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Fine-tuning of surface properties of dual-size TiO_2 nanoparticle coatings

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ABSTRACT

In this work, we focus on wetting and morphology properties of fluoroalkylsilane modified TiO_2 (FAS-TiO_2) and as-received TiO_2 nanoparticle coatings. TiO_2 nanoparticles of two sizes (30 nm and 300 nm) were spin coated onto steel substrate covered with 300 nm layer of epoxy via layer-by-layer (LbL) deposition until the desired wetting characteristics were achieved. Static water contact angles, advancing and receding contact angles and contact angle hysteresis were measured to evaluate the wetting properties of FAS-TiO_2 and as-received TiO_2 nanoparticle coatings. The morphology of coatings was analyzed with average surface roughness (S_a) measurements and SEM imaging. We have presented a simple step-like procedure to fabricate TiO_2 nanoparticle coatings with target wetting properties, either (super)hydrophobic or (super)hydrophilic. Order of the LbL deposition of dual-size nanoparticles for the fabrication of superhydrophobic/superhydrophilic coatings was found to be an important factor influencing on surface roughness and hence wettability. SEM images revealed a typical morphology and S_a difference between FAS-TiO_2 and as-received TiO_2 nanoparticle coatings reflected in the discrepancy of the average size of the agglomerates that are coating the substrate. Based on these results we can fine-tune the surface roughness and wettability by controlling the LbL deposition of dual-size FAS-TiO_2 and as-received TiO_2 nanoparticles.

1. Introduction

Manipulation of surface wettability of solid surfaces and manufacture of coatings with either water repellent (hydrophobic) or water attractive (hydrophillic) properties have been widely studied over the past two decades [1–7]. Superhydrophobic and superhydrophilic surfaces are still the most popular challenges in wetting studies for several everyday applications including self-cleaning and antifogging materials [7,8].

Superhydrophobic surface is characterized with a water contact angle larger than 150°. We have learned from nature (i.e. Lotus leaf effect) that to fabricate a superhydrophobic surface, a combination of low surface energy chemistry in combination with appropriate surface roughness is needed [9]. For this purpose, low surface energy functional group, i.e. $-CF_3$, is used together with multiscale (micro and nano) roughness structure [3,10,11]. Various methods have been reported to fabricate superhydrophobic surfaces such as spin coating [3,12], layer-by-layer deposition [13], dip-coating [14], spray-coating [15,16], etc.

Superhydrophilicity was first introduced not >15 years ago, just after the burst out of research on superhydrophobic surfaces [17]. Superhydrophilic surface is characterized with the water contact angle less than 5° or the tendency of the water to spontaneously spread over the surface. Superhydrophilic surface can be fabricated either by deposition of a molecular or microscopic film more hydrophilic than the substrate or by modification of the surface chemistry through oxidation [6]. Plasma, flame or corona treatment are the most well-known methods which create hydrophilic, polar groups, such as hydroxyl, peroxy, carbonyl, etc. on the surface [18,19]. However, it is not only about the surface chemistry, surface roughness is a necessary feature also for achieving superhydrophilicity in the same way as for superhydrophobicity [6,8]. The principle of these phenomena was found by Wenzel, Cassie and Baxter who described different wetting mechanisms on rough surfaces [20,21].

Recently, research has been focused mostly on fabrication of multifunctional superhydrophobic coatings for water-repellent and self-cleaning applications, based on multiscale roughness structures formed by various nanoparticles, i.e. silica, TiO_2, ZnO, CuO, etc. [2,22–24]. Superhydrophilic surfaces on the other hand are mostly attractive for ultrafast drying with special properties such as antifogging or evaporative cooling [7]. Considerable research has been done on photoinduced superhydrophilicity of TiO_2 thin films becoming highly hydrophilic under UV-light irradiation [25,26]. Researchers focus on improvement of these properties by combining with silica particles, doping with noble metals or transition metals [27]. A step forward presents fabrication of smart coatings combining superhydrophobic and superhydrophilic abilities or surfaces with stimuli reversible wettability, patterning wettability and gradient wetting [2].

