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Transferable Ultra-thin Multi-level Micro-optics Patterned by Tunable Photoreduction and Photoablation for Hybrid Optics

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Abstract

Next-generation hybrid optics will provide superior performances over traditional optics by combining the advantages of refractive, reflective, and diffractive optics and metasurfaces. Hybrid optics have been realized by integrating diffractive optical structures to top surface of traditional bulk refractive or reflective optics. However, high-resolution manufacturing requirement of diffractive patterns on top of free-form refractive or reflective optical surfaces have hindered the wide-spread dissemination of hybrid optics. In this paper, we demonstrate a transferable ultra-thin micro-optics having multi-level transmittance and phase profiles which are arbitrarily patterned by tunable photoreduction and photoablation of graphene oxides (GO) using femtosecond (fs) direct laser writing. A 5×5 array of multi-level ultra-thin micro diffractive lens having a focal length of 15 mm was exemplarily patterned with real-time laser power control; the resulting spot size was smaller than 14 μm with the suppression of diffractive side peaks by 14.9% at the first order and 10.8% at the second order ones. This laser-patterned diffractive lens array was successfully transferred to the surface of a refractive

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cylindrical lens via polydimethylsiloxane (PDMS) as the flexible/stretchable substrate; the resulting optical performance agrees well with the theoretical simulation result. This new fabrication method will pave a way to novel hybrid optical systems.

1. Introduction

Optical elements control the propagation of light by refraction, reflection, diffraction, or resonance effect, corresponding to refractive, reflective, diffractive optics, and optical metasurfaces, respectively. Hybrid optics refers to the combination of these different optical elements for better performances or novel functionalities. Owing to the recent advances in micro-manufacturing, micro refractive lens arrays are being utilized in 3D optical imaging based on nature-inspired compound insect eyes[1,2], precision Shack-Hartmann wavefront sensors[3,4], and array confocal microscopes for high-speed bio-medical imaging[5–7]. However, the high-precision manufacturing of metal moulds for micro refractive lens arrays requires high development cost, long process time, and special machining tools[8–11]. The simple replacement of the micro refractive lens array to diffractive planar lens array will enable a lower weight, higher density, and lower complexity to optical systems with comparable functionalities[12,13]. Furthermore, if one can integrate diffractive micro-optical elements to traditional refractive or reflective optics, hybrid optics with unprecedented superior performances or novel functionalities can be realized by combining the advantages of refractive, reflective, and diffractive optics. However, there have been very few reports on hybrid optics because the manufacturing of sub-wavelength diffractive optical structures over free-form refractive or reflective optical surfaces are extremely challenging[14–16]. A simpler solution to realize hybrid optics is to transfer the diffractive optical structures to the top of free-form refractive or reflective optical surfaces. For the efficient transfer of the diffractive micro-optic patterns, the patterns should be ultra-thin in thickness. Ultra-thin diffractive micro-optics have been recently reported based on various nanomaterials with a few hundreds

of nanometer thickness for their applications in integrated optics and on-chip photonics[17–23]. Various nanomaterials including graphene[20], carbon nanotubes (CNT)[21], tungsten chalcogenides[22], and silicon nanowires (SiNW)[23] have been utilized. However, these have not been applied so as to construct hybrid optics to date.

Standard diffractive binary Fresnel zone plates (FZPs) consist of a series of concentric rings providing amplitude or phase modulations, which diffract the incident light so as to be focused at a focal spot by constructive interference. Thus, they are categorized by the modulation types into amplitude and phase zone-plates. Because sub-wavelength features are requested in FZPs, UV photolithography is used as the basic manufacturing strategy for FZPs. Electron-beam and focused-ion-beam lithography can also be utilized in cases requiring higher resolution. The binary-amplitude FZPs based on transmittance modulation have been most widely demonstrated due to its easy fabrication by etching the concentric rings in a thin metal film (e.g., Au, Ag, Cr and so on)[24–28]. Recently, ultra-thin binary-amplitude FZPs having sub- μm structural thickness have been reported by using various nanomaterials' high optical absorption coefficient together with other benefits; the ultra-thin thickness newly enables the printed patterns to maintain their optical characteristics under large structural deformations so that they can be transferred to flexible or stretchable substrates. Moghimi *et al.* reported a Si nanowire binary-amplitude FZP microlens array on a flexible substrate by UV photolithography[23]. Li *et al.* utilized carbon nanotubes for the same purpose[21] and other materials (e.g., graphene and tungsten chalcogenides) have been also reported ever since. However, there are only two degrees-of-freedom (DOFs) in design for these ultra-thin binary amplitude FZPs, the photo-mask design and optical transmittance. The binary-phase FZPs are known to improve the optical efficiency by ~40% compared with the amplitude FZPs but require more complex fabrication; the concentric ring grooves should be etched in a transparent dielectric film (e.g., SiO_2 and Si_3N_4) to have a binary phase step of π [29–32]. There have been a few reports about the ultra-thin phase FZPs[17,21,22,33]; the

