UV-mediated tuning of surface biorepulsivity in aqueous environment

Supporting Informations

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Experimental:

Ethanol (99%, denatured with 1% PE) was freshly destilled before use. Phosphate buffered saline (PBS) contained 10 mM PO_4^{3-}, 138 mM NaCl and 3 mM KCl at pH 7.4 (25 °C). BSA was obtained from Sigma-Aldrich (albumin, from bovine serum, order no.: A7906).
As substrates for the primary SAMs gold layers on silicon were used. The substrates were prepared by thermal evaporation of 100 nm gold onto polished single-crystal silicon wafers (boron doped, (100) orientation, obtained from Wacker Siltronic AG, Germany) primed with a 2.5 nm chromium layer as adhesion promoter.

The SAMs were deposited from a 1 mM solution of $HS(CH_2)_{11}(OCH_2CH_2)_6OH$ (EG6)[1] monomer in freshly destilled ethanol at room temperature for 24 hours. Then, the samples were thoroughly rinsed with ethanol and dried in a nitrogen stream.
UV irradiation: A UV lamp equipped with a 254 nm filter (UVP, Model no. UVGL-58, typical flux 1.1 mW cm^{-2} at 5 cm distance) was used to irradiate the substrates. The power of the lamp was continuously measured with a multichannel energy meter (obtained from Ophir Photonics, equipped with a PD300-UV sensor). The substrates were rinsed with Millipore water and covered with a quartz slide (25 mm x 25 mm, thickness: 1 mm, UV quality, purchased from PGO, Germany) to create a thin water film between the slide and the substrate. After the irradiation process, the samples were rinsed with water and dried in a nitrogen stream.

To exclude oxygen, the respective experiments were performed in a nitrogen-filled glove-box and the water was de-aerated by heating it under sonication followed by purging with argon during the cooling process (at least two hours). Again, a quartz slide was used to create a thin water film.

TEM grids made by Plano, Germany, were used to fabricate patterns. For this, the TEM grid was placed between the substrate and the quartz slide within the water film.

Protein adsorption: Protein adsorption experiments were carried out with irradiated and native samples. The samples were initially equilibrated with PBS buffer for two hours and then rinsed with Millipore water. The layer thickness was determined via ellipsometry. The protein adsorption tests were performed by incubating substrates in a 1 mg/mL solution of BSA in PBS solution at pH 7.4 for two hours at room temperature. Following the incubation, the substrates were rinsed with at least 100 mL of Millipore water to remove loosely adsorbed

proteins. The amount of protein was determined via ellipsometry and XPS. For comparison, SAMs of dodecanethiol and 11-mercaptoundecanol were treated the same way.

Ellipsometry: Measurements were carried out on a Sentech SE400 ellipsometer with a 632.8 nm laser at an incidence angle of 70° with respect to the normal. A multilayer model (ambient-film-substrate) was used in the Sentech analysis software. A minimum of three different spots was measured on each sample. The substrate parameters were recorded for each substrate before the coating process. For the organic layers (EG6 SAM and the adsorbed proteins) n = 1.45 and k = 0 were used as input in the respective multilayer simulations.

IRRAS: Infrared absorption measurements were recorded on a Nicolet 6700 FT-IR spectrometer (Thermo) purged with dry and CO_2 free air and equipped with a liquid-nitrogen cooled MCT detector. Surface studies were performed with a Smart SAGA set-up utilizing p-polarized light at an incidence angle of 80° relative to the surface normal. 1024 scans were recorded at a resolution of 4 cm^{-1} from 600 to 3500 cm^{-1} at room temperature.

XPS: A Leybold−Heraeus Max100 system equipped with a hemispherical LHS 11 analyzer was used for XPS characterization. The measurements were performed using a Mg Kα X-ray source (λ = 1253.6 eV) operated at 260 W and positioned ~1.5 cm away from the sample. The spectra were recorded in normal emission geometry with an energy resolution of ~0.9 eV. The energy scale was referenced to the Au $4f_{7/2}$ peak of the gold substrate (BE of 84.0 eV). Apart from the characterization of the primary EG6 SAMs, XPS was used to monitor protein adsorption, which was performed on the basis of the characteristic N 1s signal.

SEM: SEM images were recorded using an Atomica/Amray, 1920 ECO scanning electron microscope with an acceleration voltage of 10 kV.

