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Slip length enhancement in nanofluidic flow using nanotextured superhydrophobic surfaces

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Abstract

The development of highly efficient nanofluidic devices necessitates means for enhancing and controlling fluid transport under confinement. Here we show experimentally that significant interfacial drag reduction in nanoscale channels can be obtained with hydrophobic arrays of conical textures tapering to a radius of less than 10 nanometer at their tip. This geometry maximizes interfacial slippage by trapping a highly resilient air layer at the solid/liquid interface. Further, we reveal that the composite liquid/solid-air interface bears an electrostatic charge density comparable to that

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of a flat hydrophobic solid. Altogether these properties render the nanotexture surfaces highly attractive for efficient nanofluidic transport both in pressure-driven and electro-osmotic flow.

Fluid transport through nanoscale channels underlies a variety of technological applications, including biosensing,¹ energy storage and conversion,² biological and chemical separations,³ and water desalination.⁴ Owing to the large surface to volume ratio of nanochannels, their fluid transport properties are strongly influenced by interfacial effects, such as fluid slippage and ion segregation at the solid/liquid interface.⁵ In a macroscopic fluid dynamic approach, slippage is quantified by a “slip length”,⁶ b , which is defined as an extrapolated distance relative to the wall where the tangential component of the liquid velocity vanishes. A finite slip length is highly beneficial in nanofluidic applications because it increases significantly mass transport where liquid flow is driven by either pressure or electric field gradients.^{5,7}

However, there is substantial experimental evidence that newtonian liquids obey the no-slip condition ($b = 0$) at flat hydrophilic surfaces and have only a small but non-zero slippage at flat, hydrophobic interfaces ($b \simeq 10$ nm).^{7,8} This lack of interfacial slippage greatly reduces flow rates in nanofluidic channels thereby limiting their efficiency for energy conversion and solute separation. A promising approach to further increase slip, particularly in slit shaped nanoscale channels, relies on textured hydrophobic surfaces and their ability to effectively trap air when immersed in water.⁹ The air layer provides both “superhydrophobicity”⁹ (i.e. extreme water repellency) and a shear-free interface that greatly reduces fluid drag¹⁰ (shown schematically in Fig. 1). However, conventional microtextured superhydrophobic (SH) surfaces suffer from intrinsic shortcomings that greatly limit their use in nanofluidic applications. The most serious problem is the collapse of the air layer trapped within the texture¹¹ at the relatively high pressures (> 1 atm)¹² required to drive the liquid flow in nanofluidic devices. Although, as shown recently,^{13,14} the resilience of a SH surface to water infiltration can be improved through reducing the pattern period L to ≈ 10 nm, in principle

this may be detrimental to slippage since theoretically $b \simeq L$.⁷ Nevertheless, the dependence of slippage on L has been tested only in textures with micron-scale features ($L \simeq 1 \mu\text{m}$),¹⁵ and the effect of nanometer-size textures is still largely unexplored.

Another long standing question is whether SH surfaces bear electric charge (shown schematically in Fig. 1), and whether such charge may contribute to enhancing electro-osmotic flow,¹⁶ or enable devices for efficient electrokinetic energy conversion.¹⁷ There is also no experimental consensus concerning the magnitude and even the sign of the charge accumulating at the air-water interface.¹⁸ A recent study of colloidal electrophoresis near a SH surface reported no enhancement of electro-osmotic mobility.¹⁹ However, the surface zeta potential could not be measured due to the high interfacial roughness and the study could not conclusively assign the results to the lack of surface charge.

Here we show experimentally that significant interfacial drag reduction in nanoscale, slitlike channels can be obtained with hydrophobic arrays of conical textures tapering to a radius of less than 10 nanometer at their tip. We fabricate large-area (cm^2) silicon surfaces containing features with uniform size and spacing on a length scale $\simeq 10 \text{ nm}$ using block copolymer self-assembly and plasma etching.^{13,14} The ability to control precisely the feature size and shape through the etching process and the block copolymer morphology renders these nanopatterns ideally suited to fundamental studies of water slippage and surface charge accumulation at immersed superhydrophobic solids. Tapered conical structures with either sharp (width $w \approx 5 \text{ nm}$) or flat ($w \approx 30 \text{ nm}$) tips were obtained by varying both the vertical and lateral etching rates and using a block-copolymer mask with cylindrical morphology (Fig. 2 (a,b)). Striped nanotextures with $w \approx 45 \text{ nm}$ were obtained using similar etching conditions and a block copolymer mask with a lamellar morphology (Fig. 2(c)). Silicon nanostructures were rendered hydrophobic by coating with an octadecyltrichlorosilane (OTS) monolayer, which greatly enhanced the advancing water contact angle to as high as 166° in the nanotextures with sharpest tips, compared to the 110° angle measured on a flat silane-coated surface (Table 1). These results indicate that a water drop resting on a nanotextured

surface makes contact only with the top of the textures¹³ without significantly penetrating into the structures, confirmed by direct x-ray scattering measurements.¹⁴ In this case the area fraction of solid in contact with the liquid, denoted as ϕ , can be estimated from cross-sectional SEM measurements (see Fig. 2) of the feature size at the top surface, w , and the texture period, L . For lamellar grooves, ϕ is calculated using the approximation $\phi \approx w/L$, whereas for either sharp tip and flat tip cones, $\phi \approx \pi w^2/2\sqrt{3}L^2$. The trend clearly shows that the contact angle increases with the surface area fraction of air ($1-\phi$) (Table 1).^{13,14}

