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Adhesive-Layer-Free and Double-Faced Nanotransfer Lithography for a Flexible Large-Area MetaSurface Hologram

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Supporting Information

ABSTRACT: Herein, we develop an adhesive-free doublefaced nanotransfer lithography (ADNT) technique based on the surface deformation of flexible substrates under the conditions of temperature and pressure control and thus address the challenge of realizing the mass production of large-area nanodevices in the fields of optics, metasurfaces, and holograms. During ADNT, which is conducted on a flexible polymer substrate above its glass transition temperature in the absence of adhesive materials and chemical bonding agents, nanostructures from the polymer stamp are attached to the deformed polymer substrate. Various silicon masters are employed to prove our method applicable to arbitrary nanopatterns, and diverse Ag and Au nanostructures



are deposited on polymer molds to demonstrate the wide scope of useable metals. Finally, ADNT is used to (i) produce a flexible large-area hologram on the defect-free poly(methyl methacrylate) (PMMA) film and (ii) fabricate a metasurface hologram and a color filter on the front and back surfaces of the PMMA film, respectively, to realize dual functionality. Thus, it is concluded that the use of ADNT can decrease the fabrication time and cost of high-density nanodevices and facilitate their commercialization.

KEYWORDS: adhesive-free double-faced nanotransfer lithography, polymer substrate, flexible, large-area hologram, color filter, nanopattern, PMMA film

INTRODUCTION

Nanotechnologies for the fabrication of functional nanostructures with the desired properties are of paramount importance for the production of metasurfaces,¹⁻³ optical devices,^{4,5} biosensors,^{6,7} photovoltaic devices,^{8,9} and flexible/wearable electronics.¹⁰⁻¹³ Flexible and wearable substrates have been widely used to fabricate nanostructures for a broad range of applications, and numerous patterning methods such as lithography,^{14–18} laser direct writing (LDW),¹⁹ and nano-transfer printing $(nTP)^{20-22}$ have therefore been developed. Ebeam lithography and LDW provide the advantages of high resolution and precise patterning, allowing direct photoresist patterning for three-dimensional (3D) nanostructure fabrication. However, there are some limitations; (1) the cost is very high, (2) it is very time-consuming, and (3) it is very difficult to fabricate nanostructures on the flexible substrate because of low melting of the polymer film. Conversely, nanoimprint lithography, developed to address these drawbacks, can achieve

high throughput, low cost, large area, and high aspect ratio but suffers from the difficulty of residual layer removal during postprocessing. To mitigate the above problems, many researchers have experimented with nTP techniques, which are characterized by high throughput and allow one to easily produce low-cost highly functional nanostructures and 2D/3D nanostructures. Most nTP methods employ adhesive media to achieve the transfer of nanostructures. For example, Zaumseil et al. fabricated 3D and multilayer nanostructures based on covalent bonding via chemical surface treatment,²³ while Hwang et al. employed covalent bonding-assisted nTP to fabricate various high-resolution and high-aspect-ratio structures at a low cost using a robust and fast chemical reaction.² In addition, Jung et al. developed a solvent-assisted nano-

Received: August 11, 2019 Accepted: December 11, 2019 Published: December 11, 2019



Figure 1. Schematics of the ADNT process. (a-d) Nanoimprint for repeated polymer mold formation. (e) Metal nanostructures deposited on the polymer mold. (f) Nanotransfer process at a temperature above the T_g of the polymer substrate followed by (g) detachment. (h) Double-faced metal nanostructure transferred onto the target substrate.



