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Research Article

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Posted Date: January 24th, 2024

DOI: https://doi.org/10.21203/rs.3.rs-3889556/v1

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Additional Declarations: The authors declare no competing interests.

Version of Record: A version of this preprint was published at Advanced Materials Technologies on April 25th, 2024. See the published version at https://doi.org/10.1002/admt.202400160.
3D Printed Microlattices of Transition Metal/ Metal Oxides for Highly Stable and Efficient Water Splitting

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Abstract

Developing affordable electrocatalysts is crucial for driving the sustainable energy transition to green hydrogen. Here, we report a generalizable method known as polymer infusion additive manufacturing (PIAM) for transforming 3D printed photopolymers into core-shell microlattice electrodes for electrocatalytic water splitting with transition metal/metal oxides/carbon heterointerfaces. The optimized free-standing architectures integrate Cu/CuOₓ on carbon (Cu/CuOₓ/C) microlattices, yielding high electrocatalytic activity (overpotential of 145 mV at 10 mA/cm² and a Tafel slope of 134 mV/dec) and excellent durability for HER (>100 hr), surpassing state-of-the-art Cu foams. Additionally, for oxygen evolution (OER), Co/CoOₓ on carbon (Co/CoOₓ/C) microlattices display exceptional activity with the lowest overpotential (1.40 V to gain 10 mA/cm²) among all reported PGM-free electrodes. We explore the gas phase mass-transport properties of these 3D microlattices via microscopic imaging of bubble evolution, finding that the outstanding electrocatalytic performance and long-term stability of microlattice electrodes leverages their mesoscale (100-300 μm) pores, providing accessibility of electrolytes, maximizing utilization of active sites, and ensuring rapid evolution of gas bubbles. Thus, we introduce a simple but pioneering method for manufacturing 3D mesostructured electrocatalysts with deep control of liquid and gas phase mass-transport, enhancing the efficacy of alkaline water electrolysis.
1. **Introduction**

Alkaline water electrolysis (AWE) offers a promising pathway for water splitting, presenting significant potential for the development of sustainable electrocatalysts in energy devices\[1\]. Furthermore, the advancement of platinum group metal (PGM)-free electrocatalysts holds promise for substantial cost reductions in large-scale applications\[2\]. Nevertheless, these PGM-free electrocatalysts currently face challenges regarding their catalytic efficiency\[3\]. To address this challenge, extensive studies have explored transition metal derivatives such as transition metal phosphides\[4\], transition metal nitrides\[5\], transition metal alloys\[6\], and transition metal oxides\[7\], primarily due to their moderate capacity to adsorb hydrogen, thereby enhancing kinetics. Among these derivatives, transition metal oxides (TMO) show significant promise owing to their robust stability in alkaline environments\[8\]. However, due to their low electrical conductivity and poor kinetics, there persists a substantial disparity in their water splitting performance when compared to that of PGMs. Several nanostructure-scale approaches have been proposed to enhance the water-splitting activity of TMO. These approaches include altering the electronic structure through the introduction of heteroatoms\[9\], inducing chemical defects via oxygen vacancies\[10\], and increasing porosity through synthesizing TMO with diverse nanostructures to enlarge the active surface area\[11\]. However, nanostructuring approaches encounter practical limitations as they require casting nanoparticles onto current collectors using polymeric binders such as polytetrafluoroethylene or Nafion, leading to increased resistance, blocked active sites, and hindered mass transport\[12,13\].

Three-dimensional (3D) electrocatalyst design has become a considerable focus of efforts to maximize utilization of active sites through mass-transport engineering of the liquid phase electrolyte and gas phase bubble production. The overarching goals of this strategy are to provide an inexpensive, scalable, and highly effective electrocatalyst with good activity\[14,15\]. Various wet chemical growth techniques enable the deposition nanostructures on 3D frameworks, such as nanoleaflets, nanosticks formed from spheres, and nanowires for efficient water splitting performance\[16,17\]. However, the limited adhesive force between the catalytically active materials and the 3D substrate results in easy detachment from the substrate during prolonged, high-current electrocatalysis. This limitation restricts their effective performance to lower current densities, rendering them inadequate for meeting the demands of industrial water splitting, which commonly operates at higher current densities\[18,19\]. Additionally, the gas bubbles generated during water
splitting on these 3D structures can obstruct a significant number of catalytically active sites, leading to an increase in the device resistance and limited mass transfer, impacting the overall efficiency of water splitting\[^{20}\]. Past studies therefore show that the mesoscale architecture of the electrode is of paramount importance to the overall efficiency of new earth-abundant electrocatalysts for large-scale water splitting.

