DOI: 10.1002/smll.200800564

# Sharp-Cornered Liquid Drops by Wetting of Nanoscale Features**

*Fabrice Birembaut, Nicolas Perney, Katrin Pechstedt, Philip N. Bartlett, Andrea E. Russell, and Jeremy J. Baumberg**

Nanostructured materials have become of intense interest in recent decades, driven by the realization that conventional properties on the macroscale can be completely modified. Simultaneously, it is clear that an interdisciplinary approach is inherently crucial to understand the properties of new nanostructures. Interest in exploiting enhanced optical properties for biological applications uncovers a critical question for nanobiosensors: where do molecules in solution end up on a nanostructured surface? For instance, molecular sensors can incorporate emitter–quencher coupling, or provide real-time observation of DNA pairing through luminescence tagging.[1] In the application of most interest here, molecules on a metal nanostructured surface produce intense surface-enhanced Raman scattering (SERS), which allows identification of very small numbers of unknown molecules. Discovered by Fleischman et al.,[2] the technique depends on local plasmonic electromagnetic excitations that develop on metal nanostructures and act as antennas to couple light efficiently into and out of the molecules. However, SERS applications suffer from a lack of reproducibility in the substrate preparation, and hence in their quantitative application in real environmental conditions.

Recently, a number of research groups have manufactured more reproducible substrates with nanostructured metals.[3–6] Because the huge Raman enhancements ($>10^6$) depend on the optical field to the fourth power and the field enhancements depend strongly on position within the nanostructures, it is critical to understand and control where molecules end up. Herein, we show that microstructured SERS substrates with nanoscale features have a dramatic effect in producing serrated-edged drops, and that deposition of molecules for SERS occurs in specific locations around the drop perimeter.

We explore how droplet wetting operates on such nanostructured metal surfaces, to understand how molecules will be distributed on a nanosurface that is drying. This is typified in our recent investigations of the use of a commercially available SERS substrate called Klarite, currently manufactured by D3 Technologies, for examining the potential for mass screening of patients' teardrops within the UK National Health Service. We show that the drop edges exhibit sharp, square contact lines with extreme curvatures $|R|<100$ nm. Molecules within such droplets are preferentially deposited in particular parts of this droplet edge. A simple model describing solvent flow in this highly folded drop-edge regime explains how molecules experience extreme spatial concentration.

The Klarite SERS substrates consist of square-pyramidal pits of side 1.5 μm, spaced 1.8 μm apart on a square lattice, with a maximum depth of 700 nm and an interior apex angle of 70° (Figure 1a, inset).[7] This geometry is selected for optimal control of manufacture using selective anisotropic etching of Si (for details, see Ref. [7]) to obtain atomically flat surfaces. The surfaces are Au-coated, and used here without additional cleaning procedures. Raman spectra of these clean samples show minimal contamination.

To understand the spatial deposition profile of the molecules, we studied the wetting properties of microliter droplets of water. Note that if wetting inside the pit arrays does not happen, then no SERS signal can be observed. We first measured how the droplets sit on the nanostructured substrate by allowing a 1-μL droplet to contract through evaporation (Figure 1a,b).

At the beginning, the observed contact angle is 112°, which implies that the substrate is hydrophobic. However, as it dries evaporatively the edges of the droplet initially remain pinned to the substrate, slowly decreasing the contact angle and making the droplet increasingly flatter (Figure 1b) before retracting inwards. Similar results are seen everywhere across the sample. To resolve the droplet edges, high-resolution scanning electron microscopy (SEM) images were obtained in the wet mode (Figure 1c), in which the 10-keV electrons can penetrate about 1 μm of water. The water droplet was placed on the substrate before pumping down and images were taken at a pressure of 3 Torr with the Peltier stage cooled to 5 °C. The imaged edge of the receding droplet clearly shows the pixelation of the water/air/surface interface. It appears that the droplet edges follow the pit rims, which form a "microfence" for preventing the spread of liquid wetting. As the droplet edge recedes during drying, the edges are observed to digitally snap from one pit rim to the next. The highly folded droplet edges reveal high curvatures with $|R|<100$ nm, supported by the strength of the pinning. A number of recent results support this concept.[8,9]

To assess where molecules end up on the nanostructured surface, a droplet of Rhodamine 6G (R6G) dissolved in water was deposited onto the substrate and the photoluminescence of the resulting dried pattern was recorded using a confocal microscope (Figure 2). On the patterned region, the droplet is pinned on the edges and tends to form very flat contact lines aligned along the pit sides; the R6G molecules are deposited in a thick ring inside this edge, with each pit filled.

