

Supplementary Material

Characterization of SAMs

The HBCS monolayers were characterized by XPS, NEXAFS spectroscopy, and ellipsometry. All experiments were performed at room temperature. The XPS and NEXAFS spectroscopy measurements were carried out under UHV conditions at a base pressure $< 1.5 \times 10^{-9}$ mbar. The time for these measurements was selected in such a way that no noticeable X-ray damage occurred during the spectra acquisition.^[1-4]

The XPS and NEXAFS experiments were performed at the HE-SGM beamline of the synchrotron storage ring BESSY II in Berlin, Germany. The XPS measurements were carried out using a VG CLAM 2 analyzer and a synchrotron light as an X-ray source. The photon energy was varied depending on the range of interest. The spectra acquisition was carried out in normal emission geometry with an energy resolution of 0.4-0.5 eV. The energy scale was referenced to the Au 4f_{7/2} peak at a binding energy (BE) of 84.0 eV.^[5] A wide scan spectrum and the C 1s, O 1s, S 2p, and Au 4f narrow scan spectra were measured. The spectra were fitted by symmetric Voigt functions and a Shirley-type background. To fit the S 2p_{3/2,1/2} doublet we used two peaks with the same full width at half maximum (FWHM), the standard^[5] spin-orbit splitting of ≈ 1.18 eV (verified by fit), and a branching ratio of 2 (S2p_{3/2}/S2p_{1/2}). The fits were performed self-consistently: the same fit parameters were used for identical spectral regions.

The acquisition of NEXAFS spectra was carried out at the carbon K-edge in the partial electron yield mode with a retarding voltage of -150 V. Linear polarized synchrotron light with a polarization factor of $\approx 82\%$ was used. The energy resolution was ≈ 0.40 eV. The incidence angle of the light was varied from 90° (E -vector in the surface plane) to 20° (E -vector nearly normal to the surface) in steps of 10° – 20° to monitor the orientational order of the HBC molecules within the films. This approach is based on the linear dichroism in X-ray absorption, i. e. the strong dependence of the cross-section of the resonant photoexcitation process on the orientation of the electric field vector of the linearly polarized light with respect to the molecular orbital of interest.^[6] The raw NEXAFS spectra were normalized to the incident photon flux by division through a spectrum of a clean, freshly sputtered gold sample. The energy scale was referenced to the pronounced

π^* resonance of highly oriented pyrolytic graphite at 285.38 eV.^[7]

XPS

S 2p, C 1s, and O 1s XPS spectra of HBCS/Au are presented in Figure 1. The spectra were acquired at photon energies (PE) of 400 eV (S 2p), and 660 eV (C 1s, O 1s). The S 2p spectrum exhibits two S 2p_{3/2,1/2} doublets at ~161.8 eV (S2p_{3/2}) and ~163.3 eV (S2p_{1/2}), which are assigned to the thiolate-type sulfur bound to the metal surface^[8,9] and to unbound sulfur,^[3] respectively. No features related to oxidative components or decomposition products (e.g., atomic sulfur) were seen. The intensities of both observed components are very similar, which suggest that the respective species are located not far away from each other. Taking into account, the structure of the HBCS molecule, we can reasonably assume that these components are related to the two different sulfur atoms in the disulfide ring: one of these atoms makes a thiolate-type bonding to the substrate, whereas the second one remains unbound. Thus, the HBCS molecules are bonded to the Au substrate in a SAM-like manner, by a thiolate group provided by one of the sulphur atoms in the disulfide ring. The lack of the analogous bond for the second sulphur atom can only be related to a stretching of the adjacent alkyl chain apart from the substrate, otherwise it will be energetically favourable to have both sulphur atoms bonded.

