

Supporting Information

Metasurface Photoelectrodes for Enhanced Solar Fuel Generation

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S1 – Fabrication of Single Disks and Arrays

A film of 100 nm a-GaP is RF sputtered with a rate of 1 Å/s from a GaP target onto a SiO₂ substrate, which is heated to 350 °C during the deposition. In the case of the 2D arrays, 100 nm ITO is RF sputtered with a rate of 0.5 Å/s at 350 °C from an ITO target prior to the a-GaP. In both cases, the chamber pressure is $< 10^{-7}$ mbar with an Ar flow of 20 sccm. For nanostructuring the film into single disks and 2D arrays we used a negative resist (ma-N 2403, Microresist, spin speed 3000 rpm), electron beam lithography (acceleration voltage 20 kV, aperture 10 µm), development (ma-D 525, Microresist) and subsequent ICP-RIE etching (Oxford Instruments, Plasma Pro 100). The process gases are Cl (10 sccm) and Ar (30 sccm) at a chamber pressure of 2 mTorr. The plasma is ignited by 300 W RF and 31 W ICP power. Finally, the resist mask was removed in a wet etching step (mr-Rem 700, Microresist) and the sample was cleaned in acetone and isopropanol.

S2 – Methods for Optical Characterization

The dark-field spectra of the single nanodisks are measured with a WiTec microscope in reflection using a dark-field objective (100x, NA = 0.9, Zeiss, Germany) and a halogen lamp. For transmission spectroscopy on the 2D arrays, the sample was illuminated by a nearly collimated halogen lamp (OSL2, Thorlabs) from the bottom, also using a WiTec microscope. The transmitted light was collected with a 10x objective (Olympus, NA = 0.25) and normalized by the lamp spectrum taken from the ITO/SiO₂ background. The reflectance spectra of the metasurface were measured with the same objective and a halogen lamp and the normalization spectrum were taken with an Ag mirror (Thorlabs PF20-03-P01).

S3 – FDTD-Simulations

The simulations were carried out with Lumerical FDTD-solutions. For the single particle analysis a disk with $r = 130$ nm and $h = 100$ nm was placed on a SiO₂ substrate ($n = 1.4$) using a mesh size of 5 nm. The scattering cross-section was calculated with the total-field-scattered-field analysis tool employing a plane wave source from the top. The particle absorption spectra were simulated with a power absorbed monitor that encloses the disk and also enables the display of the absorption profile. The electric near-fields, also used for the multipolar decomposition (S6) were obtained from a 3D frequency domain field profile monitor, also enclosing the disk.

For the simulation of the metasurface a 100 nm layer of ITO (complex refractive index shown in S14) was added between the disk and the SiO₂ substrate together with periodic boundary conditions in x - and y -direction. The transmission (T) and reflection (R) was obtained from two frequency domain field and power monitors and the absorption (A) is calculated by $A = 1 - T - R$.

S4 – Nanoimprint Stamp Fabrication

The master stamp is fabricated from a piece of Si wafer with 200 nm layer of thermal SiO₂ (Fig. S4a). After spin-coating a 260 nm layer of PMMA 950k A4 the sample is exposed to electron beam lithography using an acceleration voltage of 20 kV and 30 μ m aperture, that facilitated sufficient lateral resolution and a writing time of 50-60 h. The sample is then developed in MIBK:IPA (3:1) for 60 s and consecutively rinsed with IPA for 30 s. A 25 nm layer of Chromium is deposited on the sample by thermal evaporation and lifted off in acetone to generate a robust mask for the subsequent ICP-RIE etching with CHF₃/Ar plasma, achieving a SiO₂ pillar height (etching depth) of $d \approx 190$ nm. Ultimately, the residues of the Cr mask are removed in a 5 min Sigma Aldrich Cr etchant bath (KMnO₄ based) and the sample is cleaned with IPA and N₂ dry blowing. SEM images of the as-fabricates stamp are shown in Figure S4b.

