# FABRICATION OF MOLECULAR-SCALE PATTERNS WITH CHEMICALLY TUNABLE FUNCTIONALITIES

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# ABSTRACT

This paper presents a scalable hybrid molecular nanofabrication approach of sub-10 nm patterns with functionalized surfaces by combining "bottom-up" surface initiated polymerization (SIP) with "top-down" electron beam lithography (EBL). This prototype molecular nanofabrication is based on the concept of nanolithography-based molecular manipulation (NMM). The strategy is to apply free-radical SIP ("bottom-up") to the non-molecularly engineered and chemically inert nano-patterns prepared by "top-down" nanolithography, e.g. EBL. This integration can minimize feature sizes to molecular length scales (sub-10 nm) and simultaneously tune the surface chemistry of the nano-patterns through functional polymer brushes. In this work, 4 nm nanostructures have been obtained which are chemically functionalized by poly(vinyl pyridine) (PVP).

## **KEYWORDS**

Molecular Nanotechnology, Nanofabrication, Surface Initiated Polymerization, Chemically Tunable Functionality

## **INTRODUCTION**

Molecular nanotechnology is emerging as a key enabler of molecular-scale electronics, functional biomimetics, and nano-electromechanical systems (NEMs) [1-2]. To mimic biological mechanisms, it is important to realize functionalized mechanical structures at the molecular scale, e.g. for guiding position-controlled mechano-chemistry. Many examples of steric-based functional enhancement exist in the chemical and biochemical worlds including multiple classes of enzymes and catalysts. Fabrication of chemo-mechanical structures at the molecular scale opens the door for the directed design of artificial enzymes and catalysts, efficient molecular manipulators as well as validation of high-performance-computing-based models of molecular interaction [3] as illustrated in Figure 1.

Several technologies comprising both "top-down" approaches such as EBL and focused ion beam (FIB), and "bottom-up" approaches such as SIP [4] and molecular self-assembly, have demonstrated the capability of producing molecular-scale devices. However, it is still impractical and difficult to precisely fabricate structures with controlled physical dimensions as well as desired surface functionality with minimal fabrication costs. For example, "top-down" approaches have been challenged by

the issue of precise control on both the feature size and the material functionality, especially in the molecular-scale. "Bottom-up" approaches have been limited in the production of useful devices because of the inherent difficulty of exactly positioning assemblies over large areas, as well as being reliant on the spontaneous geometric assemblages available from nature as opposed to the directed design available in "top-down" approaches.

In this work, we have utilized a hybrid NMM method which combines the advantages of both "top-down" EBL and "bottom-up" free-radical SIP, and compensates for their disadvantages. The process begins with "top-down" patterning of the substrates by EBL at length scales far larger than the typical molecular sizes of sub-10nm. SIP is then used for "bottom-up" growth of functional robust polymer brushes onto the EBL patterned surface. Consequently, the feature size of the EBL pattern is reduced to a molecular scale, and the pattern functionality is varied by the covalently grafted polymers. The polymer studied in this work is the polyelectrolyte base poly(vinyl pyridine) (PVP), which has biochemical compatibility and antimicrobial properties towards specific molecules [5]. Figure 1 shows potential examples of NMM technology for the creation of artificial catalysts, steric or chiral-specific syntheses, and manipulation of macromolecules.



Figure 1: Schematic illustration of some potential applications of molecular scale chemo-mechanical structures based on NMM concept.

#### EXPERIMENTAL Materials and Reagents

All chemicals were purchased in A.C.S. grade from Sigma-Aldrich chemical company, USA. Monomer 4-vinyl pyridine (4-VP) was washed with 10% aqueous solution of sodium hydroxide followed by vacuum distillation twice. 4,4'-azobis(4-cyanopentanoic chloride) (ACPC) macroinitiator was prepared by the reaction of 4,4'-azobis (4-cyanopentanoic acid) (ACPA) with phosphorous(V) (PCl<sub>5</sub>) [6]. The product ACPC was further re-crystallized twice by n-hexane and characterized by H<sup>1</sup>-NMR.  $\gamma$ -Aminopropyltriethoxy-silane ( $\gamma$ -APS) was used without further purification.