1 photoreduction of graphene oxides (GO) was recently reported to enable the phase control[34].
2 The DOFs in design for phase FZPs, however, are still limited to two, the photo-mask design
3 and optical phase delay. Higher flexibilities in designing and manufacturing of ultra-thin FZPs
4 are the prerequisite for the realization of next-generation hybrid optics but have remained less
5 explored to date. Direct laser writing of ultra-thin multi-level diffractive optics could be a
6 promising solution candidate to meet all these requirements as the direct laser patterning can
7 be realized with lower cost in a time-efficient manner without the need for a pattern mask,
8 toxic chemicals, vacuum environment, high temperature process[35,36]. Furthermore, multi-
9 level amplitude and phase modulation can improve the optical performances of the diffractive
10 optical elements by efficient manipulation of the sub-wavefronts for stronger light
11 concentration to the focal spot[37].

12 In this paper, we demonstrate an ultra-thin transferable diffractive micro-optics array
13 based on tunable photoreduction and photoablation of GO to provide multi-level absorption
14 coefficients and refractive indices. Three different patterning regimes are realized here for
15 efficient control of the amplitude and phase profiles via parametric control of fs laser pulses:
16 the first is phase-changing less-thermal photoreduction (LTPR) regime, the second is
17 transmittance-changing thermal photoreduction regime (TPR), and the third is ablation (ABL)
18 regime. Three diffractive FZPs were fabricated at different regimes and their material
19 characteristics and optical performances were investigated. Binary, four-level, and six-level
20 diffractive FZPs were patterned to demonstrate the better light concentration to the main peak
21 with suppressed multiple foci and side peaks by tunable photoreduction in TPR regime. A
22 micro-optics array was patterned onto the ultra-thin GO and transferred to a flexible and
23 stretchable polydimethylsiloxane (PDMS) substrate, so that the patterned micro-lens array can
24 be integrated to traditional bulk refractive or reflective optics so as to realize high-
25 performance hybrid optics. The proposed method enables direct patterning of any arbitrary

designed diffractive optics with multiple amplitude and phase modulations via a lower cost and a short lead time over flexible and stretchable substrates.

2. Results and discussion

2.1 Multi-level Fresnel zone plates patterned at different patterning regimes

Ultra-thin FZPs using nanomaterials have been designed to have alternative binary layers, opaque and transparent rings, to diffract the light around the boundary of the opaque zones so that the diffracted light constructively interferes at the desired focal point. These binary FZPs based on common nanomaterials have suffered from its limited design flexibility because there has been only one available design parameter, the thickness of the nanomaterials. In this respect, GO could be promising alternative for the micro-optics which can support multi-level optical properties, such as phase and transmittance, without the complicated photolithography process. GO is a compound of carbon, oxygen, and hydrogen, whose ratio can be controlled by the reduction process. Spatially selective reduction can be induced by focusing the light to GO, which is named as the photoreduction process[38–42]. This photoreduction removes the oxygen-containing groups from GO, resulting in the increase of light absorption coefficient and optical refractive index[34,43–46]. Among various light sources, a mode-locked fs pulse laser can provide unique and extensive parametric tunability in the photo-reduction process; the pulse duration can be compressed down to a few hundreds of fs, the pulse peak power can be over MW, and the pulse repetition rate can be higher than MHz, which enables us to explore different GO reduction regimes. Therefore, we utilized a fs pulse laser as the light source here for the tunable photoreduction of GO to manufacture the multi-level Fresnel zone plates with various design parameters such as optical transmittance, reflectance, and phase shift using a common base material GO as shown in **Fig. 1a, b**. The fine tunability of photoreduction by fs pulses allows increasing the number of possible degree levels of optical properties, which realize smooth transition similar to continuous sinusoidal profile as shown in **Fig. 1b**. Ultra-thin planar GO micro-optics are arbitrarily patterned through a simple direct

