Supplementary Information

General Methods

Nanoporous anodic alumina-based gas diffusion layers for the electroreduction of CO_2

María Pilar Montero-Rama,[b] Domenico Grammatico,[c] Janine Lichtenberger,[c] Virginie Pellerin,[a] Emilio Palomares,[d,e] Laurent Billon[a], Lluis F. Marsal,*[b,e] and Aurelien Viterisi*[a]

[a]The Institute of Analytical Sciences and Physical Chemistry for Environment and Materials (IPREM),
Technopole Hélioparc, 2 avenue du Président Pierre Angot
64053 PAU CEDEX 09

[b]Departament d'Enginyeria Electrònica Elèctrica i Automàtica
Universitat Rovira i Virgili
Avinguda Països Catalans 26, 43007, Tarragona, Spain

[C] AIT Austrian Institute of Technology, Center of Energy – Power and Renewable Gas Systems, Giefinggasse 4, 1210, Vienna, Austria

[d]Institute of chemical research of Catalonia (ICIQ)
Avda. Països Catalans, 16
43007 Tarragona
[e]ICREA. Passeig Lluís Companys, 28, E-08010. Barcelona. Spain.

Experimental section

MATERIALS

Trichloro(1H,1H,2H,2H-perfluorooctyl)-silane was purchased from Aldrich and kept in a N2 atmosphere glove box. distilled under reduced pressure. Dimethyl sulfone (standard for quantitative NMR, TraceCERT@), and potassium bicarbonate (ACS reagent, 99.7%, powder, crystals, or granules) were purchased from Sigma-Aldrich. Acetone (≥99.9%, SigmaAldrich), Ethanol (>99.5%, Pharmpur®, Ph Eur, BP, NF, Sharlab were used without further purification. CDCl3 (99.8%) and D_2O were purchased from Innovachem. Aluminium sheets (99.99+%) were purchased from Advent Research Materials (UK). Deionized water (DI) refers to ultra-pure (Milli-Q) water. All electrolytes were prepared using Milli-Q water.

CHARACTERIZATION

NMR

The ^{1}H-NMR analyses were conducted using a Bruker Ultrashield spectrometer with a ^{1}H frequency of 400 MHz.

SEM-EDS

Scanning electron microscopy images of GDLs were performed ona Field Emission Scanning Electron Microscope (FESEM) (Scios 2, Thermo Fisher Scientific, Waltham, MA, USA) at a chamber pressure of 1×10^{-4} Pa with electron beam voltages set at 5 kV. An Everhart-Thornley detector (ETD) was used to detect secondary electrons (SE)

Scanning electron microscopy of GDEs (SEM) was performed on an APREO 2 SEM (Thermo-Fisher Scientific) with an EDX XFlash 6-100 (Brüker) for qualitative and quantitative elemental measurements. Measurements were carried out using a 2.00 kV accelerating Voltage and 25pA for the beam current.

FABRICATION

Anodization procedure

NAA samples were prepared following the two-step anodization process described by Masuda et al. in order to obtain hexagonally ordered nanoporous alumina membranes. Aluminium discs (0.5 mm of thickness and 20 mm of diameter) were cleaned with acetone deionised water and ethanol in order to remove residual impurities and grease. Aluminium substrates were electropolished in a solution 4:1 v/v of ethanol and perchloric acid ($HClO_4$, 70.0-72.0%, Sigma-Aldrich) at 20 V and at a temperature between 0 and 15 °C for 6 min, under stirring at 450 rpm. The first anodization step was carried out using H_3PO_4 (1% wt.) (85 wt% in H_2O) solution as the electrolyte. The first step was initiated under mild electrochemical conditions, at an anodization potential of 175 V and at an electrolyte temperature of -5 °C, which induces the formation of a protective oxide layer that prevents sample burning. After 3 h, the anodization voltage was ramped up to 195 V at a rate of 0.01 V/s. The anodization was continued for 12 h at 195 V at the same temperature. Subsequently, the NAA layer was completely removed by chemical etching in a solution consisting of an acid mixture of chromium oxide ($CrO_3 > 99.0\%$, Emsure) and H_3PO_4 for 90 min. at 70 °C. A second anodization step was conducted in a solution of H_3PO_4 (1% wt.) at an anodization potential of 195 V and at a temperature of -6.5 °C. The total charge employed in this second anodization step was of 450 C, yielding a membrane of approximately 120 μm with an area of 1.2 cm^2. Pores with diameters of about 150 nm were obtained.

