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Electrochemical 3D Printing – Advanced Manufacturing of the Future

Additive manufacturing, also commonly known as 3D printing, is rapidly becoming a part of our everyday life. From DIY use by hobbyists to industrial manufacturing, 3D printing is setting a milestone to bring the *Industry 4.0* to reality. The technologies advance quickly with faster print rates, broader choice of materials and a constantly increasing accuracy and printing resolution. Impressively, state-of-the-art techniques take the printed feature sizes to the extreme: multiphoton optical stereolithography and focused electron or ion beams are now capable to produce objects with nanoscale resolution. Although at the cutting edge to printing finest details, these advanced manufacturing methods lack the capacity to process dense and pure electrical conductors – materials very much needed to push the limits of the technologies of the future. Microelectronics, nanooptics, microrobotics and energy storage are only a few examples of application areas where 3D printing of conductive metals can make a revolution. And it seems that modern electrochemistry can make this possible.

Simple but unconventional electrochemistry

We think of electrochemistry as a science of electron transfer – to transform chemical energy into electricity in a fuel cell, to store energy in rechargeable batteries or to detect analytes on an electrode. There is of course much more to that and a curious reader can check the main avenues in modern electrochemical science via a glimpse over the symposia topics in the 72nd Annual Meeting of the International Society of Electrochemistry (https://annual72.ise-online.org/symposia.php). But in that image of an electrochemist, there is hardly any space for new advanced microfabrication technology. Nevertheless, recent progress in electrochemical research opens exciting opportunities for a rather special application – microscale additive manufacturing of metal objects with dimensions so small that even a thin human hair next to them would appear as something from a world of giants.

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The very basis for these new advances is electroplating – a galvanic technique used for making thin metallic films on objects. Some everyday articles like cutlery, car grills and wheel rims exemplify the use of this old faithful method. The science behind the process is quite well understood nowadays: a metal ion in electrolyte solution can get reduced to a solid metal when the interface (working electrode in electrochemical terms) is biased with a negative enough voltage. When something more complex than a uniform thin film is needed, structuring can be introduced by providing a template. Metal growth is then localized only in the areas where the substrate is exposed. In microfabrication this approach is commonly employed for depositing metal features on a lithographically pre-defined pattern made of a photo- or e-beam resist.

To unlock the third dimension for this essentially planar technology (with the goal of producing complex features with high or even arbitrary aspect ratio) there is a need to add the capacity for layer-by-layer fabrication typically employed in conventional 3D printing. Material has to be brought to the specified locations and form so-called voxels – by analogy to pixels, smallest volumetric elements that constitute an object. The difference to conventional 3D printing is that the material still needs to be synthesized on the spot, directly in the location of the voxel. Electrochemically this can be achieved by converting the precursor ions into a solid by local electroreduction. Electrochemists found several elegant ways of doing this and have demonstrated how these new approaches could open a door for 3D printing of conductive materials at a microscale and even below. This resolution seems unattainable for classical additive manufacturing based, for example, on the extrusion of thermoplastics or sintering metal powders. How does it work?

Electrochemical micro-3D printing

Focusing electroplating in a confined space is not a trivial task but there are, in fact, several ways of doing it. In all approaches, it is required to place an equivalent of a print nozzle – a microelectrode or a nanopipette – directly in the desired printing location. The small nozzle dimensions are complemented with a proximity of the nozzle tip from the substrate surface, which in some cases is only a few nanometers. This allows efficient focusing of the electric field that drives electrochemical reduction or enables high flux of ions to exist right in the nozzle-substrate gap. A microanode that guides local reduction, or microchanneled cantilevers (known as FluidFM) that dispense metal ion solutions via microfluidics are the state-of-the-art examples of these types of microprinting (see illustration in Figure 1).

