Metasurface holography, the reconstruction of holographic images by modulating the spatial amplitude and phase of light using metasurfaces, has emerged as a next-generation display technology. However, conventional fabrication techniques used to realize meta-holograms are limited by their small patterning areas, high manufacturing costs, and low throughput, which hinder their practical use. Herein, a high efficiency hologram using a one-step nanomanufacturing method with a titanium dioxide nanoparticle-embedded resin, allowing for high-throughput and low-cost fabrication is demonstrated. At a single wavelength, a record high theoretical efficiency of 96.9% is demonstrated with an experimentally measured conversion efficiency of 90.6% and zero-order diffraction of 7.3% producing an ultrahigh-efficiency, twin-image free hologram that can even be directly observed under ambient light conditions. Moreover, a broadband meta-atom with an average efficiency of 76.0% is designed, and a hologram with an average efficiency of 62.4% at visible wavelengths from 450 to 650 nm is experimentally demonstrated.

1. Introduction
Metasurfaces\(^1\) composed of arrays of subwavelength structures have been intensively researched due to their ability to modulate electromagnetic (EM) waves. Various practical applications of metasurfaces have been reported, such as metalenses,\(^2\) color filters,\(^3\) beam modulating devices,\(^4\) and all solid-state light detection and ranging (LiDAR).\(^5\) Moreover, high-quality, high-resolution, and large field of view (FOV) holograms have been demonstrated.\(^6\)

Metaholograms are designed to reconstruct images by manipulating the spatial amplitude and phase of light using metasurfaces, and have emerged as a next-generation display technology due to their compact form factor. In particular, many studies have been conducted to increase the efficiency of metaholograms for practical applications.\(^7\) Although plasmonic metaholograms generally exhibit low efficiency due to Ohmic losses, a reflection-type plasmonic metahologram reaching up to 80% efficiency at 825 nm has been successfully demonstrated.\(^6\) All-dielectric metasurfaces are another candidate to achieve high efficiency metaholograms. An all-dielectric Huygens’ metahologram consisting of silicon (Si) meta-atoms has been demonstrated with a transmission efficiency of 86% at 785 nm.\(^8\) Additionally, amorphous titanium dioxide (α-TiO\(_2\)) has been used to produce metaholograms reaching efficiencies of 82%, 81%, and 78% at wavelengths of 480, 532, and 660 nm, respectively.\(^6\)

Conventional fabrication techniques for realizing all-dielectric metaholograms such as electron-beam lithography (EBL) and
focused ion beam (FIB) milling, to name a few, have inherent limitations due to their small pattern areas, high cost, and low throughput, which are the biggest restrictions on commercializing metaholograms. Extreme ultraviolet (EUV) lithography can be used to fabricate nanostructures on a large scale, but is, unfortunately, still extremely expensive. To overcome these limitations, nanoimprint lithography (NIL) has been introduced as a way to easily and quickly replicate nanostructures from a master mold directly onto a substrate, which is already being applied for semiconductor and patterned media manufacturing.

As the imprinted resin generally acts as an intermediate structure, conventional NIL also requires additional operations such as deposition and etching to complete the fabrication of the final metasurface. Although the refractive index of typical resin is typically too low for use in metasurfaces, it has successfully been used to build meta-atoms by using extremely high-aspect-ratio structures. Recently, the single-step manufacturing of a metalens using NIL and a new type of nanoparticle-embedded-resist (nano-PER) has been demonstrated. The refractive index of the nano-PER can be increased at will by embedding nanoparticles (NPs) of different materials into a standard resin, which opens up exciting new possibilities of using the resin directly as functional meta-atoms. However, conventional metasurfaces consisting of nano-PER showed a low efficiency 33% in the visible regime, resulting in a reduction of performance and applicability.

