Simon Sprengel, Dmitry Momotenko

Scanning probe methods: From high-resolution imaging to nanoscale additive manufacturing

Scanning probe microscopy (SPM) is a family of powerful techniques for structural and functional imaging of interfaces using a (solid) probe. Starting with the pioneering development of scanning tunneling microscopy (STM) in 1982, the fundament for high resolution localized surface interaction was laid [1]. Already from the early age of SPM it became clear that the way the probe interacts with the surface could be adjusted to also allow local surface modification. Quickly, SPM became a tool for high resolution maskless patterning. Nowadays, SPM makes another leap in nanotechnology by extending microfabrication into the third dimension.

Manipulating molecules with high resolution

Since the introduction of SPM there has been a plethora of examples of local surface modification with high resolution. Among the most impressive ones is a stunning demonstration shown by IBM in 2011 in form of a Stop-Motion Movie called “A Boy And His Atom”, published on the video platform YouTube (Fig. 1a). An STM tip was employed to precisely manipulate CO molecules on a copper substrate. The experiment was conducted at 5 K operating temperature to ensure stationarity of adsorbed CO, which was imaged by STM after each re-organization of the surface thus creating the movie frames [2]. Another elegant example was shown by recreating a painting “Degas Dancers” by Gina Candelori (Fig. 1b) and the University of Cambridge coat of arms on a microscale (Fig. 1c). The images were patterned by red and green fluorescently labeled DNA molecules on a streptavidin-coated glass surface [3]. Evidently, read-write capabilities of many SPMs provide a vast playground for creating functional interfaces. Scanning electrochemical microscopy (SECM) is particularly suited for these tasks, as, for instance, in creating cell adhesive and repellant coatings. A microelectrode tip was used to locally etch a oligo(ethylene glycol)-terminated self-assembled monolayer (OEG-SAM) forming a pixelated portrait, which has then been visualized by electrochemical imaging (Fig. 1d-f) [4].

Simon Sprengel, M.Sc., Prof. Dr. Dmitry Momotenko
Institute of Chemistry
Carl von Ossietzky Universität Oldenburg
D-26111 Oldenburg, Germany
simon.sprengel@uni-oldenburg.de
dmitry.momotenko@uni-oldenburg.de

A journey into the third dimension

Until recently the bulk of the progress in surface modification with SPM has been made on planar interfaces and in 2D arrangement. At the same time, the demand for 3D micro- and nanostructures has grown tremendously. While 3D printing or additive manufacturing (AM) is already enjoying success across various industries, 3D-approaches in microfabrication only now start to get traction. For SPM-based techniques the trend is somewhat similar, since transitioning from 2D to 3D is not trivial and requires tight control of instrumental and materials aspects in all three dimensions.

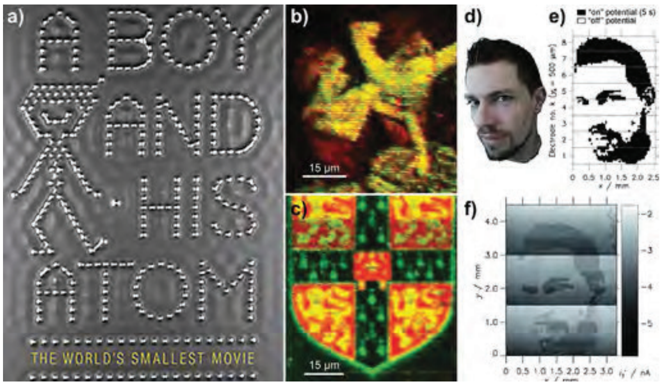

Fig. 1: Surface modification examples by SPMs. (a) IBM’s stop-motion film “A Boy and His Atom”, (b) a recreation of “Degas Dancers” by Gina Candelori and (c) The University of Cambridge emblem, formed by arranging fluorescently labeled DNA biomolecules on a streptavidin-coated glass surface. (d-f) Chemical surface modification via SECM by local etching of an OEG-SAM. © Angewandte Chemie International Edition [3, 4]. Reproduced by permission of John Wiley & Sons Ltd. and IBM/ YouTube “Fair-Use” [2]. All rights reserved.

Some examples of out-of-plane fabrication with SPMs, however, have been known for quite a while already. Electrochemical deposition using a microelectrode in SECM configuration achieved a 100 µm diameter copper pillar (Fig. 2 SECM) [5]. Also, more recently a major step towards 3D metal AM was achieved via meniscus-confined electrodeposition (MCED) that produced copper-structures with <1 µm diameter [6]. The current development of AM for microfabrication relies on similar principles but is equipped with a whole range of additional features to ensure reliable and reproducible operation even at the nanoscale, which remained unattainable for a long time.

Emerging techniques for small-scale AM

The recent advances in SPM for high resolution 3D printing are made by implementing AM-specific adjustments in SPM instrumentation. For example, FluidFM, which is based on conventional atomic force microscopy (AFM), uses a hollow cantilever filled with electrolyte solution. When the cantilever delivers precursor metal ions into the electrolyte bath, electrochemical reduction at the substrate drives the deposition of the solid metal. The AFM feedback allows tracking metal growth at individual voxel level, ensuring full automation for the fabrication of complex 3D structures with microscale resolution (Fig. 2 FluidFM) [7].

