Supplementary information for

Hydrogen Evolution Reactions Using 3D Printed Composites of Copper with Graphene and Hexagonal Boron Nitride

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Experimental Details:

Cu, h-BN and Gr powders were procured from Sigma Aldrich with 99.5 % purity, and hBN and graphene (Gr) were prepared in the laboratory through sonication to reduce the multilayer of hBN and graphite. The uniform mixing of mixtures was ensured through the tumbler machine, which performed mixing at 60 rpm for 45 mins. A water-soluble room temperature flowable 55,000 g/mol carboxymethyl Cellulose (CMC, Sigma Aldrich) was used as a binder for the preparation of DIW Cu, 2wt%hBN and 2wt%Gr mixture ink for DIW Printing. CMC is a hydrophilic by-product of hydrolyzed cellulose containing a carboxymethyl group¹. CMC was mixed in deionized water to form a cellulose-based hydrogel mixture. Then, these aforementioned mixtures were added in small increments while manually stirring to achieve uniform dispersion and thixotropic behavior. A Malvern Bohlin Gemini HR rheometer (Malvern Instruments, Worcestershire, UK) with a 25-mm cup and bob geometry fixture and a gap of 150 mm was used to determine the rheological properties of the inks for the DIW process. The high-resolution 3D printer (Hyrel 30M) was utilized to print the metal composite ink. The cold flow syringe head (SDS-30 Extruder) was used to extrude the metal composite at ambient temperature. The ink was filled in a 30mL Luer-Lock syringe and vibrated to ensure the removal of entrapped air bubbles to avoid any discontinuity during the printing. The plate onto which the Cu-Gr (Gr content vary from 1-3 wt%) and Cu-hBN (hBN content vary from 0.5-2 wt%) inks were deposited was coated with polymethylmethacrylate (PMMA) to facilitate the easy removal of the printed Cu-Gr and Cu-hBN composites. The slic3r software generated the G-code script from the CAD .stl file based on the geometry (10x10x10 mm³). The code also determines printing parameters such as extrusion width, printing speed, layer height, and printing pressure to be applied. A nozzle with a 1.5mm diameter was used for the printing to ensure optimized resolution. After printing, each green body was dried in the open air for 24 hours and then placed in an Ar purging Tube furnace for sintering at 950 °C for 4 hrs. with a heating rate of 10°C/min. This high-temperature sintering process consists of two crucial steps: de-binding and sintering^{2,3}. The de-binding process helps in the degradation of cellulose-based hydrogels and other organic components, while in the sintering stage, the individual metallic particles fuse together through various mechanisms but below melting temperature. The description of controllable parameters and optimized value is listed in Table **1**. These values have been determined based on various trial and error. Sintered composites were then polished to reveal surface morphologies. Surface morphologies were assessed through an optical and Field emission scanning electron microscopes (FEI Quanta 400) (FESEM) with 20kV accelerating voltage. To know the elemental distribution, surface mapping was also performed using EDAX embedded in the FESEM. The phase analysis was performed in Bruker D8 Advance with Lynx eye detector in the range of 20^o to 100^o with a step size of 0.35. Jeol Neoarm 200f, a high-resolution transmission electron microscope (HR-TEM) with aberration-corrected features operated at 230kV, was used to study the distribution and interfacial properties of these DIW-processed composite. X-ray photoelectron spectroscopy (XPS) analysis was also performed on a PHI 5000 VERSA PROBE III system with a monochromatic Al K α X-ray source (E = 1486.6 eV) to determine the surface chemical state change of the samples before and after the reaction.

