A superhydrophilic AFM tip as a nanosensor of hydrophobicity: a rationale for a new analytical method

A. Méndez-Vilas

Formatex Research Center SLU, 06010 Badajoz, Spain
Correspondence: e-mail: amendezvilas@gmail.com; Phone: +34644389624
Personal website: https://scholar.google.es/citations?user=XVejCGYAAAAJ

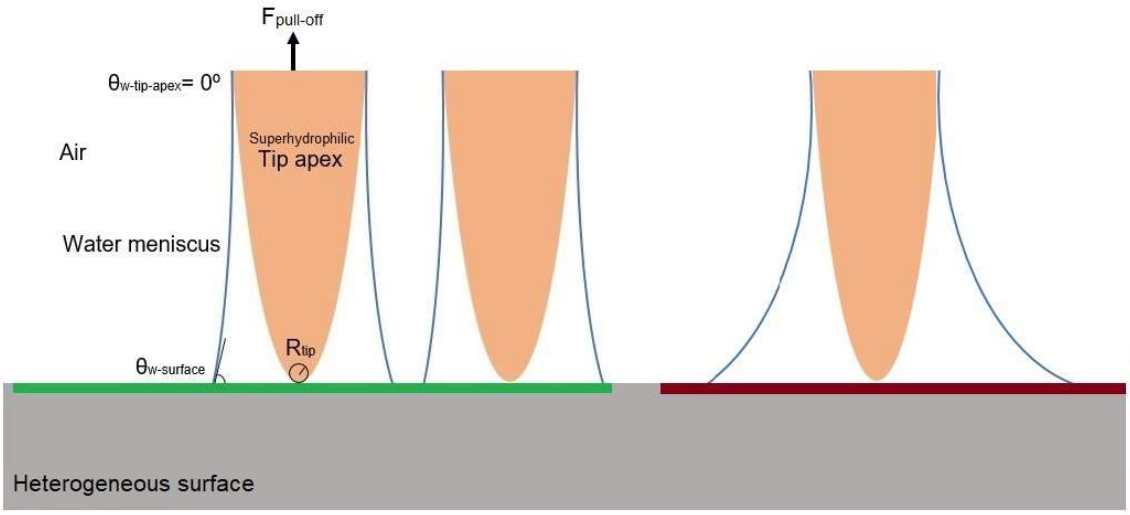
Accessing surface hydrophobicity (SH) via the water contact angle value (θ_w) at a local (nm) scale, or in a region (nm resolution), is of obvious interest in virtually any field of the natural sciences and related engineering.

To achieve that, the method proposed in this short article exploits the presence of a nanoscale water capillary formed between an AFM tip and any surface in ambient conditions, the characteristics of which depend on the value of θ_w of both the tip apex zone ($\theta_{w\text{-}tip\text{-}apex}$) and the surface under study ($\theta_{w\text{-}surface}$), as well as on the tip radius, according to the simplest possible theoretical model. This water capillary is the responsible of the pull-off force ($F_{pull\text{-}off}$) measured by the AFM. The tip radius can be precisely measured by SEM/TEM. The key of this method is that in it, the value of $\theta_{w\text{-}tip\text{-}apex}$, a quantity not directly available, is a well-defined fixed quantity. This may be achieved by using a recently released tip material (titanium nitride) instead of the common silicon nitride. Luckily for our purpose, this material bears a perfectly clean, superhydrophilic TiO_2 surface ($\theta_w = 0°$) after a simple modification (surface oxidation and UV-light illumination). The time this effect lasts is well above that taken by the AFM in getting $F_{pull\text{-}off}$ over a region. This way, for each $F_{pull\text{-}off}$ measured, a value of $\theta_{w\text{-}surface}$ can be derived.

In summary, a lucky synergy between a newly introduced tip material and the easiness of fixing its θ_w by rendering it superhydrophilic, makes it possible to obtain a map of SH ($\theta_{w\text{-}surface}$) from a raw $F_{pull\text{-}off}$ map. In other words, it potentially turns the AFM into a fast, local, high-resolution, and quantitative sensor of θ_w or SH.

