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Solar steam generation on scalable ultrathin thermoplasmonic TiN nanocavity arrays

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ultrathin plasmonic TiN absorber; solar steam generation; nanocavity array; multi-physics modelling; quasi-two dimensional heat transfer.

Abstract

Plasmonic-based solar absorbers exhibit complete light absorption in a sub- μm thickness, representing an alternative to mm-thick carbon-based materials most typically employed for solar-driven steam generation. In this work, we present the scalable fabrication of ultrathin plasmonic titanium nitride (TiN) nanocavity arrays that exhibit 90% broadband solar light absorption within ~ 250 nm from the illuminated surface and show a fast non-linear increase of performance with light intensity. At 14 Suns TiN nanocavities reach $\sim 15 \text{ kg h}^{-1} \text{ m}^{-2}$ evaporation rate and $\sim 76\%$ thermal efficiency, a steep increase from $\sim 0.4 \text{ kg h}^{-1} \text{ m}^{-2}$ and $\sim 20\%$ under 1.4 Suns. Electromagnetic, thermal and diffusion modelling of our system reveals the contribution of each material and reactor component to heat dissipation and shows that a quasi-two-dimensional heat dissipation regime significantly accelerates water evaporation. Our approach to ultrathin plasmonic absorbers can boost the performance of devices for evaporation/desalination and holds promise for a broader range of phase separation processes.

1. Introduction

The widespread availability and abundance of solar radiation as a renewable energy source have led to its application in diverse fields such as photovoltaics,[1,2] hydrogen production,[3] photocatalysis,[4,5] solar-thermal conversion,[6] and steam generation.[7–9] The latter, in particular, has recently emerged as a cost-effective solution for off-grid water desalination,[10–12] distillation[13,14] and purification,[13,15] with its potential implementation in remote locations thanks to simpler reactor designs compared to large-scale reverse osmosis desalination plants.[7,16]

Solar steam generation involves light-to-heat conversion within a broadband absorber that, by increasing water temperature in its proximity, promotes the evaporation process. The so-obtained steam can be then collected, upon condensation, as clean water.[7,8] Ideally, solar absorbers feature large absorption coefficients to dissipate solar radiation in relatively thin layers, in contrast to mm-thick commercial black paints,[17] thus minimizing the amount of required material and maximizing heat power density within the absorbers themselves. In the search of improved solar absorbers, various materials have been considered, such as plasmonic metal nanoparticles dispersed in liquid,[14,18,19] or floating three-dimensional (3D) carbon-[11–13,20–23] and/or plasmonic-based[10,24–26] structures. The great interest in plasmonic materials is motivated by the efficient light-to-heat conversion upon the dissipation of plasmonic modes[27] (i.e. collective oscillations of conduction electrons in response to the incident electromagnetic field) that can be easily tuned by controlling the size and the chemical environment of plasmonic nanostructures.[28–32] Such a high efficiency of heat generation by plasmonic materials has indeed given rise to the sub-field of the so-called thermoplasmonics.[33]

Plasmonic materials offer even more unique advantages in the form of ultrathin layers based on periodic arrays, i.e. the so-called quasi two-dimensional (2D) metamaterials or metasurfaces.[34,35] By carefully controlling the dimensional parameters of arrays of nanostructures in the sub-wavelength regime, the electromagnetic radiation can be manipulated in unusual ways, a technique that has led to scientific advancements in many optical devices.[35–37] Moreover, a 2D array of dissipative plasmonic nanostructures can effectively promote a substantial heating thanks to collective photothermal effects.[38,39] Ultrathin broadband solar absorbers with a thickness limited to $\sim 100\text{--}200$ nm have been realized employing plasmonic metamaterials.[40–42] Although solar absorbers based on periodic structures have been reported, such as anodic alumina oxide (AAO) coated by Au or TiN,[10,24,26] a further reduction of the thickness down to the ~ 100 nm scale may lead to faster evaporation dynamics because of the increased power densities in the plasmonic metasurface layer. For example, by absorbing unfocused solar radiation ($\sim 1 \text{ kW m}^{-2}$) in a ~ 100 nm thick dissipating layer would yield to an average heat power density of $\sim 10 \text{ GW m}^{-3}$. Such large power densities can trigger fast thermal processes in ultrathin devices, opening the possibility for exploiting nanoscale photothermal effects in large area systems. Here we experimentally demonstrate and numerically validate the efficacy of plasmonic metasurfaces in vaporizing water and we theoretically show how the process can be accelerated through nanoscale heat transfer.

2. Results and Discussion

We propose an ultrathin solar absorber based on plasmonic titanium nitride (TiN), an emergent thermoplasmonic material alternative to gold thanks to its similar absorption spectrum, but also ~ 40 times cheaper and showing refractory nature, complementary metal oxides compatibility, and