The goal of the imprint process is to generate a resist pattern that is used as a mask for a subsequent dry etching process to pattern the a-GaP layer. As the dry etching process will transfer the pattern of the resist into the a-GaP we need to fabricate pillars of resist on top of the a-GaP film. However, an imprinting process with the as-fabricated master stamp would generate a hole pattern in the resist instead of pillars. Therefore, we need to *invert* the structure of the stamp before the imprinting process. We conduct a replication process using OrmoPrime®, a commercial UV-curable hybrid polymer (Micro resist technology GmbH, Berlin). With the replication process we produce semiflexible pattern-inverted working stamps for the imprinting process.^[1]

For the imprinting process we apply a thin layer of mr-I8020 (Micro resist technology GmbH, Berlin) imprint resist onto our substrate via spin coating. To achieve the best results for our geometry the imprint resist layer has a thickness of 50 nm. During the imprinting process, the substrate with applied working stamp is first heated to 165 °C. This temperature is above the resist's glass transition temperature of 115 °C, which allows the resist to become viscous. Now, the stamp is pressed into the resist at a pressure of 30 bar for 3 min. Afterwards, still under pressure, the sample is cooled to 90 °C to solidify the resist again. After the pressure is released, the stamp is carefully removed from the sample. The pattern is now transferred from the stamp into the imprinting resist and the sample is ready for dry etching.

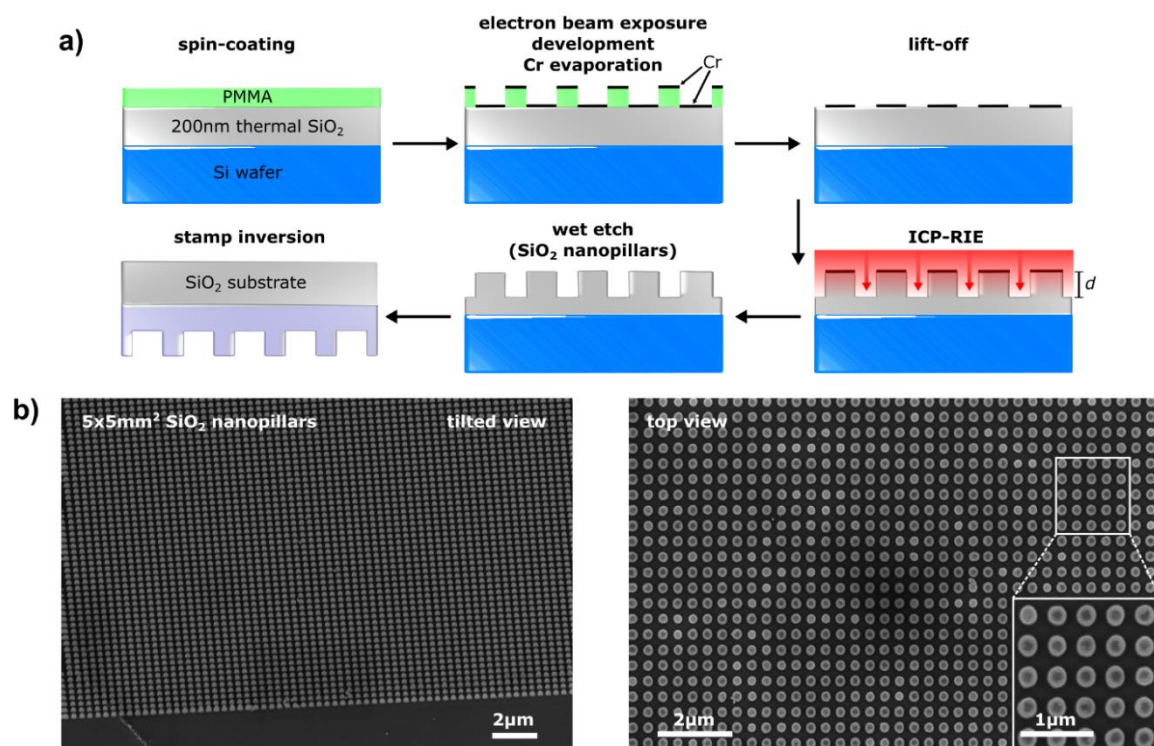


Figure S4. a) Scheme of nanoimprint stamp fabrication procedure. The SiO_2 pillar height (etching depth) is denoted as d . b) SEM images of the as-fabricated master stamp (SiO_2 nanopillars) in tilted and top view.

