Supporting Information for: A nanoscale view on oligo(ethylene glycol) self-assembled monolayer hydration

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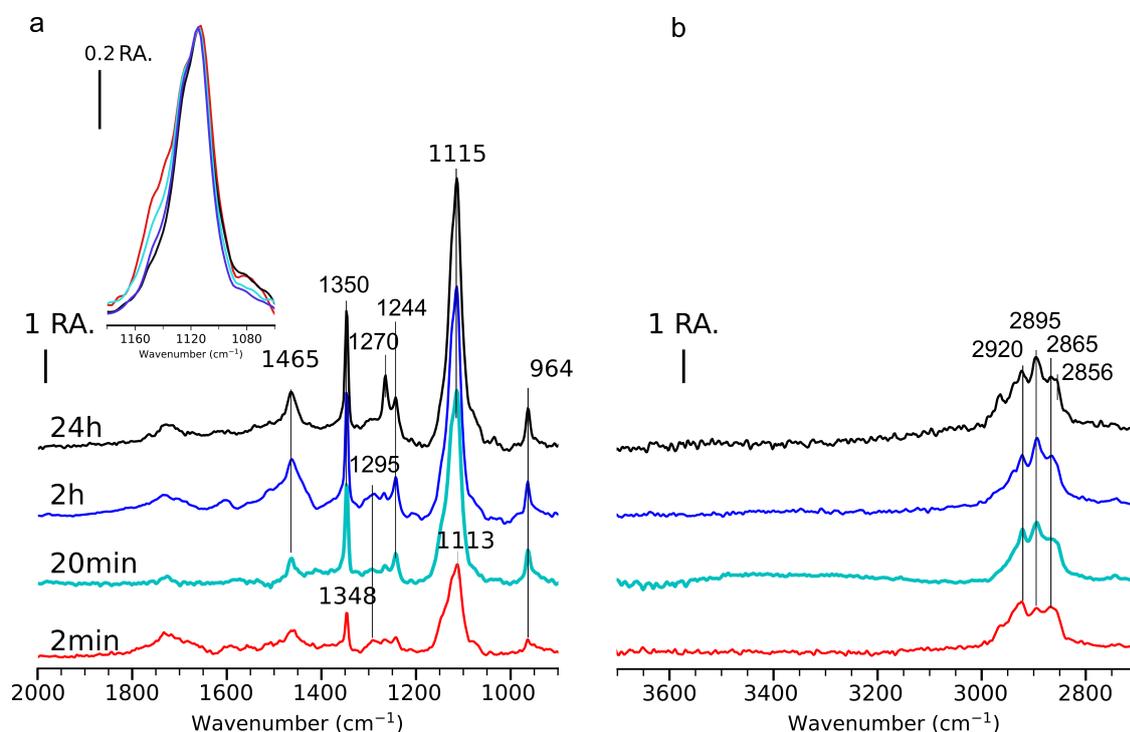
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Figure S1: IRRA spectra of Au(111)/OEG SAMs prepared from different immersion times. The peak assignments are in table 1. The inset represents the spectra normalized at COC maximum.
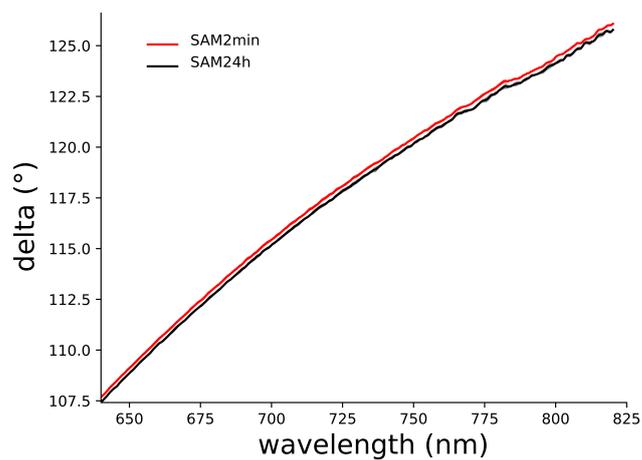
Figure S2: Averaged spectroscopic ellipsometry $\Delta(\lambda)$ recorded on AC- and HC-SAMs.
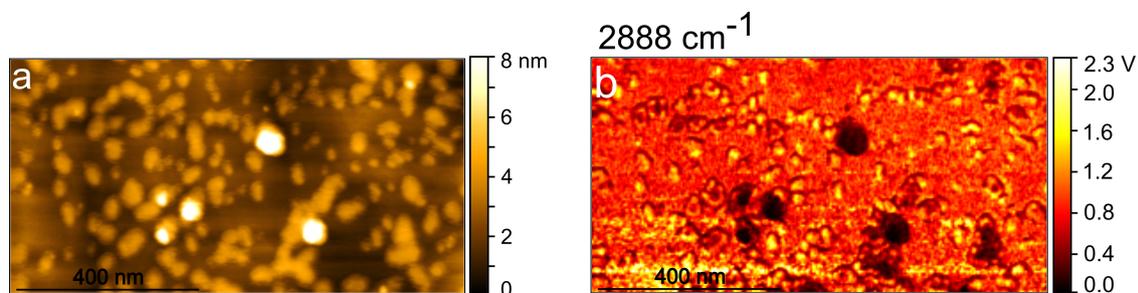
Additional AFM-IR using OPO and QCL lasers

