

Supporting Information for:

Characterisation of Non-Uniform Functional Surfaces:

Towards Linking Basic Surface Properties with Electrocatalytic Activity

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1. SKP measurements

SKP is a non-contact, non-destructive vibrating capacitor technique which measures the contact potential difference (CPD) between an electrically conductive vibrating reference probe and an electrically conductive sample. Briefly, a conventional SKP used in this work consists of a plane-ended cylindrical electrode vibrating perpendicular to a stationary sample with a frequency ω (Figure S1). In this way, both electrodes form a planar capacitor. If an external electrical contact between the two capacitor plates is formed their Fermi levels start to equalize and the resulting charge flow causes a potential gradient (U_{CPD}). Periodic modulation of the distance between the electrodes, $d = d_0 + \Delta d \sin(\omega t)$ leads to changes in the capacitance, (dC/dt) , thereby causing a so-called Kelvin current (I_{Kelvin}) to flow through the external circuit (Equation S1).

$$I_{Kelvin} = \Delta \Psi_{Sample}^{KP} * (\epsilon * \epsilon_0 * A * \Delta d * \omega) \frac{\cos(\omega t)}{(d_0 + \Delta d \sin(\omega t))^2} \quad (1)$$

where $\Delta \Psi_{Sample}^{KP}$ is the contact potential difference between the Kelvin probe and the sample, ϵ is the dielectric constant of the medium, ϵ_0 is the vacuum permittivity, A is the active tip area, Δd is the tip oscillation amplitude, ω is the tip oscillation frequency, d_0 is the main tip-to-sample distance

In the conventional nulling technique used in this work a variable backing potential (U_0) is adjusted until the Kelvin current (I_{Kelvin}) vanishes. When U_0 is equal to $-U_{CPD}$, the electric field between the capacitor plates is compensated and a zero output signal is recorded (Equation S2). In this case, the contact potential difference between the Kelvin probe and the sample is equal to the applied compensation voltage.

$$I_{Kelvin} = (\Delta \Psi_{Sample}^{KP} - U_0) * \frac{dC}{dt} = 0, \quad \text{if } \Delta \Psi_{Sample}^{KP} = U_0 \quad (2)$$

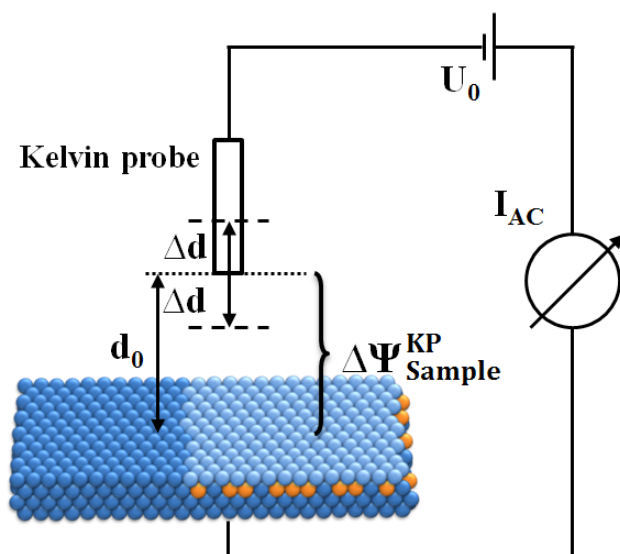


Figure S1. Schematic representation of the set-up for the measurement of the contact potential difference ($\Delta\Psi_{\text{Sample}}^{\text{KP}}$ – the contact potential difference between the Kelvin probe and the sample, d_0 – main tip-to-sample distance, Δd – tip oscillation amplitude, U_0 – variable backing potential, I_{AC} – Kelvin current).

2. The work function and CPD

The work function (Φ) is defined as the minimum work needed to extract electrons from the Fermi level of a solid carrying no net charge [1]. It is assumed that the electron is removed to a position just outside the sample (end position) where the interaction between the solid and the electron is no longer existent, i.e. the contribution from the image forces is eliminated, while the dimension of the surface is large compared to the distance between the surface of the solid and the end point (Figure S2A).

Connection of two solids with different work functions Φ^{A} and Φ^{B} leads to a flow of electrons until a uniform redistribution of electrons at the Fermi levels of both solids is reached. As the work functions of both solids are different, the equilibration of Fermi levels causes charging of one solid relative to the other. This leads to the observation of a Volta potential difference which is also called contact potential difference (CPD, denoted as $\Delta\Psi$) and is equivalent to the difference in the work functions of the two solids. As the work function of the solid is an intrinsic parameter, it remains constant after connection of two different solids while the

electrochemical potential of the electrons within both phases become identical (Fig. S2B). Therefore, as the change of the work function of the SKP-SECM tip during the experiment remains negligibly small, the observed changes of the CPD are related to changes of the work function of the sample as a consequence of its modification by intercalation of Cu.

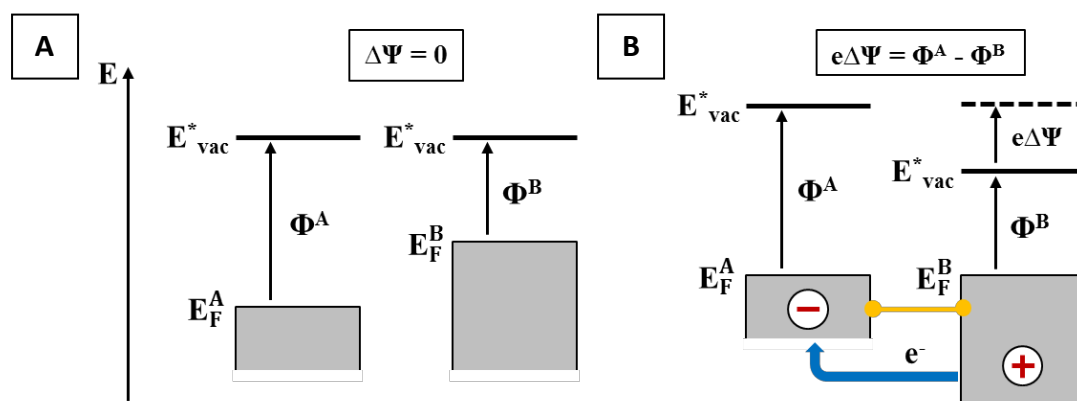


Figure S2. Schematic representation of the relationship between work function (Φ) and contact potential difference ($\Delta\Psi$).

[1] IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught, A. Wilkinson. Blackwell Scientific Publications, Oxford (1997)