Electrochemical Studies:

The electrocatalytic hydrogen evolution reaction was carried out using a Squidstat Plus potentiostat workstation. A three-electrode cell consisting of Hg/HgO, Platinum (Pt) rod and 3D-printed Cu-based composites (Cu-Gr, Cu-hBN and DIW Cu) themselves individually immersed in 1.0 M NaOH electrolyte were used as reference, counter and working electrodes, respectively. The dimension of 3D-printed composite of Cu with 2 wt% Gr is: a=6.00 mm, b= 8.00 mm and h= 2.20 mm with corresponding area is 0.154 cm². In addition, the dimension of 3D-printed pristine Cu is: I= 7.31 mm, w= 5.42 mm and h= 2.65 mm with corresponding area is 1.46709 cm². Also, the dimension of 3D-printed composite of Cu with 2 wt% h-BN is: I= 4.58 mm, w= 5.12mm and h= 2.73 mm with corresponding area is 0.99861 cm². The linear sweep voltammetry (LSV) test was conducted at a 2 mV s⁻¹ scan rate in the range of -0.3 to -0.9 V (vs Hg/HgO). All measured potentials were transformed into the reversible hydrogen electrode (RHE). Electrochemical impedance spectra (EIS) were measured in the frequency range from

0.1 Hz to 100 kHz with an AC amplitude of 30 mV. The electrochemically active surface area (ECSA) was calculated using the following relationship:

$$ESCA = \frac{C_{dl}}{C_s}$$

where, C_{dl} is the the double-layer capacitance (Cdl) of the catalysts attained by running successive CV curves in the non-Faradaic region at varying scan rates of 10-100 mV s–1 and Cs denotes the specific capacitance of the flat metal electrodes, which is 60 μ F cm⁻² for alkaline electrolytes. In order to study the durability of the designed free-standing catalysts, the Chronoamperometric measurements of HER at an overpotential of 159 mV were performed. The TOF is defined as the number of H₂ molecules evolved per site per second:

$$TOF = \frac{(j \times A)}{(2 \times F \times m/M)}$$

where j is the current density (A/cm²), A is the surface area of the electrode (cm²), n is the number of electrons transferred (typically 2 for HER), Fis Faraday's constant (96485 C/mol), M is the catalyst's molar mass in g/mol and m is the catalyst loading in g.

Theoretical Study:

To better understand the experimental results, we perform Grand Canonical Monte Carlo (GCMC) simulations using Universal Force Field potential⁴. The GCMC calculations were implemented using the Raspa software package⁵. In all cases, we used in the unit cell a (110) copper sample with 2006 atoms above a (100) structure with 2640 copper atoms, including a channel of dimensions 31 Å wide and 22 Å tall. In the first case investigated, we only used copper; however, we also considered cases where a graphene/hexagonal Boron Nitride (with 1006/960 atoms) was placed between the copper samples. In the GCMC simulations, the copper atoms are considered fixed and have no partial charges. These considerations allow the interaction between gas and host to be described only by a Lennard-Jones potential. For the hydrogen molecule, we take two hydrogen atoms bonded by a rigid bond with a length of 0.740 Å. During the GCMC simulation, we perform Monte Carlo moves on the hydrogen molecules, with probabilities of 20% for rotation, 20% for translation, and 60% for swaps (either insertion or removal of a hydrogen molecule). We used a temperature of 300 K for the gas reservoir and considered a pressure of 1 atm. The enthalpy of adsorption is calculated through the Widom insertion method, which calculates the average adsorption energy and

then adds -RT to its value, giving the enthalpy of adsorption at infinite dilution. Where R is the gas constant, and T is the temperature. The GCMC process is composed of 1x10⁵ initialisation cycles to achieve thermodynamic equilibrium, followed by 1x10⁵ Monte Carlo Cycles to obtain the adsorption data.

Table 1. Optimised Parameters used for the DIW experiment for the preparation of Cu-based composites

Parameter	Value
Slice height	0.75 mm
Path speed	20 mms ⁻¹
Extrusion width	1.5 mm
Infill density	100
Clearance	0.75mm
Material	Cu, hBN, Gr
Nozzle diameter	1.5 mm
Build temperature	25 °C

Particle Morphology and DIW Printing

The morphology of Cu, Gr and hBN powders used for ink are presented in **Fig. S1a-c**, respectively. Cu has a dendritic structure, whereas Gr presents a flake-like structure, and hBN has a spherical size.