We have measured the water slip length at the nanopatterned surfaces using colloidal probe atomic force microscopy (CP-AFM).²⁰ CP-AFM is uniquely suited to probing the effect of the nanoscale textures on slippage owing to its nm-sensitivity to changes of slip length at a flat surface.²¹ The technique relies on measurements of the hydrodynamic force acting on a spherical microscopic colloid approaching a flat surface at constant speed²² (see Fig. 2(a)). At small sphere-surface distance ($d \ll R$), where R is the colloid radius, and large enough approaching speeds ($v \simeq 10\mu\text{m/s}$), the total force on the sphere is dominated by hydrodynamic interactions which are strongly dependent on slippage properties of the colloid and the flat surface. In this regime, a quantitative analysis of the hydrodynamic force versus distance curve provides an accurate estimate of the slip length of the substrate, provided that the slip length of the colloidal probe is known precisely. Here, the high spatial uniformity of the surface textures used here as well as their nanometer dimensions ($L \ll R$) greatly facilitate the interpretation of the CP-AFM data,²³ and remove any ambiguity regarding the position of contact between the probe and the nanotextured surfaces.

In our investigations, we have taken several precautions to avoid experimental artifacts and ensure consistent and reliable results. Specifically, we chose a cantilever with a relatively large glass sphere to minimize spurious hydrodynamic effects²⁴ and improve the sensitivity of the force measurements. Further, the glass sphere was attached to the cantilever using thermal bonding rather than epoxy glue (Section S1 of the Supporting Information). This allowed proper cleaning of the sphere surface using both liquid solvents and exposure to

UV light, which significantly improved the reproducibility of the measurements. We have also thoroughly characterized the slippage properties of the colloidal probe, a crucial step for ensuring accurate slip length measurements with CP-AFM. Apparent slippage at the probe is routinely observed in experiments due to the nanometer-scale roughness of the probe surface, typically $r_s \approx 10$ nm peak-to-valley (PV).²⁵ Owing to these surface irregularities, even at physical contact, the average probe-substrate distance is finite and equal approximately to r_s (see Fig. 3(b)).

We have quantified the slip length of the probe through systematic measurements of the hydrodynamic force versus distance, d , from an atomically flat hydrophilic silicon surface (Fig. 3(c) and inset, black open dots). We obtain the plotted hydrodynamic force on the sphere after treatment and calibration of the raw AFM data (as detailed in the Section S2 of the Supporting Information). Owing to their flatness (PV roughness ≈ 1 nm) these surfaces obey the no-slip condition, so that any apparent slippage measured under these conditions can be ascribed to the probe roughness. Both sphere and substrate were exposed to UV light in air for 20 min. to render them hydrophilic (water contact angle $\approx 0^\circ$). These experiments (as well as the rest of the slippage measurements discussed here) were performed with the probe and the substrate immersed in aqueous KCl solutions with concentration $n=0.1$ M, sufficient to screen the electrostatic forces within a “Debye length”²⁶ $\kappa^{-1} = \sqrt{\epsilon\epsilon_0 kT / e^2 \sum_i z_i^2 n_i} \simeq 1$ nm, where ϵ, ϵ_0 are the permittivities of solution and the vacuum, respectively, k is the Boltzmann constant, T the solution temperature, e the electron charge, and z, n the valence and molar concentration of the ions, respectively. The approach speed of the colloidal probe was set to $v = 13.3 \mu\text{m/s}$ in order to maximize the hydrodynamic forces and reduce experimental noise. Experiments carried out at 10 times slower speeds provided similar results. Under these conditions, at sphere-surface separations $d > 5$ nm both van der Waals and electrostatic forces on the sphere are negligible compared to hydrodynamic interactions (see the Section S2 of the Supporting Information for further details). All plotted data are averages of 10 single approach curves measured at the same sample location both to improve the signal to

noise ratio and obtain statistically averaged data. We have also performed similar measurements at 10 different locations across the substrate to rule out any spatial dependence of slippage due to substrate inhomogeneities.

At large probe-substrates separations ($d > 1000$ nm) the force is constant and approximately equal to the sum of the hydrodynamic drag on the sphere, F_h , and on the cantilever body, F_{drag}^0 (for the full characterization of the total force on the cantilever see the Section S2 of the Supporting Information). At small d , the force increases due to the hydrodynamic friction at the solid/liquid interface. The experimental force-distance curve can be modeled using the Taylor equation modified for the finite interfacial slip²⁷ in the lubrication approximation ($d \ll R$):

$$F_h = \frac{6\pi R^2 \eta v_s}{d} f^* \quad (1)$$

where v_s is the instantaneous probe velocity, η is the liquid viscosity, and $f^* \leq 1$ is the correction factor.

