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Two in One: Light as a Tool for 3D Printing and Erasing at the Microscale

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The ability to selectively remove sections from 3D-printed structures with high resolution remains a current challenge in 3D laser lithography. A novel photoresist is introduced to enable the additive fabrication of 3D microstructures at one wavelength and subsequent spatially controlled cleavage of the printed resist at another wavelength. The photoresist is composed of a difunctional acrylate cross-linker containing a photolabile *o*-nitrobenzyl ether moiety. 3D microstructures are written by photoinduced radical polymerization of acrylates using Ivocerin as photoinitiator upon exposure to 900 nm laser light. Subsequent scanning using a laser at 700 nm wavelength allows for the selective removal of the resist by photocleaving the *o*-nitrobenzyl group. Both steps rely on two-photon absorption. The fabricated and erased features are imaged using scanning electron microscopy (SEM) and laser scanning microscopy (LSM). In addition, a single wire bond is successfully eliminated from an array, proving the possibility of complete or partial removal of structures on demand.

Writing and erasing are common actions in daily life, originally on paper but nowadays also on our electronic devices. In chemistry, the writing and erasing concept can be translated into the formation and cleavage of bonds, respectively. Selective cleavage of specific bonds is, for example, used in organic chemistry for the protection and deprotection of functional groups[1] or in surface chemistry.[2] In the context of 3D printing[3] there is a growing interest in the incorporation of features in the printed structures that can be partially or fully erased on demand. However, this incorporation remains a challenge as 3D printing usually results in permanent structures. The approach of removing or erasing material is often referred to as subtractive manufacturing. A high level of control over the process would enable the removal of specific parts or sections that are not required anymore (e.g., support structures or scaffolds) or, importantly, the deletion of defects in a structure without the need of disposing the entire sample.

Our group has recently developed new material systems for 3D laser lithography or laser nanoprinting, which can be written at high resolution relying on a two-photon induced radical cross-linking process and which can consequently be cleaved on demand under mild conditions, i.e., upon a defined external chemical trigger. Specifically, thiol-based 3D macro- and micro-structures prepared via stereolithography or direct laser writing (DLW) were cleaved in the presence of a reducing agent or a mild base such as ethanolamine.[4] Alternatively, we exploited the varying stability of silyl ethers with different substituents on the silicon atom.[5] A series of photoresists were prepared from bisacrylamide cross-linkers containing either methyl, ethyl or isopropyl substituents on the silyl functionality. These resists were then selectively cleaved, enabling sequential degradation when exposed to saturated, methanolic solutions of $NaCO_3$, K_2CO_3, and KF, respectively. Although these approaches are efficient, they all result in global cleavage of the fabricated microstructures.

While the use of highly focused light to trigger a multiphoton polymerization has been taken as an advantage for the preparation of structures with sub-micrometer resolution, this

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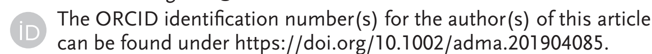
The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adma.201904085.

