Self-Assembly of Nanowires at Three-Phase Contact Lines on Superhydrophobic Surfaces

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This paper reports on a novel self-assembly method of nanowires using a superhydrophobic surface as a template. Well-defined superhydrophobic structures on a template surface can configure three-phase (liquid–solid–gas) contact lines at the structures' tips and direct the site-specific self-assembly of nanowires when the colloidal droplet of nanowires recedes in evaporation. High-aspect-ratio microstructures with tapered tips were fabricated by deep reactive ion etching (DRIE) and coated with a thin layer of Teflon for hydrophobicity. Nickel nanowires were synthesized by electrodeposition through a porous alumina membrane. A uniformly dispersed nanowire suspension was dispensed and evaporated on the superhydrophobic template surface at normal room conditions. After complete evaporation, the assembly of nanowires on the tip structures was measured by microscopy. The results show that nanowires are mostly deposited on the structural tips because the air layer retained between the hydrophobic surface structures prevent the liquid meniscus from reaching to the bottom trenches during evaporation. The assembly rate on each tip and the alignment tendency along the surface pattern vary depending on the template surface parameters and the nanowires colloidal states, requiring further systematic studies on the effects. It is envisioned that well-tailored superhydrophobic surfaces can serve as a novel template for highly-ordered and site-specific self-assembly of functional nanomaterials in simple drying processes, significantly enhancing the capability to realize future nanomaterial-based devices and systems.

Keywords: Nanowires, Self-Assembly, Evaporation, Superhydrophobic.

1. INTRODUCTION

Low-dimensional materials such as carbon nanotubes and metal/metal-oxide nanowires are promising building blocks for nanostructures and nanodevices with low power consumption, and superior electrical and mechanical properties. Practical applications, e.g., nanoelectronics, require a precise arrangement of such nanomaterials into hierarchical orders to construct the desired geometry with controllable shape, location, and direction on a large scale.1 Several techniques of nanomaterial assembly have been explored: biomolecule patterning2 and microscale contact stamping3 have high assembly resolution, but only limited biomaterials or polymers can be used; magnetic field,4 electric field,5 and dielectrophoresis6 enable a high throughput assembly, however the arrangement is often limited to one direction along the gradient of the field. The exploration of more efficient assembly techniques is demanded. Extended from previous studies,8 this paper reports on a new self-assembly mechanism for nanowires based on interfacial phenomena at the three-phase contact lines configured on a micro-patterned superhydrophobic template surface.

2. ASSEMBLY PROCESS

The basic concept of the self-assembly process studied in the paper is illustrated in Figure 1. A colloidal droplet containing well-dispersed nanowires is dispensed on a structured superhydrophobic template surface (Fig. 1(a)). Due to low surface tension and de-wetting of hydrophobic structures, the colloidal droplet sits on the top ridges of microstructures with an air layer trapped underneath the droplet.6 As the droplet evaporates, the three-phase contact line recedes and drags the nanowires along the contact line. When the dragged nanowires contact the structural tips, the adhesion and capillary forces between the nanowires and the tip surfaces will retard the movement of the nanowires. If they are greater than the interfacial drag force to the receding direction, the nanowires
will be separated from the droplet and remain on the tip surface, attaining self-ordered assembly (Fig. 1(b)). The self-assembly process will continue until the droplet completely evaporates, allowing site-specific self-alignment onto the structural ridges (Fig. 1(c)). The superhydrophobic template structures can be engineered and constructed for specific directions and patterns for desired assembly.

3. FABRICATION OF SUPERHYDROPHOBIC SURFACES

For the superhydrophobic template surface structures, high-aspect-ratio microstructures of varying surface parameters (see Fig. 2 and Table I) were created on a silicon substrate by photolithography followed by deep reactive ion etching (DRIE). A 4-inch silicon wafer was first cleaned with acetone, isopropyl alcohol, and deionized (DI) water and then dehydrated for 10 minutes on a hot plate at 150 °C. Adhesion promoter, Priming HMDS (KEM Chemical), was spin-coated at 2000 rpm for 1 minute and followed by spin-coating of SPR 3012 photoresist (PR) (Shipley) at 2000 rpm for 1 minute. The substrate was soft-baked on a hot plate at 115 °C for 1 minute and UV-exposed by using MA-6 mask aligner (Suss MicroTec). The substrate was then developed by MF-319 (Shipley). The patterned PR thickness was measured by a profilometer to be 2.2 μm. The PR-patterned silicon substrate was then etched by DRIE by using an Inductively Coupled Plasma (ICP) Etcher (Oxford PlasmaLab). Figure 3 shows the scanning electron microscopy (SEM) images of the fabricated microstructures (Type I).

