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A 3D-Printed Electrochemical Water Splitting Cell

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Abstract

3D printing offers an attractive approach in fabricating complex designs across a wide range of materials to meet the functional requirements of targeted applications. In this study, the surface-patterned metallic electrodes are printed and integrated with custom built reaction vessels produced via a polymer-based 3D printing approach to create a complete electrochemical cell. It is shown that metallic electrodes with conical surface structures can be printed from Ti and Ni. In addition to conventional flat electrodes, the design can be tailor-made to any desirable geometry such as a curved structure. The transformation of inactive Ti electrodes with the deposition of an active catalyst can be readily obtained by electrodeposition to enhance the electrode functionality. A new design of fully printed compartmented electrochemical cell with both anode and cathode facing outward, separated by a Nafion membrane, enabling the water oxidation and proton reduction reactions to occur in their respective compartments is fabricated.

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A 3D-Printed Electrochemical Water Splitting Cell

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Keywords: 3D printing, water splitting, conical arrays, electrochemical cell, additive manufacturing

ABSTRACT

3D printing offers an attractive approach in fabricating complex designs across a wide range of materials to meet the functional requirements of targeted applications. In this study, the surface-patterned metallic electrodes are printed and integrated with custom built reaction vessels produced via a polymer based 3D printing approach to create a complete electrochemical cell. We show that metallic electrodes with conical surface structures can be printed from Ti and Ni. In addition to conventional flat electrodes, the design can be tailor-made to any desirable geometry such as a curved structure. The transformation of inactive Ti electrodes with the deposition of an active catalyst can be readily obtained by electrodeposition to enhance the electrode functionality. A new design of fully printed compartmented electrochemical cell with both anode and cathode facing outwards, separated by a Nafion membrane, enabling the water oxidation and proton reduction reactions to occur in their respective compartments was fabricated.

3D printing, or additive manufacturing technologies, have grown rapidly and are revolutionising the approaches to design, development and manufacturing across a wide range of fields. Driven by a digital blueprint, and built in incrementally added layers, these technologies can replace traditional manufacturing approaches that commonly involve multiple assembly steps. The layer-by-layer fabrication process adds material from the bottom up, and has simplified the manufacturing process; reducing production cost and carbon footprint.^[1,2] The flexibility in design, high precision in fabrication of complex geometry, material savings, and ease of customisation are among the key advantages of 3D printing. To date, fabrication of 3D printed structures covers a wide range of materials including polymers, metals, alloys, semiconductors, carbons, ceramics, and biomaterials.^[1-11] Advances in additive fabrication technologies has allowed the incorporation of different materials in a single printing process.

The flexibility in fabrication from metal printing offers the reality of creating tailor-made conductive components of desirable geometries. Printing of metallic structures can involve rather large objects for aerospace and biomedical engineering applications, and is increasingly employed in fabrication of micro-scaled devices for electrochemical storage and conversion applications, such as in water splitting,^[10-13] batteries,^[14-16] supercapacitors,^[17-19] fuels cells,^[20-22] and solar cells^[23]. For the former, electrochemical water splitting to produce hydrogen offers an attractive approach for renewable fuel generation.^[24-26] The key to advancing practical usage of this technology is the development of earth abundant and low cost electrocatalysts.^[27,28] This can be achieved by printing of established and efficient earth abundant electrocatalysts, such as Ni, or post-processing them into printed electrodes that can be integrated to an electrochemical cell.

We have recently reported the use of Selective Laser Melting (SLM) to facilitate the printing of a tuneable array of Ti-based conical structures to achieve enhanced photoelectrochemical water splitting performance.^[10] This conductive metallic structure

provided a suitable platform to grow 1D nanotubular structures, resulting in 1D nanostructures on the 3D conical array. Our demonstration however, was based on single electrodes, and it would be desirable if those electrodes could be incorporated into an electrochemical water splitting cell. In this work, we design and print all aspects possible for a functioning electrochemical cell; from the metallic electrode to drive the water oxidation and hydrogen evolution reactions, to the electrochemical cell casing based on polymer printing.

