Supporting Information

Surface Wettability of 3-Aminopropyltriethoxysilane

Self-Assembled Monolayers

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1. Preparation of the APTES SAM

1.1 Pretreatment of Si (100) substrate surface

Si (100) chips (1 cm^2) were used as substrates, and were cleaned by sonication for 5 min each in acetone, chloroform and isopropanol. Si (100) chips were subsequently rinsed with excess water, sonicated for 5 min in water, and dried under a nitrogen gas stream. Cleaned substrates were then etched in hydrofluoric acid for 5 min, rinsed with water, and dried under a nitrogen gas stream. Etched substrates were oxidized in piranha solution (H_2SO_4 (98 %)/H_2O_2 (30 %), 70:30 (v/v)) at 90 ºC for 30 min, rinsed with water, and dried under a nitrogen gas stream. A completely hydroxylated SiO_2 layer with a uniform thickness of ≈2.7 nm measured by ellipsometry could then be formed on the substrate surface, such that a water contact angle less than 4° was obtained for the final surface.

1.2 Preparation of APTES SAM

The clean oxidized Si (100) substrate was immersed into freshly prepared 1×10^{-3} mol/L APTES-toluene at a strictly controlled temperature of 18.0 ± 0.1 ºC. Following surface modification, the substrate was withdrawn as quickly as possible, and immediately cleaned by sonication in toluene for 2 min, then rinsed in toluene, chloroform and isopropanol to remove any excess deposition, and finally dried under a nitrogen gas stream. Anhydrous toluene is hygroscopic, so the reaction was carried in a homemade airtight vessel to exclude atmospheric humidity.

1.3 Preparation of the phase-separated OTS/APTES mixed SAM

The clean oxidized Si (100) substrate was immersed into freshly prepared 1×10^{-3} mol/L OTS-toluene solution for 5 to 10 sec for the first phase reaction. After the first phase reaction, the substrate was quickly withdrawn from the solution and rinsed with abundant toluene to remove any excess deposits, then immediately dipped into freshly prepared 1×10^{-3}mol/L APTES-toluene solution for the second phase 30 min reaction. Following surface modification, the substrate was thoroughly rinsed in toluene,

chloroform and isopropanol, respectively, and finally dried under a nitrogen gas stream. All reaction was conducted in a homemade airtight vessels, and the reaction temperature was strictly controlled at 18.0 ± 0.1 ℃.

2. Characterization of the APTES SAM

2.1 The kinetic formation process of the APTES SAM investigated by contact angle measurements. Figure S1 represents the changes in the initial and static advancing contact angles on the sample surface with reaction time during the formation process of APTES SAM. Both the initial and static advancing contact angles increased gradually during the initial 30 min reaction, then the initial and static advancing contact angles reached the stable values of 50° and 45°, respectively. The changes in contact angles indicated that after about 30 min reaction, an APTES film with a stable structure was completely formed.
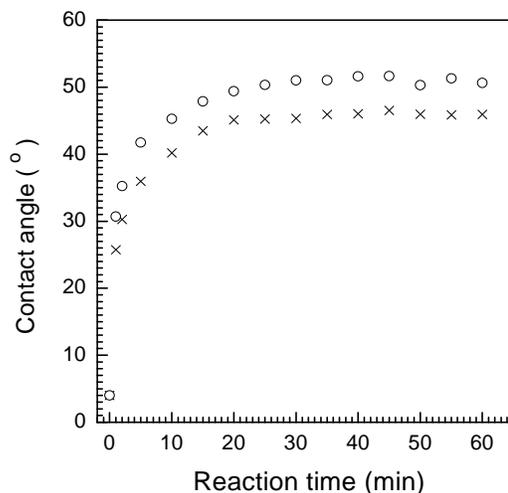

Figure S1. The changes in the initial and advancing contact angles with
reaction time during the formation process of APTES SAM.
○ - initial contact angle, × - static advancing contact angle

