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Supplementary data

Electrochromic bilayers of Prussian blue and its Cr analogue

Luke Hedley,[1] L. Porteous,[2] David Hutson, [2]Neil Robertson,[1] J. Olof Johansson*[1]

[1]EaStCHEM, School of Chemistry, University of Edinburgh, David Brewster Road, EH9 3FJ, UK

[2]School of Engineering and Computing, University of the West of Scotland, Paisley PA1 2BE, UK

**Corresponding author. Email address: olof.johansson@ed.ac.uk*

AFM measurements

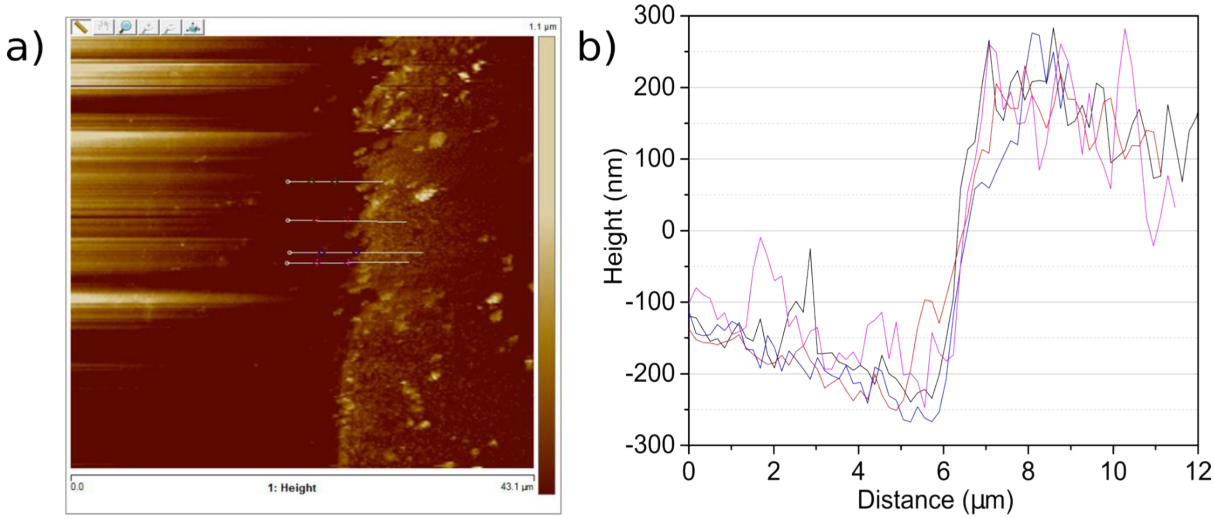

Figure S1: AFM data of a FeCr film grown for 300 s at -0.7 V. a) A razor blade was drawn across the surface of the film to generate a step from the top of the film (right-hand side) down to the surface of the FTO layer (left-hand side). The white lines correspond to the step profiles used to study the step size. b) The various step profiles for the film are shown in the graph and an average was taken. The process was carried out on various FeCr and FeFe films to determine their thickness as a function of deposition time (both deposited directly onto FTO).