Here we target the application of high-resolution additive manufacturing of a periodic 3D micro/mesostructured electrode to enhance bubble release and expedite the mass transfer of surrounding electrolyte to boost the rate and stability of electrochemical reactions for efficient large-scale water splitting. Additive manufacturing (AM), including 3D printing, has emerged as a promising method for producing customized structures with precise digital control\[^{21}\]. So far, 3D microstructured electrocatalysts have been prepared using direct ink writing (DIW)\[^{17}\], indirect fused deposition modeling (FDM)\[^{22}\], or selective laser melting (SLM)\[^{23}\]. Extrusion-based methods like FDM and DIW offer benefits including affordability, speed, and simplicity, yet they also come with limitations such as restricted design flexibility, lower spatial resolution, weaker mechanical properties, and subpar surface smoothness. Selective Laser Melting (SLM) and other powder bed fusion methods facilitate 3D metal printing, but suffer from low speed and the high cost of feedstocks. Photopolymerization based 3D printing offers an alternative route for producing large area high-resolution 3D microstructures at lower cost. Methods such as stereolithography (SLA), involve selectively solidifying a monomeric resin layer by layer, producing complex features down to the single micron scale for a variety of materials like ceramics\[^{24,25}\] and hydrogels\[^{26}\]. Additionally, SLA is adept at producing free-standing porous geometries such as microlattices that simultaneously provide high surface area and high electrical conductivity along with mechanical strength\[^{27}\]. These properties make SLA promising for engineering mass-transport in porous solids, but new chemistries and synthetic approaches are required for extending this benefit to transition metal/metal oxide catalyst materials.

In this paper, we present the fabrication and architectural design of 3D free-standing microlattices integrating highly active transition metal/metal oxides via SLA (stereolithography)\[^{27}\] (shown in Figure 1a, b) for efficient electrocatalytic water splitting under alkaline conditions. This method utilizes polymer-based 3D scaffold templates designed explicitly for high gas evolution efficiency to improve electrode stability and enhance water splitting performance. We converted these scaffolds into continuous 3D microlattices of transition
metal/metal oxides on carbon by a method we call polymer infusion additive manufacturing (PIAM) to enhance the efficiency of both the alkaline hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). In the case of HER, the 3D microlattices composed of copper oxide (CuO\(_x\)) and copper (Cu) on carbon (Cu/CuO\(_x\)/C) exhibited high performance (overpotential of 145 mV at 10 mA/cm\(^2\) and a Tafel slope of 134 mV/dec) exceeding that of previously reported Cu-based oxide electrocatalysts. Additionally, for OER, the 3D microlattices consisting of cobalt oxide (CoO\(_x\)) and cobalt (Co) on carbon (Co/CoO\(_x\)/C) displayed an exceptional overpotential of just 1.40 V at 10 mA/cm\(^2\), with a Tafel slope of 55 mV/dec. These results demonstrate superior performance compared to recently reported cobalt oxide-based 3D microstructured electrocatalysts. Through detailed characterization, we develop a mass-transport mechanism to explain the enhanced electrocatalytic performance of these 3D microlattices, the pore structure of which promotes electrolyte diffusion to the electrocatalyst surface and facilitates bubble evolution, enhancing the electrochemical reaction rate. A concomitant result of improved 3D mass-transport is that microlattices exhibit superior durability, enduring up to 240 hr of continuous hydrogen and oxygen evolution without significant change in overpotential and current density. This durability is attributed to their ordered microstructures with 100 – 300 μm pores that expose more active sites and allow for fast discharge of bubbles, ensuring mechanical and chemical stability of the electrodes.