2.2 Film thickness. By means of ellipsometry, the thickness of the APTES film obtained in this work was 0.5 ± 0.1 nm, which was very close to the theoretical thickness of an APTES monomolecular layer.[1-4] Considering the film thickness was on the edge of the

possibilities of the ellipsometry method, as well as the possible error resulting from the use of the refractive index of bulk APTES, it was necessary to further confirm that the organic film we prepared was a monolayer. By means of the phase-separated mixed SAM technique,[5] the thickness of the APTES film was further determined indirectly by AFM. Figure S2 shows the surface topographic image of the phase-separated OTS/APTES mixed SAM captured by AFM. The separate island-shaped areas in Figure S2 are the OTS SAM pieces with a reaction time of ≈10 sec, and the other areas are the APTES film with a reaction time of 30 min. It is well-known that, the thickness of OTS SAM is about 2.5 nm,[6, 7] this height was used as the benchmark to evaluate the thickness of APTES film in the mixed OTS/APTES SAM sample. In terms of the bearing analysis offered by the AFM off-line software, the average height difference between the protuberant OTS SAM islands and the rest of the flat APTES film was about 1.9 nm. The thickness of the APTES film was ≈0.6nm, which was consistent with the film thickness measured by ellipsometry.
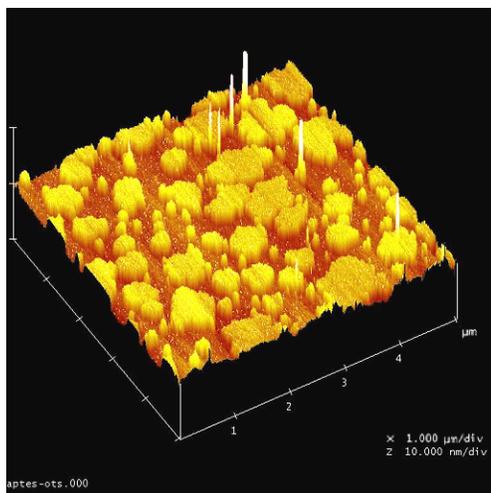

Figure S2. Topographic image of the phase-separated
OTS/APTES mixed SAM by AFM

2.3 XPS. Figure S3 shows the XPS survey spectra of an APTES-treated substrate with a reaction time of 30 min in this work. The peak at 286.2 eV was assigned to the carbon atom from the silane couple agent. A low intensity feature near 402.6 eV was found in the

spectrum, which was assigned to the nitrogen atom from the silane coupling agent. The C:N ratio of the obtained APTES SAM sample estimated by XPS was ≈6.1:1. The XPS result indicated that, the APTES molecules in the film were not fully hydrolyzed, with an average of only one to two ethoxyl groups hydrolyzed for each APTES molecule.
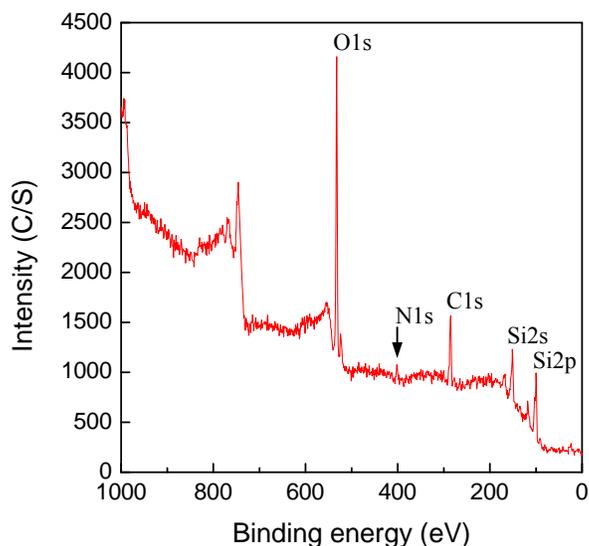

Figure S3. XPS survey spectra of APTES SAM

2.4 AFM. Figure S4 shows a typical AFM surface image of the APTES SAM sample with a reaction time of 30 min. The APTES SAM surface is rough and incompact. The calculated RMS surface roughness was ≈0.131 nm/2 μm × 2 μm.
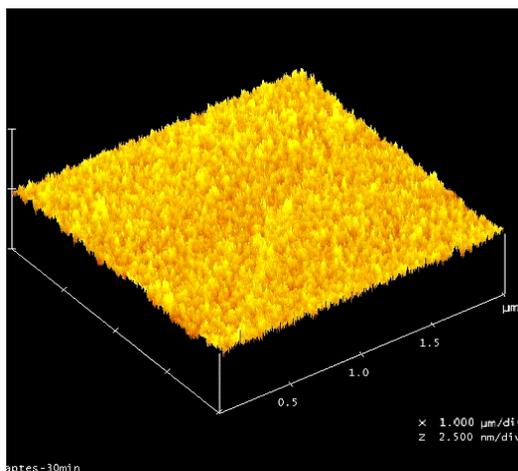

Figure S4 The AFM topographic image of an APTES
SAM sample with a reaction time of 30 min

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