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DOI: 10.1002/adma.201904085

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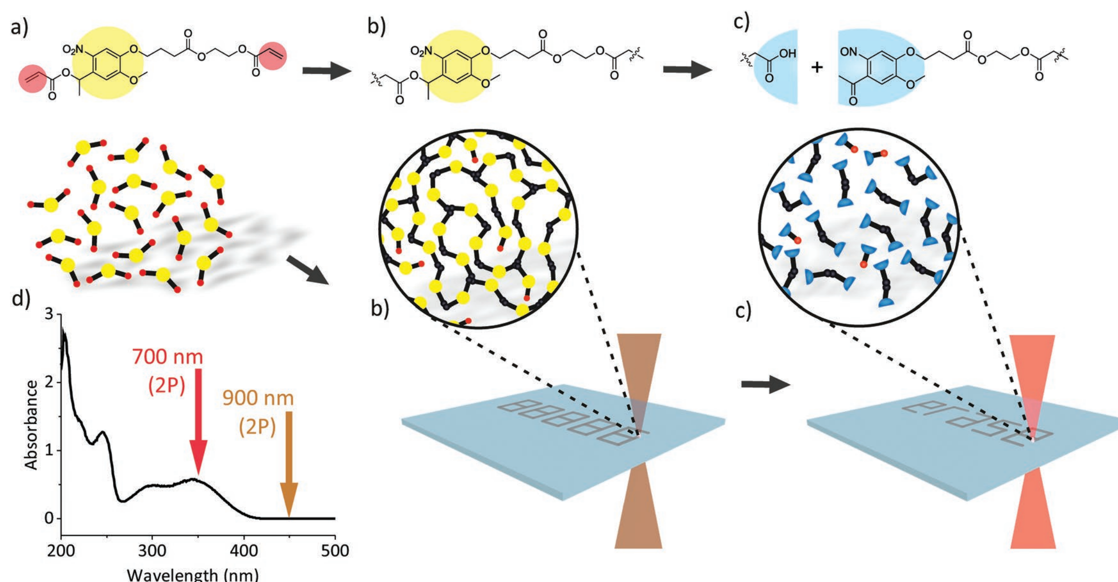

Figure 1. Schematic representation and overview of the writing and cleaving process. a) Chemical structure of the ONB monomer, b) fabrication of microstructures using DLW at 900 nm wavelength via a radical photo-polymerization process, c) selective removal of parts of the resist at 700 nm wavelength via ONB cleavage, resulting in low molecular weight segments containing the carboxylic acid and nitrosobenzaldehyde/ketone products, and d) UV–vis spectrum of the ONB monomer. Arrows highlight the associated two-photon wavelengths for writing and cleaving, respectively.

feature has not been exploited much in the reverse process. So far, only a few studies have combined additive and subtractive manufacturing using a femtosecond laser for both, two-photon polymerization and multiphoton ablation.[6] However, ablation has several disadvantages, specifically in generating features of an exact depth or width. Ablation occurs only when the material absorbs sufficient energy to be melted or vaporized. Chemically, it is an undefined process.[4] The sidewalls of the ablated parts are often rough and geometrically irregular due to explosions of the material during vaporization or due to resolidified debris.

Thus, we herein introduce an advanced approach to 3D manufacturing by introducing a photocleavable group within a photoresist, which will allow for spatially controlled additive manufacturing of 3D microstructures and subsequent cleavage or removal of specific parts. The well-known *o*-nitrobenzyl ether (ONB) motif was chosen as the photocleavable linker due to its ability to be cleaved when exposed to light. The ONB group has been utilized frequently in polymer science to, e.g., install UV degradable components into photodegradable hydrogels,[7] responsive micelles for drug delivery,[8] biocleavable conjugates,[9] surface functionalization of self-assembled monolayers (SAMs),[10] and many more. However, to date, the ONB group has not been explored in photoresists. Herein, we demonstrate the possibility to fabricate and erase 3D microstructures by employing femtosecond laser pulses at different center wavelengths. In particular, well-defined micrometer sized channels and other fine features are removed inside previously written microstructures via two-photon cleavage of the ONB moiety. As a proof of concept for its use in multimaterial systems, a single wire bond was selectively removed from an array using this technology.

ONBs are very efficient photocleavable groups. When exposed to light, the ONB moiety undergoes a Norrish II type reaction, where the photoisomerization of the nitrobenzyl alcohol derivative results in the corresponding nitrosobenzaldehyde/ketone and the release of a carboxylic acid (**Figure 1**b). In order to incorporate the ONB motif into a photo-crosslinkable photoresist, an ONB-containing diacrylate monomer (Figure 1a) was prepared from the commercially available 4-[4-(1-hydroxyethyl)-2-methoxy-5-nitrophenoxy] butyric acid in a three-step procedure (refer to Scheme S1 in the Supporting Information). After purification, the structure of the desired diacrylate was confirmed via nuclear magnetic resonance (NMR) spectroscopy (Figure S1, Supporting Information).

