Supporting Information

Tunable Geometry and Wettability of Organosilane Nanostructured Surfaces by Water Content

Experimental Section

Glass microscope slides (SAIL BRAND, China) of 25 mm× 76 mm×1 mm dimension were cut into a smaller size of 10 mm × 10 mm squares. Methyltrichlorosilane (Acros Organics) were handled under water-free conditions and used without further purification. Anhydrous toluene was used by the toluene distillation. Water-saturated toluene solution was the upper solution of a mixture of anhydrous toluene and deionized water, and then the solution was put aside for 2 days under normal temperature and pressure. Other reagents were used as received.

Initially, small glass substrates were ultrasonicaled for 30 min in a cleanser solution, rinsed with deionized water for several times, and dried in a clean oven at 120 °C for 20 min. Then the glass substrates were soaked in piranha solution (H_2SO_4 : H_2O_2 = 7: 3 by volume) at 50 °C for 2 h. After the piranha solution's activation, the substrates were ultrasonicaled for 10 min in deionized water to remove the remaining acid on the surfaces, and then dried in a clean oven at 120 °C for 20 min.

The activated substrates were used immediately for silanization reactions. All reactions were controlled at the humidity within the range of 40 ± 2 % and at normal temperatures and pressures, when the system water content and the silane concentration were varied. The representative reaction process of MTS-derived surfaces was prepared as follows. The substrates were immersed into several glass vials containing toluene (4 mL, different water content), and MTS was added immediately to the solvent with a calibrated pipettor at a specific volume. The glass vials were closed to the air during the reaction but exposed in the environment during the solution and silane introductions. 1 h later, the substrates underwent a series of rinsing with different solvents in the following sequence for several times: toluene, ethanol, ethanol: water (1:1), and water. Finally, the wafers were dried in an oven at 120 °C for 10 min.

The SEM images were taken on a field-emission scanning electron microscope at 3 kV (JSM-6700F, Japan). The contact angles were measured by a JC2000D machine (POWEREACH, China) at ambient temperature. CA values were obtained by measuring more than five different positions on the same sample.

The cross-section SEM images of the as-prepared surfaces



Fig. S1 The cross-section SEM images of the as-prepared surfaces. a) is the side view SEM image of nanoprotuberances generated under WT of 30%, c) is the side view SEM image of nanospheres generated under WT of 100%. b) and d) are the side view images at high magnification of a) and c), respectively; so nanoshperes and nanoprotuberances can be distinguished easily.

The mechanism of different surface structures reacted with different water content



Fig. S2 Possible mechanism of the reaction of Methyltrichlorosilanes with condition changes.

We know trifunctional organosilanes (RSiCl₃) are very reactive and are capable of polymerizing in the presence of water, which gives rise to a number of surfaces with different structures. In our experiment, add the MTS monomer to the toluene solution, a rough surface was obtained after the process of adsorption, hydrolysis and polymerization. The change of water content would lead to the change of hydrolysis rate, causing that the reaction to be different. With the increase of water content, MTS's hydrolysis accelerated, the trend of reaction was promoted to change from horizontal polymerization to vertical polymerization and the surface structure was changed (see above Fig. S2).