Keywords: AFM tip; adhesion force; water contact angle; surface hydrophobicity; TiO2; sensors

Graphical abstract



1. Some fundamentals on surface hydrophobicity, AFM tips and the capillary force in gaseous environments.

Surface hydrophobicity (SH) is a fundamental property that plays a fundamental role in natural phenomena like mineral flotation or protein folding and in the production of commercial goods in the automotive or aerospace (e.g., superhydrophobic coatings), in the biomedical (antibacterial paints), or textile (stain-resistant textiles or flame-retardant and waterproof clothing), to name a few. It is key in the microelectronics since prevents metal oxidation or corrosión.[1] Due to this, much attention has been paid in the past to measure SH, usually focusing on the average surface wettability (statistical average). But most materials are inherently heterogeneous. Efforts are being made to quantify SH and its distribution at local scales, therefore. AFM or its variations are techniques being used to this end, like Chemical Force Microscopy[2,3,4,5,6] or Colloidal Probe Microscopy[7]. But these methods do not provide a relationship to values of water contact angle (which is a widespread and facile method) and are conducted underwater and not at environmental conditions. In this proposal, the nanoscale heterogeneity of SH is directly mapped using an AFM derived water contact angle method, under ambient conditions, taking advantage of the ubiquitous water capillary that bridges any asperity (as the AFM tip) and another surface. This is done directly in environmental conditions, where many phenomena occur, which should aid higher comparability with the much research that uses the water contact angle.

Following the calculations by O'Brien and Hermann and the works of Israelachvili and Riedo[8,9,10], when a sphere (tip) of radius R_{tip} is in contact with a flat surface, a capillary annulus of condensed water is formed around the contact surface. The resulting capillary/adhesion (pull-off) force, the dominant force in ambient conditions, is:

$$F_{pull-off} = 2\,\pi\,R_{tip}\,\gamma_{lv}(\cos\theta_{w-tip-apex} + \cos\theta_{w-surface}) \qquad \text{Equation 1}$$

In our proposed setup, $F_{pull\text{-}off}$ is maximum, since $\cos(\theta_{w\text{-}tip\text{-}apex}) = 1$, the highest possible value, so

$$F_{pull-off} = 2\,\pi\,R_{tip}\,\gamma_{lv}(1 + \cos\theta_{w-surface}) \qquad \text{Equation 2}$$

That is, making the tip superhydrophilic maximizes the amount of water the meniscus bear. These experimental conditions make the capillary model even more justified (Fig. 1).

