Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Impurities in Graphene/PLA 3D-Printing Filament Dramatically Influence the Electrochemical Properties of the Devices

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Experimental Section

Materials and Reagents: Graphene/polylactic acid (PLA) filament (Black Magic 3D, New York, USA), *N,N'*-dimethylformamide (DMF) (Fisher Scientific, UK), absolute ethanol (Penta Prague, Czech Republic), sodium hydroxide (Lach-ner, Czech Republic). The platinum wire counter electrode, Hg/HgO reference electrode and Ag/AgCl reference electrode were purchased from CH Instruments (Texas, USA).

3D-printing parameters: Prior to the 3D-printing, the electrode was designed on the online open access program, Think-A-CAD. The 3D-printing of the graphene electrodes was conducted on an Original Prusa i3 MK3 3D-printer (PRUSA, Czech Republic). The filament used was a graphene/polylactic acid based commercial filament called Black Magic (BLACKMAGIC3D). During printing, the nozzle and printing bed temperatures were set at 220 and 55 °C, respectively.

3D-printed graphene electrode activation/treatment and Ni oxide electrodeposition: The solvent activation of the printed electrodes was carried out by immersing the electrodes in dimethylformamide (DMF) for 10 mins. The electrodeposition of the Ni oxide was carried out in a deposition bath containing 0.1 M nickel sulfate, 0.1 M sodium acetate and 0.001 M sodium hydroxide by cycling the potential between the limits of -0.9 V and 1.2 V. The counter and

reference electrodes used were a carbon rod and a Ag/AgCl reference electrode, respectively. The scan rate was 50 mV s^{-1} and the number of deposition cycles was 10.

Materials Characterisation: Scanning Electron Microscopy (SEM) was carried out using a Tescan Maia^3 Triglav high-resolution scanning electron microscope with a field-emission electron gun. The SEM images were taken in high resolution mode at an accelerating voltage of 5kV at a working distance of 5 mm with a secondary electron detector. Energy-dispersive X-ray (EDX) analysis was carried out using a X-MAX detector (Oxford Instruments). X-Ray Photoelectron Spectroscopy (XPS) was performed on a monochromated ESCAProbeP spectrometer (Omicron Nanotechnology Ltd., Germany) with an aluminum X-ray radiation source (1486.7 eV). The binding energy was calibrated to the C1s peak at 284.4 e.V.

Electrochemical performance: All electrochemical measurements were conducted in a three electrode cell in 1 M NaOH electrolyte. The electrolyte was de-gassed with argon gas for 15 mins before any measurements. The counter and reference electrode utilized for the electrochemical studies were a carbon rod and a Hg/HgO electrode, respectively. The cyclic voltammetry measurements were conducted at a scan rate of 40 mVs^{-1}. The capacitance measurements were carried out in 1M NaOH at various scan rates.

