Biomolecule and Nanoparticle Transfer on Patterned and Heterogeneously Wetted Superhydrophobic Silicon Nanowire Surfaces

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We report on the use of patterned superhydrophobic silicon nanowire surfaces for the efficient, selective transfer of biological molecules and nanoparticles. Superhydrophilic patterns are prepared on superhydrophobic silicon nanowire surfaces using standard optical lithography. The resulting water-repellent surface allows material transfer and physisorption to the superhydrophilic islands upon exposure to an aqueous solution containing peptides, proteins, or nanoparticles.

The study of wetting properties on superhydrophobic surfaces is crucial for potential applications including hydrophobic interactions, microfluidic devices, and self-cleaning surfaces.[1−3] Superhydrophobic surfaces display a water advancing contact angle higher than 150° with low hysteresis. A microdroplet deposited on a superhydrophobic surface attains a quasi-spherical shape and accordingly reduces the contact area between the droplet and the solid substrate. The reduced contact area between a superhydrophobic surface and water will have a significant impact on the interfacial chemical and biochemical reactions. We have recently shown that reversible electrowetting can be achieved on superhydrophobic silicon nanowires.[4] The result opens new opportunities for potential applications in the field of lab-on-chip and particularly in the preparation of highly functional microfluidic devices.[5]

Patterned surfaces with different wetting properties are useful for the study and manipulation of biomolecules[6] and in the fabrication of microfluidic channels.[7] Surface patterning has been achieved using several means: microcontact printing, photolithography, and scanning probes.[8] The difference in the contact angle between the patterns is, however, smaller than 90°, which may limit practical applications of the hydrophilic−hydrophobic patterns. To date, there have been only a few reports on patterned superhydrophobic−superhydrophilic surfaces.[9−13] The contrast in the wetting properties has previously been used to direct polymers selectively to hydrophilic regions of patterned superhydrophobic surfaces.[13]

In this letter, we show that superhydrophilic regions obtained through the photolithographic patterning of superhydrophobic SiNWs allow easy, fast, and selective transfer of peptides, proteins, and gold nanoparticles.

The silicon nanowires (SiNWs) investigated in this study were prepared by the chemical etching[14,15] of crystalline silicon in $AgNO_3$/HF aqueous solution or using the vapor−liquid−solid (VLS)[4,16,17] growth mechanism, according to previously published work. Figure 1A displays a top-view scanning electron microscopy (SEM) image of the nanowires synthesized by silicon dissolution in $AgNO_3$/HF solution.[14,15] The nanowire diameter is in the range of 20−80 nm, as evidenced by the cross-sectional SEM view (Figure 1B). The as-prepared SiNWs, after exposure to the atmosphere, are covered with a thin silicon oxide layer that confers superhydrophilic character to the surface. A water contact angle of <5° was measured for such a surface. Chemical modification of the surface with octadecyltrichlorosilane (OTS) led to the formation of a superhydrophobic surface with a contact angle of 160° with low hysteresis (0−2°) (inset in Figure 1B).[18,19] The surface roughness combined with the low surface energy induced by the surface modification ensured air trapping between the substrate and the liquid droplets, which is necessary to achieve superhydrophobicity.[3−5,18] The contrast between superhydrophilicity and superhydrophibicity is evident in the optical photographs displayed in Figure 2. The as-prepared SiNW

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(19) Superhydrophobic silicon nanowire surfaces were obtained by chemical functionalization of the native oxide with a 10^{-3} M octadecyltrichlorosilane solution in hexane for 16 h at room temperature in a dry-nitrogen-purged glovebox. The resulting surface was rinsed with $CHCl_3$ and i-PrOH and dried in a gentle stream of nitrogen.

