3D Nanoprinted Plastic Kinoform X-Ray Optics

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High-performance focusing of X-rays requires the realization of very challenging 3D geometries with nanoscale features, sub-millimeter-scale apertures, and high aspect ratios. A particularly difficult structure is the profile of an ideal zone plate called a kinoform, which is manufactured in nonideal approximated patterns, nonetheless requires complicated multistep fabrication processes. Here, 3D fabrication of high-performance kinoforms with unprecedented aspect ratios out of low-loss plastics using femtosecond two-photon 3D nanoprinting is presented. A thorough characterization of the 3D-printed kinoforms using direct soft X-ray imaging and ptychography demonstrates superior performance with an efficiency reaching up to 20%. An extended concept is proposed for on-chip integration of various X-ray optics toward high-fidelity control of X-ray wavefronts and ultimate efficiencies even for harder X-rays. Initial results establish new, advanced focusing optics for both synchrotron and laboratory sources for a large variety of X-ray techniques and applications ranging from materials science to medicine.

With the advent of third- and fourth-generation synchrotrons, free electron lasers, and the advanced laboratory sources, the interest in X-ray microscopy (XRM) has been steadily growing. The combination of a high-resolution and a large penetration depth gives XRM the ability to study nanoscale structures, interfaces, and buried features in their natural working conditions and under external stimuli. Thus, XRM is a powerful tool to address some of the critical scientific challenges in this century, such as energy materials and biotechnology. Accessing the soft X-ray regime by combination of XRM and near-edge spectroscopy allows addressing chemical and magnetic characteristics in an element specific manner. Nearly every element of the periodic table exhibit absorption edges in this energy regime. Furthermore, the L- and M-edges of 3d and 4f elements as most important components of magnetic media are accessible by the soft X-rays and provide superior magnetic contrast.

Development of XRM is closely correlated to improvements in the fabrication of X-ray optics, some of which require sophisticated 3D geometries with nanoscale features. As the wavelengths are in the order of a nanometer or smaller size scale, the performance of an X-ray lens is extremely intolerant to structural infidelities in comparison to the familiar visible light optics. Top-down subtractive micro- and nanofabrication methods adopted from the microelectronics industry were used for delivering high-resolution soft X-ray Fresnel zone plates (FZPs). The efficiency limits for binary absorption FZPs of 10% can be overcome by correcting the phase within each Fresnel zone by the transport of the sputtered material from the bottom of the milled trenches. This, in turn, limits the achievable efficiency at a given resolution for a certain energy range.

A route to produce arbitrary geometries on the sub-micrometer scale by using two-photon polymerization (2PP) has...
Recently emerged, with advances in laser technology and materials chemistry,[34–36] 2PP uses nonlinear absorption of the photons from an intense femtosecond infrared (IR) laser to create a subwavelength interaction volume down to 20 nm.[35] In 2PP, a photosensitive material is polymerized along computer-controlled trajectories, which are generated based on the computer-aided design (CAD) file of the desired structure. A galvo-mirror system controls the lateral laser deflection enabling a fast printing. A piezo stage moves along the vertical axis allowing layer-by-layer printing in the volume of the photosensitive material. The 3D-printing procedure and a schematic of the computer-controlled printing of the X-ray optics are illustrated in Figure S1 (Supporting Information). The rapid progress in the 2PP technology has started an expanding field of research with a long list of applications including, but not limited to, micro-optics,[26–28] microrobotics,[29] mechanical metamaterials,[30] nanoelectromechanical systems,[31] and biotechnology.[32]

Here, we fabricated high-performance kinoform X-ray lenses out of low-loss (Figure S2, Supporting Information), plastic materials by using 2PP-based 3D nanoprinting following the process schematically described in Figure 1a–c. Printing the individual lenses (Figure 1d,e) took less than 1 min, several orders of magnitude faster than alternative kinoform fabrication routes and any top-down method (Figure S3, Supporting Information). The printing was done on a standard X-ray transparent Si$_3$N$_4$ membrane of 100 nm thickness. Consequently, the lenses could be directly inserted in the X-ray microscope without any further machining process.