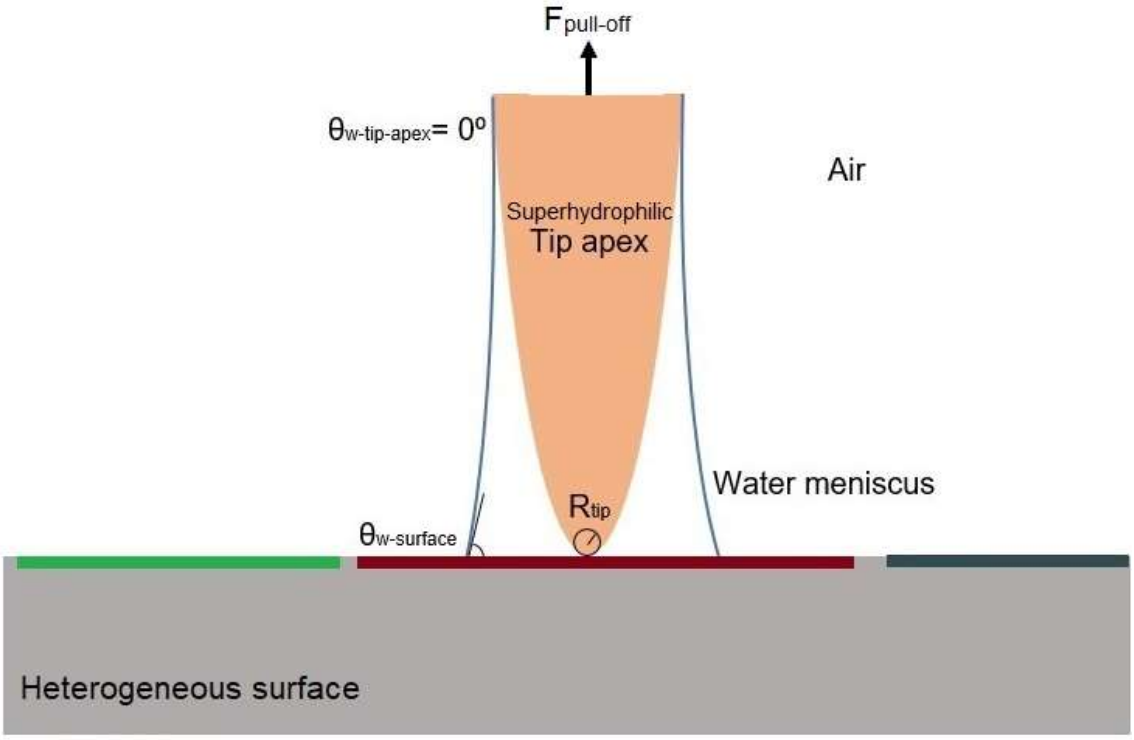


Figure 1. Schematics of a $F_{pull-off}$ measurement using a superhydrophilic AFM tip on a heterogeneous surface.

Since this is a new experimental design, we prefer to present here the simplest possible theoretical model (limitations found in other studies may not apply here, since the tip wettability is perfectly defined, and not only that, but it may be considered as clean). Depending on the success of experiments, researchers may want to use others: they shall find it easier than with conventional tips since this time the tip wettability is well defined and stable over the experimentation time (due to its self-cleaning property). But first things first: check the simplest possible model, that if successful will generate greater interest and broader use.

The research about surface forces in gaseous environment is vast and controversial. Since much of the mismatch between theory and experiment my arise from values of magnitudes not well accessible experimentally (though well defined in theory), and specially from the subtle but strong influence of airborne contaminants in both AFM and macroscopic contact angle measurements (almost any surface exposed to air increases its water contact angle, even when adsorbed organic compounds can be considered at a trace-level), this research community may benefit from this new experimental setup.

2. Easy production of a superhydrophilic (not only highly hydrophilic) tip

How can this be done? The starting point comes from nano-industry: some firms have recently introduced a novel Ti-based material, say titanium nitride (TiN), for coating their AFM tips. Why has this material been introduced? The main reasons are[11]: 1) They are conductive (in fact, these tips are usually used in electrical AFM-based measurements); 2) TiN coatings are hard and wear-resistant; 3) Resulting tip curvature are in the range of 40-60 nm after coating, which is acceptable; 4) The coating remains in the nm range (about 35 nm) and is uniform; 5) It is stress-free and does not significantly bend the cantilever; 6) Shelf life about 3 months (the limitation due to humidity). What is the scientific basis of the process of TiN coverage? These old articles accounts for it[12,13].

As specified above, these tips are not of general use, so let us describe them and their availability in some detail. These three companies are producing and selling TiN-covered tips. AIST-NT Inc. (USA) (http://nanoprobes.aist-nt.com/ Claims to have 15 years of experience in the sector, so a stable service can be expected. It has developed TiN-coated contact AFM cantilevers/tips with resonance frequencies in the range of 10-20kHz and cantilever spring constants (k_c) in the range of 0.03-0.1 N/m (k measures how stiff a cantilever is). The total tip curvature is 40-60 nm, and the height and cone angle are 7-10 μm and ≤22°, respectively. The thickness of the coating is about 35 nm. The products names are: fpC10TiN,fpC11TiN,fpC01TiN. Applied NanoStructures, Inc. (USA), known as AppNano (http://www.appnano.com). This firm develops conventional and specialized AFM probes. The facilities include a clean room with state-of-the-art characterization tools for rapid prototyping, adaptability, and versatility in designing and developing new products. From their website's age, this company has at least 15 years of experience. Their TiN covered tips for contact applications- are called TiN-FORT. They a resonance frequency of 61 kHz and a k_c of 1.6 N/m. The radius of curvature is 30 nm. They also have non-contact or intermittent-contact probes with 37 N/m and 300 kHz values. NT-MDT LLC (Russia) (https://www.ntmdt-si.com). IT develops research equipment, primarily atomic force microscopes (AFM) and their combinations with ultra-high resolution spectroscopy. It is represented by companies in Russia, Europe, the USA, and China. It has a history of more than 30 years in the sector. It commercializes TiN-cover tips, compatible with the most of commercial AFM devices. Typical curvature radius of uncoated tips is 6 nm (no data on covered ones). Cone angle at the apex: 7° - 10°.

In conclusion, luckily there are at least three reliable companies producing and selling TiN-coated AFM tips. Now the question is: How can we render these tips superhydrophilic?