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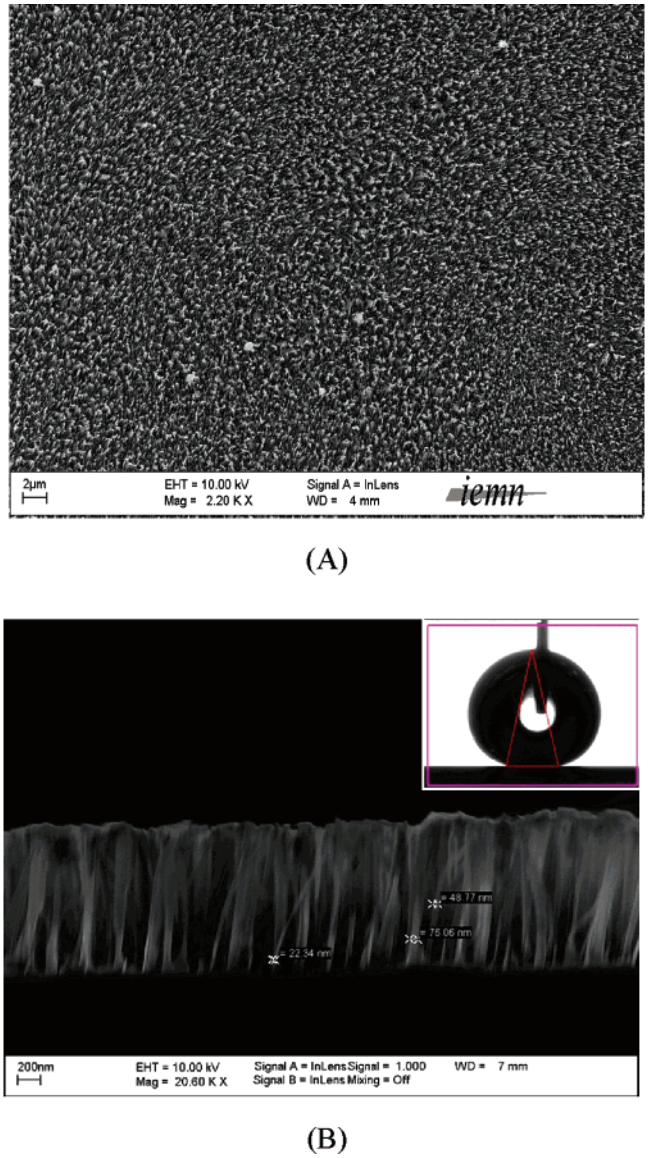

Figure 1. Top view (A) and cross-section (B) SEM images of the silicon nanowire substrate. The inset in B is the static water contact angle of the chemically modified SiNW surface with OTS.

substrate covered with a thin oxide layer displays superhydrophilic character with a contact angle of <5°. The surface is completely wetted upon immersion in a water bath (Figure 2A, bottom substrate). However, upon chemical derivatization of the substrate with OTS molecules, the SiNW surface becomes water-repellent and floats on the water surface (Figure 2A, top substrate).

The patterned surface investigated in this study consists of hydrophilic patterns between 100 μm and 1 mm in diameter obtained through optical lithography.[20] Figure 2B exhibits an optical image of the patterned superhydrophobic SiNW surface (SiNW−OTS/SiO_2) in contact with water. The droplets are self-confined in the hydrophilic areas.