laser writing method without complicated and repetitive manufacturing processes as in photolithography. Moreover, the wide tunability of optical properties provides additional DOFs to control the transmittance or phase delay of micro-optics so as to optimize the device performances, e.g. higher focusing efficiency, lower background noise, and suppressed higher-order diffraction.

In the photoreduction of GO by using ultra-short fs laser pulses, the threshold peak power for the photoreduction is generally lower than the ablation threshold. When the peak power of the incident laser pulses to GO surface is in the photoreduction regime, the pulse repetition rate determines whether thermal effects dominate the reduction process or not. If the repetition rate is relatively low compared to the heat diffusion rate of the GO film, the laser pulses photochemically remove the oxygen-containing groups in GO with negligible thermal effect; this corresponds to phase-changing LTPR regime as shown in **Fig. 1e, f**. On the contrary, the high repetition rate pulses induce the heat accumulation in GO, which relatively increases the photothermal contribution of GO reduction. This TPR in turn results in notable vertical alignment of reduced graphene oxide (rGO) flakes perpendicular to the substrate which corresponds to transmittance-changing TPR regime as shown in **Fig. 1e, g**. When the laser peak power exceeds the ablation threshold, the photoreduction converting GO to rGO takes place first, then laser ablation makes rGO thinner by removing the top layers of the rGO thin film; this ABL regime provides additional design flexibility as shown in **Fig. 1e, h**. These reduction and ablation regimes can be selected by controlling the peak power and the exposure time of GO/rGO to laser pulses via tailoring the scanning speed of the galvano mirrors.

Fig. 1. Transferrable ultra-thin multi-level Fresnel zone plates (FZPs) based on tunable photo-reduction of graphene oxides patterned by mode-locked femtosecond laser pulses. (a) Schematic of ultra-thin multi-level micro-optics to focus light for high signal-to-noise-ratio. (b) Transmittance and phase profiles, top one for binary optics and the bottom one for multi-level optics. (c) A conceptual diagram of transferrable diffractive micro-optics on a flexible/stretchable substrate. (d) A conceptual diagram of hybrid optics construct by attaching ultra-thin multi-level micro-optics on conventional refractive optic. (e) Schematic of femtosecond direct laser writing of the GO to realize ultra-thin diffractive micro lenses at three different regimes: i) less-thermal photoreduction (LTPR), ii) thermal photoreduction (TPR) and iii) photoreduction and ablation (PR/ABL), inset graph: fabrication regimes

classified by pulse energy and pulse repetition rate of fabrication conditions. (f-h)
Transmission microscope images of the patterned ultra-thin micro lenses under the three
regimes, LTPR, TPR, and PR/ABL. Scale bar: 200 μm

To investigate the optical and physical characteristics at different fabrication regimes,
three binary GO FZPs were patterned on a 500-nm thick GO film on a glass substrate in
LTPR, and TPR regimes, and subsequently on a 900-nm thick GO film in PR/ABL regimes,
respectively (See **Fig. 1f, g, h**). The patterns were designed to have 10 concentric rings with a
designed focal length of 15 mm. The physical parameters of a mode-locked Yb-doped fiber fs
laser (Amplitude, SATSUMA HP), such as central wavelength, pulse duration, repetition rate,
and peak power, were precisely controlled to realize these three fabrication regimes. The
pulse energy and repetition rate were confirmed to be the most dominant parameters which
determine the fabrication regimes (**Fig. 1e inset**). When the pulse repetition rate is 50 kHz,
which is relatively low compared to the heat diffusion rate of GO film, the laser pulses
photochemically remove an oxygen-containing group from GO with suppressed thermal
effects. Because of the limited penetration depth, this LTPR makes a very thin rGO layer only
on the top surface. This results in the phase change with a relatively weak transmittance
change as shown in the dim rGO color shown in **Fig. 1f**. In contrast, heat accumulation in GO
takes place at a high repetition rate of 500 kHz, which leads to thermal reduction inside GO
together with photochemical reduction. Therefore, the reduction process occurs in much
deeper area due to the transferred heat down to the deep penetration depth, making less-
transparent, distinct rGO lines compared to LTPR as shown in **Fig. 1g**. Even higher contrast
diffraction patterns can be printed through the combination of photoablation and
photoreduction process. A GO film was firstly irradiated by the laser pulses optimized for
photoreduction process which makes non-transparent rGO, and then highly transparent part

was patterned by focusing the high power laser pulses over ablation threshold to GO so as to remove GO layer as shown in **Fig. 1h**.