Figure 2. (a) DSC curves used to determine the T_g of PMMA films with thickness of 150 μ m, (b) SEM–FIB cross-sectional images of the nanostructures transferred onto the PMMA film under constant pressure and heating time at various heating temperatures, (c) the deformation of the PMMA film at various pressures of (i) 3 bar, (ii) 5 bar, and (iii) 7 bar after nanotransfer. (d) Nanostructures transferred onto the PMMA film at various heating times of (i) 1 min, (ii) 5 min, and (iii) 10 min. (the transferred metals were marked using red boxes).

transfer method to achieve the transfer of Au, Ag, and Pd nanowires using a solvent-dissolvable polymer master mold.²⁵ Seo et al. fabricated ultralong and fully aligned nanowires on a large flexible substrate in a highly robust manner using a material-independent mechanical interlocking-based nanowire transfer method.²⁶ Kwak et al. and Kim et al. demonstrated large-area dual-scale metal transfer by adhesive force²⁷ and a simple superhydrophobic surface,²⁸ respectively. Nevertheless, these methods could not avoid the appearance of defects during large-area transfer, are not suitable for mass production, and require medium-strength adhesives to transfer nano/ microstructures. In addition, our proposed method can not only easily achieve nanotransfer on the flexible device without

any chemical adhesive layer but also facilitate the simultaneous transfer of different nanostructures on the double surface of the flexible substrate. The double-faced transfer can be expected to improve the function of the flexible device. So far, double-faced nanotransfer has not been achieved using the conventional medium-adhesive coating method, which involves coating the donor substrate with chemical adhesives to achieve the nanotransfer of nanopatterns. This is a widely used method in the nanotransfer process. To fabricate double facednanopatterns using the conventional method, the adhesive is coated on the front side and then nanopatterns are transferred onto the substrate. Thereafter, the adhesive layer is coated on the other side of the substrate and nanopatterns are transferred

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to the back side. However, during the second adhesive coating and transfer process, the nanopatterns transferred first could be damaged. Herein, we develop adhesive-free double-faced nanotransfer lithography (ADNT) and use it to fabricate a defect-free flexible ultra-large-area metasurface hologram that has so far been impossible to produce by conventional nanofabrication methods. A transparent poly(methyl methacrylate) (PMMA) film is chosen as a substrate, as its relatively low glass transition temperature $(T_{g}, measured and evaluated$ by ultralow-temperature differential scanning calorimetry) allows one to implement nanotransfer without affecting the metal nanostructures. Various noble metal patterns are transferred onto the surface of the PMMA film under the conditions of temperature and pressure control. Sample morphologies and cross sections are observed by scanning electron microscopy (SEM) and focus ion beam (FIB), and the transfer mechanism is explained by considering the binding energy and T_{σ} of PMMA. To stress the advantage of the ultralarge area and defect-free transfer process, the proposed method is used to transfer a commercialized hologram to the surface of the flexible PMMA film and thus obtain a flexible defect-free hologram. Moreover, we successfully transfer the designed color filter and hologram with different nanopatterns on both surfaces of the PMMA film to realize the conversion of various hologram colors via the color filter. Thus, ADNT is proven to be well suited for the mass production of large-area metasurface holograms and nanodevices.

RESULTS AND DISCUSSION

Figure 1 illustrates the nanoimprinting- and e-beam evaporation-based nanotransfer process, with a detailed explanation of Figure 1a-e provided in the Experimental Section. The designed noble metal nanopatterns were deposited on the polyethylene terephthalate (PET) donor polymer mold using existing methods (Figure 1e)²⁹ and transferred to the surface of the PMMA film (110 °C, 5 bar, 5 min; Figure 1f) in the absence of any adhesive layers, which is an obvious advantage over conventional nanotransfer methods. To better explain the mechanism of the transfer process, we evaluated the T_{σ} of the PMMA film, revealing that above this temperature ($105 \text{ }^{\circ}\text{C}$), the film surface can deform and physically bond to metal nanostructures (Figure 2) and confirming that the designed method is applicable to diverse nanopatterns, metals, and donor substrate films. During the subsequent detachment process, double-faced metal nanostructures were produced on the PMMA film (Figure 1g,h). The deformation of the PMMA surface during heating was evaluated by analyzing the samples fabricated at the same pressure but at different temperatures. The results obtained are summarized in Figure S1.

