

Self-Assembly Nanofabrication via Mussel-Inspired Interfacial Engineering

Young Joo Choi, Hyeon Min Jin, Bong Hoon Kim, Ju Young Kim, and Sang Ouk Kim

Department of Materials Science and Engineering, KI for the Nanocentury
Korea Advanced Institute of Science and Technology (KAIST)

305-701, Daejeon, Republic of Korea
sangouk.kim@kaist.ac.kr

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Abstract. We present that polydopamine-assisted interfacial engineering can be synergistically integrated with block copolymer lithography for surface nanopatterning of low-surface-energy substrate materials, including Teflon, graphene, and gold. Block copolymer lithography is a self-assembly based nanofabrication that holds great promise for sub-10-nm scale patterning. The directed self-assembly of block copolymers into device-oriented nanopatterns generally requires organic modification of a substrate surface. In this work, the versatility of the polydopamine treatment was demonstrated by the surface modification.

Introduction

Interfacial engineering is of particular significance for self-assembling materials, such as liquid crystals, [1] amphiphiles, [2] and block copolymers. [3,4] The molecular ordering and the nanodomain alignment of self-assembling materials are delicately influenced by the surface energy and functionality. To date, various interfacial engineering methods, ranging from the simple deposition of a surface modifier to a self-assembled monolayer (SAM) [5] or layer-by-layer assembly, [6] have been exploited. Nevertheless, currently available methods are substrate-specific and unable to modify low surface energy or chemically inert surfaces. Recently, polydopamine treatment, inspired by the adhesive proteins secreted by marine mussels, has been suggested as a facile and universal strategy for surface modification. The versatile catechol unit provides a unique opportunity to modify virtually all types of material surfaces, regardless of their chemical functionality or surface energy. Moreover, the robust polydopamine treated surface can accommodate the surface reaction site for the formation of secondary ad-layer. [7-11]

Surface Modification

Simple immersion of a substrate in an aqueous dopamine solution generates an ultrathin adherent polydopamine layer. [7] In this work, the versatility of the polydopamine treatment was demonstrated by the surface modification of a raw cherry tomato. A raw cherry tomato is a challenging object for surface modification due to its non-planar morphology consisting of soft biomolecules. [12-14] Figure 1 compares two cherry tomatoes. The left one is a raw cherry tomato with a fairly low energy surface. Water droplets readily dewetted from the raw cherry tomato surface. The right one is the polydopamine treated cherry tomato, whose surface energy was greatly enhanced such that water droplets were stably stuck at the non-planar geometry.



Figure 1 Mussel-inspired surface engineering of cherry tomato.

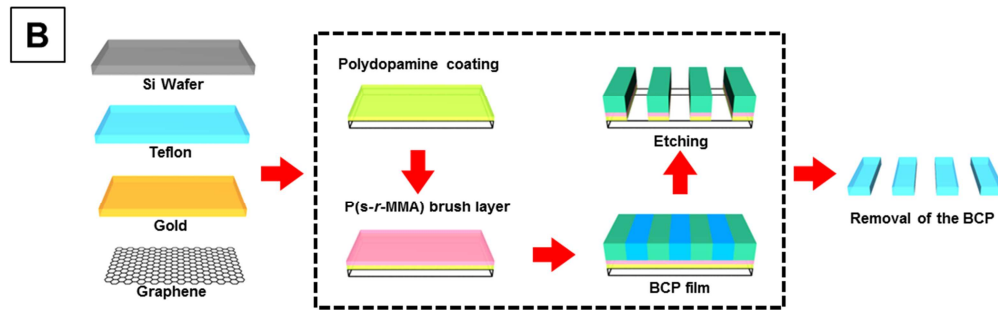


Figure 2 Schematics for mussel-inspired block copolymer lithography for low surface energy substrates.

Mussel-Inspired Self-Assembly

Figure 2 illustrates the procedure for mussel-inspired self-assembly of block copolymer. A low surface energy substrate was immersed in a dopamine solution (1 mg/mL), buffered to a pH typical of marine environments (10 mM Tris-HCL, pH = 8.0). Upon immersion for several hours, a thin and robust adherent polydopamine film was spontaneously deposited on the substrate surfaces. [7] A hydroxyl terminated poly(styrene-ran-methyl methacrylate) P(S-*r*-MMA) brush thin film was spin-cast on the polydopamine-treated substrate. We note that without the polydopamine layer polymer films readily dewetted from the low surface energy substrates. Subsequent thermal annealing facilitated the covalent reaction between the hydroxyl terminal group of the polymer brush with the catechols of the polydopamine layer. The resultant brush-treated surface was chemically neutral (balanced identical surface tension) to PS and PMMA components with the optimized chemical composition of the random copolymer. [3, 4] Any excess polymer brush molecules were thoroughly spin-washed. Finally, a thin film of polystyrene-block-poly(methyl methacrylate) (PS-*b*-PMMA) was spin-cast on the neutralized substrates and thermally annealed. Upon the neutralized surface, the substrate surface enforced surface parallel block copolymer molecule alignment and, thus, surface perpendicular lamellar alignment. The resultant block copolymer thin films with vertical nanodomain morphology were employed for further additive or subtractive nanopatterning of the underlying low surface energy materials.

Surface Chemistry and Wetting Property

The variation of surface chemistry and surface wettability upon surface treatment was monitored with X-ray photoelectron spectroscopy (XPS) and water contact angle measurements. [7] Figure 3 shows the XPS spectra of a Teflon substrate measured at each processing step. [15] After polydopamine treatment for 5h, O1s and C1s peaks became enhanced and a new N1s peak emerged, elucidating the formation of a polydopamine layer. After P(S-*r*-MMA) brush ad-layer (6–7 nm thick) deposition on the polydopamine layer, the intensity of the N1s peak greatly decreased.