superior heat dissipation.[41,43–46] The TiN-based solar absorber (TSA) is enclosed within a thermally-insulating polytetrafluoroethylene (PTFE) cell having, in its top section, a cylindrical through-hole (1 cm diameter) working as basin to collect water, reminiscent of a solar still (Figure 1A). Solar-simulated light is then focused at the top surface of the water collector (i.e. the light spot has a diameter of ~ 1 cm) to heat water and the TSA, driving the steam generation. The TSA consists of three different layers, as a result of the fabrication process (Figure 1B, see also Supplemental Notes). The first layer is made of a TiN nanocavity array (Figure 1C) with optimized thermoplasmonic properties for improved light-to-heat conversion.[47] The array is obtained by anodizing a commercial 125 μm -thick Ti foil in acidic solution, which leads to the self-organization of TiO_2 nanocavities in a hexagonal array,[48,49] and then by nitridation in NH_3 atmosphere (see Experimental and Numerical Methods). The so-obtained TiN nanocavities exhibit a typical diameter of ~ 80 nm, height of ~ 180 – 200 nm, and center-to-center distance of ~ 100 nm (Figure 1D).[47] Anodization was employed as a scalable process to obtain nanostructures over cm-scale areas.[50] The nitridation process, on the other hand, leads to a stoichiometric TiN composition in the nanocavities, as confirmed by high-resolution transmission electron microscopy (HRTEM)-energy dispersive X-ray spectroscopy (EDS) elemental mapping (Figure 1D) and X-ray diffraction (Figure S1). The second layer is a Ti_2N layer of ~ 1 μm thickness, which is formed beneath the TiN nanocavities as a result of diffusion of NH_3 through the Ti plate (Figure 1B). Finally, the third layer is the rest of the substrate, which remains in the form of metallic Ti (Figure 1B). We employ finite element method (FEM)-based electromagnetic numerical simulations to show that the optical power absorption at visible wavelengths (Figures 1E, 1F and S2) is actually confined in a thickness of ~ 250 nm, corresponding to the height of TiN nanocavities, while in the near IR region it increases to ~ 350 nm (Figure S2). This is reflected by Figure 1F,

which shows that the modulus of the vertical component of the Poynting vector $|\mathbf{P}_z|$, quantifying the power flow through the structure, exhibits a rapid decay in the nanocavities height h_{TiN} . Such an efficient optical absorption and subsequent heat generation is attributed to the collective photothermal effects of the TiN nanocavity array.[47] As such, the TSA can be considered as a promising quasi-bidimensional absorber for efficient heat dissipation in confined volumes over large areas.

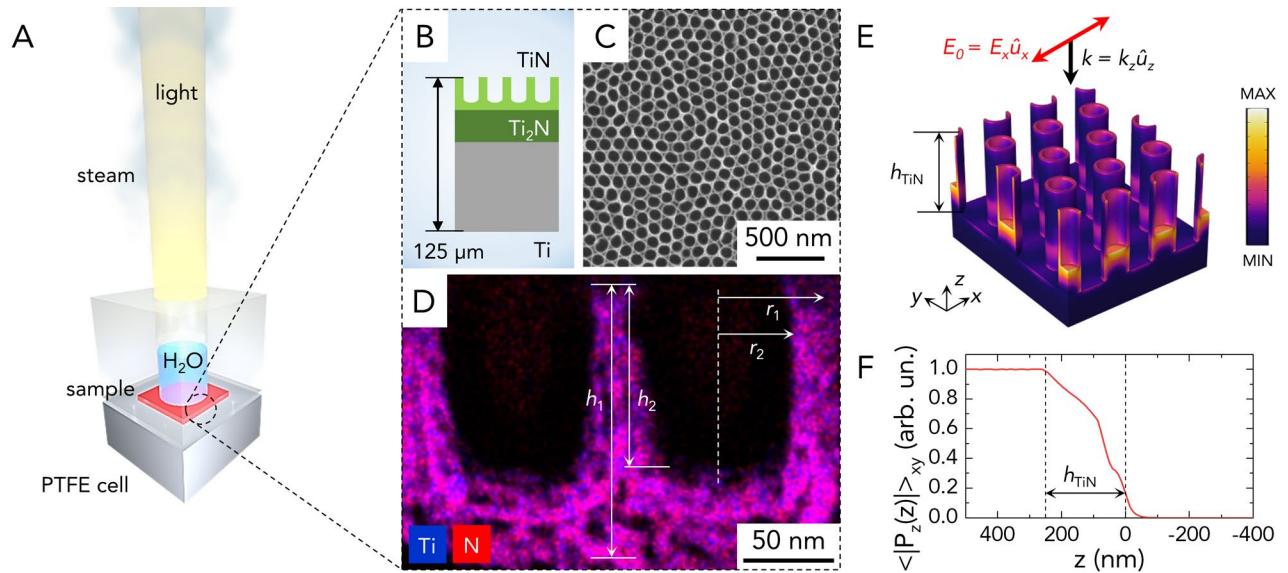


Figure 1. Steam generation by the TSA. (A) Schematic of water evaporation and steam generation by the TSA under moderate light concentration in a custom-made PTFE cell. (B) Schematic structure of the TSA: TiN nanocavities (250 nm thickness), Ti₂N thermal layer (~1 μm), and rest of the Ti substrate. (C) Top-view SEM image of TiN nanocavities. (D) HRTEM-EDS elemental mapping for Ti (blue) and N (red). The panel also reports the geometrical parameters of the nanocavities: external height h_1 , cavity depth h_2 , external radius r_1 , and internal radius r_2 . (E) Simulated power absorption across the nanocavities array upon plane wave illumination (normal incidence with linearly-polarized electric field \mathbf{E} along x -axis, exemplary excitation wavelength $\lambda = 500$ nm), computed following Joule dissipation. The electromagnetic power is then converted

into heat following this same spatial pattern. (F) Modulus of the vertical component of the Poynting vector, $|\mathbf{P}_z|$, averaged over horizontal (xy) planes as a function of the direction normal to the structure (z -axis), shown for $\lambda = 500$ nm and normalized to its incident value.

