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| **Citation**     | Hegde, C., Yan, Q., & Li, H. (2018). 3D printing electro-
|                  | catalysts for hydrogen production. Proceedings of the 3rd
|                  | International Conference on Progress in Additive
|                  | Manufacturing (Pro-AM 2018), 625-630. doi:10.25341/D4K88V |
| **Date**         | 2018                                                   |
| **URL**          | http://hdl.handle.net/10220/45993                      |
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3D PRINTING ELECTRO-CATALYSTS FOR HYDROGEN PRODUCTION

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ABSTRACT: The rising pollution and depleting fossils fuels urgently demand alternative renewable sources of energy. Hydrogen is one of the promising fuels with zero pollution which can be abundantly produced by electrolysis of water. But, the challenge is to produce hydrogen with least energy consumption via renewable sources from electrolysis of water. This has led to extensive research in synthesis of novel low-cost catalysts with high performance. However, there is still a need for a robust catalyst with low cost and long-term stabilities. Herein we demonstrate an alternative approach to synthesize these catalysts in which nickel-based catalysts are synthesized by extrusion-based 3D printing (3DP). The catalyst precursor is initially 3D printed by nickel-based powder. The precursor is oxidized and further sulfurized to convert them to catalysts with remarkable performance. The oxidized 3DP nickel (3DP nickel @NiO) shows remarkable performance for hydrogen evolution reaction (HER) with a low overpotential of 113.56 mV at 10 mA cm$^{-2}$. The sulfurized 3DP nickel (3DP nickel@NiS) can act as a bifunctional catalyst with a low overpotential of 166.17 mV at 10 mA cm$^{-2}$ for HER and 220 mV at 20 mA cm$^{-2}$ for oxygen evolution reaction (OER). Thus, this work demonstrates 3D printing as a promising way of synthesis to produce robust, binder-free catalysts in industries for mass scale application.

KEYWORDS: (Electrocatalyst, 3D printing, Tafel slope, overpotential)

1. INTRODUCTION: Hydrogen is one of the promising fuels for the future. High energy density and the zero pollution of hydrogen make it one of the efficient and environmentally benign energy carriers. Hydrogen can be abundantly produced by electrolysis of water. Therefore, the efficiency of the catalyst for this reaction process is critical. Platinum and IrO$_2$ are the best performing catalysts reported to date. However, due to their high cost and low abundance, the widescale application is limited. Therefore there has been increasing interest in earth abundant transition metal-based catalysts for this application. Nickel, cobalt and iron-based catalysts have shown appealing performance for HER and OER. For example, NiS (Chen et al., 2017), NiP (Lin, Zhang, Pan, & Liu, 2017), CoS (Sun et al., 2013), CoP (Tian, Liu, Asiri, & Sun, 2014), NiFe double hydroxides (Dutta, Indra, Feng, Song, & Paik, 2017) are few of the many reported transition metal-based catalysts with superior catalytic performance. However, in many cases, the catalysts are produced in powder form and require a binder to be attached to the electrode. This method is highly inefficient and not suitable for a wide-scale
application. Therefore synthesis of binder-free catalyst on a conductive substrate is necessary. Typically, researchers use commercially available foams of nickel, cobalt, titanium, etc. to synthesize binder free catalyst (Y. Wang, Zhang, Pan, Ma, & Zhang, 2017). But, the porosity and surface area of these foams are difficult to be tuned. Therefore, creating structures with tunable porosity and surface area can significantly facilitate manufacturing robust binder free catalysts with the large surface area. 3D printing can create structures with highly complex shapes, which also affords a high degree of customization and relatively easy way of fabrication (de la Osa, Pérez-Coll, Miranzo, Osendi, & Belmonte, 2016). Applications of 3D printing for the synthesis of catalysts are reported for methane conversion (Michorczyk, Hćdrzak, & Węgrzyniak, 2016), detection of methylene blue (Z. Wang, Wang, Li, Sun, & Liu, 2014) and battery electrodes (Jian Qin, 2014). Inspired by this, herein we demonstrate a facile method to synthesize catalysts for electrolysis of water. We 3D printed nickel plates through extrusion-based 3D printing. The printed parts are chemically treated to convert them to catalysts with superior activity.

2. EXPERIMENTAL SECTION:

2.1 Materials: Nickel powder (325 mesh- 99% purity), polyethylenimine (PEI), sulfur powder (99.5%), sodium hydroxide (NaOH, 99.5%), ammonium persulfate ((NH₄)₂S₂O₈, 99.5%) are used as obtained from Sigma Aldrich Pte. Ltd.

2.2 3D printing of nickel: 50 g of nickel powder is mixed with 1 ml of PEI and 4 ml of ethanol and mixed with mortar and pestle. The paste is loaded onto 5 ml syringe with 1.2 mm diameter nozzle and extruded using Choc creator chocolate printer. The printed pattern is dried in an electric oven at 60 °C overnight. The dried sample is sintered in a tube furnace with Ar flow. Initially, the temperature is raised to 300 °C at a ramping rate of 5 °C min⁻¹ and maintained for 2 hours for de-binding. After de-binding the temperature is raised to 1100 °C at 10 °C min⁻¹ and maintained for 6 hours and cooled to room temperature naturally.

