

# Wafer-scale epitaxy of TiN nanoarrays on fluorophlogopites for flexible, refractory, and multifunctional plasmonic metamaterials

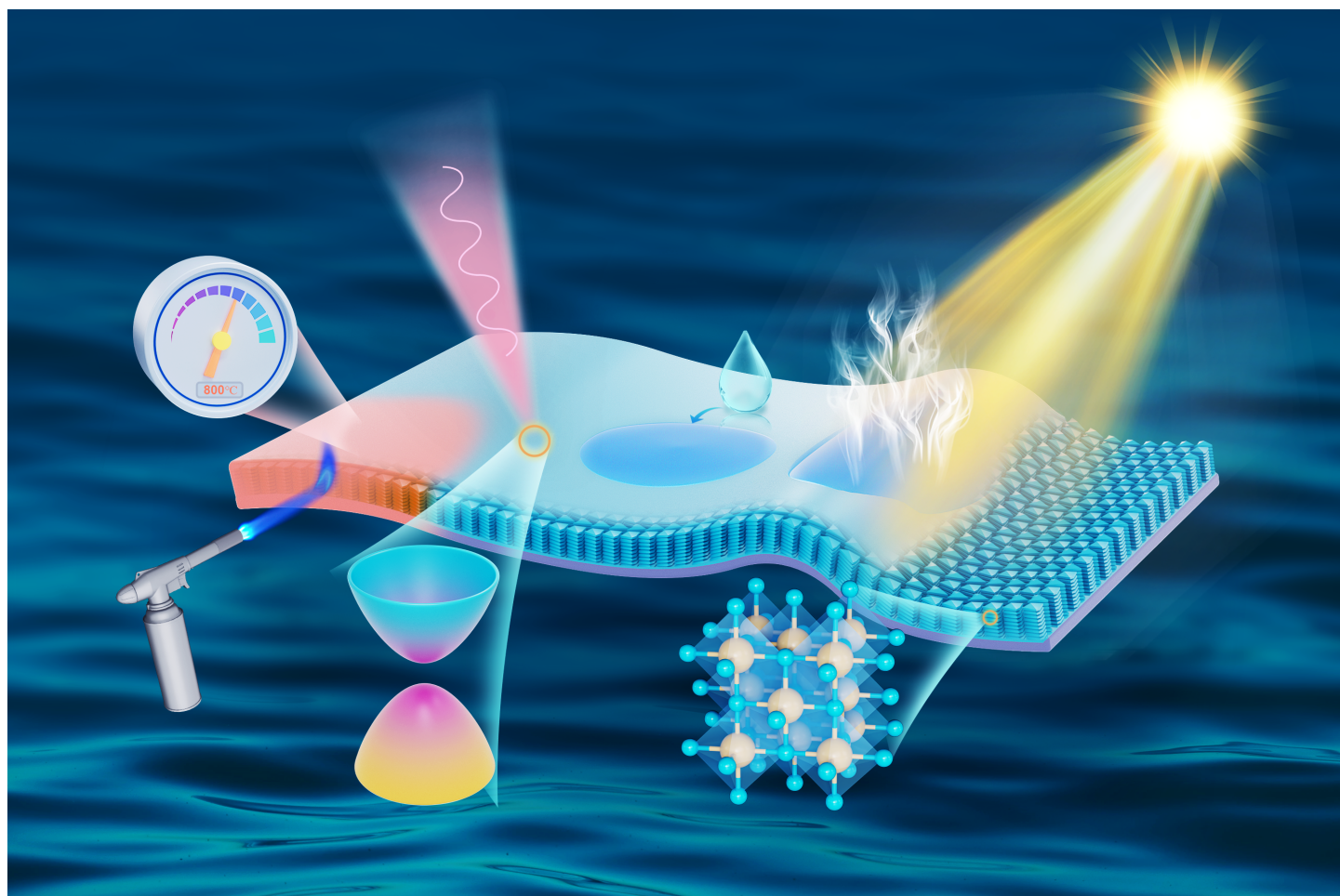
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## GRAPHICAL ABSTRACT



## PUBLIC SUMMARY

- To overcome challenge of fabricating flexible and single-crystalline plasmonic nanostructure arrays (PNAs).
- A wafer-scale route by epitaxy of TiN nanoarrays on fluorophlogopites was demonstrated.
- Flexible TiN nanoarrays show plasmonic hyperbolic dispersion, superhydrophilicity, and solar steam generation.
- The excellent thermal stability of flexible TiN nanoarrays far surpasses that of ordinary flexible PNAs.

# Wafer-scale epitaxy of TiN nanoarrays on fluorophlogopites for flexible, refractory, and multifunctional plasmonic metamaterials

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Developing strategies for flexible, single-crystalline, but refractory plasmonic nanostructure arrays (PNAs) is important for flexible, high-performance, and reliable plasmonic metamaterials, which have broad applications in refractory plasmonics, nanophotonics, sensors, and photothermal conversion. However, the scalable fabrication of flexible, single-crystalline, but refractory PNAs is extremely challenging due to the incompatibilities of synthesis temperatures, crystal structures, and thermal expansion coefficient between typical plasmonic materials and conventional flexible organic substrates. Here, an easy and scalable route to the flexible single-crystalline PNAs is demonstrated by self-assembled growth of TiN nanopillar arrays on flexible van der Waals fluorophlogopite mica substrates using a reactive magnetron sputtering epitaxy system. Remarkably, the wafer scale flexible TiN nanopillar arrays exhibit several intriguing properties, including tunable plasmonic hyperbolic dispersions, superhydrophilicity, strong light absorption, and efficient solar steam generation. Moreover, these flexible TiN nanoarrays demonstrate excellent thermal stability at 800°C, far exceeding the operating temperature (below ~ 200°C) of current flexible noble-metal PNAs on organic substrates. This work offers an easy and scalable approach for fabricating flexible, wafer-scale, single-crystalline, but refractory PNAs with versatile and tunable properties, which can significantly expand the applications of flexible PNAs in flexible electronics, nanophotonic, and photothermal devices.

## INTRODUCTION

Recently, plasmonic metamaterials consisting of metallic nanostructure arrays (e.g., nanorod, nanoparticle, and nanopillar arrays) have attracted significant research interests due to their great capability to confine light in a subwavelength manner. These excellent properties of plasmonic metamaterials enable strong light-electron-matter interactions for a wide range of important applications, including subwavelength imaging, nonlinear optics, biochemical sensing, surface-enhanced Raman spectroscopy, perfect light absorption, solar steam generation, and photochemistry.<sup>1–8</sup> Therefore, extensive efforts have been devoted to the design, fabrication, and processing of plasmonic nanostructure arrays (PNAs), which are mainly fabricated on planar and rigid substrates.<sup>1–6</sup> Meanwhile, the continuous pursuit of smart, lightweight, and wearable devices has aroused great interests in flexible PNAs, which offer unique advantages such as mechano-photon coupling and geometric degrees of freedom.<sup>9–13</sup> However, there remain many technical obstacles for the large-scale and low-cost fabrication of flexible PNAs, especially in a single-crystalline way.

So far, the PNAs have been fabricated by either top-down or bottom-up techniques.<sup>1,4,14–15</sup> Though top-down techniques (e.g., photolithography, electron-beam lithography, focused ion-beam, etc.) can fabricate accurate, well-defined, and reproducible PNAs, the disadvantages including complexity, high-cost, and low throughput have limited their suitability for the wide application of PNAs.<sup>2–4</sup> On the other hand, the bottom-up techniques, which mainly exploit various microscopic forces (e.g., van der Waals force, electrostatic force, capillary force, hydrogen bonding force, etc.) to realize self-assembled growth of PNAs, have attracted intensive research attentions lately due to the obvious advantage of large-scale and low-cost.<sup>2–4,15</sup> To make the PNAs flexible, various fabrication strategies combining the top-down and bottom-up techniques have been developed recently.<sup>4,12–13,16</sup> For example, the flexible

PNAs can be fabricated by transferring the PNAs prepared by various top-down techniques onto flexible organic substrates, such as polyvinyl alcohol (PVA), Polymethyl Methacrylate (PMMA), polyethylene terephthalate (PET), and polydimethylsiloxane (PDMS), after selectively etching a sacrificial layer.<sup>12–13</sup> Flexible PNAs can also be fabricated using the bottom-up techniques by direct self-assembly of nanostructure arrays on the flexible organic substrates.<sup>13</sup> Recently, single-crystalline PNAs have also attracted considerable interests due to their high crystalline quality, low defect density, low optical loss, and high reliability.<sup>2</sup> Despite the wide applications of flexible organic substrates, the incompatibilities of synthesis temperatures, crystal structures, and thermal expansion coefficient between flexible organic substrates and typical plasmonic materials, such as noble metals (e.g., Au, Ag), transition metal nitrides (e.g., TiN, NbN, ZrN, HfN), transparent conducting oxides (e.g., ITO, AZO), make it extremely challenging to directly fabricate single-crystalline PNAs on these flexible organic substrates.<sup>12,16</sup> Moreover, organic substrates are extremely vulnerable to high temperature and intensive light illumination, which limits conventional flexible PNAs in many applications such as nonlinear optics, solar/thermophotovoltaics, and solar steam generations.<sup>11–13,17</sup> Therefore, a scalable and low-cost method for fabricating flexible, single-crystalline, but refractory PNAs is still lacking, which could greatly enhance their potential applications in flexible electronics and nanophotonics.

