Two-photon nanolithography for patterning ionic liquid-polymer composites

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The lithographic capabilities of a photoresist-based material facilitate direct 3D manufacturing of electrically conductive and transparent nanostructures.

An important challenge in micro- and nanotechnology is direct patterning of functional structures. Moreover, the manufacture of 3D structures that have additional properties (e.g., conductivity and optical transparency) already in the directly patterned materials is highly desirable in a number of modern applications. Such applications include sensors, solar cells, and electro-optical display devices (e.g., LCDs and electroluminescent display devices). Transparent conductive oxides (TCOs), such as indium tin oxide (ITO), antimony-doped tin oxide, and cadmium stannate (cadmium tin oxide), are commonly used materials for the functional 3D structures (e.g., as transparent electrodes). Of these, ITO is the most prominent on a commercial scale, and sputtered ITO films have conductivities of up to $10^4 \text{S cm}^{-1}$. However, high substrate temperature conditions during coating of ITO, the complexity of fabrication methods, and the high cost of indium limit the range of potential ITO applications.

Intrinsic conductive polymers, such as poly(3,4-ethylenedioxythiophene), also known as PEDOT, as well as electrically conductive polymer composites (ECPCs), have emerged over the past few years as alternatives to TCOs. In several ECPCs, a photoresist (an electronic insulator in its pure state, typically used for the direct manufacture of permanent patterns) is mixed with various conductive filler particles to significantly increase the conductivity of the polymerized material. Such composites allow the fabrication of low-cost devices with new properties. For instance, flexible plastic substrates with an electroconductive polymer layer can be produced through the use of continuous hopper or roller coating methods (rather than a batch process such as sputtering). The resulting organic electrodes enable straightforward fabrication of electronic devices that are more flexible and have lower costs and lighter weights. Efforts in this direction to date, however, have yielded sub-optimal results. This is because the polymer composites had low optical transparency across visible wavelengths, they were only slightly conductive, or they were incompatible with high-resolution structuring.

In previous work, we presented three novel, cross-linkable, conductive, and highly transparent composite materials that are based on a photoresist. The photoresist materials we used were SU-8 3010 (from MicroChem Corp.), IP-L 780, IP-G 780 (both from Nanoscribe GmbH), and OrmoComp (from micro resist technology GmbH). ILs are examples of new materials that provide advantageous characteristics and facilitate a combination of optical and electrical properties. They are potentially unique solvents, with a wide range of physicochemical properties, as well as extremely low vapor pressure and high thermal, chemical, and electrochemical stability. Furthermore, a wide variety of

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anion/cation combinations (i.e., tunability) can be easily adjusted to tailor their properties, including ionic conductivity, viscosity, melting point, water miscibility, and density. Although ILs are conductive, their liquid nature is an obstacle to applications where a predefined physical shape is required (i.e., 3D functional structures). For such applications a process of solidification is necessary to enable the immobilization of ions. This process allows the formation of a branched polymer or a 3D solid structure, i.e., a polymer matrix porous network that entraps the IL. In our so-called ionically conductive polymer composite (ICPC), liquid-like properties (e.g., charge transport) originate from the IL, whereas solid-like properties originate from the host polymer. This contributes to material flexibility, but also prevents the system from flowing.

We have also developed approaches for the patterning of our ICPC, with the use of conventional and two-photon photolithography techniques.\textsuperscript{10,11} Two-photon polymerization (2-PP) is a fabrication technology that allows exact reconstructions of specific volume shapes to be achieved. This novel, rapid prototyping technique—also known as 3D direct laser lithography—is used for the fabrication of complex structures that have feature sizes smaller than 100nm (i.e., far beyond the diffraction limit of the applied laser’s wavelength).\textsuperscript{12} The key aspect of this method is that polymerization takes place only inside the focus of the laser beam. The 2-PP process is therefore a one-step 3D patterning approach and provides superior nanometer resolution, in combination with an accurate control of topology.