This is not difficult. Simple treatments are available for a medium sized surface science/materials science lab to oxidise the surface of TiN to TiO_2, the best known self-cleaning superhydrophilic material (only needs UV-light illumination). One simple way is the ozonisation of the original TiN tip. As described in[14], O_3 oxidizes TiN to form a layer of TiO_2 on the surface. The oxidation reaction, thermodynamically favourable, proceeds as follows:

$$TiN + 3O_3 \rightarrow TiO_2 + NO + 3O_2$$ Equation 3

This produces a stable and self-passivating TiO_2 layer that impedes further oxidation. An alternative way, called thermal oxidation, is using heat to oxidize TiN since this material oxidizes to titanium dioxide (TiO_2) at relatively low temperatures, as low as 350 °C in air (Fig. 2).[15,16,17]

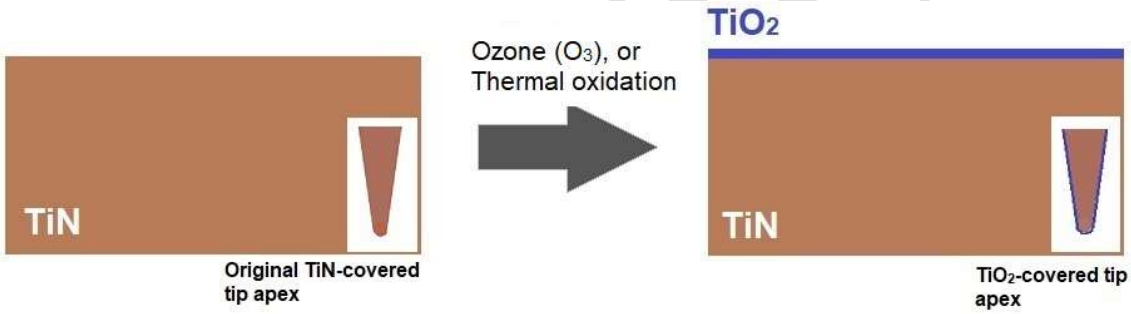


Figure 2. Schematics of the process of getting TiO_2 over the surface of TiN.

How can we render a TiO_2-covered tip superhydrophilic? The phenomenon of turning TiO_2 superhydrophilic is well known. It was first reported in a *Nature* paper in 1997 by the group of Prof. Akira Fujishima, from University of Tokyo.[18] They discovered that a TiO_2 surface, whose water contact angle may vary considerably (from hydrophilic to hydrophobic) depending on environmental conditions, becomes superhydrophilic ($\theta_w = 0°$) after being exposed to UV radiation during some hours. Nowadays, this is called the superhydrophilic self-cleaning effect, being this the basis of important applications and product develolopments[19,20]. The phenomenon is explained by the production of radical species due to the formation of oxygen vacancies at the bridging sections of TiO_2, which has two effects: it induces complete wetting of water and the decomposition of organic contaminant adhered. Particles adsorbed are also carried away by a thin water layer formed at the illuminated surface. Hydrophobic recovery occurs when the material is kept in dark during some (typically some days) or

exposing it to heat (typically hours or even minutes[21,22,23]. Luckily for our purposes, TiO_2 is one of the few materials that becomes superhydrophilic in such a simple way. UV illumination is therefore the last step in getting our TiO_2-covered tip superhydrophilic and clean (Fig. 3).

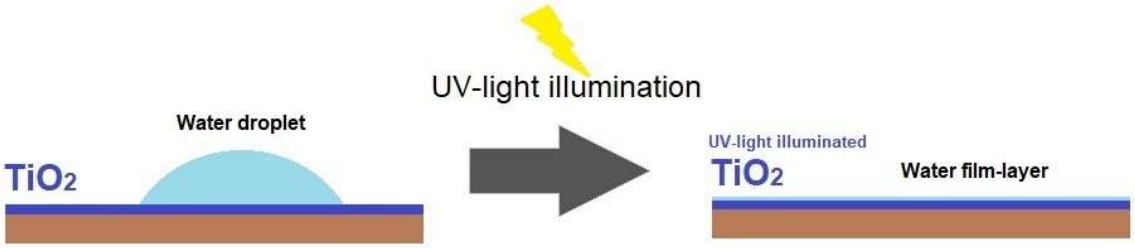


Figure 3. Schematics of how to transform TiO_2 into superhydrophilic.

