TiO$_2$ metasurfaces: From visible planar photonics to photochemistry

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TiO$_2$ metasurfaces have been intensively studied in the past few years. To date, the TiO$_2$ metadevices only used their high reflective index ($n$). The controllable light extinction coefficient ($k$) of TiO$_2$ has not been exploited yet. Here, we converted TiO$_2$ metasurfaces to black TiO$_2$ metasurfaces and explored their new opportunities in photochemistry. A complementary metal oxide semiconductor (CMOS)–compatible technique has been developed to reversibly and precisely control the absorption of TiO$_2$ metasurfaces without spoiling their internal nanostructures. Consequently, two types of black TiO$_2$ metasurfaces were realized for photochemical experiments. The metasurface with an ultrawide absorption band can substantially enhance the white light absorption and accelerate the solar-based photochemistry process by a factor of 18.7. The other metasurface with an absorption band of <20 nm only responded to the resonant wavelengths, making the photochemistry process capable of being monitored in real time. In addition, the reversible switch between normal and black states makes TiO$_2$ metasurfaces suitable for dynamic metadevices as well.

INTRODUCTION

A CMOS-compatible technique has been developed to switch between TiO$_2$ and black TiO$_2$ without spoiling their internal nanostructures, successfully extending the practical applications of TiO$_2$ metasurfaces from static planar visible photonics to dynamic metadevices and photochemistry. The field of metasurfaces has been one of the important driving forces for the advancement of nanophotonics (1–4). By constructing nanoparticles with subwavelength spaces, the planar metasurface enables many new physics and phenomena, providing a unique capability to fully control the incoming light and realize planar photonic circuits. In the past decade, while various metadevices have been demonstrated with silicon and plasmonic materials, their performances are limited by the material losses in the visible spectrum (1–10). Recently, TiO$_2$ has shown a series of intrinsic advantages for visible metasurfaces. It is transparent in the entire visible spectrum, and its refractive index is high enough to support Mie magnetic (electric) dipole resonances in a single nanoparticle. In 2016, Khorasaninejad et al. experimentally demonstrated the first TiO$_2$ metasurfaces with efficiency above 70% in the entire visible range (11). Soon after, TiO$_2$ metasurface–based holograms, color nanoprinting, and spin orbital conversion were reported by different groups (12–15). Very recently, the chromatism of TiO$_2$ metasurfaces has also been successfully corrected (16–19). To date, the physics of TiO$_2$ metasurfaces are almost complete, and the research attention gradually switches to practical applications. However, despite the above progresses and the recent advances on x-ray photoelectron spectroscopy (20) and optical coherence tomography (21), research on TiO$_2$ metasurfaces is mostly restricted in static photonic devices.

Titanium dioxide can absorb light with energy larger than its bandgap and then generate excited electrons and holes in the conduction and valence bands (22). Such excited charges have the ability of migrating individually to the surfaces of nanoparticles and performing photocatalytic reactions. Consequently, the combination with photocatalysis can be an emerging opportunity for TiO$_2$ metasurfaces. However, there is a barrier between these two research areas. The TiO$_2$ metasurfaces usually work in visible spectrum, whereas TiO$_2$ catalysts absorb ultraviolet (UV) light. While the conversion of TiO$_2$ to black TiO$_2$, pioneered by Chen et al. in 2011 (23), can reduce the bandgap to ~1 eV and increase the absorption in visible to near-infrared regions, the typical conversion techniques are strongly dependent on high pressure/high temperature (23–26), which spoil the internal nanostructures and thus are incompatible with TiO$_2$ metasurfaces.