Here, we introduce a metahologram made of a nano-PER reaching a record high of 96.9% efficiency, fabricated using a high-throughput one-step NIL manufacturing process. We verify that the optical properties of the nano-PER are sufficient to produce high efficiency metaholograms and even outperform other low-loss dielectric materials. For the synthesis of the nano-PER, titanium dioxide (TiO$_2$) NPs, that have a high refractive index in low-loss dielectric materials, are dispersed in an ultraviolet (UV)-curable resin. Using a single step of NIL, the meta-atoms patterns are transferred from a master mold and cured through UV light to directly imprint the metasurface without the need of any secondary operations. We theoretically verify that the metahologram composed of the TiO$_2$ nano-PER can achieve a 96.9% conversion efficiency while being almost free of zero-order diffraction (0.2%) at a wavelength of $\lambda = 532$ nm. We confirm this high performance by experimentally demonstrating a metahologram with a measured conversion efficiency of 90.6% with no twin image. Furthermore, we reveal the broadband property of TiO$_2$ nano-PER by designing a single meta-atom with high efficiency over the visible regime. We theoretically calculate an average efficiency of 76.0% and experimentally demonstrate a metahologram with an average efficiency of 62.4% for different wavelengths from 450 to 650 nm. This low-cost and high-throughput realization of high-efficiency metaholograms could prove to be a valuable method for the commercialization of optical metasurfaces.

2. Results and Discussion

2.1. Optical Properties of TiO$_2$ Nano-PER

The key to using NIL as a one-step fabrication method is to utilize the printable resin as the desired meta-atom directly. Typically, resins used in NIL have a refractive index ($n$) of around $n=1.5$, and therefore cannot be used as meta-atoms in optical metasurfaces without extremely large structure parameters. In order to increase the $n$ of the resin in the visible regime, we use the well-understood and inexpensive synthesis of TiO$_2$ NPs to create a TiO$_2$ nano-PER. This is done by dispersing 30 nm diameter TiO$_2$ NPs into a UV-curable resin, which acts as a matrix to enable the direct transfer of nanostructures from the master mold. The result is a homogeneous effective medium with an increased effective index, closer to that of TiO$_2$ than the bare resin.

The optical properties of the nano-PER are determined by the weight ratio of the NPs. Here, we use a TiO$_2$ nano-PER with a weight ratio of 80%. To determine the $n$ and extinction coefficient ($k$) of the TiO$_2$ nano-PER, an 84.9 nm thin film of TiO$_2$ nano-PER was spin-coated onto a Si substrate (Figure 1b) and the amplitude ratio ($\Psi$) and phase difference ($\Delta$) between the s and p components of the thin film were measured using ellipsometry (Figure 1c). The measured $\Psi$ and $\Delta$ data are fitted using the Cauchy dispersion model, which is expressed as follows:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \cdots$$

where $n(\lambda)$ is the dispersive refractive index, $\lambda$ is the wavelength of the light with the unit of $\mu$m, and $A$, $B$, $C$ are coefficients to fit the model with the measured $\Psi$ and $\Delta$ data. Model coefficients of $A = 1.87600$, $B = 0.02025 \mu$m$^{-2}$, and $C = 0.00216 \mu$m$^4$ were determined, with a mean squared error (MSE) of 19.070. This confirms the validity of treating the TiO$_2$ nano-PER as a homogeneous effective medium. The measured $n$ of 80% weight ratio TiO$_2$ nano-PER and typical resin at a wavelength of 532 nm is 1.9754, and 1.5288, respectively (Figure 1d). The simulated refractive index from COMSOL Multiphysics version 5.6 was measured using the Maxwell–Garnett mixing formula:

