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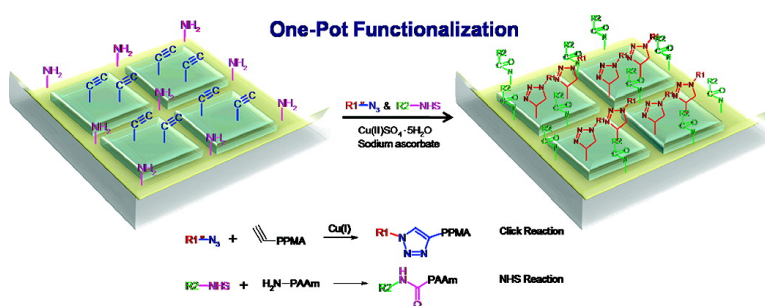
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Designed bioactive patterned functional surfaces can offer advantageous properties such as controlled adsorption and site-specific affinity.^{1,2} In particular, area-selective functionalization of multiple components onto a predesigned surface^{2–6} is highly desirable. Such a system can be utilized to detect and identify more than one analyte in biosensor applications, which enables fabrication of more effective biodevices.³ Moreover, the multifunctional surface can be used as a template to monitor the interaction among the adsorbed components from a complex mixture, such as an extracellular environment. To achieve this goal, a highly efficient, orthogonal functionalization scheme with high fidelity is desirable.

Although various multicomponent patterning strategies are well-established for semiconductor industries, the direct application of these schemes for bioactive platforms is still challenging because many biological components such as proteins and nucleic acids are susceptible to degradation during patterning.⁷ For example, conventional photolithography (PL) utilizes harsh organic solvents and UV irradiation that can potentially lead to the destruction of bioactivity.^{3,7} Soft lithography techniques often result in the dehydration of biofunctionalities during the inking of stamps.⁶ For these reasons, patterned surfaces had been primarily functionalized only with one component on a selected area.^{8,9} To achieve bioactive multifunctional surfaces, J. Katz et al. synthesized a new photo-sensitive terpolymer that can be processed under mild biocompatible conditions;³ however, the process involves a complicated synthesis. J. M. Slocik et al. used shadow mask patterning and plasma enhanced chemical vapor deposition (PECVD) for patterning of multiple components, but the resolution does not reach the nanometer scale domain and the use of thiol agents limits the type of substrates that can be used.⁵ For nanometer scale multifunctional surfaces, a solventless patterning process that can be performed under mild conditions using commercial reactants is highly desirable.

In this report, we propose a facile solventless method for synthesizing nanopatterned multifunctional surfaces. One nanodomain contains an acetylene group which can be functionalized via click chemistry. The other nanodomain contains surface amine groups which can be functionalized by carbodiimide chemistry with *N*-hydroxysuccinimide (NHS).^{4,8} Both the click reaction and amine functionalization (NHS reaction, afterward) are well-understood and have attractive characteristics such as high selectivity, high yield, fast reaction in aqueous phase at room temperature, and biocompatibility.^{4,8} Moreover, the click and NHS reactions are highly orthogonal to each other so that nonspecific immobilization can be minimized.⁴ With these functionalities, we demonstrated the covalent functionalization of two independent components in a one-pot, self-sorted area-selective process, performed in an aqueous solution at room temperature, having conditions which are biocompatible. Considering the versatility and generality of the thin

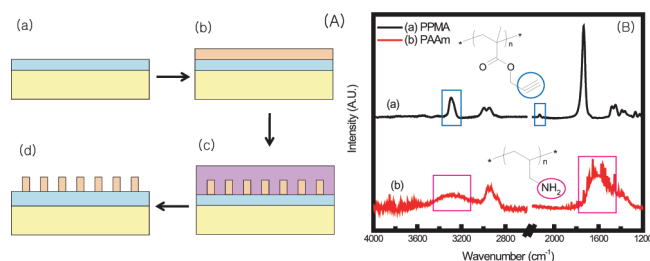


Figure 1. (A) Schematic procedure of nanopattern fabrication: (a) PECVD of PAAm; (b) iCVD of PPMA; (c) apply CFL mold to induce capillary rise; (d) remove CFL mold to complete the nanopattern. (B) FTIR spectra of (a) iCVD PPMA and (b) PECVD PAAm.

film deposition methods used here, we believe this platform can be easily extended to various biodevice applications.

In Figure 1A, capillary force lithography (CFL)¹⁰ nanopatterns the upper layer of a bilayer structure, exposing regions of the bottom material, thus creating a dual functional surface. Cross-linking allows the bottom layer to remain immobile during the CFL step. Vapor deposition allows the insoluble bottom layer to be directly synthesized. For the top layer, the use of solventless vapor deposition is also critical, as solvents used in conventional solution processing have the potential to dissolve the underlying layer of a multilayer.¹¹ Additionally, residual solvent can lead to a biocompatibility issues.¹² In contrast to conventional photolithography, CFL does not require resists, developers, solvents, or chemically destructive irradiation that can deactivate the reactive functional groups.¹⁰ Moreover, since the patterning process of CFL utilizes solely thermal movement of polymer film regardless of the chemical properties of polymer films, we believe this procedure can be applicable to many different sets of functional polymer films.

To create a bilayer with amine and acetylenic functional groups, first a 100 nm thick poly(allylamine) (PAAm) film using PECVD to achieve cross-linking was synthesized. Next, a 50 nm thick noncross-linked poly(propargyl methacrylate) (PPMA) film was synthesized via initiated chemical vapor deposition (iCVD). Conveniently, the monomers required for both layers are commercially available.

The Fourier Transform Infrared (FTIR) spectrum (Figure 1B) clearly shows the N–H stretching peak ($\sim 3200\text{ cm}^{-1}$) and the N–C stretching peak ($\sim 1650\text{ cm}^{-1}$), demonstrating retention of the amine functionality in the PECVD PAAm layer.¹³ Similarly, the characteristic peaks of the acetylene group (C–H stretch peak at $\sim 3300\text{ cm}^{-1}$ and C \equiv C stretch peak at $\sim 2100\text{ cm}^{-1}$)¹³ were clearly observed in the FTIR spectrum of iCVD PPMA. The PECVD film was insoluble in common solvents for PAAm including water, methanol, and acetone, suggesting the presence of cross-linking commonly found in plasma deposited materials.¹⁴

