Supplementary Information.

1. Independence of EW operation parameters.

A series of test experiments were performed to demonstrate that the conclusions regarding charge trapping are independent of the operation conditions of the EW measurements. Figure S 1 demonstrates that the Asymmetry between positive and negative bias voltage does not depend on the rate at which the applied voltage is ramped up and down. The test was carried out with a triangular waveform with an amplitude of 40V at sweep frequencies ranging from 1-40mHz on Teflon AF samples that were previously aged in water at pH 6 for 2h. The experiments do not display any substantial variation within the parameter range explored.

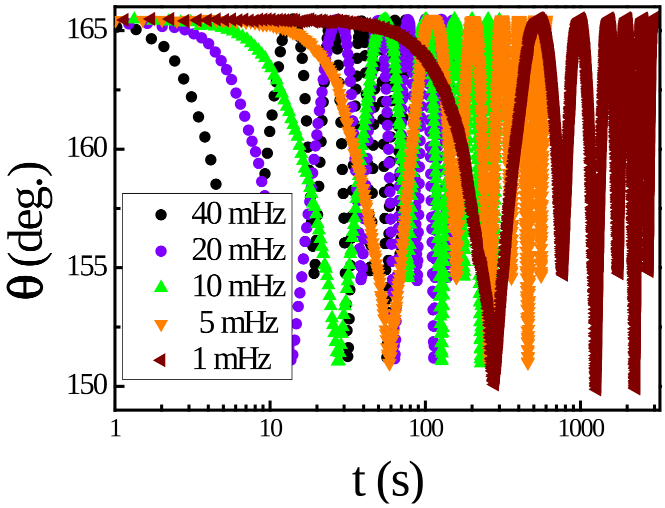

Figure S 1. EW response on Teflon AF for $t_w = 2h$ at pH 6 for sweep frequencies of 1-40 mHz.

Similarly, test experiments with variable amplitude of the voltage ramp do not display any effect on the asymmetry of the EW response curve. The same trapping voltage U_T is obtained for over a wide range of amplitudes, as shown in Figure S 2.

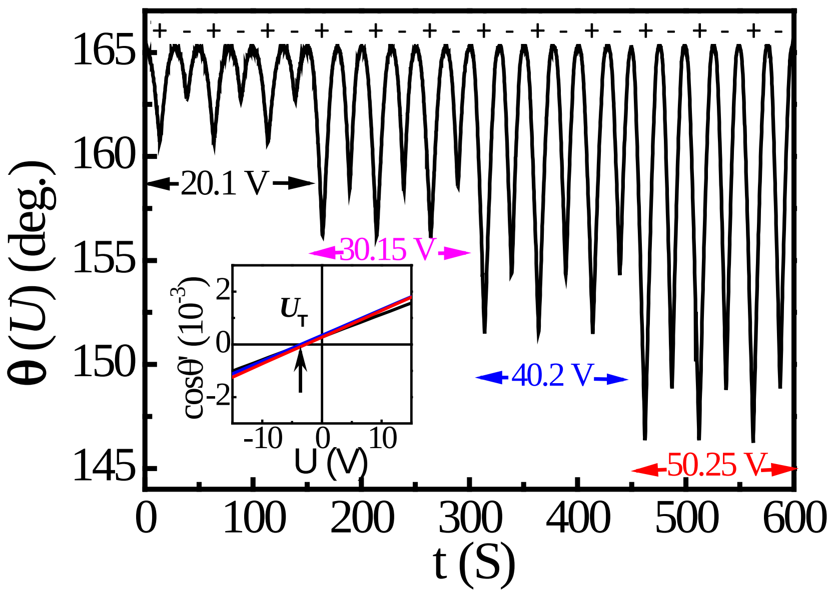

Figure S 2. EW response vs. time for variable amplitude of the applied voltage. from $\pm$ 20.1 to $\pm$ 50.25 V as indicated. Same type of samples as in Figure S 1. + and – signs indicate moments of maximum positive and negative bias voltage on the drop. Inset: $d\cos\theta\,/dU$ vs. U illustrates that U_T does not vary for variable amplitude.

2. Aging in humid atmosphere.

Figure S 3 shows the contact angle response of a pristine Teflon AF sample (a) and another one that was aged in humid air (ambient humidity ≈ 98%) for 36h.