S5 – Metasurface Transmission under Variation of the Angle of Incidence

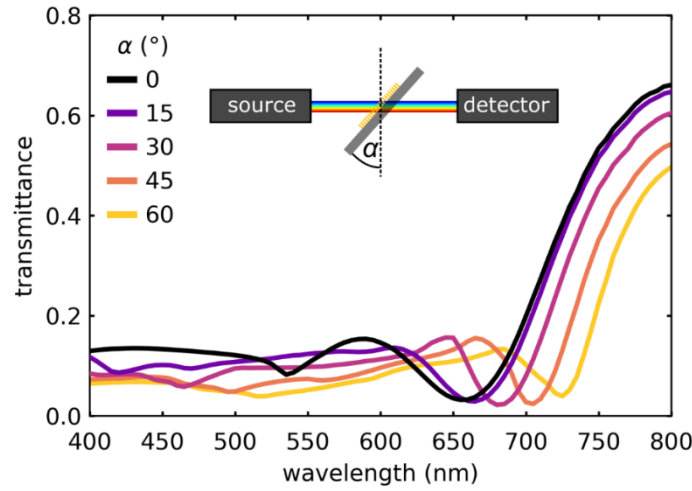


Figure S5. Transmission through the metasurface under variation of the angle α between normal incidence and sample rotation. The LR redshifts with increasing angle of incidence.^[2] However, $\alpha > 45^\circ$ is required to push the transmission minimum above 700 nm, which is a typical benchmark for minimum photon energy required for solar water splitting.^[3] This good spectral robustness over 90° of total angle of incidence makes this metasurface design attractive for solar energy harvesting without the need of costly tracking systems.

S6 – Multipolar Decomposition of Fundamental Mie-Modes

To investigate the LR-assisted absorption enhancement a multipolar decomposition was carried out from the simulated, internal electric fields of a single and an embedded nanodisk (Figure S6). The data suggest that the LR leads to a suppression of the electric dipole in the presence of the electric toroidal dipole, showing a reduced total far-field scattering and thus, a strong analogy to the AE. Therefore, we attribute the LR-assisted absorption enhancement to a lattice induced creation of a further non-radiative state with increased light confinement into the resonator, but a full understanding of this effect requires further investigations beyond the scope of our study.

