Supplementary information for

Nanoscale Electrochemical Movies and Synchronous Topographical Mapping of Electrocatalytic Materials

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Supplementary Movie Captions:

Movie S1. Spatially-resolved electrochemical movie (2500 pixels over a 2.5×2.5 μm scan area, 400 pixels μm^{-2}, 384 image frames) obtained with the voltammetric hopping mode SECCM protocol, visualizing HER activity on a cleaved MoS_2 surface. The nanopipet probe (diameter, $d \approx 30$ nm) contained 100 mM $HClO_4$. Experimental parameters were as follows: voltammetric scan rate (v) = 10 V s^{-1}, total scan time (t_s) = 635 s (*ca.* 0.25 s per pixel), approach voltage (E_a) = –0.947 V, initial potential (E_i) = 0.053 V and final potential (E_f) = –0.947 V (all vs. RHE). The data presented are not interpolated.

Movie S2. Spatially-resolved electrochemical movie (2520 pixels over a 3.5×1.8 μm scan area, 400 pixels μm^{-2}, 230 image frames) obtained with the voltammetric hopping mode SECCM protocol, visualizing ORR/HER activity on GC-supported AuNCs. The nanopipet probe ($d \approx$ 30 nm) contained 100 mM H_2SO_4. Experimental parameters were as follows: v = 10 V s^{-1}, t_s = 671 s (*ca.* 0.27 s per pixel), E_a = –0.708 V, E_i = 0.142 V and E_f = –0.458 V (all vs. RHE). The data presented are not interpolated.

Supplementary Figures:

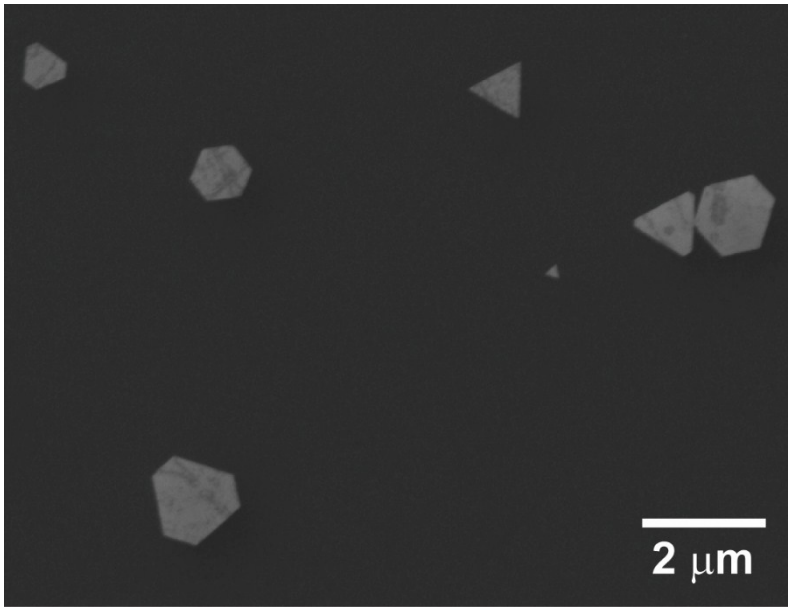

Figure S1. A **r**epresentative SEM image of the two-dimensional (2D) Au nanocrystals (AuNCs), supported on glassy carbon (GC). The AuNCs range in size from *ca.* 100 nm to >1 μm.