Needless to say, the k_c and R_{tip} might have changed to some degree due to the TiO_2 layer grown. Therefore, they must be measured before using the tip. This is straightforward, as they are usual calibration steps in AFM-based experimentation if one does not want to settle for the data provided by the companies. R_{tip} can be measured directly by SEM/TEM or indirectly by the blind estimation algorithm, available in various AFM software packages, such as Gwyddion, WSxM and SPIP [24,25]. k_c can be measured using the thermal noise method, among others.[26] The whole process of getting a superhydrophilic tip from a bare TiN one is schematized in Fig. 4.

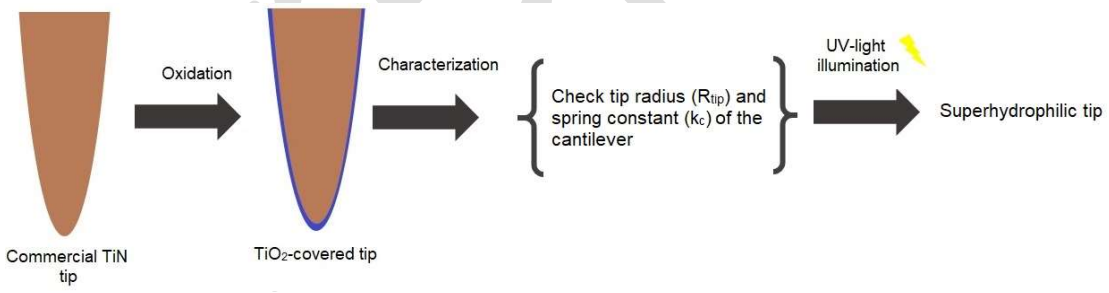


Figure 4. Schematics of the whole process of getting a superhydrophilic tip from a bare TiN one.

3. Other surface science research that might benefit from this new experimental design.

Though I am a experimentalist, I feel that many previous works reporting a mismatch between the theoretical models available or developed could be repeated with a well-defined and stable AFM tip like the one proposed in this note: the mismatches might had been

absolutely "impossible to check" factors at time they were conducted: relying in the measurement of the wettability of a macroscopic surface of the “same material” than the tip may a good decision since the tip status may vary, even erratically, during an experiment, behaving like a "collector" of adsorbed contaminants[27] or simply due to differences arising from the different methods used for synthesizing or processing, even having the same bulk composition. In the case of using superhydrophilic, self-cleaning tips, their properties remain stable for days.

If experimental results require to use other refined theoretical models available in the literature, other variables might be required, such as the tip-surface distance (usually denoted as D), relative humidity (RH), or the rms roughness of the substratum (R_q), which are accessible from AFM data or the environmental chamber

Eventually, depending on how successful experiments are, a kind of method-specific “hydrophobicity” (e.g., superhydrophilic AFM tip derived SH) could be developed, that would add to other existing: for example, the “hydrophobicity-index” used in the biological field to get a numerical estimate of how hydrophobic the cell surface of a bacteria or a fungus is[28], the SH derived from capillary AFM interactions with chemically modified tips[29], from Chemical Force Microscopy[2,3,4,5,6] or Colloidal Probe Microscopy interactions[7], or that derived from ESEM images of water micro (not nano) droplets.[30]

4. A singular configuration: both superhydrophilic tip and substratum

This configuration is particularly interesting because it predicts a fixed value of $F_{pull\text{-}off}$ for a chosen tip. $F_{pull\text{-}off}$ takes here its maximum value (both cosines equal 1), say

$$F_{pull-off} = 4\,\pi\,\gamma_{lv} R_{tip} \qquad \text{Equation 4}$$

Thus, a measured value of $F_{pull\text{-}off}$ can be used to retrieve a measure of R_{tip}:

$$R_{tip} = \frac{F_{pull-off}}{4\,\pi\,\gamma_{lv}} \qquad \text{Equation 5}$$

In summary, we could measure $F_{pull\text{-}off}$ on a TiO_2 irradiated substratum previous to the material of interest as a way of obtaining R_{tip}. This is straightforward: extended TiO_2 surfaces are commercially available (check, for example, MSE supplies,

https://www.msesupplies.com, or Shinkosha, https://www.shinkosha.com). Researcher who have not got access to a SEM or TEM apparatus might find this useful.