$$n_{MG} = \sqrt{\frac{1 + 2f\alpha}{1 - f\alpha}}$$

where $\alpha = (\varepsilon_{TiO_2} - \varepsilon_1)/(\varepsilon_{TiO_2} + 2\varepsilon_1)$; $f$ is the volume fraction of TiO$_2$, and $\varepsilon_{TiO_2}$ and $\varepsilon_1$ are the permittivity of TiO$_2$ and resin, respectively. Using the Maxwell–Garnett mixing formula, we estimate the volume fraction to be 44% for TiO$_2$ weight ratio of 80% (Figure 1d). The simulated refractive index from COMSOL Multiphysics version 5.6 using the calculated filling ratio agrees well with the measured refractive index indicating the credibility of the estimated filling ratio. Furthermore, this is also confirmed by the Bruggeman mixing formula (Note S3, Supporting Information). The scattering due to the finite size of the TiO$_2$ NPs in the nano-PER are visualized using 2D finite element analysis (FEM) simulations. In a nano-PER with 30 nm diameter TiO$_2$ NPs, negligible scattering occurs and the directionality of the beam is maintained (Figure 1e), however, with 100 nm diameter TiO$_2$ NPs, the scattering is severe and directionality of the beam is maintained. The optical properties of the nano-PER are determined by the weight ratio of the NPs. Here, we use a TiO$_2$ nano-PER with a weight ratio of 80%. To determine the $n$ and extinction coefficient ($k$) of the TiO$_2$ nano-PER, an 84.9 nm thin film of TiO$_2$ nano-PER was spin-coated onto a Si substrate (Figure 1b) and the amplitude ratio ($\Psi$) and phase difference ($\Delta$) between the s and p components of the thin film were measured using ellipsometry (Figure 1c). The measured $\Psi$ and $\Delta$ data are fitted using the Cauchy dispersion model, which is expressed as follows:

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Figure 1. Optical properties of TiO$_2$ nanoparticle-embedded-resin (nano-PER). a) Schematic of the high-efficiency metahologram made up of nano-PER meta-atoms. b) Scanning electron microscope (SEM) image of a cross-section of the spin-coated nano-PER films with a TiO$_2$ weight ratio of 80%. Scale bar: 1 μm. c) Ellipsometry analysis of the TiO$_2$ nano-PER film. d) The measured refractive index of the nano-PER film with 80% weight ratio (blue solid line) and a typical resin (blue dotted line). The measured extinction coefficient of the nano-PER with 80% weight ratio (orange solid line). Calculated effective refractive index by the Maxwell–Garnett formula (blue circles). Simulated effective refractive index by Comsol Multiphysics version 5.6 (blue squares). e) Visualizing the propagation of a Gaussian beam in a nano-PER thin film using 2D finite element analysis (FEM) simulations.

2.2. Design of High-Efficiency Meta-atoms

Rigorous coupled-wave analysis (RCWA)\cite{18} was used to simulate the optical properties of the TiO$_2$ nano-PER-based meta-atoms using the measured $n$. Anisotropic meta-atoms were designed to modulate the incident light using the concept of Pancharatnam–Berry phase (PB phase), also known as geometric phase (Figure 2a), to allow for broadband operation. PB phase achieves a full $2\pi$ phase modulation by modifying the in-plane orientation angle of the anisotropic meta-atoms in the metasurface and can be understood by analyzing the meta-atoms with a Jones matrix $J$\cite{19} given by

$$J = \begin{bmatrix} t_{xx} & 0 \\ 0 & t_{yy} \end{bmatrix}$$

(3)

where $t_{xx}$ and $t_{yy}$ represent the complex transmission coefficients for light polarized along the long and short axes of the anisotropic meta-atoms, respectively. The Jones matrix $T$ for meta-atoms rotated by an angle $\theta$ can be calculated using a rotation matrix $R(\theta)$, as follows\cite{19}

$$T = R(\theta^\ast) \cdot J \cdot R(\theta)$$

(4)

The transmission coefficients for rotated meta-atoms can then be calculated as follows

$$E_T = T \cdot E_{CP} = \frac{t_{xx} + t_{yy}}{2} E_{co-pol} + \frac{t_{xx} - t_{yy}}{2} e^{i2\theta} E_{cross-pol}$$

(5)

where $E_T$, $E_{CP}$, $E_{co-pol}$, and $E_{cross-pol}$ represent the electric fields of the transmitted light, the circularly polarized incidence, and the co- and cross-polarized components, respectively. The $e^{i2\theta}$ term indicates that the phase of the cross-polarized part of the transmitted light is retarded by $2\theta$, and depends solely on the orientation angle of the meta-atom. The co-polarized component of the...
light causes zero-order diffraction, which leads to a low signal-to-noise ratio and poor-quality holograms. Therefore, the conversion efficiency, which is defined as the amplitude of the cross-polarized component, is directly connected to the efficiency of the hologram. To demonstrate high-quality holograms, the conversion efficiency should be maximized, while the co-polarized light is simultaneously suppressed.

