Wetting Behavior of Zirconia nanotubes

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In this work, we investigate the wettability of ZrO₂ nanotubes (ZrNT) synthesized via electrochemical anodization of Zirconium. The ZrNT surface shows super-hydrophilic behavior while the octadecylphosphonic acid (C₁₈H₃₇PO(OH)₂) modified surface shows super-hydrophobic behavior. We demonstrate that the wetting properties are independent of ZrO₂ nanotube geometry and length.

Electrochemical anodization is a facile technique used to fabricate highly ordered structures in the sub-micron range. Several metals have successfully demonstrated self-organized porous nanostructure growth under appropriate anodization parameters.[1] Fluoride rich electrolytes contributed a significant advancement to the field, enabling the synthesis of high-aspect ratio nanostructured arrays on 'valve metals' such as zirconia.[2],[3],[4] Tuneable surface properties can exploit applications that are surface-interaction dependent, such as e.g. catalysis, filtration or coatings.[5],[6],[7][22] Zirconia is a biocompatible, high band-gap material that has reportedly demonstrated superior surface properties for the enhanced attachment of molecules.[8],[9],[10] It is used in biomedical devices, sensors and more recently for photocatalytic applications.[11],[12] With this intent, ZrNT surfaces are modified by a monolayer of octadecylphosphonic acid rendering it super-hydrophobic.[13] Wang et al. previously investigated the pristine ZrNT surface wettability, observing highly hydrophilic properties.[14] In the present study, we synthesize ZrO₂ nanotubular structures in a single step anodization process without the pre-requisite dip-etching process using HF-acid based etchants. This one-pot synthesis allows for less hazardous and safer working conditions. Further, we investigate the influence of nanotube-geometry on the extent of super-hydrophobicity. Zr foils (99.2 % purity, Goodfellow UK, 0.125mm thickness) were ultrasonically cleaned in acetone, methanol and ethanol followed by rinsing in deionized water and dried under a nitrogen stream. Electrochemical anodization was carried out using a high-voltage potentiostat (Jaisle IMP 88-200 PC) in electrochemical cells with a working area of 1cm² and larger cross-sections were fabricated via dip-anodization in an electrochemical bath-type setup. In both cases, a platinum counter electrode was used in a two-electrode setup. Anodization was carried out in a standard glycerol-based electrolyte consisting of 30% formamide, 2wt% NH₄F (Merck) and 2wt% H₂O under various conditions to obtain the respective morphologies. 20nm wide-tubes were synthesized via-dip anodization at 30V for 45 minutes without ramping and 40nm wide-tubes, with ramping the potential at 1Vs⁻¹ from OCP and kept at 50V for 2h. Thick-

walled ~ 100nm wide tubes (inner wall 'd' ~ 80nm, wall-thickness 't' ~ 20nm) were synthesized at 50V for 30min without ramping, with the difference of 4wt% distilled water in the electrolyte. Thin-walled ZrNTs (~ 100nm wide, 't'~ 3nm) were achieved in 30min at 90V (ramp 1Vs⁻¹). The tube length was varied from 3 to 9µm by adjusting the anodization time. Zr (and Ti) compact oxide (CO) films were prepared on Zr (and Ti) foils under a constant potential of 30V for 30min in a 1M H₂SO₄ (Merck) electrolyte. As anodized samples were rinsed with ethanol and distilled water and dried with nitrogen. To impart surface hydrophobicity, samples were placed in solutions containing 10mM octadecylphosphonic acid (OPA, C₁₈H₃₇PO(OH)₂) in tetrahydrofuran (THF, Roth) for a period of 24h at ambient conditions, forming self-assembled monolayers (SAMs). Further, the samples were rinsed in pure THF for 30s and dried under a filtered nitrogen stream. Scanning electron microscopy (Hitachi SEM FE 4800) was employed for the structural and morphological characterization of the anodized zirconia specimens. For chemical characterization, surface modification with OPA was evaluated using a ToF-SIMS V instrument (ION-TOF, Münster) and coverage was evaluated via XPS (Perkin-Elmer Physical Electronics 5600). Static water contact angle (WCA) measurements were performed using a Leica Suite Application and for ZrNTs with d ≤ 20 nm * using an Ossila-Contact Angle Goniometer (DI water droplet volume, 10µl) to determine wetting behavior. Figure.1(a), shows a zirconia substrate with a native oxide film (as received condition), having a hydrophilic WCA of (~30°) owing to surface hydroxyl groups.[15],[16] All porous samples depicted here showed superhydrophilic behaviour due to the improved oxide quality and enhanced liquid the improved oxide quality and enhanced liquid impregnation when compared to the native oxide surfaces. The water droplets spread entirely, covering the pores, an example is shown in Figure.1(b), in agreement to literature.[14]

Figure.1: Optical images of water droplet on ZrO₂ surface. (a) Native oxide (b) bare ZrNTs (c) ZrNTs after attaching OPA SAM. Inset shows SEM top and cross-section of ~100nm ZrNTs.