Due to the optically opaque nature of the TSA, the optical properties were evaluated by UV-visible-NIR spectroscopy in reflectance (R) mode, from which the absorption was retrieved as $A = 1 - R$, being zero the transmittance (T). The experimental reflectance and absorption spectra in air are shown in Figure 2A, together with their simulated counterparts (see Figure S3 and Note S1 for the electromagnetic modelling of the TSA). These results clearly show the capability of TiN nanocavities to efficiently absorb the solar light in a broadband range, which is the first requirement to achieve an efficient photothermal conversion and heat generation both in air and water environments, confirming previous studies on the same material.[47] The experimental overall absorption in air, weighted for the solar irradiance spectrum in the range 200–1100 nm, is ~90%, in good agreement with simulations (Figure 2A). The slight mismatch between the experimental and the theoretical curves can be due to the fact that numerical simulations do not take into account neither size distribution effects of the nanocavities nor local imperfections in the hexagonal array.[47] Since the TSA is placed at the bottom of the water reservoir in the PTFE cell for steam generation experiments, its optical properties in water must be considered. In particular, the absorption spectrum in water was numerically simulated and the contributions of each layer constituting the TSA were disentangled (Figure 2B and Figure S3): the TiN nanocavities layer (green), a 100-nm thick Ti layer beneath them (cyan), and the further substrate (blue). Consistently with previous investigations,[47] optical simulations did not explicitly include the Ti₂N layer due to its similar electronic properties to TiN (see also Note S1).[51] As a first remark, the overall

absorption in water is very similar to that in air in the range 300–800 nm, after which the former drops to values < 80% due to the increasing absorption coefficient of water in the IR region.[52] Moreover, by evaluating dissipation spectra separately, it was possible to ascribe spectral features of the total absorption to the different components of the TSA. In the UV-visible range, light absorption is efficiently confined within the TiN nanocavities layer, in agreement to the results of Figures 1E and 1F. At $\lambda > 800$ nm, conversely, the substrate has a crucial role in maintaining the total absorption above 65%. Interestingly, a substantial contribution is given by a 100 nm-thick Ti underlayer under TiN, while all the remaining Ti substrate only gives ~5% absorption at $\lambda > 1800$ nm. In other words, almost all the optical absorption of solar radiation within the TSA occurs in the first few hundreds of nm, i.e. in the TiN nanocavities and the immediate Ti underlayer. Light absorption in TiN nanocavities is affected by the excitation of plasmonic modes, as illustrated by the simulated spatial maps of electric field enhancements across a single nanocavity (Figure 2C). In particular, at $\lambda = 500$ nm the absorption is due to pure cavity modes,[53,54] resulting in the electric field mainly concentrated in the hollow core. At $\lambda = 1700$ nm, on the other hand, the absorption is related to the localized surface plasmon resonance (LSPR) at the cavity corners, producing an electric field enhancement mostly concentrated at the external surface of the cavities.[47]

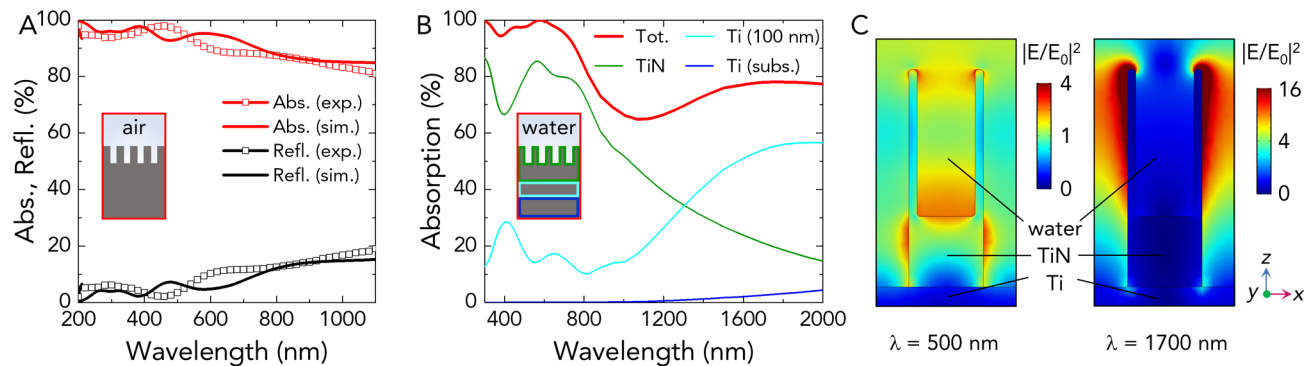


Figure 2. Optical properties of the TSA. (A) Experimental (symbols) and simulated (solid lines) absorption (red) and reflectance (black) of the TSA in air. (B) Simulated absorption of the TSA in water (red), disentangled in terms of contributions arising from the TiN nanofurnaces (green), the 100 nm-thick Ti underlayer (cyan), and the Ti substrate (blue). (C) Spatial maps of electric field enhancement across a single TiN nanocavity, numerically computed at $\lambda = 500$ nm (left) and $\lambda = 1700$ nm (right).