A similar experiment was carried out by looking at the deposition of copper from a 2-μL droplet of copper sulfate solution, which was allowed to dry on the Klarite substrate. By

---

[*] K. Pechstedt, N. Perney, Prof. J. J. Baumberg
School of Physics and Astronomy
University of Southampton
Highfield, Southampton SO17 1BJ (UK)
E-mail: j.j.baumberg@phy.cam.ac.uk
Dr. F. Birembaut, Prof. P. N. Bartlett, Prof. A. E. Russell
School of Chemistry, University of Southampton
Highfield, Southampton SO17 1BJ (UK)

[**] We thank Caterina Netti, Martin Charlton, and D3 Technologies for samples, and UK EPSRC for funding grants EP/C511786/1 and EP/C011902/1.

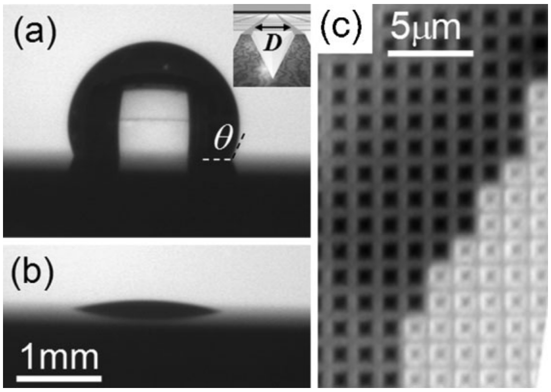

**Figure 1.** a) Image of a 1-μL water droplet on a Klarite substrate, with a contact angle $\theta$ of 112°. Inset: Cross section of a square-pyramidal pit nanostructure, with square aperture side *D*. b) The same water droplet after evaporation where the edges of the droplet remain pinned to the substrate. c) SEM (wet mode) image of a receding droplet of water (dark) highlighting the "pixelated" edges.

using energy-dispersive X-ray (EDX) mapping of the L$\alpha$ edge of copper in an SEM image (Figure 3a), the distribution is found to be strongly concentrated in the pits, with little deposition on the rims between them. This combined evidence that molecules are left inside the pits, where they experience strong SERS enhancements (enabling signature detection), implies the substrate indeed wets. We also measured the plasmonic reflectivity as the drying drop edge recedes under an optically interrogated spot (not shown), and found that it exhibits a plasmonic resonance appropriate for the water-filled gold pit (i.e., the resonance tunes with the refractive index of water).

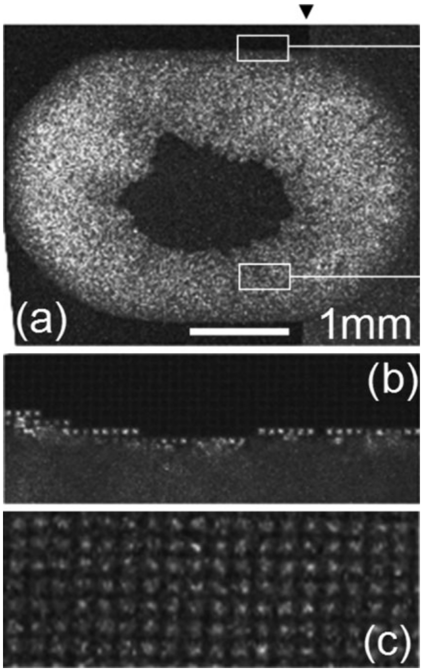

**Figure 2.** Confocal luminescence microscopy images of a $2 \times 10^{-4}$ mol solution of R6G in a dried water drop a) on the edge of the nanostructured substrate. Nanostructures (square pits 1.5 μm across) are to the left of the vertical arrowhead, with flat Au on the right. b) Edge of the drop and c) inside the droplet ring (rectangular areas in (a)).