2. Results and Discussion

Our polymer infusion additive manufacturing (PIAM) technique, derived from stereolithography, facilitates the preparation of diverse 3D microstructured transition metal derivatives from common acrylate photopolymers and metal salts. We use 3D architected polymer scaffolds as platforms for the subsequent in situ synthesis of transition metal and transition metal oxide interfaces on conductive graphitic carbon lattices, as depicted schematically in Figure 1c. Stereolithography is employed to create various 3D scaffold templates\(^{[27]}\) with adjustable lattice structure, pore size, and volumetric porosity. After the printing phase, the 3D scaffold templates are immersed in an aqueous solution of a metal nitrate salt precursor, facilitating its infusion into the polymer –similar to the hydrogel additive manufacturing (HIAM) approach developed by Saccone, et al\(^{[26]}\). Calcination in a vacuum converts the metal-salt-infused polymer to coatings consisting of metal...
oxides on carbon. Subsequent reduction in forming gas (95% N\textsubscript{2}, 5% H\textsubscript{2}) yields transition metal and transition metal oxide interfaces on the carbon 3D microlattices (details available in the experimental methods section). Showing the versatility of this (PIAM) technique, we fabricate two different kinds of catalytic 3D microlattices of Cu/CuO\textsubscript{x} on carbon (Cu/CuO\textsubscript{x}/C), and Co/CoO\textsubscript{x} on carbon (Co/CoO\textsubscript{x}/C). Compared to current approaches that rely on particle-laden slurries or resin precursors, PIAM allows the exploration of a considerably broader range of catalyst compositions while ensuring the protection of the conductive carbon core. From optical microscopy images (displayed within red circles in the inset of Figure 1c), it is confirmed that during calcination, the polymer scaffold structures shrink by approximately 50% but maintain the high resolution 3D microlattice features while incorporating transition metals and transition metal oxides on carbon – ensuring the ability to design a variety of optimal architectures for enhancing mass-transport.

2.1 Microscale and nanoscale structural characterization of 3D microlattice electrodes
The morphologies of the 3D microlattices of transition metals and transition metal oxides interfaces on carbon were investigated by scanning electron microscopy (SEM). SEM imaging revealed that 3D microlattices of Cu/CuO\textsubscript{x}/C, and Co/CoO\textsubscript{x}/C retained their precise lattice shape during thermal treatment (Figure 1d, g), with beam diameters of approximately 250 μm. Cross-sectional SEM images illustrate the defect-free core-shell structures of Cu/CuO\textsubscript{x}/C (Figure 1e) and Co/CoO\textsubscript{x}/C (Figure 1h), a unique feature of this method that strategically integrates electrochemically active material onto surfaces exposed to the electrolyte. The magnified SEM of Cu/CuO\textsubscript{x}/C also shows a continuous lamellar structure originating from the layer-by-layer SLA process (Figure 1f), whereas the Co/CoO\textsubscript{x}/C exhibits a similarly dense structure with micron-sized particles on the surface (Figure 1i). Energy dispersive X-ray spectroscopy (EDS) mapping shows conformal distribution of Cu/CuO\textsubscript{x} shell on carbon (Figure 1j-l), and homogenous distribution of Co/CoO\textsubscript{x} on carbon (Figure 1m-o), confirming a well-defined core-shell structure of each individual beam in the 3D microlattices. Furthermore, transmission electron microscopy (TEM) characterization of the Cu/CuO\textsubscript{x}/C microlattices confirm the homogeneous dispersion of Cu/CuO\textsubscript{x} on carbon, with a mean size of 30-40 nm, as shown in Supporting Information Figure S1.

2.2 Material characterization of metal/metal oxide phase

To understand the phase and chemical evolution of the microlattices throughout calcination and reduction processes, we analyzed the phase composition using X-ray diffraction (XRD) and investigated chemical composition through X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA). Figures 2a,d show the XRD measurements of calcined 3D CuO\textsubscript{x} on carbon microlattices derived from PIAM of Cu(NO\textsubscript{3})\textsubscript{2} and 3D CoO\textsubscript{x} on carbon microlattices derived from Co(NO\textsubscript{3})\textsubscript{2}, respectively. Notably, the CuO\textsubscript{x}/C and CoO\textsubscript{x}/C XRD patterns show the presence of the only the oxide phases of Cu and Co after calcination. Partial reduction of these metal oxides in forming gas (500 °C) converts copper oxides to Cu / CuO\textsubscript{x} heterointerfaces (Cu/CuO\textsubscript{x}/C) and cobalt oxide to Co/CoO\textsubscript{x} heterointerfaces (Co/CoO\textsubscript{x}/C), respectively. From these findings, it is evident that the mixed phase of transition metals and their oxides is formed without impurities and that the duration of post-annealing in forming gas can control the relative percentage of the metal/metal oxide to engineer its electrochemical properties.