Here, we develop a CMOS-compatible technique to produce black TiO$_2$ metasurfaces and explore their new opportunities in photochemistry. Basically, the TiO$_2$ film was deposited onto an Indium tin oxide (ITO)–coated glass substrate with the electron-beam (E-beam) evaporation technique (see Materials and Methods). The structural characterizations show that the deposited TiO$_2$ is an amorphous film with surface roughness <2 nm (fig. S1A). Then, the deposited TiO$_2$ film was placed into an inductively coupled plasma (ICP) etcher (Oxford PlasmaPro 100 Cobra) and implanted with H$^+$ ions for 4 min (see schematic picture in Fig. 1A and details in Materials and Methods). After the ion implantation, the color of the TiO$_2$ film changed from transparent to dark brown (see inset in Fig. 1A). The corresponding absorption spectra before and after H$^+$ ion implantation are plotted as solid and dashed lines in Fig. 1B. The absorption is significantly increased over the full visible spectrum, although a dip appeared at 400–480 nm. The corresponding x-ray photoelectron spectroscopy measurements show that Ti$^{4+}$ species and oxygen vacancies are produced during the ion implantation (fig. S2, C and D) (27, 28). All these observations are consistent with previous reports (23–26) and confirm the formation of black TiO$_2$ (fig. S2). The transition process between TiO$_2$ and black TiO$_2$ was reversible. By implanting O$^-$ ions into the black TiO$_2$ film with ICP, the oxygen vacancies were recovered by oxygen ions. Then, both the absorption spectrum (dash-dotted line in Fig. 1B) and the color were restored.

Compared with previous techniques (23–26), the reversible transition process with ICP has several intrinsic advantages. More than the black and white, a series of interstates of the TiO$_2$ film can be
Figure 1. The properties of the black TiO\textsubscript{2} film. (A) Schematic picture for the transition process between conventional TiO\textsubscript{2} and black TiO\textsubscript{2}. The insets show the corresponding microscope images of TiO\textsubscript{2} films. (B) Dashed, solid, and dash-dotted lines are the absorption spectra of TiO\textsubscript{2} film before and after 4-min H\textsuperscript{+} ion implantation and the recovered TiO\textsubscript{2} film. (C) and (D) show the refractive index \( n \) and light extinction coefficient \( k \) as a function of ion implantation time.

generated by controlling the ion implanting time. Figure 1 (C and D) shows the experimentally measured \( n \) and \( k \) as a function of ion implanting conditions. With the increase of implanting time from 0 to 4 min, the refractive index is kept around its initial value (\( n > 2.1 \)), whereas the light extinction coefficient increases from 0 to 0.15 at 800 nm. The high-resolution scanning electron microscope (SEM) images show that the nanostructures of TiO\textsubscript{2} are well preserved during the transition processes (figs. S1 and S3, B and C). In this sense, the preserved refractive index and nanostructure can ensure the designed eigenmode of each TiO\textsubscript{2} nanoblock, whereas the tunable \( k \) value is able to precisely tailor the absorption and intensity of the incident light.

To further confirm adaptability, we fabricated TiO\textsubscript{2} metasurfaces and measured their reflection spectra before and after conversion to exclude the global changes (29) (see Materials and Methods and fig. S3). The TiO\textsubscript{2} metasurfaces were composed of periodic TiO\textsubscript{2} nanoblocks with lattice size \( l \) and side width \( w \) (see Fig. 2A). The cross section of each TiO\textsubscript{2} nanoparticle in the vertical direction was a trapezoid with a thickness of 200 nm and an angle of 72° (see fig. S3). The coupling between the magnetic (electric) dipole resonances and the reflection of the periodic structure can greatly enhance the reflectance and narrow the full width at half maximum (FWHM) (30). One example with \( l = 400 \) nm and \( w = 330 \) nm is illustrated in the bottom panel of Fig. 2B. A resonant peak with reflectance \( \sim 70\% \) and FWHM \( \sim 20 \) nm can be seen at 637 nm. The reflectance at other wavelengths is close to zero. As a result, a distinct red color was obtained under a bright-field microscope (see inset). With the decrease of lattice size, the reflection peak gradually shifted from 637 to 607, 590, 561, 529, 513, and 481 nm in Fig. 2B. The recorded bright-field colors change from red to green and lastly to blue. In our experiment, 15 TiO\textsubscript{2} metasurfaces with different sizes have been investigated (see fig. S7B). Their reflection spectra were recorded and summarized as white dots in a International Commission on Illumination (CIE) 1931 color map, which covered a large area and indicated the potential of the TiO\textsubscript{2} metasurface in color nanoprinting.