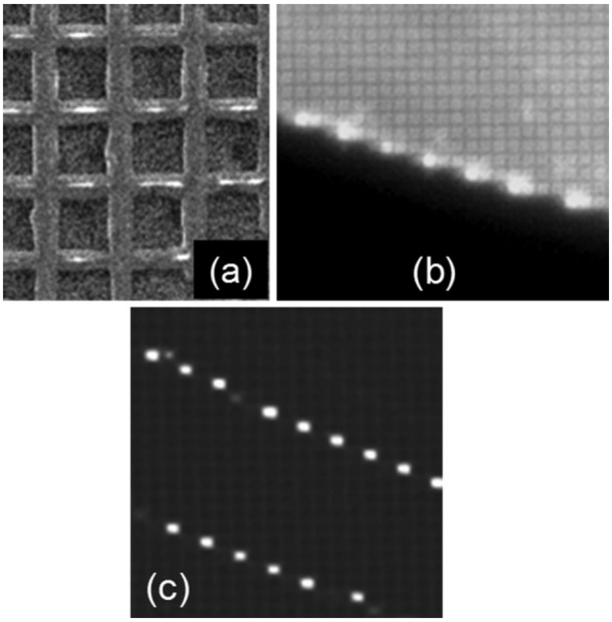

**Figure 3.** a) Map of Cu distribution by EDX from a drop of copper sulfate. b,c) Confocal luminescence images of the edge of the dried drop containing 0.2 μmol CdSe semiconductor QDs suspended in b) water and c) toluene.

However, there remain two possibilities for the dynamics of the drop edges: they can remain statically in place depositing molecules before jumping to a new location, or they can retract by leaving behind a microdroplet in each pit which then dries. We gained insight into the deposition by measuring the photoluminescence image in a confocal microscope of a dried droplet of CdSe semiconductor quantum dots (QDs) suspended in both water and toluene (Figure 3b,c). While for a toluene droplet the evaporation process is much faster than that of water, similar features are observed. However, an additional feature is "drying rings" along which QDs are preferentially located (as well as concentrated in a central clump). The most unusual feature of these rings, which record the position at which the rim has been temporarily pinned, is that the QDs are deposited selectively in only certain pits to form a "dotted line" with discrete gaps. While less pronounced on the water/QD drop edges (Figure 3b), there is a clear concentration of molecules into particular pits along the edge.

We believe that this peculiar phenomenon can be explained from the shape of the pixelated droplet edge (Figure 1c). We first consider the typical flows inside a drying drop. Under the conditions here, the rate-limiting step of evaporation is the diffusion of solvent vapor away from the droplet vicinity rather than the transfer rate across the liquid/vapor interface. In this condition, evaporation proceeds faster at the droplet edges because the probability of molecules escaping the vicinity of the drop edge is higher than that above the center (Figure 4a). When the droplet edge is pinned, a decrease in the droplet height has to be produced mostly by vapor escape from the drop circumference near the substrate; hence, there has to be a significant flow of liquid into this edge region from the droplet bulk.[10] This flow carries molecules and particles into the edge region, thus

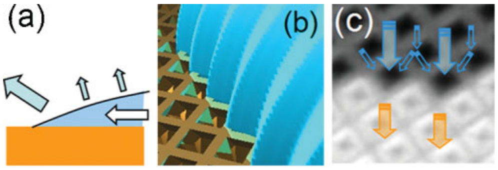

**Figure 4.** a) Vapor and liquid flows at a droplet edge. b) Schematic geometry of the edge of a drop on a nanostructured surface, with c) faster flow of liquid to the sharp, convex edges where evaporation is faster.

forming the traditional coffee-ring effect.[10] In the system here, the droplet edge is severely corrugated by the pixelated edge (Figure 4b). Convex regions of this corrugation have a higher diffusion probability for vapor to leave the droplet vicinity, and hence the flow into these regions needs to be faster. Conversely, in the concave regions, vapor escapes more slowly and hence the flow into these regions is reduced (Figure 4c). This leads to the QDs/molecules being preferentially deposited in the pits that are surrounded by convex outer drop edges, and hence produces the dotted line effect. Once the evaporation is strong enough so that the contact angle provides a strong inward force, the edge of the droplet then jumps back allowing the process to be repeated.