There were reports on the assembly of prototype 3D-printed electrochemical cells. Ponce de Leon and co-workers fabricated a flow reactor made from acrylonitrile butadiene styrene (ABS) and 3D printed nickel electrodes.^[29] Cronin and co-workers electrodeposited Ag catalyst on Ag coated polypropylene (PP) flow plates,^[12] as well as Pumera and co-workers on polylactic acid (PLA) plates with catalyst electrodeposited on the stainless steel electrodes.^[30] Here, we demonstrate the impact of surface patterning of the electrode topography towards enhanced electrocatalytic performance. We show the feasibility of designing electrodes with a concave base, as well as its integration to the full water splitting cell. Furthermore, the new design with both anode and cathode facing outward offers the possibility of using such a cell for photoelectrochemical water splitting application.

The 3D printed Ti and Ni electrodes were fabricated with conical array features using SLM and the work flow as described previously.^[8] In brief, the desired electrode geometry was modelled using computer aided design (CAD) software and was subsequently translated to standard tessellation language format (.stl), which was then sliced into layers. The sliced file is then converted to a metal printing file format, where the required laser parameters are linked to each individual layer. Each material has a unique set of values for fabrication via SLM, and associated post-processing (thermal treatment). These values vary on the basis of the printability of the metallic powder (assuming the powder is spherical in nature and dimensionally within a finite diameter range); properties such as thermal conductivity,

wavelength reflectance and melt temperature heavily dictate the fabrication process, while phase diagrams govern post-processing temperatures.

The conical-array features provide the desirable effect of enhancing surface area, in comparison to that of the similarly sized flat electrode. This electrode patterning offers a platform upon which further enhanced surface functionality and roughness can be introduced by post-processing via electrochemical or other approaches. We employed electrodes with the conical sizes with height of 800 μm , base of 250 μm , and distance between cones of 700 μm (Figure S1). Such surface structures will also facilitate enhanced contact with the reactant, as in this case of aqueous electrolyte for both water oxidation and proton reduction reactions. The distribution of products, oxygen and hydrogen, may also be facilitated by such design. As a proof-of-concept in the flexibility of 3D printing to tune electrode features, we further fabricate a concave-based electrode structure (Figures 1b and 1d) which differs to the flat-based structure (Figures 1a and 1c). Inset in Figures 1c and 1d show the optical images of the fabricated electrodes with flat- and curvy-based structures producable in both Ti and Ni. Our calculation of mathematical surface area indicates both flat and curvy-based structures provide almost an identical surface area. From a design perspective, such a concave-based structure could offer advantage in task-specific configurations. We focus here the fabrication of an all printable 2-compartment electrochemical cell from the electrode to the cell designs.

Figure 1 Schematic diagram of a flat (a) and a curvy (b) based 3D printed conical array electrodes. Optical images of a flat (c) and curvy (d) electrodes taken from the side views. Inset shows the optical photograph of the whole electrodes. SEM images of the (e) conical Ti electrode electrodeposited with Ni, and (f) higher magnification image showing Ni particles.

(g) XRD spectra of Ni and Ti electrodes, and Ni catalyst electrodeposited on Ti electrode. (h) EDX of Ti and Ni elements on Ni electrodeposited Ti electrode.

Ni is an abundant and cheap metal that is known to be an efficient catalyst for electrochemical water splitting. Conversely, Ti is relatively inefficient and in comparison results in a significantly large overpotential. Nevertheless Ti is the most widely employed 3D printed materials with matured printing capability, and it is of interest to examine if this material can be transformed as a support by post-processing of a layer of electrocatalytically active material. Taking advantages of Ti as a conductive metallic structure, we electrodeposited an active metal to enable efficient electrochemical water splitting. The Ni catalyst was deposited on Ti by a simple electrodeposition in nickel sulphate solution containing sodium citrate. Figures 1e and 1f show the SEM images of Ni catalyst deposited onto conical arrays of Ti. The Ni catalyst with particle sizes of $\sim 0.5\ \mu\text{m}$ formed a layer on the Ti electrode surface. XRD data in Figure 1g indicates the peaks corresponding to Ni and Ti, with the Ni electrodeposited on Ti resulting in peaks containing both mixed Ni and Ti. Energy Dispersive X-Ray Analyser (EDX) analysis in Figure 1h confirms the presence of both Ni on Ti elements with the Ni homogeneously electrodeposited on Ti electrode.

Figure 2 Comparison between the nickel electrode without (Ni) and with conical structure (Ni Con), with (a) showing linear sweep voltammograms, and b) cyclic voltammograms. c) Comparison of the linear sweep voltammograms of conical structure based on Ni and Ti. d) Comparison of linear sweep voltammograms of nickel electrodeposited on conical structure of titanium.