In addition to the original microstructures, nanogras structures were also created on the bottom trench by controlling the etching parameters of DRIE. The nanograd structures formed by the so-called black silicon method is to provide the surface with more robust superhydrophobicity (i.e., de-wetting stability) by preventing the liquid meniscus from filling the air voids even though the meniscus touches the bottom trench surface due to the increased Laplace pressure of the droplet during evaporation.

After fabricating the microstructures, a thin layer of Teflon was coated to make the surface superhydrophobic.

<table>
<thead>
<tr>
<th>Type</th>
<th>G (μm)</th>
<th>P (μm)</th>
<th>L (μm)</th>
<th>H (μm)</th>
<th>W (μm)</th>
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<td>40</td>
<td>10</td>
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<tr>
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<td>20</td>
<td>20</td>
<td>10</td>
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</table>
Teflon solution was prepared by dissolving 0.2 wt% of Teflon AF1600 powder (DuPont) in FC-75 (DuPont) solvent. After rolling agitation for 4 days and filtered by a Millipore filter (SLGV033RS, 0.22 μm), Teflon solution was spin-coated on the microstructured surface at 1000 rpm for 30 seconds and baked at 112°C, 165°C, and 330°C for 10, 5, and 15 minutes, respectively, to give the film thickness of ∼20 nm. Figure 4 shows the contact angles of a droplet of water on a planar surface (control) and the microstructured template surface (Type II) after the Teflon coating. A theoretical contact angle of a liquid droplet on a superhydrophobic surface with a composite interface (i.e., solid and air) can be estimated by the Cassie-Baxter equation,

$$\cos \theta_c = f \cos \theta_0 + f - 1 \tag{1}$$

where $\theta_c$, $\theta_0$, and $f$ are the apparent contact angle on a composite surface, referential contact angle on a planar surface, and area fraction of a wetted solid surface, respectively. The wetting fraction of the microstructured superhydrophobic surfaces (Type II) was estimated to be $f = 0.1$, and the referential contact angle of Teflon on a planar surface was $\theta_0 = 123^\circ$ (Fig. 4(a)). The theoretical contact angle on such conditions is $\theta_c = 162^\circ$ by the Cassie-Baxter Eq. (1), which agrees well with our measurement (∼160°) (Fig. 4(b)) and indicates that the fabricated microstructures support the composite Cassie (de-wetted) state.

4. SYNTHESIS OF NANOWIRES

Nickel (Ni) nanowires were grown by electrochemical deposition through a nanoporous anodized alumina membrane.19–22 A silver layer was thermally evaporated on one side of the alumina template membrane (Anodisc, Waterman Inc), serving as a seed layer. Ni nanowires were then electrodeposited from a nickel electroplating solution of 300 g/l NiSO$_4$·6H$_2$O, 45 g/l NiCl$_2$·6H$_2$O, and 45 g/l H$_3$BO$_3$ at a constant current density of 2.0 mA/cm$^2$ with a 263A galvanostat (Princeton Applied Research, Oak Ridge, TN).23 After the electrodeposition, the silver seed layer was removed by concentrated nitric acid. The alumina template membrane was selectively removed by dissolving in a 5 M NaOH solution. The nanowires were subsequently washed and transferred to DI water. Figure 5 shows the electrodeposited Ni nanowires fabricated using the anodized alumina membrane as a scaffold. Ni nanowires of 5, 10, and 20 μm lengths and 200 nm diameter were synthesized and tested in this study. To make a well-dispersed suspension, the nanowires suspension was agitated by sonication (ultrasonic bath) for 30 minutes before the assembly test on the superhydrophobic template surfaces.