Wavelength selectivity between the writing process (photoinitiation wavelength) and photocleavage is essential. ONB cleavage takes place under irradiation typically between 300–400 nm wavelength for one-photon absorption.[10] Thus, in order to avoid photocleavage during the fabrication process, the photoinitiation wavelength must exceed 400 nm for one-photon absorption (i.e., 800 nm for two-photon absorption). Ivocerin ((bis-(4-methoxybenzoyl) diethylgermane), a symmetrical germane-based radical initiator was selected as the photoinitiator. Ivocerin has been used exclusively as a visible light initiator (λ_{max} = 408 nm) for dental materials,[11] and has not been used in multiphoton systems so far. Thus, the employed photoresist is composed of the diacrylate ONB monomer and Ivocerin as photoinitiator in dimethylformamide (DMF), a good solvent for both components (30 mg monomer and 1.5 mg Ivocerin in 30 µL DMF).

As mentioned above, the determination of the adequate femtosecond laser center wavelength for the fabrication of the microstructures is crucial. The selected wavelength needs to efficiently activate the photoinitiator to trigger the photopolymerization of the acrylate groups without degrading the ONB groups. First, simple line patterns (100 µm long lines with a distance of 5 µm, see Figure S6a in the Supporting Information) were fabricated using a custom-made setup, allowing for the possibility to tune the wavelength of the laser. In particular,

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femtosecond laser pulses derived from a Ti:sapphire laser oscillator, with center wavelengths ranging from 800 to 900 nm (above 400 nm for one-photon absorption), were employed. Since the photoinitiator Ivocerin was never used before for two-photon lithography, the system was first tested using a commercially available pentaerythritol tetraacrylate (PETA) monomer as a model system. The writing wavelength as well as the concentration of photoinitiator were varied and best results were observed when using Ivocerin at a concentration of 4–5 wt% at a center wavelength of 900 nm. The same line patterns were repeated using the ONB-containing photoresists at 900 nm. The threshold for the writing process at these conditions was found to be around 6–7 mW and optimum writing was achieved at a speed of 100 µm s^{-1} and a laser power of 8 mW.

Once the writing wavelength was optimized, the wavelength at which the photocleavage takes place efficiently was assessed. Initially, a solution study employing an NMR and LEDs as light sources (leading to one-photon absorption) was conducted to assess at which wavelength the photocleavage takes place efficiently. As such, the photocleavage was investigated quantitatively at three different wavelengths (365, 385, and 410 nm). Monomer samples in $CDCl_3$ were irradiated for specific time intervals and analyzed after each step. The photocleavage reaction was monitored through the disappearance of the α-proton and methyl protons resonances at 6.55 and 1.68 ppm, respectively, and through the appearance of a methyl ketone resonance at 2.94 ppm (Figure S2, Supporting Information). The reaction was found to progress rapidly under irradiation at 365 nm with 75% of monomer having undergone cleavage after 30 min. A rapid decrease of the photocleavage reaction occurred when the wavelength was red shifted, with only 25% and 22% cleaved after 30 min under 385 and 410 nm, respectively (Figure S3, Supporting Information).

Secondly, in order to establish the degradability of the system under conditions of one-photon absorption, simple microstructures (2D line patterns with a separation distance of 5 µm and text, see Figure S6 in Supporting Information) were written using the photoresist containing ONB groups alongside the control resist. A droplet of dimethyl sulfoxide (DMSO) was placed on top of the structures and the sample was exposed to light at 365 nm wavelength for several hours. Subsequently, the sample was washed with acetone and water and analyzed by SEM. Degradation of the ONB photoresist is clearly evident with the thinning and disappearance of the written structures (Figure S6a,c, Supporting Information). The PETA microstructures, however, showed no change in their appearance under identical conditions (Figure S6b,d, Supporting Information).