Fig. 2. Characterization of fs-laser-patterned rGO at three patterning regimes, thermal photoreduction (TPR), less-thermal photoreduction (LTPR), and photoreduction/ablation conditions (PR/ABL). (a) SEM images of the GO surface after fs laser pulse irradiation. (b) Reflected light microscope images showing the different light reflection and scattering from the surface. (c) Confocal microscopy images and the related surface profiles. Scale bar = 100 μm . (d) Raman spectra of the fabricated samples. (e) Light attenuation level at resultant GO layers of LTPR and TPR patterned at different peak powers.

Three fabricated FZPs under different patterning regimes were characterized using SEM, reflected light microscope, and confocal microscope, as shown in **Fig. 2a-c**. In SEM images, all rGO's surface morphologies under the photoreduction look fluffy because the high incident peak power instantaneously removes oxygen-containing groups, which leads to explosive evaporation of the water vapors within the structure. Especially, TPR shows more complex surface structure with large rGO flakes because the reduction reaches deeper region inside the GO film. The reflected light microscope images in **Fig. 2b** show the clear difference between two rGO surfaces, one patterned at LTPR and the other at TPR regime; TPR makes brighter surface images due to higher light scattering at the rough top surface. The confocal microscope images in **Fig. 2c** show the thickness variation along the radial direction from the center. LTPR makes smaller thickness deviation less than 400 nm which agrees well with smoother surface morphology as observed in both SEM and reflection microscope. TPR causes slightly larger thickness variation of $\sim 1.0 \mu\text{m}$. When the photoreduction and photoablation processes are alternatively applied, the resultant thickness variation becomes significantly larger up to $\sim 6.9 \mu\text{m}$ ($2.8 \mu\text{m}$ in average), which can provide us higher phase or transmittance contrast.

The degrees of photoreduction at LTPR and TPR regimes were tested in the Raman spectra (See **Fig. 2d**). Two dominant peaks were observed in GO which assigned as the D and G band respectively. After the irradiation of fs pulses, both the D and G bands exhibit narrower bandwidth, decrease of intensity ratio (I_D/I_G), and appearance of 2D band peak; these confirms that higher degree photoreduction was realized under the TPR regime[42]. The chemical composition of GO and rGOs produced with different photoreduction strategies were comprehensively characterized using X-ray photoelectron spectroscopy (XPS) and UV-vis spectroscopy. The high-resolution C1s spectra of GO and rGOs are displayed in XPS results as shown in **Fig. S1**. The spectra was de-convolved into three peaks, which are centred at ~ 284.6 (C-C/C=C bond), 286.8 (C-O-C bond), and 288.7 eV (C=O bond), respectively.

The C-O percentage of GO decreases with the higher laser peak power in both LTPR and TPR samples. This can be explained by the enhanced removal of OCGs by irradiated pulses with a higher repetition rate. The UV-vis spectra were compared in **Fig. S2**. The optical absorbance at two different regimes was also measured using a 638 nm continuous-wave diode laser with the rGO samples patterned at 50 and 500 kHz repetition rates with different peak powers as shown in **Fig. 2e**. As the incident peak power increases, the absorbance increases to a certain point and then starts to decrease; this transition is made by the photoablation of the reduced rGO at high peak powers. At a low repetition rate of 50 kHz, the threshold peak power for this absorbance decrease is more than four times higher than the threshold at a high repetition rate of 500 kHz. This difference is expected to come from the heat accumulation effect inside rGO at high repetition rates. The accumulated heat can increase the base temperature of the rGO thereby lowering the laser power required for the subsequent rGO ablation. When one wants to fine-tune the optical absorbance for multi-level FZPs, the LTPR could be better because the absorbance can be easily controlled by selecting the proper peak power with a relatively large process control bound. On the other hand, the TPR works better for the high-speed patterning because a lower peak power is required for the same absorbance change.

