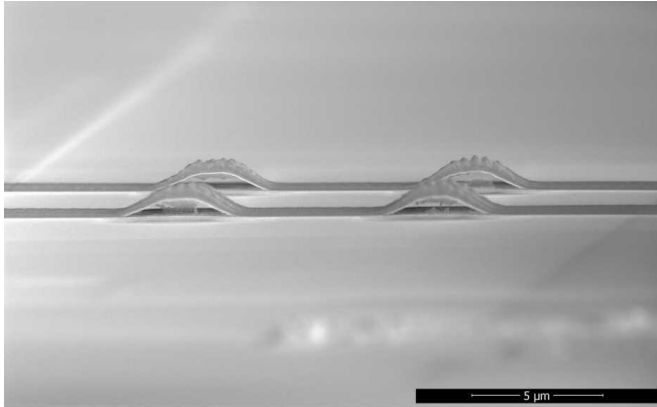


3-D printing of metallic micro-objects

30 April 2019, by Oliver Morsch



These silver stripes with arched bridges were realized with the help of a supporting structure made of copper, which was subsequently etched away. Credit: Alain Reiser / ETH Zurich

3-D printing has become an increasingly important production method. Researchers at ETH have now developed a new 3-D printing technique by which micrometre-sized objects made of several metals can be produced with high spatial resolution.

3-D printers can print almost anything these days, from production prototypes to artificial organs all the way to entire houses. Particularly on a microscopic scale, [additive manufacturing](#), as 3-D [printing](#) is also known, makes it possible to produce structures which cannot be realized using other techniques such as lithography. Up to now, a weak point of additive manufacturing has been the realization of metallic structures at the micrometre scale. A team of researchers at ETH Zurich led by Ralph Spolenak, professor at the Laboratory for Nanometallurgy of the Department of Materials, together with Dimos Poulikakos of the Department of Mechanical and Process Engineering as well as Renato Zenobi of the Department of Chemistry and Applied Biosciences, have now developed a [technique](#) that even allows one to print two metals at the same time with a spatial resolution of 250 nanometres.

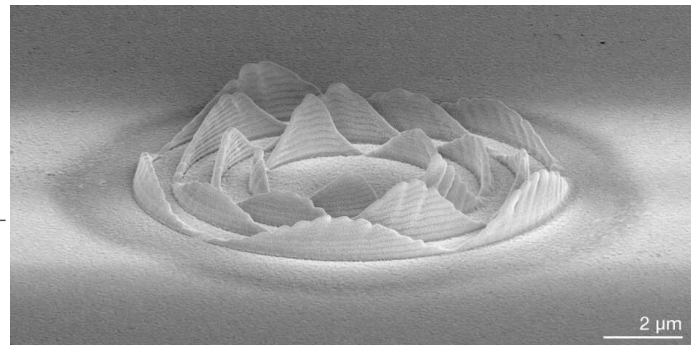
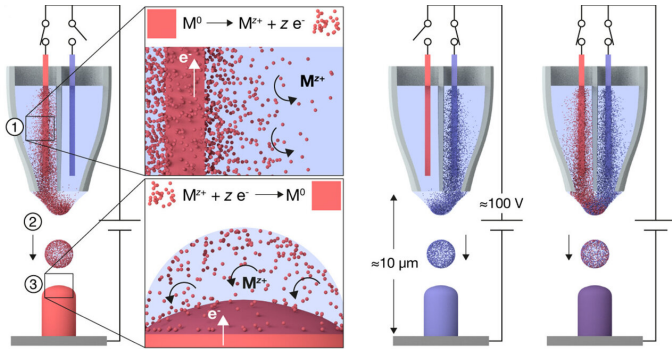
Alternatives to ink

Conventional methods for 3-D-[metal](#) printing are ink based, which means that the desired metal is dissolved as nanoparticles in a suspension and delivered to a surface through a printing nozzle. An advantage of such inks is that they can be made with a variety of materials, but they also have important disadvantages. "Those techniques require a post-printing treatment that involves heating, which results in a shrinking and pronounced porosity of the material," explains Alain Reiser, a Ph.D. student in Spolenak's group and first author of the study recently published in *Nature Communications*. "Typically, this means that the metallic structures are less conductive, mechanically unstable and, moreover, often contaminated with the organic compounds of the liquid solvent."

Printing with ions

To solve this problem, the researchers at ETH chose the direct route: the metals is no longer deposited as a nanoparticle, but rather transported in the shape of electrically charged metal ions. Those ions are created by applying an electric voltage to a "sacrificial anode" consisting of the desired metal inside the printing nozzle. The ions are then sprayed by electric forces inside a solvent onto the printing surface, where they lose their electric charge and reassemble as a metal.