Figures 2a and 2b show the comparison of electrocatalytic water oxidation of 3D printed Ni with and without conical structures in 1.0 M KOH. The conical arrays exhibit enhanced peak current in comparison to the flat Ni. This is consistent with the increment in the peak area under the redox peak at ~ 1.40 V vs. RHE which indicates that conical array structure resulting in enhanced surface area. At 10 mA cm⁻² and 40 mA cm⁻², water oxidation overpotentials of

400 mV and 530 mV were required, respectively for the conical structure electrodes. To drive the water oxidation for control electrodes at the aforementioned current densities, larger overpotentials of 490 mV and 740 mV were needed in the flat nickel structure. In compare to the nickel electrodes, the use of titanium electrodes exhibited almost negligible catalytic peaks at both oxidative and reductive potential regions were obtained (Figure 2 c and 2d). Upon the electrodeposition of nickel catalyst on the titanium electrode surface, catalytic peaks corresponding to water oxidative and proton reduction were readily observed.

Based on the fabricated electrode, we further designed an assembly that intergrated the electrodes in a two-compartmental electrochemical cell seperated by a nafion membrane as schematically shown in Figure 3a. Figure 3b shows a Ti-plate with 1 cm x 1 cm exposed area, which was deposited with Ni. A small hole in the middle of the electrode allows electrolyte contact between anodic and cathodic compartments via the nafion membrane. A small tab on top of the electrode enables electrical connection. We employed a Stratasys Connex 350 high resolution 3D printing platform to print polymeric water-tight cathodic and anodic chambers using translucent proprietary photopolymer material (Stratasys - MED610). Meanwhile, a simple low cost fused deposition modelling system was employed to produce the ABS plastic locating base. Ethylene propylene diene monomer (EPDM) rubber gaskets were produced using a laser cutter and assembled between the plate, nafion membrane and cell compartment, ensuring water and gas tight sealing of the cell assembly. When necessary, the cell can be converted to a photoelectrochemical water splitting cell by placing quartz glass at the entrance port for light illumination on the electrode. O₂ and H₂ gases can be collected in their respective anodic and cathodic compartments. In the assembled cell, Ni electrodeposited Ti electrodes were employed as both anode and cathode. The assembly of full water splitting cell employed with printed anode and cathode. Instead of 1 cm x 1 cm electrode as previously reported,^[8] the electrode was printed to be integrated for the cell assembly. The fabrication of a larger electrode meant the heat-generation is greater, therefore the internal stresses within the printed structures

from the fabrication process was managed by supporting the electrodes at a small angle of inclination to allow gradual introduction of the welded cross sectional area, and then the excess support material and post-processed by heat-treatment at 950 °C. This temperature profile was selected so as not to introduce phase transitions into the material, but rather to eliminate internal thermal stresses produced as a result of the fabrication process.

Figure 3 (a) Schematic diagram of the assembly of 3D printed electrochemical water splitting cell consists of printable components. (b) The electrode with design allowing direct integration to the cell. (c) The optical photograph of the cell assembly, with the bottom white support to hold the cell.

Figure 4 (a) The comparison of a full cell with both anode/cathode consists of either conical arrays of Ti or Ni modified conical arrays of Ti, with experiment performed in 1.0 M NaOH solution at a scan rate of 5 mV s^{-1} . (b) The controlled potential electrolysis performed on Ni modified conical arrays of Ti at the applied potential of 1.87 V .

Figure 4 shows the full water splitting cell by the employment of electrodes with Ti coated with Ni catalyst in both anodic water oxidation, and cathodic proton reduction reaction. Comparison was also made with the Ti sample without further modification. As expected Ni electrodeposition was essential for full water splitting to be performed at a lower overpotential. The use of titanium alone resulted in a very low electrocatalytic current. The applied potential of 1.87 V was required for the water splitting to occur with a current density of 10 mA cm^{-2} . Using the nickel modified Ti conical array electrode, about 80 % of current retention after 1 h electrolysis (Figure 4b). Comparison of the SEM images show that there is no obvious change in the surface morphology of the electrodeposited Ni after 1 h electrolysis (Figure S2). There is a room of improvement with respect to the electrodes performance and stability, which requires further optimisation of the electrodeposition parameters.