The advantage of our method is that it only requires the operating temperature to exceed the $T_{\rm g}$ of the polymer substrate and does not require the use of adhesives and chemical bonding agents. To illustrate this point, we performed X-ray photoelectron spectroscopy (XPS) analysis of three kinds of Au nanostructures (a 30 nm-thick 200 nm line and space structure, a 30 nm-thick nanodisc pattern, and a 50 nm-thick film without any pattern), as shown in the Supporting Information Figure S2. All samples were transferred to the PMMA substrate and etched downward with a 200 μ m × 200 μ m area to analyze the binding energy at the interface between the PMMA film and transferred Au. The obtained spectra featured only the typical peak of Au at the interface between Au and PMMA. Peaks due to Au oxidation

were not observed, as transfer was conducted at 110 °C, that is, at a temperature higher that the $T_{\rm g}$ of the PMMA film and lower than the oxidation temperature of Au (150 °C).³¹ It was concluded that above its $T_{g'}$ the deformed PMMA film covers the interface of the deposited materials, which are thus physically detached from the donor polymer stamp and transferred onto the PMMA substrate (Figure S3). To explain the mechanism of adhesive-free transfer, we evaluated the T_{σ} of PMMA film and the binding energy of the metal-polymer interface. Advantageously, the proposed method allows transfer to be conducted at low temperature that is independent of the employed material. In our previous works, we found that Au, Al, and Ag nanostructures can be melted and oxidized below 150 $^{\circ}C_{1}^{30,31}$ which highlights the importance of performing transfer at low temperature. Consequently, we selected PMMA as a flexible substrate with a low $T_{\rm g}$ and used DSC analysis to show that the T_g of the PMMA film with the thickness of 150 μ m (Figure 2a). The T_g of the employed PMMA film (83 °C) was suitable for the transfer of nanoscale metal structures without melting and oxidation. To confirm the applicability of our method to films other than PMMA, we employed a commonly used PET film for transfer, with the obtained results provided in Figure S4. Because the substrate thickness is very important for micro-nanodevices, PMMA films with thicknesses of 30 and 75 μ m were used to perform the nanotransfer, and their DSC data and photo after transfer has been provided in Supporting Information Figure S5.

In order to elucidate the mechanism of our proposed nanotransfer, different pressures and heating temperatures were used to achieve nanotransfer and the changes in the PMMA substrate were analyzed. Figure 2 demonstrated the various nanostructures transferred on the flexible PMMA substrate using various pressures, heating temperatures, and heating times, which were based on the DSC curve used to determine the $T_{\rm g}$ of PMMA films with a thickness of 150 μ m. Figure 2a shows DSC curves used to determine the T_g of PMMA films with a thickness of 150 μ m. As reported in previous studies,^{32,33} T_g is an important property when considering polymers for a particular end-use. The T_g is the temperature below which the physical properties of plastics change to those of a glassy or crystalline state. Above the $T_{g'}$ they behave like rubbery materials. Below the T_{o} , plastic's molecules have relatively little mobility. The three kinds of states can be observed in the DSC curves in Figure 2a. Based on the DSC curve, the nanotransfer process was implemented at different heating temperatures to observe the shapes of the polymer substrate under constant pressure and heating time. From Figure 2b, we can observe that metal nanopatterns cannot be transferred onto the PMMA film at 80 °C because of the relatively low mobility of the PMMA film. As the heating temperature increases, the deformation of PMMA films can be observed during the transfer process. When the heating temperature was applied to the above rubbery states, we found that the PMMA substrate showed large deformation. When the heating temperature is sufficiently high, the imprinted depth h_3 could be greater than the polymer mold h, thereby causing the metal nanostructures fabricated at the bottom of the polymer mold to be simultaneously transferred onto the PMMA substrate. It is known that the pressure can cause the deformation of the polymer below the relative heating temperature. Therefore, to better explain the physical bonding of nanotransfer, the FIB cross-sectional images were compared and analyzed above $T_{\rm g}$ under different pressures.