We calculate the conversion efficiency of the meta-atoms by sweeping lengths ($l$) from 290 to 430 nm and widths ($w$) from 60 to 200 nm, with a fixed height ($h$) of 910 nm and periodicity ($p$) of 450 nm, and a residual layer of 128 nm (Figure 2b). The residual layer acts as an antireflection layer, resulting in near-unity transmission (97.0%) and suppression of reflection (2.7%) (Note S5, Supporting Information). $h$ is determined to produce the maximum efficiency (Note S6, Supporting Information), while $p$ is chosen to be smaller than the operating wavelength (532 nm) to suppress the unwanted diffraction of light. The meta-atom with $l = 411$ nm and $w = 121$ nm reaches up to the 96.9% conversion efficiency with almost zero (0.2%) zero-order diffraction at a wavelength of 532 nm, while only absorbing 0.2% due to the extremely low $k$ of the TiO$_2$ nano-PER. Considering that reflection inevitably occurs when light passes through the interface of media with different refractive indices, the reflection should be reduced to achieve high efficiency. We design the residual layer of the metasurface to act as an antireflective (AR) film, along with negligible absorption from the TiO$_2$ nano-PER, thus achieving high efficiency with only 2.7% reflection. Moreover, many candidate structures near the target geometry have an efficiency of over 90% near the target structure, therefore some fabrication errors are acceptable. To confirm that the $l$ and $w$ of the chosen meta-atom provides a $\pi$-phase difference between the $x$ and $y$ components of the electric field ($E_x$ and $E_y$), we simulate the propagating electric field profiles of $x$- and $y$-polarized light in the optimized meta-atom at 532 nm (Figure 2c). The results clearly show that the meta-atom acts as a half-wave plate, therefore producing the maximum efficiency.

Furthermore, we reveal the broadband properties of the nano-PER based metahologram. To find the meta-atom that maximizes the broadband properties, we calculate the conversion efficiency of meta-atoms with lengths from 390 to 420 nm, and a fixed width of 116 nm, height of 940 nm, and periodicity of 450 nm (Figure 2d). Width and height are determined to maximize efficiency from 450 to 650 nm wavelength (Note S7, Supporting Information). The meta-atoms show high efficiency over the broadband visible range from 450 to 650 nm. Moreover, we calculate the average efficiency from 450 to 650 nm along each length (Figure 2e). As the length increases, the average efficiency increases from 73.4% (390 nm) to 75.9% (420 nm), and fabrication errors are acceptable because meta-atoms show broadband property with high efficiency over a wide range of lengths. The conversion efficiency and zero-order diffraction efficiency of the meta-atom with a length of 410 nm is calculated over the entire visible regime (Figure 2f) to confirm the high efficiency broadband properties over the visible regime.
2.3. One-Step Nanofabrication Using Nano-PER for High-Efficiency Metaholograms