The experimental force recorded on flat silica is systematically less than the ideal no-slip curve (dot-dashed line in Fig. 3(c), obtained assuming $f^* = 1$), due to the effective slippage on the probe. This slip was modeled using the correction factor $f^* = d/(d + r_s)$,²⁸ which simply assumes that at physical contact the probe-substrate distance is finite, $d = r_s$. An alternative choice would be to model the slippage of the probe using an effective slip length b_s , rather than a roughness parameter. However, the two methods lead to results that are indistinguishable within the experimental error (see Section S2 of the Supporting Information for further details). We model the data by solving numerically the full differential equation describing the probe motion using measured values for all the geometrical and physical parameters and determining the best-fit value for the probe roughness. The obtained $r_s = 8.85$ nm provides an excellent description of the measurement (see Fig. 3(c) solid black line) and is consistent with the roughness parameter of the spherical probe as obtained by AFM imaging. By averaging 10 measurements at different substrate locations we obtained

$r_s = 9 \pm 2$ nm where the little data dispersion reflects the high homogeneity of the flat hydrophilic silica sample.

We performed similar force-distance measurements under identical experimental conditions (i.e., using the same colloidal probe, aqueous solution, and temperature) on flat hydrophobic silicon (OTS, red open triangles) and on the three different surface nanotextures: flat tip cone (FTC, green left-pointing open triangle), sharp tip cone (STC, open blue diamonds), and lamellar groove (LG, orange right-pointing open triangle) (Fig. 3(c)). Quantitative differences in the force-distance characteristics of these surfaces are most evident at small probe separation distances $d < 300$ nm (inset to Fig. 3(c)) where the data for all the hydrophobic surfaces falls below the control hydrophilic (silica) curve (black open dots), indicating increased slip on these surfaces. Although the behavior of OTS, FTC, and LMG surfaces is quantitatively similar to that of the no-slip hydrophilic control, the STC pattern (blue diamonds) exhibits significantly larger slip.

We extract the intrinsic slip length of the hydrophobic surfaces by modeling their force-distance curves using measured sample and experimental parameters, a probe roughness of $r_s = 9$ nm, and using a best fit to determine the correction factor accounting for the finite slip length at the substrate, b (boundary conditions illustrated schematically in Fig. 3(b)). Full analysis details are in Section S2 of the Supporting Information. The best fits represent the measured data very accurately (solid lines in Fig. 3(c)). Flat OTS and nanotextured FTC and LG surfaces exhibit slip lengths larger than the flat hydrophilic control by only a few nanometers. The small data dispersion indicates our high sample homogeneity. However, the STC nanotexture exhibits an order of magnitude larger slip length ($b = 44$ nm) than the other hydrophobic surfaces studied here (Table 1). We have also verified that this effect depends on the superhydrophobic nature of pattern because STC patterns without the hydrophobic coating (uSTC) showed a slip length comparable to flat OTS (see Table 1). Further, the results of the slip length measurements were independent of the time the samples were immersed in water (up to several hours). These findings suggest that nanometer scale

roughness is essential to maintaining dry surfaces under water, consistent with previous reports.²⁹ The reported slip lengths represent averages of ten individual measurements carried out at distinct locations across each substrate. The uncertainties reflect both instrumental errors and the effects of sample heterogeneity.

Our finding that flat hydrophobic coatings lead to modest slippage enhancement is consistent with previous experimental⁷ and theoretical work.³⁰ For example, molecular dynamic simulations of slippage at OTS ($\theta_{adv} = 110^\circ$) predict $b < 5$ nm.³⁰ The observed dependence of slippage on the texture's geometry is also consistent with theory. The theoretical slip length on the LG pattern can be estimated using the analytical solution:³¹

$$b_{LG} = \frac{3L}{4\pi} \ln \left[\csc \left(\frac{\phi\pi}{2} \right) \right], \quad (2)$$

where b_{LG} is the arithmetic average of the slip lengths in the direction transverse and longitudinal to the grooves under the assumption of no slip boundary condition at the solid surface. Similarly, the slippage on the hexagonal arrays of cones with either sharp or flat tips can be estimated using the semi-analytical model³²(which also assumes no slip at the solid):

$$b_{FTC,STC} = L \left(\frac{0.325}{\sqrt{\phi}} - 0.44 \right). \quad (3)$$

Using the geometrical parameters in Table 1, the models predict a modest increase of slippage at the grooves and flat tip cones textures, $b_{LG} = 4$ nm and $b_{FTC}=8$ nm, respectively. These predictions are close or slightly higher than the measured values of 4 and 3 nm, respectively. However, theory predicts a significantly larger slip for textures covered by sharp nanocones, $b_{STC}=41$ nm, in close agreement with the experiment. The slightly smaller slip enhancement on LG and FTC patterns, compared to the theoretical predictions, could be explained by considering that in the experiments the liquid/air interface is not pinned at the top of the structures (as assumed in the models) but is in fact recessed several nm inside

the texture.³³ In this case, slippage is significantly reduced compared to the case of no liquid penetration modeled by Eq. (2) and (3).

The interfacial slip measurements were complemented by studies of spontaneous charge separation at the nanotextured surfaces and its dependence on the texture’s chemistry and geometry. The surface charge density was inferred through CP-AFM measurements of the electrostatic force acting on the colloidal probe as a function of its distance from the surface.³⁴ The force curves were measured at approach speeds of $0.2 \mu\text{m/s}$ – two orders of magnitude slower than used in the slippage experiments – and low salt concentrations (0.5 mM KCl, pH=5.5) in order to reduce the effect of hydrodynamic interactions compared to electrostatic and van der Waals forces. The residual long-ranged hydrodynamic force was subtracted from the data by averaging the force curves acquired during approach and retraction of the probe.