After surface modification with a monolayer of octadecylphosphonic acid, the nanotubes become super-hydrophobic as shown in Figure.1(c). In Figure.2, the coverage of ZrO₂ and TiO₂ compact oxides with long chain aliphatic molecules with various functional groups was determined using XPS. OPA showed the highest adhesion to

both oxides, followed by octadecyl-trimethoxysilane. Both molecules form denser layers on ZrO₂, as reflected by the enhanced coverage. Stearic acid and octadecylamine yielded significantly lower surface coverages, showing a slightly enhanced adsorption to TiO₂. Phosphonic acid-based SAMs consequently offer the highest potential for the formation of superhydrophobic coatings on both ZrO₂ and TiO₂ among the investigated functional groups. ToF-SIMS measurements were performed to evaluate the OPA-attachment and the resulting spectra in Figure.3 confirm the presence of the phosphonic acid on ZrNT via the detection of the characteristic quasi-molecular signal of OPA ($m/z=333.29$, C₁₈H₃₈PO₃⁻, M-H⁻) in accordance to reported literature.[10],[17],[18]

Figure.2: Adsorption of organic molecules to ZrO₂ and TiO₂ substrates – C1s and substrate signals measured using XPS for 18-C carbohydrate molecules with different anchoring groups (OPA- octadecylphosphonic acid, ODMS – octadecyltrimethoxysilane, ODA – stearic acid, ODAM – octadecylamine).

Figure 3. ToF-SIMS spectra of ZrNTs before and after coverage with octadecylphosphonic acid SAMs; (a) Zr⁺ isotopic pattern; (b) OPA-H⁻ molecular signal.

Figure.4 (a) depicts the morphology of ZrNT ($d \leq 20\text{nm}$), and the WCA* ($162^\circ \pm 1^\circ$). This is the currently smallest reported ZrNT diameter achieved via a single-step anodization. When functionalized with a SAM, it reports a superhydrophobic WCA. Moreover, in Figure.4 the WCAs on zirconia test surfaces with larger pore configurations: 'd' nm ~ 40, ~100nm- thick and thin-walled NTs and CO, (b, c, and d) reveal that changing the porosity (difference in surface area made up of the solid), did not affect the extent of hydrophobicity, thereby maintaining a nearly constant WCA of ($160^\circ \pm 1^\circ$) on the respective nanotubular surfaces. The only difference appeared when comparing ZrNTs to a ZrCO surface, for which a WCA of 120° (Figure.4(e)) was recorded. It may be noted that the Zr-substrates have poor conductivity resulting in challenges such as excessive charging and lower focusing abilities while performing SEM characterization. Images shown in Figure 4 have uniform scale-bars (SEM - 500 nm and WCA - 1 mm). Table.1

summarizes the influence of these pore geometries on WCAs. In Figure.5, WCA measurements were performed on OPA modified ZrNT of varying lengths to evaluate the influence of tube length on the wettability, yielding no statistical changes in dependence of tube length. A uniform nanoporous array is a homogenous surface with an increased roughness factor when compared to a 'flat' surface and hence in Figure.1(a,b), the transition from hydrophilic to super-hydrophilic state is well accommodated by the Wenzel approach.[19] This phenomenon is represented as an enhanced wetting process that occurs as a result of liquid-solid interaction in the absence of air resistance. After successful surface modification with OPA (Figure.1(c)), the methyl-terminated SAM surface is strongly water-repellent. This results in some cases where the water droplets continue to bounce of the surface and if they do adhere, they form high WCAs ($\geq 150^\circ$). The super-hydrophobic state is stabilized and explained by the Cassie-Baxter model (CBM) as a result of a greater interaction with trapped air in-between the liquid-solid layers.[20] As represented in Figure.4(a-d), the average WCAs measured were ($\sim 160^\circ$) for the ZrNT surfaces. The WCA values (θ^*) can be expressed according to the Cassie-Baxter equation