Once the one-photon cleavage was proven, two-photon cleavage was investigated. ONB susceptibility to two-photon absorption[12] has also allowed for precise spatial degradation within hydrogels for cell migration,[13] but there is currently no study of two-photon cleavage of dense networks. First, 2D line structures were written 5 µm apart at 900 nm wavelength and then some parts were selectively removed by focusing a femtosecond laser operating at 700 nm wavelength in a perpendicular fashion at 20 µm s^{-1} focus speed and 10 mW laser power. The smooth surface of the cleaved sections is particularly noticeable, especially when compared to the PETA resist lines, which under the same cleaving conditions, resulted in irreproducible, rough cleavage of different widths, consistent with the ablation of PETA. (Figure S8a,b, Supporting Information).

In order to exploit the 3D possibilities of two-photon cleavage of our photoresist, 3D cuboids with a volume of $15 \times 15 \times 5$ µm^3 were written using the laser emitting at 900 nm center wavelength and subsequently developed. In a second lithography step, different fine features were removed inside the block using 700 nm center wavelength (for further details, see Section 3 in the Supporting information). First, cylinders and smaller blocks were cleaved. It should be noted that in order to avoid heating and undesired degradation of the sample, the cleavage experiments were performed with the structures immersed in solvent (DMSO). On the one hand, the solvent helped to dissipate the heat generated. On the other hand, the cleaved fragments are instantaneously dissolved due to their lower molecular weight. Upon completion of the laser scanning, the structures displayed well-defined cleaved features with smooth edges under SEM inspection (**Figure 2**a). The average laser power required for the cleavage process was around 10 mW. This relatively high power might be due to the low two-photon absorption cross-sections of ONB as already reported in the literature.[12a,14] To ensure that the observed material removal is due to two-photon cleavage of the ONB units and not the result of an uncontrolled degradation of the material, 3D blocks from the noncleavable photoresist composed of the commercially available PETA and the same photoinitiator (Ivocerin) in DMF were prepared as controls and cleaved using the conditions as before. In this case, yet slightly higher powers were needed (14–20 mW). More importantly, during the laser scanning, micro-explosions were observed, which are most probably due to the heat caused by ablation. The resulting cleaved holes contained substantial debris and pitted surfaces (Figure S8d, Supporting Information), in sharp contrast to the smooth and fine cleaved features achieved by employing the ONB-containing photoresist (Figure S8a,c, Supporting Information). In the case of the erased lines, a lateral linewidth of around 500 nm was achieved. In addition, the fluorescent properties of the cleaving product (nitrosobenzyl derivatives) were exploited to visualize the surface of the cleaved areas by imaging using laser scanning microscopy (LSM). In order to obtain a signal in the noncleaved material as well, a dye emitting in the red region (Atto 647N) was added to the photoresist prior to writing. Post cleavage, a 3D reconstruction of the blocks was performed. From Figure 2a, the cleaved surface of the block can clearly be seen in blue (cleaved product) against the red colored block (emission of Atto dye).

To further demonstrate the opportunities that the photoresist offers, fine channels were removed inside the microstructures. Further blocks ($15 \times 15 \times 5$ µm^3) were written at 900 nm wavelength using the same conditions mentioned above. Submicrometric tunnels and crosses were then cleaved into the blocks with the 700 nm wavelength laser. The SEM image of the same block (Figure 2b) confirms that the tunnel is written inside with the exit holes clearly visible (see Figure S9 in the Supporting Information for a magnified view of the exit holes). Due to the presence of solvent during the cleaving process, some shrinkage can be observed after development. Additionally, making use of the fluorescent characteristics described above, LSM was employed to check the quality of the channels