Again, if experimental data dot not fit the theoretical models and the cause might be insufficient water adsorbed for capillary condensation to occur (as some authors have claimed in studies made with conventional tips), relative humidity (RH) inside the environmental chamber could be raised until fulfilling the theoretical requirements. This configuration maximizes the amount of water available for formation of the capillary, so my impression is that it worth making the experiments, analysing the data with the simplest model first, and using refined models available in the literature available, if necessary.

5. A singular configuration: a non-superhydrophilic tip and superhydrophilic substratum

An accessory unexpected advantage may come from the measurement of $F_{pull\text{-}off}$ when using a conventional tip and a superhydrophilic substratum (Fig. 5). In this case, equation 1 reads:

$$F_{pull-off} = 2\,\pi\,R_{tip}\,\gamma_{lv}(\,cos\,\theta_{w-tip-apex} + 1) \quad \text{Equation 6}$$

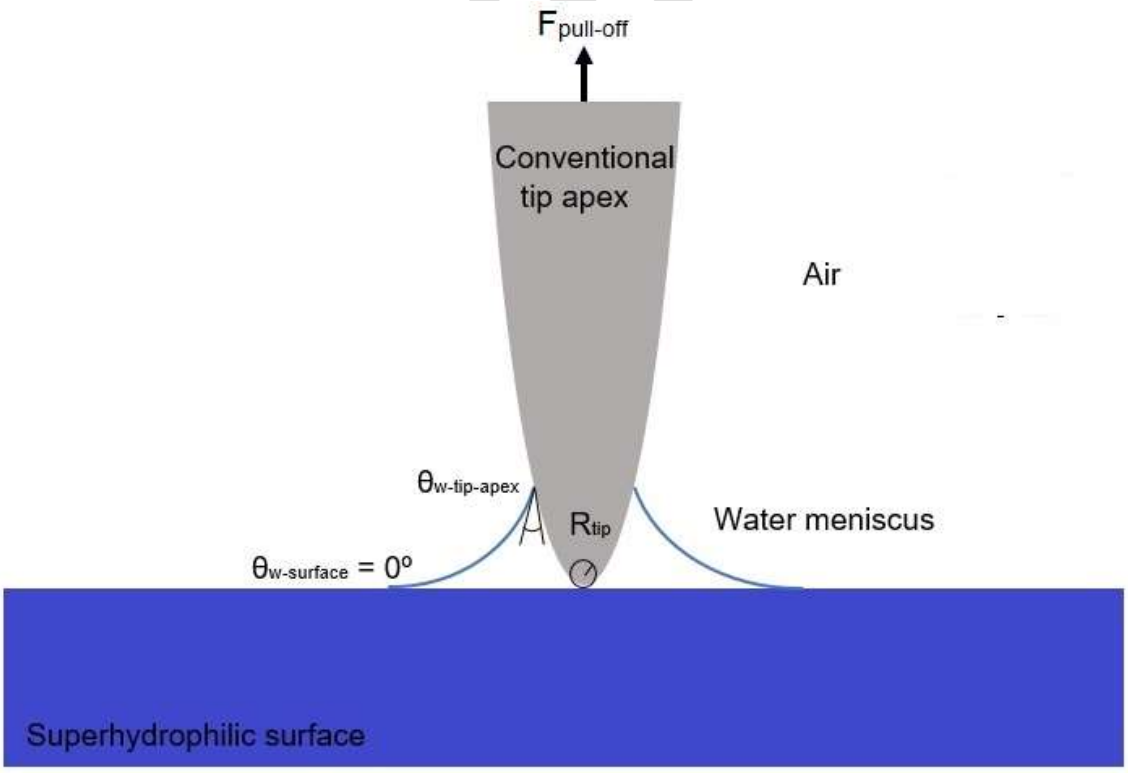


Figure 5. Schematics of a $F_{pull\text{-}off}$ measurement using a superhydrophilic AFM tip on also superhydrophilic superhydrophilic surface.

Therefore, the only unknown is $\theta_{w\text{-}tip\text{-}apex}$. That is, measuring $F_{pull\text{-}off}$ on a superhydrophilic substratum could be a facile method for measuring/calibrating the wettability of the tip apex. This value could further be used in ulterior studies using another substrate of interest. This would make possible another physical quantity (wettability) of the tip apex, which is the real sensing part, to be accessible experimentally.