The kinoforms nominally had 32 µm apertures and 800 nm outermost periods (effective Δr of 400 nm) with 2–6 µm thicknesses leading to aspect ratios of up to 7.5. The structure of the 3D-printed lenses is in good agreement with the design geometry according to the scanning electron microscopy (SEM) images (Figure 1c–e). Lenses printed with the same laser parameter resulted in outer diameter of 31.83 ± 0.16 µm.

Direct imaging and ptychography studies were conducted between 800 and 1800 eV in a state-of-the-art scanning transmission X-ray microscope (STXM, MAXYMUS), located at the Berlin Synchrotron Radiation Facility (BESSY II). Imaging properties of two lenses with 2 and 4 µm optical thicknesses are investigated in detail, as summarized in Figure 2. The half-pitch cutoff resolution of a 4 µm thick lens was estimated to be 240 nm via direct imaging of a linear test sample shown in Figure 2a. The deduced line profile (Figure 2b) was used to calculate the contrast transfer function (CTF, Figure 2c), which follows that of an unobstructed lens. Another STXM image of the Siemens star, captured using a 2 µm thick lens, shows astigmatism-free imaging (Figure 2d). Fourier ring correlation (FRC) analysis returns a resolution of 558 nm (half-pitch of 279 nm, Figure 2e). The outermost zone periods, expected and achieved focus sizes of other relevant work is compared to the present work (Table S1, Supporting Information).

Ptychography was used to reconstruct the amplitude and phase images of the Siemens star (Figure 3a,b) resolving innermost 30 nm features, with a reconstructed pixel size of 19 nm, given by the actual NA of the used system. The reconstructed pixel size can be reduced to 3.4 nm by changing the camera distance in a future study. In our case, the distance is bound from below to 4 cm by the design of our experimental setup. The simultaneously reconstructed illumination function was used to calculate the three-dimensional wavefield for 1.8 mm along the optical axis (Figure 3c). The magnitude of the reconstructed probe at the object plane, which is defocused by 230 µm (Figure 3d), was propagated to the focal plane revealing an Airy pattern (Figure 3e), slightly larger than the expected pattern (Figure 3f). Full width at half maximum (FWHM) of the reconstructed spot in x- and y-directions were found to be 485 and 491 nm, respectively, compared with the FWHM of an ideal Airy pattern 1.028 × 1.028 x dr = 411 nm, it is in good agreement with the direct imaging results. The results of the printed kinoforms show that such lenses can perform very well as focusing optics in ptychographic imaging.

Theoretically, efficiencies of 3D-printed plastic kinoforms excel at both hard and soft X-rays (Figure 4a,b) thanks to the

Figure 1. Overview of the fabrication method. a) Schematic illustration of the 3D nanoprinting of plastic X-ray lenses on X-ray transparent Si$_3$N$_4$ support membranes. A tightly focused high-power infrared laser creates an intense focus to promote nonlinear absorption of photons in the central portion of the Gaussian focus causing a two-photon polymerization of the photoresist. This allows exposing features smaller than the wavelength. b) A CAD file was generated from a mathematical model of the kinoform lens. Half of the structure is hidden to better illustrate the geometry of the structure. c) An SEM image of a nanoprinted half-kinoform lens shows the cross-section profile. Scale bar is 5 µm. d) A portion of an array of kinoform lenses printed with different parameters. Scale bar is 10 µm. e) Magnified central part of a kinoform lens exhibits a high-quality surface and very well-defined features. Scale bar is 2 µm.
favorable properties of the material and the geometry. Focusing efficiencies of lenses with 2, 4, and 6 µm thicknesses were measured from 900 to 1800 eV using a pinhole scan method depicted in Figure 4c and detailed in the Experimental Section. The pinhole scan method is a straightforward method to measure the efficiencies of X-ray focusing optics. It allows measurement of incident flux, zeroth and first-order intensity simultaneously in a single scan even for multiple optics. Moreover, this measurement method is insensitive to variations in the synchrotron beam current or intensity fluctuations. The profile of the intensity across the pinhole scan shows the suppression of the zeroth order, confirming the high quality of the optic. To study the effect of laser dose on focusing efficiency, four lenses with the same optical thickness (2 µm) were printed in the peak laser intensity range of 0.239 (1.231 µJ dose at the focal spot) – 0.247 TW cm⁻² (1.435 µJ dose at the focal spot) (Table S2, Supporting Information). The highest focusing efficiency among 2 µm thick lenses was obtained for a laser dose of 0.239 TW cm⁻² (1.28 µJ dose at the focal spot) (Figure 4d). It was observed that the lenses printed with the similar parameters had very close focusing performances (Figure 4d top and middle). It should be noted that the mechanism of polymerization reaction initiated by two-photon absorption during printing is under an active debate.[33,34] Considering the peak
laser intensity, pulse power, and pulse duration (Table S2, Supporting Information) the polymerization is expected to be influenced by both two-photon absorption and avalanche ionization.\[33–36\]

