

Supporting information

for

Self-assembled anchor layers/polysaccharide coatings on titanium surfaces: a study of functionalization and stability

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Additional Experimental Information

Table S1: Influence of the surface treatments on the surface concentration of titanium oxides, Al₂O₃, SiO₂ and hydroxyl groups as determined by peak fitting of the O 1s XPS spectra reported in Figure 2. The contributions are reported with respect to the total surface composition (Table 1).

Treatment	Total O1s	Ti oxides	Al ₂ O ₃	SiO ₂	Hydroxyls
	(atom %)				
Pristine	50.3	18.2	16.7	13.1	2.3
NH ₄ OH:H ₂ O ₂ :H ₂ O	59.0	50.0	–	–	9.0
NaOH	58.4	43.9	8.1	–	6.4
HCl/H ₂ SO ₄	58.6	47.0	5.4	–	6.2
H ₂ SO ₄ /H ₂ O ₂	55.5	44.7	–	2.2	8.7
Flat surface	56.7	48.9	–	–	7.9

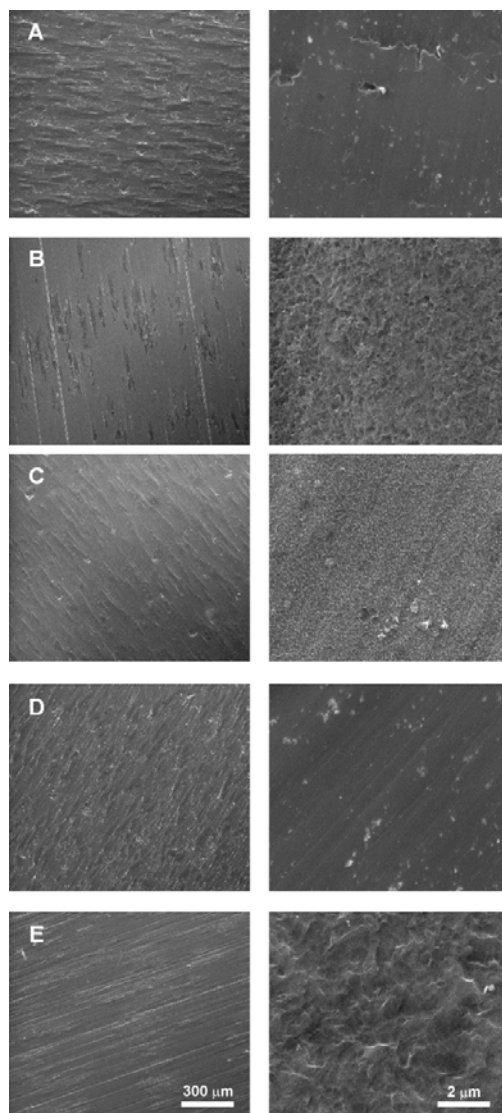


Figure S1: Scanning electron microscopy of pristine titanium surfaces (A) and surfaces treated using alkaline piranha (B), 0.5 M NaOH (C), mixture of concentrated acid (HCl and H₂SO₄) (D) and piranha (concentrated H₂SO₄ and 30% H₂O₂) (E). The scale bar for the left micrographs is 300 μm the right is 2 μm. All treated samples show uniform topography. While the treatment using a mixture of concentrated acids resulted in surfaces with unchanged surface morphology, the other activation treatments gave surfaces with increased microtexture. Such a microstructure has been reported to have an inherent ability to increase the rate of bone formation.

Table S2: Changes in root mean squared roughness (R_{RMS}) and root mean squared waviness (W_{RMS}) due to the surface treatments as determined by stylus profilometry. The resulting changes in surface wettability, that is, advancing (θ_{A}) and receding (θ_{R}) contact angle between the samples and water, were tested by the Wilhelmy plate method.