The C 1s spectrum of HBCS/Au shows a single emission peak at a binding energy (BE) of 284.45 eV (PE = 660 eV). No features related to contamination are observed. The single ester group incorporated into anchoring chain provides obviously too small XPS signal to be clearly seen in the C 1s spectrum. The specific BE position of the C 1s emission is related to the mixed character of this molecule, containing both HBC core and aliphatic chains, contributions of which can not be distinguished in the spectra. It is quite common that the C 1s spectra of SAMs formed from hybrid aliphatic-aromatic molecules exhibit a single emission at BEs ranging between the typical values for pure aliphatic (~284.95 eV)^[9] and pure aromatic (~284.1 eV)^[10] films.^[11, 12]

The O 1s spectrum of HBCS/Au exhibits a weak emission peak at ~531.6 eV, which can be related to the ester group incorporated into the anchoring chain of the HBCS molecule.^[5]

On the basis of the C 1s and Au 4f (not shown) XPS data, the thickness of the HBCS films was estimated to be 28.9 ± 0.5 Å. A standard evaluation procedure

was applied, i.e. an exponential attenuation of the XPS signal was assumed and standard^[13, 14] attenuation lengths for the Au 4f and C 1s emissions were used.

NEXAFS spectroscopy

C K-edge NEXAFS spectra of HBCS/Au acquired at different X-ray incident angles are presented in Figure 2. The spectra exhibit an absorption edge at ~287.0 eV and several characteristic absorption resonances, namely two sharp π^* resonances at 284.4 and 285.1 eV, a low-intense resonance at 286.1 eV (presumably, a further π^* resonance or a R*/C-S* feature), R* resonance at 287.5 eV, and several broad σ^* resonances at higher photon energies (the assignment has been performed in accordance with refs [10] and [15]). Among these features, the π^* and R* resonances are exclusively related to the HBC core and aliphatic part of the HBCS molecule, respectively, and can be consequently used as fingerprints of the respective entities. The splitting of the π_1^* resonance, which is located at 285.0 eV for benzene,^[16] to several ones is typical for strongly conjugated aromatic systems.^[17]

The NEXAFS spectra of HBCS/Au in Figure 2 exhibit a pronounced linear dichroism, i.e. a dependence of the absorption resonance intensity on the incidence angle of X-rays, which suggests an orientational order in these SAMs. The dichroism is additionally highlighted by the differences between the spectra acquired at 90°, 20°, and 55° presented in Figure 3. The sign of the peaks in the respective difference spectra suggests an upright orientation of both HBC cores and aliphatic chains (at the average), since the transition dipole moments of the π^* and R* resonances are oriented perpendicular to the plane of the aromatic rings and the axis of alkyl chain, respectively.^[18,19]

Apart from these qualitative conclusions, average tilt angles of the HBC cores in the HBCS films can be derived by numerical evaluation of the NEXAFS data,^[6] which is slightly modified for the case of aromatic SAMs (see refs [20] and [21] for details). For the evaluation, the π^* resonance at 285.1 eV as the most distinct one in the spectra has been selected. The derived value of the average tilt angle of the HBC moieties in HBCS/Au is around 30-35°.

The average tilt angle of the aliphatic chains in the HBCS films can not be precisely determined, since the respective resonance (R*) has a low intensity and overlaps with the absorption edge. In addition, this parameter is an average over

the side and anchor alkyl chains, which definitely have different orientation. Taking into account that at least a part of the side chains should be oriented parallel to the surface, average vertical orientation of the alkyl part of the HBCS molecules mean that the anchoring chain has such orientation, i. e. is strained away from the substrate.

Figures :