The recent breakthroughs in AM in terms of feature size have been achieved by introducing an intermittent meniscus formation as feedback in MCED. This boosted the level of automation, allowing to monitor metal growth with kHz bandwidths, opening the way to achieve 25 nm voxel size (Fig. 2 MCED) [8]. At larger dimensions, MCED has also demonstrated for printing complex structures. Several other important advances in small scale SPM-based AM have been achieved using electrohydrodynamic redox printing (EHD-RP) (which shares many similarities with SPM-based AM without strictly being an SPM). EHD-RP utilizes electric field induced nanodroplet ejection from electrolyte-filled nozzles. As the droplets land on the biased substrate, the metal ion content gets converted into solid metal via electroreduction. As shown recently, a tight droplet control can allow metal structures with diameters down to 50 nm, with a complexity level approaching that somewhat between FluidFM and MCED (Fig. 2 EHD-RP) [9].

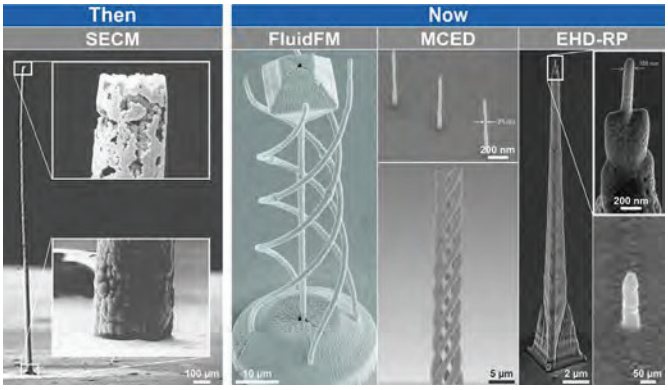

Fig. 2: Advances of 3D SPM Then vs Now. A comparison of early SECM copper deposition vs current techniques of FluidFM, MCED, and EHD-RP techniques. © The Electrochemical Society [5], © Advanced Engineering Materials [7], © Small [9]. Reproduced by permission of IOP Publishing Ltd., John Wiley & Sons Ltd., and under CC-BY-NC-ND 4.0 [8]. All rights reserved.

Challenges and future directions of SPM-based 3D printing techniques

The rising interest to small scale AM has led to significant advances in SPM-based 3D printing, but further development is yet restricted by various challenges. One remains within fundamental aspects that govern many functional SPMs – mass-transport. The limitations of ion transport at the nanoscale, typical for techniques like FluidFM, limit the available range of printing rates and resolution. Mass-transport-related broadening in liquid is difficult to take control of by simply reducing the nozzle opening. Similar limitations apply for EHD-RP where the resolution is linked to the droplet size, which becomes independent of the nozzle diameter at the nanoscale. For MCED, which currently champions the resolution, fabrication of more complex structures remains challenging. Despite success in printing overhangs and coils (Fig. 3a) reliable printing of more complex shapes and making connections between structures is still difficult (see missing part of "H" in Fig. 3a) [8].

Further advances also require extensive understanding of materials growth and microstructure control. Electrochemical AM offers fully dense as well as porous materials (like shown in Fig. 3b-c) [8, 10]. For advanced nanoscale applications, varying porosity could become very beneficial. Further progress in materials design needs means of surface structure engineering, as well as understanding of nanoscale mechanics (which for small scale AM becomes its own playground [11]). Electrical properties of the additively manufactured nanostructures are also a focus of current research activities. This requires extensive combination of high-resolution techniques, including electron microscopy, nanomechanical characterization, as well as advanced sample preparation techniques.

Additionally, macroscopic electrodeposition chemistries are not always directly transferrable to nanoscale AM. Although chemical composition of the printed features is typically given by the purity of the metal precursor (see EDX of the pure copper structures shown in Fig. 3d-e) [8], chemical composition control is often needed for new materials and processes. An extension of the material library is central for advanced applications along with the development of techniques to combine multiple materials into a single design.

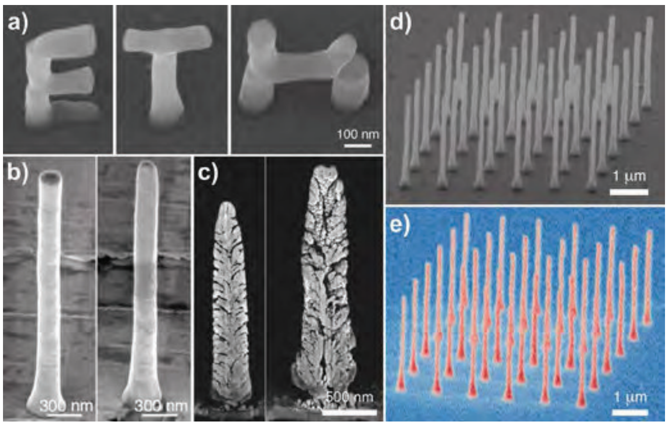

Fig. 3: Microstructure and chemical composition of additively manufactured metals. (a) Advances in MCED towards printing overhangs, focused ion beam (FIB) milling of (b) MCED- and (c) EHD-RP-fabricated Cu pillar porosity comparison, and (d-e) SEM/EDX analysis of MCED-printed structures, confirming high copper purity. Reproduced from [8] and [10] under CC-BY-NC-ND 4.0.