Figure S1. SEM morphology of (a) Cu, (b) Gr, (c) hBN

Cu has a particle size of 19 μ m, as evident from Fig. S1a. The key binding agent is the carboxymethyl cellulose (CMC), which was selected for this study because of its low-

temperature degradation point. For each 10 g composite, 5.5 g of binder solution was used to prepare the metallic composite ink. As the DIW process relies on the continuous deposition of ink, the rheological properties are tailored to facilitate the ejection of ink through the orifice of the syringe in the DIW process. The ideal ink should be able to extrude with minimal pressure and retain its shape under shear thinning conditions. As the shear rate increases, the ink particles experience shear stress across different flow layers, weakening their entanglement and causing shear thinning. This allows the ink to flow smoothly through the nozzle during extrusion, preventing blockages. Thus, the prepared inks and their compositions are ideal for the DIW process to create Cu composite models. The DIW process provides a uniform distribution of the reinforcement in each layer during the ejection through the nozzle, as demonstrated in the previous study⁶. As the properties of a composite depend upon the distribution and uniformity of secondary particles, the DIW process can enhance the mechanical properties. The sintering temperature of 950 °C was selected so that the bonding between Cu particles occurred effectively, as well as the binder particles are removed effectively^{7,8}. The sintering process mechanism works in three stages: curing, de-binding and sintering. The curing process consists of the removal of water, de-binding to ensure all binders are removed, and finally, sintering where densification occurs. The low-temperature region ensures the removal of binder and water, and the high-temperature regime ensures the sintering of Cu and the particles. As the melting temperature of Gr and hBN is much higher than the investigated sintering temperature, the atomic diffusion of these refractory elements is smaller compared to cu⁹.



Figure S2. Rheological profile of the ink: (a) Variation of shear viscosity (η) with shear rate and (b) variation of shear stress with shear rate for pristine Cu, Cu-Gr and Cu-hBN composites ink at room temperature.

The analysis of the shear viscosity and shear stress behavior of different inks reveals that Cu-2wt%Gr ink is more suitable for Direct Ink Writing (DIW) printing than Cu-2wt%hBN ink. Cu-2wt%Gr ink exhibits a lower viscosity across a wide range of shear rates, which is beneficial for DIW as it facilitates smoother extrusion through the print nozzle. Additionally, its moderate shear stress values, compared to Cu-2wt%hBN, ensure better shape retention and consistency during printing, preventing the ink from either collapsing or spreading too much after deposition. This behavior is attributed to the shear-thinning properties of Cu-2wt%Gr, where the viscosity decreases with increasing shear rate—ideal for controlling flow during the printing process. On the other hand, Cu-2wt%hBN ink shows higher viscosity and increased shear stress at lower shear rates, which could impede its printability and consistency, potentially leading to more challenges during the extrusion and deposition process. Therefore, based on these rheological characteristics, Cu-2wt%Gr composite inks are considered more appropriate for DIW printing than Cu-hBN composites, ensuring better print resolution and accuracy.



Figure S3. Distribution of hBN and Gr with elemental mapping of the investigated composites



Figure S4. TEM micrographs of (a) Cu-Gr and (b) Cu-hBN.



Figure S5. Experimental Density (ED) and porosity of investigated composites.

From the porosity measurement it is confirmed that addition of Gr has a strong impact on the pore generation. The shape and surface area of the Gr particle have modified the sintering mechanism owing to which there is a difference in microstructure as observed in micrographs presented in **Figure 1**. We have achieved an optimum combination of densification and porosity for our investigated composites which is required for the HER and sustaining various load bearing application.



Figure S6. HER catalytic performance of 3D printed Cu-Gr, Cu-hBN composites with varying Gr (1, 2 and 3 wt%) and h-BN content (0.5, 1 and 2 wt%) at a scan rate of 2 mV s⁻¹ in 1.0 M KOH electrolyte solution: a) polarisation curves for Cu composites with varying Gr content; b) corresponding EIS plots; c) comparison of polarisation curves for Cu composites with varying h-BN content and d) corresponding EIS plots.