Treatment	R_{RMS} (nm)	W_{RMS} (nm)	θ_{A} ($^{\circ}$)	θ_{R} ($^{\circ}$)
Pristine	40 ± 10	330 ± 150	52	12
$\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$	140 ± 20	650 ± 180	3	^a
NaOH	50 ± 30	500 ± 230	27	13
HCl/ H_2SO_4	60 ± 20	610 ± 220	14	12
$\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$	190 ± 60	780 ± 200	15	^a

^aMissing values signify complete wetting during measurement of the receding water contact angle

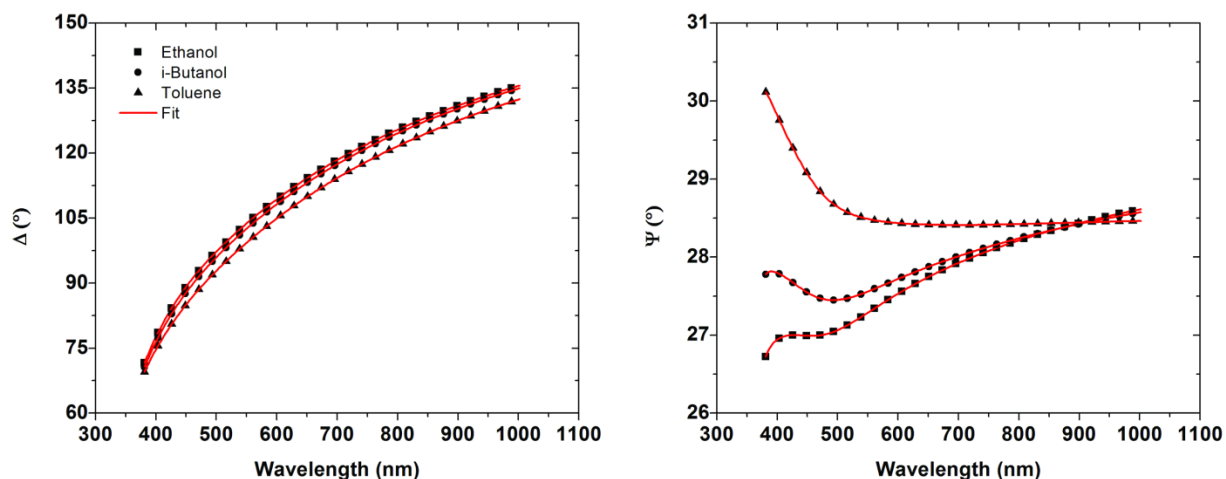


Figure S2: Multiple environment *in situ* spectroscopic ellipsometry. Δ and Ψ ellipsometric spectra of neat titanium surfaces were measured in ethanol (■), isobutanol (●) and toluene (▲). The red lines represent the fitted data. The measured data of a neat titanium layer in different solvents was simultaneously fitted with the parameters of a Drude–Lorentz model (amplitude: 24.268 eV^2 , broadening: 1.648 eV) and two Lorentz oscillator functions ($E_1 = 2.808 \text{ eV}$ with amplitude: 5.191 eV^2 , broadening: 1.585 eV ; $E_2 = 2.998 \text{ eV}$ with amplitude: 28.077 eV^2 , broadening: 1.585 eV).

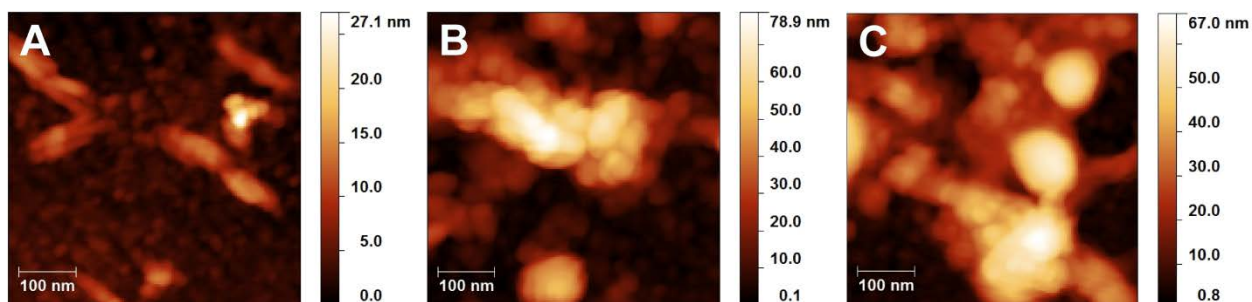


Figure S3: AFM images of ALG films immobilized on neridronate (A), APTES (B) siloxane and PDA (C) anchor layers. The AFM measurements were performed on regions with pronounced topography arising from surface immobilized aggregates of alginate. The determined roughness of these films was in the range of 5–15 nm.