XPS analysis of 3D microlattices of CuO\textsubscript{x}/C, and Cu/CuO\textsubscript{x}/C show the presence of Cu, C, and O, as illustrated in Supporting Information Figure S2a. Figure 2b shows the Cu 2p XPS spectra and fitting curves of CuO\textsubscript{x}/C, and Cu/CuO\textsubscript{x}/C. The binding energy of 932.1 eV is
distinctive of the Cu$_2$O phase within copper oxide, whereas the prevailing binding energy at 940.5 eV signifies CuO in the XPS spectra of CuO/C [28]. After reduction, it is observed that the CuO peak disappears in Cu/CuO/C, and the 932.1 eV peak shifts to 932.1 eV, confirming the presence of copper in the 3D microlattices of Cu/CuO/C. Additionally, the XPS spectra of Cu/CuO/C reveal a narrower and higher binding energy shift of the O 1s peak compared to CuO/C, confirming the reduction of oxygen in the copper oxide phase. The XPS survey scans of 3D microlattices of CoO/C, and Co/CoO/C show the presence of Co, C, and O, shown in Supporting Information Figure S2b. Figure 2e shows the Co 2p XPS spectra and fitting curves of CoO/C, and Co/CoO/C. The shift of the peak at 784.7 eV to 782.3 eV for Co 2p$_{3/2}$, typically indicative of Co$^{2+}$, towards a lower binding energy, confirms the reduction of CoO to elemental Co. The shift of the peak at 779.7 eV, which is less significant (0.5 eV), indicates the presence of Co$^{3+}$ rather than Co$^{2+}$, confirming a lower degree of reduction of Co$_3$O$_4$ to elemental Co$^{2+}$[29]. Furthermore, the XPS analysis of Co/CoO/C exhibits a shift in binding energy to a higher value for the O 1s peak in comparison to CoO/C, serving as additional confirmation of the oxygen reduction occurring within the cobalt oxide structures. During the TGA analysis of the Cu(NO$_3$)$_2$ precursor within the 3D microlattices, it was observed that the material retained 25.4 % of its initial mass, signifying
complete conversion at 450 °C, shown in Supporting Information Figure S3. In contrast, the uncoated 3D microlattices made of polymer retained 3.8 % of their original mass, reaching full conversion at 450°C. This reveals a weight ratio of 75 % Cu/CuOx to 25 % C. However, the TGA analysis of the Co(NO₃)₂ precursor within the 3D microlattices revealed that the material retained 12.5 % of its initial mass, confirming a weight ratio of 87.5 % Co/CoOₓ to 12.5% C.

2.3 Electrochemical characterization of HER activity

Controlling the oxygen stoichiometry of the microlattice coating through post-annealing enables the optimization of the mixed Cu/CuOₓ phase for HER. The electrocatalytic activity of 3D-microlattices of Cu/CuOₓ/C was characterized in a 1.0 M KOH electrolyte. Firstly, we compared HER activity of CuOₓ/C, and Cu/CuOₓ/C 3D microlattices with a powdered control sample of identical composition by linear sweep voltammetry (LSV) curves, shown in Figure 3a. Fully oxidized CuOₓ/C 3D microlattices exhibit electrochemical activity for HER, but require a higher overpotential of 210 mV to produce a current density of 10 mA/cm² and 502 mV for a current density of 50 mA/cm². The reduction of CuOₓ/C to form Cu/CuOₓ/C microlattices notably
enhances the HER activity, achieving a remarkable low overpotential of 145 mV at 10 mA/cm², which is lower than that of other 3D Cu based electrocatalysts[30–34]. Moreover, when compared to powdered controls, the 3D microlattices demonstrate 3X greater electrocatalytic activity normalized by surface area. The calculation of the surface area of microlattices follows a methodology similar to that outlined in our previous report (details available in the experimental methods section).[27] This validates that the 3D microlattices both expose a higher abundance of active sites and decreases interface resistance between the electrolyte and the electrode, thereby boosting electrocatalytic efficiency. We derived the Tafel plots from the polarization curves to delve into the reaction kinetics occurring on each electrode, shown in Figure 3b. The Tafel slope of Cu/CuOₓ/C microlattices is 134 mV/dec⁻¹, which is approximately 4X lower than that of Cu/CuOₓ/C powder (392 mV/dec⁻¹), confirming that active materials coupled with appropriate 3D microstructuring facilitates the binding between the catalyst and the adsorbates, enhancing HER kinetics. The improved dynamics observed in 3D microlattices could stem from the effective release of generated gas bubbles, which creates new surface-active sites for adsorbates, as illustrated in Figure 3c.