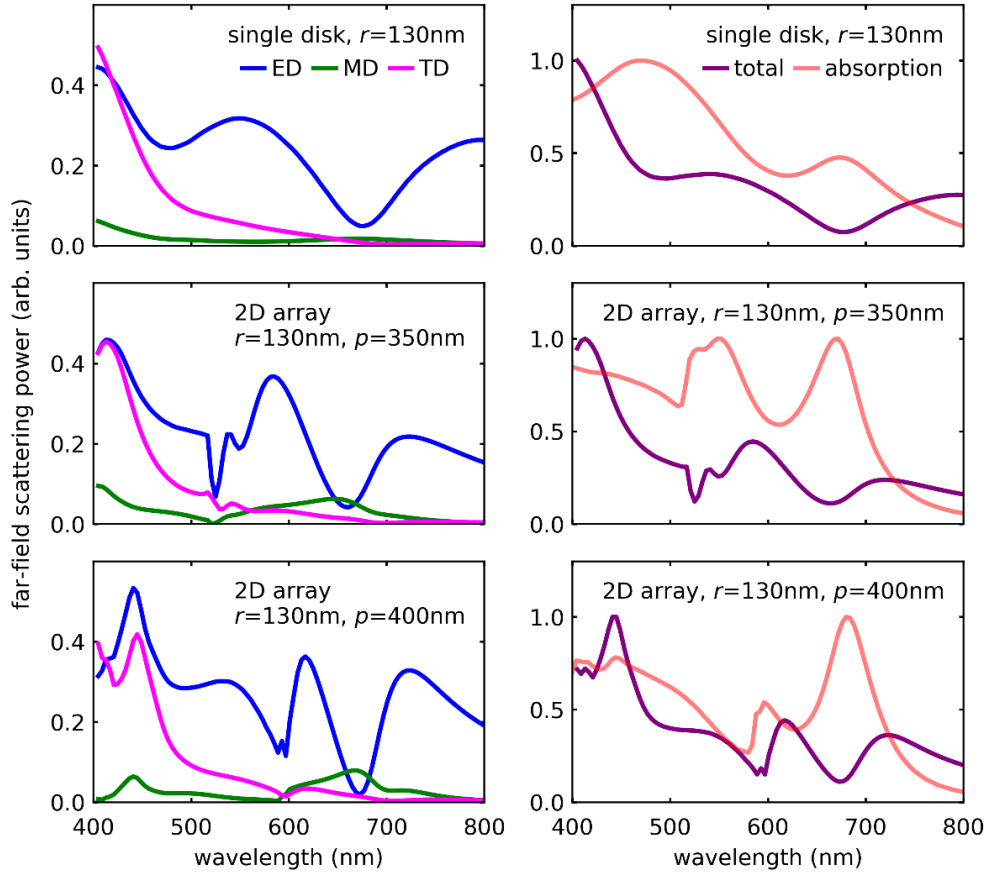


Figure S6. Left column: multipolar decomposition into far-field scattering power of fundamental Mie-modes electric dipole (ED), magnetic dipole (MD) and toroidal electric dipole (TD). From top to bottom: isolated a-GaP disk, single disk embedded in an infinite 2D array with $p = 350\text{ nm}$ and $p = 400\text{ nm}$. Right column: total far-field scattering power (ED+MD+TD) overlaid with the power absorbed by the disk, both are normalized to unity. The non-radiative excitations (minima of total) coincide with absorption maxima. The respective equations are taken from reference^[4], simulation details are given in reference.^[5]

S7 – Determination of the Doping-Type of a-GaP

The doping type of the GaP layer was determined by measuring its surface photovoltage (SPV) in a GaP/ITO/glass stack with the underlying ITO serving as an electrical contact to the layer. The measurement was carried out in air using a KPTechnology KP020 Kelvin probe system is equipped with an Au electrode. A 455 nm LED was applied to illuminate the sample. In order to determine the SPV, the contact potential difference was recorded in alternating periods of darkness and illumination. The SPV can be calculated by the negative difference of both values:

$$SPV = -\Delta CPD \quad \text{with} \quad \Delta CPD = CPD_{light} - CPD_{dark} . \quad \text{Figure S7 displays the CPD}$$

measurement. The CPD signal shows a decrease upon illumination corresponding to a positive SPV, which is indicative of an upward surface band bending due to the population of surface states, typically present in n-type semiconductors. Since the photon energy is well below the band gap of ITO of around 4 eV, measuring effects from the buried interface can be excluded.^[6] Furthermore, the relatively small SPV suggests a small excess carrier density in the material. We attribute this behavior to the unintentional inhibition of n-doping during sputtering of the material. Driving a bare GaP photoelectrode at anodic bias for the oxygen evolution reaction (OER), where n-doping is favorable, is reported to lead to rapid degradation due to the formation of Gallium Oxide and consequent blocking of charge carrier transfer to the electrolyte.^[7] Thus, for the sake of sample stability we drive the electrode at cathodic bias and examine the performance of the HER.

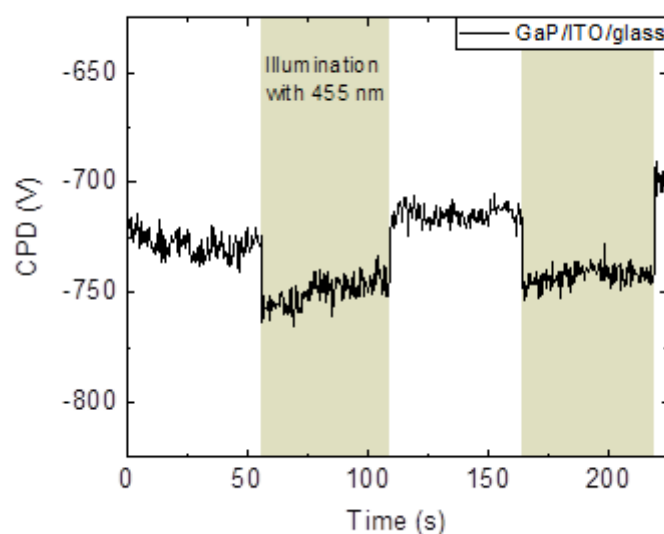


Figure S7. Contact Potential Difference (CPD) on an a-GaP/ITO stack as a function of time under alternating illumination with 455nm.

