Supporting Information

In-Situ XPS Monitoring and Characterization of Electrochemically Prepared Au Nanoparticles in an Ionic Liquid

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Experimental Details

Au electrodes were sputtered on PEM using a conventional SEM-sputter and 5 µl of DEME-TFSI inserted between the electrodes. After the immediate spread of IL-drop over the entire device line scans were recorded from electrified electrode toward grounded electrode.

Figure S1. Schematics of the two electrode device with the IL medium in between (a), and the photoemission process (b).
**Chemical Composition of the PEM+IL Medium**

A survey XP spectrum of the PEM+IL is given in Figure S2, which indicates that no major surface impurities exist. Detailed spectra of the N1s and F1s regions are also given to reveal the integrity and the stoichiometry of the IL (see also Figure S3). However, the C1s signal consists of peaks from both IL and the PEM.

*Figure S2.* XP survey spectrum of the polymer + IL surface in the scanning mode and with higher resolution of the regions.

Assuming the probed surface composition to be uniform, we can estimate the probed top 10 nm of the surface to contain one Ion-Pair of the IL for ~60 Carbon atoms of the polymer membrane, which means that the final IL medium within the device is not very thick. This is obtained by using the relative intensity ratio of the two strong peaks observed, i.e. F1s/C1s, and working backwards.

*Figure S3.* High resolution XP spectra of C1s and O1s regions of IL-only, together with experimentally determined and theoretical atomic ratios.

experiment

\[ F : O : N : S : CF_3 = 1 : 0.88 : 0.39 : 0.38 : 0.32 \]

theoretical

\[ F : O : N : S : CF_3 = 1 : 0.83 : 0.33 : 0.33 : 0.33 \]
Current Measurements

Figure S4. Current measurements.

Time variations of the current to 0 to +3 and 0 to -3V voltage pulses, plotted both in linear and logarithmic time scales, are given in Figure S4. The current at the onset is exponentially decaying in time very similar to the F1s signal recorded with 1s time resolution as shown in Figures 3 and 4 in our previous work.¹
Potential Drop Across Electrodes

The binding energy shift at the Au electrode is 3 eV upon the application of +3V D.C. potential. When the potential is applied to an electrode that is in contact with electrolyte, DEME-TFSI in our case, Electrical Double Layer (EDL) forms through screening of the charge on the electrode by the oppositely charge ionic fragments DEME-TFSI (anions in this case e.g. purple spheres corresponding to TFSI anions reoriented themselves at the positively charged electrode/IL interfacial region.) The half of the applied potential (+1.5 V) prevails on the IL-medium in between electrodes and until the oppositely charged electrode/IL interface at the grounded electrode then drops to zero-potential. The details of EDL formation and the voltage drop were heavily discussed in our previous work and the related photoelectron spectra is not re-represented here. Only the schematic illustration of potential drop across the electrodes are given in Figure S5.

**Figure S5.** Schematic representation of EDL formation and potential drop under +3V D.C. potential.
**Crystallographic Planes in TEM images**

Au has Face Centered Cubic (FCC) crystal structure and the interplanar spacing in a FCC – cell crystallographic structure is calculated by $d_{xyz} = \frac{a}{\sqrt{x^2 + y^2 + z^2}}$ where $d$ is the distance between two planes, $a$ is the lattice parameter that is 0.408 nm for Au and $xyz$ corresponds to the coordinates of the plane e.g. for (111) plane $x=1, y=1, z=1$. For instance, basically in the following Figure S6 interplanar distance values are determined for the particular planes.

**Figure S6.** Schematic representation corresponding to Au Face Centered Cubic Structure

The TEM images at high magnifications the distance between two planes was found ~0.20 ±0.05 nm and from the interplanar distance calculations within the error margin this can be attributed to both (111) and/or(200) planes of Au which has $d_{111} = \frac{0.408nm}{\sqrt{1^2 + 1^2 + 1^2}} = 0.235$ nm and $d_{200} = \frac{0.408nm}{\sqrt{2^2 + 0^2 + 0^2}} = 0.204$ nm

**Figure S7.** (a) TEM images of Au NPs at different resolution. (b) At higher magnification reflecting the crystallographic planes and the distance between two planes from the marked-region in distance-profile.
Laterally Resolved XP Spectra of F1s under 10 mHz 5V SQW Modulation

Similar time resolved F1s spectra, recorded at 1600 μm intervals across the two metal electrodes and DEME-TFSI medium (without Au NPs) in between, are displayed in Figure S8.

**Figure S8.** Time-resolved F1s XP spectra recorded at 5 different positions across the metal electrodes.

(1) Camci, M.; Aydogan, P.; Ulgut, B.; Kocabas, C.; Suzer, S. *Physical Chemistry Chemical Physics* **2016**, 18, 28434.