EDX

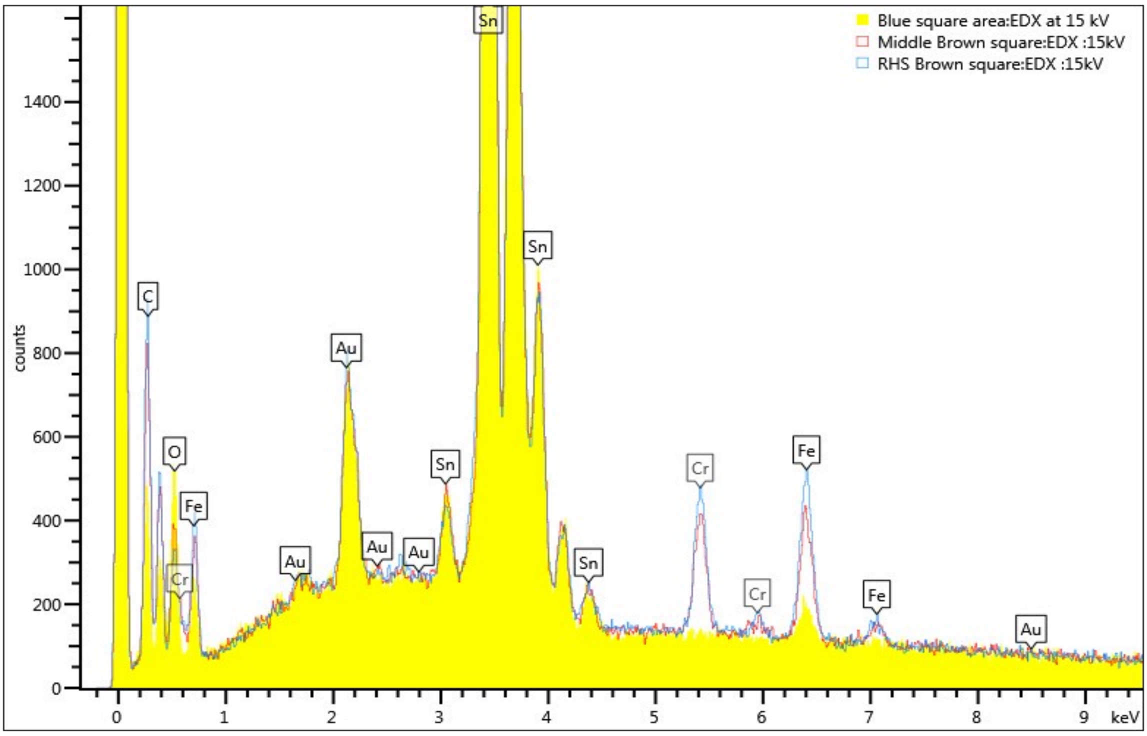

Figure S2: EDX data taken from an FeFe film deposited directly on FTO ("Blue square"), FeCr film ("Middle brown square") and a bilayer film ("RHS Brown square"). The peaks of note are those coming from Fe and Cr ions at 5.4 and 6.4 keV in the FeCr layer, the highlighted yellow area corresponds to the blue FeFe layer. The gold peaks are present to aid with SEM analysis of the films and was added post synthesis.

FeCr film coverage on FTO substrate

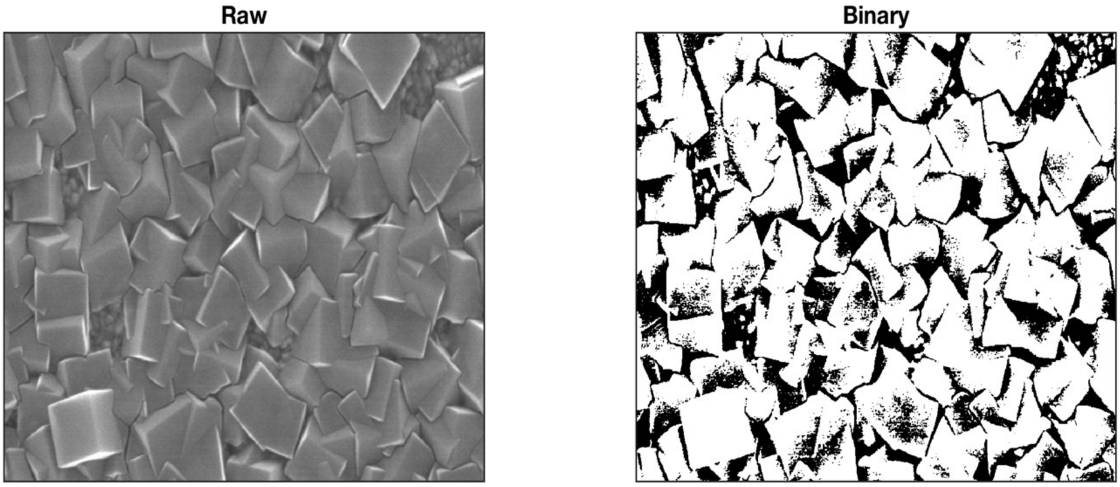

Figure S3: Analysis of surface coverage of FeCr films from raw SEM images (left). The MATLAB image processing toolbox was used to convert the SEM images to binary images to separate the FTO layer (pixel value 0) from the FeCr layer (pixel value 1) (right). The number of pixels with value one was then compared to the total number of pixels to estimate the surface coverage. The threshold between 0 and 1 in the binary image was set manually by carefully comparing to the raw SEM image. The SEM images were recorded with a zero-degree incidence angle to the substrate surface normal. In this analysis, we found that the first FeCr layer covers 70 – 80 % of the substrate area. However, this analysis does not take into account the 3D morphology of the crystal grains, which means that the film surface area is underestimated by the top-view from the SEM images. Therefore, the film-to-substrate ratio should be even larger than that estimated from the SEM images.