### Fabrication

The hybrid NMM fabrication procedure is outlined in Figure 2. It begins with a "top-down" process (Fig. 2a). A thermally oxidized Si substrate bearing ~100 nm SiO<sub>2</sub> was patterned by EBL (JEOL JBX-9300FS EBL system, 100 kV) followed by reactive ion etching (RIE) to create a series of nano-trenches in the SiO<sub>2</sub> layer. Trench widths of 85 nm and 65 nm were produced with depths of ~70 nm. The sample was then treated by piranha solution (98% H<sub>2</sub>SO<sub>4</sub> and 30% H<sub>2</sub>O<sub>2</sub> in volume ratio of 2:1 at 100°C for 1 hour) to create a defined monolayer of silanols on the surface. In the subsequent processes (Fig. 2b-d), all of the reactions were performed in a closed dry-N<sub>2</sub> system using the setup illustrated in Figure 3. An oil pump was applied first to remove air followed by a N<sub>2</sub> purge flow to maintain the



Figure 2: Schematic illustration of NMM. (a) electron beam lithography followed by RIE, (b) surface functionalization of  $SiO_2$  nano-patterns with amino groups, (c) surface modification of  $SiO_2$  nano-patterns with azo- based initiators, (d) free radical surface initiated polymerization (SIP) to covalently grow functional polymer PVP brushes,  $SiO_2$ -PVP.



Figure 3: Reaction apparatus for SIP process.

entire system in a dry-N<sub>2</sub> atmosphere. This procedure was repeated three times to ensure complete removal of O2. All chemicals are injected separately under N2 flow, and an oil or ice bath was used to control the reaction temperature. Samples were stacked separately on a quartz frame, and the entire assembly was kept inside a beaker with a magnetic stirrer. Before the initiation of each chemical reaction, a degassing treatment was applied to the entire system by using ultrasonication for approximately 2 hours to remove air trapped inside the nano-patterns. The silanol groups were reacted with  $\gamma$ -APS in ethanol solution to functionalize the sample surface with reactive amino groups (SiO<sub>2</sub>-NH<sub>2</sub>) (Fig. 2b). The reaction was kept at 130°C for 6 hours with a  $V_{\gamma-APS}$ :  $V_{ethanol}$  ratio of 3:20. The resulting sample (SiO<sub>2</sub>-NH<sub>2</sub>) was repeatedly washed by ethanol and deionized (DI) water and then dried in N<sub>2</sub>. To the amine-terminated oxide sample (SiO<sub>2</sub>-NH<sub>2</sub>) and azo-based ACPC initiators in THF solution (4mg/ml) an excess amount of pyridine (0.4ml) was added dropwise and the reaction was allowed to proceed for 24 hours. The resulting sample (SiO<sub>2</sub>-azo) (Fig. 2c) was washed a few times with THF and DI water followed by drying in N<sub>2</sub>. Free-radical SIP of 4-vinyl pyridine onto the SiO<sub>2</sub>-azo surface was performed at 60 °C for 4 hours in ethanol solution. The resulting surface was covalently coated in functional PVP brushes (SiO<sub>2</sub>-PVP) (Fig. 2d). The resulting sample was repeatedly cleaned by ethanol and DI water followed by drying in a vacuum oven at 60  $^{\circ}$ C for 24 hours. The grafted PVP thickness can be varied between 5 and 30 nm by varying the initial monomer concentration.

### **RESULTS AND DISCUSSION**

Figure 4 shows SEM (Zeiss SEM Ultra60) images of a series of  $SiO_2$  nano-trenches before and after SIP. As observed, the feature size is significantly reduced from the original 85 nm pattern produced by "top-down" EBL/RIE (Fig. 4a) to 35-45 nm (Figs. 4(b) and 4(c)) after SIP, resulting in a 50 nm size reduction of the trench widths. Additionally, the surface composition and functionality are

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Figure 4: SEM images of  $SiO_2$  nano-trenches (top view) (a) with 85nm in width before SIP, (b) and (c) with the reduced width of 45nm and 35 nm after SIP, respectively, and (d) in a lower magnification after SIP. The insets are cartoon illustrations before and after SIP.

chemically modified from the original hydrophilic SiO<sub>2</sub> to organic polyelectrolyte PVP (Fig. 6) with tailored biochemical compatibility [5]. The grafted PVP molecules appear as particles in varied sizes of 5-30nm (Figs. 4(b)). In general, the size (the radius of gyration) of specific polymer molecules is affected by the molecular weight (M<sub>w</sub>), its polydispersity (PDI,  $M_w/M_n$ ), and the external environment [7]. Thereby the observed variation in size of obtained PVP molecules can be explained by two main reasons: 1) the compact self/inter-entanglement of polymer chains since the sample surface was completely dried; and 2) a high molecular weight polydispersity (PDI) resulting from the free radical polymerization mechanism. The variation in size of grafted PVP molecules results in nano-trenches with zigzag profiles which are curved on the grafted polymer's molecular scale as illustrated in the insets of Figures 4(a)and 4(b).