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Figure 3. Morphologies and cross-sectional images of samples with different thicknesses, pattern sizes, and compositions fabricated at variable pressures. (a) Images of dot nanopatterns captured before and after transfer at 1 bar. (i,i-1) Dot nanopatterns transferred onto the PMMA film. (i,ii-1) Nanopatterns remaining on the polymer mold of the PET film after transfer. (iii,iii-1) Nanopatterns on the polymer mold of the PET film after transfer at 4 bar. (i,i-1) Nanowires transferred onto the PMMA film. (ii,ii-1) Nanopatterns remaining on the polymer mold of the PET film after transfer. (c) Images of dot nanopatterns before and after transfer (i,ii-1) Nanowires transferred onto the PMMA film. (ii,ii-1) Nanopatterns remaining on the polymer mold of the PET film after transfer. (c) Images of dot nanopatterns before and after transfer at 6 bar. (i,i-1) Dual layer formed on the PMMA film after nanotransfer. (ii,ii-1) Polymer mold after nanotransfer. (d) Large-area photos, morphologies, and cross-sectional images of nanopatterns with different thicknesses, pitches, and shapes. (i) Large-area photo (120 mm × 120 mm). (ii) Morphologies and cross-sectional images of Au nanowires with a thickness of 50 nm, width of 100 nm, and a pitch of 200 nm. (iii) Morphologies and cross-sectional images of Au nanowires (iv) Morphologies and cross-sectional images of Au nano

From the FIB images, we found that our proposed nanotransfer was well achieved based on the mechanical interlocking adhesion during the $T_{\rm g}$ and cooling process. Mechanical interlocking adhesion theories have been pre-viously studied.³⁴⁻³⁶ Figure 2c demonstrates the mechanism of the transfer process under different pressures. Figure 2c(i) shows the results of transfer below a temperature of 110 °C, pressure of 3 bars, and heating time of 5 min. In the figure, h is the depth of the polymer mold, t is the thickness of the metal Au, and h_1 , h_2 , and h_3 are depths of deformation after transfer based on the various pressures. The Au nanostructures easily transferred onto the surface of the PMMA substrate, when a relatively low pressure of 3 bars was applied. The corresponding cross-sectional image is displayed on the right. We can observe that the small deformation of the PMMA surface can strongly capture the metal nanostructure after the cooling process (red arrows represent the capture force in three directions). This is because mechanical interlocking adhesion causes the capture of the metal patterns during the cooling process. With the increase in the applied pressure, greater deformation can be observed in the PMMA surfaces, such as imprinting [see Figure 2c(ii,iii)]. Therefore, we believe

that our proposed method can not only easily transfer metal nanostructures onto flexible substrates without any chemical adhesives but also control the shape of the polymer substrate depending on the pressure and heating temperature. In order to explain the effect of heating time on nanotransfer, the nanostructures were transferred to the PMMA film at varying heating times under constant pressure and heating temperature. The corresponding results are demonstrated in Figure 2d. From Figure 2d, it is clear that heating time has an important effect on the nanotransfer based on the $T_{\rm g}$. Therefore, the shape of nanostructures transferred onto the PMMA film can be adjusted by modifying the heating temperature, heating time, and pressure.

To verify the practicality of the proposed method for nanofabrication, we employed it to produce various nanopatterns and observed their morphologies and cross sections by SEM and FIB (Figure 3). Specifically, three kinds of nanostructures were fabricated by controlling the pressure during nanotransfer, and facile large-area nanotransfer was achieved in the absence of any chemical adhesive-based coating layer. Figure 3a demonstrates SEM and cross-sectional FIB images of Au nanopillars (diameter = 200 nm, pitch = 400



Figure 4. Transfer of a flexible large-area ring hologram onto the PMMA film. (a) Schematic representation and an image of the flexible ring hologram. (a.1 and a.3) Schematic of the ring hologram for different light colors. (a.2) Photo of a flexed hologram. Representations and images of (b) the ring hologram fabricated on the polymer mold, (c) transferred onto the PMMA film, and (d) the remaining PET polymer mold. Corresponding blue, red, and green dotted boxes represent the morphologies, cross-sectional images, and large-area photos. (e) Images captured under illumination with red and white light-emitting diodes (LEDs) with an angular spectrum of -9, -6, -3, 0, +3, +6, and $+9^{\circ}$.

nm, thickness = 30 nm) acquired before and after nanotransfer (1 bar, 105 °C, 3 min). Figure 3a(i,i-1) demonstrates that the nanopillars were well transferred to the PMMA surface because of their thermal deformation, with the detailed mechanism of this adhesive-layer-free transfer discussed in Figure 2. In addition, the sample surface was found to be coated with Pt nanoparticles originating from the ultrathin Pt coating layer deposited to enhance image clarity.