The solar steam generation performance of the TSA was evaluated by a custom-made setup, in which the PTFE cell enclosing the TSA, 800 mg of water and a thermocouple were placed on a high-precision balance and illuminated by solar-simulated light with various intensities (see Experimental and Numerical Methods and Figure S4 for further details). Water evaporation experiments under light irradiation were run for 25 minutes, while no appreciable water evaporation was measured in the dark. Each TSA sample was tested several times over a period of few months showing stable performance after several runs of water evaporation. Figure 3A shows the time-dependent experimental and simulated evaporation rate for the TSA under 1.4–9.8 Suns (see below for more details on the simulations). The time-dependent evaporation rate $\dot{m}(t)$ ($\text{kg h}^{-1} \text{m}^{-2}$) was calculated from the mass change Δm (Figure S5) for each specific time interval Δt by the formula $\dot{m}(t) = \Delta m / \Delta t$. It is possible to observe a monotonic increase of the evaporation rate with

time because of the variation in the slope of the mass change (Figure S5), and with the incident light intensity (from $\sim 0.4 \text{ kg h}^{-1} \text{ m}^{-2}$ at 1.4 Suns to $\sim 5.5 \text{ kg h}^{-1} \text{ m}^{-2}$ at 9.8 Suns). Moreover, we found a good agreement between the experimental and calculated curves. Only for the case at 9.8 Suns a mismatch occurs (evaporation rate $\sim 4.4 \text{ kg h}^{-1} \text{ m}^{-2}$), which is ascribed to the limitations of the numerical model in reproducing the phenomenon of boiling and bubble formation (see Note S2). Bubbles were indeed observed at high irradiation conditions, but their origin (either steam or air) could not be identified. For the same reason, no simulations were performed for the highest irradiation conditions (12.6 and 14 Suns). In addition, it is possible to note that the evaporation rate reaches a relatively stable value only for the lowest irradiation condition (1.4 Suns), meaning that in our experimental conditions no steady state could be achieved, likely due to the limited (800 μL) and continuously decreasing volume of water in the PTFE cell. The corresponding temperatures measured in water slightly above the TSA surface are reported in Figure 3B, ranging from $\sim 37 \text{ }^\circ\text{C}$ at 1.4 Suns to $\sim 96 \text{ }^\circ\text{C}$ at 9.8 Suns. Also in this case it is possible to appreciate a good agreement between the experimental and the numerical data. The slight underestimation of the simulations compared to experiments could be accounted for the additional temperature rise induced in the thermocouple by the solar-simulated light. The evaporation rate and the temperature profiles vs. time for water alone, without TSA, are instead reported in Figures 3C and 3D, respectively. As expected, both the evaporation rates (maximum $\sim 1.5 \text{ kg h}^{-1} \text{ m}^{-2}$ at 9.8 Suns) and the temperatures (maximum $\sim 75 \text{ }^\circ\text{C}$ at 9.8 Suns) are lower than those measured in the presence of the TSA, especially at higher irradiation conditions (i.e. 7 and 9.8 Suns). Conversely, at low irradiation conditions (especially at 1.4 Suns), light from the solar simulator is mostly absorbed in the water volume close to the upper surface of the reservoir, thus accounting for the similarity with the data in Figures 3A and 3B. The small deviation between experimental and numerical curves,

in the case of water only (Figures 3C and 3D) is observed at short times only, where evaporation rates tend to exhibit a less reliable trend.

An overview of all the experimental evaporation rates in all the investigated irradiation conditions is reported in Figure 3E. This figure not only reports the data for the TSA (both measured and simulated) and for water, but also for a Ti plate (i.e., the substrate on which TiN nanocavities were grown) and for a commercial solar absorber material as benchmark for solar-thermal applications. The latter consisted in a multilayer metallic spectrally-selective absorber, TiNOX[®], in which the solar absorber layer is a cermet structure. It is possible to note that, while at 1.4 Suns the evaporation rates for all the cases are almost the same ($\sim 0.3\text{--}0.4 \text{ kg h}^{-1} \text{ m}^{-2}$), their values spread by increasing the light intensity. In particular, a non-linear increase of the evaporation rate and efficiency was found, consistently with previous studies,[11] and the maximum value was achieved by the TSA at 14 Suns ($\sim 14.9 \text{ kg h}^{-1} \text{ m}^{-2}$). Notably, the TSA outperformed the Ti plate, i.e. the substrate itself ($\sim 8.5 \text{ kg h}^{-1} \text{ m}^{-2}$), but also the commercially available TiNOX[®] ($\sim 11.1 \text{ kg h}^{-1} \text{ m}^{-2}$), positioning the TSA as a promising candidate for large-scale ultrathin absorbers. Additional solar steam generation experiments featuring a TSA covering a ten times higher surface area than before confirmed the role of plasmonic enhancement in the water evaporation process, reaching similar performances to those obtained with the small-scale PTFE reactor (Figure S6). Detailed theoretical insights on the scalability of the TSA are reported in the Supporting Information (Figure S7 and Note S3).