This is a non-trivial advantage: due to the its nm size, potentially irregular shape or contamination, methods to probe its physico-chemical status urge. Whereas it is "easy" to check its physical (shape and general status) by SEM or TEM, which do have nm resolution[31,32] or using advanced reconstruction algorithms applied to AFM images taken with it, the precise chemical status under the working ambient conditions might be impossible to access, since only TOF-SIMS has the required resolution (nm)[27], but as SEM/TEM requires high vacuum and is its capacity of revealing the of molecular nature of the substances present is limited due to the aggressive nature of the ionic bombardment of the surface. Surface wettability $\theta_{w\text{-}tip\text{-}apex}$ is an intermediate physico-chemical parameter, but its measurement to such a ultrasmall region is also challenging. Measuring $F_{pull\text{-}off}$ on a superhydrophilic substratum could provide a solution. If successful, we could well characterize the wettability of an arbitrary tip without relying on the macroscopic water contact angle acquired over a substratum of the “same material” whose surface status might not be "sufficiently equivalent" to reality in the context of magnitudes so exquisitely dependent on the “true surface” as contact angles and surface forces are.

Finally, I would suggest another way of testing this obtained value. It would be worth imaging microscopic water droplets nucleated on the tip in an ESEM apparatus, trying to locate the droplets as close to the apex as possible. I only know about microscopic and not nm scale water droplets imaged by ESEM (see my review[30] for details), but potentially useful and complementary information may arise in dedicated works.

Acknowledgments

I acknowledge my former colleagues at the Biosurfaces and Interfacial Phenomena (led by Prof. González-Martín) group of the University of Extremadura, where I spent many years performing applied research, for the much I learned there on the topic of this note.

References

1. Nanomaterials and Nanotechnology, Volume 12: 1–21, 2022.

2. Dynamic Cell Surface Hydrophobicity of *Lactobacillus Strains* with and without Surface Layer Proteins, Vadillo-Rodríguez, V.; Busscher, H.J.; Norde, W.; Vries, J.; van der Mei, H.C. *J Bacteriol.* 2004, 186(19), 6647–6650.

3. Dufrêne, Y.F. Direct characterization of the physicochemical properties of fungal spores using functionalized AFM probes. *Biophys J.* 2000, 78(6), 3286-91.

5. Xie, L.; Wang, J.; Shi, C.; Cui, X.; Huang, J.; Zhang, H.; Liu, Q.; Liu, Q.; Zeng, H. Mapping the Nanoscale Heterogeneity of Surface Hydrophobicity on the Sphalerite Mineral. *J. Phys. Chem. C* 2017, 121, 5620–5628.

6. Acharya, H.; Vembanur, S.; Jamadagni, S.N.; Garde, S. Mapping hydrophobicity at the nanoscale: Applications to heterogeneous surfaces and proteins. *Faraday Discuss*., 2010,146, 353-365

7. Babel, B.; Rudolph, M. Characterizing mineral wettabilities on a microscale by colloidal probe atomic force microscopy. *Miner. Eng*. 2018, 121, 212–219.

8. Obrien, W.J.; Hermann, J.J. Strength of liquid bridges between dissimilar materials. *J. Adhes*. 1973, 5, 91–103.

9. Israelachvili, J.N. Intermolecular and Surface Forces, 2nd Edition, Academic Press, London (1991).

10. Riedo, E., Levy, F.; Brune, H. *Phys. Rev. Lett*. 2002, 88, 185505

11.http://nanoprobes.aist-nt.com/index.php?main_page=index&cPath=68_127_135 (accessed 25-06-2022).

12. Bernard, P.S.; Liu, H. Ion-beam-sputter deposited titanium nitride thin films for conductive atomic forcé microscope probes. *Thin Solid Films* 2013, 529, 317-321.

13. Shevyakov, V. ; Lemeshko, S. ; Roschin, V. Conductive SPM probes of base Ti or W refractory compounds, *Nanotechnology* 1998, 9, 352-355.

14. Thermal Atomic Layer Etching of Titanium Nitride Using Sequential, Self-Limiting Reactions: Oxidation to TiO2 and Fluorination to Volatile TiF4. Lee, Y.; George, S.M. *Chem. Mater*. 2017, 29, 8202−8210.

15. Goya, S.; Murai, S.; Tanaka, K. Thermal oxidation of TiN nanocylinder arrays: effects of insulator coatings by atomic layer deposition. *Opt. Mater. Express* 2019, 9(12), 4751-4764.