The morphologies and cross-sectional images of the extra parts of nanostructures on the PET donor substrate after transfer are displayed in Figure 3a(ii,ii-1), respectively, while Figure 3a(iii,iii-1) shows the images of metal nanostructures deposited onto the designed polymer patterns on the PET donor substrate before transfer. The nanopillars shown in Figure 3a(iii) were fabricated using nanoimprinting and ebeam evaporation (fabrication process details are provided in Figure 1a-e). Thus, it was concluded that the thermal deformation of PMMA allows one to fabricate nanostructures with variable shapes using different pressures. In addition, to confirm the adaptability of the proposed method to different nanopatterns, it was employed to transfer metal nanowires at different pressures. Figure 3b displays the morphologies and cross-sectional images of Au nanowires (width = 200 nm, pitch = 400 nm, thickness = 30 nm) before and after nanotransfer at

4 bar, showing that the PMMA film became suitable for nanoimprinting under the conditions of high pressure and temperature. Interestingly, the nanoimprinted thickness of PMMA could be easily controlled. Figure 3b(ii,i) shows images of Au nanowires before and after nanotransfer at 4 bar, respectively. Figure 3b(i-1,ii-1) reveals that these nanowires were well transferred to PMMA and that the nanoimprinted thickness of PMMA was well controlled and increased with increasing pressure. At an applied pressure of 6 bar, the metal deposited on the channel could be transferred to PMMA. Figure 3c shows the morphologies and cross-sectional images of Au nano-pillars (diameter = 200 nm, pitch = 400 nm, thickness = 30 nm) before and after transfer, revealing that nanopatterns located on the top and bottom sides of the polymer mold could be simultaneously transferred onto the PMMA substrate. To explain the broad sample thickness, pitch, and shape scope of the transfer process, we fabricated various specimens on the PMMA substrate. Figure 3d demonstrates the morphologies and large-area and crosssectional images of Au nanowires with different thicknesses, pitches, and shapes transferred onto the PMMA substrate, revealing that no defects were observed after transfer.

To demonstrate the possibility of flexible large-area transfer for different metals, we used computer-generated holography



Figure 5. Large-area photos, morphologies, and cross-sectional images of the hexagonal nanodot pattern (a) after and (b) before transfer. (i) Largearea photo, (ii) SEM-observed morphologies, and (iii) FIB-observed cross sections. (c) Fabrication of a hologram and a color filter on opposite sides of the PMMA film by double-faced nanotransfer. (i) Photo of the PMMA film with double-faced nanopatterns. (ii) Schematic of the ring hologram and color filters irradiated with white light. (ii-1) Front and back photos of the ring hologram and a color filter. (iii) Morphologies and cross-sectional images of the front and back surfaces of the PMMA film. (d,e) Images of the fabricated double-faced hologram captured under illumination using white LEDs with an angular spectrum of 0 and $+5^\circ$, respectively.

to design and fabricate a ring hologram. The corresponding Si master was prepared via KrF lithography and used to fabricate the polymer stamp. The Ag metal was deposited on the replicated polymer mold to form a ring hologram that was transferred onto the PMMA film using ADNT at a temperature exceeding substrate T_g. Figure 4 presents hologram morphologies, cross-sectional and large-area images, and other parameters. Holograms with different designs, widely studied and applied in the field of optics,^{37–39} are mostly fabricated on glass and Si substrates using e-beam lithography.40,41 In this work, we used the polygon-based computer-generated hologram (CGH) synthesis algorithm.⁴²⁻⁴⁵ There are several design methods for CGH such as point clouds, depth-maps, and polygons. The polygon-based CGH is not very popular because of its difficulty in implementation, yet its rigor and accuracy in the modeling of holographic 3D scenes and algorithmic flexibility are very well recognized. The diffraction efficiency of the five-ring hologram sample presented in this paper is theoretically 100% when the hologram is complexmodulated. In this work, the hologram pattern was approximated in the form of a binary pattern. In this case, the theoretical diffraction efficiency decreased to about 15% because of dc, conjugate, and higher-order diffraction noise. However, in contrast to ADNT, these methods are not well suited for nanofabrication and are of limited applicability to the mass production of large-area patterns on flexible substrates. Figure 4a shows a schematic representation and a photographic image of a ring hologram, while Figure 4a.2 reveals that