In order to understand the role of varying content of Gr (1, 2 and 3 wt%) on HER performance, LSV at 2 mV s⁻¹ and EIS have been analyzed. **Fig. S6a** depicts the LSV plots of all Cu-Gr composites. Notably, Cu-Gr2 exhibits lowest overpotential (20 mV) at 10 mAcm⁻² which is almost 47.6 mV lower than Cu-Gr3 and 108 mV lower than Cu-Gr1, revealing the optimum loading of Gr is 2 wt%. EIS plots for all the composites is shown in **Fig. S6b**, suggesting Cu-Gr2 exhibits lowest charge transfer resistance (R_{ct}) (1.06 ohm). On the contrary, Cu-Gr1 presents almost similar R_{ct} (~7 ohm) with pristine 3D-printed Cu (~8 ohm) and Cu-Gr3 shows R_{ct} of 3.4 ohm, confirming 2 wt% of Gr in Cu is the optimal loading which balances the conductivity,

structural integrity, and HER efficiency of 3D printed Cu composite. The content of h-BN (0.5, 1 and 2 wt%) in Cu has also been varied to investigate their effect on HER performance. **Fig. S6c** shows the LSV plots of Cu-hBN composites. It is observed that overpotential gradually decreased with increasing h-BN content from 0.5 to 2 wt% due to the improved surface interaction of h-BN with Cu. However, higher concentration of h-BN (3 wt%) was not further used for HER study owing to the sluggish kinetics, agglomeration of hBN in Cu and difficult to printing for obtaining particular shape. Therefore, 2 wt% of h-BN was selected as the optimum concentration for balancing HER activity as well as structural integrity. Notably, current density and overpotential are significantly lower for Cu-hBN composites than those for Cu-Gr composites, validating the conducting nature of Gr (and insulating nature of h-BN) to assist fast ion diffusion. Nyquist plots in **Fig. S6d** reveals that R_{ct} remains almost unchanged with varying h-BN content as Cu remains the primary conductor and h-BN acts as a surface modifier, not as a charge carrier.

 $H_2O + e^- + M \rightarrow M-H_{ads} + OH^-$ (Volmer reaction) $H_2O + e^- + M-Ha_{ds} \rightarrow H_2 + M + OH^-$ (Heyrovsky reaction) $M-H_{ads} + M-H_{ads} \rightarrow H_2 + 2M$ (Tafel reaction)

Figure S7. Reaction mechanism of HER for 3D printed Cu-based catalysts in alkaline electrolyte¹⁰. In alkaline/neutral conditions, the Volmer and Heyrovsky steps involve the hydroxide ion, while the Tafel step remains unchanged.



Figure S8. Determination of exchange current density from Tafel slopes of DIW-processed (a) Cu and Cu-hBN and b) Cu-Gr



Figure S9. Cyclic voltammograms (CVs) measured in the scan rate range from 10 to 100 mV s⁻¹ in the non-Faradaic regions of the polarisation curves of DIW-processed a) Cu, b) Cu-Gr, c) Cu-hBN.

The consecutive CV curves for all the self-standing catalysts recorded in the non-Faradic region at various scan rates are presented in **Fig. S9a-c**. C_{dl} was determined from the slope of current density (by averaging cathodic and anodic current) versus scan rate.

Post-HER Characterization:

After the electrocatalytic assessment, the composites were analysed using XRD and the corresponding XRD plot is shown in **Fig. S10a**. The XRD plot reveals extra peaks indicating the presence of CuO, Cu₂O and Cu(OH)₂ compared to the XRD plot before electrolysis, as evident from **Fig. S10a**. The presence of oxides on the composites surface is due to the electrolytic process where interactions of oxygen with the surface