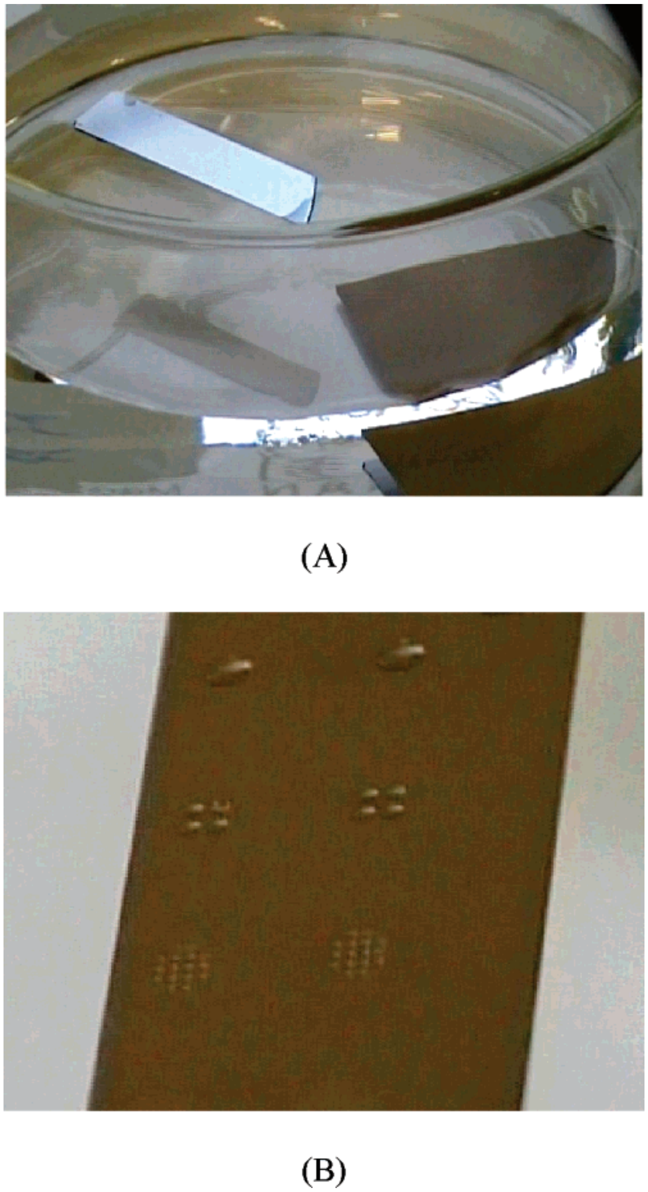

Figure 2. Optical images of superhydrophobic (top) and superhydrophilic (bottom) silicon nanowire substrates in contact with water (A) and liquid droplets transferred onto superhydrophilic islands on the patterned SiNW surface (B).

This property was further exploited to transfer other molecules such as short peptides, proteins, and nanoparticles. To test the strategy, the patterned surface was exposed to an aqueous solution of rhodamine-labeled streptadivin (1.6×10^{-8} M) for 30 min at room temperature. After drying in air, fluorescence analysis clearly indicates the successful transfer of the protein in the hydrophilic regions (Figure 3).[21] The fluorescence signal is observed in all patterns down to 100 μm. Moreover, there is no evidence of any protein adsorption on the superhydrophobic surface. In a similar way, a short peptide labeled with rhodamine (Arg-Lys-rhodamine) was transferred after only 5 min of exposure of the patterned surface to an aqueous solution of the peptide (10^{-6} M) (data not shown).

Furthermore, the transfer of gold nanoparticles with a mean average diameter of 20 nm was achieved using the patterned superhydrophobic SiNW substrate. Figure 4A displays an SEM image of the resulting surface after exposure to an aqueous solution

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(20) Hydrophilic apertures between 100 μm and 1 mm in diameter were obtained on SiNW superhydrophobic surfaces using standard optical lithographic techniques. Optical resist AZ4562 from Hoeschdt was spin coated onto the surface and soft backed at 110 °C for 2 min to remove excess solvent. The thickness of the coated films is ~3 μm. Optical writing was carried out by exposure of the resist to UV light for 3 s through a chromium quartz mask. The sample was then dipped in AZ451 revelation solution for 400 s, thoroughly rinsed in deionized water, and dried in a flow of nitrogen. Removal of the OTS molecules was achieved using an O_2 plasma etch for 30 s. Finally, the resist was removed with acetone, and the sample was further cleaned in acetone, isopropyl alcohol, and deionized water.

(21) Array imaging was performed using the Cy3 channel of an Affymetrix 418 array scanner at a resolution of 10 μm.

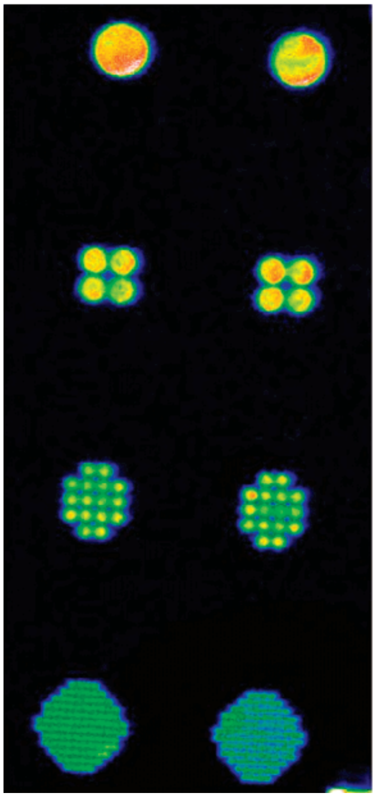

Figure 3. Fluorescence image of transferred rhodamine-labeled streptavidin onto SiO_2 patterns.