Then, the TiO\textsubscript{2} metasurfaces were converted to black TiO\textsubscript{2} metasurfaces via ion implantation. Taking three metasurfaces with red, green, and blue colors as examples, we have carefully studied their performances with the ion implanting time. The experimental results are shown in Fig. 3A. The initial reflectance of three metasurfaces was around 70% at 627 nm, 60% at 550 nm, and 50% at 472 nm. After 1-min H\textsuperscript{+} ion implantation, while the reflection peaks were kept at their original wavelengths, the intensities were greatly reduced to \( \sim 30\% \), and the corresponding structural colors became pale. By increasing the H\textsuperscript{+} ion implantation time to 4 min, the intensities of reflection peaks further reduced to \( < 10\% \), and the structural colors were all dark. To exclude the structural changes, we have converted the black TiO\textsubscript{2} metasurfaces back to TiO\textsubscript{2} metasurfaces...
with 5-min O− ion implantation. As shown in the bottom panel of Fig. 3A, all the reflection peaks and the distinct colors were recovered. Figure 3B summarizes the reflectance of three metasurfaces as a function of transition rounds. No obvious reductions in reflectance were observed even after 20 TiO2–black TiO2–TiO2 transition rounds (fig. S7A). Associated with the SEM images, the reflection spectra confirmed that our ion implantation process did not damage the TiO2 nanostructures. Therefore, the CMOS-compatible technique has the capability of breaking the barrier and extending the applications of TiO2 metasurfaces to photochemistry.

The color erasure with transition to black TiO2 was quite generic. Figure 3C summarizes the recorded colors of 15 metasurfaces before and after H+ ion implantation. We can see that the designed rainbow colors were all erased, and only the dark backgrounds were left (Fig. 3C). The corresponding CIE 1931 map in Fig. 3D shows that all the colors contracted significantly. This kind of post-synthetic control of structural color can produce by-products for TiO2 metasurfaces. Figure 3E shows the top-view SEM image of the metasurface. Two types of TiO2 metasurfaces with \( l = 300 \) nm and \( l = 290 \) nm were selected to construct the information and background, respectively. When the metasurface was illuminated with a white light source, a yellow “color” appeared in a green background (Fig. 3F). Once the metasurface was implanted with H+ ions for 4 min, all the distinct colors disappeared, and the encoded information was fully concealed in Fig. 3G. Owing to the similar structural sizes between the information and background, the encoded information was even hard to resolve in the SEM image without the guiding lines (fig. S8), making the optical encryption more difficult to crack. The optical encryption process has also been concealed and recovered for many rounds, like their plasmonic counterparts (31, 32). This technique has a series of intrinsic advantages for optical encryption.

The brightness can be precisely controlled at will. It is independent of the cumbersome external instruments and compatible to modern CMOS technology, which are key factors for commercial applications.

Figure 2. The conventional TiO2 metasurfaces. (A) Top-view SEM images of TiO2 metasurfaces. Scale bars, 200 nm. The insets show the corresponding structural colors under a bright-field microscope. (B) Measured (solid lines) and numerically calculated (dashed lines) reflection spectra. From bottom to top, the lattice size decreases from 400 to 380, 370, 350, 330, 320, and 300 nm. The gap is kept at \( w = 70 \) nm. The insets are the recorded (left) and calculated (right) structural colors. (C) Corresponding structural colors of 15 metasurfaces in the CIE 1931 map.

We then demonstrated the influences of the black TiO2 metasurface on photochemistry by immersing the black TiO2 metasurface in AgNO3 solution (0.25 M) and illuminating it with a white light lamp.
(0.1 mJ/cm²), the UV light has been filtered out (fig. S9). Here, the immersing time was fixed at 60 s, and the illuminating time changed from 0 to 60 s. The morphological changes of black TiO₂ metasurfaces were characterized by SEM. Additional particles appeared after immersing the metasurface in AgNO₃ solution. With the increase of illumination time, the sizes of the nanoparticles also increased (Fig. 4D). The corresponding transmission electron microscope measurements confirmed that these new generated nanoparticles were Ag nanoparticles (fig. S10C). By measuring all the particles in a 6-μm² area on the metasurface, the mean sizes of Ag particles have been statistically analyzed and plotted in Fig. 4E. With the increase of illumination time from 0 to 20, 40, and 60 s, the mean sizes of Ag nanoparticles increased linearly from 0.09 to 0.53, 0.78, and 1.12 μm (see fig. S11A and examples in fig. S10). The nanoparticle with 0-s illumination is caused by the spontaneous reduction that relates to oxygen vacancies at the surfaces (37).