SPM has come a long way from its origins as a purely imaging approach to a powerful tool for surface modification and nanofabrication. The transition from 2D to 3D structures has opened new frontiers, but significant challenges remain. While recent advancements in SPM-based techniques such as FluidFM, MCED, and EHD-RP have enabled higher resolution and wider material library, technical issues and questions about material properties require further research. The immense opportunities that these techniques are yet to offer in micro- and nanofabrication fuel the growing interest in these developments.

References

[1] Binnig, G.; Rohrer, H.; Gerber, C.; Weibel, E., Surface Studies by Scanning Tunneling Microscopy. *Physical Review Letters* 1982, **49** (1), 57-61.

[2] IBM Research Almaden, *A Boy And His Atom*. https://www.youtube.com/watch?v=oSCX78-8-q0 (accessed 11.03.2025).

[3] Rodolfa, K. T.; Bruckbauer, A.; Zhou, D.; Korchev, Y. E.; Klenerman, D., Two-component graded deposition of biomolecules with a double-barreled nanopipette. *Angew Chem Int Ed Engl* 2005, **44** (42), 6854-9.

[4] Lesch, A.; Vaske, B.; Meiners, F.; Momotenko, D.; Cortes-Salazar, F.; Girault, H. H.; Wittstock, G., Parallel imaging and template-free patterning of self-assembled monolayers with soft linear microelectrode arrays. *Angew Chem Int Ed Engl* 2012, **51** (41), 10413-6.

[5] El-Giar, E. M.; Said, R. A.; Bridges, G. E.; Thomson, D. J., Localized Electrochemical Deposition of Copper Microstructures. *J. Electrochem. Soc.* 2000, **147** (2), 586-591.

[6] Hu, J.; Yu, M.-F., Meniscus-Confined Three-Dimensional Electrodeposition for Direct Writing of Wire Bonds. *Science* 2010, **329** (5989), 313-316.

[7] Ercolano, G.; Zambelli, T.; van Nisselroy, C.; Momotenko, D.; Vörös, J.; Merle, T.; Koelmans, W. W., Multiscale Additive Manufacturing of Metal Microstructures. *Adv. Eng. Mater.* 2019, **22** (2).

[8] Hengsteler, J.; Mandal, B.; van Nisselroy, C.; Lau, G. P. S.; Schlotter, T.; Zambelli, T.; Momotenko, D., Bringing Electrochemical Three-Dimensional Printing to the Nanoscale. *Nano Lett* 2021, **21** (21), 9093-9101.

[9] Menetrey, M.; Kupferschmid, C.; Gerstl, S.; Spolenak, R., On the Resolution Limit of Electrohydrodynamic Redox 3D Printing. *Small* 2024, **20** (46), e2402067.

[10] Menetrey, M.; Koch, L.; Sologubenko, A.; Gerstl, S.; Spolenak, R.; Reiser, A., Targeted Additive Micromodulation of Grain Size in Nanocrystalline Copper Nanostructures by Electrohydrodynamic Redox 3D Printing. *Small* 2022, **18** (51), e2205302.

[11] Zhang, W.; Li, Z.; Dang, R.; Tran, T. T.; Gallivan, R. A.; Gao, H.; Greer, J. R., Suppressed Size Effect in Nanopillars with Hierarchical Microstructures Enabled by Nanoscale Additive Manufacturing. *Nano Lett* 2023, **23** (17), 8162-8170.

Simon Sprengel, M.Sc.

Simon Sprengel studied chemistry at the Carl von Ossietzky Universität Oldenburg, Germany. With the focus on technical electrochemistry he joined the group of Dmitry Momotenko at the Department of Chemistry. During his master's thesis he started the development of a microfluidic printing platform for single cell bioprinting technology for biomedical applications. Continuing his journey in Prof. Dmitry Momotenko's working group, he started as PhD candidate performing research on the development of micro- and nanoscale electrochemical additive manufacturing processes.

Prof. Dr. Dmitry Momotenko

Dmitry Momotenko studied analytical chemistry at the M. V. Lomonosov Moscow State University, Russia, and obtained his PhD at École Polytechnique Fédérale de Lausanne (EPFL, Switzerland) in 2013 in the Group of Prof. Hubert H. Girault. Main focus of his thesis was on electrochemistry for local chemical analysis. After the PhD studies, he received a Marie Curie Fellowship at the University of Warwick (UK) with the project on nanoscale ion sensing with 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, where he is currently leading the Electrochemical Nanotechnology Group with research centered on nanoscale 3D printing, chemical sensing, scanning probe microscopy and electrocatalysis.