Figures:

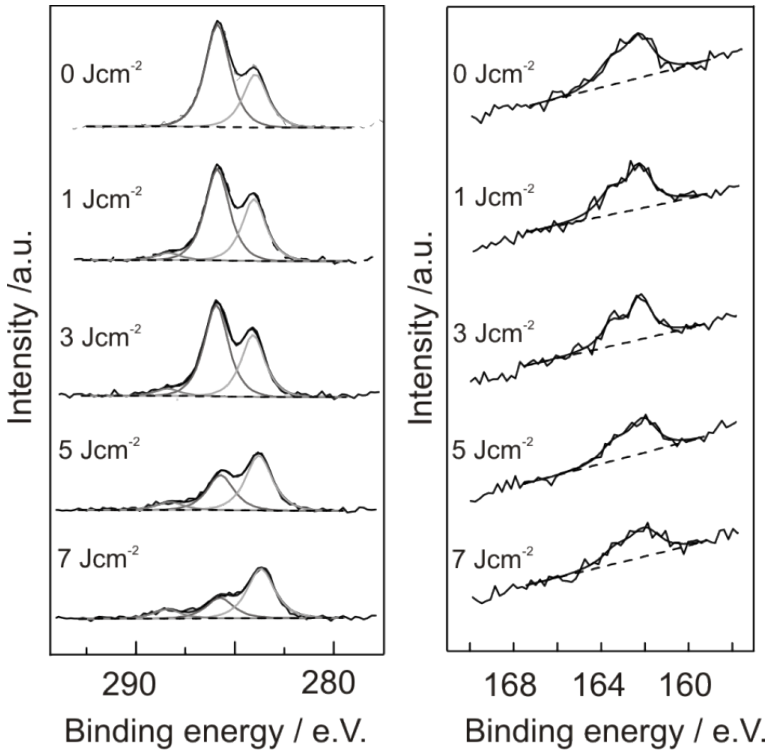

Figure SI 1: XP spectra (left: C 1s, right: S 2p) of EG6 SAMs irradiated in oxygen-containing water at different doses.

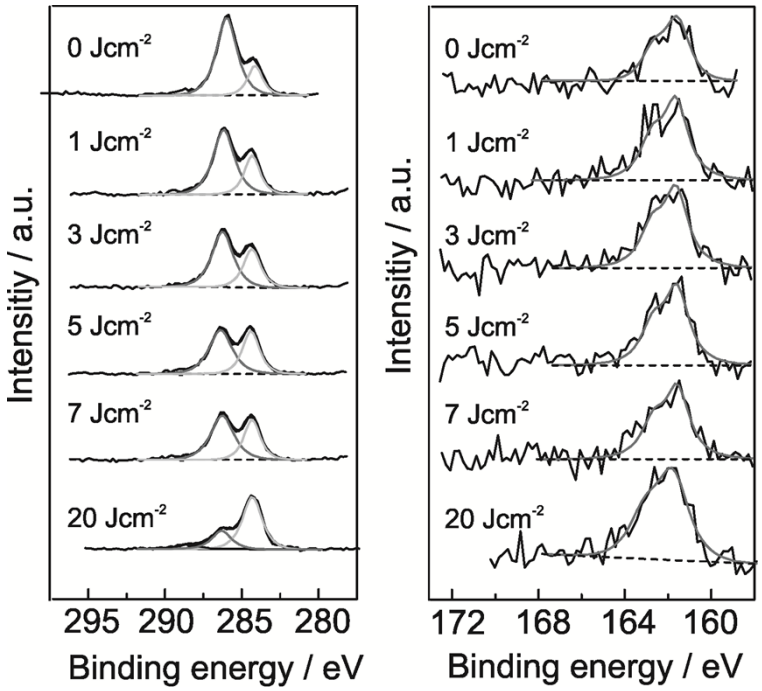

Figure SI 2: XP spectra (left: C 1s, right: S 2p) of EG6 SAMs irradiated in oxygen-free water at different doses.