Here, an easy and large-scale method of fabricating flexible, single-crystalline, but refractory PNAs using a self-assembled way has been developed. Epitaxial titanium nitride (TiN) nanopillar arrays have been successfully grown on a 5 nm-thick single-crystalline TiN seed layer atop wafer-scale (2 in.) van der Waals fluorophlogopite mica (F-mica) using an RF magnetron sputtering system. By mechanically exfoliating the F-mica substrate, the TiN nanopillar arrays exhibit highly stability under repeated bending. The lateral sizes (height) of TiN nanopillars are on the order of tens of nanometers (hundreds of nanometers), and their microstructures, stoichiometry, and resulting optical properties can be tuned by deposition parameters. Remarkably, these flexible TiN nanopillar arrays present many intriguing properties, including superhydrophilicity, plasmonic hyperbolic dispersions, light absorption, and solar steam generation. Thanks to the refractory nature of the TiN and F-mica, these nanopillar arrays demonstrate exceptional thermal stability at 800 °C, make them promising for many refractory plasmonic applications. This work offers an easy and scalable route to the wafer-scale, flexible, single-crystalline, but refractory PNAs with superhydrophilicity, plasmonic hyperbolic dispersions, light absorption, and solar steam generation, which can be widely applied in flexible electronics, nanophotonics, and photothermal devices.

## MATERIALS AND METHODS

### Materials

High-purity (99.999%) titanium targets (2 in.) and fluorophlogopite-mica substrates (10×10 mm) and wafers (2 in.) were purchased from Shanghai Fenglin Co., Ltd. and Changchun Taiyuan Fluorophlogopite Co., Ltd., respectively.

### Preparation of flexible TiN nanopillar arrays

Nanostructured TiN films were fabricated on fluorophlogopite-mica (F-mica) by reactively sputtering the high-purity Ti target in high-purity N<sub>2</sub> or mixed Ar/N<sub>2</sub> atmospheres using a homemade RF magnetron sputtering epitaxy system. The target-substrate distance was kept at about 10 cm

during deposition. Prior to the growth of single-crystalline TiN nanopillars at 500°C, 5 nm thick epitaxial TiN seed layers were deposited on F-mica substrates and wafers in a pure N<sub>2</sub> atmosphere at 1000°C. The deposition pressure for the TiN seed layer was kept at 20 mTorr with growth time of about 10 min. Samples grown under 20 mTorr pure N<sub>2</sub> atmosphere, 20 mTorr mixed Ar/N<sub>2</sub> (with a mass flow ratio of 19:1) atmosphere, and 5 mTorr mixed Ar/N<sub>2</sub> (with mass flow ratio of 19:1) atmosphere were labeled as NA1, NA2, and NA3, respectively. As a comparison, the sample directly grown on F-mica substrates under 5 mTorr mixed Ar/N<sub>2</sub> (with mass flow ratio of 19:1) atmospheres at 500°C without the 5 nm thick epitaxial TiN seed layers was named as NA4. The power applied to the sputtering gun was kept at 100W regardless of the growth of 5 nm thick epitaxial TiN seed layers or TiN nanopillar arrays. The growth times of TiN nanopillar arrays were kept at about 2 hours. All samples follow the same cooling rate of 50 °C/min under the same atmospheres after deposition as used for the deposition of TiN nanopillar arrays. Subsequently, the F-mica substrates supporting the TiN nanopillar arrays were thinned to ~ 5 µm for bending stability tests up to 1000 cycles.

### Characterizations

The crystal structures of all films were characterized by  $2\theta$ - $\omega$  scans,  $\varphi$  scans, and reciprocal space mappings (RSMs) performed on a high-resolution X-ray diffractometer (HRXRD, Bruker D8 Discovery) with a wavelength of 1.5406 Å. The surface morphology and cross-sectional microstructure of all films were examined by scanning electron microscopy (SEM, Hitachi Regulus 8230). To evaluate bending stability, the thinned TiN nanopillar arrays were mounted on a displacement actuator using a stepper motor. Thermal stability was assessed by annealing the TiN nanopillar arrays at 800°C for 4h under vacuum. The optical properties of all films were characterized by a spectroscopic ellipsometer (SE, J. A. Woollam M-2000DI) with variable angle (45°, 55°, and 65°) covering wavelengths from 300 to 1700 nm. A uniaxial anisotropy model incorporating Drude-Lorentz oscillators was employed to extract the dielectric constants and s-/p-polarized reflectivities of all films by fitting the SE  $\Psi$  and  $\Delta$  data based on the effective medium approximation. Experimental s- and p-polarized reflectivities were measured at incidence angles 45°, 55°, and 65° to compare with the fitted polarized reflectivities. The absorption and transmittances of all films were measured by the ultraviolet-visible-near infrared (UV-vis-NIR) spectrometer (Lambda 1050) at room temperature. The surface wettabilities of all films were evaluated by static water contact angle (WCA) measurements using a contact angle goniometer (Dataphysics OCA 20, Germany) equipped with a high-speed CCD camera. A deionized water droplet (~0.5 µL) was gently dropped onto the surface of all samples under ambient conditions. A custom-built solar steam generation platform was used to evaluate the photothermal performance of the samples. All films with an area of 1 cm<sup>2</sup> were placed on a piece of sponge with a recessed groove matching the sample dimensions to ensure stable support and reduce heat transfer to the underlying surface. The solar steam generation measurements under simulated solar illumination (one sun, 100 mW/cm<sup>2</sup>) were carried out with a Xenon lamp (PLS-FX300HU, Beijing Perfectlight) equipped with an AM 1.5G filter. Before illumination, approximately 10 µL of deionized water was gently dropped onto the surface of the sample using a calibrated micropipette. Water mass loss was measured by a high-precision analytical balance (PX224ZH, OHAUS, accuracy: 0.0001 g) under ambient conditions.

### FDTD simulation

The optical response of the structure was numerically investigated using the finite-difference time-domain (FDTD) method. Periodic boundary conditions in the in-plane (x and y) directions were applied to the 3D simulation domain to model a periodic array. Perfectly matched layers (PMLs) were applied along the out-of-plane (z) direction to absorb outgoing waves and avoid non-physical reflections. The light source was set as a plane wave incident in the z-direction, covering the wavelength range from 300 nm to 1000 nm. The optical constants used for the TiN nanopillars were derived from ellipsometric fitting of an oxidized TiN film, which are presented in Figure S1 of the Supplementary Information. The optical constants of an oxidized TiN film rather than that of pristine TiN film were adopted due to high specific surface area of TiN nanopillars and noticeable oxidation through nanogaps.

Then, a mesh size of 0.2 nm was employed for the simulations. To evaluate the optical performance of the structure, frequency-domain power monitors were employed to record the transmitted and reflected light intensities. Specifically, a monitor was placed directly below the TiN nanopillar array film to collect the transmitted power and calculate the transmittance ( $T$ ), while another monitor was positioned above the incident plane wave source to capture the reflected power and determine the reflectance ( $R$ ). The absorption ( $A$ ) was then calculated as  $A = 1 - T - R$ .