S8 – Stability of Bare a-GaP with Alkaline Electrolyte and Anodic Bias

While a-GaP in 1M KOH remained stable for 2h without any visible changes, cyclic voltammetry under anodic bias lead to immediate dissolution even with 0.1 M KOH and small anodic potentials of 0.1 V (vs. Ag/AgCl).

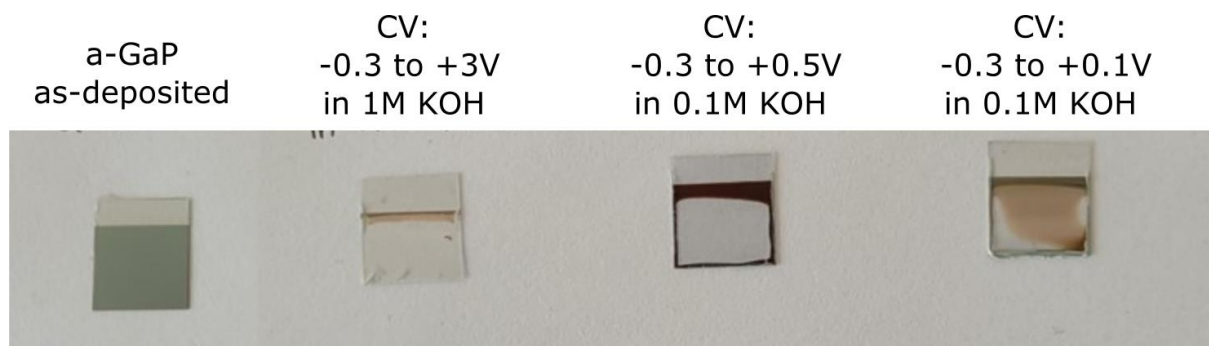


Figure S8. Photographs of a-GaP substrates after cyclic voltammetry (CV) in alkaline electrolyte with anodic bias. The dissolution occurred immediately when applying anodic potentials. All potentials are vs. Ag/AgCl reference electrode.

S9 – Stability of Metasurface under Constant Cathodic Bias

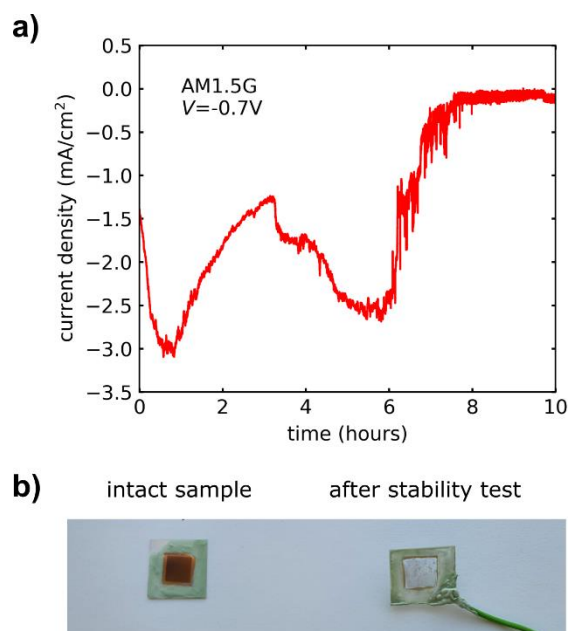


Figure S9. a) Chronoamperometric (I - t)-curves of a metasurface a-GaP photoelectrode with 15 Å Pt under AM 1.5G illumination and constant applied potential of -0.7 V vs. Ag/AgCl. b) Photograph of (left) intact sample and (right) sample after the stability test. Contact probe measurements on the used electrode showed no conductance on the previously active area. In contrast to voltage cycling, constant cathodic bias leads to degradation of the electrode after 6-7 hours. Despite the observed degradation, future integration of a corrosion protection layer provides a route to long-term operational stability.^[8]

S10 – Cyclic Voltammograms of Bare a-GaP

The bare a-GaP film on ITO is characterized by cyclic voltammetry under cathodic bias and illumination with different wavelength ranges. The photoresponse is considerably weak and high illumination powers are required to measure sizable photocurrents (Figure S10 and table), which is an indication for extremely short charge carrier diffusion lengths and lifetimes at the catalyst-electrolyte interface.

