerization. Acetonitrile (ACN), tetrahydrofuran (THF), and tetrabutylammonium hexafluorophosphate (TBAH) were obtained from Sigma–Aldrich (St. Louis, MO). Sodium n-dodecyl sulfate (SDS; 99% pure), hydrogen tetrachloroaurate (III) hydrate (99.999%), and perchloric acid (70 vol.% in aqueous solution) were purchased from Alfa Aesar (Ward Hill, MA).

### *2.2. Preparation of conductive substrates*

Gold- and indium tin oxide (ITO)-deposited glass slides are the primary conductive substrates used for patterning. Au substrates are prepared by thermally evaporating high-purity gold pellets onto pre-cleaned glass. Glass slides (BK7) are sonicated alternately in MilliQ water and acetone, then immersed in Piranha solution ($H_2SO_4$: $H_2O_2$, 7:3 v/v). *Caution: The Piranha solution is highly corrosive and very reactive toward organic materials! Using this solution requires extreme precaution.* After the substrates have been thoroughly rinsed with MilliQ water and then treated with $O_2$ plasma, approximately 20 nm of Cr is thermally evaporated onto the glass under high vacuum conditions. Cr will act as an adhesive layer for Au, which was subsequently evaporated at a rate of 0.8–1.2 Å/s until film thickness reaches 100 nm. For SPR studies however, Cr and Au thicknesses should be kept close to 0.5 and 50 nm respectively.

On the other hand, ITO substrates (pre-cut into 0.6″ × 1″ pieces) were cleaned using a detergent solution (Alconox) and sonicated in isopropanol, hexane and toluene for 15 min each. After drying with $N_2$, the substrates treated with $O_2$ plasma for 3 min.

### *2.3. Assembly of PS colloidal microsphere masks*

A highly ordered array of hexagonally closed packed polystyrene (PS) microspheres with 500 nm diameter was assembled

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