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Page No. – Page No.

Title

Supplementary Materials:

Photoelectron spectroscopy at the graphene-liquid interface reveals the electronic structure of an electrodeposited cobalt/graphene electrocatalyst

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Electron transparent membrane fabrication

Graphene was grown by chemical vapor deposition (CVD), in an Aixtron BM Pro (4 inch) reactor, using 25 μm thick Cu foil (Alfa Aesar, 99.8%) as the catalyst and CH_4 (diluted in Ar and H_2) as the precursor at 1050°C ^[17]. The CVD grown graphene is polycrystalline with relatively large grain sizes of $\sim 20\mu\text{m}$, as confirmed by scanning electron microscopy (SEM) of a sample for which growth was interrupted prior to complete coverage. A polymer support (polymethylmethacrylate, 4 wt.% in anisole, 950 k molecular weight) is spin coated onto the surface of the graphene covered Cu foil, and floated on a 0.05M aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ to remove the copper foil. The polymer supported graphene is then rinsed in deionized water and transferred onto another graphene covered Cu foil. This is dried at $\sim 50^\circ\text{C}$ for 5 min, floated again on the $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution to remove the Cu, and then rinsed in deionized

water. The polymer supported bilayer graphene (BLG) is lifted onto perforated TEM membranes (PELCO[®] Holey Silicon Nitride Support Films), consisting of a 200 nm thick Si₃N₄ layer with a 40 x 40 array of 1 μm circular pores at a 2 μm pitch, with a Cr(3 nm) adhesion layer and Au(30 nm) conductive layer thermally evaporated on top. After drying, the polymer is then dissolved by immersion in acetone to leave BLG completely covering the array of pores (as confirmed by SEM and Raman mapping). The presence of tears and holes due to the transfer process is suppressed by the deposition of the second graphene layer. Figure S1 shows the Raman characterization of such samples including spatial mapping of the G and 2D band intensities. The presence of the G peak at ~1580 cm⁻¹ and 2D peak at ~2700 cm⁻¹ across the area of the membrane confirms that complete coverage with BLG is achieved^[17]. The presence of only a small D peak at ~1350 cm⁻¹ (<5% of the G peak intensity), confirms the BLG is of high-quality with a low density of defects in the graphene lattice. The relatively small hole size of 1 μm reduces the likelihood of the graphene breaking during the removal of the support polymer and when maintaining a ~1 bar pressure difference between the liquid and the vacuum chamber. The use of the Au layer has numerous advantages: Firstly, it enhances the electrical contact to the electrode. Secondly, it minimizes the intercalation of water between the graphene and the substrate^[31,32] due to the hydrophobicity of gold^[33] in spite of the reported hydrophilicity of UHV-clean gold^[34]. Finally, it passivates the Si₃N₄ from damage induced by the formation of radicals in the radiolysis process^[35].

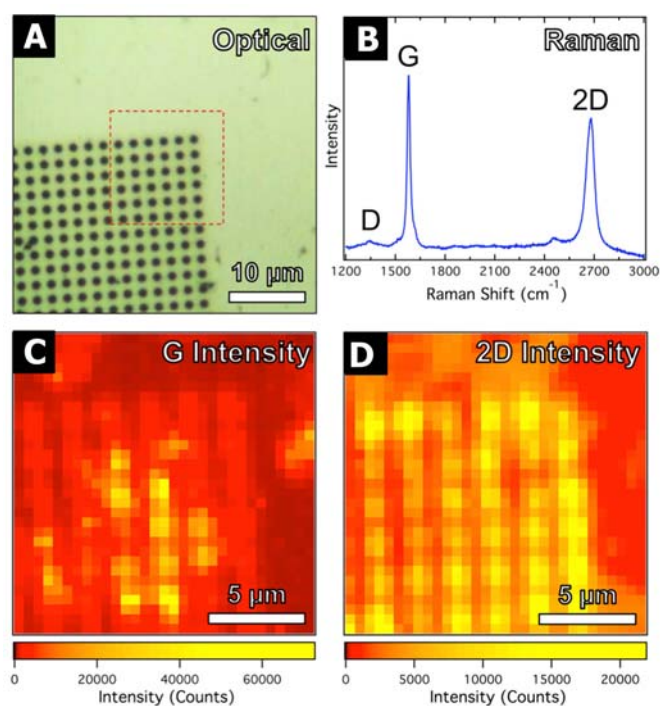


Figure S1. (A) Optical image of the BLG coated Si₃N₄ grid. (B) Representative Raman spectrum of BLG suspended over a hole in the Si₃N₄ grid. (C) G band mapping and (D) 2D band mapping. Raman spectroscopy was performed using a Renishaw Raman InVia Microscope, with 100x objective and 532 nm excitation.