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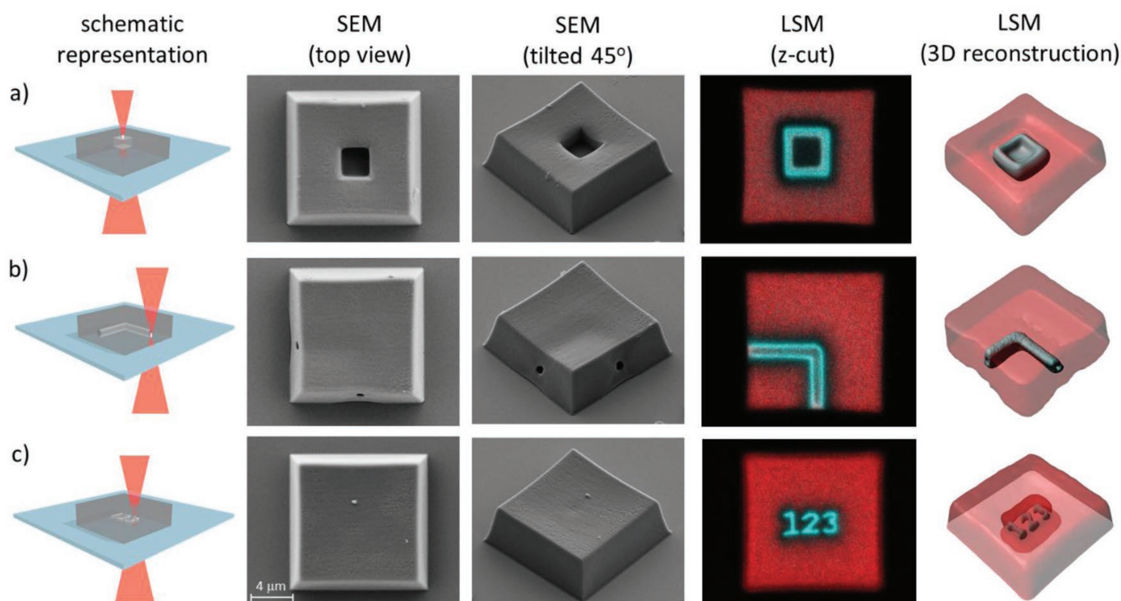

Figure 2. Examples of removed features inside previously written micrometric 15 × 15 × 5 µm^3 blocks using a 700 nm femtosecond laser. a) 3 × 3 µm^3 block, b) 90° 1 µm diameter tunnel, and c) simple text "123."

inside the block. By imaging a plane inside the written block, we can detect the open 90° channels as blue (fluorescence of the cleavage product) inside the red square (Figure 2b). The 3D reconstructions clearly show the presence of the smooth and open micrometer sized channels inside the block. Additionally, other sub-micrometric features such as numbers ("123") (Figure 2c), crosses (Figure S10, Supporting Information), and letters (Figure S11, Supporting Information) were also cleaved inside a block. Although the SEM images showed an intact block, LSM allowed us to image the erased shapes inside the block (Figure 2c) using the fluorescence of the cleaved product (blue). It should be noted that for complete removal of the cleaved material, "open features" such as channels are required.

As a further demonstration, the ONB-containing photoresist was combined with other commercially available photoresists to create multimaterial structures taking the advantage of the cleavage properties of one component to selectively delete parts on demand. In detail, an array of 5 × 5 µm^2 patches were written at 900 nm wavelength using the cleavable photoresist (**Figure 3**a), which serve as sacrificial components. In a second lithographic step, a commercially available acrylic photoresist (Nanoscribe, IP-L 780) was utilized to fabricate wire bonds anchored on top of the previous structures using a commercially available Nanoscribe setup (Figure 3b). Since the conversion of the photoreactive groups is never complete and reactive groups were still available in the ONB-containing structures, covalent bonding of the wire bonds was achieved. Subsequently, it was possible to delete a specific wire bond just by scanning the laser focus, with the femtosecond pulses tuned to 700 nm center wavelength, in the sacrificial area (Figure 3d). After removing the two supporting patches, the wire bond was no longer attached to the substrate and was washed away with the solvent (Figure 3e). This experiment demonstrates well the possibility of selectively erasing individual structures, while preserving the other structures.