2.2 Optical performance evaluation of the laser-patterned ultra-thin micro lenses.

Optical performances of the three fabricated FZPs were carefully characterized as shown in **Fig. 3**. Firstly, the focal intensity distributions along the z-axis were measured (See **Fig. 3a, b**). A well-collimated 638 nm laser beam was incident on the zone plates and the beam profiles along the propagation direction were captured by a CCD camera. The CCD camera was translated from the lens surface to the focal plane with 0.1 mm steps. **Fig. 3b** shows the resulting intensity distribution of the propagating light on xz-plane and the xy-plane beam profile at the focal distance. When the propagating light firstly encounters the lens

surface ($z=0$ mm), the opaque rGO part of the lens blocks the light, whereas the transparent GO part transmits the light. At this position, the optical diffraction occurs at the border lines between the transparent and opaque regions; thus, the beam profile in xy-plane looks similar with the shape of FZP. When the light propagates on, the diffracted beams converge to a focal point, while some scattered lights diverge away; then, the converging beams are finally focused into a small spot by constructive interference of the diffracted beams at the focal distance ($z=15$ mm). In all three fabrication regimes, the beams were well converged to the focal spots; the spot size in full-width-half maximum (FWHM) was $12.2\text{ }\mu\text{m}$ at LTPR, $13.2\text{ }\mu\text{m}$ at TPR, and $12.0\text{ }\mu\text{m}$ at PR/ABL regime, respectively. In LTPR regime, the strength of the diffracted beams from the lens is weaker than the other two cases due to the smaller difference of the transmittance at FZP as discussed in **Fig. 2b**. The photoreduction/ablation regime exhibits the most efficient light focusing out of the three regimes thanks the higher transmittance difference and lower light scattering from FZP. The peak intensities at the focal spots for LTPR and TPR lenses are about 48% and 78% of the peak intensity for the PR/ABL lens were as shown in **Fig. 3c**. This superior optical efficiency of PR/ABL lens could be attributed to the higher transmittance at the transparent ablated part and higher contrast between the transparent and opaque areas. The relative strengths of the background noise at the focal plane was 9.4% at LTPR, 5.8% at TPR, and 4.5% at PR/ABL regimes, respectively. Due to higher diffraction orders, FZPs can exhibit harmonic focal points along the z-axis; the measurement results along the focal plane (See **Fig. 3d**) did not show noticeable harmonic foci at the integer division of the designed focal length (e.g. $f/2$, $f/3$, and so on). The depth of foci of the lenses were measured along the z-axis as 1.15 mm for LTPR, 1.93 mm for TPR and 1.77 mm for PR/ABL lenses, respectively.

Fig. 3. Beam propagation after the ultra-thin diffractive lenses fabricated at three different patterning regimes of LTPR, TPR, and PR/ABL. (a) Schematic of the beam propagation test. A collimated laser beam was incident to a binary FZP and the resulting beam propagation was recorded by measuring the beam profiles at different focal depths by CCD. (b) Measured beam propagation; the intensity distribution cross-sections along with the z-axis. (c) Light intensities across the x-axis at the focal plane. (d) Light intensities along the z-axis of the focal plane. Comparison between experimental and simulation results for (e) beam profile at the focal plane, and (f) the depth of focus.

In order to confirm the optical performances of the printed FZPs, the experimental results were compared with the simulation results (obtained by modeling the FZP by Zemax Opticstudio) in terms of three key parameters, the spot size, side lobes and depth of focus. Firstly, the beam profiles, one by simulation and the other by experiment, show good agreement with each other within 5% deviation; the beam size was $12.0\ \mu\text{m}$ by experiment

and 11.4 μm by simulation (See **Fig. 3e**). Secondly, the radial position of side lobes also agrees well for simulation and experiment as shown in **Fig. 3e** and its inset. Thirdly, the depth-of-focus along the z-direction was evaluated by the sectional beam profiles as shown in **Fig. 3f**. The experimental depth-of-focus, 1.77 mm matched well with the simulation result, 1.70 mm within 4% deviation. These deviations are expected to be made by the patterning errors due to the imperfect calibration of the galvano scanner and the background noise induced by the light scattering at FZPs. These results confirm that our ultra-thin FZPs work well in good accordance with the design.