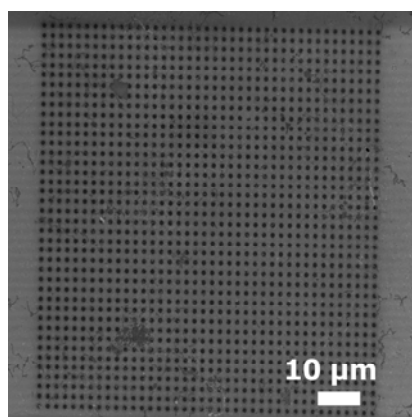


Figure S2

SEM image of the BLG coated Si_3N_4 grid, the grid size is $80\ \mu\text{m} \times 80\ \mu\text{m}$ and contains an array of 40×40 holes of $1\ \mu\text{m}$ diameter.

Electrochemical cell detection tests

Iridium nanoparticles 2-5 nm in size (see TEM measurements in figure S4b) were sputter-deposited on the graphene layer which was placed on top of a Pd foil (figure S4a) to evaluate the photoelectron transmission of the BLG. The XPS peaks obtained from the Pd 3p, Ir 4f and Au 4f excitations, with photoelectron kinetic energies of 1000 eV (Figures S4c and S4d), demonstrate excellent photoelectron transmission through BLG. These measurements were performed at the ISSIS beamline of BESSY II (Germany). The membrane was subsequently mounted in the liquid cell and filled with ultrapure MilliQ-water. The liquid flow cell (figure S3) was operated inside a vacuum chamber with a pressure of $\sim 10^{-7}$ mbar, while aqueous solutions circulated on the back side of the membrane. The cell holds three electrodes: Pt counter electrode, Ag/AgCl reference electrode and the working electrode is the graphene membrane that is mounted in the cell using a special sample holder. The main body of the cell is made of PEEK and provides liquid inlet and outlet. With this setup we can investigate electrochemical reactions using XPS under aqueous conditions (~ 1 bar), in a flow-through scheme without the need for high kinetic energies of several keV. Iridium nanoparticles were deposited on the backside of graphene used to test the XPS detection under aqueous conditions. The intensity of the Ir 4f peaks is weak at photoelectron KEs below 500 eV (figure S5a, top curve), but quite intense at higher KE of 950 eV (figure S5a, bottom curve). This provides a reference for the attenuation of photoelectron intensity through 2 layers of graphene, which is consistent with reported values of the mean free path for 500eV photoelectrons^[36]. Subsequently, the pure water was replaced by a 10 mM KOH solution and the C 1s and K 2p spectra recorded at KEs of 450 eV and 950 eV (figure S5b). The observation of K peaks demonstrates that with this setup we are able to detect ions concentrations as low as 10 mM. After the measurement, flowing MilliQ-water through the cell again caused the K XPS signal to disappear, as shown in figure S5b, which confirms that no significant leakage of solution to the vacuum side of the membrane through potentially defective holes has occurred.