To further understand how 3D porous microlattices impact the reaction kinetics, the overall turnover frequencies (TOFs) per surface site were quantified (details of these calculation are supplied in the Supporting Information), as shown in Figure 3d. The TOF value of the 3D microlattices composed of Cu/CuOₓ/C is 0.82 s⁻¹ at an overpotential of 150 mV – 4X higher than that of powdered Cu/CuOₓ/C (0.21 s⁻¹) and higher than that of reported 3D structured Cu/CuOₓ.[35]. The increased TOF strongly aligns with the enhanced catalytic performance for HER, indicating that the improved activity of 3D microlattices is a direct result of their 3D printed porous micro-architecture. Furthermore, electrochemical impedance spectroscopy (EIS) was used to calculate charge-transfer resistance (R_{ct}), shown in Figure 3e. The R_{ct} of the 3D microlattices composed of Cu/CuOₓ/C is 5X lower (7.0 Ω) than that of the powder control (36.2 Ω), which matches with the other kinetics and suggests the formation of gas bubbles obstructs a significant portion of the catalytically active surface area within the powdered sample, leading to heightened ohmic resistance. To evaluate the electrochemical durability of the 3D Cu/CuOₓ/C microlattices, uninterrupted electrolysis (chronoamperometry) was conducted in 1 M KOH at a fixed potential of 210 mV versus RHE, maintaining an initial current density of 20 mA/cm². As depicted in Figure 3f, the 3D microlattice exhibits minimal reduction in activity over 120 hrs of continual operation.
an indication of its remarkable stability. By comparison, however, the stability of the Cu/CuO$_x$/C powder is inferior, showing large fluctuations even under low current density. These fluctuations could arise as bubbles form on the powder surface, impeding active sites and elevating resistance between these sites and the electrolyte.

To characterize the influence of the specific 3D microarchitecture on electrocatalytic activity, we printed various microlattices including cubic, body-centered cubic, and octet structures, as depicted in Figure 4a. The highest electrocatalytic activity was observed in cubic Cu/CuO$_x$/C microlattices, as revealed by LSV (Figure 4b). The superiority of cubic architectures can be attributed to the directional structure of the microlattices, which facilitate the diffusion of electrolytes into the 3D electrodes and efficient bubble release without any obstacles. This, in turn, reduces the resistance between the electrolyte and the electrode while maximizing the utilization of active sites for electrocatalytic activity. Tafel plots from the polarization curves (Figure 4c) show that cubic microlattices exhibit optimal reaction kinetics. In addition, when comparing the performance of our cubic 3D microlattices composed of Cu/CuO$_x$/C with reported Cu catalysts,
particularly Cu/CoOₓ foams[36], our 3D microlattices demonstrate a 2X increase in electrocatalytic activity and exhibit superior kinetics, as shown in the literature comparison of our electrodes’ electrochemical activity in terms of overpotential and tafel slope (Figure 4d). This underscores the significance of periodic 3D electrode architectures for enhancing performance beyond the limits of random porous foams.

To clarify the impact of the variable lattice structure, we extracted the electrochemically active surface area (ECSA) for the microlattices by conducting cyclic voltammetry (CV) measurements to determine the electrical double-layer capacitance (EDLC) (C<sub>dl</sub>) (shown in supporting information Figure S4), which is directly proportional to ECSA. At each scan rate, the cubic 3D microlattices of Cu/CuOₓ/C exhibit excellent anodic and cathodic current densities and a quasi-rectangular shape, suggesting a larger active surface area and more electrochemically active sites compared to other electrodes. The plots of differences of charging current density against scan rates (Figure 4e) reveals C<sub>dl</sub> of 23.2, 18.6, and 2.3 mF/cm² for cubic, BCC, and octet Cu/CuOₓ/C, respectively. The octet electrode exhibits a minimal C<sub>dl</sub> due to its dense morphology, wherein the dense structures trap gas bubbles, elevating resistance and limiting available active sites. These factors likely contribute to its comparatively lower HER activity. The charge-transfer resistance (R<sub>ct</sub>) of the cubic lattice (7.0 Ω) is smallest compared with the BCC (9.8 Ω), and octet (25.9 Ω) (shown in Figure 4f), matching the kinetics results. The optimal R<sub>ct</sub> of the cubic lattice further demonstrated its efficient electron transfer ability, contributing to its excellent HER activity. Indeed, chronopotentiometry (at 200 mV) measurements of the cubic microlattices showed impressive chemical stability with little overpotential variation over 120 hrs (Supporting Information Figure S5). This result is among the highest stability reported for 3D Cu based electrodes, affirming the reliability of electocatalysts fabricated by our PIAM method.