The metals printed in this way are dense and have electrical and mechanical properties that are on a par with those of traditionally produced thin films. The new printing technique, moreover, offers a resolution of 250 nanometres with a printing speed of ten voxels per second (a voxel is a volume element, similarly to a pixel in 2-D printing). This makes the technique ten times faster than existing electrochemical printing methods.

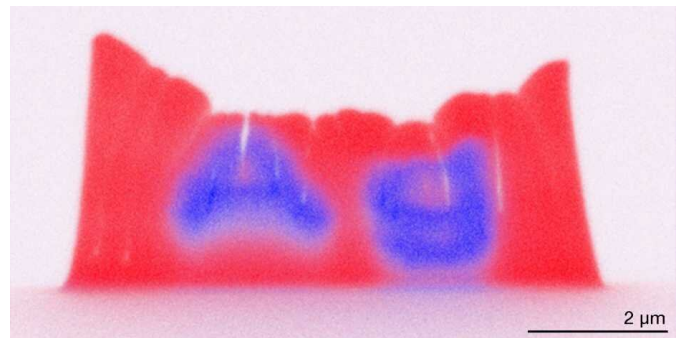


Working principle of 3D printing with metal ions. By applying appropriate voltages one can print, for instance, copper (left), silver (centre) or both metals at the same time (right). Credit: Alain Reiser / ETH Zurich

Copper structure printed layer by layer with a spatial resolution of around 200 nanometres. Credit: Alain Reiser / ETH Zurich

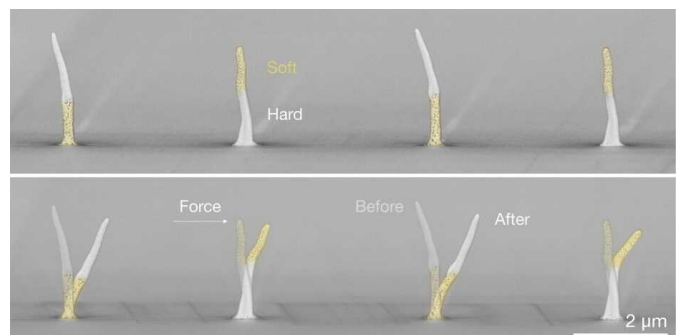
Alternating metals

The new "electrohydrodynamic redox printing technique" has another crucial advantage, as Reiser points out: "By printing directly with [metal ions](#), without the detour via an ink, we can even print two metals simultaneously or in alternation. This allows us to produce metal structures with locally controllable chemical, electrical or mechanical properties." To achieve that, the researchers use a double printing nozzle, inside of which there are two different sacrificial anodes. Which metal to print when, where and in what concentration can now be controlled simply through the applied voltages.



Chemical imaging of a printed 3-D structure with a varying distribution of the elements in the alloy (red: copper, blue: silver). The local chemical properties can be controlled with a resolution of 250 nanometres during the printing process. Credit: Alain Reiser / ETH Zurich

Using a single printing nozzle also makes it easier to position both metals exactly. It is possible to switch between the two metals up to ten times per second. In that way, Spolenak and his collaborators were able, for example, to print tiny pillar measuring only 250 nanometres in width and which contained alternating sections made of copper and silver. By adjusting the composition of the two-metal alloy, the local porosity—and hence the stiffness and stability—of the nano-pillar could be precisely controlled.



Silver nano-pillars: by etching copper away from the sections with a silver-copper alloy (yellow), their porosity was increased. In those places the material is less stable,

which becomes visible when a force is applied (bottom figure). Credit: Alain Reiser / ETH Zurich

The new technique has a multitude of possible applications. The researchers at ETH are currently collaborating with experts on printed [electronic circuits](#) in order to produce extremely thin connecting wires to organic semiconductors using their 3-D printing method. Furthermore, in the future they aim to extend the range of metals used (so far, copper, silver and gold have been tested) to include, for instance, magnetic materials. According to Reiser, in the long run the production of photosensors, printed integrated circuits and mechanical metamaterials should be possible.

More information: Alain Reiser et al. Multi-metal electrohydrodynamic redox 3D printing at the submicron scale, *Nature Communications* (2019).
[DOI: 10.1038/s41467-019-09827-1](https://doi.org/10.1038/s41467-019-09827-1)

Provided by ETH Zurich

APA citation: 3-D printing of metallic micro-objects (2019, April 30) retrieved 23 October 2021 from <https://techxplore.com/news/2019-04-d-metallic-micro-objects.html>

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