Partial barrier layer etching

Following the second anodization step, all NAA samples were immersed in an etching solution (H_3PO_4, 4% wt.) at temperature of 35 °C and for a time of 1 h. With this chemical etching the thickness of the barrier layer was reduced from 200 nm in the as-produced samples to a final thickness of approximately 80 nm. Notice that this process also results in a reduction of the pore wall thickness, but only partially in order to maintain the structural integrity of the porous structure.

Selective dissolution of the barrier layer

To obtain open-through NAA membranes, the aluminium substrate at the bottom of the samples was dissolved using a mixture of HCl (37 %) and $CuCl_2$ solution at room temperature for 8 min. Subsequently, the barrier layer was selectively etched by placing the substrates in a two-cell compartment vessel, in which the bottom part of the substrates (barrier layer side) was brought into contact with the etching solution (4 wt% H_3PO_4) and the other was filled with DI water. The substrates were kept in the etching bath for 2h30 minutes at 35 °C, after which they were thoroughly rinsed with DI water.

Metal deposition procedure

Sputter deposition was performed in a Leybold Univex sputter system with a base pressure of 1×10^{-7} mbar. Substrates were sputtered in direct current (DC) magnetron mode from a 4-inch in diameter Ag or Cu target at a process pressure of 2 μbar, and 5 μbar, respectively, in Ar atmosphere. The sputter power was set to 80 W for Ag, yielding a deposition rate of 0.28 nm/s, while a power of 120W was used for Cu yielding a deposition rate of 2.3 nm/s. The sputter deposition rates were determined by a surface profilometer (KLA-Tencor, Alpha-Step IQ), measuring the step height.

Flow Cell electrochemical characterisation

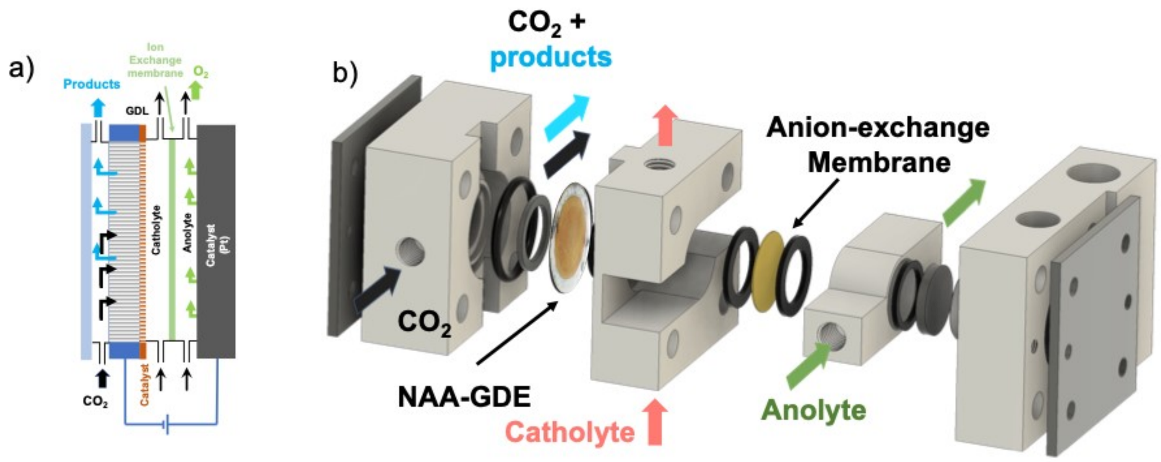

Figure S1: a) General scheme of the flow cell electrolyzer functioning principle b) 3D printed Flow Cell design showing the NAA-GDE placed in the cathode compartment.

Chronopotentiometry experiments were performed on a custom-made Flow cell (Figure S1). It was designed to fit a 3cm² NAA-GDE with a window of 1cm² to the catholyte compartment. The anode was a platinum-coated titanium electrode, and the potential was measured using a micro Ag/AgCl electrode (3M KCl). The 2 electrolyte compartments were separated by a Fumasep FAB-PK membrane (AEM). The catholyte and anolyte consisted of $KHCO_3$ (1M) circulated at a flow rate of 2.5mL/min using a peristaltic pump. The CO_2 flow rate was fixed at 10 mL/min using a Mass Flow Controller (Bronkhorst EL-FLOW prestige FG-201CV).