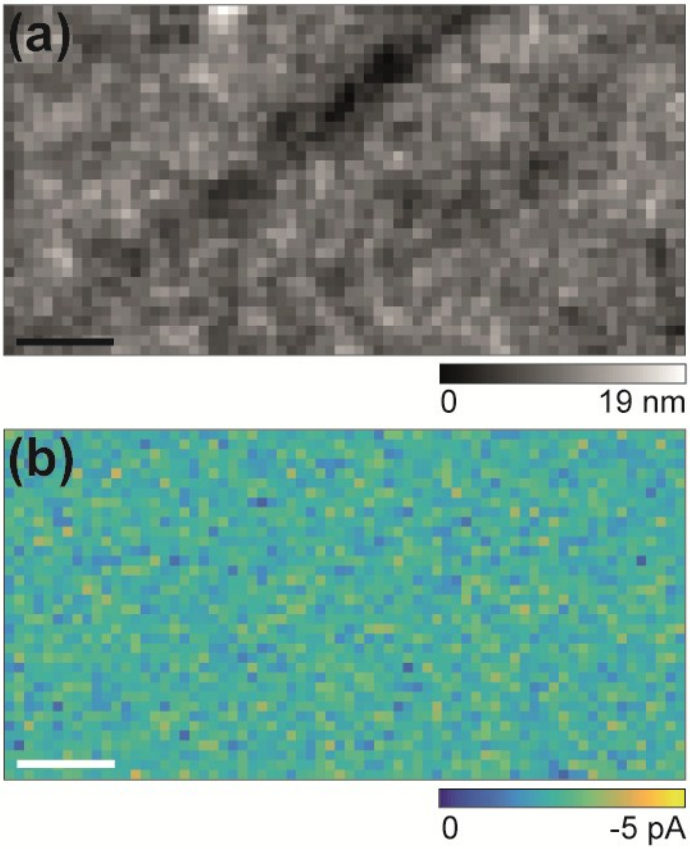

Figure S2. (a) Topographical and **(b)** spatially-resolved electrochemical maps (2520 pixels over a 3.5×1.8 μm scan area, 400 pixels μm^{-2}) obtained with the voltammetric hopping mode SECCM configuration, obtained on a GC support surface. The nanopipet probe ($d \approx 30$ nm) contained 100 mM H_2SO_4. The electrochemical map was obtained at –0.43 V vs. RHE. Experimental parameters are as follows: $v = 10$ V s^{-1}, $t_d = 260$ μs, $t_s = 671$ s (*ca.* 0.27 s per pixel), $E_a = -0.708$ V, $E_i = 0.142$ V and $E_f = -0.458$ V (all vs. RHE).