Here we report on the systematic study of the qualitative correlation between surface roughness generated by the LbL deposition of dual-size fluorosilane modified TiO_2 (FAS-TiO_2) and as-received

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Table 1
Comparison of static water contact angles (θ^W) and average surface roughness (S_a) of dual-size double-layer FAS-TiO_2 and as-received TiO_2 nanoparticles. Diamond polished AISI 316L and AISI 316L coated with 300 nm layer of epoxy (AISI + E) were used as a reference.

	Contact angle	Roughness	Contact angle	Roughness
	FAS-TiO_2		TiO_2	
Substrate	θ^W [deg]	S_a [nm]	θ^W [deg]	[nm]
AISI	57,2	31,2	57,2	31,2
AISI + E	70,8	50,1	70,8	50,1
AISI + E + 30 + 300	125,0	219,9	80,6	84,4
AISI + E + 300 + 30	116,7	173,7	79,7	92,2

TiO_2 nanoparticles (30 nm and 300 nm), and resulting (super)hydrophobicity or (super)hydrophilicity of the coatings. We analyze the wetting properties of the fabricated coatings and their morphology. In addition, we point out the importance of the order of the LbL deposition of dual-size nanoparticles for the fabrication of superhydrophobic/superhydrophilic coatings in view of surface roughness and hence wettability. We show that controlled LbL deposition of FAS-TiO_2 and as-received TiO_2 nanoparticles via simple spin-coating method offers the possibility to fine-tune the surface roughness and wettability.

These findings serve as an excellent base for our further studies in progress, as TiO_2 nanoparticles were chosen for their widespread use in antimicrobial coatings and our general priority is to study the antimicrobic effect on hydrophobic/hydrophilic surfaces.

2. Materials and methods

2.1. Materials

Epoxy resin (Epikote 816, Momentive Specialty Chemicals B.V.) was mixed with a hardener Epikure F205 (Momentive Specialty Chemicals B.V.) in the ratio % wt 100: 53. TiO_2 nanoparticles with mean diameters of 30 nm (anatase) were provided by Cinkarna Celje, whereas 300 nm (rutile) by US Research Nanomaterials, Inc.

Austenitic stainless steel AISI 316L (17% Cr, 10% Ni, 2.1% Mo, 1.4% Mn, 0.38% Si, 0.041% P, 0.021% C, <0.005% S in mass fraction) was used as a substrate.

2.2. Surface functionalization

For hydrophobic effect, TiO_2 particles were functionalized in 1 vol% ethanolic fluoroalkylsilane or FAS17 ($C_{16}H_{19}F_{17}O_3Si$) solution.

2.3. Steel substrate preparation

The steel sheet with a thickness of 1.5 mm was cut into discs of 25 mm diameter. Prior to the application of the coating, the steel discs were diamond polished following a standard mechanical procedure and then cleaned with ethanol in ultrasonic bath.

2.4. Coating preparation

Prior to TiO_2 nanoparticles adsorption, diamond polished AISI 316 L substrate was spin-coated with 300-nm layer of epoxy (as determined by ellipsometry) [28] and then cured for 1 h at 70 °C and post-cured at 150 °C for another hour. We have decided for a thin base epoxy layer to improve TiO_2 nanoparticles adhesion as the oxide layer growing on the surface of clean AISI 316L substrate prevents adhesion and is very difficult to remove. In this way we were able to synthesize stable TiO_2 nanoparticle coatings which is mostly important for our further studies on corrosion protection, biocompatibility and antimicrobial properties.