To confirm the effects of the black TiO₂ metasurface, two control experiments with a regular TiO₂ metasurface and a black TiO₂ film have also been performed under the same conditions. By immersing the regular TiO₂ metasurface into AgNO₃ solution and illuminating with white light, the displayed colors were well kept, and no additional nanoparticles have been generated (fig. S10D). The black TiO₂ film indeed produced some additional Ag nanoparticles. However, the particle sizes were much smaller than the ones on black TiO₂ metasurfaces (fig. S10F). The two control experiments have also been plotted as a triangle line and a dot line in Fig. 4E. We can see that the speed of photoreduction on the black TiO₂ metasurface was ~18.7 times faster than the value on the black TiO₂ film. Then, we confirmed that the black TiO₂ metasurfaces can improve the photochemical processes and are more suitable for weak light–based photochemistry.

In addition to increasing the reaction speed of weak-light reactions, some photochemical experiments require real-time monitoring to precisely understand the internal process, e.g., Raman spectrum and nonlinear optical measurements. For such applications, it is essential to avoid the influences of probe light or lasers. The black TiO₂ metasurfaces can perfectly solve this problem. According to Fig. 1D, the absorption of black TiO₂ is dependent on the ion implantation time. If TiO₂ is implanted with H⁺ ions for a very short time, the increased absorption in the visible spectrum is negligibly...
small. However, once the TiO$_2$ film is patterned to the metasurface, the resonance of the metasurface can greatly enhance the absorption around the reflection peak and thus form a narrow absorption band. One example is shown in Fig. 5. A metasurface with lattice size $l = 400$ nm produced a narrow-band reflection at 630 nm (see the solid line in Fig. 5A). Then, the TiO$_2$ metasurface was implanted with H$^+$ ions for a minute. In contrast to the small change of absorption in TiO$_2$ film, the reflection peak significantly decreased from 50 to 30%, and an obvious absorption peak emerged (see Fig. 5A and fig. S9C).

The slight increase in absorption and the resonant enhancement of incident light (solid line in Fig. 5B) makes the light-implanted TiO$_2$ metasurface essential for wavelength-dependent photochemistry. To test this application, we have immersed the black TiO$_2$ metasurface into AgNO$_3$ solution and illuminated it with a tunable laser (see Materials and Methods). Here, the pumping density and time were kept at 10 $\mu$J/cm$^2$ and 90 s, respectively. The laser wavelengths scanned from 700 to 600 nm. From the corresponding SEM images (fig. S11, B to I), the sizes of Ag nanoparticles have been analyzed and plotted as a function of incident laser wavelength in Fig. 5B. The photochemical reaction was fastest at 640 nm. The sizes of Ag nanoparticles decreased rapidly when the incident wavelength deviated from the resonant peak, giving an FWHM of around 20 nm. Both the peak position and the FWHM matched the retrieved enhancement factor in solution very well. We thus can confirm the importance of the TiO$_2$ metasurface in wavelength-dependent chemical reactions and chemical processes requiring real-time measurement.