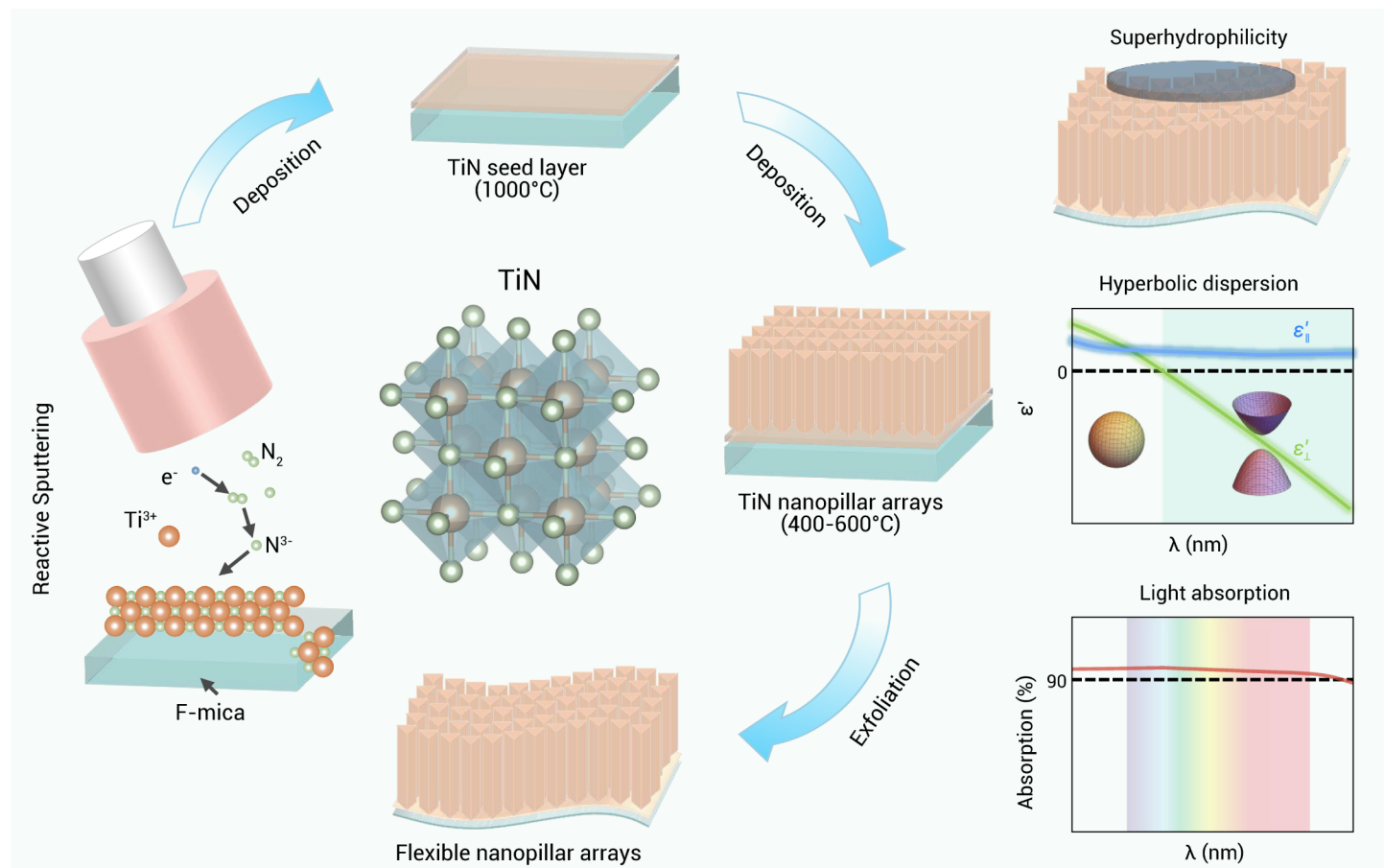
## RESULTS AND DISCUSSION

### Preparation and structural characterizations of flexible TiN nanopillar arrays

Figure 1 illustrates the fabrication process for the flexible single-crystalline TiN nanopillar arrays by sputtering high-purity (99.999%) Ti target in a nitrogen atmosphere using a home-made magnetron sputtering system. As a representative plasmonic TMN, the rocksalt-structured TiN was selected due to its superior properties including remarkable chemical/thermal/mechanical stabilities, high compatibility with standard CMOS technology, and excellent plasmonic performance comparable with noble metals (e.g. Ag, Ag).<sup>17-25</sup> F-mica [KMg<sub>3</sub>Al(Si<sub>3</sub>O<sub>10</sub>)F<sub>2</sub>] was chosen as the substrate due to its two-dimensional crystal structure with quasi-hexagonal sublattices and high thermal stability (up to 1000°C), which support epitaxial growth of many oxide (e.g., SrTiO<sub>3</sub>, CoFe<sub>2</sub>O<sub>4</sub>) and nitride (e.g., TiN, ScN) films and allows mechanical exfoliation for flexible applications.<sup>23,26-31</sup> It is noted that we employ a two-stage method for growth of the single-crystalline TiN nanopillar arrays. At growth stage I, a thin (about 5nm-thick) epitaxial TiN layer was directly deposited on the F-mica substrates in a pure (99.999%) N<sub>2</sub> atmosphere at 1000°C, providing a single-crystalline seed layer for the growth of epitaxial TiN nanopillar arrays. At growth stage II, a low temperature (400-600°C) was employed to limit the diffusion rate of adatoms, enabling the growth of single-crystalline TiN nanopillar arrays. Finally, the F-mica substrates were mechanically exfoliated to less than 5 µm, rendering the TiN nanopillar arrays highly bendable for flexible applications. The resulting flexible TiN nanopillar arrays exhibit several notable properties, including highly tunable plasmonic hyperbolic dispersion, superior mechanical and thermal stability, superhydrophilicity, and light absorption. These features make them a versatile platform for various important applications, such as flexible plasmonic devices with strong optical anisotropy, and solar steam generation.

The crystal structures of TiN/F-mica nanopillar arrays are shown in Figure 2. F-mica is a synthetic two-dimensional van der Waals layered material with lattice parameters  $a = 5.31$  Å,  $b = 9.18$  Å,  $c = 10.14$  Å,  $\alpha = 90^\circ$ ,  $\beta = 100.07^\circ$ ,  $\gamma = 90^\circ$ .<sup>32</sup> Rocksalt TiN holds lattice parameters of  $a = 4.24$  Å. As seen in Figure 2A, the single-crystalline TiN seed layer and nanopillar arrays can be grown on F-mica substrates by following the epitaxial relationship expressed as, TiN[11-2]||F-mica[100] and TiN[1-10]||F-mica[010] for the in-plane directions and TiN(111)||F-mica(001) for the out-of-plane direction. Figure 2B shows the detailed  $2\theta$ - $\omega$  scans around F-mica (004) and (005) diffractions for the nanostructured TiN films with different growth conditions. Samples NA1, NA2, and NA3 employed the two-stage growth method (stage I and II), whereas sample NA4 was grown using only stage II without a 5 nm-thick epitaxial TiN seed layer. All samples used a mixed Ar/N<sub>2</sub> (gas flow ratio of 19:1) atmosphere except for the NA1 sample with a pure N<sub>2</sub> atmosphere used during the growth stage II. In the growth stage II, the pressures were kept at 20 mTorr for the samples NA1 and NA2 and 5 mTorr for the samples NA3 and NA4. The TiN seed layer and nanopillar arrays are (111)-oriented in the samples NA1, NA2, and NA3 without any secondary phases (as shown by the wide range  $2\theta$ - $\omega$  scans in Figure S2 of the Supplemental Information). In a sharp comparison, the NA4 samples have non-epitaxial TiN (002) diffraction apart from the TiN (111) diffraction. The substrate temperature of 500°C used for the direct growth of TiN nanoarrays on F-mica in NA4 samples can't offer enough diffusion energy for the adatoms to avoid non-epitaxial crystallization, resulting in a TiN (002) diffraction. However, the epitaxial growth of TiN nanopillars on the TiN seed layer requires much lower substrate temperature (e.g., 500°C) due to homoepitaxy without mismatch of lattice parameters and crystal symmetries. Therefore, the TiN seed layers are indispensable for the low-temperature growth of TiN nanopillar arrays on the F-mica substrates. It is noted that we employ a mixed Ar/N<sub>2</sub> atmosphere (gas flow