The non-linear increase of the evaporation rate with the TSA (+3700% from 1.4 to 14 Suns, Figure 3E) is higher compared to the linear increase typically reported in previous studies concerning plasmonic absorbers (Figure S8A).[10,24,25,55,56] In particular, at low irradiation conditions other systems showed a higher evaporation rate, such as anodic alumina oxide membranes

combined with Al,[10] Au[24] or HfN[55] nanoparticles, likely due to the interfacial configuration arrangement. However, in these cases the evaporation rate increased linearly (e.g. +1570% for black Au film from 1 Sun to 13 Suns),[25] our system showed a better performance at moderate light concentrations. For example, even under 17 Suns the black Au film[25] showed an evaporation rate of $\sim 13 \text{ kg h}^{-1} \text{ m}^{-2}$, lower than the TSA at 14 Suns (Figure S8A). The non-linear increase found here could be related to the exponential (Beer-Lambert-like) increase of light penetration through the water layer above the TSA and to the exponential increase of the saturation vapor pressure of water with temperature.[11]

The evaporation efficiency (η) was calculated by the following formula[7,20]

$$\eta = \frac{\dot{m}h_{LV}}{C_{opt}q_i} \quad (1)$$

where \dot{m} is the evaporation rate (calculated at the end of the experiments), h_{LV} is the total enthalpy of liquid-vapor phase change (kJ kg^{-1}), C_{opt} is a concentration factor (from 1.4 to 14), and $q_i = 1 \text{ kW m}^{-2} = 1 \text{ Sun}$ is the nominal solar flux. The term h_{LV} , in particular, was calculated as[7]

$$h_{LV} = c_{H_2O}\Delta T + h_{fg} \quad (2)$$

where $c_{H_2O} = 4.186 \text{ kJ kg}^{-1} \text{ K}^{-1}$ is the specific heat capacity of water at constant pressure (which negligibly changes in the temperature range 0–100 °C), ΔT is the temperature change from the beginning to the end of the experiment, and h_{fg} is the latent heat of vaporization (kJ kg^{-1}), whose temperature dependence was instead taken into account by an empirical polynomial equation.[57] The data for all the investigated conditions are accordingly reported in Figure 3F, as well as for the simulated TSA up to 9.8 Suns. As in Figure 3E, the values at 1.4 Suns are similar for all the samples, with efficiencies falling in the range 16–19%. By increasing the light intensity, an initial

drop at 4.2 Suns is observed probably due to optical losses related to light concentration[20,25] and to the baseline evaporation rate (Figure S9), while at higher solar intensities the efficiency remained almost constant for water (from ~11% to ~14%) and increased when a solar absorber is employed. In particular, for the TSA the efficiency ranged from ~15.6% at 4.2 Suns to ~76% at 14 Suns, outperforming TiNOX[®] (maximum η ~56%) and the Ti plate (maximum η ~43%). In addition, the simulated efficiency for the TSA was in good agreement with the experimental one up to 7 Suns. Despite the relatively low efficiency values for the TSA at low irradiation condition, likely due to the TSA location far from the water surface, a remarkable ~4-fold efficiency improvement by increasing the light intensity from 1.4 to 14 Suns was found (Figure 3F). Other plasmonic-based absorbers showed higher efficiencies in interfacial configuration[10,24,25,55,56] (e.g. η ~99% for anodic alumina membranes filled with HfN at 4 Suns,[55] Figure S8B), which indeed is more suitable to reach higher performances due to the efficient heat localization at the liquid surface.[7,8] Such a configuration was, however, not feasible in this work due to the non-floating and non-porous nature of the Ti substrate on which TiN nanocavities were prepared. Nevertheless, other 2D plasmonic arrays based on Au have shown fifty-times smaller increase compared to TSA (e.g. only +3% for black Au film from 1 Sun to 13 Suns[25], Figure S8B).