2.3 Synthesis of the catalyst: the 3D printed nickel (3DP nickel) is cleaned with 6 M HCl and subsequently ultrasonicated in acetone and ethanol for 10 minutes each to clean the surface off oxides and impurities. The cleaned nickel foam is dried in Ar gas. In the meantime, in another beaker 40 mmol NaOH and 10 mmol (NH₄)₂S₂O₈ are dissolved in 40 ml DI water. The dried 3DP nickel is immediately immersed in this solution for 4 hours under ultrasonication and oxidized to form nickel oxide nanowires on 3DP nickel. This precursor is washed with DI water and ethanol and dried in an electric oven at 60 °C. The oxidized 3DP nickel is put in a porcelain boat with sulfur powder on the upper side. The porcelain boat with reactants is placed in a furnace under Ar gas flow and annealed at 400 °C for 2 hours with a ramping rate of 3 °C per minute.

2.4 Characterization: JEOL field emission scanning electron microscope (JSM-7600F, JEOL Ltd. Tokyo, Japan) is used to image the nanostructures formed during the synthesis. The phase of the synthesized samples is determined using Shimadzu XRD-6000 with Cu-Kα radiation operated at 40 kV and 30 mA.

2.5 Electrochemical measurement: The electrochemical measurements are done using Solartron analytical equipment (Model 1470E). The 3DP nickel samples of size 0.4 cm * 0.5 cm size are used for the measurements. The tests for HER and OER performance are conducted using a typical 3 electrode system with Hg/HgO as the reference electrode and Pt mesh as the counter electrode for OER, carbon electrode as a counter electrode for HER, and 1 M KOH as the electrolyte. The HER performance is measured by linear sweep voltammetry (LSV) from -0.7 V to -1.7 V at 5 mV per second, and the OER performance is measured from 0 V to 1 V vs. the reference electrode at 1 mV per second. The measured potential is converted to potential vs. reversible hydrogen electrode (RHE) by using the relation ERHE = Ehg/HgO + 0.098 + 0.059* pH.
3. RESULTS AND DISCUSSION: The 3D printing ink is synthesized using PEI as dispersant and ethanol as solvent. The XRD pattern of the nickel powder used confirms the pure phase of nickel as shown in Figure 1 (d). The ink is extruded through a nozzle of 1.2 mm diameter, and after sintering, the printed part retains its shape as shown in Figure 1 (c). Addition of foaming agents in ink will help to tailor the porosity of the printed parts. However, in the current study, we have not investigated the efficacy of various foaming agents and their effect on catalyst performance. Therefore, this study serves as a proof of concept to use 3D printing for catalytic applications. The 3D printed nickel is converted to an efficient catalyst by a facile method. The mixture of ammonium persulfate and sodium hydroxide is a strong oxidizing agent is well reported for the synthesis of Cu(OH)_2 nanowires on copper foam. However, to our knowledge, there is no report of this method to generate Ni-based nanostructures. We have implemented this approach to generate Ni-based nanostructures. The technique is simple and time-saving and can be used for a large surface area structures. Cleaned nickel foam is immersed in a solution containing 40 mmol NaOH and 10 mmol (NH_4)_2S_2O_8 dissolved in 40 ml of DI water for 4 hours under ultrasonication. After the reaction, the color of the foam changed to black and on drying the foam turned yellowish. The suggested reaction for the above process is

\[
\text{Ni} + 4 \text{NaOH} + (\text{NH}_4)_2\text{S}_2\text{O}_8 \rightarrow \text{NiO} + 2 \text{Na}_2\text{SO}_4 + 2 \text{NH}_3 + 3\text{H}_2\text{O}
\]  

The XRD pattern of the oxidized 3DP nickel confirms the formation of rhombohedral NiO (PDF no. 00-044-1159) as shown in Figure 1 (e). The peaks at 2θ of 37.25, 43.28, 62.85, 75.4, 79.5 correspond to (101), (012), (110), (113), (006) planes of the rhombohedral NiO. The FESEM images of the oxidized 3DP nickel show the formation of nanowires as seen in Figure 1 (a). The nanowire morphology furnishes large surface area suitable for catalysis. This precursor is later annealed in Ar flow with sulfur on the upper side for sulfurization. The FESEM images show the formation of nanowires on the nickel foam as shown in Figure 1 (b). The nano-wire morphology possesses very high surface area and can play a vital role in the catalytic activity. The XRD results confirm the formation of rhombohedral NiS (PDF no. 04-007-0707) as shown in Figure 1 (f). The peaks at 2θ of 32.25, 35.77, 40.54, 48.92, 50.21, 52.73, 57.51, 59.83 correspond to (300), (021), (131), (410), (401), (330), (012) planes of rhombohedral NiS. The major peaks are seen at 2θ of 22, and 44.95 correspond to (101) and (202) planes of trigonal Ni_3S_2 (PDF no. 01-075-6275).