As a control experiment, we have initially carried out force measurements on a flat silicon wafer bearing a native SiO_2 layer. Both the substrate and the probe were cleaned by UV-ozone exposure immediately before the measurements. A representative force curve (Fig. 4(a), open black dots) exhibits a repulsive force increasing monotonically with decreasing distance d until an instability occurs at $d \simeq 10 \text{ nm}$ where the probe is rapidly attracted to the surface. The details of the force curve are highly reproducible but the exact position of the instability varies slightly between measurements. Similar experiments, carried out on uncoated silicon STC (uSTC) textures (which also bears a native SiO_2 layer) show an equally repulsive albeit weaker interaction compared to the flat silica substrate (see Fig. 4(a), open magenta squares).

The repulsive interaction is understood considering the very similar chemical composition of the probe (soda lime glass containing up to 75% SiO_2) and the substrate. Both surfaces become negatively charged in water due to the dissociation of the silanol groups: $-\text{SiOH} \rightleftharpoons -\text{SiO}^- + \text{H}^+$.³⁵ The surface charge and surface potential of the flat and nanotextured surface can be estimated through quantitative analysis of experimental force curves based on solutions of the Poisson-Boltzmann (PB) equation with appropriate boundary con-

ditions (constant charge density at the solids). In our investigations, where the measured surface potentials are relatively low (<30 mV), the PB equation can be solved in the linear approximation²⁶ such that the total force on the colloidal probe is:

$$F(d) = 4\pi R\epsilon\epsilon_0\kappa\psi_s\psi_p e^{-\kappa d} - \frac{A(d)R}{6d^2}, \quad (4)$$

within the Derjaguin approximation and at separations $d > \kappa^{-1} = 13.6$ nm, where the effect of charge regulation is less important and the surface charge density is independent of d , in good approximation. The first term in (4) represents the (repulsive) electrostatic interaction where ψ_s, ψ_t are the surface potential of the substrate and the probe, respectively, and the substrate charge density is $\sigma_s = \epsilon\epsilon_0\kappa\psi_s$. The second term accounts for the (attractive) van der Waals interactions in the retarded regime $d > \kappa^{-1}$ through the empirical, distance-dependent Hamaker constant:³⁶ $A(d) = A_H(1 + 28d/\lambda)/(1 + 14d/\lambda)^2$ where $A_H = 0.6 \times 10^{-20}$ is the nonretarded silica-water-silica Hamaker constant and $\lambda = 100$ nm is the interaction range.

Our experimental data on both planar and nanotextured SiO₂ are well described by the model of Eq. (4) using the experimentally calibrated probe surface potential of $\psi_p = -23$ mV to determine free parameters ψ_s and κ^{-1} (Fig. 4(a), solid black lines). The best fit surface potential for silica $\psi_s = -23.2$ mV is in good quantitative agreement with literature³⁷ (at salt concentration and pH used here), and matches ψ_p . Further, the average fitted $\kappa_{fit}^{-1} = 14.1$ nm is consistent with the value expected at the solution salt concentration. On the uSTC nanotexture (silica surface) we measure an effective surface potential $\psi_s = -8$ mV, significantly lower than that measured on flat silica. This result is understood qualitatively considering the structure of the diffuse electric double layer and the nanotexture's geometry. The probe can not access regions within the nanocones and, since the texture feature height $h \gg \kappa^{-1}$, it experiences an effective surface charge density smaller than the flat silica, as illustrated schematically in the inset to Fig. 4(a).

Flat and nanotextured hydrophobic surfaces (coated with OTS) exhibit a very different

charging behavior compared to hydrophilic samples as shown in Fig. 4(b) (where each curve represents the average of 10 single approach curves measured at the same sample location). Although these surfaces also show repulsive forces, consistent with a negative surface charge, their surface potentials are all smaller in magnitude than that of silica surfaces. Remarkably, the magnitude of ψ_s is constant for all hydrophobic surfaces regardless of their very different morphologies. Fits to the data in Fig. 4 (b) yielded a potential (charge density) of -5.2 mV (-0.24 mC/m²) for planar OTS (open red triangles), -4.4 mV (-0.21 mC/m²) for both LG and STC textures (open right-pointing orange and open blue diamonds, respectively), and -4.7 mV (-0.22 mC/m²) for FTC texture (left-pointing open green triangles)). We understand the lower surface charge of OTS compared to SiO₂ as due to differences in the charging mechanisms of the two substrates. Differently from the silanol groups, the terminal methyl groups of OTS are nonpolar and therefore do not dissociate in water. Rather, charging is believed to result from the adsorption of OH⁻ groups at the OTS/water interface. Although Cl⁻ and H⁺ also adsorb at the hydrophobic interface, the hydroxide ions have the highest adsorption energy and saturation coverage.³⁸

Our numerical results for the surface charge density of OTS are close to the literature values of methyl-terminated surfaces, in the range of -0.5 to -1 mC/m² (measured at pH=5.5 and salt concentrations <1 mM).^{37,39,40} The important finding that the surface charge of hydrophobic textures is similar to the flat hydrophobic surface – regardless of their different solid area fraction – is a strong indication that the air-water interface is negatively charged with a surface density very close to OTS. Indeed, if the air-water interface carried no charge, or a positive charge, the repulsive force should be smaller particularly for the STC texture where the surface is composed almost exclusively of air at $\phi = 0.07$. The excellent agreement between the measured surface potential of the STC texture and the experimental values of surface potential of air bubbles,^{41,42} further strengthens our conclusions.