of gold nanoparticles for 1 h at room temperature. A high-density distribution of nanoparticles on the surface was observed. In this case, the patterns were modified with aminopropyltriethoxysilane[22] to favor electrostatic interactions of the NH_2 terminal groups and the gold colloid. An examination of a single nanowire within the pattern shows that the nanoparticles are homogeneously distributed on the nanowire (Figure 4B).

In conclusion, a simple method for biomolecule and nanoparticle transfer using a patterned superhydrophobic surface is demonstrated. The method is based on the difference in the wetting properties (superhydrophilic/superhydrophobic) of the substrate. The material transport is believed to be limited by the diffusion of molecules to the patterned islands. The technique developed in this work holds promise for single-cell transfer and patterning, and applications in digital microfluidic devices based on electrowetting on dielectrics (EWOD).

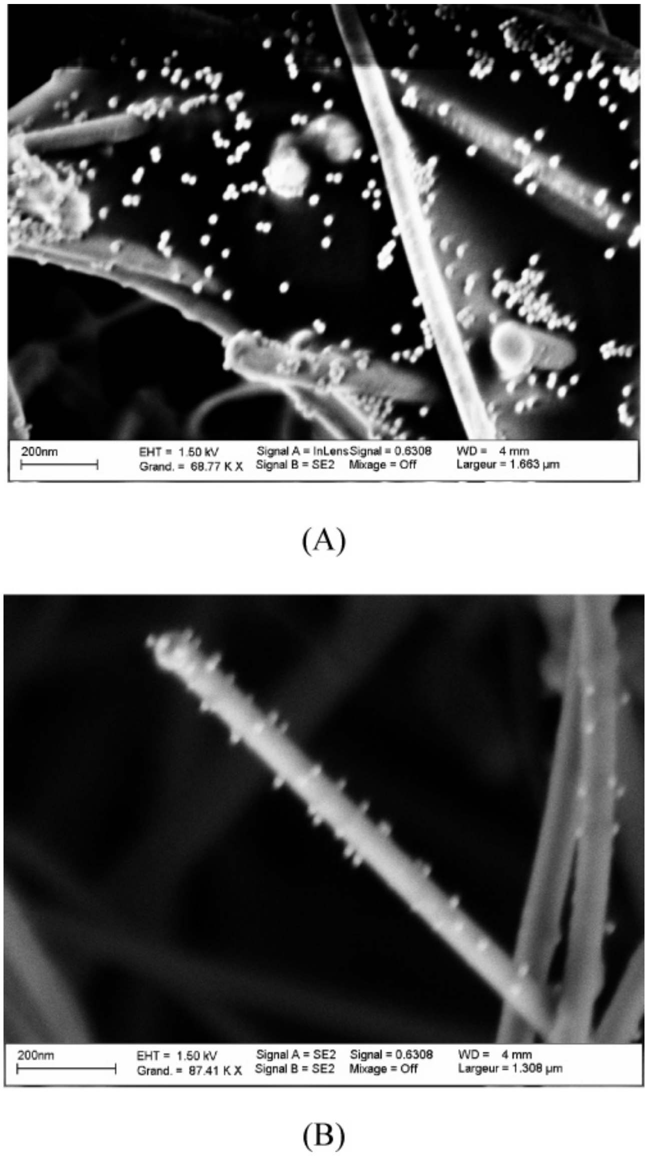

Figure 4. SEM images of 20-nm-diameter gold nanoparticles transferred onto NH_2-terminated regions (A) and a single nanowire coated with nanoparticles (B).

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[22] The oxide patterns were amine-terminated by reaction with 3% aminopropyltriethoxysilane (APTES) in 95/5 v/v methanol/water for 1 h under stirring. The resulting surfaces were washed with methanol (two times) and isopropanol and then dried in a gentle stream of nitrogen.