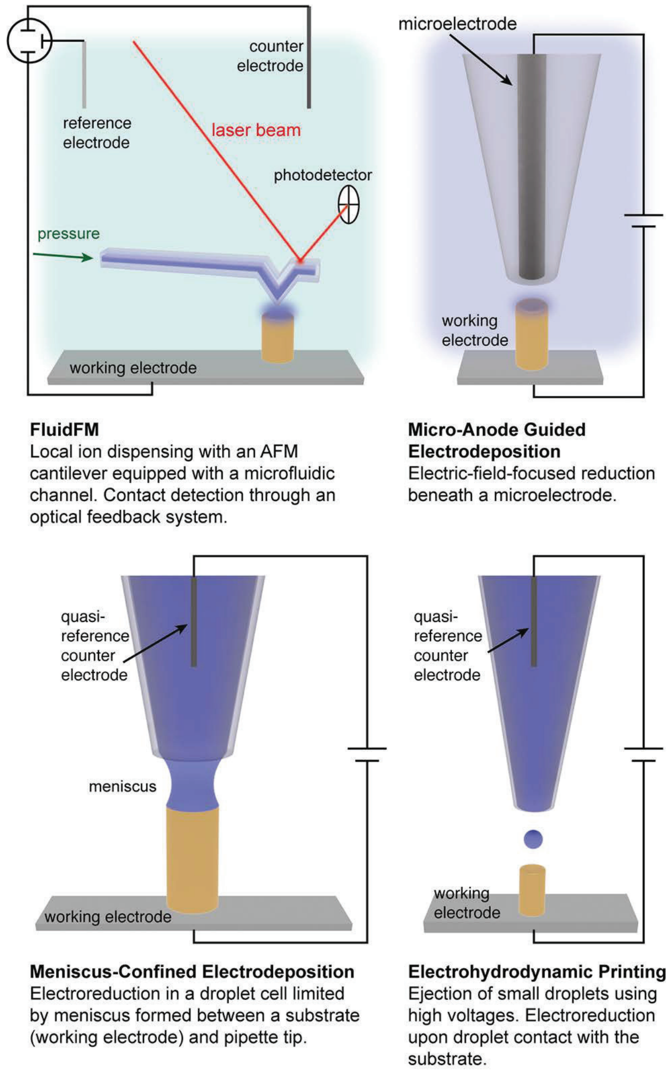

Fig. 1: A variety of approaches for electrochemical 3D printing.

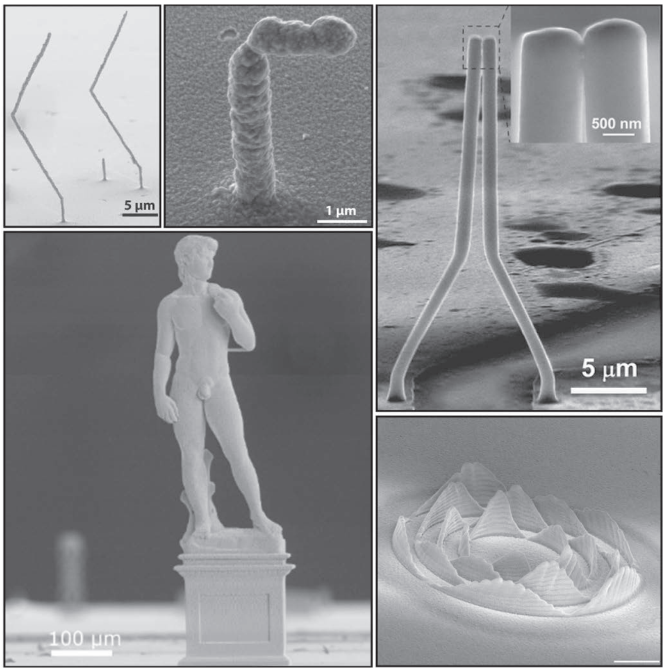

Fig. 2: Electrochemically printed micro-objects: free-standing zigzags and overhangs, vertically printed capacitive switch, Michelangelo's David replica and a sine wave pattern. Reproduced with permission from [1], copyright 2016 American Chemical Society, and [2-4] under CC BY 4.0 (http://creativecommons.org/licenses/by/4.0/).

Another way of focusing the electroplating is to limit the electrolyte cell itself to sub-microscale dimensions, eliminating the need to immerse the nozzle into an electrolyte. When the nanopipette with dimensions as small as 100 nm is brought to the substrate a liquid meniscus is formed. The footprint of this meniscus limits the active electrode area and the deposition occurs essentially in an electrochemical cell with attoliter (10^{-18} L) volume. In another approach, tiny droplets of electrolyte can be brought to substrates locally by high voltage ejection from nanopipettes (similarly to Taylor cone formation in electrospray ionization mass-spectrometry), and the metal ion content of the droplets is electrochemically transformed into solid metal.