**Figure 1. Schematic process of synthesizing flexible single-crystalline TiN nanopillar arrays with multifunctionalities including superhydrophilicity, plasmonic hyperbolic dispersion, and light absorption.**

ratio of 19:1) to grow nanopillar arrays for most of our samples (e.g. NA2, NA3, NA4) rather than the pure  $N_2$  used for the growth of TiN seed layer and sample NA4. The reason is that titanium nitrides tend to be nitrogen-rich (i.e.  $TiN_{1+\delta}$ ,  $0 < \delta < 0.3$ ) at low growth temperature,<sup>33</sup> which can be counterbalanced by using a mixed  $Ar/N_2$  (gas flow ratio of 19:1) atmosphere. As seen, the  $TiN(111)$  diffraction angle of  $37.1^\circ$  for the sample NA1 is higher than  $36.8^\circ$  of sample NA2 and  $36.9^\circ$  of samples NA3 and NA4, indicating the shrinkage of lattice parameters of nitrogen-rich titanium nitride, as also reported in a previous study.<sup>34</sup> Much higher intensities of  $TiN(111)$  diffractions for samples NA1 and NA2 compared to those of NA3 and NA4 samples suggest that 20 mTorr deposition pressure favors higher crystalline qualities than 5 mTorr deposition pressure. Figure 2C is the photo image of a 2 in. sample of NA3 with black color due to strong light absorption behavior in visible light range in a sharp comparison to the golden color demonstrated by the TiN films without any nanostructures. It is worth noting that the wafer-scale growth capability of flexible TiN nanopillar arrays using a complementary metal-oxide-semiconductor (CMOS) compatible technology of magnetron sputtering is crucial for their wide applications. The  $\varphi$  scans of sample NA3 performed around the F-mica (202) and  $TiN(111)$  diffractions in Figure S3 of the Supplemental information confirm the epitaxial relationship as revealed in Figure 2A. 6-fold symmetry rather than 3-fold symmetry for the  $TiN(002)$  diffractions indicates twin domains of TiN, which are also widely reported in other oxide and nitride films grown on F-mica.<sup>24,29,35-36</sup> The reciprocal space mappings (RSMs) performed around the F-mica (-207) diffractions of samples NA1, NA2, and NA3 are presented in Figures 2D-F. The intensities of TiN (113) diffractions follow the order  $NA2 > NA1 > NA3$ , in good agreement with the observations from the detailed  $2\theta-\omega$  scans in Figure 2B. According to these RSM data, the out-of-plane lattice spacings  $d_{111}$  (in-plane lattice spacings  $d_{11-2}$ ) are 2.42, 2.44 Å, and 2.43 Å (1.72, 1.73 Å and 1.73 Å) for samples NA1, NA2 and NA3, respectively. As seen, the sample NA1 exhibits significantly smaller lattice parameters than samples NA2 and NA3, further

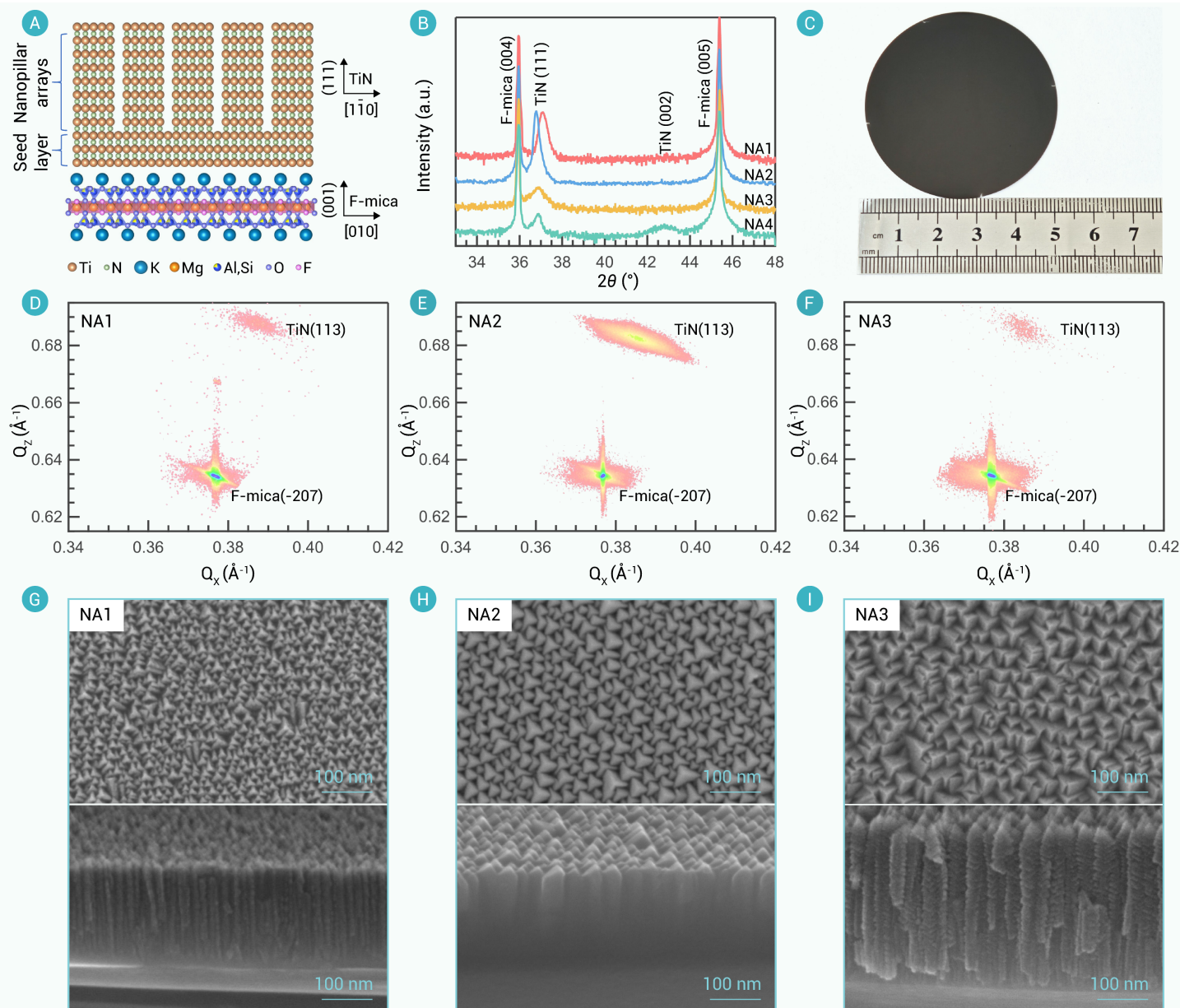
suggesting that titanium nitrides deposited under pure  $N_2$  at low temperature are nitrogen-rich.<sup>34</sup>

Figures 2G-I are the top-view and cross-sectional-view SEM images of the samples NA1, NA2, and NA3. All three samples show triangular pyramids atop densely-packed nanopillar arrays. Both the deposition atmospheres and pressure during growth stage II strongly influence the microstructures of TiN nanopillar arrays. Sample NA1 deposited under 20 mTorr pure  $N_2$  atmosphere and sample NA2 deposited under a 20 mTorr mixed  $Ar/N_2$  atmosphere have average lateral sizes (heights) of nanopillar arrays of  $\sim 17$  nm ( $\sim 198$  nm) and  $\sim 25$  nm ( $\sim 199$  nm), respectively, suggesting that mixed  $Ar/N_2$  atmosphere can facilitate the lateral growth of TiN nanopillar arrays. Compared to the smooth sidewalls of sample NA2, sample NA3 deposited under a 5 mTorr mixed  $Ar/N_2$  atmosphere exhibits hierarchical structures with rough sidewalls composed of smaller nanostructures. The hierarchical structures resemble pine trees with height of  $\sim 320$  nm, averaged lateral sizes of  $\sim 38$  nm, and countless branches of nanometer scale along the sidewalls. It is noted that NA3 samples with two different nanopillar height (i.e.  $\sim 320$  and  $\sim 640$  nm) have been prepared for the measurements of light absorption. It is apparent that lower deposition pressure of 5 mTorr compared to 20 mTorr can induce more hierarchical structures to the TiN nanopillar arrays due to a faster deposition rate. These hierarchical structures also lower the crystalline qualities as demonstrated in Figure 2B. The tunable microstructures of TiN nanopillar arrays achieved through deposition parameters provide high flexibility in tailoring their properties, which will be further addressed later.