no defects were observed in the flexible large-area hologram after transfer. Figure 4a.1,a.3 displays the shape of the ring hologram using light of different colors. Figure 4b-d shows the ring hologram fabricated on the PET donor polymer mold, the hologram transferred onto PMMA, and the post-transfer PET donor polymer mold. The corresponding blue, red, and green dotted boxes represent the corresponding morphologies, crosssectional images, and large-area images.

Figure 4c reveals that ring hologram nanopatterns were well transferred onto the surface of the PMMA film. Interestingly, the imprinted thickness (h) of PMMA could be controlled by pressure adjustment, as confirmed by the related results in Figure 3. Figure 4c.3 shows that ring hologram nanopatterns were transferred onto the transparent PMMA film without any defects. Thus, in combination with the existing roll-to-roll nanofabrication technology, the developed simple nanotransfer method was concluded to be applicable to the mass production of large-area arbitrary nanopatterns. To restress, the proposed technology only requires the operating temperature to exceed the T_{σ} of the substrate film. The ring hologram fabricated on the PMMA film was evaluated using red and white LEDs depending on the different angular spectrum, with details of the measurement method provided in the Experimental Section. The optical layout, experimental setup, and illustration of the measured angle of the hologram used for evaluation are provided in Figure S6. Figure 4e.1 shows images captured at different viewing directions using LEDs with a central wavelength of 660 nm (red) and a full width of half maximum of 30 nm. Figure 4e.2 shows images captured using fibercoupled white LEDs manufactured by Thorlabs. The corresponding videos are provided in the Supporting Information.

To demonstrate the unique features of our method, we transferred nano/microstructures onto both sides of a polymer substrate to achieve dual functionality and confirmed the success of this transfer using a plasmonic four-color filter. The above approach allows one to easily change the colors of the signed hologram to elevate the density of nano/micro-structures for nanodevices. The corresponding Si master comprised four kinds of hexagonal nanohole array color filters (based on the extraordinary transmittance (EOT) phenomenon^{46,47}) with different hole sizes and periods (Figure S7). The polymer stamp was prepared from the Si master following the procedure in Figure 1 and was coated with Ag to a depth of 50 nm (Figure 5b).

The deposited Ag was transferred to the PMMA substrate by applying a pressure of 5 bar at 110 °C for 5 min. Figure 5a(i) shows the fabricated flexible plasmonic color filter on a large area (photo of the flexed device is shown in the inset). Because of the EOT phenomenon, the geometric figures showed different colors determined by nanohole size and period.^{46,47} Figure 5a(ii,iii),b(ii,iii) demonstrates the corresponding morphologies and cross-sectional images of one of the four kinds of hexagonal nanohole patterns with the results obtained for other patterns before and after transfer provided in Figure S8. The corresponding transmissions were provided in Figure S9. As mentioned above, unlike conventional patterning methods, our method enables the fabrication of nano/micro patterns on both sides of the substrate and thus allows one to significantly decrease the volume and thickness of the corresponding devices and fabricate merged items on a single substrate. As shown in Figure 5c, when a 150 μ m-thick PMMA stamp was placed between the color filter polymer stamp and the hologram polymer stamp and a pressure of 5 bar was applied for 5 min at 110 °C, a double-faced hologram with a color filter was obtained after the above stamps were detached from the PMMA film (Figure 5c(i)). This method makes designed ring hologram produce a different performance assisted color filter. Figure 5c(ii) displays a schematic of the hologram and a color filter irradiated with white light, with the corresponding morphologies and cross-sectional images of the front and back surfaces shown in Figure 5c(iii-1-iii-4). Figure 5c(ii) shows a photo of the ring hologram and a color filter fabricated on both sides of the PMMA film, confirming the successful formation of the four-color ring hologram. The corresponding images were captured under illumination with white LEDs with an angular spectrum of 0 and +5°. Thus, the proposed ADNT method is believed to be of high importance for the field of nanofabrication.