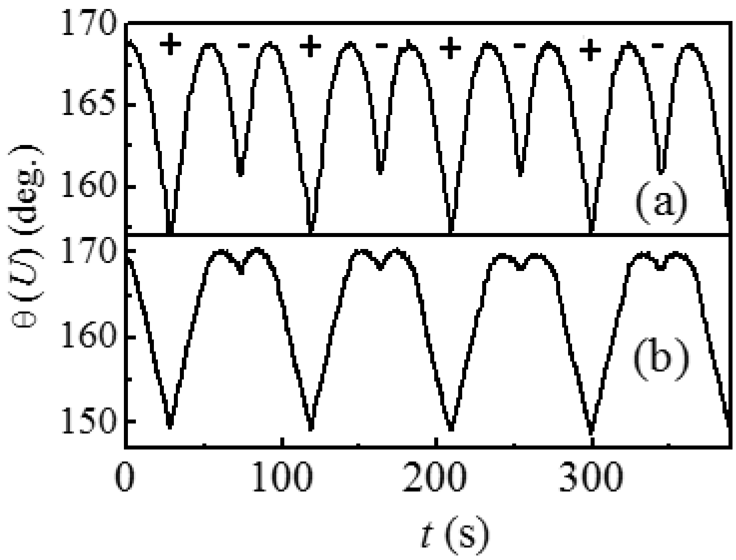

Figure S 3. EW response curve vs. time for Teflon AF. a) pristine surface. b) after $t_w = 36h$ in humid air. (voltage amplitude: 40V). + and – signs indicate moments of maximum positive and negative bias voltage on the drop.

3. Thermal annealing of water-aged Teflon AF films

The thermal stability of trapped charges on Teflon AF was tested by subsequent annealing of Teflon AF films at elevated temperature in a vacuum oven for 1h. Following the annealing step, the sample was cooled down in ambient atmosphere and loaded back into the oil-filled cuvette for characterization by EW. As shown in Figure S 4, the thermal annealing step did not affect the trapping voltage U_T in any appreciable manner. Apparently, the trapped charges are thus stable – at least for the short annealing time tested here – even at temperatures well above the glass transition temperature $T_g = 160°C$ of Teflon AF 1600.

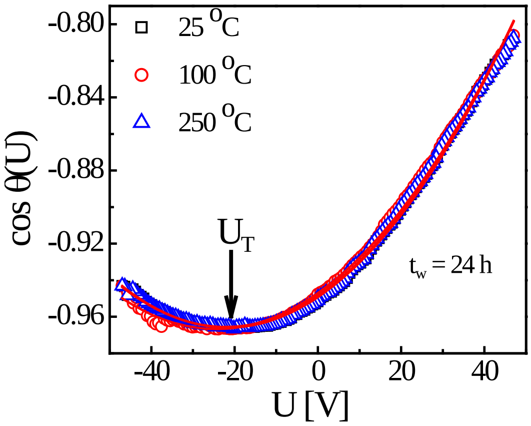

Figure S 4. EW response of a water-aged Teflon AF film after annealing for 1 hour at temperatures 25 °C (□), 100 °C (○) and 250 °C (△) in a vacuum oven.

4. Water-induced spontaneous nano-roughening of Teflon AF surfaces.

The roughness and morphology of Teflon AF samples were assessed by Atomic Force Microscopy in tapping mode in air (Icon, Bruker). For the measurements Scan Asyst-Air-HR probes are used (resonant frequency r_f=130 kHz, spring constant k=0.40 N/m, nominal tip radius <7 nm). Figure S 4a shows the taping-mode AFM height image of a Teflon AF surface in air, as prepared. The image is featureless, without any discernable spatial structure, with R_q = 0.27 nm. After aging in de-ionized water of pH 6 and 9, and the streaming potential experiment, the Teflon AF surface was imaged again with AFM in taping mode in air to check the surface topography changes. The topography images and height profiles show that surface is nanostructured. The observed surface structuration seems to correlate well with the values of the surface charge density as derived from the measured zeta potential of the surfaces using the Grahame equation (see Figure 10): the higher the value of the surface charge density, the larger is the effect of the aqueous phase on the structure of the Teflon AF surface. At pH 6 the height and width of these objects are ≈1.5 nm and 20 nm; at pH 9 ≈5 nm and 50 nm, respectively. Aging in water solution and/or high pressure during streaming potential lead hydroxyl ions to go closer to the interface. They originate an electric field which polarizes the Teflon AF surface, generating the rearrangement of the polymer surfaces. Similar patterns were observed by exposure of a Teflon AF film to degassed solutions.