2.4 Electrochemical characterization of OER activity

To generalize our polymer infusion additive manufacturing (PIAM) for electrolyzer integration, we prepared cubic CoOₓ/C and Co/CoOₓ/C microlattices for performing OER in alkaline media (1M KOH). Additionally, we compared the OER activity of Co/CoOₓ/C microlattices at variable reduction temperatures. The reduced Co/CoOₓ/C microlattices annealed at 700 °C exhibit the best performance, which is able to achieve a remarkable low overpotential of 1.40 V vs RHE at 10 mA/cm² (shown in Figure 5a). For additional context, we highlight that this result is even lower than that observed for the benchmark RuO₂ (1.42 V vs RHE at 10 mA/cm²).
and lower than the overpotential of leading PGM-free electrocatalysts\[^{37–40}\]. This finding that both HER and OER electrocatalyst performance can be enhanced via 3D microlattice integration reveals the advantage of these architectures in producing a greater number of active sites and reducing the resistance at the interface between the electrolyte and electrode. This superiority can be attributed to the synergistic effect of a directional 3D structure and reduction of cobalt oxide to cobalt and cobalt oxide interfaces, which facilitates the diffusion of electrolytes and improves the kinetics for OER activity.

To understand the enhanced kinetics, we extracted the Tafel plots from the polarization curves, as illustrated in Figure 5b. The Tafel slope of Co/CoO\(_x\)/C is approximately 51 mV/dec\(^{-1}\), which is the best among reported 3D structured noble metal free electrocatalysts\[^{40,41}\], shown in Figure 5c. Furthermore, we have measured EIS to extract the charge transfer resistance (R\(_{ct}\)) (shown in Supporting Information Figure S6). The extremely low R\(_{ct}\) of the Co/CoO\(_x\)/C microlattice is just 2 Ω, the smallest among reported OER electrocatalysts, which aligns well with the other kinetic results\[^{42}\]. Stability testing plotting the charge transfer resistance against time for both the Co/CoO\(_x\)/C and Co/CoO\(_x\)/C powder samples is shown in Supporting Information Figure S7. The comparison reveals that for the 700 ºC reduced Co/CoO\(_x\)/C microlattices, the R\(_{ct}\) remains unchanged. However, in the case of the Co/CoO\(_x\)/C powder, the R\(_{ct}\) gradually increases over time. This observation suggests that the efficient evolution of bubbles on the Co/CoO\(_x\)/C microlattices can also enhance the stability of the electrode. Chronoamperometry measurements of the 700 ºC reduced Co/CoO\(_x\)/C microlattices operated at 1.50 V vs RHE (Figure S8) show robust stability by maintaining greater than 96% of its initial current density after 90 hrs continuous operation.
2.5 Characterizing bubble evolution kinetics in microlattices

To gain insight into the effects of the 3D microlattice pore structure on gas phase mass transport, we conducted experiments examining gas bubble evolution in both random (Figure 6a, iv, v) and ordered microlattices (Figure 6a, i, ii, iii) using gas injection and high-speed imaging. Bubble propagation was tracked for both microlattices and commercially available random foams, recording images from a side view using a high-speed camera. In this configuration, N\textsubscript{2} gas was supplied at a flow rate of 1 mL/s through a syringe needle into slabs of 3D structured electrodes approximately 4 mm thick, comparable to the catalyst microlattice dimensions. The initial injection of gas produces singleton bubbles that then propagate through the lattice due to the upward buoyant force (F\textsubscript{B}). Our video analysis of the bubble propagation time (\Delta t) for cubic microlattices shows the shortest time (\Delta t = 100 ms) among the set of 3D printed microlattices. Interestingly, this bubble evolution in cubic and BCC lattices is also significantly faster than evolution through random foams (\Delta t \sim 200 – 400 ms) (shown in Figure 6b), and even lower than

Figure 6. Bubble release dynamics. (a) Schematics illustration of different types of printed 3D microlattices and random foams and respective side view images to show the bubble release with the guide of buoyant force (F\textsubscript{B}). (b) High-speed camera images of bubble release from printed 3D microlattices and random foams to evaluate the time for bubble release time. (c) Schematics illustration of bubble evolution in bare and with microlattices. (d) Normalized velocity of bubble in different 3D microlattices and random foams.
that reported for other 3D printed structures\textsuperscript{[17]}. The slower evolution of gas bubbles within random foams can be attributed to the disordered pore structure, which leads to indirect pathways and trapping in narrow cavities (shown in Figure 6a). In contrast, in cubic microlattices, the bubbles move vertically in alignment with the buoyant force without undergoing scattering. Figure 6c shows a definition of the bubble evolution velocity in pure electrolyte ($v_0$) and the velocity of evolution in porous solids such as microlattices ($v_1$). To quantify the ordered pore arrangement effects on the bubble release through the 3D electrode, we have calculated normalized bubble velocity ($v_1/v_0$) on different 3D ordered microlattices and random structures, as shown in Figure 6d. The normalized bubble velocity in 3D printed cubic microlattices is highest (~0.8) among 3D printed microlattices and random structures, further confirming that 3D printed cubic microlattices are efficient for bubble release for achieving excellent electrocatalytic activity.