CONCLUSIONS

Herein, we proposed a novel nanotransfer lithography method allowing the transfer of nano/microstructures onto large-area flexible substrates without the introduction of defects. The proposed method does not require the use of adhesive materials and chemical bonding agents and hence allows one to fully preserve the properties of the transferred materials. The slight deformation of the polymer substrate at temperatures above its T_g resulted in the detachment of materials deposited on the polymer stamp, and the shape of transferred structures was determined by the pressure applied during nanotransfer. Moreover, the developed technique was found to be applicable to the fabrication of double-faced nanostructures on a single substrate. To prove the practical utility of our method, we applied it to the fabrication of an ultra-large metasurface hologram, a plasmonic color filter, and a double-faced color embedded metasurface. Thus, our method is applicable to large-area flexible substrates and hence is well suited for the fast fabrication of high-density flexible devices at a low cost.

EXPERIMENTAL SECTION

Fabrication. Si masters with different line and dot patterns were prepared using KrF lithography (Figure S9). RM311 polyurethane resin (Minuta Technology Co., Ltd. Korea) was chosen to repeatedly replicate the polymer mold. First, the above resin was coated on the Si master, and rolling was implemented to make the imprint resin infiltrate the master nanopatterns (Figure 1a,b). Subsequently, full resin polymerization was achieved by UV-curing (2×90 s; Figure 1c). The polymer mold was separated from the Si master (Figure 1d) and coated with the target metal to form nanopatterns (Figure 1e). Finally, the PMMA film was employed as a donor substrate to implement adhesive-free double-faced transfer (Figure 1f–h). The results of T_g evaluation indicated that our method is applicable to a variety of films.

Characterization. Sample morphologies and cross sections were observed by SEM (Sirion, FEI Netherlands) and FIB (Helios Nanolab, FEI Netherlands), respectively. Metal nanostructures were fabricated on the polymer mold using e-beam evaporation (DAEKI HIOTECH Co, Ltd. Korea). The T_g of PMMA films was measured by ultralow-temperature differential scanning calorimetry (DSC214 Polyma, Netzsch). The binding energies of metal and film surfaces were probed by XPS (K-Alpha+, Thermo Fisher Scientific, Inc.), and hologram images were observed using an optical system.

Ring Hologram Evaluation. Light was delivered by an optical fiber and collimated before entering the hologram. As the reconstruction image changes with the viewing direction, a telecentric lens (58-428, Edmund) was used to capture a narrow portion of the angular spectrum. A CCD camera with a resolution of 2016 × 2016 pixels was mounted on a two-axis rotation stage to measure the full angular spectrum of the reconstruction wave (Figure S4). Two different LEDs were used as the source of light, which was delivered through a 200 μ m-diameter optical fiber. Light diverged at the end of the fiber and was then collimated by a lens with a focal length of 150 mm and a diameter of 50 mm. The incident wave was modulated by the hologram, and a large field of view was reconstructed.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.9b14345.

- Additional results of morphological characterization and cross-sectional imaging, design of the four-color color filter, optical layout and experimental setup used for hologram characterization, and the effect of temperature on the shape of the PMMA film (PDF)
- Red light-emitting diodes (AVI)

White light-emitting diodes (MP4)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Center for Advanced Meta-Materials (CAMM) funded by the Ministry of Science, ICT and Future Planning, Korea, through the Global Frontier Project (CAMM-no. 2014M3A6B3063707), (CAMM-No. 2019M3A6B3030637), and the Basic Research Program of KIMM (Korea Institute of Machinery and Materials, NK218B).

ABBREVIATIONS

ADNT, adhesive-free double-faced nanotransfer lithography LDW, laser direct writing

nTP, nanotransfer printing

SEM, scanning electron microscopy

EOT, extraordinary transmittance

XPS, X-ray photoelectron spectroscopy

PMMA, poly(methyl methacrylate)

FIB, focus ion beam

PET, polyethylene terephthalate

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