16. Milošv, I.; Strehblow, H.; Navinšek, B.; Metikoš-huković, M. *Surf. Coat. Technol*. 1995, 74-75, 897-902.

17. Milošv, I.; Strehblow, H.-H.; Navinšek, B.; Metikoš-Huković, M.. Electrochemical and thermal oxidation of TiN coatings studied by XPS. *Surf. Interface Anal*., 23, 529-539

18. Wang, R.; Hashimoto, K.; Fujishima, A.; Shimohigoshi, M.; Watanabe, T. Light-induced amphiphilic surfaces. *Nature* 1997, 388, 431–432.

19. Wen, L.; Tian, Y., Jiang, J. Bioinspired super-wettability from fundamental research to practical applications. *Angew Chem Int Ed Engl,* 2015, 9;54(11), 3387-99.

20. Banerjee, S.; Dionysiou, D.D.; Pillai, S.C. Self-cleaning applications of TiO2 by photo-induced hydrophilicity and photocatalysis. *Appl. Catal. B: Environ*. 2015, 176–177, 396-428.

21. Guckenberger, D. J., Berthier, E., Young, E. W., & Beebe, D. J. Induced hydrophobic recovery of oxygen plasma-treated surfaces. *Lab Chip*. 2012, 7; 12(13), 2317–2321.

22. Teisala, H.; Tuominen, M.; Stepien, M.; Haapanen, J.; Mäkelä, J.M.; Saarinen, J.J.; Toivakka, M.; Kuusipalo, J. Wettability conversion on the liquid flame spray generated superhydrophobic TiO2 nanoparticle coating on paper and board by photocatalytic decomposition of spontaneously accumulated carbonaceous overlayer. *Cellulose* 2013, 20, 391–408.

23. Teisala, H.; Tuominen, M.; Haapanen, J.; Aromaa, M.; Stepien, M.; Mäkelä, J.M.; Saarinen, J.J.; Toivakka, M.; Kuusipalo, J. Review on Liquid Flame Spray in paper converting: Multifunctional superhydrophobic nanoparticle coatings. *Nord. Pulp Pap. Res. J.,* 29(4), 747-759.

24. Flater, E.E.; Zacharakis-Jutz,G.E.; White, D.B.G.; Clifford, C.A. Towards easy and reliable AFM tip shape determination using blind tip reconstruction. *Ultramicroscopy* 2014, 146, 130-143.

25. Xu, L.; Guo, Q.; Qian, S.; Wu, S. Self-Adaptive Grinding for Blind Tip Reconstruction of AFM Diamond Probe. *Nami Jishu yu Jingmi Gongcheng/Nanotechnol. Precis. Eng.* 2018, 1, 150-155.

26. Force Calibration Cantilevers, Bruker Support Note 013-000-000, https://www.bruker-afmprobes.com/images/product/specPDF/3242.pdf)

27. Ievlev, A.V., Brown,C .; Burch, M.J., Agar, Velarde, J.C.; Martin, G.A.; Maksymovych, L.W.; Kalinin, P.; Sergei, V.; Olga, S. Chemical Phenomena of Atomic Force Microscopy Scanning. *Anal. Chem*. 2018, 90, 3475−3481.

28. M. Rosenberg. Microbial adhesion to hydrocarbons: Twenty-five years of doing MATH. *FEMS Microbiol. Lett*. 2006, 262, 129–134.

29. Chen, L.; Gu, X.; Fasolka, M.J.; Martin, J.W.; Nguyen, T. Effects of Humidity and Sample Surface Free Energy on AFM Probe−Sample Interactions and Lateral Force Microscopy Image Contrast. *Langmuir* 2009, 25, 6, 3494–3503.

30. Méndez-Vilas, A.; Jódar-Reyes, A.B.; González-Martín, M.L. Ultrasmall liquid droplets on solid surfaces: production, imaging, and relevance for current wetting research. *Small* 2009, 5,1366–1390.

31. D. Passeri, A.; Bettuccia, M.; Germano, M.; Rossi, M.; Alippi, A. Effect of tip geometry on local indentation modulus measurement via atomic force acoustic microscopy technique. *Rev. Sci. Instrum*. 2005, 76, 093904.

32. Liu, J.; Notbohm, J.K.; Carpick, R.W.; Turner, K.T. Method for Characterizing Nanoscale Wear of Atomic Force Microscope Tips. *ACS Nano* 2010, 4, 3763–3772.