In conclusion, we show that the wetting of metallic microstructures with nanoscale features, which are suitable for highly sensitive molecular detectors, can produce extremely unexpected results. The sharp bending of the droplet edges produced by tethering of the liquid/air/substrate contact line induces flows of analyte to particular locations. We show that molecules are preferentially deposited in the pyramidal pits on these structures. Such measurements are crucial to engineer the fluidics of deposition in optimized devices. Our results have implications for a much wider range of nanostructures and these are currently under investigation.

## Experimental Section

*Contact angle measurements*: Contact angles were determined with a purpose-built arrangement assembled on a vibration-isolated platform. Measurements were made in a sealed glass chamber at 100% humidity (unless stated otherwise). The sample was illuminated and observed through an optical window in the side of the cell using a Krüss DSA100 drop shape analysis system. A 1-μL droplet was placed on the surface of the substrate, and the apparent contact angle $\theta^*$ was measured automatically using the drop shape analysis program (DSA1 v1.9). All reported contact angles are the average of at least five measurements taken at different locations on the substrate and have a maximum error of ±3°.

*SEM*: An environmental scanning electron microscope (Philips XL30 ESEM) was used to study the morphology and thin drop wetting. The humidity was controlled inside the chamber to ±5% to stabilize the evaporation rate.

*Confocal microscopy*: Standard confocal microscopy was used to image the nanostructured surfaces (Zeiss LSM 510), with laser excitation at 488 nm and blocking filters to observe the luminescence of the R6G dye on QDs at wavelengths beyond 550 nm.

**Keywords:**
microdroplets · nanostructures · Raman spectroscopy · surfaces · wetting

[1] P. Zhong, Y. Yu, J. Z. Wu, Z. Y. Long, C. S. Liang, *Anal. Sci.* **2007**, *23*, 1085.
[2] M. Fleischman, P. J. Hendra, A. J. McQuilla, *Chem. Phys. Lett.* **1974**, *26*, 163.
[3] L. M. Shen, Z. L. Yang, B. Ren, D. Y. Wu, R. A. Gu, Z. Q. Tian, *Chem. J. Chin. Univ.* **2005**, *26*, 1732.
[4] J. F. Li, J. W. Hu, B. Ren, Z. Q. Tian, *Acta Phys. -Chim. Sin.* **2005**, *21*, 825.
[5] M. E. Abdelsalam, P. N. Bartlett, J. J. Baumberg, S. Cintra, T. A. Kelf, A. E. Russell, *Electrochem. Commun.* **2005**, *7*, 740.
[6] L. A. Dick, A. D. McFarland, C. L. Haynes, R. P. Van Duyne, *J. Phys. Chem. B* **2002**, *106*, 853.
[7] N. M. B. Perney, J. J. Baumberg, M. E. Zoorob, M. D. B. Charlton, S. Mahnkopf, C. M. Netti, *Opt. Express* **2006**, *14*, 847.
[8] M. Gleiche, L. Chi, E. Gedig, H. Fuchs, *ChemPhysChem.* **2001**, *3*, 187.
[9] A. Ahuja, J. A. Taylor, V. Lifton, A. A. Sidorenko, T. R. Salamon, E. J. Lobaton, P. Kolodner, T. N. Krupenkin, *Langmuir* **2007**, *24*, 9.
[10] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel, T. A. Witten, *Phys. Rev. E* **2000**, *62*, 756.

Received: March 28, 2008
Revised: June 26, 2008