It is also not surprising that the air-water interface carries a charge similar to hydrophobic (OTS-water or oil-water) interfaces because their charging mechanism is thought to be

the same, namely the adsorption of excess hydroxide ions. This enrichment could arise from the disruption of the hydrogen bond network of water at the interface. The charge density of the nanotextures surfaces, albeit weak, can be further enhanced by increasing the solution pH.^{38,40,43} Nevertheless, even at low charge density ($|\sigma_s| \simeq 1 \text{ mC/m}^2$), electrokinetic energy conversion efficiencies of up to $\approx 20\%$ could be achieved theoretically¹⁷ using nanofluidic channels decorated with tapered nanocone textures ($b = 50 \text{ nm}$) (in the regime of strong double layer overlap). These results highlight the importance of high surface slip for improving significantly the efficiency of existing devices, which presently remains poor. Future work will investigate the dependence of slippage and surface charge on the electrolyte characteristics (chemical composition, pH, etc.), with the goal of identifying the conditions leading to optimal device efficiency.

In conclusion, we have investigated the slippage properties and surface charge of model hydrophobic nanotextures in contact with electrolyte solutions. Our results suggest that tuning the texture morphology allows maximizing fluid slippage at the interface in excellent agreement with theoretical estimates. Moreover, the presence of negative charges at the composite air/liquid and solid/liquid interfaces – comparable to that of flat hydrophobic interfaces – also enables amplification of electro-osmotic flow. These findings improve our basic understanding of liquid flow and charge separation at complex, nanostructured interfaces and may benefit a large spectrum of nanofluidic applications, from energy harvesting, to ultrafiltration and macromolecules sorting.

Experimental Section

PS-b-PMMA Thin-Film Preparation: Polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA) block copolymers (Polymer Source, Inc.) with molecular weights of $MW = 99 \text{ kg/mol}$ (PS:PMMA 64:35, polydispersity $PD = 1.09$) were cast into thin films by spin-coating from solution (1.0 wt% in toluene) at 2000 revolutions per minute (RPM) (dwell time of 45 s) and self-assembled into ordered structures by annealing in vacuum ($< 1 \text{ Torr}$)

at 200 °C for 12 hours. Prior to spin coating the block copolymer, the silicon substrates were coated with a hydroxyl-terminated PS-r-PMMA random copolymer brush ($MW \simeq 11$ kg/mol, PS:PMMA 52:48), formed by spin casting the random copolymer (0.5 wt% in toluene, 600 RPM), thermally annealing for 4 hours, and then rinsing the substrate in toluene to remove ungrafted copolymer chains. PS-b-PMMA templates were converted to aluminum oxide nanostructures by sequential infiltration synthesis, wherein ordered PMMA domains were converted to aluminum oxide nanostructures with similar sizes. This process consisted of three sequential exposures to tri-methyl aluminum and water vapor (for 300 s each at > 5 Torr and 85 °C) in a commercial atomic layer deposition system (Cambridge Nanotech Savannah S100). After this process, all remaining organic material was removed by oxygen plasma (20 W radio frequency (rf) power at 100 mTorr for 2 minutes) using a March Plasma CS1701.

Reactive Ion Etching: Reactive ion etching of the silicon nanostructures was performed using an Oxford Instruments PlasmaLab 100. A conical-shaped vertical etch profile was achieved using a 50:50:10 ratio of HBr, Cl₂, and O₂ gases at 10 mTorr, 60 W rf power, and 250 W inductive plasma power at room temperature. The process included a brief breakthrough step using BCl₃ and Cl₂ (20:5 standard cubic centimeter per minute, 10 mTorr, 100 W rf power, 800 W inductive plasma power) for 10 s in order to uniformly initiate silicon etching. The flat tip and lamellar etch profiles were achieved using a 100:20 combination of HBr and Cl₂ (10 mTorr, 60 W rf power, 250W inductive plasma power) at room temperature. This process included a breakthrough step using SF₆:O₂ (40:50 standard cubic centimeter per minute at 12 mTorr, 40 W rf power, 800 W plasma power) for 10 s. After etching, the remaining Al₂O₃ was removed using dilute hydrofluoric acid (50:1 in water) for 30 s. Samples were characterized by scanning electron microscopy (Hitachi S4800) operating at 20 kV.

Hydrophobic Coatings: Nanostructured silicon surfaces were rendered hydrophobic by passivation with a 2.5 nm thick octadecyltrichlorosilane (OTS) monolayer (immersion in 5 mM solution of OTS molecules in toluene for 10 h) after first cleaning in piranha solution

(a mixture of sulfuric acid and hydrogen peroxide in a 3:1 volume ratio. Warning: piranha solution reacts strongly with organic compounds and should be handled with extreme care). The conformal OTS coating does not significantly alter the surface topography as verified by comparing SEM images of the surfaces before and after silanization.

