Metal Support Effects in Electrocatalysis at Hexagonal Boron Nitride

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Section S1. Materials and Methods.

Chemicals and materials. Copper (Cu) foil was purchased from Alfa Aesar (purity 99.8 %, 0.025 mm thick). Perchloric acid (HClO₄, 70%) and ammonia borane (NH₃-BH₃, 97%) were purchased from Sima-Aldrich and used as received. All aqueous solutions were prepared from ultrapure water (18.2 M Ω cm resistivity at 25 °C) produced by a Purite Integra HP system (U.K.). The silver/silver chloride (Ag/AgCl) quasi reference counter electrode (QRCE) was prepared by anodic polarization of an Ag wire (0.125 mm diameter, Goodfellow, 99.99 %) in saturated KCl solution. The QRCE potential was calibrated against a commercial saturated calomel electrode (SCE) in 0.1 M HClO₄ solution after each experiment, and was found to possess a stable potential¹ of *ca*. 0.21 V vs. SCE.

Preparation of h-BN. Hexagonal boron nitride (h-BN) was grown on polycrystalline Cu foil with a thickness of 25 μ m by the atmospheric pressure CVD method.² In order to achieve this, the Cu foil was first chemically polished using a solution of 0.4 M FeCl₃ in 0.8 M HCl. After drying with compressed N₂ gas, the polished foil was loaded into the center of a 25 mm diameter tube furnace, before being pumped to a pressure of 15 mTorr. After pre-annealing at 1015 °C for 30 min with a mixture gas of 16 standard cubic centimeters (sccm) of H₂ (99.99 %) and 260 sccm of Ar (99.99%), 1 mg ammonia borane was placed in a specially designed boat and loaded in the upstream of the CVD growth tube as the precursor of h-BN. The precursor temperature was controlled by a heating belt around the tube, separated from the heating zone of the furnace. The growth of h-BN was achieved in 60 min at 1065 °C. After growth, the system was quickly cooled down to <200 °C under the same gas flow. The rear surface of the sample was fixed to an evaporated Au (300 nm) film on SiO₂/Si wafer by using silver paint (Agar Scientific, Ltd, U.K.). The whole sample was then connected to a copper wire for subsequent electrochemical measurements.

For preparing the transferred h-BN/Au using polymethyl-methacrylate (PMMA) method,^{3,4} a PMMA (AR-P. 679.04, ALLRESIST, GmbH) layer was spin-coated on the surface of as-grown h-BN on Cu foil at 4000 rpm for 50 s. The h-BN film is released by protecting the h-BN with PMMA and etching the underlying Cu foil with an aqueous solution of 0.4 M FeCl₃ for 5 h. After that, the film was washed by floating on deionized water. Subsequently, the film could be transferred on the Au substrate, which consisted of an evaporated Au film (300 nm) on SiO₂/Si. The sample was then heated to 150 °*C* to remove any adventitious water, as well as promote good adhesion of the film to the Au substrate. Following this, the sample was immersed in acetone solution to dissolve the PMMA layer and was then annealed under nitrogen gas at 350 °*C* for 5 min." Similar to above, the sample was connected to a copper wire for electrochemical characterization. After scanning (see below), the h-BN/Cu and h-BN/Au substrates were imaged using a ZEISS GEMINI 500 FE-SEM, at 2 keV with the InLens mode.

Fabrication and characterization of nanopipets. Single-barrel nanopipets were pulled from glass capillaries (GC120F-10, Friedrich & Dimmock, Inc, U.S.A., with filament) using a P-2000 laser puller (Sutter Instruments, USA) with a two-step protocol. For the first step, the parameters were heat 330, filament 3, velocity 30 and delay 220. For the second step, the parameters were heat 350, filament 3, velocity 40, delay 180 and pull 120. The dimensions of the nanopipet orifice were measured using field emission scanning electron microscopy (FE-SEM) on a Zeiss Supra 55VP system, which was operated at an accelerating voltage of 2 kV. Representative images of the nanopipet probes used in this work are shown in Figure S1. After fabrication, the nanopipet probes were back filled with 0.1 M HClO₄ solution and a layer of silicone oil (DC 200, Fluka) sequentially using a MicroFil syringe (World Precision Instrument Inc., U.S.A.), before inserting the Ag/AgCl QRCE (detailed above) for electrochemical measurement.

The instrumental setup of single-barrel SECCM has previously been reported^{5,6} and is shown in the main text, Figure 1a. During operation, the prepared nanopipet probe (detailed above) was mounted on a z-piezoelectric positioner (P-753.3CD, Physik Instrumente), and the substrate (i.e., h-BN/Cu or h-BN/Au) was mounted on an xy-piezoelectric positioner (P-622.2CD, Physik Instrumente). SECCM was operated in the voltammetric hopping mode, as previously reported.^{7,8} In this mode, the nanopipet probe is approached to the surface of interest at a series of pre-defined locations in a grid. During z-approach, contact between the meniscus (droplet) cell located at the end of the nanopipet probe and substrate surface (note that the nanopipet itself did not make contact) was detected through surface current (i_{surf}) feedback, using a threshold current of 1 pA herein. Upon each landing, a linear-sweep voltammogram (LSV) measurement was carried out at a voltammetric scan rate (v) of 1 V/s. After each measurement, the nanopipet probe was retracted and moved laterally (*i.e.*, in xy space) to the next point that was located at a pre-defined distance away ('hopping distance', equal to 500 nm herein), where the same procedure was implemented. The potential applied $(-E_{app})$ to the QRCE (with respect to the ground) was controlled, and h-BN sample (working electrode, ground) current, namely i_{surf} , was detected. The current was measured every 4 μ s, which was averaged 513 times to give a data acquisition rate of 2052 µs per point. The current signal was filtered using an 8th order low-pass filter at a time constant of 2 ms.

To perform LSV measurements using SECCM in the absence of air, the nanopipet tip and h-BN/Cu sample were placed in an environmental chamber that was constantly purged with humidified argon gas, as previously reported.^{9,10}

Data acquisition and fine control of all the instruments were obtained by using an FPGA card (PCIe-7852R) controlled by a LabVIEW 2016 (National Instrument, U.S.A.) interface running the Warwick Electrochemical Scanning Probe Microscopy (WEC-SPM,

www.warwick.ac.uk/electrochemistry) software. After collection, the raw data were processed with Matlab R2015b and OriginPro 2016 software packages.



Figure S1. Representative FE-SEM images of the end (tip) of single-barrel nanopipets used in experiments on the **(a)** h-BN/Cu and **(b)** h-BN/Au substrates.



presence and absence of air



Figure S2. Typical LSVs at the surface of h-BN/Cu obtained from the (a) 12 points (transparent blue) in the presence of air and representative average LSV (blue), and (b) 12 points (transparent red) in the environmental chamber (*i.e.*, absence of air) and representative average LSV (red). (c) HER activity comparison between the average LSVs obtained in the presence (blue) and absence (red) of air. Note that all measurements were performed with the same probe. These LSVs were obtained from a 0.1 M HClO₄ solution at a voltammetric scan rate (v) of 1 V s⁻¹.

Section S3. LSVs extracted from the exposed Cu and Au substrates during SECCM.



Figure S3. Representative linear sweep voltammograms (LSVs) obtained the (a) Cu and (b) Au support substrates during SECCM. Also shown in (b) is an average LSV (red trace) obtained from all points on exposed Au. These LSVs were obtained from a 0.1 M HClO₄ solution at a voltammetric scan rate (v) of 1 V s^{-1} .

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