3. Conclusions

In this work, we have developed a rapid and robust polymer-infused additive manufacturing 3D printing method for fabricating transition metal-based electrocatalysts for alkaline electrolysis. We show how the design of optimal 3D architectures and post-treatments yield microlattice electrodes with increased active sites and greatly improved electrolytic properties of transition metal-based materials. Overall, for alkaline HER Cu/CuO$_x$/C has efficient electrocatalytic activity with low overpotential (145 mV to gain 10 mA/cm$^2$), and for OER Co/CoO$_x$/C electrode demonstrates exceptional activity with the lowest overpotential (1.40 V to gain 10 mA/cm$^2$) among all reported PGM-free electrodes. Additionally, we experimentally demonstrate the deeper connection between 3D electrode architecture and electrochemical stability via 120 hr continuous electrolysis, showing minimal morphological or compositional alterations. The enduring stability of these structures is credited to the rapid elimination of gas bubbles within precise, directional 3D microlattices. This underscores the method's reliability, presenting a viable alternative for fabricating free standing, integrated catalyst / electrode structures in a single scalable process with a high degree of design freedom. The suggested approach allows for the creation of electrocatalytic structures that explicitly optimize mass-transport beyond the limits of random porous architectures.

4. Experimental Methods

\textit{Fabrication of 3D microlattices of transition metal/transition metal oxide/carbon}
First, the Kudo3D stereolithography system was utilized to print 3D polymer microlattices employing Kudo’s Ultra High Resolution (UHR) positive resin based on an acrylate photopolymer. For further details about the 3D polymer lattice fabrication, please refer to our latest publication for in-depth protocol information\cite{43}. As shown in previous work, this system can be used to produce lattices with features as small as 20 micron after post-annealing processes. 3D microlattices of transition metal/transition metal oxide/carbon are fabricated by simply polymer infusion additive manufacturing. Briefly, first 3D polymer microlattices are infiltrated by respective metal salts. To prepare Cu/CuO\textsubscript{x}/C, 3D polymer microlattices were infiltrated by an aqueous solution of 1 M Cu(NO\textsubscript{3})\textsubscript{2}, while for Co/CoO\textsubscript{x}/C, polymer microlattices were infiltrated by an aqueous solution of 1 M Co(NO\textsubscript{3})\textsubscript{2} at 90 °C for 72 hours. The infused 3D polymer structures are then calcined at 450 °C in vacuum, and reduced at 500 °C in forming gas in a tube furnace. We observed that the calcined 3D infused polymer structures formed respective oxide phases of transition metals on carbon (CuO\textsubscript{x}/C and CoO\textsubscript{x}/C). However, reduction leads to the formation of the transition metal/transition metal oxide on carbon (Cu/CuO\textsubscript{x}/C and Co/CoO\textsubscript{x}/C).

Chemical Composition and Microstructural Characterization

The X-ray photoelectron spectroscopy (XPS) (Kratos, Axis Supra), powder X-ray diffraction (XRD) (Rigaku, Miniflex), transmission electron microscopy (TEM) (JEOL, 300 KV), scanning electron microscopy (SEM) (Helios 660), and thermogravimetric analysis (TGA) were employed to explore the chemical composition, perform microstructure analysis, and assess the mass ratio analysis of 3D microlattices consisting of transition metal/transition metal oxide/carbon. TGA tests were performed in a pure N2 atmosphere.

Bubble Evolution Measurements

Bubble evolution experiments were performed with a high-speed video camera focused on a slab of microlattice or foam that was 3D printed by similar methods to those used for the catalysts. Frame by frame analysis was used to assess the average bubble velocity in each respective lattice or foam sample oriented perpendicular to the direction of buoyant force, an identical orientation to how each catalyst microlattice was tested electrochemically.

Electrochemical Characterization

Electrochemical characterization was performed with a VersaSTAT electrochemical workstation from Princeton Applied Research is equipped with a three-electrode system for studying the activity of the research for the Hydrogen Evolution Reaction (HER) and Oxygen Evolution
Reaction (OER). The setup includes a working electrode consisting of the 3D microlattices, a reference electrode of Ag/AgCl in 3M KCl, and a counter electrode using Pt wire, all immersed in a 1.0 M KOH electrolyte solution. We note that the 3D microlattices function as the working electrode without requiring any additional additives or binders. All potentials are adjusted relative to a Reversible Hydrogen Electrode (RHE) using the formula

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \, \text{pH} + E^\circ_{\text{Ag/AgCl}}, \]

where \( E^\circ_{\text{Ag/AgCl}} = 0.1976 \, \text{V} \).