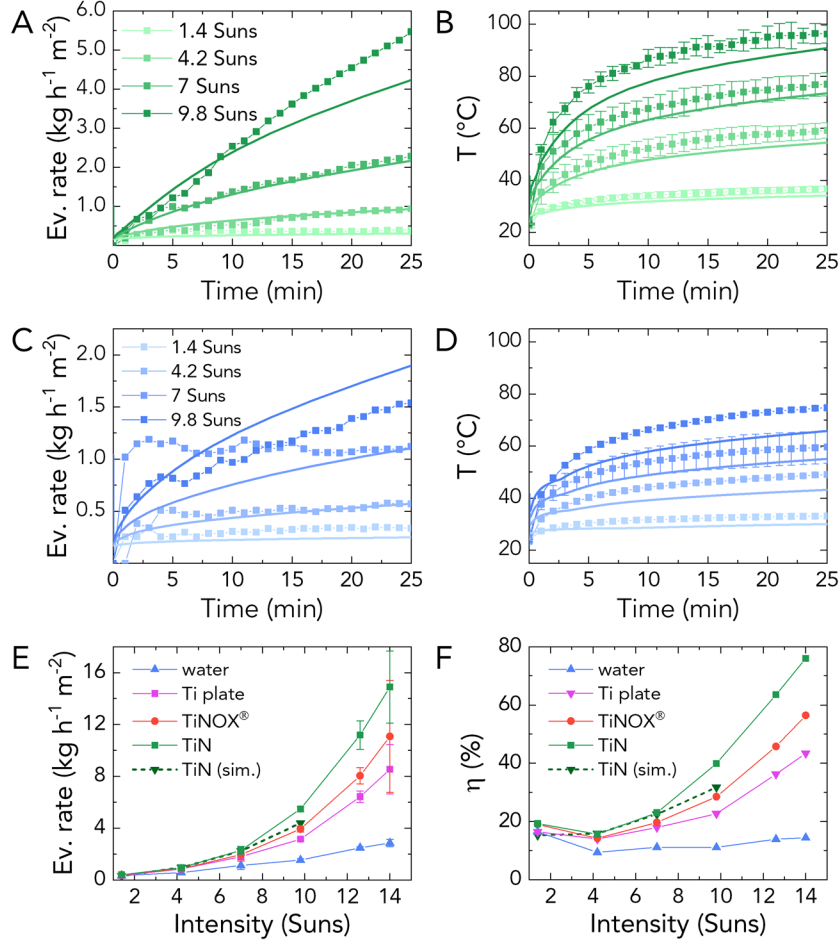


Figure 3. Solar-driven steam generation by the TSA. (A and B) Time-dependent water evaporation rate with the TSA (A) and corresponding temperatures (B) under different light intensities (symbols: experimental; solid lines: simulated). (C and D) Same as (A and B), respectively, but without the TSA. (E and F) Water evaporation rate and corresponding solar-to-vapor conversion efficiency, respectively, under different light intensities for different materials, evaluated at $t = 25$ min; for TiN, the simulated data are also included (dark green dashed line).

The simulations of the TSA-assisted steam generation experiments (Figure 3) were achieved by a comprehensive multiphysics and multi-scale thermo-fluid modelling of all the interlinked phenomena involved in the evaporation process, i.e. optical absorption, heat generation and

transport, fluid dynamics, and photon scattering. This model is schematized in Figure 4A, while Supporting Information reports additional details regarding the geometry of the model itself (Figure S10) and typical results for the temperature distribution (Figure S11), convective flow in the water reservoir (Figure S12), and water vapor concentration in the surrounding air (Figure S13). A thorough discussion of the model is reported in Note S2. More schematically, Figure 4A shows that radiation coming from the solar simulator and focused by the Fresnel lens impinges on the water volume on top of the TSA, the two surrounded by PTFE. Considering that light absorption in the TSA mostly occurred in the TiN nanocavities and in the thin Ti underlayer (Figure 2B), only these two layers were considered as dissipaters in the TSA region. The dissipation in water was taken into account by weighing its wavelength dependent absorption coefficient over the solar spectrum (see also Figure S10 and Note S2). Moreover, the spatial arrangement of TiN nanofurnaces was neglected and the TiN layer was considered as a homogeneous 250 nm-thick layer. From the heat dissipation point of view, indeed, any spatial inhomogeneity of sub- μm -thick dissipaters can be neglected when the dimensions of the adjacent domains (i.e. the water volume and the PTFE cell) are orders of magnitude larger (see Figure S14 and Note S4 for a more detailed description).[39] Moreover, due to the large light scattering provided by PTFE, the cell effectively concentrates the incoming radiation in the active area additionally to its thermal insulation role, resulting in a higher solar intensity reaching the TSA surface. The paths of few exemplary photons were calculated through a Monte Carlo based approach within the PTFE and are sketched in Figure 4A, depicting the randomizing effect of PTFE on the photon propagation direction (see Figure S15 and Note S5). Due to the non-trivial paths of photons, radiation dissipation is modified in the whole structure, resulting in a more

complex heat source distribution for the thermal model describing the experimental system. A further heat source due to the non-negligible lens heating was included as well (Note S2).

Beyond the time-dependent numerical results shown in Figure 3, the model was employed to predict the system performances in the stationary regime as well. Such regime could not be tested experimentally due to the complete evaporation of water at longer times. A disentanglement of heating contributions was also performed to distinguish the terms related to different dissipating elements. The simulated steady-state evaporation rates as a function of light intensity associated to the individual components of the experimental setup are reported in Figure 4B. Numerical predictions clearly show to what extent each component has a role in the evaporation process. Clearly, the main contributions are associated to TiN and water. Nevertheless, the radiation confinement produced by the PTFE cell (Figure S15) and the additional heating induced by the Fresnel lens further contribute to the evaporation process promoted by the TSA, resulting in the evaporation rates experimentally measured (Figure 3).

Furthermore, we numerically investigated the time needed to reach the stationary state for water evaporation (Figure 4C) moving from 3D heat transfer conditions to a quasi-2D scenario, in which the confined dissipation in the ultrathin TSA can be fully revealed. While the full geometrical features of a metasurface should be considered when the water layer thickness h_w becomes comparable to the TiN layer thickness h_{TiN} , here we employ a simplified model to highlight the time dependent heat transfer properties of different layers spanning size over orders of magnitude. Our model is composed of a passive water layer on top of an active TiN layer (inset of Figure 4C and Figure S16), the latter characterized by the same thermal properties as the TiN layer in the previous model (see Note S6 for further details). The radius of both TiN and water layers is 0.5 cm. The system is considered insulated on its lateral walls but can exchange heat by conduction