2.3 Multi-level micro Fresnel zone plate by tunable photoreduction and ablation.

The optical performances of the patterned micro FZPs can be further improved by tunable photoreduction and photoablation by controlling the optical parameters of the ultra-short fs laser pulses. Compared to traditional binary zone plates manufactured by photolithography, the laser-patterned multi-level transmittance and phase profiles enable better light concentration to the central main peak with suppressed side peaks; this can be explained as follows. A diffractive FZP employs the diffraction of light from the rotationally symmetric sub-wavelength rings to make the constructive interference at the focal spot. Therefore, a single ring is an important base diffractive element whose diffraction behaviour directly determines the focusing performance of the zone plate. For the traditional binary FZP, each ring segment generates a diffraction pattern with a zero-order Bessel function at the target focal plane; therefore, the final optical performance is also determined by the combination of these multiple zero-order Bessel functions. Whereas, when a multi-level amplitude profile is applied instead of a single step profile, the diffracted field profile can be redistributed so as to be concentrated more to the focal spot with suppressed higher order side lobes. In order to demonstrate this, we fabricated binary, 4-level, and 6-level FZPs having three concentric diffractive rings with the same designed focal length of 150 mm as shown in **Fig. 4a**. The peak power of the laser pulses was precisely controlled for the transmittance to meet the

designed values; the power-to-transmittance relationship shown in **Fig. 2e** was utilized here for the control. **Fig. 4b** shows the transmission microscope images of the fabricated FZPs with different numbers of transmittance steps. The resulting intensity profiles at the focal points with different step numbers are as shown in **Fig. 4c** (in the x-y domain) and 4d (in the r-theta domain). The focused intensity's leakage to high-order side peaks (See **Fig. 4c-1, c-2, d-1, d-2**) are significantly suppressed with the increased number of transmittance steps as shown in **Fig. 4c-3** and 4d-3. For binary and four-level lenses, the first- and second-order side peaks appeared as horizontal lines in **Fig. 4d-1** and 4d-2 over the whole angles. On the other hand, the six-level lens shows smoother decrease of intensity distribution along the vertical axis without noticeable horizontal lines. The sectional intensity distributions along the radial direction in **Fig. 4e** provide clearer quantitative understanding. For the binary and four-level lenses, one can observe the first intensity minimum at 0.11 mm apart from the zero-order central intensity peak and then the first- and second-order side peaks at 0.17 mm and 0.36 mm from the central peak. Contrary to binary and four-level lenses with the six-level transmittance, the large dip between the zeroth- and first-order peaks almost disappeared and the first- and second-order peak strengths were lowered by 14.9% and 10.8% compared to the case in binary zone plate. Based on these experimental results with only three diffractive rings, the light focusing performance becomes comparable to that of discussed refractive lenses. We foresee the effective reduction of unwanted diffraction orders will get better with the increased number of diffractive rings. Considering the simplified fabrication process, material saving, light-weight, and structural compactness, the ultra-thin micro-optics with multi-level transmittance or phase profiles could be a promising alternative to refractive optics while maintaining similar optical performances.

Fig. 4. Multi-level Fresnel zone plates (FZPs) based on tunable photoreduction (a) Fresnel zone plate design with multi transmittance levels. (b) Microscope images of binary, 4-level, and 6-level transparency lens. (c) Focal spot images when a collimated laser beam was illuminated to the fabricated FZPs. (d) Light intensity profiles along the radial axis with respect to the center of focus point at the focal plane. (e) Light intensity (Summation in all 360 degrees) profiles along the radial axis with respect to the center of focus point at the focal plane.

2.4 Flexible/stretchable micro Fresnel zone plates and their transfer to conventional optics

Flexibility and stretchability are of great interest in wearable, flexible, and integrated electronics; this trend will also apply to optoelectronic devices. One more key advantage of the ultra-thin GO micro-optics is that they can be easily transferred to elastomer substrates.

