

Supporting information

Adsorption and Reaction of Sub-Monolayer Films of an Ionic Liquid on Cu(111)

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Experimental

The experiments were performed in a commercial ultrahigh vacuum (UHV) system (SPECS GmbH) with a base pressure of 2×10^{-10} mbar. It consists of two chambers, one containing an Aarhus type STM/AFM system (SPECS Aarhus SPM150 with Colibri sensor), which is capable of measurements in a temperature range of 90 K and 370 K by cooling with LN₂ and resistive heating, the other one is equipped with an x-ray source (SPECS XR50, Al + Mg K _{α}) and a hemispherical analyzer (SPECS, DLSEGD-Phoibos-Has3500) for XPS measurements.

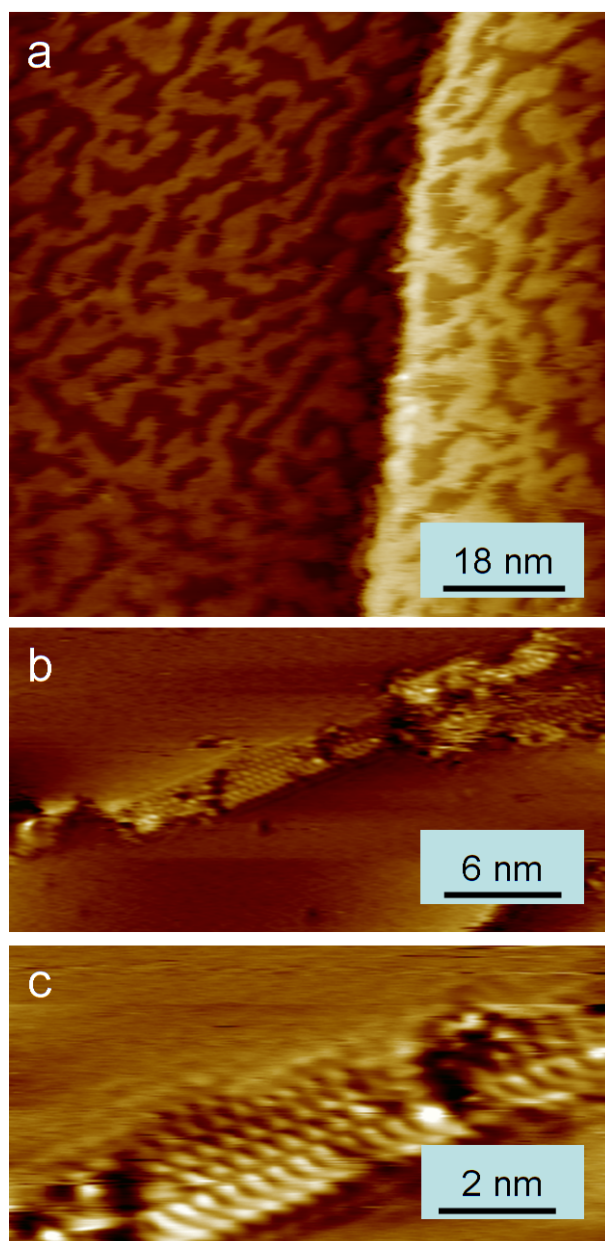
The Cu(111) single crystal was purchased from MaTeck GmbH (purity 5N). It has a hat shape form with a diameter of 9 mm, one side is polished with a roughness of the (111) surface smaller than 30 nm and an orientation accuracy better than 0.1°. The ionic liquid [BMP][TFSA] was purchased from Merck in ultrapure quality. The Cu(111) surface was cleaned by several cycles of Ar⁺-ion sputtering (1 kV) and heating to 770 K. With this procedure atomically flat terraces were obtained; a few remaining surface cavities were found on the Cu terraces which we relate to small amounts of adsorbed oxygen (the amount is too small to be detected by XPS). Therefore another cycle of 5 min of Ar⁺-ion sputtering was performed, followed by annealing in the LN₂ cooled manipulator head. This reduced the density of the cavities to a neglecting amount ($< 0.008 \text{ nm}^{-2}$) – see also STM image in the supporting information of ref. [1]. The ionic liquid is filled in a quartz crucible, which is mounted in a Knudsen effusion cell (Ventiotec, OVD-3). The IL was degassed for at least 24 hours under UHV conditions at room temperature, followed by several hours of degassing at up to 400 K. The quartz crucible itself was also baked prior to use at 870 K in UHV. The cleanness of the IL vapour was tested with a quadrupole mass spectrometer (Pfeiffer HiQuad QMA 400). To generate IL adlayers on the Cu(111) surface, the IL was evaporated at a temperature of the IL source of 450 K onto Cu(111). The Under these conditions the deposition rate is around 0.1 ML min^{-1} . During evaporation the Cu(111) sample was held at temperatures between 80 K and 420 K, depending on the experiment.

STM measurements were performed in constant current mode with currents between 15 pA and 50 pA, bias voltages between 0.1 V and 1.5 V applied to the sample, and at temperatures between 90 K and 350 K.

For XPS measurements we used an Al K $_{\alpha}$ x-ray source (1486.6 eV), operated at a power of 250 W (U = 14 kV, I = 17.8 mA). The spectra were recorded at a pass energy of 100 eV under a detection angle of 80° relative to the surface normal, which enhances the surface sensitivity. The IL adlayers show beam damage upon extended irradiation, therefore the duration of the XPS measurements was minimized to 1 scan for the C1s, O1s, N1s and F1s regions and 5 scans for the S2p signal (overall irradiation ~8 min), which on the other hand lowers the signal to noise ratio (see, e.g., S2p signal at 80 K in Fig. 3b). Because of the irradiation induced decomposition, STM measurements were never performed after XPS measurements on the same sample. Before analysis of the spectra, the background was subtracted from all C1s, O1s, N1s, F1s and S2p signals. In the peak fitting procedure, a Voigt-type peak shape was applied, which was approximated by a weighted sum of Gaussian and Lorentzian functions.

1. F. Buchner, H. Farkhondeh, M. Bozorgchenani, B. Uhl, R. J. Behm, *Phys. Chem. Chem. Phys.*, 2014, **16**, 11191.

Supporting STM data



(a) Large scale STM image recorded after vapor deposition of [BMP][TFSA] at 80 K (STM measurement at ~ 100 K). It shows the same island morphology as depicted in Figure 3 upon vapor deposition at 200 K. (b) STM image recorded after vapor deposition of [BMP][TFSA] on Cu(111) at 80 K and subsequent heating to ~ 300 K, showing the same square structure as observed after vapor deposition at ~ 300 K (see Figure 1). The structure is highlighted at a magnified scale in (c).