Tunnelling AFM (TUNA) measurements

To test the conductivity of the FeCr layer, tunnelling AFM (TUNA) measurements were carried out. Fresh FeCr films were prepared on a FTO/glass substrate under identical conditions to those used for the bilayers. The films were rinsed with deionised water (bubbled with N_2) and dried under N_2 flow. The TUNA measurements were carried out in air using a titanium nitride AFM tip. A voltage of 200 mV was applied between the FTO substrate and the AFM tip. As the tip approached the surface, the current tunnelling through the tip was measured. This therefore made it possible to measure the conductivity of an individual crystal between the FTO and AFM tip. This measurement was carried out on six different positions on the FeCr film. The values were very similar for all positions and an example is shown in Fig. S4. The average peak current for these measurements was 285 ± 50 fA. The size of the FeCr crystal grains was approximately 600x600 nm the height was *ca*. 400 nm. The estimated conductivity was therefore on the order of 10^{-5} to 10^{-6} S/m. Scaling up the measured current for the total (estimated) number of grains in the whole film gives a current on the order of 100 μA, which is comparable to what is measured in the electrochemical measurements.

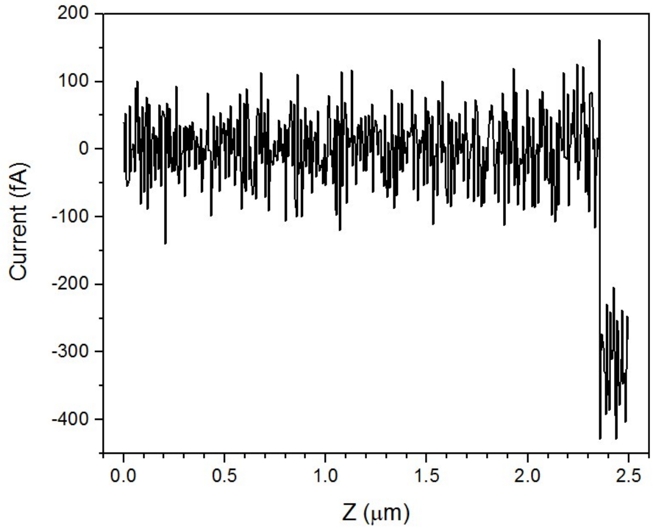

Figure S4: Tunnelling AFM conductivity measurement carried out by applying a voltage bias of 200 mV between tip and surface. The current as a function of distance Z between the tip and surface was measured. Here, Z = 0 corresponds to the beginning of the measurement when the tip is far away from the surface (the surface is close to Z = 2.35 μm). For 6 different positions on the FeCr film the average peak current for these measurements was 285 ± 50 fA.

Electrochromic switching

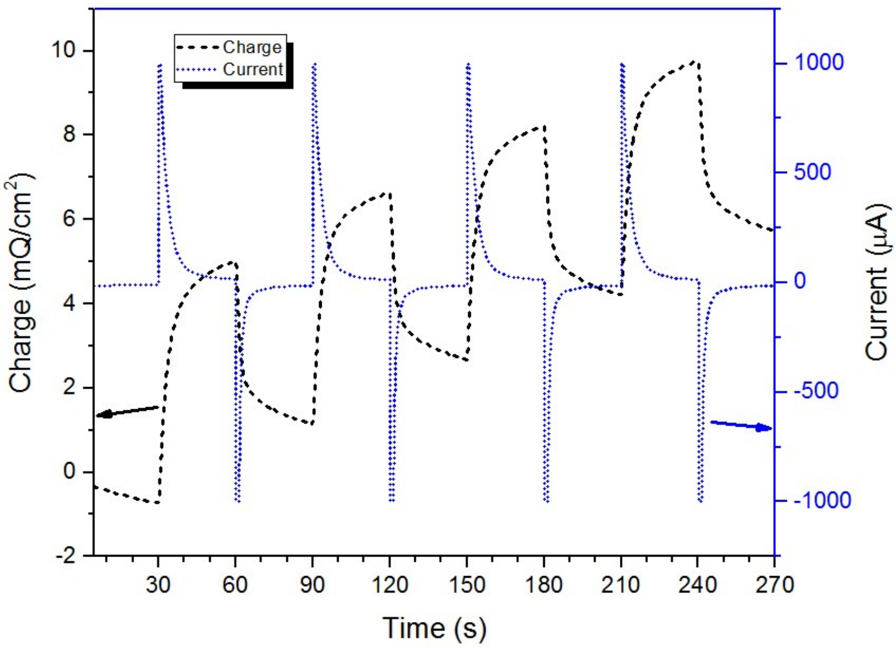

Figure S5: Current and charge data for the electrochromic switching of the FeCr-FeFe bilayer structure. When potentials of 0.5 and -0.2 V are applied there is a large increase in the current flowing through the system, this decreases to 0 as the system nears full oxidation/reduction. Note the gradual increase in the charge flowing through the system while the charge due to the switching increases and decreases with each switch. This is thought to be charging up of the FeCr layer between the electrode surface and the electrochromically active FeFe layer.