These electrochemical printing technologies allow microfabrication with rather impressive complexity. Microscale metal objects with shapes from simple vertical pillars with sub-microscale dimensions to zigzags, overhangs, multi-helices, walls and "houses" are only a few examples to name. A 1:10'000 replica of Michelangelo's David shown in Figure 2 demonstrates the full capacity of these new technologies. High level of detail is given by the possibility to construct an object just as small as 1/2 of a millimeter with hundreds of thousands of voxels. Importantly, the printed metals contain almost unnoticeable number of defects/voids and exhibit large bulk material-like electrical and mechanical properties.

Facing the challenges

Despite the progress in electrochemical printing within the last years, there is still a lot to be done to bring this technology from research labs to the real world. First of all, the resolution is still far from where it should be and the nanoscale (<100 nm) remains mostly unconquered. However, many interesting phenomena including variations in electrical conductivity, ballistic electron transport or spin-selectivity exist only within these dimensions. Such high resolution is still to be achieved by electrochemical printing. This is a huge challenge – those electrochemical techniques that operate in electrolyte are limited by feature broadening due to ions intrinsically escaping away from the printing area, while the meniscus-confined techniques suffer from high propensity of nozzle clogging by feature growth within the meniscus.

Another major technological obstacle is printing speed. In most 3D printing methods the material is already synthesized and just needs to be transferred to the desired area. In electrochemical printing the synthesis has to occur during the deposition and that is often a relatively slow process with its own chemical kinetics and mass-transport limits. Parallel approaches with multiple nozzles operating simultaneously and independently can be a possible solution, but are rather difficult technologically, especially, at the nanoscale.

Finally, the materials palette is currently limited to only a few metals: copper, platinum, nickel to name a few. However, the range of electroplatable materials is significantly broader. The challenge is to make electrodeposition chemistry and process conditions compatible with 3D electroprinting. Fabrication of other material types, e.g. seminconductors, is also very much desired as this will open exciting possibilities in electronics. Probably the most important feature of all is the capacity to operate a multi-material printing process for fabrication of complex multi-component objects as well as for multi-compound complex substances (e.g. alloys). This is a major challenge for a variety of 3D printing techniques across all length's scales.

With these future developments one can expect a tremendous breakthrough in a multitude of advanced technologies. In addition to practical interest, technological development in 3D printing at the micro- and nanoscale raises its own fundamental research questions, from the physics of electron transfer to confined material growth and nanoscale mechanics. This makes us believe that the flexibility of 3D printing coupled with the high printing resolution almost undoubtedly will open new avenues in numerous research applications, and eventually will be taken further to a manufacturing site.

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Dmitry Momotenko studied analytical chemistry at the M. V. Lomonosov Moscow State University, Russia, and obtained his PhD at École Polytechniques Fédérale de Lausanne (EPFL, Switzerland) in 2013. Main focus of his thesis was on electrochemistry for local chemical analysis. After the PhD studies, he received a grant within the European Marie Curie Fellowship program to come to the University of Warwick (UK) with the project on new nanoscale ion sensing approaches using glass nanopores to track heterogeneous chemical reactions. In 2017 he joined ETH Zürich (Switzerland) as an independent group leader with an Ambizione Grant from the Swiss National Science Foundation to work on new nanoparticle manipulation methods. In 2020 he obtained an ERC Starting Grant and in 2021 he joined the Carl von Ossietzky University of Oldenburg, Germany, as a Junior Research Group Leader, where his current main research interests are nanoscale 3D printing, chemical sensing, scanning probe microscopy and electrocatalysis.

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Julian Hengsteler studied electrical engineering and information technology at ETH Zürich, Switzerland. At the end of his bachelor and during his master studies he moved his focus to the fields of sensor- and biomedical technology. His interest in these two disciplines led him to join the Laboratory of Biosensors and Bioelectronics (LBB) led by Prof. Janos Vörös for a master thesis. There he applied machine learning algorithms to investigate stimulation dependent activity in in-vitro neuronal cell cultures. In 2020 he started his PhD at LBB on micro- and nanoscale 3D printing under the supervision of Dr. Dmitry Momotenko. His research interests include electrochemical 3D printing, scanning probe microscopy, biosensing, and nanotechnology for life sciences.