Measured efficiencies regularly exceeded 15% in the full energy range (Figure 4d), peaking up to 20% for a 2 \( \mu \)m thick kinoform at 1200 eV. The measured efficiency at 1500 eV corresponds to 95% of the theoretical calculations at (Figure 4e). The discrepancies at lower energies can be partly attributed to the high harmonic contributions from the undulator. A second cause may be attributed to the increase of the volumetric mass density of the resin after cross-linking, which was not taken into account for theoretical calculations. The polymers used in 3D printing offer superior optical properties for X-rays, whereby the amorphous (see X-ray diffraction (XRD) analysis in Figure S4, Supporting Information) nature eliminates the undesired diffraction present in polycrystalline media. Also, the photore sist used in printing the kinoform structures (IPL-780) has a large phase shift (1–\( \delta \)) combined with a low absorption (\( \beta \)) (Figure S2a–e, Supporting Information). As depicted in Figure S2f (Supporting Information), the \( \delta/\beta \) ratio of IPL-780 is significantly greater than that of aluminum, similar to that of diamond. Beryllium has a slightly larger \( \delta/\beta \) ratio (Figure S2f, Supporting Information) but its nanofabrication is troublesome with a nonideal microstructure. Also, it is a highly toxic material that is difficult to handle.

We envisage that the 3D nanoprinting now enables realization of kinoform lenses, as well as on-chip stacking of different optics, which were impossible to fabricate before. These new types of integrated, high-efficiency, high-performance X-ray optics can unlock new applications in both hard and soft X-ray imaging. The integration of various optical elements is conceptually shown in Figure 5a. Focusing optics can be integrated together with any optical device such as wavefront shaping and correction plates and combine various functions even for hard X-rays. As an example, on-chip horizontal stacking of nine kinoform lenses of 2 \( \mu \)m optical thickness achieving an effective aspect ratio of 45 is shown in Figure 5b. The estimated theoretical focusing efficiency as a function of number of stacked lenses significantly expands the energy range to several tens of keV (Figure 5c). This configuration offers the same focal spot size as the single lens configuration, which is an order of magnitude smaller than the recently realized printed hard X-ray compound refractive lenses.\[38\] A concern in using polymeric lenses for focusing X-rays could be the radiation damage. In this study, no degradation was observed in the imaging properties of lenses over extended exposure to synchrotron radiation over several days. The SEM imaging after testing of the kinoform lenses showed no signs of structural change (Figure S5, Supporting Information). However, long-term stability remains to be examined in future.

In summary, high-resolution kinoform zone plates with high focusing efficiencies are realized for the first time by using 3D nanoprinting from plastic materials in a single step. The printing time for each kinoform lens was less than a minute presenting the cost-effectiveness of the described route. Synchrotron radiation tests between 900 and 1800 eV revealed that the lenses achieved up to 95% of their theoretical efficiencies, meeting the demands of the emerging coherent diffractive imaging method called ptychography excellently. Direct

Figure 3. Results of the X-ray ptychography tests. a,b) Reconstructed magnitude of the Siemens star test object obtained by ptychographic imaging and the corresponding reconstructed phase, respectively. Nominal period of the smallest features is 60 nm. c) YZ-slice of the normalized magnitude of the wavefield, propagated from \(-600\) till 1200 \( \mu \)m. Color-bar is valid for all density plots. d) Magnitude of the reconstructed illumination function at the object plane shows a defocused probe. e) Illumination function propagated to the focal plane. f) X- and Y-slices through the focal spot show the Airy disc created by the kinoform lens. Slices in X- and Y-directions are shifted in to align with the perfect Airy disc.
imaging and ptychography experiments matched up with theoretical estimations confirming the high quality of the optics, and the fabrication method.