and vaporization through the water/air interface. We have studied the dependence of the evaporation rate, normalized to its stationary value, for $h_w = 100$ nm and varying values of h_{TiN} , from 1 mm to 0 thickness that represents the limiting case of surface heating dissipating 1 Sun. For each other thickness, the heat dissipation density has been set to $1 \text{ kW m}^{-2} / h_{TiN}$, thus maintaining constant the total input power. The time dependent evaporation dynamics is shown in Figure 4C. While the curves follow similar trends, the timescale strongly depends on the TiN layer thickness. Thinner layers imply faster thermalization, as expected by heat dynamics at smaller scales. Interestingly, the case $h_{TiN} = 100$ nm is virtually equivalent to the 0 nm limit case where pure surface heating is considered. This observation shows how thin plasmonic metasurfaces can indeed accelerate thermal processes. In Figure 4D we report the thermalization times (the time required to reach 90% of the steady state evaporation rate), τ , for h_{TiN} spanning from 10 nm to 1 mm in the case of three different layers of water: 100 nm, 10 μm and 1 mm. As expected, the larger the overall system (TiN+water), the longer it takes for reaching steady state. However, the plot clearly shows how sub- μm absorbers are required if water thicknesses below $\sim 10 \mu\text{m}$ are considered. For example, only a few tenths of seconds are required for thermalize a system with $h_{TiN} = 100$ nm and $h_w = 100$ nm, compared to the hundreds of seconds a combination with $h_{TiN} = 1$ mm and $h_w = 100$ nm would require. Moreover, it should be noticed that such thermalization times are calculated for a relatively large $w = 1$ cm diameter system. Since τ is expected to decrease with the volume of the heated system, for given layer thicknesses we can infer $\tau \propto w^2$. Therefore, even faster dynamics are expected if smaller scales can be managed, depending on the intended application. This observation suggests the great promise plasmonic metasurfaces hold in accelerating thermal processes beyond steam generation, such as phase changes or Arrhenius-type chemical reactions, within light driven micro/nanofluidics devices. The fast thermalization may

also allow the use of non-continuous irradiation, paving the way to the study of nanoscale thermal processes under pulsed or intermittent illumination.

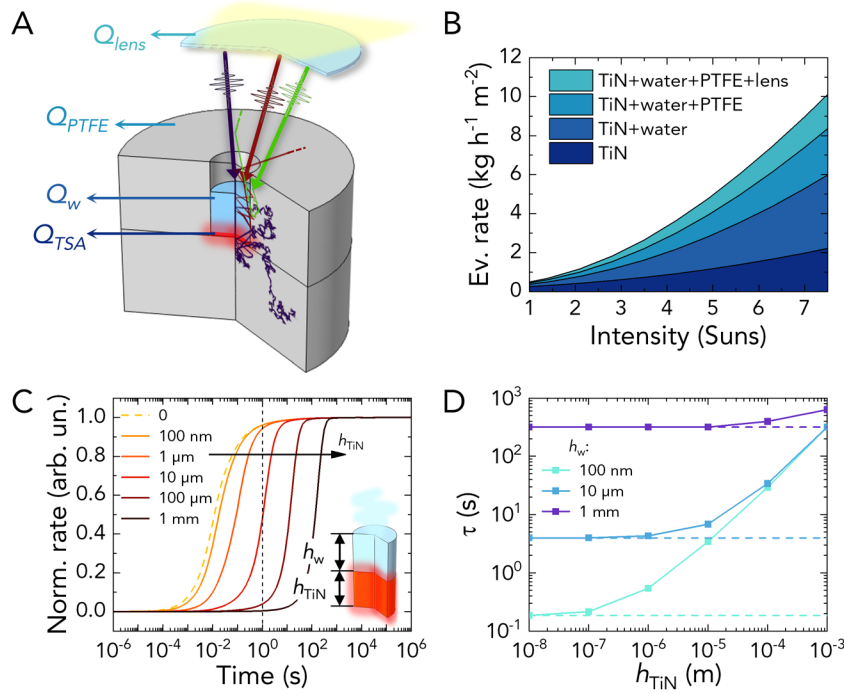


Figure 4. Modelling of TSA-assisted steam generation. (A) Schematic of the thermal modelling of the experimental set-up, where the paths of few exemplary photons within the scattering PTFE cell are shown. Heat sources included in the modelling are also highlighted. (B) Simulated evaporation rate in stationary regime, disentangled in terms of the dissipation contributions due to single heat sources. (C) Evaporation rates normalized by the stationary value computed for the simplified model (see right inset) for a 100 nm-thick water layer and varying TiN thickness (h_{TiN}), from 0 (limit case of surface heating) to 1 mm. The vertical dashed line marks the time $t = 1$ s. (D) Characteristic time τ the system, as in (C), takes to reach the steady state, as a function of h_{TiN} for different h_w : 100 nm, 10 μm and 1 mm. The dashed lines represent the zero-thickness limit scenario for a fixed h_w .

3. Conclusion

In summary, we introduced an ultrathin solar absorber based on TiN nanocavities and demonstrated its thermoplasmonic properties in solar steam generation experiments. The periodic array of nanocavities was easily achieved by a scalable method, based on anodization and thermal nitridation, ensuring a broadband light absorption confined in few hundreds of nm in thickness thanks to plasmonic and cavity resonances. Efficient steam generation under moderate light concentration was achieved with an evaporation rate of $\sim 15 \text{ kg h}^{-1} \text{ m}^{-2}$ and efficiency of $\sim 76\%$ at 14 Suns, outperforming commercially available solar absorbers and showing a higher and non-linear performance enhancement compared to other cases in the literature. A comprehensive electromagnetic and thermal modelling of the involved materials and of the overall experimental system, including a light diffusing thermally-insulating PTFE cell, revealed the substantial light absorption confinement in the TiN nanocavities. This effect confined the heat dissipation volume at the surface layer of the absorber. Further light concentration was found to be due to photon scattering within the PTFE cell. Such multiphysics thermo-fluid modelling successfully reproduced the experimental steam generation data and was further employed to study the transition from 3D to 2D heat transfer regime, demonstrating the acceleration by up to two orders of magnitude of the evaporation process in case of a sub- μm thickness of both the TiN absorber and water overlayer. The outcome of simulations thus provides a guidance to further improve the performance of the ultrathin TiN-based solar absorber, not only by engineering the components of the reactor, but also adjusting the thickness of the absorber itself and of water. Our work opens to fast water evaporation dynamics, which is relevant not only for solar steam generation, but also for nano-optofluidics, confined chemical reactions, sensing, fast phase separation, and smart surfaces.