A brief schematic diagram of the one-step nano-PER printing is provided in Figure 3a. First, a master mold with the desired meta-surface is fabricated on a Si substrate using traditional EBL, lift-off, and etching processes (details in the Experimental Section). Figure 3b shows a scanning electron microscope (SEM) image of the Si master mold. The master mold is hydrophobically coated with a vaporized fluorine solution for the subsequent demolding process of a soft mold. Next, a hard-polydimethylsiloxane (h-PDMS) solution is coated and solidified on the master mold to replicate the metasurface precisely. The h-PDMS is preferred as it can transfer nanopatterns at a higher resolution than standard PDMS due to its high modulus ($\approx 9$ N mm$^{-2}$). The PDMS is then coated onto the h-PDMS layer to adjust the thickness of the soft mold, which is important because if the soft mold is too thin, it will shrink overly while absorbing the solvent in the nano-PER. The PDMS layer is then heated and combined with the h-PDMS layer, and the soft mold is completed by separating the h-PDMS layer from the master mold (Figure 3c). For the highest efficiency hologram, the residual layer of nano-PER which can be finely controlled by modulating the revolutions per minute (RPM) is spin-coated at 2000 RPM to produce a thickness of 130 nm (Note S8, Supporting Information). For the broadband high efficiency hologram, both the mechanical design of the soft mold and chemical absorption of the solvent in the nano-PER help to make a uniform, minimal thickness spin-coated nano-PER film (Note S9, Supporting Information). After the coating of the nano-PER on the soft mold, the coated nano-PER contacts conformally with the substrate without air traps and particles. Finally, the correct amount of pressure and UV light is applied to the substrate-PER-soft mold structure. When the nano-PER is fully cured, the soft mold is detached, leaving the high-aspect-ratio metasurface on the substrate, as can be seen in Figure 3d. As the reactive ion etching (RIE) used to etch the silicon mold is not completely anisotropic, the fabricated meta-atoms are slightly trapezoidal as shown in Figure 3b,d. We confirmed that this minor fabrication error does not significantly affect the results (Note S10, Supporting Information).

This mechanical single-step printing process of NIL with nano-PER is very attractive as it not only allows for the high-throughput fabrication of metasurfaces but also can be easily complemented by enhancing or weakening the work of adhesion...
(\(W_a\)) between interfaces to fabricate high-efficiency metaholograms with higher aspect ratio. While the soft mold is hydrophonically coated to decrease the \(W_a\) between the soft mold and the nano-PER, the PMMA layer is coated on pretreated substrates by \(O_2\) plasma simultaneously to increase the interaction between the nano-PER and substrates, which facilitating the replication of metasurfaces with an aspect ratio of about 8. The \(W_a\) between two interfaces can be calculated precisely by harmonic-mean equation,[21] given by

\[
W_a = \frac{\gamma_i^d \gamma_i^d l}{\gamma_i^d + \gamma_i^d l} + \frac{\gamma_i^p \gamma_i^p l}{\gamma_i^p + \gamma_i^p l} + \frac{\gamma_p^d \gamma_p^d l}{\gamma_p^d + \gamma_p^d l} + \frac{\gamma_p^p \gamma_p^p l}{\gamma_p^p + \gamma_p^p l}
\]  

(6)

where the subscript \(s\) is for the interface of solid and the superscripts \(d\) and \(p\) are for the dispersive and polar components of the surface tension \(\gamma\), respectively. At this point, surface tension is determined by the geometric-mean equation,[21] given by

\[
(1 + \cos \theta) \gamma_l = 2\left(\gamma_1^l \gamma_2^l\right)^{\frac{1}{2}} + 2\left(\gamma_2^l \gamma_1^l\right)^{\frac{1}{2}}
\]  

(7)