The catalytic performance is estimated in a typical three-electrode system, with Hg/HgO as a reference electrode, Pt as a counter electrode for OER and graphite electrode for HER in 1 M KOH solution. The linear sweep voltammetry (LSV) is carried out at 1 mV sec^{-1} for OER and 5 mV sec^{-1} for HER. The oxidized 3DP nickel plate shows a remarkable performance with a low overpotential (η) of 113.56 mV at 10 mA cm^{-2} as seen in Figure 2 (a). Such a low overpotential is indicative of the superior performance of the catalyst. The Tafel slope of the catalyst is 160 mV dec^{-1} as shown in Figure 2 (d). Such a performance is expected from the synergistic effect between Ni and NiO as reported previously (Gong et al., 2014). The catalyst shows an overpotential of 450 mV at a current density of 30 mA cm^{-2} for OER. The Tafel slope for OER is not impressive.
Figure 1 (a) SEM images of the oxidized 3DP nickel; (b) SEM images of the 3DP nickel@NiS; (c) Optical images of the 3D printed nickel; (d) XRD pattern of the nickel powder used for 3DP; (e) XRD pattern of the oxidized 3DP nickel; (f) XRD pattern of the 3DP nickel after sulfurization.

Figure 2 (a) HER performance of oxidized 3DP nickel; (b) HER performance of 3DP nickel@NiS; (c) OER performance of 3DP nickel@NiS; (d) Tafel slope of HER performance derived from (a); (e) Tafel slope of HER performance derived from (b); (f) Tafel slope of OER performance derived from (c).
For 3DP nickel@NiS the performance of the catalyst is improved. The OER performance is remarkable with an extremely low overpotential of 165 mV at 10 mA cm\(^{-2}\) as shown in Figure 2 (c, f). The Tafel slope is 142.74 mV dec\(^{-1}\) with the catalyst reaching current densities of 20 mA cm\(^{-2}\) and 50 mA cm\(^{-2}\) at 220 mV and 411 mV respectively. Similar performance was reported in the past for catalysts synthesized on commercially available nickel foam (Zhou et al., 2013). Herein the catalyst synthesized on 3D printed nickel shows comparable performance confirming the effectiveness of 3D printing in catalysis. The catalyst also is highly active for HER with a low overpotential of 166 mV at 10 mA cm\(^{-2}\) and a Tafel slope of 151 mV dec\(^{-1}\) as shown in Figure 2 (b,d). Hence 3DP nickel@NiS can act as a bifunctional catalyst for water splitting. The remarkable performance may be attributed to a synergistic effect between nickel sulfide and nickel foam (Zhou et al., 2013).

### Table 1. Summary of the performance of the synthesized catalysts.

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<th>Catalyst</th>
<th>Electrolyte</th>
<th>HER performance</th>
<th>OER performance</th>
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<td></td>
<td></td>
<td>Overpotential</td>
<td>Tafel slope</td>
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<tr>
<td>Ni 3DP oxidized</td>
<td>1 M KOH</td>
<td>113.56 mV @ 10 mA cm(^{-2})</td>
<td>160 mV dec(^{-1})</td>
</tr>
<tr>
<td>Ni 3DP@NiS</td>
<td>1 M KOH</td>
<td>166.17 mV @ 10 mA cm(^{-2})</td>
<td>151 mV dec(^{-1})</td>
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As shown in Table 1 the synthesized catalysts from 3D printed nickel show remarkable performance for electrolysis of water. The synthesis route aids in manufacturing binder free catalysts that are robust and show high catalytic activity. The 3D printed metal base gives robust and highly conductive support, and the catalyst on the surface is active for chemical conversions. The process is versatile and can be similarly implemented for synthesizing catalyst based on cobalt, iron, vanadium and their compounds with sulfur, phosphorous, nitrogen, etc. Also, since 3D printing can produce complex shapes, the porosity and surface area of the foam structure can be easily tailored to suit the required application. The porous structure can be optimally designed to facilitate bubble interaction kinetics for reactions involving gases. In conclusion, we have demonstrated the benefit of 3D printing to create electrodes for catalytic and energy storage applications.

### 4. CONCLUSIONS:

In summary, we have 3D printed nickel and converted it into a catalyst with remarkable performance for water splitting. The process is highly repeatable and can be applied to catalysts based on various other elements. Also, by using a mixture of different metal powders the alloys and their compounds can be synthesized which can act as catalysts for water splitting. It is worthwhile to note the versatile nature of this synthesis. Similar synthesis routes can be used to fabricate electrodes for other catalytic systems such as fuel cells, oxidation of ammonia, batteries and in applications which need high surface area like supercapacitors. By using advanced 3D printing techniques such as selective laser melting, electron beam melting, etc. more complex structured electrodes can be designed that have large surface area and the architecture suitable for gas bubble release. Therefore, this study serves as a proof of concept for the synthesis of catalytic systems via 3D printing.
ACKNOWLEDGMENTS:
The authors gratefully acknowledge the research facilities at Singapore Center for 3D Printing for synthesis and 3D printing of nickel. Also, we would like to acknowledge the Facility for Analysis, Characterization, Testing and Simulation, Nanyang Technological University, Singapore, for the use of their electron microscopy and X-ray facilities.

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