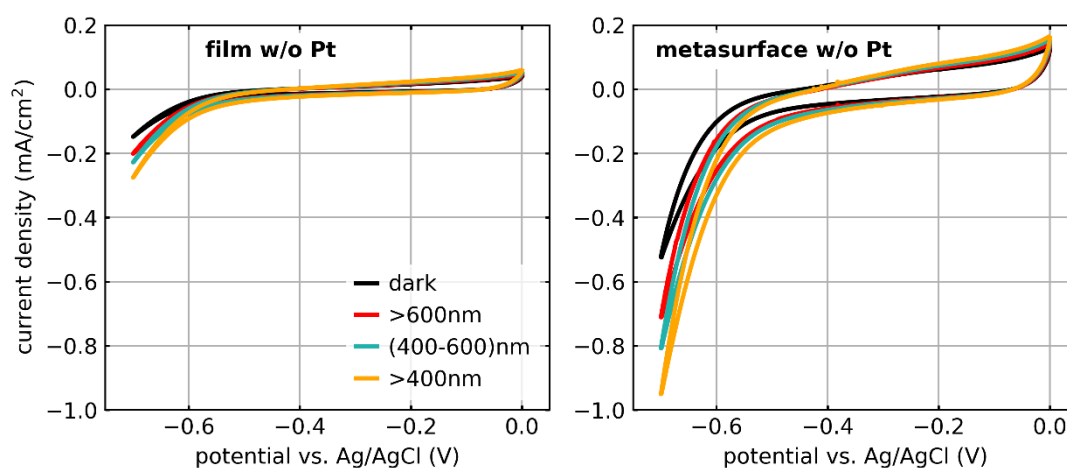


Figure S10. *I-V*-curves of the last out of ten cycles for the a-GaP film (left panel) and the metasurface (right panel) without the platinum co-catalyst. The lamp powers are listed in the following table and the same is used as in Figure 4b:

wavelength range (nm)	power density (mW/cm ²)
>400	1076
400-600	207
600-1000	780

S11 – Metasurface and Film Transmission with Platinum Coating

Because of the moderate photoresponse of bare a-GaP, we performed additional measurements using a co-catalyst by coating the metasurface and the flat film with a Pt layer of 15Å, which has only minor effects on optical properties of the metasurface (Fig. S11), but facilitates better electron transfer (Fig. S10).

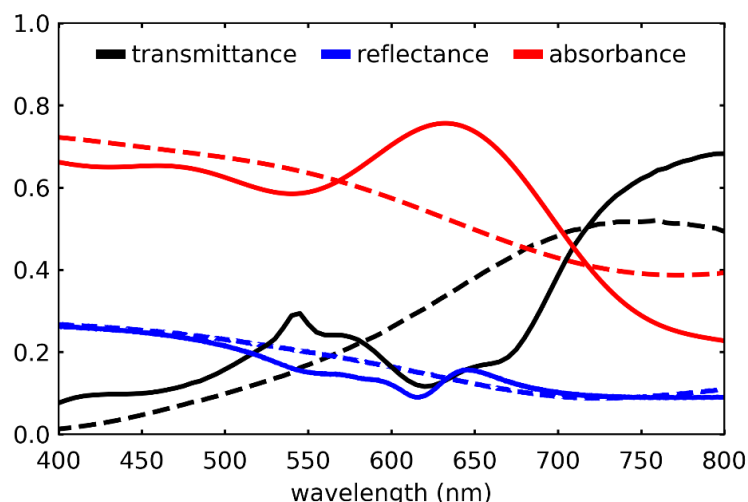


Figure S11. Transmittance, Reflectance and calculated absorbance ($T + R + A = 1$) of a-GaP film (dashed lines) on ITO and of the metasurface (solid lines) with 15Å Platinum as co-catalyst. For the metasurface, the Pt is sputtered on the a-GaP film before dry etching to guarantee that it is not in contact with the ITO and the Pt is located only on the top face of the disks. The Pt coating leads to a broadening of the resonances but maintains the optical characteristics of the metasurface.