#### Plasmonic hyperbolic dispersion and extreme optical anisotropy

The plasmonic hyperbolic dispersion and extreme optical anisotropy of TiN nanopillar arrays were characterized by a variable-angle spectroscopic ellipsometer (VASE) as demonstrated in Figure 3. The plasmonic hyperbolic dispersions manifest as opposite signs of dielectric constants along direc-

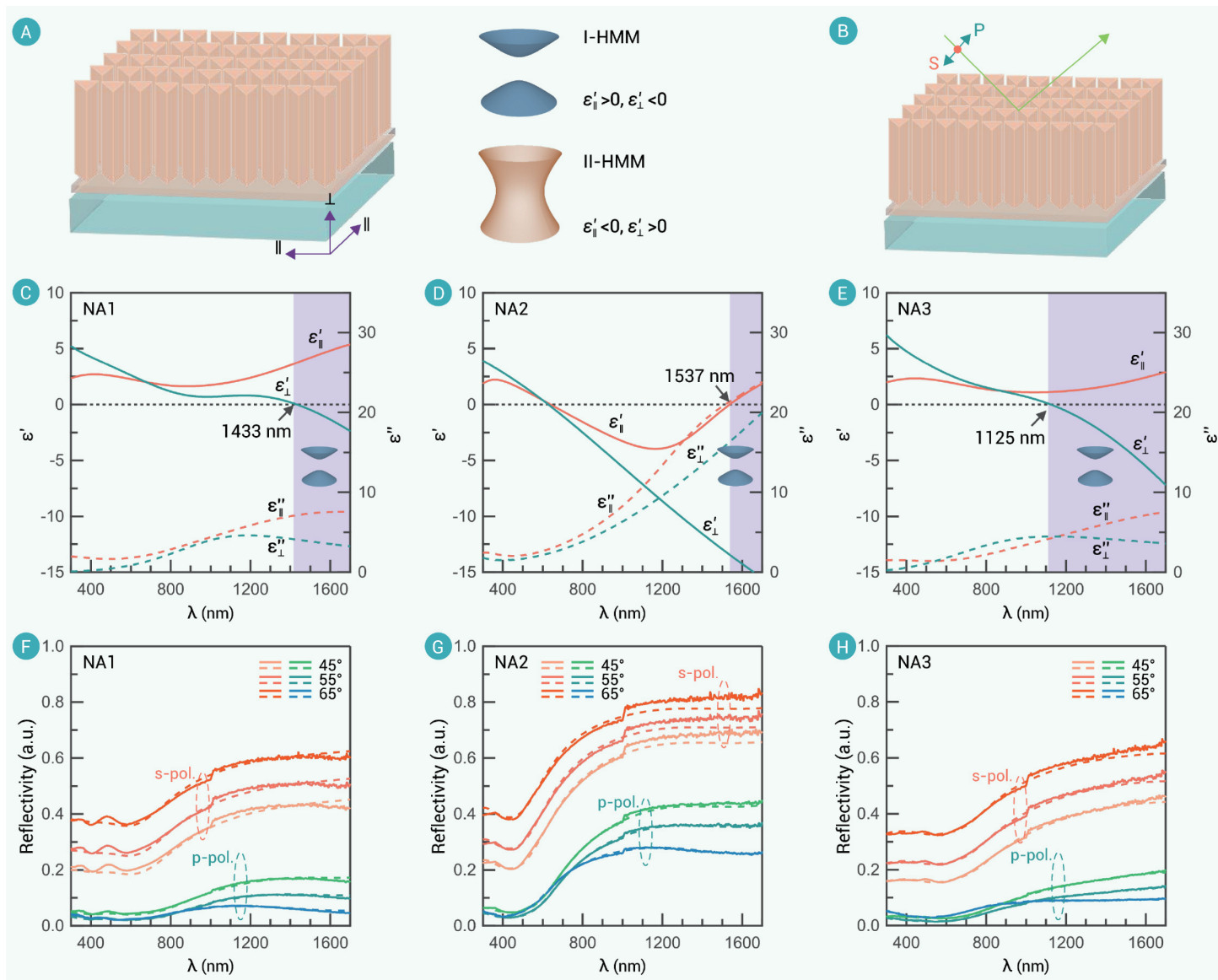




**Figure 2. Crystal structures, photo image, and structural characterizations of TiN nanopillar arrays deposited on F-mica substrates** (A) the crystal structure showing the epitaxial relationship between TiN nanopillar arrays and F-mica substrate, (B) detailed  $2\theta$ - $\omega$  scans around F-mica (004) and (005) diffractions, (C) the photo image of wafer-scale (2 in.) TiN nanopillar arrays of sample NA3, (D-F) RSMs patterns recorded around F-mica (-207) diffractions for samples NA1, NA2, and NA3. (G-I) top-view and cross-sectional SEM images for samples NA1, NA2, and NA3.

tions parallel and perpendicular to the optical axis. Figure 3A depicts two types of hyperbolic dispersions, i.e. type-I ( $\epsilon'_\perp < 0$  and  $\epsilon'_\parallel > 0$ ) and type-II ( $\epsilon'_\perp > 0$  and  $\epsilon'_\parallel < 0$ ) hyperbolic dispersions. Due to their open isofrequency surfaces (see Figure 3A), plasmonic metamaterials with hyperbolic dispersions (i.e. hyperbolic metamaterials, HMMs) are fundamentally important to many intriguing applications, including negative refraction, subwavelength-resolution imaging, spontaneous emission engineering, and highly sensitive sensors.<sup>37–40</sup> Figure 3B shows the optical configurations for the measurements of polarized reflectivities of the TiN nanopillar arrays. Figures 3C–E are the dielectric constants in the orientations parallel ( $\epsilon'_\parallel$ ) and perpendicular ( $\epsilon'_\perp$ ) to the film plane for the samples NA1, NA2, and NA3, which are extracted by well fitting the VASE data using the uniaxial anisotropy model with small MSE below 10 (see fitting details in Figure S4 of the Supplemental information). It is important to note that the uniaxial anisotropy model is valid as the lateral sizes of TiN nanopillars are much smaller than the wavelength of interest (300 – 1700 nm) due to the effective medium approximation (EMA). As seen, the samples NA1, NA2, and NA3 present type-I hyperbolic dispersion with

wavelength ranges above 1433 nm, above 1537 nm and above 1125 nm, respectively. The titanium nitride nanopillars in NA1 samples are nitrogen-rich due to deposition in pure  $N_2$  atmosphere, making them less metallic than the nanopillars in NA3 samples.<sup>41</sup> Consequently, the sample NA1 has much smaller absolute values of  $\epsilon'_\perp$  at near-infrared (NIR) ranges and a blueshift hyperbolic dispersion range compared to that of the sample NA3. The sole type-I hyperbolic dispersion is also observed in the NbTiN nanopillar arrays deposited on the rigid MgO (001) substrates and can be well simulated by EMA in our previous study.<sup>42</sup> The type-I hyperbolic dispersion and small dielectric loss (e.g.,  $\epsilon''_\parallel$ ,  $\epsilon''_\perp < 8$ ) demonstrated by samples NA1 and NA3 are very useful for hyperlens applications.<sup>43</sup> The sample NA2 has both  $\epsilon'_\parallel$  and  $\epsilon'_\perp$  below zero in the range 640 – 1537 nm probably due to its much better crystalline qualities and more closely-packed nanopillar arrays compared to other samples, which give rise to strong metallicity, negative signs for both  $\epsilon'_\perp$  and  $\epsilon'_\parallel$ , and relatively large dielectric loss (e.g.,  $\epsilon''_\parallel = 20.7$ ,  $\epsilon''_\perp = 15.5$  at 1500 nm). The simulations based on EMA analogous to a previous study<sup>42</sup> have also been performed to gain a deeper insight into the extreme optical anisotropy



**Figure 3. The plasmonic hyperbolic dispersions and polarized reflectivities for the samples NA1, NA2, and NA3** (A) type-I and type-II hyperbolic dispersions and their equivalent frequency surfaces, (B) the optical configurations for the s- and p-polarized reflectivity measurements, (C-E) dielectric constants and hyperbolic dispersion ranges for type-I (purple region) and type-II (green region), (F-H) the experimental (solid lines) and fitted (dashed lines) for the s-polarized (s-pol.) and p-polarized (p-pol.) reflectivities with incidence angles of 45°, 55°, and 65°.