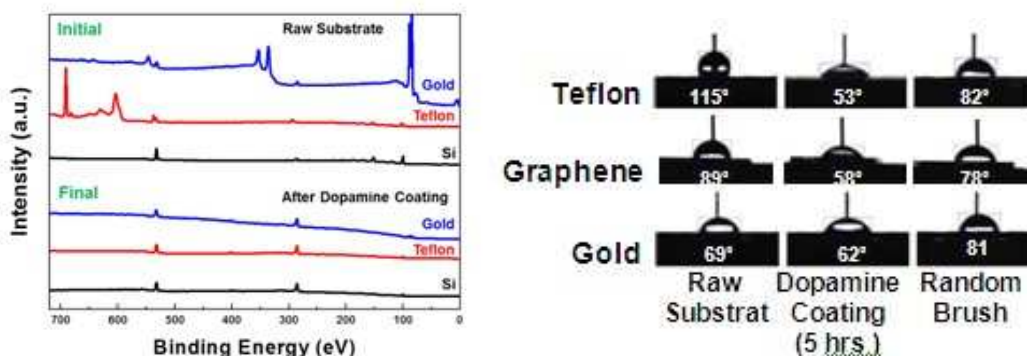


Figure 3 X-ray photoelectron spectroscopy (XPS)

Table 1 shows the variation of the advancing water contact angle during the interfacial engineering of various substrates. While the raw Teflon surface revealed a highest angle of $\sim 120^\circ$, graphene and Au substrates showed moderate angles of $\sim 90^\circ$ and $\sim 70^\circ$, respectively. The piranha-treated silicon substrate showed the lowest angle of 0° . During polydopamine treatments for 5h, the water contact angles gradually increased or decreased to converge to 55° - 60° , regardless of the wide spectrum of initial values. Finally, all contact angles reached values of 75° - 80° after P(S-*r*-MMA) brush layer deposition, which is consistent with the value for a neutral surface for PS and PMMA components. We note that the lowest energy Teflon surface underwent a rapid variation of the contact angle in the early period of polydopamine treatment. This behavior was due to the oxygen atom present in Teflon AF. The hydroxyl or C=O groups in polydopamine can form a hydrogen bond network with the oxygen atoms in the solution processible Teflon AF. This spontaneous adsorption of polydopamine used the large decrease in the contactangle during the early stage of polydopamine treatment.

Table 1 The variation of the advancing water contact angle

| | Bare Substrate | 1 hr Polydopamine coating | 3 hr Polydopamine coating | 5 hr Polydopamine coating | P (S- <i>r</i> -MMA) Brush Treatment |
|--------------------|----------------|---------------------------|---------------------------|---------------------------|--------------------------------------|
| Teflon | 115° | 60° | 52° | 53° | 82° |
| CVD-Grown Graphene | 89° | 83° | 76° | 58° | 78° |
| Au | 69° | 62° | 61° | 62° | 81° |
| Si Wafer | 0° | 30° | 52° | 58° | 80° |

Fabrication of the Hydrophobicity of the Teflon nanowires

Figure 4 shows Teflon nanowires replicating a block copolymer lamellar morphology prepared by mussel-inspired block copolymer lithography. The nanowires were fabricated by a dry etching employing a PS-*b*-PMMA thin film mask with vertical lamellar morphology. After formation of a lamellar nanotemplate upon a neutrally modified Teflon surface, CF₄ dry etching was employed to selectively remove PMMA lamellae. The remaining nanopatterned PS lamellae film played the role of an etching mask for the further etching of the underlying Teflon film with CF₄ and Ar. We note that O₂ etching was avoided to prevent any surface oxidation. It is well-known that nanopatterning can enhance the surface energy effect of a surface. A hydrophobic surface becomes more hydrophobic with a surface roughness and, particularly, with the involvement of an air pocket. [16, 17] The water contact angle on the Teflon surface increased from 290° to 151° upon the nanowire morphology formation. This extremely high value indicates a superhydrophobic behavior.

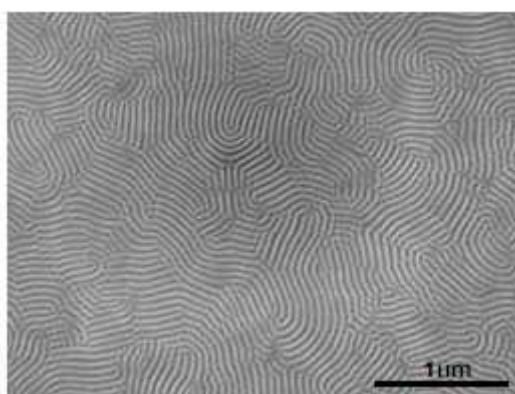


Figure 4 Lamellar morphology of Teflon nanowires

Summary

We have demonstrated a facile and universal method for surface nanopatterning, which is particularly useful for low surface energy substrates, such as Teflon, graphene, and gold. Those materials have been longstanding challenges for surface nanopatterning thus far. Our strategy, inspired by a genuinely universal adhesive protein secreted by marine mussels, can serve as a versatile platform for surface energy modification and further surface nanopatterning. A lesson from nature greatly strengthened the potential of block copolymer lithography. Moreover, the universal adhesive polydopamine treatment can be synergistically combined with any other nanopatterning technology, especially for nonplanar or soft/flexible geometry.^[18, 19]

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