Gas quantification

Permanent gases were identified and quantified using gas chromatography (GCMS-QP2010-plus, Shimadzu, Japan) equipped with a micropacked column (ShinCarbon ST, 2m; 0.53 mm, mesh80/100, Restek, USA) for permanent gases separation. Helium (6.0, Alphagaz 2, AirLiquide) was used as carrier gas. A Dielectric-Barrier Discharge Ionisation Detector (BID, Shimadzu, DL < 0.1ppm) was used to quantify all permanent gases (H_2, CO, Methane, Ethane, ethylene) with a range of calibration curves made from 0.1, 1 and 10% standard mixtures of H_2, CO, CH_4, C_2H_4 and C_2H_6 in CO_2 with at least 4 points for each calibration curve ($R^2>0.98$). A high linearity is observed between calibration curves indicative of an accurate quantification method. Sampling from the electrolysis cell's headspace was carried *via* a proprietary automated-sampling system operating solenoid valves at timed intervals transferring a sample of the cell's head space to a GC-sample loop (500 µL) followed by the subsequent injection to the GC column.

Faradaic efficiency was obtained by direct quantification of the gas products:

$$Faradaic\ efficency\ (\%) = \frac{Q_{exp}}{Q_{theo}} \times 100 = \frac{z \times n \times F}{Q} \times 100.$$

Equation S1

Where z is the number of electrons involved in the reaction, n the number of moles of generated product, F the faraday constant and Q the charge passed during the catalytic experiment.

Liquid products

After each experiment, the electrolyte from the cell was replaced and analyzed by quantitative NMR. Quantitative spectra were recorded following a procedure based on an article from T. Chatterjee et al.[2], employing a water suppression method. The measured spectra consisted of 512 scans with a delay time of 25 seconds (T1= 5s), and $DMSO_2$ was used as an internal standard for quantification. The NMR tubes were prepared by mixing 392 µL of the electrolyte, 40 mL of a 4mM $DMSO_2$ solution, and 48 µL of D_2O. The chemical shifts were calibrated based on the peak of the standard at 3.1 ppm. The following equation was used to quantify the liquid products:

$$C_{product\ of\ interest,\ tube} = C_{internal\ standard,\ tube} \frac{\frac{I_{product\ of\ interest}}{H_{product\ of\ interest}}}{\frac{I_{internal\ standard}}{H_{internal\ standard}}}$$

Equation S2

FE-SEM images of GDLs

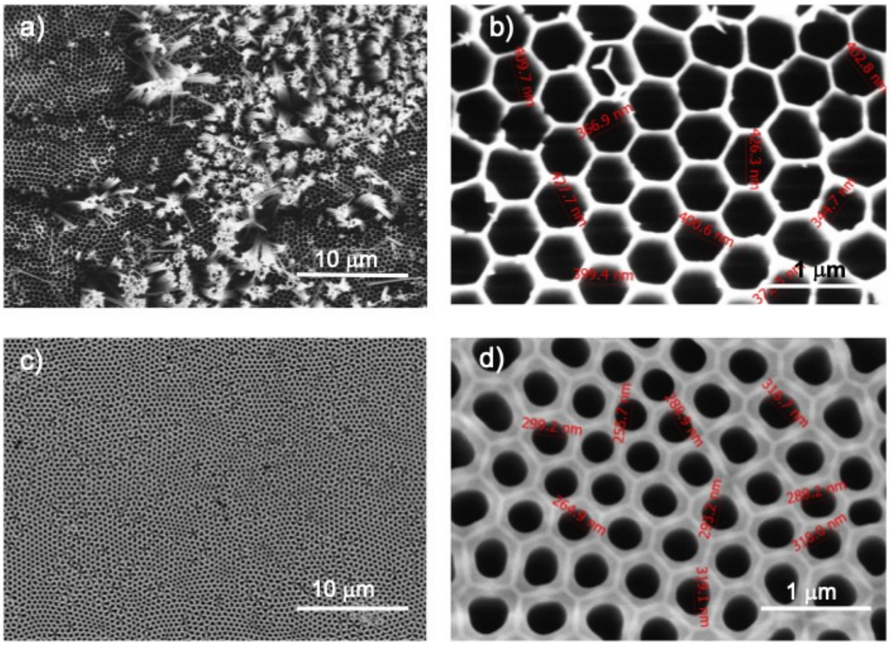

Figure S2: a) and b) Topview micrographs and c) and d) bottom view micrographs of NAA membranes that have undergone barrier layer removal under less-than-optimum etching conditions. Image a) shows how the topside of the pores is widened to a extreme extent, while a zoomed out image b) shows how a significant amount of pores have collapsed.