Wetting Measurements: Contact angles of Millipore water droplets on passivated silicon surfaces were measured with a Dataphysics model OCA 15+ goniometer. Advancing (receding) angles were measured by slightly increasing (decreasing) the volume of the droplet (radius $\simeq 1$ mm) using a motorized syringe with the needle immersed in the droplet.

CP-AFM measurements: Colloidal Probe AFM measurements were carried out using a commercial atomic force microscope (Agilent 5500) equipped with a 100 μm range, XYZ closed-loop scanner previously calibrated using a known standard, and a dedicated cell for operation with the probe and sample immersed in a liquid. In order to remove any uncertainty associated to the temperature dependence of the liquid viscosity, the liquid temperature in close proximity to the substrate was measured using a thermistor. Details of the colloidal probe assembly, data treatment, and modeling are reported in the sections S1 and S2 of the Supporting Information.

Supporting Information

Details of CP-AFM data acquisition and analysis.

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Table 1: Geometrical parameters, advancing/receding contact angle ($\theta_{adv}/\theta_{rec}$), slip length (b), surface potential (ψ_s), and surface charge (σ_s) of textured surfaces described in the main text.

surface	L (nm)	h (nm)	$\theta_{adv}/\theta_{rec}(^{\circ})$	ϕ	b (nm)	ψ_s (mV)	σ_s (mC/m ²)
flat SiO ₂	n/a	n/a	0/0	1	reference	−23.2	−1.09
flat OTS	n/a	n/a	110/103	1	4 ± 2	−5.2	−0.21
LG	80 ± 8	265 ± 10	150/130	0.6	4 ± 3	−4.4	−0.21
FTC	52 ± 5	205 ± 5	155/130	0.3	3 ± 2	−4.7	−0.22
STC	52 ± 5	190 ± 5	166/162	0.07	44 ± 4	−4.4	−0.21
uSTC	52 ± 5	190 ± 5	0/0	n/a	3 ± 2	−8.2	−0.38

Figure 1: Schematics of hydrodynamic flow on superhydrophobic surfaces. The presence of air inside the texture voids leads to a larger effective slip length, b , compared to a flat, hydrophobic solid. Charge accumulation at both solid/liquid and air/liquid interfaces is required to sustain a significant electro-osmotic flow.

Figure 2: Oblique side-view SEM pictures of silicon surfaces patterned with (a) hexagonal arrays of sharp tip nanocones, (a) hexagonal arrays of flat-tip nanocones, and (a) lamellar grooves (the scale bar is 100 nm for all pictures).

Figure 3: (a) Schematics of the CP-AFM experiment and (b) boundary conditions used to model the experimental data, where r_s is the roughness factor of the probe and b the slip length of the substrate. (c) CP-AFM force-distance curves measured at $v = 13.3 \mu\text{ m/s}$ and 0.1 M KCl for flat silica (open black dots) flat OTS (open red triangles), FTC texture (left-pointing open green triangles), LG texture (right-pointing open orange triangle), and STC texture (open blue diamonds). Dash-dotted line is the theoretical no-slip force and solid lines are fits to the respective data as detailed in the main text.

Figure 4: CP-AFM force-distance curves measured at $v=0.2 \mu\text{ m/s}$, 0.5 mM KCl , and $\text{pH}=5.5$ for (a) hydrophilic flat silica (open black dots) and uncoated STC texture (open magenta squares), and (b) flat OTS (open red triangles), LG texture (right-pointing open orange triangle), FTC texture (left-pointing open green triangles), and STC texture (open blue diamonds). Solid lines are fits to the data using Eq. (4) and insets illustrate schematically the charge sign and density at the solid/liquid and liquid/air interfaces.

Slip length enhancement in nanofluidic flow using nanotextured superhydrophobic surfaces

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Supporting Information

Colloidal Probe AFM measurements

S1: Colloidal probe-cantilever assembly

The colloidal probe was assembled by bonding a spherical soda lime glass bead of radius $R=26.5\text{ }\mu\text{m}$ (Polyscience, Inc., Niles, IL, USA), to a tipless silicon cantilever (Model CSC12 MikroMasch USA, San Jose, CA, USA). The process for fabricating the cantilever-bead

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assembly consisted of two steps. Initially, the bead was placed in contact with the free end of a cantilever previously wet with a small (diameter $\simeq 10\mu\text{m}$) drop of glycerol. The capillary force exerted by the liquid on the sphere was sufficient to hold it in place during further processing. Subsequently, the assembly was annealed in an oven at 650°C for 30 min. At this temperature, the glycerol boiled off and the glass reached its softening point thereby binding permanently to the oxidized silicon surface of the cantilever. Before each measurement, the cantilever-bead assembly was cleaned by immersion in chloroform for 5 min. followed by UV/ozone treatment for 20 min.