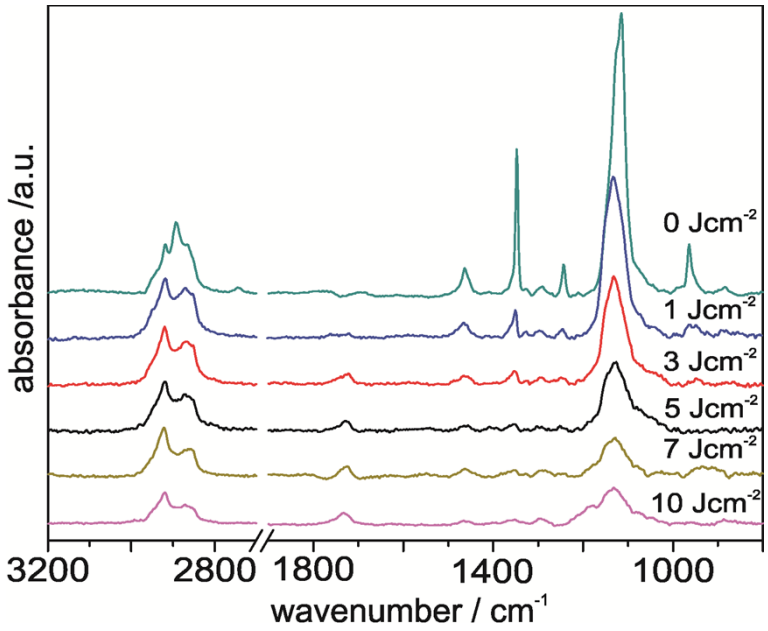

Figure SI 3: IRRA spectra of EG6 SAMs irradiated in oxygen-containing water at different doses.

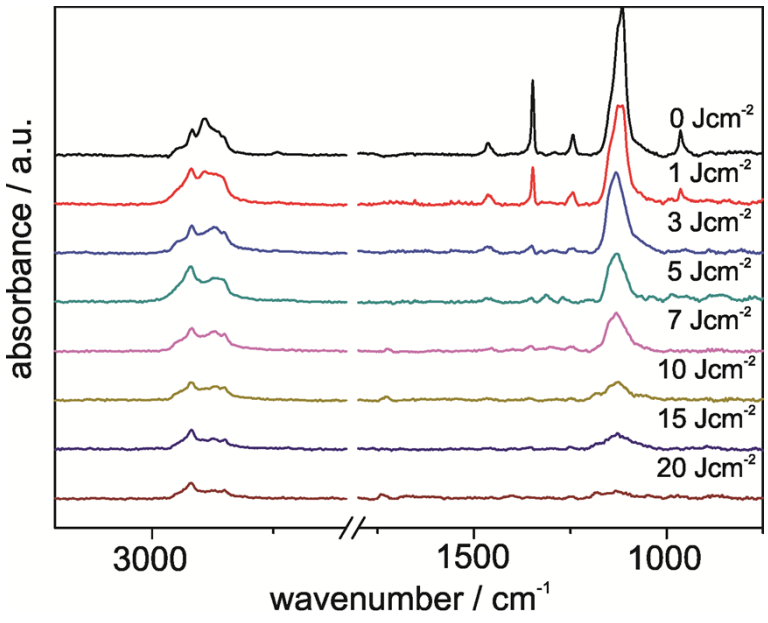

Figure SI 4: IRRA spectra of EG6 SAMs irradiated in oxygen-free water at different doses.

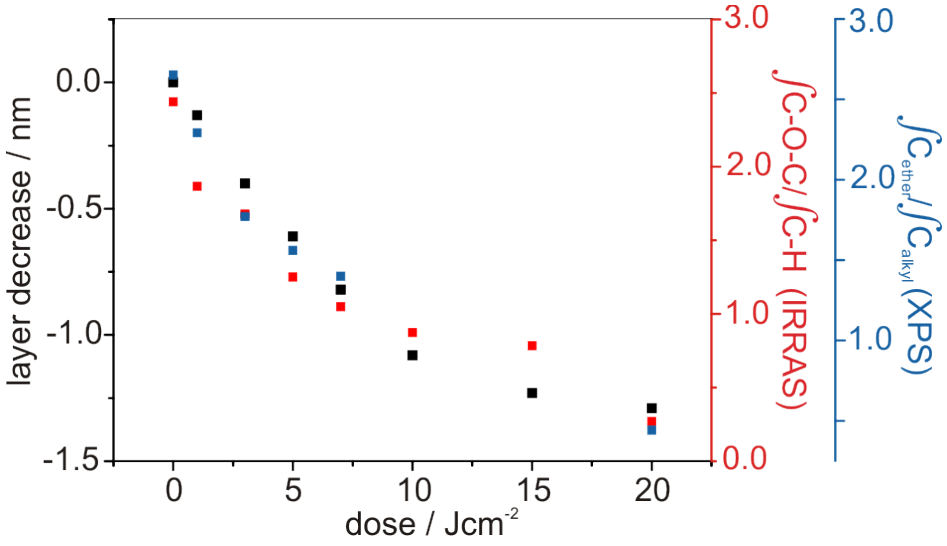

Figure SI 5: Correlation of ellipsometry, IRRAS, and XPS data of EG6 SAMs irradiated in air-containing water at different irradiation doses. The layer thickness decrease (as determined by ellipsometry, black squares) correlates well with the loss of the signals of EG part: Ratio between the integrals of the C-H stretching mode (2900 cm^{-1}) and the C-O stretching mode (1120 cm^{-1}) as determined by IRRAS (blue squares). Ratio between the C-C (284 eV) and the C-O (286 eV) signals in C 1s XPS (blue dots).