FE-SEM images of GDEs

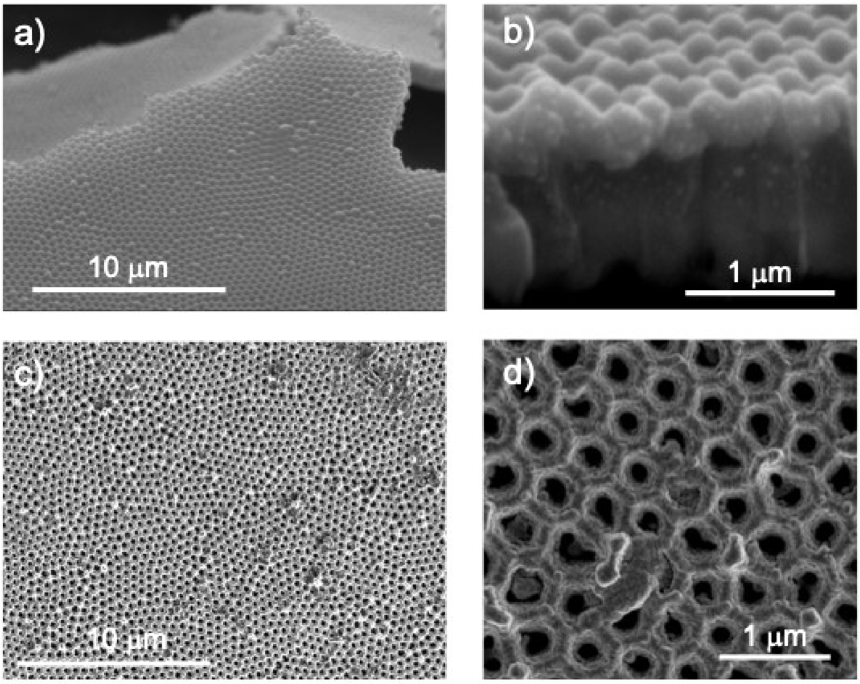

Figure S3: a) and b) Topview and sideview micrographs of NAA membranes covered with 300 nm of silver deposited *via* thermal evaporation; c) and d) Topview micrographs of NAA membranes covered with 300 nm of silver deposited via DC magnetron sputtering.

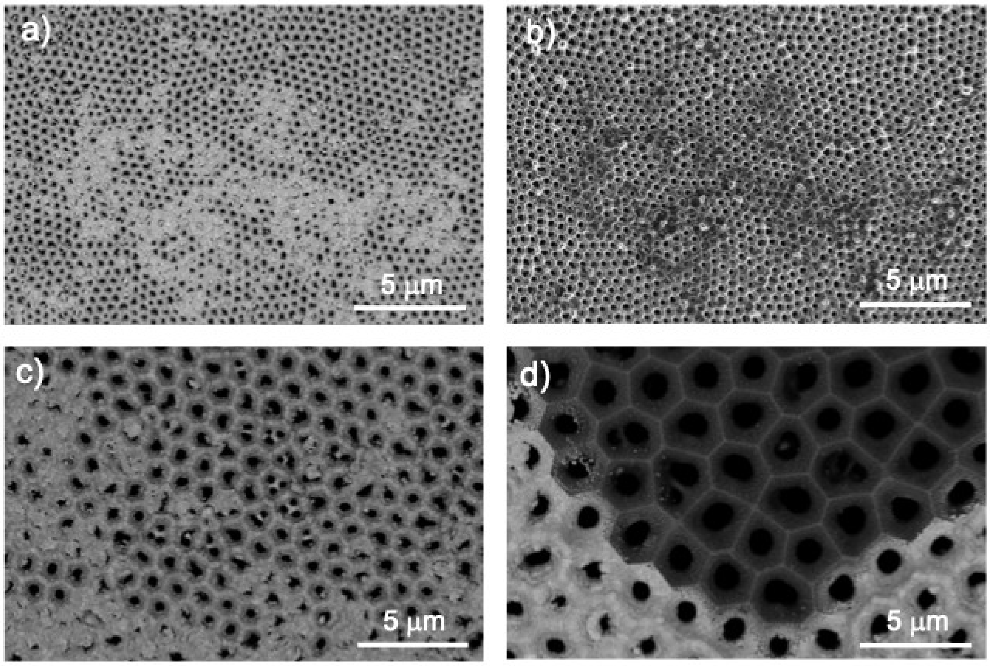

Figure S4: Topview micrographs of NAA membranes covered with 300 nm of silver deposited *via* DC magnetron sputtering showing regions with excess metal a) and c) and metal-depleted regions b) and d)