S12 – Transmission Curves of Optical Filters in PEC Setup

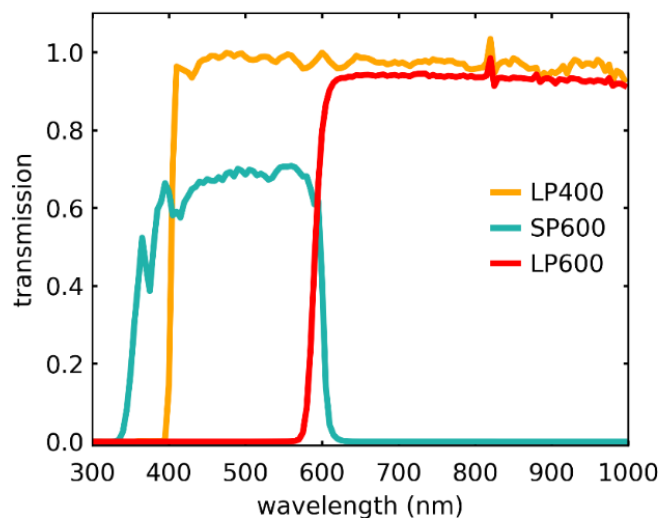


Figure S12. Measured transmission of the default 400 nm long pass (LP400), 600 nm short pass (SP600) and 600 nm long pass (LP600) filters.

S13 – Full Set of Cyclic Voltammetry of Photoelectrodes with Platinum

In the main text, Figure 4b presents the last cycle of voltammograms, from which the values are used to calculate the PEF and the MFE factors. Figure S13 shows the full set of 10 cycles for each measurement. The extracted values from the averaged current densities at -0.7 V are summarized in Table S13 together with the calculated photoenhancement factors (PEF).

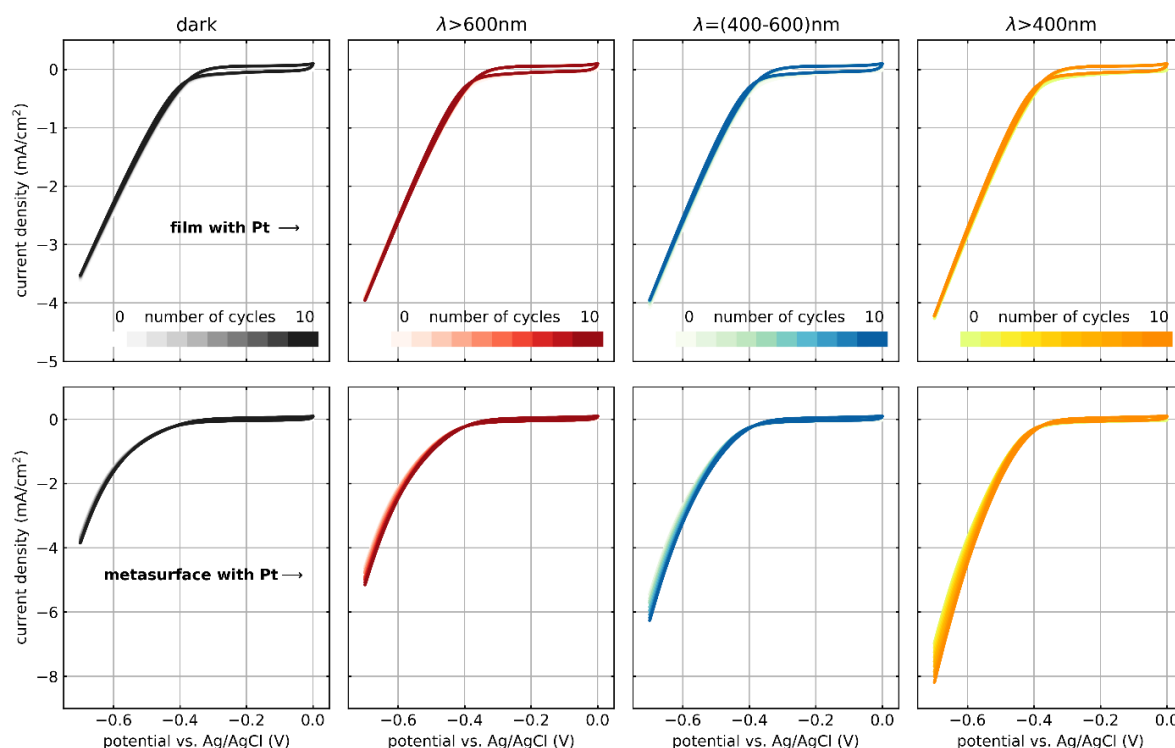


Figure S13. Cyclic voltammetry *I*-*V*-curves of the photoelectrodes with the a-GaP film (upper panels) and the metasurface (lower panels). The current is normalized by the active area of the electrodes immersed in the electrolyte. Each measurement consists of 10 cycles, the lamp powers are given in the table of section S10.