of composite take place. Notably, Cu-Gr composites show the presence of peaks around 29.34°, 36.20°, 42.02°, 43.07°, 50.21°, 61.28°, 73.86° and 89.69° (JPCDS card no. 89–5898), confirming the formation of Cu(OH)₂ along with Cu₂O¹¹. The SEM surface morphology of the electrocatalysed composites is depicted in Fig. S10b-d. Pristine Cu shows the presence of CuO and Cu₂O, whereas Cu-Gr shows the existence of both Cu_2O and $Cu(OH)_2$. The generation of $Cu(OH)_2$ is more advantageous to boost the HER kinetics as it increases active sites for catalytic reactions, enlarges active surface area and facilitates the modification of the electronic structure for enhancing its electrical conductivity and catalytic activity in alkaline medium^{12,13}. Fig. S10d clearly shows that the 3D-printed architecture of the Cu–Gr electrode remains intact and well-preserved, with no visible signs of structural collapse, delamination, or surface degradation. These results confirm the excellent mechanical and structural robustness of the DIW-printed Cu–Gr composite electrode during prolonged electrochemical operation. Furthermore, surface features indicative of Cu₂O and Cu(OH)₂ formation suggests controlled surface oxidation during HER without compromising the electrode's physical framework. The stability of the printed structure is attributed to the synergistic effect of the Cu matrix and the presence of graphene as reinforcement, which not only enhances electrical conductivity but also provides structural resilience during prolonged exposure to alkaline electrolyte and potential cycling. XPS survey spectra of the electrolysed composites are presented in Fig. S10e-g, corrected with reference to C1s peak at 284.5 eV¹⁴. The oxygen signal has originated due to the surface oxidation of the composites. The XPS survey indicates the presence of Cu and O without any impurities in the composites. In the Cu 2p spectrum, two peaks at 932.5 and 952.3 eV are ascribed to the 2p3/2 and 2p1/2 of Cu⁺, while two peaks at around 934.1 and 956.7 eV reveal the presence of Cu(OH)₂ after the electrocatalytic proces¹⁵. All the composites show O 1s core level peak after Shirley background subtraction, suggesting multiple co-ordination of O2 in the composite. The high-resolution C 1s, O 1s and Cu 2p peaks for DIW printed Cu-Gr composite are shown in Fig. S10h-j. C 1s peaks for Cu-Gr composite (Fig. S10h) are observed at 284.6 and 285.8 eV, corresponding to the C-C bond within a graphitic structure and C-O bond, confirming the oxidation of surface and generation of copper hydroxide. Deconvolution of O1s peaks of Cu-Gr shows binding energy at 530and 531.2 eV corresponding to Cu₂O and Cu(OH)₂, respectively (Fig. S10i). The presence of the oxides and hydroxides is reaffirmed from the XPS deconvoluted peaks of Cu 2p of Cu-Gr, as shown in **Fig. S10j**.



Figure S10. a) XRD patterns of representative DIW processed composites after electrocatalysis, SEM surface morphology of b) DIW Cu, c) Cu-hBN and d) Cu-Gr after electrocatalysis and XPS survey spectra of e) DIW Cu, f) Cu-hBN and g) Cu-Gr respectively. XPS deconvoluted spectra of h) C1s, i) O1s and j) Cu 2p for DIW Cu-Gr.

The deconvoluted peaks of DIW Cu and Cu-hBN composites are shown in **Fig. S11**. For DIW Cu, the presence of CuO and Cu₂O is confirmed by the deconvoluted peak of O 1s (**Fig. S11b**), whereas DIW printed Cu-hBN (**Fig. S11e**) exhibit the presence of Cu(OH)₂ after the electrolysis process. These oxides are known to develop as thin, passivating

layers that protect the bulk Cu from further corrosion or dissolution^{16,17}. In this context, their presence does not indicate instability but rather preserves the structural and electrochemical integrity of Cu under alkaline HER conditions. Importantly, the presence of Cu(OH)₂ in addition to Cu₂O in Cu-composites indicates a favorable surface transformation in alkaline media, where Cu reacts with OH⁻ ions to form a stable hydroxide layer. This layer acts as a protective passivation film, helping to preserve the underlying Cu matrix from further oxidation or corrosion. Notably, the formation of Cu(OH)₂, rather than more aggressive oxidation products like CuO, is likely influenced by the presence of graphene and hBN, which modulate the local surface chemistry and stabilize the electrode interface. While Cu(OH)₂ itself is not the primary HER-active species, its coexistence with conductive Cu and uniformly dispersed 2D additives ensures retained HER performance and long-term electrode stability, as supported by stable current density value (**Fig. 2g**). These results confirm that the Cu-based electrodes maintain their chemical integrity and electrochemical stability in alkaline media.