In addition, we have demonstrated a proof-of-concept multifunctional sensor for temperature and relative humidity sensing. As we have continued our research, we have aimed to increase the resolution of this sensor and to extend the spectrum of its applications. In our current work,\textsuperscript{13} we have therefore used our ICPC to address the technical problems associated with current conductive photolithographic compositions. The composition of our ICPC has several advantages for this purpose. First, minimal effort is required with respect to material handling (i.e., no control of ambient conditions or special pre-/post-processing is needed). Second, during deposition there is no need to control the viscosity and sedimentation of the filler particles. Accordingly, uniform film deposition can be performed on quartz wafers by spin coating and drop casting. A third benefit is that the cured material has a transmission value of 40% for a 170µm-thick film over visible wavelengths. Last, the ICPC exhibits good ionic conductivity (about 8–12mS cm\textsuperscript{-1}), over a wide frequency bandwidth (100kHz to 1MHz). This represents the very strong ionic conductor behavior of our ionic liquid-in-polymer composite.\textsuperscript{14}

The lithographic capabilities of our material facilitate time and cost savings for the direct manufacture (via 2-PP) of 3D transparent, electrically conductive microcomponents that have good optical and electrical characteristics. High-resolution scanning electron microscope images of our patterned ICPC are shown in Figure 1. These images represent the highest spatial resolution (down to 150nm) that we have achieved to date and clearly show our fabricated, high-aspect-ratio 3D structures.\textsuperscript{13}

In summary, we have developed a novel composite material that combines a light-sensitive non-conductive photoresist (as the host network) with an ionic liquid. This material provides several advantageous material characteristics. Furthermore, the compatibility of our composite with the 2-PP process enables time and cost savings to the direct manufacture of high-resolution transparent, electrically conductive components and opens up a variety of potential applications. For example, the newly enabled components could be used to monitor the mobility of small model organisms (e.g., Caenorhabditis elegans), which is a challenge for in situ manipulation and stimulation. Real-time monitoring of such motile micro-organisms is an efficient method of investigating a variety of biological processes. In our current work, therefore, we are focused on tracking of Caenorhabditis elegans. In our approach, we integrate electrodes (fabricated via 2-PP nanolithography) into a microfluidic platform. The transparency and conductivity of our ICPC, combined with our highly standardized electrodes, may facilitate additional visual control of the tracking process. Numerous experiments could thus be performed in parallel on the same chip, with fewer reagents, improved sensitivity, and increased resolution. Our work could therefore lead to more precise quantitative and qualitative in vivo analyses for novel 3D applications.

We gratefully acknowledge financial support from the European Research Council (contract 290586).

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Neil MacKinnon obtained his BSc from the University of Toronto, Canada, in 2004. He continued his studies at the University of Toronto, obtaining his PhD in chemistry under the supervision of Peter M. Macdonald in 2009. He then joined Ayyalusamy Ramamoorthy’s group at the University of Michigan as a postdoctoral researcher, where he developed a nuclear magnetic resonance-based metabolomic approach to prostate cancer detection. He joined Jan Korvink’s group in 2013, where he is the group leader. His research focus is determining metabolomic profiles from in vivo systems.

Jan Korvink studied at the University of Johannesburg and the University of Cape Town, South Africa, and at the Swiss Federal Institute of Technology (ETH) Zurich, Switzerland. He joined the University of Freiburg, Germany, in 1997, where he was a professor in the Department of Microsystems Engineering and co-director of the School for Soft Matter Research of the Freiburg Institute for Advanced Studies. His is also a curatory board member of the Fraunhofer Institute for Physical Measurement Techniques and a research advisory panel member of the Council for Scientific Research’s Materials Science and Manufacturing activities in South Africa. He was the recipient of a Red Dot Design Concept Award in 2011, and a European Research Council Advanced Grant. Since April 2015 he has been the head of IMT.

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