In summary, we have developed a CMOS-compatible technique that can gently and reversibly convert TiO$_2$ metasurfaces to black TiO$_2$ metasurfaces without spoiling their internal nanostructures. Consequently, we expanded the practical applications of TiO$_2$ metasurface from planar visible photonics to photochemistry. By controlling the conversion time, TiO$_2$ metasurfaces can either accelerate the chemical reaction speed or selectively respond to designed wavelengths. In addition, by-products of active metadevices have also been demonstrated. The research on black TiO$_2$ metasurfaces shall open new routes to novel photonic devices and even beyond photonics.
MATERIALS AND METHODS

Numerical simulation

The reflection spectra and corresponding field distributions were numerically calculated with a commercial finite element analysis software (COMSOL Multiphysics). In our numerical calculations, the whole structure was composed of TiO$_2$ and settled on top of a 15-nm ITO-coated glass. The optical constant of TiO$_2$ was determined from spectroscopic ellipsometry measurements. The dielectric constant of ITO was taken from (19). The glass substrate was considered as lossless with a refractive index of $n_{\text{sub}} = 1.52$. To mimic the infinite large periodic sample, a periodic boundary condition was applied.

Fabrication of the TiO$_2$ metasurface

The TiO$_2$ metasurfaces were fabricated with E-beam lithography, followed by a lift-off process. The ITO glass substrates were cleaned in ultrasound bath in acetone, isopropyl alcohol, and deionized (DI) water for 15 min, respectively, and dried under clean nitrogen flow. Then, 350 nm of ZEP520 film was spin-coated onto the ITO glass substrates and baked at 180°C for 10 min. Afterward, the designed nanostructures were patterned with an electron beam in an E-beam writer (Raith eLINE, 30 kV) and developed in ND510 solution and methyl isobutyl ketone at 0°C for 60 and 10 s, respectively. The samples were transferred into an E-beam evaporator and directionally coated with 200-nm TiO$_2$ films (deposition rate, 0.8 Å/s; base vacuum pressure, $2 \times 10^{-7}$ torr). After immersing the samples in acetone for 8 hours, the ZEP patterns were removed and the designed TiO$_2$ metasurfaces were obtained.

Transition between TiO$_2$ and black TiO$_2$

The TiO$_2$ metasurfaces were transferred to black TiO$_2$ metasurfaces in an ICP (Oxford Instruments Plasma Technology 380) treatment system. The chamber was pumped to reach a degree of vacuum of around $10^{-9}$ torr. Then, the metasurfaces were implanted with H$^+$ plasma with a flow rate of 50 standard cubic centimeters per minute. Meanwhile, the chamber pressure was stabilized at 15 mtorr, and the temperature of the platform was maintained at 70°C. The ICP power was 700 W, and the radio frequency (RF) power was 10 W. Under the same conditions, the black TiO$_2$ can be oxidized back to TiO$_2$ by using O$^-$ plasma.

Optical characterization

The sample was placed onto a three-dimensional translation stage under an optical microscope (ZEISS, Axioscope AI). Basically, a collimated white light beam was focused onto a sample by an objective lens (numerical aperture = 0.4). The reflected light (R) was collected and collimated by the same objective lens and coupled to a charge-coupled device (CCD) coupled spectrometer (Acton Research 2750, Princeton Instruments CCD). The transmitted light was collected by another optical lens and coupled to the same spectrometer. The experimental setup of optical characterization is shown in fig. S6A, and the specific method to achieve absorption curve is shown in fig. S6B. The bright-field microscopy images were taken with a Canon EOS 100D camera under the optical microscope.

Photoreduction of Ag nanoparticles

Silver nitrate was prepared as a 0.25 M solution as a silver ion source. First, the sample was immersed in AgNO$_3$ solutions and illuminated with white light or a single-wavelength laser. After illumination, the sample was rinsed with deionized water and then blow-dried with a nitrogen gun. Then, the sizes of the Ag nanoparticles generated on the surface of TiO$_2$ metasurfaces or films were characterized by SEM. The details and experimental setup are shown in the Supplementary Materials (fig. S9).
Section S4. Characterization of TiO$_2$ metasurfaces

Fig. S4. The numerical simulation of Mie resonance.

Fig. S9. Setup for photoreduction and the characterization of the TiO$_2$ metasurface in AgNO$_3$ solution.

Fig. S8. The SEM image of "COLOR" pattern without guide lines.

Fig. S3. Numerical calculation and the Mie resonances in TiO$_2$ metasurfaces.

Fig. S2. Fabrication process and characterization of the nanostructures.

Fig. S1. The deposition and transition of TiO$_2$ film.