where \(\theta\) is for the contact angle of the liquid on the solid and subscripts \(l\) and \(s\) are for the liquid and solid components of the \(\gamma\), respectively. By solving above equations about the two different liquids of which know the dispersive and polar surface tensions, typically deionized (DI) water and diiodomethane, we can decide dispersive and polar surface tensions of various surfaces and calculate the \(W_a\) (Note S11, Supporting Information). While the bare glass without pretreatment has a \(W_a\) of about 67.2 mJ m\(^{-2}\) for the \(TiO_2\) nano-PER, polycarbonate (PC), polypropylene (PP), and curved glasses based polyethylene terephlate (PET) have poor \(W_a\), measured to be 62.4, 51.5, and 59.1 mJ m\(^{-2}\), respectively. By applying the PMMA layer on substrates for the adhesive layer, the \(W_a\) is increased by 68.8 mJ m\(^{-2}\). In the same manner, the \(W_a\) of the fluor-coated soft mold for the \(TiO_2\) nano-PER becomes lower than the non-treated soft mold, measured to be 43.6 and 52.8 mJ m\(^{-2}\), respectively. Consequently, by achieving the \(W_a\) difference between the pretreated substrate and the soft mold of 25.2 mJ m\(^{-2}\), we can easily fabricate metasurfaces with a high aspect ratio over 8 on any flexible substrate. In addition, the controlled residual layer of the \(TiO_2\) nano-PER increases the relative contact area of substrates for the nano-PER than the nonresidual layer, maximizing the \(W_a\) difference when considering contact areas (Note S11, Supporting Information). We further confirm that the surface treatment of the soft mold allows the metasurfaces to be transferred without any additional defect, while metasurfaces transferred by the non-treated soft mold are easy to contain defects such as bending or breaking of the meta-atoms during detaching the soft mold (Note S12, Supporting Information). The improved transfer capacity can be observed directly by replication of palette nanopillars with various sizes, validating that the adhesion modulation between interfaces can be one major element for the replication of metaholograms with higher efficiency (Note S13, Supporting Information). Synthetically, the optimization of the one-step nano-PER printing in many ways enables perfect transfer to any kind of substrate, from soft and flexible films to arbitrary hard surfaces such as PC, PP, and curved glasses (Figure 3e–g), maintaining the designed holographic images (Note S14, Supporting Information).

2.4. Design and Demonstration of a High-Efficiency Hologram

We designed a simple Fraunhofer hologram with the name of our research group, “RHO’s LAB,” as the holographic image to be reconstructed in the far-field (Figure 4a). The Gerchberg–Saxton (GS) algorithm was used to retrieve a high-quality phase-only hologram.[22] The recovered hologram exhibits a pincushion-like distortion due to the property of the Fraunhofer approximation. We compensate for the distortion using barrel distortion and retrieve a phase map of the hologram using the GS algorithm (Figure 4b). We use 200 iterations of the GS algorithm to retrieve a high quality phase-only hologram (Note S15, Supporting Information). As the phase is only dependent on the angle of rotation of the meta-atoms, we discretize the phase into 16 steps in order to limit the noise added to the hologram at this step. We confirm that the phase map is calculated well and 16 steps of discretized phase are enough to recover the hologram by recreating the holographic image from the discretized phase-only hologram (Figure 4c). By modulating the phase with the designed meta-atoms, we experimentally realize a high-efficiency hologram using \(TiO_2\) nano-PER (Figure 4d). In order for metaholograms to be used in general lighting conditions, it is important that the holographic images appear clearly even under ambient lighting. The low efficiency of conventional metaholograms is a limiting factor for achieving this. Furthermore, it is hard to display large holographic images with low efficiency holograms since the intensity of light per unit area decreases as the hologram size increases. The far-field holographic image of our metahologram is clear, vivid, free from twin images, and over 60 cm in size. The high-efficiency means that it is also visible under ambient lighting, proving its validity for practical applications.

High-efficiency holograms have the advantage of being able to demonstrate various steps of brightness. Low-efficiency holograms are unable to achieve this due to the small difference in contrast between the bright and dark shades. To experimentally verify this, we confirm that various steps of brightness are possible by implementing a gradient palette with high-efficiency holograms with different brightness (Figure 4e) and demonstrate that our high efficiency holograms have a much better performance compared to gradient palette holograms with the efficiencies of 70%, 50%, and 30% (Note S16, Supporting Information). A schematic of the experimental setup used to reconstruct the hologram is provided in Note S17 (Supporting Information). A linear polarizer (LP) and a quarter-wave plate (QWP) are used to produce circularly polarized light, which is incident on the sample and is converted to the opposite handedness by the metasurface, generating a holographic image. A standard plastic viewing screen was used to observe the hologram in the far-field.