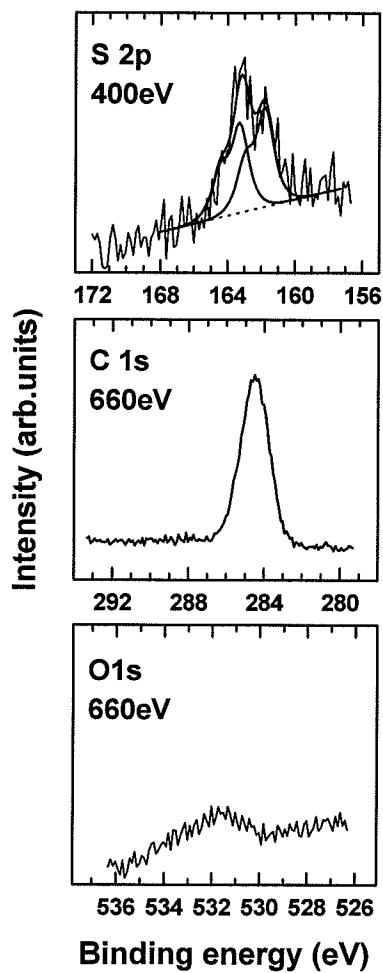


Figure 1. S 2p, C 1s, and O 1s XPS spectra of HBCS/Au acquired at photon energies of 400 eV (S 2p) and 660 eV (C 1s and O 1s). The decomposition of the S 2p spectra in two doublets is shown (see text).

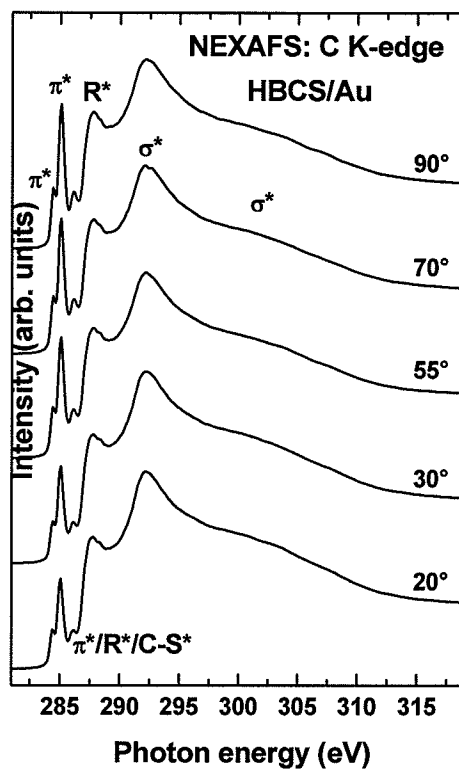


Figure 2. Carbon K-edge NEXAFS spectra of HBCS/Au acquired at different X-ray incidence angles, given at the respective curves. The most important absorption resonances are marked.

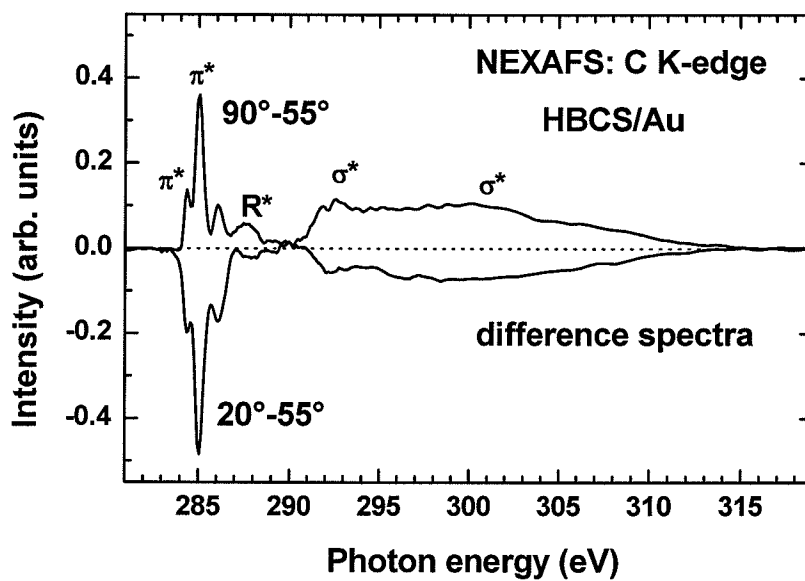


Figure 3. The difference between the NEXAFS spectra collected at X-ray incidence angles of 90° and 55° and 20° and 55°. Most important absorption resonances are marked.

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