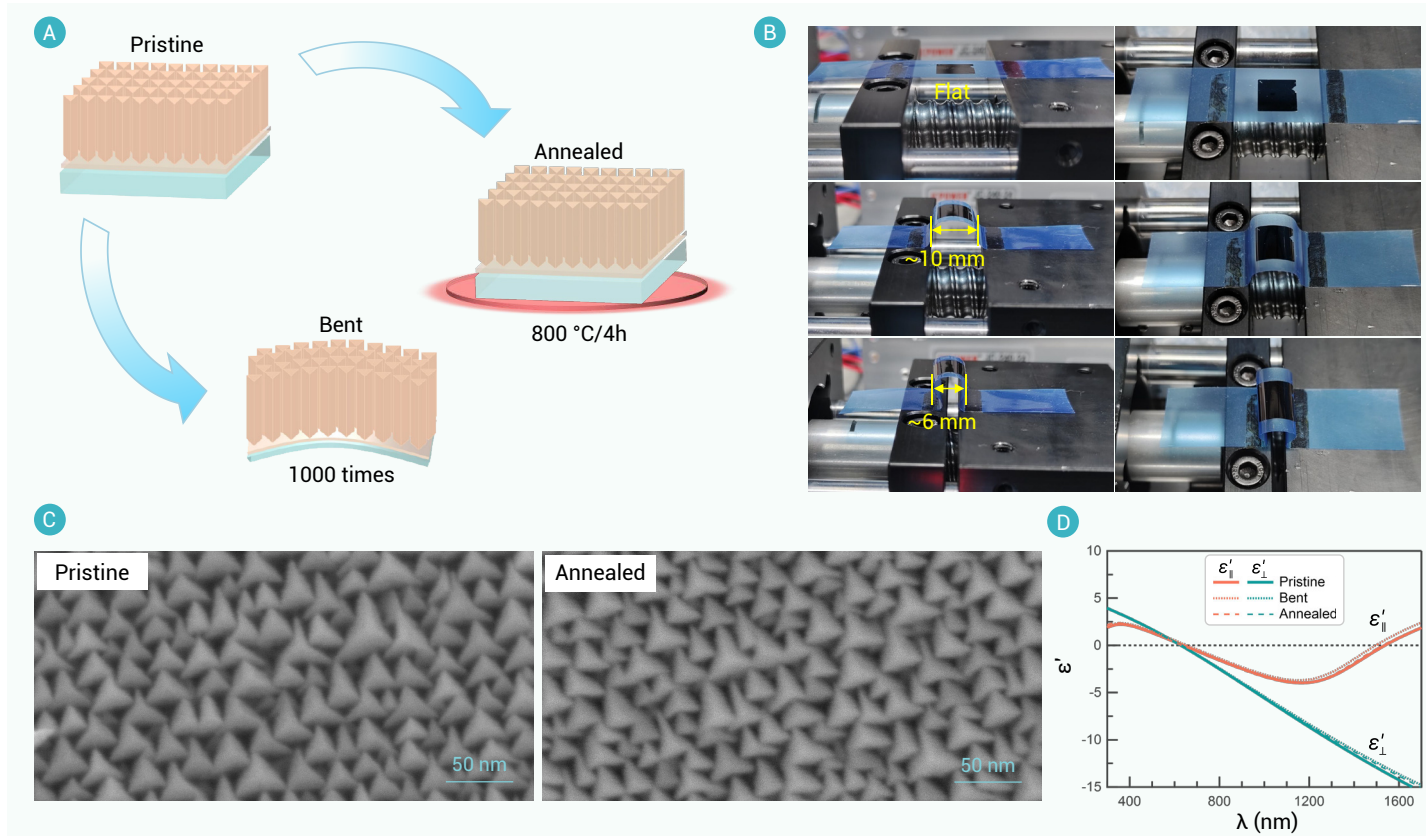
and hyperbolic dispersion, the results of which can be seen in Figure S5 in the Supplemental Information. To the best of our knowledge, such flexible and single-crystalline PNAs with tunable plasmonic dispersions have not been reported previously.

The extreme optical anisotropy of the samples NA1, NA2, and NA3 is demonstrated in Figures 3F-H by the experimental (solid lines) and fitted (dashed lines) polarized reflectivities with incidence angles of 45°, 55°, and 65°. The fitted polarized reflectivities were calculated by using the same uniaxial anisotropy model for deducing the dielectric constants in Figures 3C-E. As seen, the fitted polarized reflectivities are in excellent match with the experimental ones, further validating the effectiveness of the uniaxial anisotropy models. The s-polarized reflectivities are always higher than the p-polarized reflectivities in all samples. With the increase of incidence angles, the s-polarized reflectivities increase whereas the p-polarized reflectivities decrease. It is noted that with the incidence angle fixed, the s- and p-polarized reflectivities of sample NA2 are always higher than those of samples NA1 and NA3. For example, the s-polarized (p-polarized) reflectivity at incidence angle 65° is above 0.7 (0.2) at wavelength range above 1000 nm for the sample NA2, suggesting strong metallicity in good agreement with the results from the dielectric constant in Figure 3D. These results demonstrate

that deposition parameters (i.e., deposition atmosphere and deposition pressures) enable tunable plasmonic behavior and optical anisotropy in TiN nanopillar arrays, providing high flexibility for tailoring their optical properties for practical applications.

#### Flexibility and thermal stability

Next, the stabilities of TiN nanopillar arrays upon repeated bending and high-temperature treatment were evaluated (see Figure 4A). Firstly, the mica substrates of TiN nanopillar arrays were mechanically exfoliated to less than 5  $\mu\text{m}$  and adhered to blue tapes. Then, the samples were mounted on a displacement actuator using a stepper motor for repeated bending tests (see the Supplemental movies). As shown in Figure 4B, the TiN nanopillar arrays on blue tape can be gradually bent from a flat state to a concave curvature (bending radius of  $\sim 3$  mm) without inducing cracks. To assess thermal stability, the surface morphology and dielectric constants of TiN nanopillar arrays were measured before and after post-annealing at 800°C in vacuum for 4 hours. Figure 4C shows that the nanopillar arrays remain structurally unchanged after high-temperature annealing for the sample NA2, which is remarkable. Figure 4D shows the derived dielectric constants of the pristine NA2 sample, the sample NA2 after 1000 times bending, and the sample NA2



**Figure 4. Stability of flexible TiN nanopillar arrays upon repeated bending and high-temperature treatment** (A) schematic illustration showing the tests of mechanical and thermal stability, (B) the photo images showing the bending test, (C) the top-view SEM images for the pristine and annealed NA2 samples, (D) the derived dielectric constants of the pristine, bent, and annealed NA2 samples.

**Table 1. Comparison of TiN nanoarrays with conventional Au/Ag-Based flexible plasmonic nanostructures (PNAs).**

|    | PNAs/Flexible substrate | Fabrication process                                                                | Crystallinity         | Operating temperature (°C) | Application                       | Ref.      |
|----|-------------------------|------------------------------------------------------------------------------------|-----------------------|----------------------------|-----------------------------------|-----------|
| 1  | Au/PDMS                 | Holographic lithography + Metal deposition + Stripping                             | Non-singlecrystalline | <200                       | Adjustable near-field enhancement | 45        |
| 2  | Au/PDMS                 | Plasma treatment + Turkevich method                                                | Non-singlecrystalline | <200                       | Control of heat generation        | 46        |
| 3  | Au/PDMS                 | Nanoimprint + E-beam evaporation                                                   | Non-singlecrystalline | <200                       | SERS                              | 47        |
| 4  | Au/PET                  | DUV lithography + Magnetron sputtering                                             | Non-singlecrystalline | <180                       | SERS and Biosensing               | 48        |
| 5  | (Au, Ag)/PET            | Plasma treatment + Thermal evaporation                                             | Non-singlecrystalline | <180                       | SERS imaging                      | 49        |
| 6  | Ag/PUA/PET              | AAO template + Thermal evaporation                                                 | Non-singlecrystalline | <180                       | High-sensitivity SERS             | 50        |
| 7  | Au/PC                   | E-beam evaporation + 2D stretching                                                 | Non-singlecrystalline | <150                       | Conformal SERS sensors            | 51        |
| 8  | (Au, Ag)/PC             | Nanoimprint + AAO template                                                         | Non-singlecrystalline | <150                       | Highly- uniform SERS              | 52        |
| 9  | Au/COC                  | Interference lithography + Electroplating + Thermal imprint + Nanopattern transfer | Non-singlecrystalline | <140                       | Plasmonic biomolecular sensing    | 53        |
| 10 | Ag/PMMA                 | Photoreduction + Drop and peel-off                                                 | Non-singlecrystalline | <105                       | Pesticides sensors                | 54        |
| 11 | TiN/F-mica              | Magnetron sputtering                                                               | Single Crystalline    | ≤800                       | Plasmonic metamaterial            | This work |

PDMS: Polydimethylsiloxane, PET: Polyethylene terephthalate, COC: Cyclic olefin copolymer, PC: Polycarbonate, PDMS: Polydimethylsiloxane, AAO: Anodic aluminum oxide, SERS: surface-enhanced Raman scattering.

after annealing at 800°C. As seen, the repeated bending and high-temperature annealing only cause slight drift (< 40 nm) of type- I hyperbolic regions, suggesting robustness of hyperbolic dispersion and superior mechanical and thermal stabilities for the flexible TiN nanopillar arrays. Moreover, the absorp-

tion, transmittance, and reflectance spectra of flexible NA2 sample after 1000 times bending show little variations compared to the spectra of the pristine NA2 sample, further validating the robustness of flexible TiN nanopillar arrays upon repeated bending (see Figure S6). Owing to the high melting tempera-