To determine the efficiency of the \(TiO_2\) nano-PER hologram, we experimentally measured the conversion efficiency. A schematic of the experimental setup and a detailed explanation of the calculating efficiency is provided in Note S18 (Supporting Information). The light diffracts during the propagation through the sample and is focused through the lens. The focused light passes through an analyzer consisting of the quarter-wave plate and linear polarizer. Depending on the rotation of the quarter-wave plate, only the intensity of the converted or zero-order light is measured by the photodetector. The measured conversion efficiency with 532 nm laser is a record 90.6%, with a measured...
Design and experiment of the high-efficiency metahologram. a) Designed holographic image. b) Phase map of the computer-generated Fraunhofer hologram. c) Simulated hologram. d) Captured image of the hologram when illuminated with a 532 nm wavelength laser under ambient lighting conditions. A 2-dollar bill is pictured next to the holographic image for scale. e) Captured image of the gradient palette hologram with conversion efficiency of 96.9%.

Broadband property of the high-efficiency metahologram covering the visible spectrum. a) Holographic images with different visible wavelength inputs. All images are obtained from proposed meta-atom with broadband property. b) Measured (solid line) and simulated (dashed line) data of conversion (blue) and zero-order (orange) efficiency. Firstly, we experimentally verify the broadband properties of TiO$_2$ nano-PER based metahologram by reconstructing high efficiency holograms with lasers of various wavelengths from 450 to 650 nm (Figure 5a). We measure and calculate the conversion efficiencies of each demonstrated holographic image (Figure 5b). We experimentally confirm that the designed broadband metahologram has an average efficiency of 62.4% for nine different wavelengths from 450 to 650 nm. The measured and theoretical efficiencies match and prove the excellent broadband property. Finally, we confirm that our work has both higher theoretical and experimental efficiencies compared to previously reported TiO$_2$ nano-PER metasurfaces and high efficiency metaholograms and metalenses, particularly in the visible regime (Note S19, Supporting Information).

3. Conclusion

In summary, we have demonstrated an almost perfectly noise-free hologram, reaching, to the best of our knowledge, a record high of 96.9% theoretical efficiency and 90.6% experimental efficiency at a wavelength of 532 nm using the mechanically and chemically advanced one-step printing method. We synthesized the TiO$_2$ nano-PER by combining TiO$_2$ NPs with a typical nanoimprint resin to increase its refractive index to allow it to be...
used directly as a meta-atom in metasurfaces that operate in the visible regime. One step further, we practically improved this TiO$_2$ nano-PER printing to the both mechanically and chemically variable process for the uniform fabrication of metasurfaces with critical resolution about 40 nm and high aspect ratio over 8. Using this method, we numerically designed and characterized a metahologram with a conversion efficiency of 96.9% and zero-order efficiency of 0.2% at a wavelength of 532 nm. We experimentally demonstrated the metahologram and measured values of 90.6% conversion efficiency and 7.3% zero-order efficiency, respectively. Due to the extremely high efficiency of the hologram, the designed holographic image was clearly visible even under ambient lighting conditions, proving the applicability of our device in holographic displays and augmented reality devices. Moreover, we reveal the broadband property of TiO$_2$ nano-PER by designing a meta-atom which has an average efficiency of 76.0% from 450 to 650 nm. We confirm that experimentally demonstrated metahologram has an average efficiency of 62.4% for various wavelengths from 450 to 650 nm.

Although the concept of the nano-PER has been introduced before, we prove the high-performance capabilities of nano-PER, showing that they can be comparable or even outperform exiting materials by achieving high efficiency. Moreover, we reveal the broadband property of nano-PER with high efficiency. Finally, we show the feasibility for nano-PER to be applied to various practical applications by transferring nano-PER metasurface to the various curved, flexible, and ultrathin surfaces. Our high-aspect-ratio metasurface made up of TiO$_2$ nano-PER structures was fabricated easily by using both mechanical and chemical methods, as mentioned above. This advanced printing method has additional benefits of high-throughput and low fabrication cost. Specifically, each sample takes around 15 min and costs less than 1.4 USD to realize high-efficiency metahologram (Note S20, Supporting Information). Moreover, we confirm that our method enables the transfer of high-aspect-ratio metasurfaces even to any arbitrary surface. We also note that multifunctional metaholograms could be fabricated by integrating the nano-PER meta-atoms with conventional tuning techniques, thus proving their promise as candidates for holographic display technology, as well as in augmented and virtual reality devices. Over the area limitation of metasurfaces due to the limitation of EBL to fabricate the master mold, we believe this work could lead to new breakthroughs for the commercialization of metaholograms by extending mechanical or chemical modulation of our process to scalable and uniform nanofabrication.