In summary, the combination of metallic and polymeric based 3D printing approaches allows the fabrication of a 3D printable compartmental electrochemical water splitting device. The metal printing approach facilitates tailor-made electrode designs of desirable structures that can be readily integrated into a polymeric housing to serve as a full water splitting cell. The metallic electrode such as titanium which is a non-active water oxidation catalyst can be employed as a support for catalyst loading to facilitate electrocatalytic reaction, in this study by the electrodeposition of nickel. The used of other more active catalysts, is expected to lead to enhanced electrocatalytic performance.³¹⁻³⁴ The next strategy that can be employed is direct incorporation of a second metal during SLM printing, to obtain novel alloys that may offer enhanced electrocatalytic performance.

Experimental Section

Materials and Chemicals: All materials and chemicals employed in this work were used as received without further purifications. Deionized water that was purified by a Mili-Q system was used for preparation of all solutions and for the purpose of rinsing.

3D Printing: Metallic and polymeric 3D printing approaches were employed for electrodes, and the compartmented cell fabrication, respectively. 3D metal printing utilised a Realizer SLM50 metal printer (Realizer, Germany) with Ti and Ni based electrodes produced using a Grade 2 Ti metal (Fe 0.03, O 0.19, C 0.02, N 0.04, H 0.005 wt %, TLS TechnikSpezialpulver) and Ni metal (Ni 99.99%, TLS TechnikSpezialpulver) powders. The printed parts were removed from the build plate manually using a cutting process and underwent post-processing sonication in iso-propyl alcohol (Sigma Aldrich) for 60 minutes. This sonication process would remove any loosely bound titanium particles, which may have adhered to the surface during the print process, but had not completely bonded to the component. The electrodes were sonicated

with the array facing downwards to prevent any loose powder accumulation in the conical array. Samples were then dried using pressured nitrogen. In the fabrication of a larger 3D printed electrode for cell assembly, the internal stresses within the printed structures arising from the fabrication process were managed by supporting the electrodes at a small angle of inclination to allow gradual introduction of the welded cross sectional area, and then the excess support material. The formed structure was post-processed by heat-treatment at 950 °C. The locating base for the cell assembly was produced in ABS plastic using a simple low cost fused deposition modelling platform. The cathodic and anodic chambers were produced in a translucent proprietary photopolymer (MED610, Stratasys) via a Stratasys Connex 350 high resolution 3D printing platform.

Electrodeposition: The nickel nanoparticle was electrodeposited onto the Ti conical array electrodes in solution consisting of 0.1 M nickel sulfate hexahydrate and 0.2 M sodium citrate, at -1.0 V for 20 min.

Electrochemical water splitting experiments: Electrochemical water splitting measurements were performed in a three-electrode configuration using an Ag/AgCl (3 M NaCl, BASi) electrode as a reference electrode, platinum foil as a counter electrode and the 3D-printed metallic electrodes as anode and cathode, measured with a potentiostat (CH Instrument 650D). The measurements were performed in 1.0 M NaOH (Sima-Aldrich) and the potential value was converted to a RHE scale using the relationship $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \times \text{pH} + 0.1976 \text{ V}$.

Characterization: The electrodes were analysed by X-ray diffraction (XRD, GBC MMA diffractometer) with Cu K α radiation at a scan rate of 2 degree per min. The morphology of the samples was investigated by field emission scanning electron microscopy (FESEM, JEOL

JSM-7500FA). The resulting electrodes were imaged using a Leica M205 optical microscope and the associated dimensions compared to the CAD counterparts for physical reference.

Supporting Information

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

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The combination of 3D metal and polymer printings allow the fabrication of full water splitting cell. Direct integration of electrodes design is achievable with the tailored made printed design. New design with both anode and cathode facing outward is demonstrated, with 3D printed metallic electrodes also allow an ease of functional post-processing modifications.

Keyword

3D printing, water splitting, conical arrays, electrochemical cell, additive manufacturing

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A 3D-Printed Electrochemical Water Splitting Cell

Supporting Information

A 3D-Printed Electrochemical Water Splitting Cell

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Figure S1 The top (a) and side (b) views of optical images of the 3D printed conical arrays Ti electrodes.

Figure S2 Comparison of the SEM images of Ni electrodeposited on Ti electrode, in the conditions of as prepared electrode (a1, a2) and electrode after performed 1h electrolysis at 1.87 V (b1, b2).