

## Electronic Supplementary information

# Recognizing Conductive Islands in Polymeric Redox Surface Using Electrochemical-Coupled Vibrational Spectromicroscopy

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### Chemicals

Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98%) and aniline monomer (99%) were purchased from Synth and Sigma-Aldrich, respectively. Aniline was further purified before use. The solutions were prepared with deionized water.

### Electrodeposition of the PANI film

A thin film of Au (~20 nm) was obtained through vacuum evaporation on glass substrate, previously evaporated with Ti (~10 nm) as adhesion layer. The resultant Au-coated glass substrate, from here onward named as flat Au mirror electrode, was used as working electrode and modified with the PANI film by applying a potential of 0.8 V vs Ag/AgCl<sub>sat</sub> electrode in a solution containing a freshly distilled aniline (0.1 mol L<sup>-1</sup>) and H<sub>2</sub>SO<sub>4</sub> (0.5 mol L<sup>-1</sup>) for 100 s. A one compartment, three electrodes electrochemical cell controlled by the potentiostat/galvanostat (Autolab, PGSTAT128N) was used for this purpose, consisting of the flat Au mirror as the working electrode, Pt wire counter electrode, and Ag/AgCl<sub>sat</sub> reference electrode. All the potentials are quoted against Ag/AgCl<sub>sat</sub>.

### Electrochemical assembly

The spectroelectrochemical measurements were performed in a home-built polytetrafluoroethylene (PTFE) three electrodes electrochemical cell containing the PANI modified flat Au mirror as the working electrode, Pt wire sealed in a glass tube as counter electrode and Ag/AgCl<sub>sat</sub> as reference electrode. The electrochemical cell was connected to the potentiostat/galvanostat (autolab, PGSTAT128N), where the potential of the working

electrode was maintained at fixed value through the technique of steady-state staircase voltammetry for a fixed duration of time, before switching to the next potential.