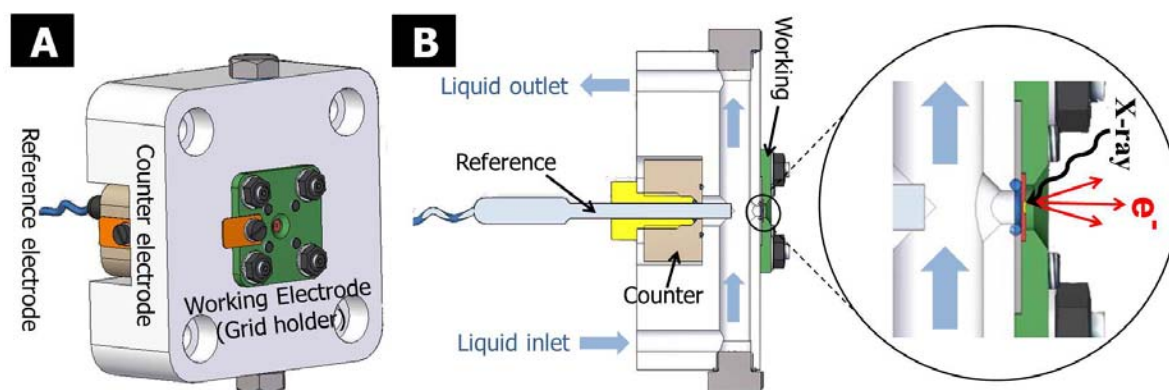


Figure S3

(A) Sketch of the liquid flow cell with the main body made of PEEK and with a stainless-steel 3 mm diameter wafer holder. (B) Liquid flow cell cross-section: The blue arrows indicate the electrolyte flow. The cell has three electrodes counter, working and reference. The working electrode is transferred directly onto the grid.

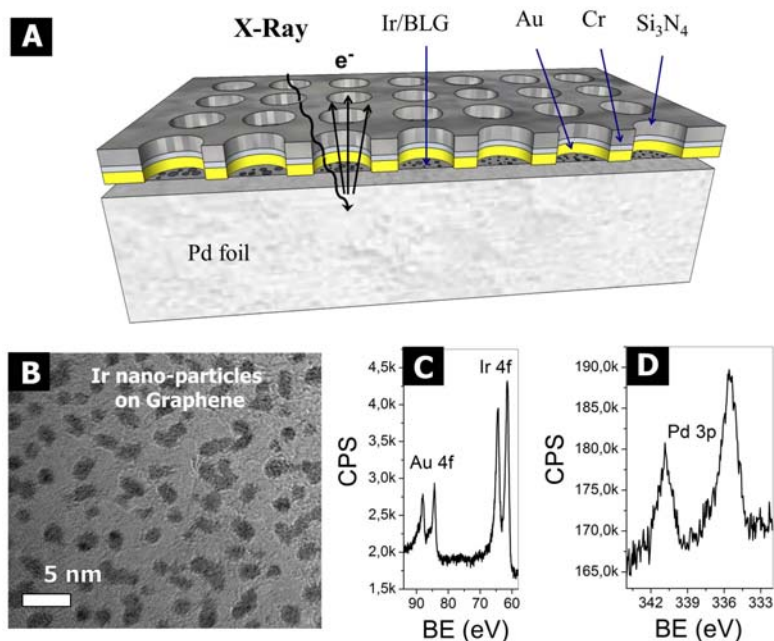


Figure S4

(A) Schematic drawing of the grid covered by graphene with sputtered Ir nano-particles on top of a Pd foil. (B) TEM of the iridium nanoparticles sputtered onto the graphene membrane. Their size ranges from 2-5 nm. The coverage is approximately 30 % of the total area. (C) Ir 4f XPS spectra of the nanoparticles sputtered on the graphene membrane and the (D) Pd 3p of a palladium foil located underneath (spectra were recorded at 1000 eV KE).

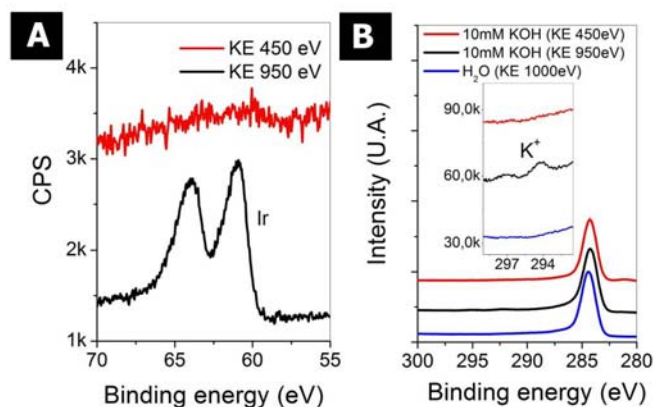


Figure S5

(A) XP spectra of Iridium nanoparticles deposited on the solution side of the graphene membrane. Ir 4f peaks with 950 eV and 450 eV KE are shown in the presence of deionised water. Notice the higher attenuation of the low kinetic energy peaks (B) C 1s and K 2p spectra in 10 mM KOH (red 450 eV and black 950 eV KEs curves) and in deionized water (blue curve at 1000 eV KE).

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