In summary, we developed a photocleavable resist capable of spatially resolved subtractive manufacturing. Upon two-photon absorption at 900 nm wavelength, 3D microstructures were fabricated using Ivocerin as the radical photoinitiator. The utilization of the photolabile *o*-nitrobenzyl linker allowed the spatially resolved cleavage upon two-photon absorption at 700 nm wavelength. To demonstrate the selective

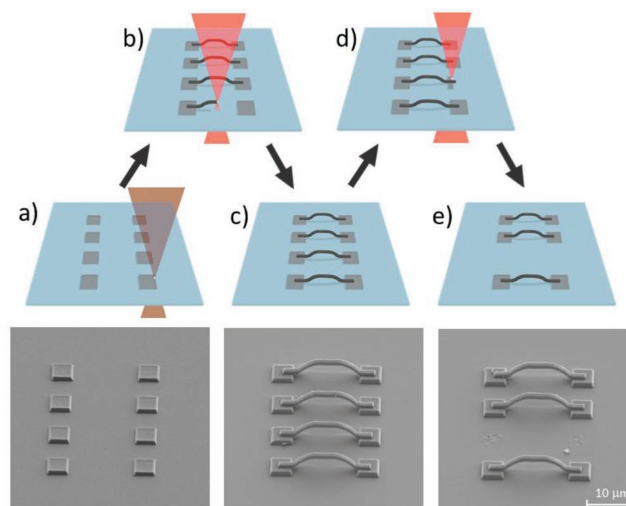

Figure 3. Graphical reconstruction of a multimaterial system prepared from ONB and IP-L 780 resists and the selective removal of one wire bond component as well as SEM images of the completed writing and cleaving processes. a) An array of ONB patches written at 900 nm, b) wire bonds connecting parallel patches were written at 780 nm using IP-L 780, c) completed wire bond array, d) selective removal at 700 nm of a wire bond through cleavage of the underlying ONB patch, and e) wire bond array after development, showing the absence of one wire bond and its ONB supports.

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photocleaving, well-defined features such as micrometer sized cylinders, blocks, channels, and text were written into the previously written microstructures. To further showcase the potential of this material, an array of wire bonds was connected to the ONB resist followed by the selective removal of one wire bond through the removal of the sacrificial ONB resist. The new photoresist enabled the clean and easy removal of single microstructures or selective parts of structures. The versatility of this system allows for the possibility to combine it with other compatible photoresists opening up new opportunities for multimaterial structures that have so far been unattainable.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

R.B. and T.M. contributed equally to this work. The current research has been funded by independent funds of the C.B.-K. and E.B. team, the Helmholtz program "Science and Technology of Nanosystems" (STN), by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy via the Excellence Cluster 3D Matter Made to Order (EXC-2082-390761711), and by the Carl Zeiss Foundation through the "Carl-Zeiss-Focus@HEiKA." The authors thank Martin Bastmeyer (KIT) for providing the access to the LSM equipment, Vincent Hahn (KIT) for help with the SEM imaging, Dr. Patrick Müller (KIT) for his assistance with the laser setup and Prof. A. Hashidzume and Dr. T. Michikata (Osaka University) for fruitful discussions. C.B.-K. acknowledges the Australian Research Council (ARC) for a Laureate Fellowship funding his overarching photochemical research program as well as the Queensland University of Technology (QUT) for continued key support.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

3D printing, direct laser writing, laser lithography, photocleavage, two-photon polymerization

Received: June 27, 2019
Revised: July 26, 2019
Published online: August 16, 2019

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