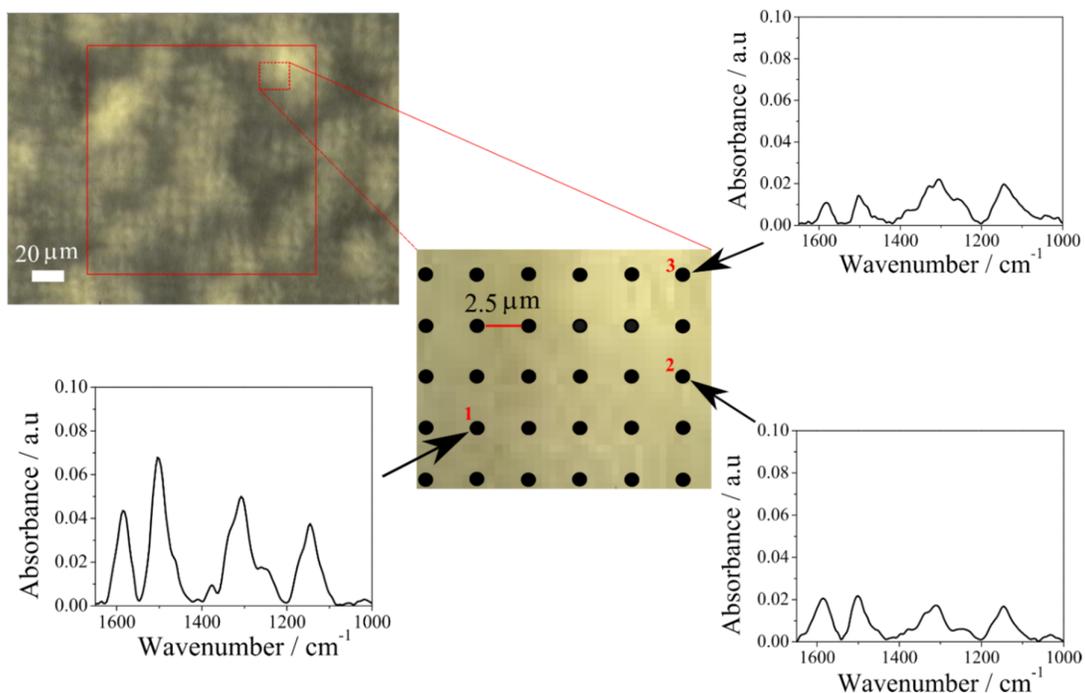
### **Micro-FTIR experiments**

We initially characterize the PANI film through FTIR spectromicroscopy without coupling it to the electrochemistry. These analysis were conducted in the reflectance mode using a spectral resolution of  $4\text{ cm}^{-1}$  and 32 scans in the  $4000\text{--}900\text{ cm}^{-1}$  spectral window using an FTIR spectrometer (Vertex 70v, Bruker) coupled with an FTIR microscope (Hyperion 3000) equipped with liquid  $\text{N}_2$  and cooled  $64\times 64$  elements focal plane array (FPA) detector.

### **Electrochemical coupled vibrational spectromicroscopy (EVSM) setup**

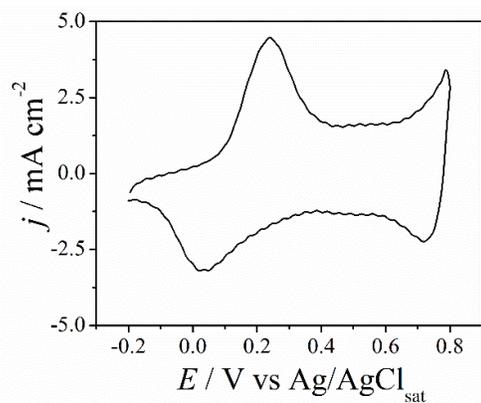
The spectroelectrochemical cell was mounted in the motorized stage of the FTIR microscope (Hyperion 3000) coupled to FTIR spectrometer (Vertex 70v, Bruker), which provides the facility of moving the electrochemical cell and hence the measurement can be performed at any desired position of the working electrode by initially focusing the visible and then IR light through  $\text{CaF}_2$  window, when the measurement is performed. The  $\text{CaF}_2$  window also controls the thickness of the electrolyte layer above the working electrode. A gasket made of PVC was placed between the  $\text{CaF}_2$  window and the surface of the working electrode (Fig. 1d, main manuscript) to entrap approximately  $8\text{ }\mu\text{m}$  thick electrolyte layer between  $\text{CaF}_2$  window and the sample surface. The FTIR spectra were recorded with the FPA detector at each applied potential ranging from  $-0.2\text{ V}$  to  $+0.8\text{ V}$  and the FTIR chemical maps were then obtained through the integration of the specific spectral bands at particular applied potential. Each potential was applied to the working electrode for 240s before the spectrum was recorded. This allows sufficient time for the system to reach the steady state and ensure that the perturbed ions reach the equilibrium before shifting to the next applied potential. The reference spectrum was recorded initially during the application of the  $-0.2\text{ V}$  potential to the working electrode and used for consequent measurements of the spectra and chemical maps. The resultant spectra are called as subtractively normalized interfacial FTIR (SNIFTIR) spectra. These spectra were collected in the spectral range from  $4000\text{ -- }900\text{ cm}^{-1}$  at a spectral resolution of  $8\text{ cm}^{-1}$  with the 32 scans co-added.

### S1: Spatial resolution of the electrochemical coupled vibrational spectromicroscopy (EVSM)



**Fig. S1:** Illustration of the spatial distribution of the electrochemical coupled vibrational spectromicroscopy technique: A sub-scanned area of the electrode partly covered with polymeric molecules is selected from the optical microscopic image and evaluated for spatial distribution. The black dots correspond to the individual pixels, each composed of single spectrum and the distance between them is  $2.5\ \mu\text{m}$ . Spectra are extracted from three different regions of the microscopic image and each spectrum shows a different level of intensity of the peaks depending on the region from where it is taken. The spectrum from region 1, which is apparently darker and contain larger contents of the polymeric materials show the highest intensity as compared to region 3, containing relatively smaller contents. The spectrum from region 2 shows the intermediate intensity.

**S2:** Testing of the EVSM system by performing the cyclic voltammetry



**Fig. S2:** Cyclic voltammogram of the PANI modified Au mirror electrode performed in the EVSM setup in  $\text{H}_2\text{SO}_4$  ( $0.5 \text{ mol L}^{-1}$ ) in the potential range of -0.2 to +0.8 V. Scan rate =  $50 \text{ mV s}^{-1}$