$$\cos(\theta^*) = f^* \cos(\theta) - (1 - f^*) \quad (1)$$

where, (θ) is the WCA measured on the SAM modified flat zirconia surface, ' f^* ' is a morphological factor and is defined as the area fraction of solid-liquid contact and ($1 - f^*$) is the area fraction of air-liquid interface. These surface fractions were calculated from high resolution SEM images as represented in Figure.4, by estimating the ratio between pore walls to the total area respectively and complemented with ImageJ analysis. The morphological factor ' f^* ' for values represented in Table.1 was calculated to be 0.020, 0.047, 0.131, 0.052 for ('d' nm = 20, 40, 100- thick-walled and thin-walled) ZrNTs, respectively. Recently, it was reported that the wettability of titania nanotubes is dependent on tube diameter and the observations were perfectly supported by Eq.(1) as proposed by the CBM.[21] For this result to hold true in the case of zirconia, the dimensionless factor ' f^* ' in Equation 1 is represented as the ratio between the 'projected area' to the 'total area' where, the projected area P is

$$P = 2 \pi r \epsilon \quad (2)$$

where, ' ϵ ' denotes the wall thickness, while ' r ' is the radius of the pore. The newly calculated morphological factor ' f^* ' using Eq. (2) for values represented in Table.1 was calculated to be 0.015, 0.048, 0.079, 0.066 for ('d' nm= 20, 40, 100-thick-walled and thin-walled) ZrNTs, respectively, indicating that the thin-walled NTs are more densely packed than the thick walled. Theoretical values continue to be greater than experimentally measured WCAs for all three morphologies. The experimental values are identical on all substrates, averaging at a value of ($\sim 160^\circ$). This value is at the physical limit of experimental measurements for low-energy surfaces and, hence, acts as a limiting criterion while quantifying the 'extent' of an already super-hydrophobic surface.[21]

Figure.4: Optical images of water droplets on SAM modified ZnNT structures of different porosity and corresponding SEM images of the surfaces. Diameters, a) $d \leq 20\text{nm}$ (measured on an Ossila goniometer), b) $d = 40\text{nm}$, c) thick walled $d = 100\text{nm}$, d) thin walled $d = 100\text{nm}$ and e) compact anodic oxide.

This essentially means that the surfaces measured experimentally may indeed have higher WCA values that are in reality closer to the theoretical calculations. Additionally, the proposed modification to CBM accounts for the super-hydrophobic phenomenon exhibited by ZnNTs irrespective of pore-diameter, because the ' f ' factor is comparable due to the type of packing exhibited by all three substrates. Implying that for a droplet of fixed volume, the drop-contact line interacts with similar solid fractions. Thus, superhydrophobicity observed for ZnNTs even at smaller pore-diameters is consistent with the constant WCAs reported for titania (increasing diameters will increase surface hydrophobicity).^[21] Nevertheless, the droplet always remains balanced in CBM.^{[19],[20]} There appear a few variations in theory and experimental and may be

attributed to the physical limits of experimental measurement as described earlier.

Table.1: Influence of pore-diameter of ZnNTs on WCAs, measured and calculated values (according to Cassie-Baxter model and the proposed modification to it)

Pore Diameter (nm)	Experiment	Water Contact Angle (°) - Cassie-Baxter Model	
		Theoretical	Proposed-theoretical
~ 20	162 ± 1	172	173
~ 40	159 ± 2	168	167
Thick-wall (~ 100)	160 ± 1	159	164
Thin-wall (~ 100)	160 ± 1	167	165
Compact Oxide	120 ± 2		

In comparison to previous reports by Wang et al.,^[14] this is the first reported observation of superhydrophobic WCA on functionalized ZnNT for ($d \leq 20\text{nm}$) produced via a single-step anodization. Additionally, the WCA of ZnNTs is also independent of length.

Figure.5: Optical images of water droplets on SAM modified ZnNT structures of different oxide-layer thickness and corresponding SEM images of the cross-sections. length a) $\sim 3\mu\text{m}$, b) $\sim 4.5\mu\text{m}$ and c) $\sim 9\mu\text{m}$.

In conclusion, the nanoporous ZrO_2 layers produced via anodization show a transition from super-hydrophilic to super-hydrophobic surfaces when modified with a (non-fluorinated) octadecyl phosphonic acid monolayer. Within the investigated range, WCAs remain constantly super-hydrophobic ($\sim 160^\circ$), irrespective of the change in pore diameters and length, thereby following the Cassie-Baxter model. By including the influence of a geometric parameter accommodating the wall thickness, the roughness factor is balanced and continues to remain within the transition threshold of the super-hydrophobic state. Such an observation is of importance as it offers insights into material behavior and is responsible for enhanced degrees of freedom during the fabrication process, such that both simple and complex geometries may still be able to elicit identical surface response. This level of flexibility offers the possibility to work with wider operating parameters involving the anodization process.

SNVR- Conceptualization, Data curation, Methodology, Investigation, Writing- original draft. MSK- Conceptualization, Funding acquisition, Project

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There are no conflicts to declare

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