**Figure 5. Contact angle measurements** (A) static contact angle for the sample NA1, (B) static contact angle for the sample NA2, (C) the dynamic contact angles for the sample NA3.

ture for TMNs, including TiN (typically over 2500°C),<sup>17</sup> high thermal stability (~1000°C) for F-mica substrates,<sup>23,30</sup> the flexible TiN nanopillar arrays show superior thermal stability. It is noteworthy that the flexible TiN nanopillar arrays show high-temperature endurance up to 800°C, far exceeding the working temperature of conventional flexible PNAs and even noble metal PNAs on rigid substrates. As ordinary flexible PNAs are constructed upon organic substrates, the typical working temperatures are limited below about 200°C.<sup>12-13,16</sup> On the other hand, the nanostructures of noble metal PNAs can change significantly at about 400°C due to low melting temperature of noble metals (below 1000°C) and small size effect.<sup>44</sup> As shown in Table 1, most Au/Ag-based flexible PNAs rely on various patterning techniques (e.g., photo/holographic/interference lithography, nanoimprint, and AAO template), metal deposition techniques (e.g., magnetron sputtering, thermal evaporation, and e-beam evaporation), and many other techniques, which are complex and low-yield.<sup>45-54</sup> Therefore, the superior mechanical/thermal stabilities and simplified fabrication processes demonstrated by the flexible TiN nanopillar arrays offer unprecedented advantages compared to ordinary flexible PNAs, enabling their wide applications such as flexible nonlinear optics, solar/thermophotovoltaics, and solar steam generation.

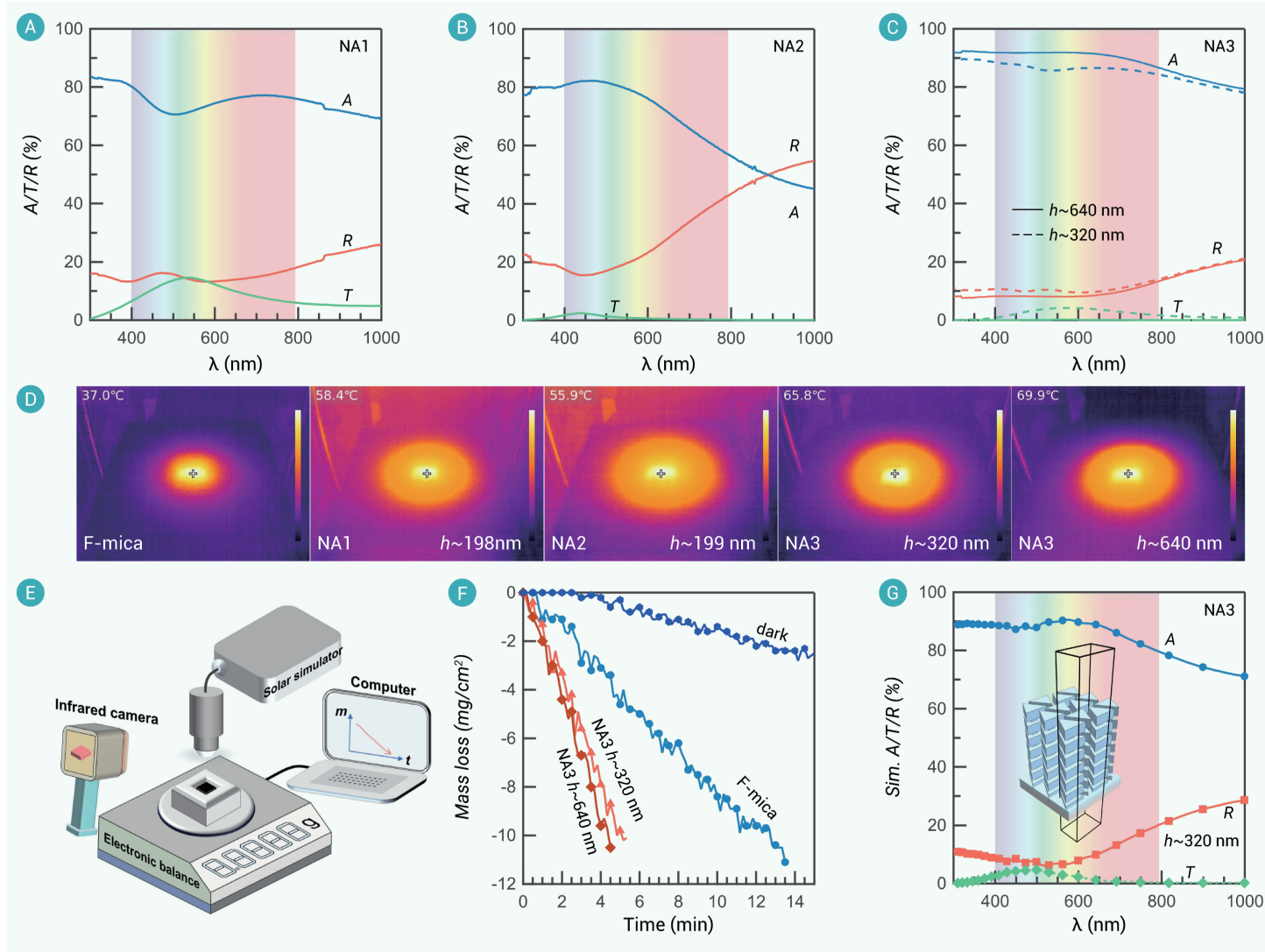
### Superhydrophilicity

Hydrophilicity, or surface water wettability, is critical for the uniform spreading of liquids across plasmonic surfaces, which significantly enhances the performance of PNAs in plasmonic sensors, surface enhancement Raman scattering devices, photocatalysis, and solar steam generation.<sup>55-57</sup> Thus, the surface wetting behaviors of the samples NA1, NA2, and NA3 were evaluated by water contact angle (CA) measurements using a contact angle goniometer (see Figure 5). As seen from Figures 5A-B, the samples NA1 and NA2 have static CA of 14.9° and 16.7°, respectively, showing good hydrophilicity. It is very striking that the video of water droplet spreading across the surface of NA3 demonstrates an extremely fast wetting process for the sample NA3 (see Figure 5C). The sample NA3 reaches a CA of only 9.7°, 5.9°, and 0° in just 0.02 s, 0.12 s, and 0.48 s, respectively, demonstrating liquid superspreading behavior, defined as the ability to achieve a contact

angle of 0° within subsecond timescales.<sup>58</sup> The liquid superspreading surfaces including the surface of the sample NA3 excel in many applications including efficient heat dissipation, rapid medical diagnosis, and fast liquid transport.<sup>58</sup> It is noteworthy that the hierarchical structure of sample NA3 significantly enhances its liquid superspreading behavior, resulting in superior hydrophilicity compared with samples NA1 and NA2. The extremely fast wetting process is also beneficial for interface solar-driven steam generation of TiN nanoarrays, as it facilitates rapid water evaporation by minimizing heat loss to the bulk water.<sup>59-61</sup>

### Light absorption and solar steam generation

Next, the light absorption performance for the flexible nanostructured TiN films was evaluated by the UV-vis-NIR spectrometer. The unpolarized reflectance ( $R$ ) and transmittance ( $T$ ) were measured for the samples NA1, NA2, and NA3. The absorption ( $A$ ) of the samples can be calculated by the equation  $A = 1 - R - T$ . Figures 6A-C shows the  $A$ ,  $R$ , and  $T$  curves for the samples NA1, NA2, and NA3 (including two different nanopillar arrays with nanopillar height  $h$  of about 320 nm and 640 nm, respectively). Despite noticeable light transmittance resulting from weakened metallicity of TiN nanopillars, sample NA1 exhibits light absorption above 70% across 300–1000 nm wavelength range. In comparison, the sample NA2 has high light absorption (> 80%) below 500 nm. However, above 500 nm the light absorption (light reflectance) of sample NA2 continuously decreases (increases) with increasing wavelengths, consistent with the trends observed in Figure 3. It is remarkable that the samples NA3 have the highest light absorption among all flexible nanopillar arrays. The light reflectance/transmittance decreases and light absorption increases as the nanopillar height  $h$  increases from 320 nm to 640 nm for the samples NA3. The hierarchical structure promoted light absorption demonstrated by the samples NA3 has also been observed elsewhere.<sup>57</sup> The light absorption performance of the samples NA3 is comparable to the light absorption of 75.0–91.4% for the hierarchically structured black gold film with excellent solar steam generation efficiency.<sup>55</sup> These bendable black gold films were either fabricated on flexible substrates (3M tape and sponge) or were freestanding with operating temperature below



**Figure 6. Light absorption and solar steam generation** (A–C) absorption (A), transmittance (T), and reflectance (R) curves for the samples NA1, NA2, and NA3 (including two different nanopillar arrays with nanopillar height  $h$  of about 320 nm and 640 nm, respectively), (D) infrared images of different samples under illumination of 1 Sun for 5 minutes, (E) experimental configuration for solar steam generation, (F) evolution of mass loss of water droplet for different samples under illumination of 1 Sun, (G) simulated A, R, T curves for the sample NA3 ( $h \sim 320$  nm) based on the periodic nanostructures in FDTD simulation.