4. Experimental Section

Synthesis of TiO$_2$ Nano-PER: The TiO$_2$ nano-PER was prepared by mixing TiO$_2$ NPs dispersed in MIBK (DT-TIOA-30MIBK (N30), Ditto Technology), monomer (dipentaerythritol penta-/hexa-acrylate, Sigma-Aldrich), photoinitiator (1-hydroxycyclohexyl phenyl ketone, Sigma-Aldrich), and DI water. At first, precleaned substrates were processed by O$_2$ plasma pretreatment of the soft mold and the substrate. Chromium (Cr) layer was deposited using electron beam evaporation (KVT, KVE-ENS4000). The lift-off Cr meta-atoms were used as an etching mask for the Si substrate. Cr patterns were transferred onto the Si substrate using a dry etching process (DMS, silicon/metal hybrid etcher). The remaining Cr etching mask was removed by Cr etchant (CR-7).

Fabrication of the Soft Mold: h-PDMS was prepared by mixing 3.4 g of vinylmethyl copolymers (VDT-731, Gelest), 18 µL of platinum-catalyst (SiP6831.2, Gelest), 0.1 g of the modulator (2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclooctasiloxane, Sigma-Aldrich), 2 g of toluene, and 1 g of siloxane-based silane reducing agent (HMS-301, Gelest). The h-PDMS was spin-coated on the master mold at 1000 rpm for 60 s, then baked at 70 °C for 2 h. A mixture of a 10:1 weight ratio of PDMS (Sylgard 184 A, Dow Corning) and its curing agent (Sylgard 184 B, Dow Corning) was poured on the h-PDMS layer and cured at 80 °C for 2 h. The cured soft mold was detached from the master mold, then used to replicate the nano-PER structure.

Preparation of the Soft Mold and the Substrate: Fluorosurfactant [(tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane] was coated on the h-PDMS soft mold by vaporized coating at 130 °C for 5 min to decrease the surface tension of the soft mold. Various substrates were also treated to increase the surface tension after the cleaning process using acetone, IPA, and DI water. At first, precleaned substrates were processed by O$_2$ plasma (CUTE-1MPR, Femto Science Inc.) at 100 W power and 100 sccm O$_2$ gas flow rate for 5 min. Then, the 60 nm-thick PMMA layer (495 PMMA A2, MicroChem) was spin-coated at 5000 rpm for 1 min on pretreated substrates and subsequently heated at 180 °C for 5 min for the glass substrate and at 70 °C for 60 min for polymeric substrates to fasten the uniform adhesive PMMA layer on the surface of respective substrates.

Optical Measurement: A 532 nm laser (532 nm diode-pumped solid-state lasers, Thorlabs) was incident on a linear polarizer (Ø 1 in. unmounted linear polarizers, Thorlabs), half-wave plate (Ø ½ in. mounted achromatic half-wave plates, Thorlabs), and quarter-wave plate (Ø ½ in. mounted achromatic quarter-wave plates, Thorlabs) to form right circular polarized (RCP) light. A 500 µm diameter pinhole [P500HD – Ø ½ in. (12.7 mm) Mounted Pinhole, Thorlabs] was used to block the unnecessary light. A photodiode power sensor (S120C, Thorlabs) and a compact power and energy meter console (PM100D, Thorlabs) were used to measure the intensity of the light.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.
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high-efficiency metaholograms, metasurface holography, nanoparticle-embedded-resin, one-step nanoprinting, scalable nanomanufacturing