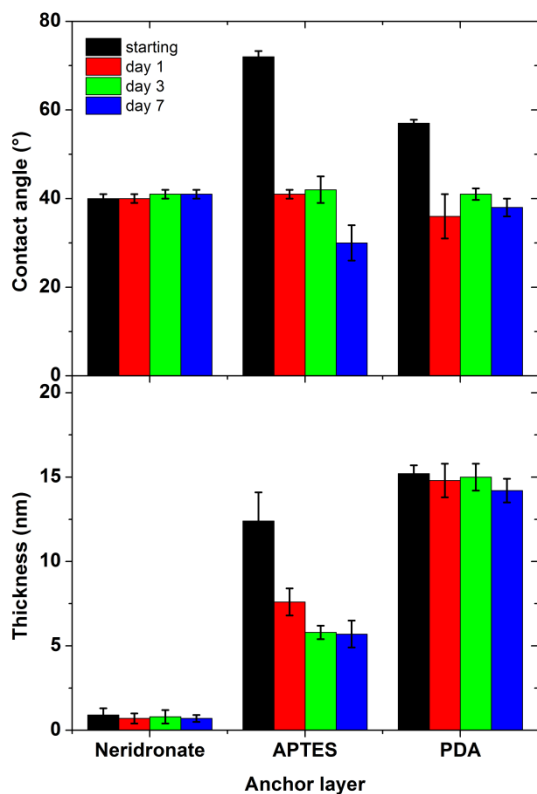


Figure S4: Ellipsometric thickness and water contact angle evolution of neridronate, APTES siloxane and PDA during the immersion in PBS (37 °C, pH = 7.4) (mean value \pm SD, n = 15). The pronounced decrease in thickness and water CA during the immersion indicate strong deterioration of the APTES siloxane layers. The changes in the water CA of PDA are most probably a result of structural reorganization.

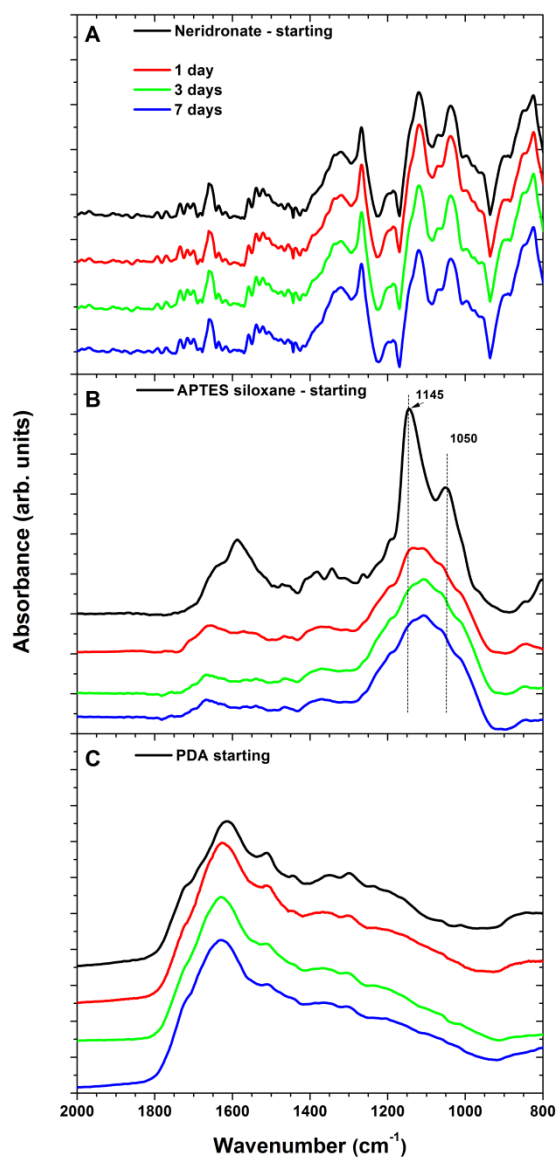


Figure S5: Evolution of IRRAS spectra of neridronate (A), APTES siloxane (B) and PDA (C) upon immersion in PBS at 37 °C for 7 days.