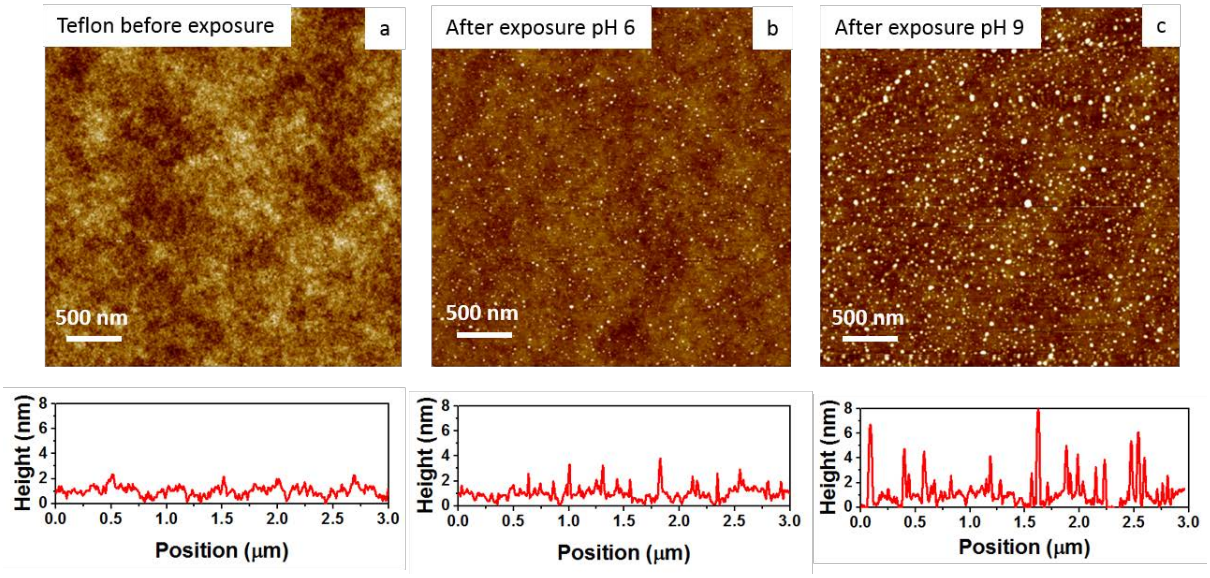

Figure S 5. AFM topography images of Teflon AF films in pristine state (a), after aging in ambient water at pH 6 b), and after aging at pH 9 (c).

5. **Independence of Water Salinity**

We also explored the effect of salinity (drop conductivity) on offset voltage.

Figure S5 shows plot of U_T and corresponding charge density for insulating water drop (Millipore water) and saline drop with conductivities varying from 5 to 26.6 mS/cm. These experiments are performed on Teflon surface submerged in water for 8 hrs. Figure S 5 clearly shows that average offset voltage U_T remains unchanged as function of droplet conductivity.

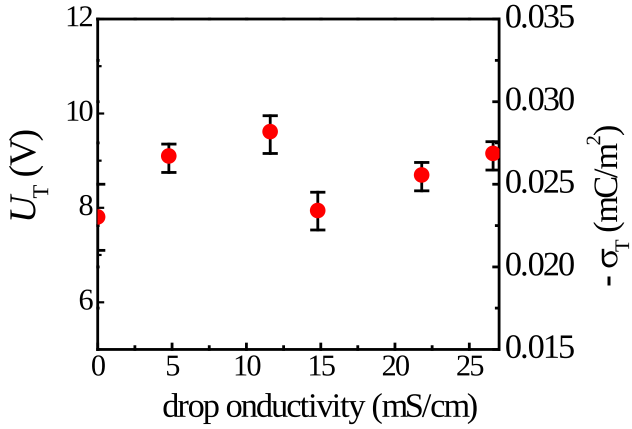

Fig. S-5: Plot shows offset voltage U_T and corresponding charge density for various drop conductivity values on Teflon sample submerged in water for 8 hrs.