Sub-10 nm trench patterns with functionalized surfaces were also obtained as shown in Figure 5. Both top and lateral views of the nano-trenches are compared. The observed feature size is apparently reduced from the original 65 nm (Fig. 5(a)) to a molecular scale of sub-10 nm, e.g. 4 nm (Fig. 5(b)) with a scalar reduction of approximately 55 nm. There is a noticeable size variation of approximately 15nm between the minimum and maximum widths of the nano-trenches (i.e. 4 nm and 20 nm, see Fig. 5(b)) which is of the same dimensions as the grafted PVP molecules. This implies that the resolution of this hybrid approach is affected by the size of the entangled polymer chains. When the patterned feature size and the grafted polymer molecules are on the same scale, the feature size variation in the nano-pattern becomes apparent. Furthermore, Figure 5(d) shows a 20nm thick continuous polymer layer which conformally coats the sub-70 nm nano-trenches, demonstrating the ability of SIP in



Figure 5: SEM images of  $SiO_2$  nano-trenches (a) with 65nm in width before SIP (top view), (b) with reduced size down to 4 nm after SIP (top view), (c) lateral view of nano-trenches with 65nm sized opening before SIP, (d) lateral view of nano-trenches with reduced opening size after SIP.

conformally depositing ultrathin PVP polymer brushes onto the entire patterned region. Compared to this SIP chemical deposition method, physical deposition or physisorption, including spin-casting and spray coating, can in principle also produce an ultrathin polymeric layer (a few nanometers) on nano-patterned substrate surfaces. However, the non-covalent adsorption may result in instability of the deposited ultrathin layer.



Figure 6: Wide-scan XPS spectra of SiO2 nano-pattern surface (a) after "top-down" nanolithography, (b) after surface modification with amino groups (SiO2-NH2), and (c) after SIP (SiO2-PVP). The insert is N1s XPS spectra from sample b.

Table 1: Elemental Compositions

Sample No.	Atom Weight %		
	Cls	NIs	Ols
a	15.42	0	84.58
b	40.21	5.08	54.71
с	64.38	9.40	30.22



Figure 7: SEM images of  $SiO_2$  nano-trenches after SIP (a) without and (b) with degassing.

The sample surface elemental composition was characterized by X-ray photoelectron spectroscopy (XPS) (SSX-100, Al K- radiation, 1486.6 eV). Figure 6 shows a series of XPS wide-energy scans on the sample after nanolithography (EBL and RIE) (Fig. 6a), after surface modification with amino groups (SiO<sub>2</sub>-NH<sub>2</sub>) (Fig. 6b), and after SIP (SiO<sub>2</sub>-PVP) (Fig. 6c), respectively. It is observed that the peak counts of C1s and N1s increase while O1s counts decreases for the samples SiO<sub>2</sub> (6a), SiO<sub>2</sub>-NH<sub>2</sub> (6b) and SiO,-PVP (6c), indicating successful introduction of amino groups and PVP brushes during fabrication schematically illustrated in Figures 2(b) and 2(d). C, N and O atomic weight ratios for each sample calculated from XPS results are listed in Table 1. The calculated ratio of C to N in SiO<sub>2</sub>-PVP sample obtained after SIP, 6.8, is very close to the theoretical value for PVP equal to 6, indicating that PVP brushes were properly grafted onto nano-patterns at the molecular scale.

In general, a recessed nano-pattern is technically more difficult than a protruding structure to achieve a proper SIP. In addition, patterning nano-sized recessed features becomes even more challenging when the feature size becomes smaller than 100 nm. A few studies have reported successfully grafting polymers on protruding nano-patterns to amplify the pattern profile [8-10], but very few have reported the polymer grafting on recessed nano-patterns at the sub-100 nm scale. In our study, one of the key factors that determined the success of grafting polymer brushes on the side walls of nano-trenches was effective removal of the air trapped inside the nano-trenches prior to any chemical reaction. This problem was solved by degassing the device under ultrasonication. As shown in Figure 7, only after degassing can the reactive chemicals enter into the nano-trenches and allow the functionalization to occur.

The utilization of free-radical SIP in this hybrid NMM is more convenient compared to hybrid methods involving atom transfer radical polymerization (ATRP) [8] or living free-radical polymerization [9] for surface grafting, since it requires less stringent experimental conditions and reaction steps. In addition, this work does not require the specific performance of "nanometer-scale lift-off" processes to pattern gold for anchoring thiol-based initiators [8, 10].

#### **CONCLUSION**

In this paper, we have demonstrated a hybrid nanofabrication approach based on the concept of NMM by integrating "bottom-up" SIP into "top-down" EBL. The proposed method enables the capability of precisely producing molecular-scale structures down to 4nm at a reduced cost. Also, it allows the potential of chemically tuning the pattern with proper bio/chemical functionalities to interact with the molecules of interest simply by choosing specific polymers. Further, this approach would be useful to fabricate extensive functional nano-machines including artificial heterogeneous enzymes/catalysts for activating favorable reactions as well as molecular manipulators for molecular assembly, conformation control, and hierarchic integration. Also it provides the possibility to experimentally validate a variety of programmed molecular interaction models based on high-performance computing.

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