5. RESULTS AND DISCUSSION

A planar hydrophobic and a microstructured uncoated (i.e., hydrophilic) surfaces were first tested as controls.
The current results demonstrate that well-tailored superhydrophobic template surfaces can direct the self-assembly of nanomaterials in a simple drying process by exploiting the unique three-phase contact line dynamics on the hydrophobic structures. However, there are several challenges that remain to be overcome. The first issue is the assembly yield and the controllability of the assembly. Our current results show that only ~10% of the surface structures are deposited with nanowires. Furthermore, the assembly rate was not uniform over the surface, i.e., higher assembly population at the initial contact boundary region. The low yield rate with non-uniform deposition suggests that the number density assembled on
the structural tips varies so that some tips have multiple nanowires deposited onto them, while others have none. The assembly of nanowires on the tips is determined by interfacial forces between nanowires, solvent, and contact surface. The movement of liquid meniscus (i.e., kinetics of three-phase contact line) can be controlled by drying conditions such as ambient pressure, humidity, and temperature so as to manipulate the balance of the interfacial forces.\textsuperscript{24–27} The deposition patterns and uniformity are also influenced by the gradients of evaporation rate and interfacial tension along the droplet surface,\textsuperscript{24,25,28–30} which also affect the convective flow inside of the droplet and the distribution of nanowires. Hence, further systematic studies of the three-phase contact line dynamics and the dynamics of nanoparticles inside of the droplet are necessary in varying evaporation conditions to understand how to regulate the deposition coverage and uniformity to have better yield rate and controllability of the self-assembly.

The second issue is to maintain the de-wetted (air-retained) state throughout the entire evaporation stage. When a droplet evaporates, its radius of curvature decreases and thus increases the internal Laplace pressure of the droplet. If the Laplace pressure exceeds a threshold pressure where the surface tension force of the structure can balance, the liquid meniscus collapses by the excessive pressure force and the surface becomes wetted and thus loses air. In this study, it was observed that on denser structures (i.e., small P and G in Fig. 2), the de-wetted state was maintained over the evaporation, while on wider structures (i.e., large P and G), the air layer disappeared and the surface became totally wetted before the evaporation completed. Figures 7(a and b) show the optical micrograph images taken at the same location of the sample Type IV (P = 10 µm, G = 10 µm) with the focus on the tip surface (Fig. 7(a)) and the bottom trench (Fig. 7(b)), respectively. Figures 7(a and b) clearly show that the nanowires are deposited only on the structural tips and no nanowires are found at the bottom trench. The tested nanowires (20 µm) are longer than the structural gaps (P = 10 µm, G = 10 µm) and they are deposited onto multiple surface structures bridging them. In contrast, Figures 7(c and d) show the optical micrograph images taken at the same location of the sample Type V (P = 20 µm, G = 20 µm) with the focus on the tip surface (Fig. 7(c)) and the bottom trench (Fig. 7(d)), respectively. Figures 7(c and d) show that few nanowires are placed on the tip surface and most nanowires sink down to the bottom trench. This result indicates that the dimensions of surface pattern are important design parameters for the durable and robust self-assembly process of the colloidal droplet evaporation on superhydrophobic template surfaces, e.g., a denser surface pattern will provide better stability and applicability.\textsuperscript{31–33}

If such issues are resolved through further extensive studies, the new self-assembly approach explored in this study possesses several advantages than conventional assembly techniques, e.g., soft-lithography based microcontact printing.\textsuperscript{34} Instead of planar contact printing where the control of deposition density and selectivity...
is not efficiently attainable, discrete droplets can be selectively dispensed on arbitrary locations of the template surfaces with regulated droplet sizes and nanowire compositions (e.g., sizes and concentrations), which will allow great flexibility of pattern design and device architectures. It has recently been demonstrated that the distribution and deposition of nanomaterials on superhydrophobic surfaces can be manipulated by control of surface patterns and the sizes/concentrations of nanoparticles.52–55 Hence, in addition to the evaporative conditions such as humidity and temperature, the physical/mechanical/chemical conditions of the template surface structures as well as the nanowire compositions in the colloidal droplet can be conveniently modulated to allow greater controllability in the self-assembly process. The droplet-based drying process also allows multiple layer-by-layer depositions. After the first layer of assembly is made, the second layer assembly can be applied on top of the first layer by dispensing new colloidal droplets with a variety of nanomaterial compositions and evaporation modes. As such layer-by-layer assembly is repeated, the high-aspect-ratio 3-D nanostructures of customizable nanomaterial compositions and functionalities can also be achieved along the vertical direction.

6. CONCLUSIONS

In this study, we explored a new nanowire self-assembly mechanism based on interfacial phenomena configurable at the three-phase contact line of a superhydrophobic surface. A superhydrophobic template surface enabled the site-specific self-assembly of nanowires on the structural tips as a colloidal droplet of nanowires receded in a simple evaporation process. The primary design parameters acquired from this study provides an insight into the essential design parameters of superhydrophobic template surfaces for an efficient self-assembly. An optimization of superhydrophobic template surfaces and evaporative processes will enable successful development of a simple and efficient self-assembly scheme for a wide range of functional nanomaterials.

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References and Notes


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