Figure S3: Results of tapping mode AFM-IR measurements on AC Au(111)$_{sc}$/OEG SAM $t_{im} = 3\,\text{min}$ in dry atmosphere (RH 3%). Topography (a), nano IR-mapping at maximum of $\nu_s(\text{C}-\text{H}_2)$ 2888 cm^{-1}
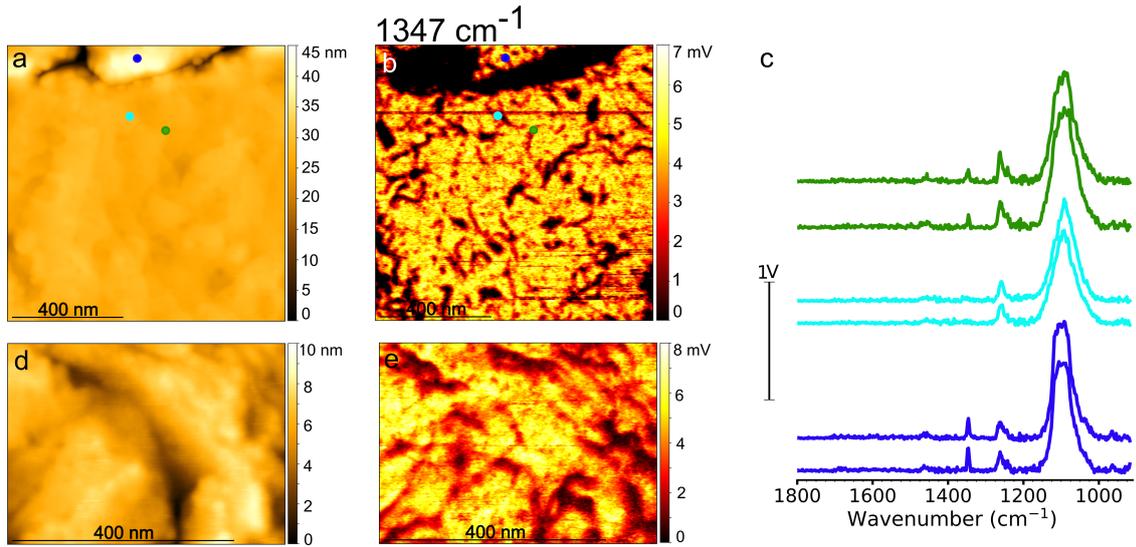
Figure S4: Results of tapping mode AFM-IR measurements on HC Au(111)/OEG SAM t_{im} = 10 min in 20 µM; topography and nano IR-mapping at maximum of $\omega(C-H_2)$ 1347 cm^{-1} in large (a, b) and small (d, e) scan area. Nano-IR point spectra recorded on SAM are indicated by corresponding colors on topography and IR maps. For each position, 2 spectra were recorded.