The nanoparticles were coated onto AISI 316L + epoxy (AISI + E) surface by spin-coating 20 μl of 3 wt% TiO_2 nanoparticle ethanolic solution. We then started with the preparation of dual-size dual layer coatings consisting of 30 nm and 300 nm FAS-TiO_2 nanoparticles. On the AISI + E surface we first spin-coated 30 nm FAS-TiO_2 nanoparticles, followed by spin-coating 300 nm FAS-TiO_2 nanoparticles resulting in AISI + E + 30 + 300 coating. In the same manner, by first spin-coating 300 nm FAS-TiO_2 nanoparticles followed by spin-coating 30 nm FAS-TiO_2 nanoparticles, we prepared the coating consisting of the reversed sequence of FAS-TiO_2 nanoparticles, AISI + E + 300 + 30. Prior to further analysis, both coatings were dried in an oven for approximately 20 min at 100 °C.

According to the results we focused on the further analysis of AISI + E + 30 + 300 coating and continued with spin-coating the sample with additional layer of 30 nm FAS-TiO_2 nanoparticles (AISI + E + 30 + 300 + 30) and then drying in an oven. We followed by adding 300 nm FAS-TiO_2 nanoparticles on the top (AISI + E + 30 + 300 + 30 + 300) and then drying in an oven. In the same manner we spin-coated one more layer of 30 nm and one more layer of 300 nm FAS-TiO_2 nanoparticles (AISI + E + 30 + 300 + 30 + 300 + 30 + 300).

The same procedures were repeated for the preparation of coatings with as received, non-functionalized TiO_2 nanoparticles.

2.5. Scanning electron microscopy (SEM)

SEM analysis using FE-SEM Zeiss SUPRA 35VP was employed to investigate the morphology of the TiO_2 coatings' surfaces which were sputtered with gold prior to imaging.

2.6. Contact-angle measurements

The static and dynamic (advancing/receding) water contact angles on a clean AISI 316 L diamond polished sample, on the epoxy coated AISI 316L (AISI 316L + E) substrate and on a sequence of TiO_2 nanoparticles coated AISI 316L + E substrate were performed using an optical tensiometer Attension Theta (Biolin Scientific). For static water contact-angle measurements, liquid drops of 5 μl were deposited on different spots of the substrates to avoid the influence of roughness and gravity on the shape of the drop. The drop contour was analyzed from the image of the deposited liquid drop on the surface with the Attension software and the contact angle was determined by using Young-Laplace fitting. To minimize the errors due to roughness and heterogeneity, the average values of the contact angles of the drop were calculated approximately 20 s after the deposition from at least five measurements per sample.

Advancing/receding contact angles were measured on at least three different positions on each substrate. A 5 μl water droplet was placed on a horizontal substrate and then the substrate was tilted slowly till 90° at an angular speed of 1° s^{-1}. The development of the drop contour was again analyzed with Attension software via Young-Laplace fitting.

All the contact-angle measurements were carried out at 22 °C and ambient humidity.

Table 2
Surface properties of AISI 316L substrate when blended with pure epoxy and LbL FAS-TiO_2 nanoparticles. Static water contact angles (θ^W), advancing (θ_{ADV}) and receding (θ_{REC}) contact angles, contact angle hysteresis ($\Delta\theta = \theta_{ADV} - \theta_{REC}$) and the average surface roughness (S_a) are listed.

Substrate	θ^W [deg]	θ_{ADV} [deg]	θ_{REC} [deg]	$\Delta\theta$ [deg]	S_a [nm]
AISI + E + 30 + 300	124,4	124,8	103,2	21,6	219,9
AISI + E + 30 + 300 + 30	147,8	146,6	110,9	35,6	376,2
AISI + E + 30 + 300 + 30 + 300	160,9	165,0	106,7	58,3	489,6
AISI + E + 30 + 300 + 30 + 300 + 30	163,6	161,6	98,7	62,9	520,9
AISI + E + 30 + 300 + 30 + 300 + 30 + 300	162,4	162,0	99,2	62,8	618,4