These first results show that 3D-printed plastic kinoforms are powerful and promising new, advanced X-ray optics, whereby a simple one-step preparation route realizes complex and

Figure 4. Focusing efficiency performance of the nanoprinted plastic kinoforms. a,b) Focusing efficiency according to thin grating approximation, as a function of energy and lens thickness at hard and soft X-rays, respectively. c) (Top) A STXM image of a 4.4 μm wide pinhole taken without an OSA between the pinhole and the lens, showing the relation of the first-order focus intensity to the zeroth order and the incident intensity. Energy: 1300 eV, step size: 500 nm, dwell time: 1 ms. Scale bar: 10 μm. (Bottom) 3D surface profile of the image on top, showing that the zeroth order is completely suppressed. d) The measured focusing efficiencies of kinoform lenses with optical thicknesses 2 μm (bottom graph), 4 μm (middle graph), and 6 μm (top graph). Four kinoform lenses with an optical thickness of 2 μm were evaluated. Each of those 2 μm thick kinoforms was printed using different printing dose as labeled in the figure legend. For testing the reproducibility of the fabrication method two lenses with the same printing parameters were tested both for 4 and 6 μm optical thicknesses. e) 2 μm thick kinoform lens with highest focusing efficiency (1.28 μJ μm⁻¹) compared to its theoretical focusing efficiency.

Figure 5. Applications of 3D nanoprinting to advanced X-ray optics. a) The conceptual design that allows integrating any type of X-ray optical element into a stack of lenses. The optical elements can be achromatic elements, beam splitters, phase plates, wavefront shaping, and aberration correcting elements. b) Horizontally stacked kinoform lenses, each lens having 2 μm optical thicknesses. A 1 μm thick support element is printed along with the kinoforms. The combined filtering of incident radiation due to the support structure is in the order of a few percent at 8 keV, and strongly decreases as energy increases. Scale bar: 10 μm. c) Focusing efficiency of stacked lenses as a function of energy and number of lenses each having a 2 μm optical thickness (does not include the effect of support).
high-aspect-ratio 3D structures. An ample room for improvement regarding focal spot size is present and can be met by materials and design file optimization and printing refinements.

The attractive possibility for arrangements of multiple lenses and other optical elements in the near field will allow reaching the ultimate performance especially in the hard X-ray range where absorption is less, allowing higher efficiencies. The integration of several additional optical components would allow aberration correction and wavefront manipulation with ease. Therefore, the 3D-printed plastic kinoforms and FZPs combined with other types of X-ray optics will open new capabilities in X-ray focusing and have a strong impact for the optimal use of new highly brilliant X-ray sources as well as advanced laboratory sources, where the source brightness is still the most critical issue.

**Experimental Section**

**Chemical Composition Determination:** The chemical composition of the IPL-780 photoreisist was determined by ELTRA-CS-800 Carbon-Sulfur determinator and ELTRA-ONH-2000 Oxygen-Nitrogen-Hydrogen determinator. The composition of the polymer was estimated to be 3.0 wt% hydrogen, 24.9 wt% oxygen, 0.8 wt% nitrogen, and 71.2 wt% carbon.

**Preparation of the 3D CAD Files:** CAD files of the kinoform lenses were generated using Wolfram Mathematica v. 10.4. The Wolfram Language allows generation of such 3D structures with only a couple of lines of script. The scripts are available from the authors upon request. The CAD files were then sliced using DeScribe 2.5 of Nanoscope GmbH for feeding to the Photonic Professional two-photon lithography instrument.