Humidity dependent SE measurements on Au substrate

SE measurements were done on two Au(111) to deteremine the thickness of the water layer in elevated RH %. The absolute thickness of interfacial water (d) was measured by fitting the $\Delta(\lambda)$ with a 3-layer optical model (Au(111) | water film | ambient (n=1)). The Au(111) dispersion layer was calculated by point-wise inversion of one set of experimentally measured (Δ, Ψ) angles and used in the model. The dispersion of the water film's refractive index was derived from 3-term Sellmeier's dispersion formula[1] for HPLC water. The thickness increases almost linearly with elevated RH%, as the gold substrate is an impermeable material, the increase is solely attributed to the averaged thickness of the adsorbed water film. The error bars represent the maximum variation of thickness change on two samples (0.06 nm at RH80%) (figure 5). During the increase of RH from 3 % to 70 %, no significant increase in the thickness was measured. The average water thickness increases to 0.5 Å at 70%, to 0.9 Å at 85%, and 1.6 Å at RH 95%, which indicates the formation of an incomplete water layer on Au(111). As if the water molecules is assumed to bind to Au(111) via one of the oxygen atoms[2] then the minimum thickness for a dense layer of water should be at least 2.8 Å which is the molecular diameter of one water molecule.[3]
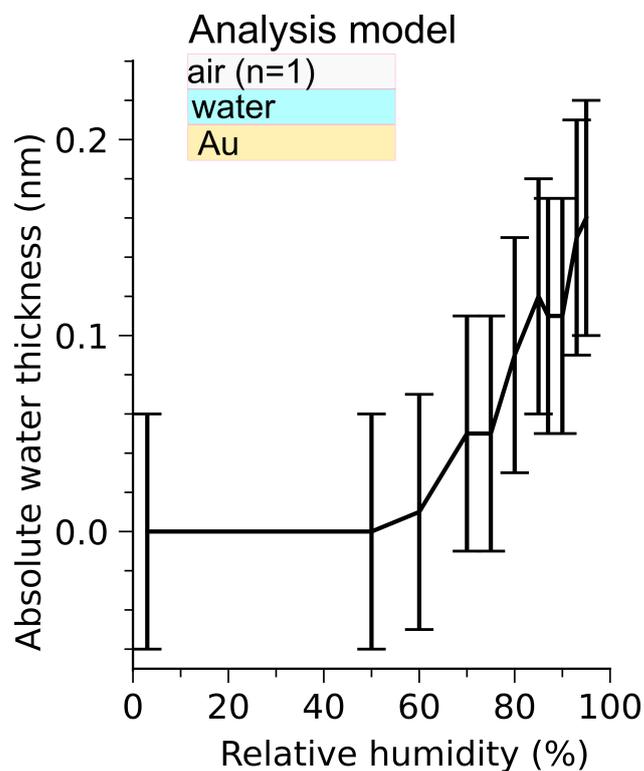
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Figure S5: The absolute thickness of adsorbed water on Au(111) measured by spectroscopic ellipsometry.

References

1. Daimon, M.; Masumura, A. Measurement of the refractive index of distilled water from the near-infrared region to the ultraviolet region. *Applied Optics* **2007**, *46*, 3811.

2. Groß, A.; Sakong, S. Ab Initio Simulations of Water/Metal Interfaces. *Chemical Reviews* **2022**, *122*, 10746–10776.

3. Chen, L.; He, X.; Liu, H.; Qian, L.; Kim, S. H. Water Adsorption on Hydrophilic and Hydrophobic Surfaces of Silicon. *The Journal of Physical Chemistry C* **2018**, *122*, 11385–11391.