Moreover, the current is normalized based on the surface area of the calcined microlattices. We utilize calculations of the microlattice surface area of the octet, BCC, and cubic lattices that were reported in our previous publication based on a graph theory model summing the surface of each individual strut element and accounting for beam intersections.[27]

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Acknowledgements**

Measurements reported in this publication were conducted through the University of New Hampshire's Center for Integrated Biomedical and Bioengineering Research (CIBBR). M.S.R. receives support from the Dartmouth PhD Innovation program.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

**References**


Supporting Information

3D Printed Microlattices of Transition Metal and their Oxides Interfaces for Highly Stable and Efficient Water Splitting

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Figure S1. TEM images of a) Cu/CuOₓ/C, and high resolution transmission electron microscope image of b) Cu/CuOₓ/C.

Figure S2. XPS survey spectra of a) Cu/CuOₓ/C, b) Co/CoOₓ/C.
**Figure S3.** Thermogravimetric analysis of bare, Cu(NO$_3$)$_2$, and Co(NO$_3$)$_2$ soaked microlattices measured in pure N$_2$ gas.

**Figure S4** Cyclic voltammetry of a) cubic, and b) BCC, and c) Octet 3D microlattices with different scan rates.
**Description of calculations for turn over frequency (TOF) for H\textsubscript{2} of microlattice catalyst samples:**

The structural data of Cu/CuO\textsubscript{x} are as follows:

Density of Cu/CuO\textsubscript{x} = 6.31 g cm\textsuperscript{-3}. Average size of nanoparticle (determined from the Scherrer equation) = 30 nm. The shapes of the nanoparticles are approximated to spherical.

Loading amount on the electrode is 1 mg/cm\textsuperscript{2}.

Total volume of Cu/CuO\textsubscript{x} particles present on the electrode

\[ = (1 \times 10^{-5}) / 6.31 = 1.6 \times 10^{-6} \text{ cm}^3 \]

Total number of Cu/CuO\textsubscript{x} nanoparticles present on the electrode

\[ = (1.6 \times 10^{-6}) / [(4/3) (\pi) (r^3)] \]
\[ = (1.6 \times 10^{-6}) / [4.18 \times (15 \times 10^{-7})^3] \]
\[ = 1.1 \times 10^{11} \text{ particles} \]

Surface area of one Cu/CuO\textsubscript{x} nanoparticle

\[ = (4) (\pi) (r^2) \]
\[ = (4) (\pi) (15)^2 \text{ nm}^2 \]
\[ = 1.9 \times 10^{-15} \text{ m}^2 \]

Total surface area of all Cu/CuO\textsubscript{x} the nanoparticles present

\[ = (1.1 \times 10^{11}) \times (1.90 \times 10^{-15}) = 2.1 \times 10^{-4} \text{ m}^2 \]

The area of per unit cells of Cu/CuO\textsubscript{x} = 1.1 \times 10^{-19} m\textsuperscript{2}

There are 4 Cu atoms in this unit cell.

Hence, the total number of surface Cu atoms present

\[ = [4 / (1.1 \times 10^{-19} \text{ m}^2)] \times (2.1 \times 10^{-4} \text{ m}^2) \]
\[ = 7.6 \times 10^{15} \text{ atoms} \]

We assume that all the surface Cu atoms participate in the HER. Hence, the turnover frequency of H\textsubscript{2} production at Overpotential = 150 mV (current density measured = 10 mA cm\textsuperscript{-2}, electrolyte = 1 M KOH).

\[ = [(10 \text{ mA/cm}^2) (10^{-3}) (0.196 \text{ cm}^2) (6.02 \times 10^{23})] / [(96485.3 \text{ C/mol}) (2) (7.6 \times 10^{15})] \]
\[ = 0.83 \text{ s}^{-1} \]
Figure S5. Long-term stability (Chronopotentiometry) test of cubic Cu/CuO/C 3D microlattices for HER.

Figure S6. Nyquist plots for cubic CoO/C, and Co/CoO/C microlattices for OER.

Figure S7. Enlarged plot of impedance vs. time with the details of bubble growth and detachment on powder and 3D microlattices of Co/CoO/C for OER activity.
Figure S8. Long-term stability (chronoamperometry) test of cubic Co/CoOx/C 3D microlattices for OER.