Optimization of the pores' bottom size

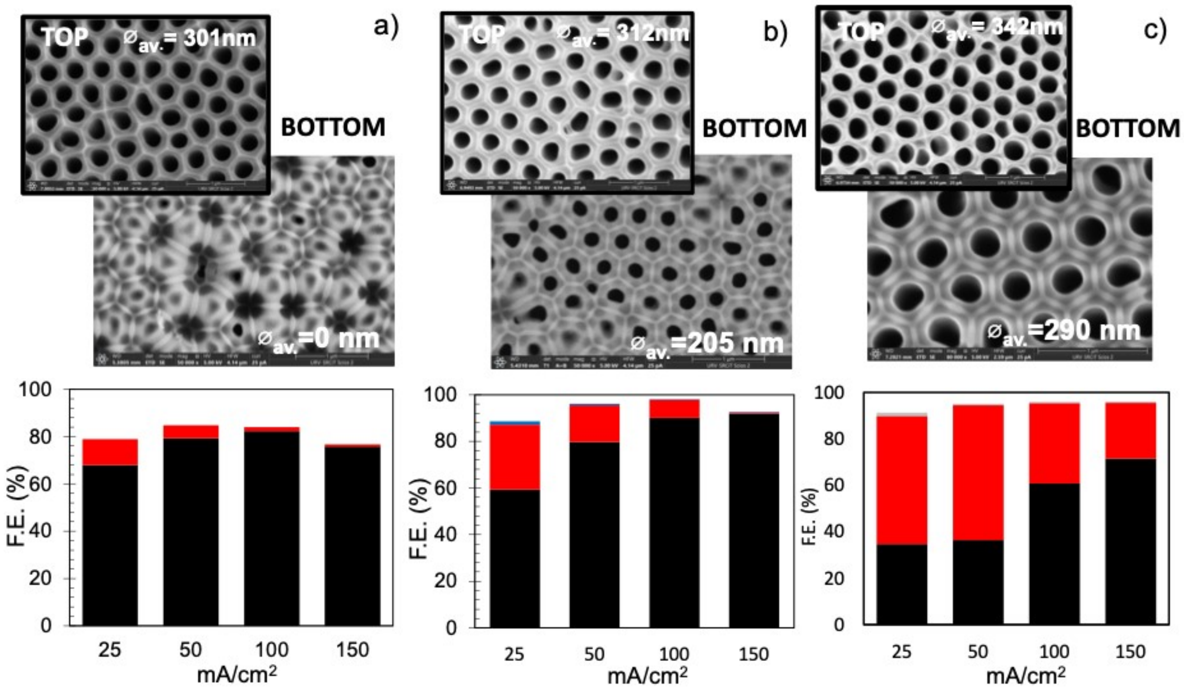

Figure S5. Study of the impact of the GDLs bottom's pore size on Ag-GDE's selectivity. The H2 and CO's FE are represented in the hystograms (CO is in red, H_2 is in black)