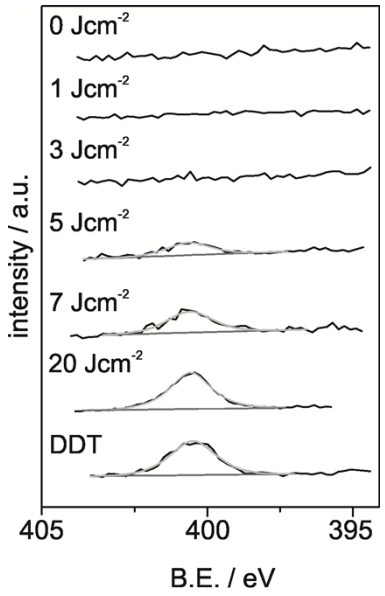

Figure SI 6: N 1s XP spectra of BSA layers adsorbed onto EG6 SAMs irradiated in oxygen-containing water at different doses.

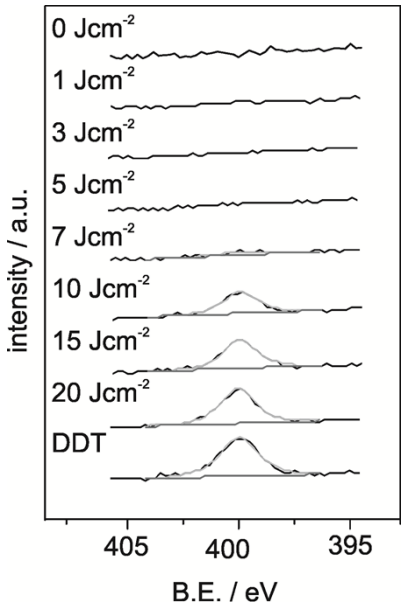

Figure SI 7: N 1s XP spectra of BSA layers adsorbed onto EG6 SAMs irradiated in oxygen-free water at different doses

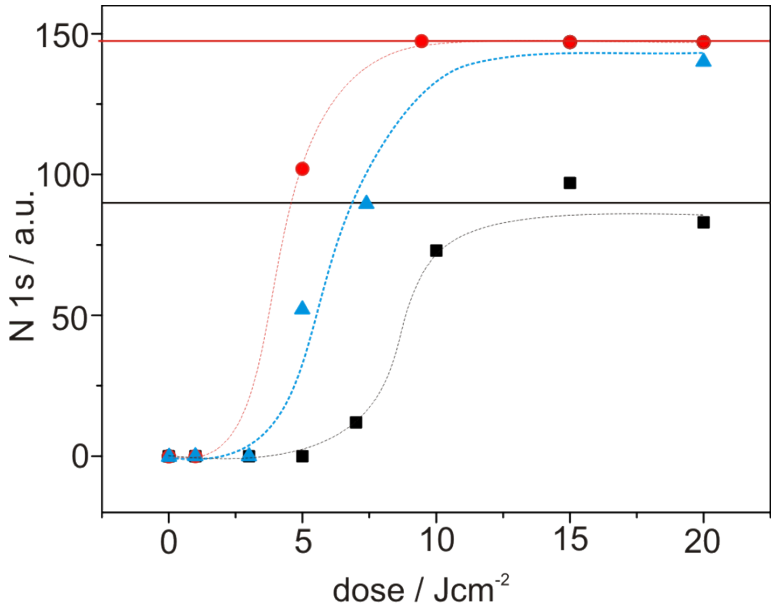

Figure SI 8: N 1s integrals of BSA layers adsorbed onto EG6 SAMs irradiated at different doses in oxygen-free water (black), in oxygen-containing water (blue), and under air (red). Curves are guide to the eye. Values obtained for the BSA layers on dodecanethiol SAM (red line) and 11-mercaptoundecanol SAM (black line) are shown for comparison.

Reference

[1] Tobias Winkler, Nirmalya Ballav, Heidi Thomas, Michael Zharnikov, Andreas Terfort. *Angew. Chem. Int. Ed.* **2008**, *47*, 7238 –7241.