350°C (see Table S1), significantly lower than the operating temperature of about 800°C for the flexible TiN nanoarrays in this work. To assess the light-thermal conversion efficiency, infrared images of different samples under 1 Sun illumination for 5 minutes are presented in Figure 6D. As seen, the maximum temperatures of infrared images for TiN nanopillar array can reach 58.4 – 69.9°C, which is significantly higher than that of F-mica substrate (temperature of 37.0°C). The highest temperature in each infrared image follows the order NA3 ( $h \sim 640$  nm) > NA3 ( $h \sim 320$  nm) > NA1 ( $h \sim 198$  nm) > NA2 ( $h \sim 199$  nm), in good agreement with the light absorption performances shown in Figures 6A–C. Figure 6E illustrates the experimental configuration for solar steam generation using a solar simulator, electronic balance, infrared camera, and computer. Figure 6F shows the mass change of water droplet on the surfaces of NA3 ( $h \sim 640$  nm), NA3 ( $h \sim 320$  nm), and F-mica under continuous illumination of 1 Sun accompanied by the mass change on F-mica without illumination (dark condition). The evaporation rate on F-mica substrate under 1 Sun illumination is  $0.47 \text{ kg m}^{-2} \text{ h}^{-1}$ , 4.3 times higher than that ( $0.11 \text{ kg m}^{-2} \text{ h}^{-1}$ ) for the dark condition. Owing to the good light-thermal conversion efficiency of TiN nanopillar arrays and good thermal isolation of sponge, the evaporation rate for the samples NA3 ( $h \sim 640$  nm) and NA3 ( $h \sim 320$  nm) can reach  $1.33 \text{ kg m}^{-2} \text{ h}^{-1}$  and  $1.24 \text{ kg m}^{-2} \text{ h}^{-1}$ , respectively, 2.8 and 2.6 times faster than that on F-mica substrate. The evaporation rate achieved here is much higher than  $\sim 0.4 \text{ kg m}^{-2} \text{ h}^{-1}$  under 1.4 Sun reported for the thermoplasmonic TiN nanocavity arrays in the previous study.<sup>62</sup> Then, the solar-to-

vapor conversion efficiency ( $\eta$ ) of the sample NA3 ( $h \sim 640$  nm) can be calculated with following relationship expressed as,<sup>62–64</sup>

$$\eta = \frac{\dot{m} h_{LV}}{C_{opt} q_i}$$

where  $\dot{m}$ ,  $h_{LV}$ ,  $C_{opt}$ , and  $q_i$  are the mass flux, total enthalpy of sensible heat and liquid-vapour phase change, concentration factor, and nominal solar flux, respectively. In this work,  $\dot{m}$  equals  $1.22 \text{ kg m}^{-2} \text{ h}^{-1}$  after subtracting the dark evaporation ( $0.11 \text{ kg m}^{-2} \text{ h}^{-1}$ ) and  $q_i$  equals  $1 \text{ kW m}^{-2}$  (1 Sun illumination). Typically,  $C_{opt}$  equals 1. Then,  $h_{LV}$  was calculated by following equation expressed as,<sup>62</sup>

$$h_{LV} = c_{H_2O} \Delta T + h_{fg}$$

where  $c_{H_2O}$ ,  $\Delta T$ , and  $h_{fg}$  are the specific heat capacity of water at ambient temperature, the temperature variation of water, and the latent heat of vaporization, respectively.  $c_{H_2O}$  equals  $4.186 \text{ kJ kg}^{-1} \text{ K}^{-1}$ . The water temperature increases from ambient temperature of  $\sim 22^\circ\text{C}$  to an average surface temperature of  $\sim 45^\circ\text{C}$  after 1 sun illumination, leading to a  $\Delta T$  of  $\sim 23^\circ\text{C}$ . The value of  $2394.352 \text{ kJ kg}^{-1}$  for the  $h_{fg}$  can be referred to a previous study.<sup>65</sup> Therefore, the solar-to-vapor conversion efficiency  $\eta$  for the sample NA3 with nanopillar height of 640 nm reaches 84.4%, which is comparable to the  $\eta$  values ranging from 50% to 85.9% for commercially available solar vapor

generation materials (e.g., TiNOX®, black carbon) summarized in Table S2 in the Supplemental Information. Therefore, the flexible TiN nanopillar arrays exhibit a high solar steam generation rate, showing great potential in photothermal applications. To reveal the origin of high light absorption and solar steam generation for the sample NA3, we have conducted the finite-difference time-domain (FDTD) simulations. The periodic structures consist of triangular nanopillar arrays with a nanopillar height of  $\sim 320$  nm and a gap between nanopillars of  $\sim 2.5$  nm. To mimic the hierarchical structures of NA3, many nanogaps have been created along the side wall of each nanopillar. As seen, the simulated curves resemble the experimental one with high light absorption and low light reflection in the visible range. The FDTD simulation in Figures 6G & S7 suggest that the hierarchical structure can increase an overall light absorption by 1.8% by reducing light reflection in the visible to near infrared (NIR) ranges. The TiN nanoarrays with lateral sizes of nanogaps 2.5 nm (corresponding to the experimental NA3 sample) can increase an overall light absorption by 10.7% compared to TiN dense films without nanogaps according to the simulation. Thus, the hierarchical structure, localized surface plasmon resonance effect (LSPR) of nanopillars, and the presence of numerous nanogaps contribute to the broadband light absorption behavior for the samples NA3.<sup>4, 57, 60, 66</sup> Increasing the nanopillar height (e.g., 640 nm) can further increase the light scattering in the sample, reduce light transmittance, and increase the light absorption performance.

## CONCLUSION

In conclusion, an easy and scalable strategy to fabricate flexible, single-crystalline, but refractory plasmonic metamaterials has been developed in this work. These flexible plasmonic metamaterials were fabricated by self-assembled growth of epitaxial TiN nanopillar arrays on F-mica substrates via reactive sputtering. Deposition parameters, such as atmosphere and pressure, can control the size, microstructure, and stoichiometry of the TiN nanopillars, enabling highly tunable plasmonic hyperbolic dispersion, extreme optical anisotropy, and light absorption. By mechanical exfoliation of F-mica substrate, the TiN nanopillar arrays become highly flexible. These flexible TiN nanoarrays show robust plasmonic hyperbolic dispersions upon repeated bending. Thanks to the high thermal stability of both TiN and F-mica, the flexible TiN nanopillar arrays maintain excellent stability even at 800°C, far exceeding the typical working temperature ( $< 200^\circ\text{C}$ ) of noble metal-based PNAs on flexible organic substrates. Their superhydrophilicity combined with high light absorption ( $> 90\%$  in the visible range and  $> 70\%$  in the NIR range), enables highly efficient solar steam generation. This work offers an easy and scalable route to the flexible, wafer-scale, single-crystalline, but refractory PNAs with highly versatile and tunable properties. The method introduced in this work can significantly expand the applications of flexible PNAs in flexible electronics, nanophotonic, and photothermal devices, particularly in nonlinear optics, solar/thermophotovoltaics, and solar steam generation devices.

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## AUTHOR CONTRIBUTIONS

R.Z. and Y.C. conceived the project. S.P. and R.Z. prepared the samples. S.P., X.W., J.B., S.Z., T. Z. J.S., and R.Z. performed the HRXRD, SEM, SE, and UV-Vis-NIR characterizations. S.P. and R.Z. performed the SEM characterizations and analyzed the SEM images. R.Z., S.P., and H.C. conducted the fittings and analyses of SE data. R.Z. and S.P. wrote the draft. All authors contributed to the manuscript and approved the final version.

## DECLARATION OF INTERESTS

The authors declare no competing interests.

## DATA AND CODE AVAILABILITY

Data are available from the corresponding author upon reasonable request.

## SUPPLEMENTAL INFORMATION

It can be found online <https://doi.org/10.59717/j.xinn-mater.2026.100189>.