S2: Data acquisition and treatment

Representative CP-AFM data of cantilever photodiode deflection signal (U_{pd}) versus piezo-electric transducer position (H) obtained upon approach (filled red dots) and withdrawal (open red dots) of the colloidal probe to a flat silica surface at constant transducer velocity $v = 13.3\mu\text{m/s}$ are shown in Fig. 1 (a). The data represent an average of 10 single approach/withdrawal curves measured at the same substrate location. U_{pd} increases monotonously upon approach (decreasing H), until a crossover to a linear regime is observed when the probe comes into contact with the substrate. In this compliance regime, where the cantilever deflection is small ($\sim 100\text{ nm}$), $U_{pd} \propto H$ and the slope of the data is used to calibrate the deflection sensor. The withdrawal and approach curve differ in that a strong adhesion is observed upon retracting the probe from the surface. Owing to this effect, we have measured the hydrodynamic force on the probe through analysis of the approach curves only.

Similarly averaged data acquired with the probe $\simeq 50\mu\text{m}$ away from the surface show that – even in the absence of any probe-surface interaction – the deflection exhibits a small, linear dependence on H (see Fig. 1(b)). This artifact is caused by the elastic deformation of the AFM scanning head.¹ The apparent slope of the data, obtained by a linear fit (straight line in (b)), is approximately constant over the whole Z range of the piezo-transducer. Hence,

Figure 1: (a) Photodiode signal versus piezo-transducer position during approach (solid red dots) and withdrawal (open red dots) of the probe to a silicon oxide surface. (b) Same data and in (a) but with the probe located far away from the substrate. The solid red line denotes a linear fit to the data.

we have corrected for this artifact by subtracting the fitted slope from the data in Fig. 1(a). The corrected and calibrated cantilever deflection, denoted as δx , is plotted versus H in Fig. 2(a). In this plot, the point of zero probe-substrate separation, $(\delta x_0, H_0)$, denotes the crossover to the linear deflection regime (see inset to Fig. 2(a)).

The typical uncertainty of H_0 is $\simeq 5$ nm, however, we have estimated that this uncertainty translates in a small error of less than 2% on the slip length. The probe-substrate separation, d , was obtained from the data in Fig. 2(a) using the following relationship:

$$d = H + \delta x - (H_0 + \delta x_0), \quad (1)$$

and the cantilever deflection is plotted versus d in Fig. 2(b). In the limit of small deflections, the restoring force of the cantilever, F_{res} , is well approximated by the harmonic oscillator model:

$$F_{res} = k_c \delta x. \quad (2)$$

where k_c is the spring constant of the cantilever. We have measured k_c using the hydrodynamic method,² which assumes that at large separations $d > 1 \mu\text{m}$, and in absence of

Figure 2: (a) Cantilever deflection versus piezo-transducer position. Inset shows the coordinates of the point of zero separation ($\delta x_0, H_0$). (b) Cantilever deflection versus probe-substrate distance.

interfacial slip (hydrophilic probe and substrate), the restoring force of the cantilever equals the sum of Taylor's drag on the probe and the drag force on the cantilever body, F_{drag}^0 , namely:

$$k_c \delta x = \frac{6\pi\eta v R^2}{d} + F_{drag}^0, \quad (3)$$

where η is the viscosity of the aqueous solution (at the known solution temperature). We have obtained k_c and F_{drag}^0 through a linear fit to the data in Fig. 2(b) recast in a δx vs $1/d$ plot in the range $1000 \text{ nm} < d < 1700 \text{ nm}$. A statistical average (over 20 independent measurements) provided:

$$k_c = (0.0334 \pm 0.0023) \text{ N/m} \quad \text{and} \quad F_{drag}^0 = (0.037 \pm 0.010) \text{ nN}. \quad (4)$$

These parameters were used to calibrate and fit the force measurements to obtain the slip length of the various substrates described in the paper.

Hydrodynamic force-distance curve analysis

We have described the colloidal probe motion using the Newtonian equation:

$$F_h + F_{vdW} + F_{es} + F_{drag} + F_{res} = m\ddot{d}. \quad (5)$$

where F_h , F_{vdW} , and F_{es} are the hydrodynamic, van-der-Waals, and electrostatic force on the probe, respectively, F_{res} is the cantilever restoring force, F_{drag} is the hydrodynamic drag of the cantilever body, and m is the probe mass. In our experiments the probe motion is characterized by a low Reynolds number $\text{Re} = \frac{\rho v R}{\eta} \approx 0.37$ (ρ and η are the fluid density and viscosity, respectively) therefore the inertial term was safely neglected. Moreover, our measurements were carried out in (100 mM KCl) aqueous solutions where the electrostatic interaction was negligible up to separations on the order of the Debye length $\kappa^{-1} \approx 1$ nm. The van der Waals force in the sphere-plane geometry was approximated by the expression:

$$F_{vdW} = -\frac{A_H R}{6d^2},$$

where $A_H = 6 \cdot 10^{-21}$ J, is the non-retarded Hamaker constant. At separations $d > 20$ nm investigated here, $F_{vdW} < 0.1$ nN and therefore negligible compared to F_h . Consequently, Eq. (5) reduces to:

$$F_h + F_{drag} + F_{re} = 0. \quad (6)$$

The restoring force of the cantilever for small deflections was approximated by the harmonic oscillator model:

$$F_{res} = -k_c[d(t) - d_0 + v \cdot t], \quad (7)$$

where d_0 is the initial probe-substrate separation, and v the (absolute) velocity of the piezo-

electric transducer. The drag on the cantilever body was described using an empiric model:³

$$F_{drag} = a \left(1 - \frac{v + \dot{d}}{v} \right) F_{drag}^0 + (1 - a) F_{drag}^0, \quad (8)$$

where F_{drag}^0 is the drag force on the cantilever far from the surface (measured as described in the previous section) and a is an empirical parameter accounting for velocity dependence of the drag. Our data were well described using $a = 0.8$. However, since F_{drag}^0 is small compared to F_h and F_{re} our results do not depend significantly on the choice of a (in the range $0.7 < a < 1$).