4. Experimental and Numerical Methods

4.1. Samples preparation. TiN nanocavities were prepared according to the procedure reported in a previous work.[47] Briefly, 125- μm thick Ti plates (Goodfellow, England) were anodized to form TiO_2 nanocavities in a two-electrode electrochemical cell (Pt counter electrode) in a $\text{HF}/\text{H}_3\text{PO}_4$ solution[48,49] and, upon drying, thermally treated at 600 °C in NH_3 to convert them to TiN. Ti plate and TiNOX[®] Energy (Almeico GmbH, Germany) were cut in $\sim 1.5 \times 1.5 \text{ cm}^2$ pieces and ultrasonically cleaned in acetone, ethanol and deionized water before experiments.

4.2. Materials characterization. The morphology of the studied materials was investigated by scanning electron microscopy (SEM, Hitachi FE-SEM 4800) and high-resolution transmission electron microscopy (HRTEM, Titan G2). The chemical composition was analyzed by energy-dispersive X-ray spectroscopy (EDS) in scanning TEM mode (STEM) using the Super-X system with four silicon drift detectors (Bruker). STEM images were taken with a high-angle annular dark-field imaging (HAADF) detector (Fischione, model 3000). TEM lamella was prepared with a FEI Helios Focused Ion Beam/SEM (Thermo Scientific).

The crystalline structure of the studied materials was investigated by X-ray diffraction (XRD) using a high-resolution X-ray powder diffractometer (PANalytical X'Pert Pro MPD) with $\text{Co K}\alpha$ radiation ($\lambda = 0.1789 \text{ nm}$). The measurements were performed in grazing incidence geometry ($\omega = 3.6^\circ$) in a 2θ range of 25° – 85° with a step size of 0.016° and a time step of 40 s.

The optical properties of the materials in air were investigated by reflectance spectra measured with a PerkinElmer Lambda 950 spectrometer equipped with an integrating sphere.

4.3. Numerical simulations. A multiphysics and multiscale approach was necessary to account for all phenomena triggered by Sun-like illumination and inducing water-to-vapor conversion. A finite-element-method (FEM) based model was developed using a commercial software

(COMSOL Multiphysics 5.4) to simulate all processes occurring in the experimental system. First, a full-vectorial three-dimensional electromagnetic problem was numerically set to estimate the absorption of radiation in a hexagonal array of TiN nanofurnaces. With this information at the nanoscale, light-induced dissipation in the macroscale sample was evaluated and the thermal modelling of the experimental structure was subsequently addressed. To do so, a simulation coupling laminar flows (for the natural convection in water and air), diffusion (for the water vapor concentration at the water/air interface) and thermal transport (for the heating of the whole structure) was settled. Dissipation contributions produced in the TSA sample itself, water, the PTFE cell and the lens respectively upon Sun-like illumination were accounted for. Moreover, due to the highly scattering nature of the PTFE cell, a thorough estimation of the actual amount of radiation exciting each component was necessary. Thus, a FEM-based Monte Carlo-like approach was developed to quantify, on the one hand, the percentage of incoming photons which effectively excite the TiN nanostructures, and, on the other hand, the effective length of the average trajectory of photons in the water reservoir. A detailed discussion of the modelling approach pursued in each of its part is reported in the Supporting Information (Notes S1–S6).

4.4. Water evaporation experiments. The reactor consisted in a PTFE cell made of two parts to allow a firm positioning and an efficient thermal insulation of the sample: a top part ($4.4 \times 4.7 \times 1.7 \text{ cm}^3$) with a 1 cm-diameter through-hole in the middle, as cylindrical water reservoir, and a bottom part ($4.4 \times 4.7 \times 2.0 \text{ cm}^3$). The sample was centered along the water container and positioned in the PTFE cell, together with a type K thermocouple (RS PRO, 0.075 mm diameter). The PTFE cell was then placed on a high-precision analytical balance (Kern & Sohn GmbH, 0.1 mg accuracy) and 800 μL (800 mg) of deionized water were inserted in the water reservoir. Afterwards, light under a 1000 W solar simulator (Sciencetech A4 Lightline C250) equipped with

an AM 1.5G filter and the light spot was focused with a Fresnel lens (Thorlabs FRP251) on the top surface of the PTFE cell to match the diameter of the water reservoir. The light intensity was measured prior to experiments by a thermopile power meter (Standa 11UP19K-30H-H5).

Appendix A. Supporting Information

Supplementary data associated with this article can be found in the online version at...

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Author Contributions

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Declaration of Interests

L. M., P. S., R. Z., Š. K., and A. N. are coinventors on the provisional patent application relating to the research presented in this paper.

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