**Nanoprinting of Kinoform Lenses:** The kinoform lenses were printed directly on silicon nitride membranes (500 μm × 500 μm × 100 nm) as illustrated in Figure 1. Briefly, the silicon frame was placed on a glass coverslip. A Si frame of 100 μm thickness was chosen to accommodate the short focal length of the objective lens. In between the membrane and the glass substrate, immersion oil was filled to minimize the refraction at the interface. A minute amount of IP-L 780 photoreisist (less than 3 μL) was dropped on the top of the membrane. Commercially available Direct Laser Writing system (Photonic Professional, Nanoscope GmbH) equipped with a 63× oil-immersion objective (numerical aperture: 1.4) was used for two-photon polymerization. The printed kinoform lenses were developed in propylene glycol monomethylether acetate and isopropanol. The structures were then dried with critical point drying to effectively preserve the high-aspect features. Printing parameters of the evaluated lenses are listed in Table S2 (Supporting Information). The horizontally stacked kinoform lenses were printed on standard glass substrate of 100 μm thickness. For the printing of horizontally stacked kinoforms IP-S photoreisist was used.

**X-Ray Microscopy Tests:** The X-ray focusing tests were done at a state-of-the-art scanning transmission X-ray microscope located at UE46-PEG2 beamline in BESSY II, MAXYMUS.[38] The kinoform lens was mounted as a focusing optic at MAXYMUS. The microscope setup is a typical scanning probe microscope where the probe is a tightly focused X-ray beam. The X-rays coming from an APPLE 2 type undulator are focused by the lens and filtered by an order selecting aperture (OSA) onto a sample, which is raster scanned while the total transmitted light is collected by an avalanche photodiode to form an image. The FRC was calculated from two independently acquired images after alignment, using the Fourier Ring Correlation plugin of the ImageJ software.[40]

Psychography was done using a 2 μm thick kinoform at 800 eV using the third undulator harmonic with exit slits set to 15 × 15 μm. The image with a 3 μm field of view was recorded with a dwell time of 100 ms pixel$^{-1}$, 50 nm steps (60 points) with a sample-to-camera distance of 15.5 cm. The direct X-ray detection camera consists of 264 × 264 pixels. At the energy of 800 eV this corresponds to a reconstructed pixel size of 19 nm. The reconstruction was done using the SHARP ptychography package[41] performing 1000 iterations of relaxed averaged alternating reflection (RAAR) algorithm. Fourier beam propagation method was used to propagate the beam backward/forward.

For estimating the focusing efficiency of the kinoform lenses, a pinhole diameter of 4.4 μm was raster scanned in the first-order focal plane recording the incident intensity, projected zeroth order of the lens, and the first-order focal spot at the same time. This is shown in Figure 2c,d. The ratio of the mean focal intensity (average intensity of selected 9 pixels in the yellow spot of Figure 2c) to the X-rays incident on the kinoform area gives the focusing efficiency of the kinoform lens.

**Electron Microscopy Analysis:** For the SEM analysis, a ZEISS Gemini 500 SEM with a field emission electron source was used. The samples were coated with 20 nm of carbon prior to SEM analysis. To minimize charging effects, beam deceleration was used while acquiring the SEM images.

**Theoretical Efficiency Calculations:** The theoretical focusing efficiency of a kinoform lens can be calculated by assuming the phases making up the optic contribute equally to the efficiency and represent the overall efficiency of the optic. By following a thin grating approximation, the sum of amplitudes at the first order, $A_1$, is given by the following equation[17]

$$A_1 = \frac{C}{2\pi} \int_\delta \frac{d\Phi}{\lambda} e^{i \left( \frac{2\pi d_1}{\lambda} \right)} d\theta$$

where $C$ is the incident amplitude, $\beta$ is the imaginary part of the complex refractive index, $\delta$ is the decrement in the real part (1 − $\delta$) of the complex refractive index, $\Phi_0 = 2\pi\delta/\lambda$ is the phase shift in the material of thickness $t$, $\lambda$ is the wavelength of the radiation, and $\theta$ is the optical path length difference to the focal spot over one lens period, that is, a pair of zones in a FZP and one ridge in the kinoform. Then, the focusing efficiency (FE) is then given by the following equation

$$FE = A_1^2 / C^2 \times 100$$

**Supporting Information**

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

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**Conflict of Interest**

Max Planck Society has filed a patent for the described process.