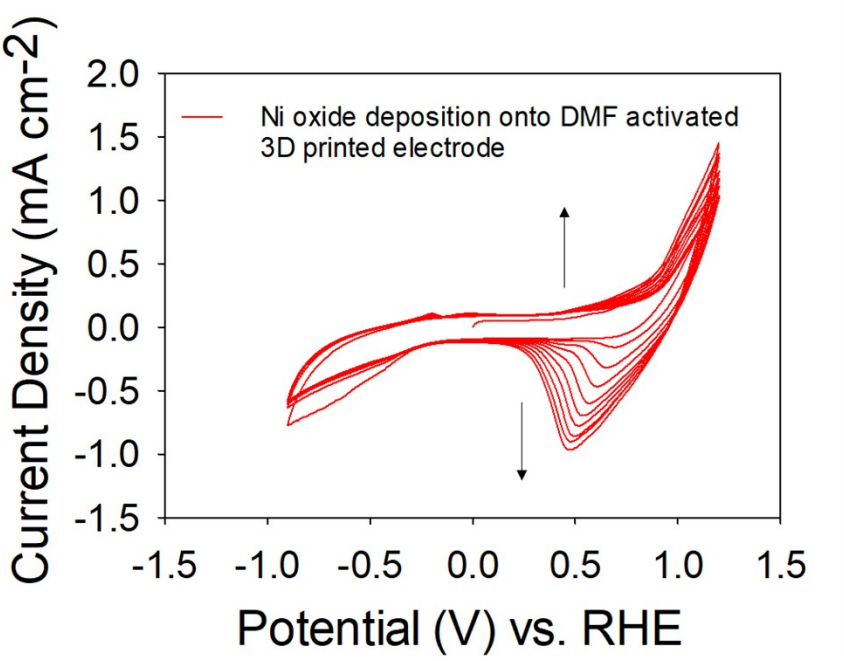

Figure S1. Electrodeposition of Ni oxide onto DMF activated 3D-printed electrode

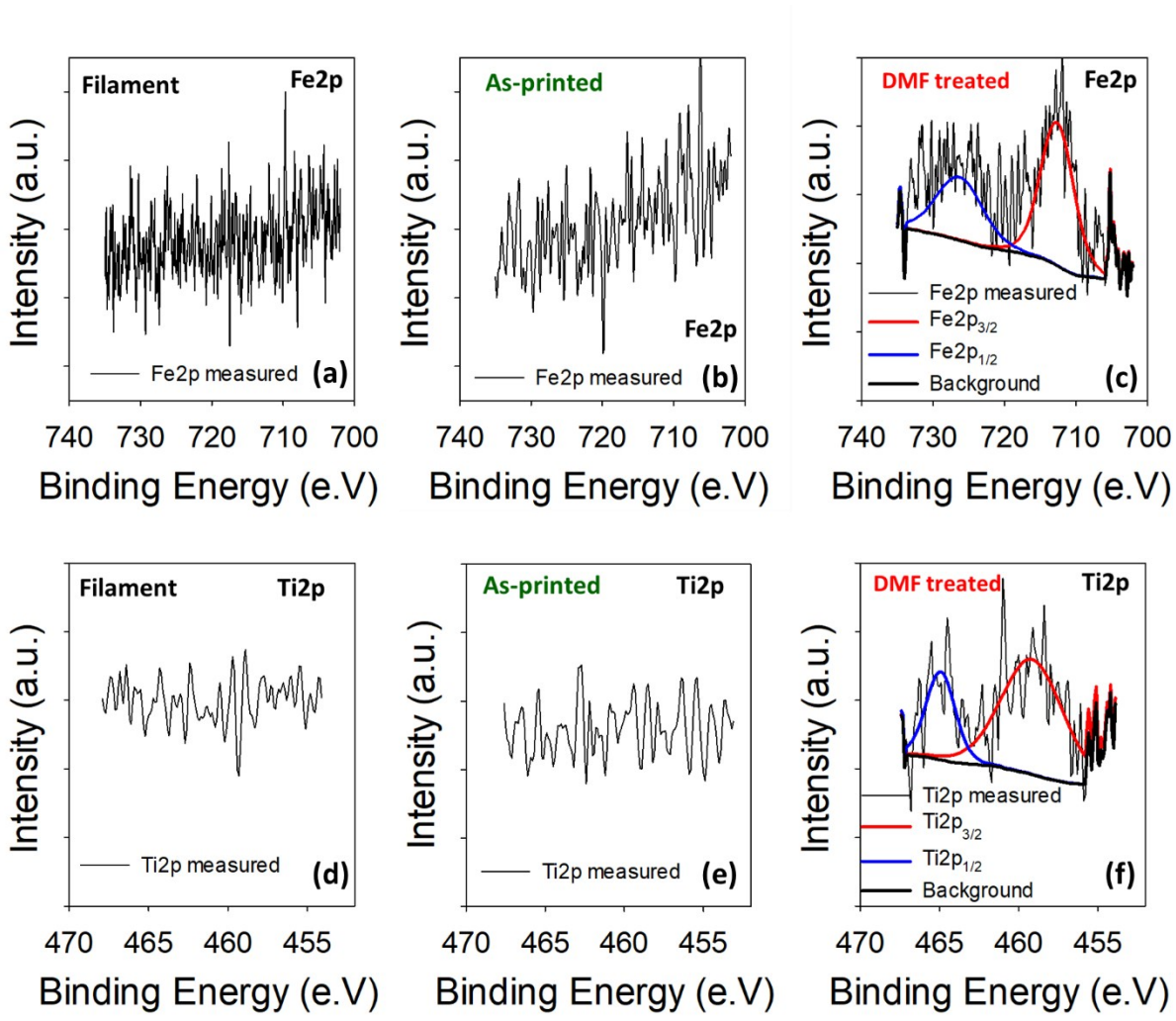

Figure S2. XPS high resolution core levels of the Fe2p region for the **(a)** filament **(b)** as-printed electrode and **(c)** DMF treated electrode. XPS high resolution core levels of the Ti2p region for the **(d)** filament **(e)** as-printed electrode and **(f)** DMF treated electrode.

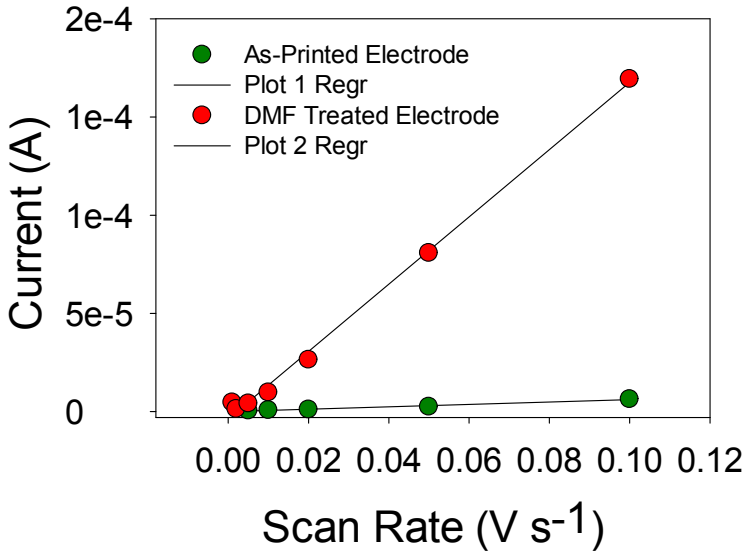

Figure S3. Electrochemcial surface area measurements of the as-printed and the DMF treated 3D printed electrodes

Further to the CV studies of the as-printed and DMF treated electrodes in Figure 2(e) in the main manuscript, we conducted electrochemical surface area (ECSA) measurements on these aforementioned electrodes, Figure S3. The plot shows that the capacitance, and hence the ECSA, of the 3D printed electrodes significantly increases after DMF activation. This result is consistent with the CV curves in Figure 2(e) in the main manuscript and further suggests that the surface of the electrode has been modified i.e. with metal impurities. From the XPS analysis, Figure 2(c-d) and Figure S2, we can confirm the introduction of metal impurities to the surface of the electrode.