

Supplementary Information

Inherent Impurities in 3D-Printed Electrodes are Responsible for Catalysis towards Water Splitting

Michelle P. Browne^{a1}, Veronika Urbanova^{a1}, Jan Plutnar^a, Filip Novotný^a and Martin Pumera^{abcd}*

^aCenter for Advanced Functional Nanorobots, Department of Inorganic Chemistry, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic

^bDepartment of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 03722, Korea

^cDepartment of Medical Research, China Medical University Hospital, China Medical University, No. 91 Hsueh-Shih Road, Taichung, Taiwan

^dCentral European Institute of Technology, Brno University of Technology, Purkyňova 656/123, Brno, CZ-616 00, Czech Republic

¹Joint first author

E-mail: pumera.research@gmail.com

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Experimental Section

3D-printing of electrodes

The electrode design was created on an online computer aided design (CAD) software called 'Tinkercad.com'. Once the electrode design was completed, the design was converted to a .STL file and then converted to a .gcode file in the PRUSA slicer. The 3D-printing of the electrode was carried out using a commercial conductive graphene/PLA filament (BlackMagic3D) in an Original

Prusai3MK3 3D-printer (PRUSA). For the printing, the nozzle and the bed temperatures were 220 °C and 55 °C, respectively. The diameter of the nozzle opening was 0.6 mm.

DMF

Treatment of the bare 3D-printed electrode

The 3D-printed electrodes were immersed in DMF for 10 minutes. After the electrodes were rinsed with ethanol and then allowed to dry overnight at room temperature.

Thermal treatment of the bare 3D-printed electrode

The 3D-printed electrode was inserted into a vacuum chamber filled with nitrogen (500 Pa) and gradually heated to 350 °C (at a rate of 5 °C/min) and held at this temperature for 3 hours.

Materials characterisation parameters: Inductively coupled plasma emission spectroscopy was carried out using a Spectro ARCOS spectrometer (SPECTRO Analytical Instruments, Germany) in a Paschen-Runge configuration with a Rowland circle polychromator. The measurements of the various elements were conducted simultaneously with 32 charge coupled device (CCD) detectors in the spectral range of 130-770 nm. Scanning electron microscopy (SEM)/energy dispersive X-ray (EDX) spectroscopy was conducted on a Tescan Maia3 Triglav high-resolution microscope (SEM) coupled with a XMAX 150 EDX detector. The accelerating voltage was 20 kV and the working distance was 5 mm. X-Ray Photoelectron spectroscopy (XPS) was carried out on a SPECS XPS spectrometer equipped with an Al (1486.7 eV) XR 50 MF X-ray source. The pass energy for the survey and high-resolution core level scans were 50 eV and 30 eV, respectively. The XPS data was fitted using XPS Casa software.

Electrochemical measurements

All electrochemical measurements were carried out in a three electrode cell consisting of working, reference and counter electrodes. The reference electrode for the HER and PEC measurements was an Ag/AgCl electrode and the counter electrode was a graphite rod. The electrolytes used for the HER and PEC measurements were 0.5 M H₂SO₄ and 1M NaOH, respectively. For the HER measurements, the scan rate for the linear sweep voltammetry was 5 mVs⁻¹. For the PEC water oxidation measurements, a homemade LED set-up consisting of three 390-400 nm LEDs was used to illuminate the 3D-printed electrodes. The PEC measurements were carried out at a constant potential of 1.23 V vs. RHE.