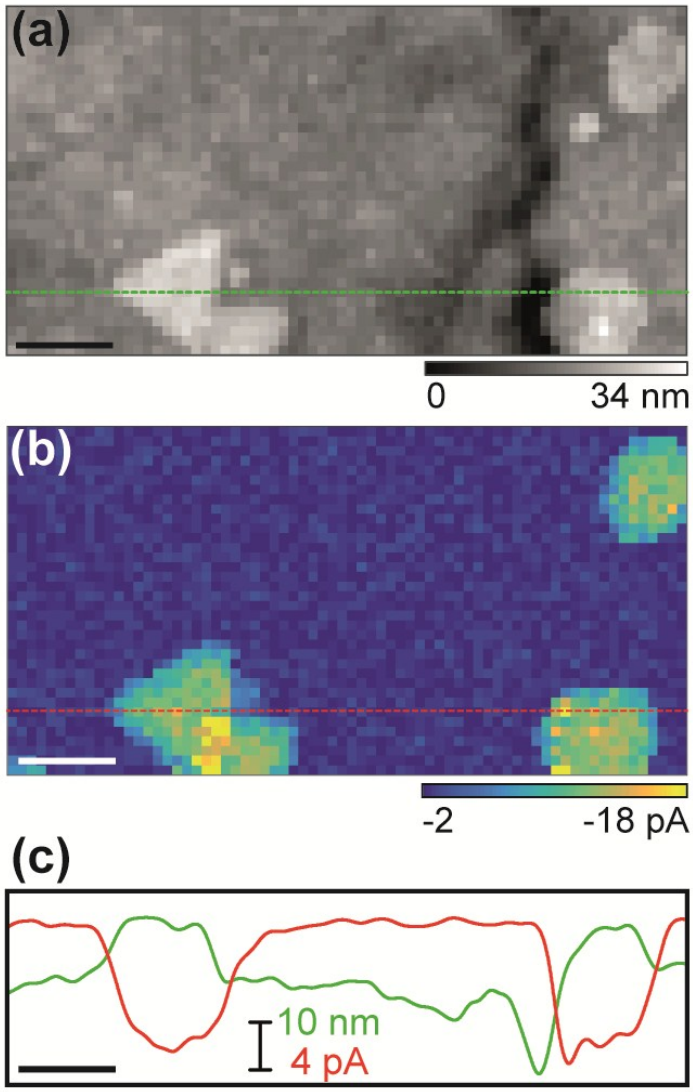

Figure S3. (a) Topographical and **(b)** spatially-resolved electrochemical maps (2520 pixels over a 3.5×1.8 μm scan area, 400 pixels μm^{-2}) obtained with the voltammetric hopping mode SECCM configuration, visualizing ORR/HER activity on GC-supported AuNCs. The nanopipet probe ($d \approx 30$ nm) contained 100 mM H_2SO_4. The electrochemical map was obtained at –0.43 V vs. RHE. **(c)** z-position and i_{surf} line scan profiles of the area indicated by the green and red dashed lines in **(a)** and **(b)**, respectively. 0 nm and 0 pA are the bottom-left and top-left corners of the plot, respectively. Experimental parameters are as follows: $v = 10$ V s^{-1}, $t_d =$ 260 μs, $t_s = 671$ s (*ca.* 0.27 s per pixel), $E_a = –0.708$ V, $E_i = 0.142$ V and $E_f = –0.458$ V (all vs. RHE). All *xy* scale bars indicate 500 nm. The data presented in **(a)** and **(b)** are not interpolated.

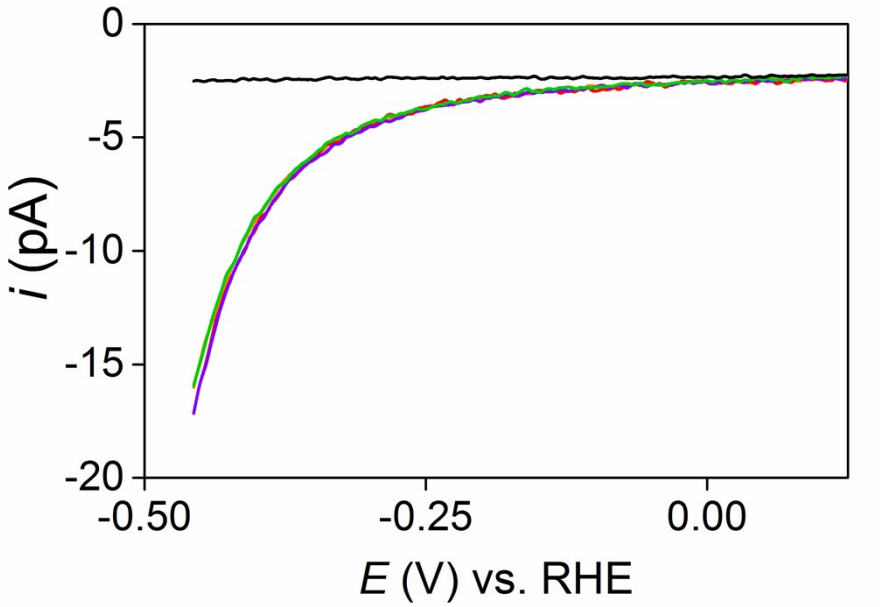

Figure S4. Average LSVs obtained on GC (black trace, $N = 138$, selected at random across the surface), AuNC-1 (orange trace, $N = 68$), AuNC-2 (red trace, $N = 35$), AuNC-3 (purple trace, $N = 74$) and AuNC-4 (green trace, $N = 56$), labelled in Figure 4c of the main text. Experimental parameters are as follows: Experimental parameters are as follows: $v = 10$ V s^{-1}, $t_d = 260$ µs, $E_i = 0.142$ V and $E_f = -0.458$ V (both vs. RHE).