

Localized Electrochemical Deposition of Multi- Metal Structures by Hydrodynamic Flow Confinement

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We present a device and method that leverages hydrodynamic flow confinements to enable localized electrochemical deposition of microscale multi-material metal structures.

Localized electrochemical deposition is a well-established method for additive manufacturing of micrometer scaled metal structures^[1]. At its core, the method relies on localized reduction of a metal salt electrolyte over a negatively charged substrate. The state-of-the-art methods, which offer sub-micron resolutions, utilize nano-channels for ion transport of the dedicated electrolyte. However, these methods are limited to a single metal, as in situ switching of ions within the nano-channels cannot currently be achieved.

We here leverage the liquid confinement ability of a vertical microfluidic probe (MFP) to precisely control the composition of a salt metal electrolyte between an integrated platinum electrode and a charged substrate^[2]. The MFP is a non-contact scanning device that combines hydrodynamic confinement of liquids with precision motion control. Upstream liquid switching and mixing allows for in-situ adjustment of the electrolyte composition, enabling precise control of the printed metal structure composition. Important to note, that in this system, the metal printing resolution is dictated by the integrated electrode dimension and distance from the charged substrate, not the flow confinement. It is in this way, that we are capable of maintaining micron scaled resolution, within a millimeter scaled flow confinement. By scanning with the microfluidic probe over a designated path, we print micrometer scale multi-material metallic structures containing smooth gradients in metal composition.

^[1] X. Li, P. Ming, S. Ao, W. Wang, *Int J Mach Tools Manuf* 2022, 173, 103848.

^[2] G. v. Kaigala, R. D. Lovchik, U. Drechsler, E. Delamarche, *Langmuir* 2011, 27, 5686.

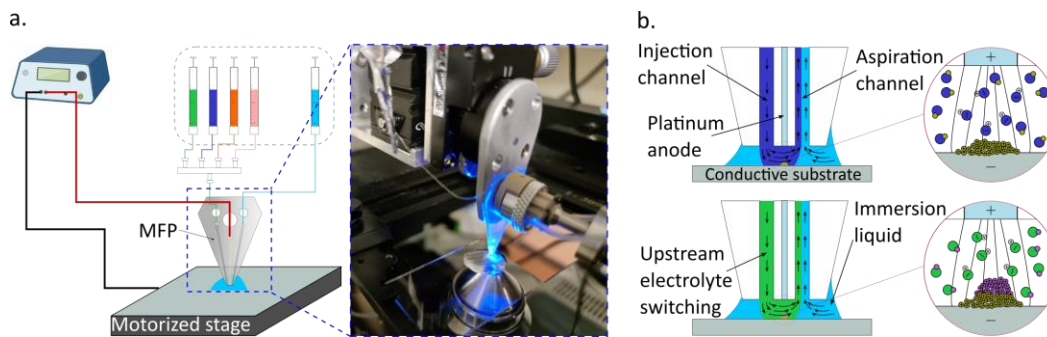


Figure 1: A schematic of the experimental setup and the working principle of HLECD. **(a)** Experimental setup schematic and image. The MFP is connected to a set of syringe pumps for injecting and aspirating the different electrolytes. A DC power supply is connected to the platinum micro-anode integrated to the MFP and to the charged substrate. A set of X,Y and Z motors control the alignment and movement of the MFP with relation to the charged substrate. **(b)** A schematic of the MFP apex during HLECD. The MFP is submerged within an immersion liquid and an electrolyte is confined by injecting it through the injection channel and aspirating it at a higher flow rate through the aspiration channel. When a DC voltage difference is applied between the platinum anode and the conductive surface, localized electro deposition of metal cations occurs. Upstream switching of the injected electrolyte results in seamless alteration of the metal being deposited.

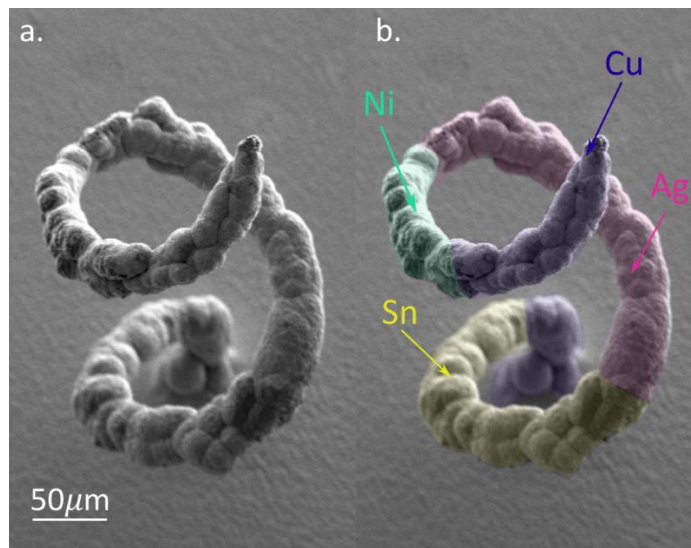


Figure 3: **(a)** SEM micrograph of a multi-metal micro coil deposited through HLECD. A tin base was printed confining a Sn HCl electrolyte at 10 V, followed by silver confining a AgNO₃ electrolyte at 7 V, then nickel confining a NiSO₄ electrolyte at 4.6 V and finally, copper using a CuSO₄ electrolyte at 2.6 V. The coil is 700 μm in height and its inner diameter is approximately 400 μm. It was fabricated with upstream liquid switching at an injection rate of 2 μl/min and an aspiration rate of 9 μl/min. At the apex of the MFP is a 100 μm diameter electrode. **(b)** EDS mapping, showing the different metal composition of the fabricated coil.