We fabricated an ultra-thin GO micro-optics array and transferred it to a PDMS substrate for realizing flexible and stretchable micro-optics functioning over a wide wavelength range. Through the simple GO coating on any substrate and subsequent fs direct laser writing, a micro diffractive lens array with arbitrary lateral patterns can be fabricated. **Fig. 5a** shows the working principle of the ultra-thin GO lens array, patterned to the shape of ‘NTU’ on a glass substrate, a real sample image, and the focal plane captured by a CCD at the focal plane. Each micro FZP has 10 concentric opaque rGO rings designed to have a focal length of 15 mm at 638 nm wavelength; the outer diameter of each structure is 875 μm . The incident collimated laser beam was focused by the each subset lens without a significant power loss or field deviation from the design as shown in **Fig. 5a**. The ultra-thin micro-lens array was firstly patterned to the GO film which was previously drop-casted on a glass substrate as shown in **Fig. 5b**. The patterned micro-optics array was then transferred to a flexible and stretchable substrate. For the transfer, PDMS was spin coated on the patterned GO film at 1000 rpm for 60 s so as to make PDMS be immersed into rGO and form an elastic film with a few hundreds of micrometers in thickness. Thanks to the porous rGO structure after the photoreduction, the rGO patterns can be efficiently transferred into PDMS to form a rGO/PDMS composite after the post-curing at 80°C. Finally, the PDMS film was peeled off from the glass substrate, where the ultra-thin rGO micro-optics array was obtained consisting of rGO rings without GO since GO has a flat surface morphology and is not easily transferred. This transferred rGO structures can provide better transmission contrast than GO/rGO and can have better optical characteristics at the focal plane. **Fig. 5b** shows the fabricated 5×5 rGO lens array transferred from the GO/rGO film to PDMS. The combination of PDMS and rGO offers high flexibility and stretchability to rGO so that rGO can preserve its optical performances without notable degradation even under high mechanical deformations, such as bending, rolling and twisting. This flexibility and stretchability offer new wavefront shaping capability to ultra-thin diffractive micro-optics by simply transferring them to the top of existing bulk refractive or

reflective optical elements (as shown in **Fig. 5c**). While traditional rigid optics need to be carefully aligned with much mechanical support, the proposed method is efficient to realize hybrid optics. The flexible and stretchable thin-film micro-optics can be simply attached on top of existing optics without much loading nor supports. **Fig. 5d** shows an example of hybrid optics combines a flexible rGO/PDMS diffractive FZP array of a 15 mm focal length to a bulk cylindrical lens of a 50 mm focal length. The rGO micro-lens array part was installed to make direct contact with the cylindrical lens and PDMS works as a thin flexible substrate following the surface of rigid lens with uniform thickness. The propagation characteristics of the hybrid optics was confirmed by comparing the experimental results with simulation (using Zemax Opticstudio) and the case with the FZP array only without the cylindrical lens. While the FZP array maintains the circular beam shape to the focal length of 15 mm, the hybrid optics transformed the circular beam to ellipse at 11.5 mm (See **Fig. 5d-1, d-2**) having a longer horizontal axis for both experimental (132.8 μm in horizontal and 15.5 μm in vertical axis (FWHM)) and simulation results; then, the beam was changed into circular back at 14 mm and transformed to ellipse with a longer vertical axis at 15 mm (17.1 μm in horizontal and 115.3 μm in vertical axis (FWHM); See **Fig. 5d-1, d-2**). This good agreement of the experiment and simulation confirms that our method for realizing hybrid optics by transferring of ultra-thin diffractive optics works efficiently. We envisage that this concept for manufacturing hybrid optics will enable us to combine the advantages of refractive, reflective, diffractive optics, and metasurfaces without requiring precision manufacturing of micro-patterns on top of the free-form optics.

Fig. 5. Hybrid optics realized by transferring ultra-thin diffractive micro-optics array to traditional rigid refractive optics. (a) Schematic of the fabricated GO/rGO lens array and the focused light images by the array. (b) 5×5 lens array patterned on GO film which is coated on a cover glass and subsequently transferred onto a thin PDMS film. Scale bar: 5 mm. (c)

The lens array on PDMS film conforms to various hybrid optics applications. Scale bar: 5 mm. (d) Comparison between simulation and experiment by illuminating a collimated laser beam through the ultra-thin flexible/stretchable micro lens array (focal length: 15 mm) before and after transferring to a rigid cylindrical lens (focal length: 50 mm).