Figure S11. Core level XPS of a) C1s, (b) O1s and (c) Cu2p for DIW Cu, d) C1s, e) O1s and f) Cu2p for DIW Cu-hBN.

Computational Study for HER Efficiency:

To obtain a deeper understanding of the improved HER activity of the DIW printed composites and verify how the addition of Gr and hBN in copper changes the interaction energy of the solid with molecules located within a cavity in the material, we performed Grand Canonical Monte Carlo (GCMC) simulations of hydrogen molecules interacting with (i) pristine copper, (ii) copper + graphene, and (iii) copper + hBN. The results of the Enthalpy of Adsorption for the three investigated type of structures, which is a measure of the heat release during molecular adsorption, is also shown. More negative values of this quantity indicate a stronger interaction of the solid host with guest molecules (hydrogen in the simulations). The addition of graphene/hBN increased the Adsorption enthalpy from -2.60 kJ/mol to -4.79/-4.90 kJ/mol. To examine how the addition of graphene/hBN changes the adsorption sites, we examined snapshots of various equilibrium configurations of the hydrogen molecules inside copper. The first point to note is that, for the considered unit cell, the average number of adsorbed hydrogen molecules increased from 7 to 9 with the addition of either Gr or hBN. Inspection of the snapshots reveals that the majority of molecules are adsorbed in the proximity of the graphene/hBN monolayer, indicating the significant interaction of the 2D materials with the adsorbates.

We can list three structural merits that graphene-based HER catalysts have¹⁷: (1) availability of a large surface area, leading to faster transport of the electrolyte to the active centers; (2) a high electrical conductivity¹⁸, which contributes to fast catalytic reaction kinetics, (3) significant chemical stability allowing the catalyst structure to be preserved even under unfavorable electrocatalytic conditions. Furthermore, it is well established in the literature that both the catalytic activity and the lifetime of catalysts are highly correlated with their composition, morphology, and structure^{17,19}. Previous works have already demonstrated the successful incorporation of graphene flakes into copper matrices during the production of samples via DIW²⁰, with the observation of an increase in the electrical conductivity of the Cu-Gr samples²¹. As a result of this higher conductivity, the composite is easier to transfer charge during chemical reactions²². Like graphene, h-BN can be considered chemically stable; however, h-BN is highly electrochemically inert and acts as an insulator, exhibiting a large electronic bandgap of around 6 eV.²³Thus, even if h-BN still has some catalytic activity, it is constrained by the charge transfer limit. Study conducted by Liu *et al.*²⁴,

have compared the electrocatalytic activity of Cu/h-BN and Au/h-BN composites, obtaining an overpotential of 0.47 V for the Au/h-BN ones, while for Cu/h-BN composites, an overpotential of 0.77 V was obtained. This difference shows that h-BN does not have an effective electronic coupling to copper as it does to Au. Therefore, a possible explanation for the significant difference between the overpotential seen in Cu/Gr and Cu/h-BN composites comes from the conductive nature of graphene and the insulating nature of the h-BN. We have obtained adsorption enthalpies of -4.79/-4.90 kJ/mol for graphene/h-BN, respectively. Qualitatively, those values of enthalpies follow the same trends observed in the experimental data since, at a current density of J=10 mA/cm², we have an overpotential (η) of 20 mV for the Cu/Gr sample. In contrast, for the Cu/h-BN sample, we have a value higher than that of Cu-Gr, with η =268 mV, but around 34% lower than the overpotential of pristine copper. We must emphasize that the GCMC simulations and the enthalpy model alone cannot capture all the structural complexity present in the experiment, given that they are approximations of a more complex topology. However, when we consider the enthalpy and overpotential values, they offer a plausible explanation for the enhanced performance of the Cu/Gr composites.

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