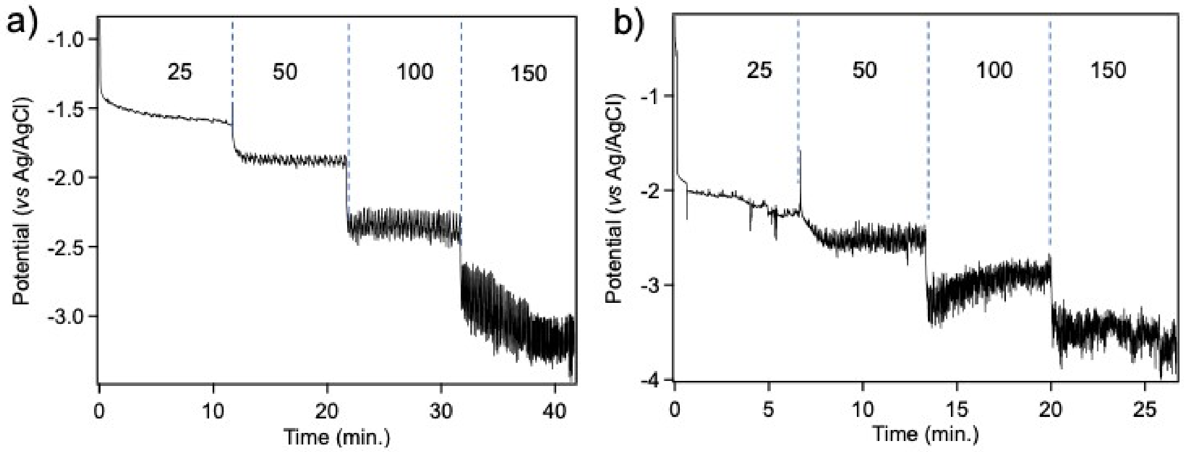

Figure S6. Cathode potential (vs Ag/AgCl) of the experiment whose FE is shown in Figure 5. a) Ag-NAA-GDE, b) Cu-NAA-GDE

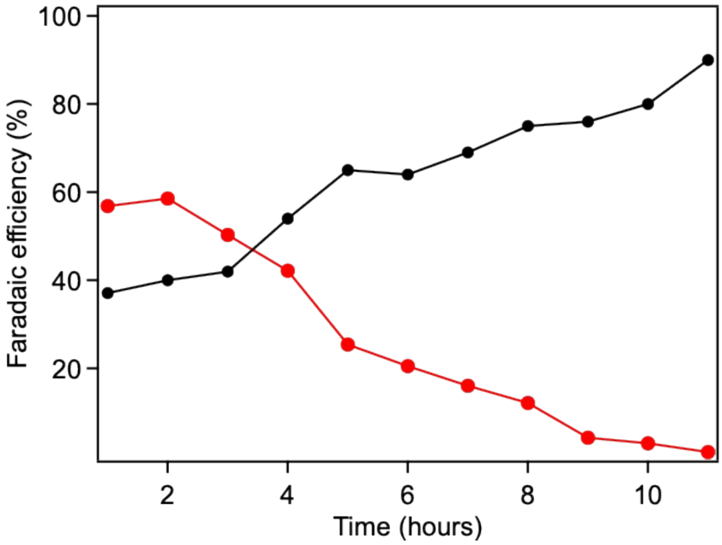

Figure S7. Extended stability assessment: evolution of the FE over a 11h chronopotentiometry experiment.

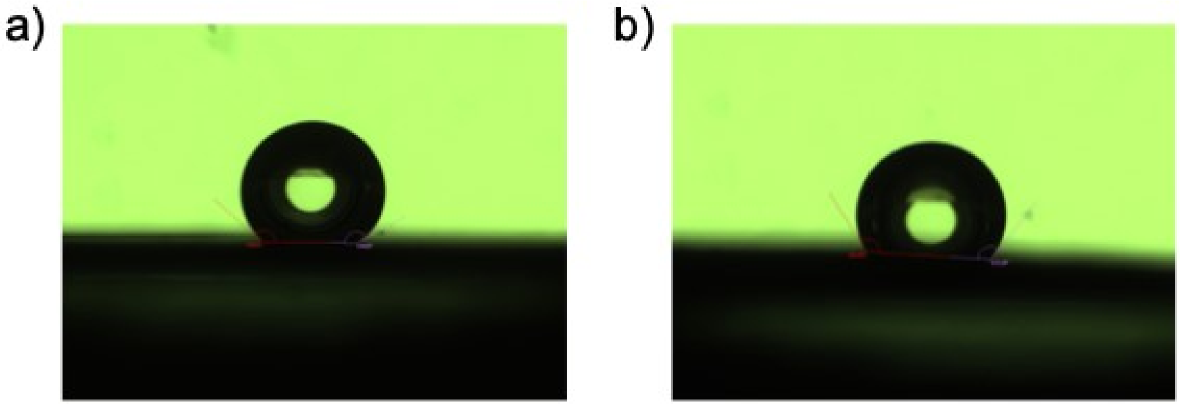

Figure S8. Contact angle (145° (average)) of NAA-GDL before a) and after copper (300nm) was deposited on top (126° (average)) b)