The hydrodynamic force on a sphere approaching a flat substrate was modeled using the the Taylor equation modified for the the finite interfacial slip at the probe and substrate surface⁴ (in the limit $h \ll R$):

$$F_h = -\frac{6\pi R^2 \eta \dot{d}}{d} f^*, \quad (9)$$

where

$$f^* = -\frac{2Ad}{BC} - \frac{2d}{C-B} \left[\frac{(B+d)(B-A)}{B^2} \log \left(1 + \frac{B}{d} \right) - \frac{(C+d)(C-A)}{C^2} \log \left(1 + \frac{C}{d} \right) \right], \quad (10)$$

is the slip correction factor, and b_s , $b = b_s(1+k)$ (with $k \in [-1, \infty]$) are the slip lengths of the probe and substrate respectively. The constants A , B , and C are defined by:

$$A = b_s(2+k), \quad B = 2b_s(2+k + \sqrt{1+k+k^2}) \quad \text{and} \quad C = 2b_s(2+k - \sqrt{1+k+k^2}). \quad (11)$$

In the case of finite slippage at the substrate only (i.e. $b_s = 0$), f^* reduces to:

$$f^* = \frac{1}{4} \left(1 + \frac{6d}{4b} \left[\left(1 + \frac{d}{4b} \right) \log \left(1 + \frac{4b}{d} \right) - 1 \right] \right). \quad (12)$$

Figure 3: Experimental force-distance data measured on a hydrophilic flat substrate (open red dots) and fit to the data assuming a probe roughness r_s (solid green line) or a probe slip length b_s (solid red line). The dotted blue line denotes the theoretical no-slip curve.

We have initially characterized the slippage properties of the probe. A no-slip boundary condition at the probe surface is expected to hold in the case of ideally smooth, hydrophilic probe. However, in a real experiment, the roughness of the probe surface introduces a significant apparent slip. For this reason, we have modeled force-distance curve on flat hydrophilic surfaces using the following correction factor:⁵

$$f^* = \frac{d}{d + r_s}, \quad (13)$$

which simply assumes that at physical contact the probe-substrate distance is equal to r_s , the probe roughness parameter.

r_s was obtained by fitting numerical solutions of Eq. (6) (with f^* defined by Eq. (13)) to force-distance curves recorded on flat hydrophilic silica surface as shown in Fig. 3. The best fit (solid green line) provided an excellent description of the experimental data using $r_s = 8.85$ nm as the only fitting parameter. A statistical average over 10 independent measurements yielded $r_s = 9 \pm 2$ nm. We have obtained the slip length of the various flat and nanopatterned substrates by fitting numerical solutions of Eq. (6) to the corresponding

hydrodynamic force-distance curves where f^* was defined by Eq. (12) assuming a contact probe-substrate distance of $r_s = 9$ nm. The only fitting parameter was the slip length of the substrate, b .

An alternative, but less physical approach for modeling the probe slippage would be to ignore the probe roughness and to introduce a probe slip length b_s . We have verified that this choice leads to very similar results of substrate slip length. b_s was obtained by fitting numerical solutions of Eq. (6) to the data in Fig. 3 where the correction factor was defined by Eq. (10) with $b = b_s$. The best fit (solid red line) also provided an excellent description of the data with $b_s = 10.65$ nm. A statistical average over 10 independent measurements yielded $b_s = 11 \pm 2$ nm. The slip lengths of the various flat and nanopatterned substrates were obtained by fitting numerical solutions of Eq. (6) to the corresponding hydrodynamic force-distance curves with f^* defined by Eq. (10) and fixed $b_s = 11$ nm. The results, summarized in Table 1, show that both approaches provide equally good fits to the data (quantified by chi-square parameters) with slip length results that are indistinguishable within the uncertainty of the measurement.

Table 1: Fitted slip length of various substrates, and chi-square parameter obtained assuming either slippage on the probe (b_{b_s}) or probe roughness (b_{r_s}).

substrate	b_{b_s} (nm)	$\chi^2_{b_{b_s}}$ (nN)	b_{r_s} (nm)	$\chi^2_{b_{r_s}}$ (nN)
flat OTS	4 ± 2	0.21 ± 0.04	4 ± 2	0.23 ± 0.05
FTC	2 ± 2	0.14 ± 0.01	3 ± 2	0.15 ± 0.01
LG	3 ± 2	0.14 ± 0.04	4 ± 3	0.14 ± 0.04
STC	42 ± 3	0.17 ± 0.03	44 ± 4	0.17 ± 0.03

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