3. Conclusion

In conclusion, a hybrid optics based on a combination of ultra-thin diffractive micro-optics array and refractive optics was realized by tunable photoreduction and photoablation of GO with the aid of fs laser pulses. Three different GO patterning regimes, namely LTPR, TPR, and ABL, were studied in detail to constitute ultra-thin diffractive micro-optics. Binary, four-level, and six-level diffractive FZPs were patterned to demonstrate the better light concentration to the main peak with suppressed multiple foci and side peaks by tunable photoreduction in TPR regime. A 5×5 array of multi-level ultra-thin micro lens having a focal length of 15 mm was exemplarily patterned, whose resulting spot size smaller than $14\text{ }\mu\text{m}$ with the suppression of diffractive side peaks by 14.9% at the first order and 10.8% at the second order ones. This diffractive lens array was transferred to the surface of a refractive cylindrical lens using PDMS as the flexible/stretchable substrate to form a hybrid optics array. The optical performance of the hybrid optics correlates well with theoretical simulation result, which confirms the validity of our scheme for realizing hybrid optics. This transferable multi-level ultra-thin micro-optics expected to pave a way to novel hybrid optics such as nature-inspired insect's micro-optic hybrid compound eyes for 3D imaging and hybrid Shack-Hartmann wavefront sensors over a wider dynamic range, compact heads-up displays for automobiles, higher performance optics with ultra-thin aberration-tailored hybrid optics and efficient dispersion compensation for ultrafast photonics.

4. Experimental Section

4.1 Material preparation

GO thin-films were fabricated through the drop-casting method on a glass substrate using 0.5 and 1.0 mg/ml aqueous GO solution (Product number: 777676, Sigma Aldrich) and dried on the hot plate at 30 °C to form a 500 nm thick and 900 nm film on glass substrate. Diffractive micro-optics were then patterned on it. For a flexible rGO/PDMS diffractive FZP array, the ultra-thin micro-lens array was firstly patterned to the GO film. Subsequently, PDMS was spin coated on the patterned GO film at 1000 rpm for 60 s so as to make PDMS be immersed into rGO and form an elastic film with a few hundreds of micrometers in thickness. Finally, the PDMS film was peeled off from the glass substrate after the post-curing at 80°C for 2 hours.

4.2 Sample characterization

Optical performance was collected by an optical setup consisting of a continuous wave laser source of 638-nm wavelength (Thorlabs MCLS1) being collimated to each FZP samples and images at the focal plane are captured using CMOS camera (Thorlabs DCC1240M). The surface morphology was performed on scanning electron microscope (JEOL 7600). The film thickness properties was performed by 3D laser scanning microscope (KEYENCE VK-250). The UV–vis spectra were captured with a spectrometer (Shimadzu Corp. UV-1800). Raman spectra were acquired using confocal Raman system (Renishaw, inVia Raman microscope) with laser source of 633 nm wavelength. XPS was performed using a spectrometer (Physical Electronics PHI-5400) with Al K α (1486.6 eV) radiation.

4.3 ZEMAX simulation

Zemax OpticStudio® was used for simulating the optical properties of the FZP and hybrid optics. Zemax offers two methods for simulation, namely physical optical propagation

(POP) and geometrical ray tracing. Geometrical ray tracing offers a ray approximation based optical propagation solution while the POP mode takes in to account of the wave nature of the irradiation. Hence for simulating the FZP and hybrid optics, we used the sequential POP simulation method and analyzed the diffraction patterns and focusing properties. The FZP was realized using circular obscurations designed with dimensions exactly matching to the fabricated rGO FZPs. The cylindrical lens was designed using appropriate surface curvatures and refractive index based on the actual lens used for the experiments (material = N-BK7, radius of curvature = -25.8 mm, thickness = 6.8 mm, clear semi diameter = 11.7 mm). A collimated Gaussian light source of 0.8 mm diameter (FWHM) was used as the illumination source in the simulations of single FZP. For the 3×3 FZP array, a collimated Gaussian source of 3 mm diameter was used as the illumination source. A sampling of 4096×4096 was used at the illumination surface, while a sampling of $16k \times 16k$ was used at the focused image surface.

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