	film		metasurface	
spectral range (nm)	averaged current density @ -0.7 V (mA/cm ²)	PEF ($I_{\text{light}}/I_{\text{dark}}$)	averaged current density @ -0.7 V (mA/cm ²)	PEF ($I_{\text{light}}/I_{\text{dark}}$)
dark	-3.56	-	-3.73	-
>600	-3.93	1.10	-4.84	1.29
400-600	-3.98	1.12	-5.81	1.56
>400	-4.23	1.19	-7.50	2.01

Table S13. Extracted values for the calculation of the photo-enhancement factors (PEF).

S14 – Optical and PEC Characterization of ITO

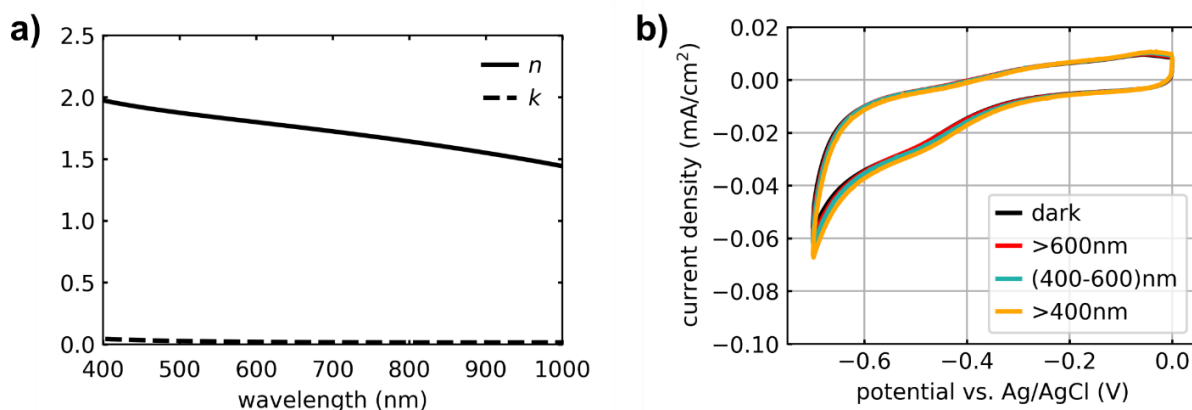


Figure S14. a) Spectral ellipsometry of 100nm ITO sputtered on SiO₂. b) Cyclic voltammetry of bare ITO in dark and highest illumination powers (table S10).

S15 – Power Dependence of Photo-Enhancement Factor of the a-GaP Film with Platinum

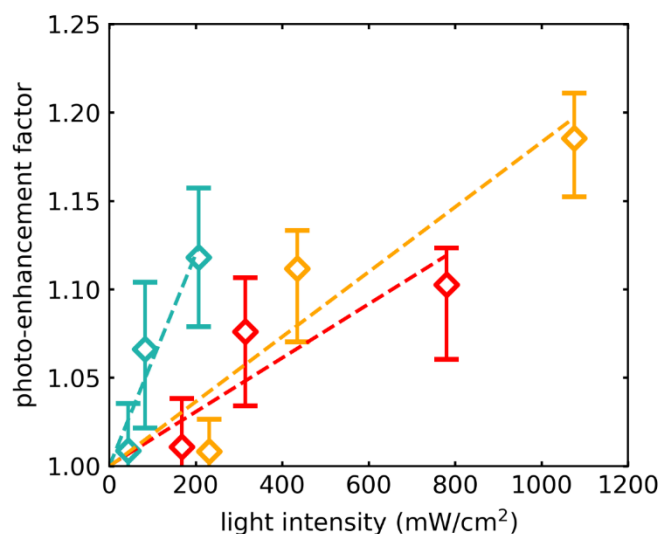


Figure S15. Power dependence of Photo-Enhancement Factor of the a-GaP Film with Pt. For the calculation, the same procedure as explained in Figures 4a-c is applied.

S16 – Cyclic Voltammograms of the Photoelectrodes under Simulated Solar Light

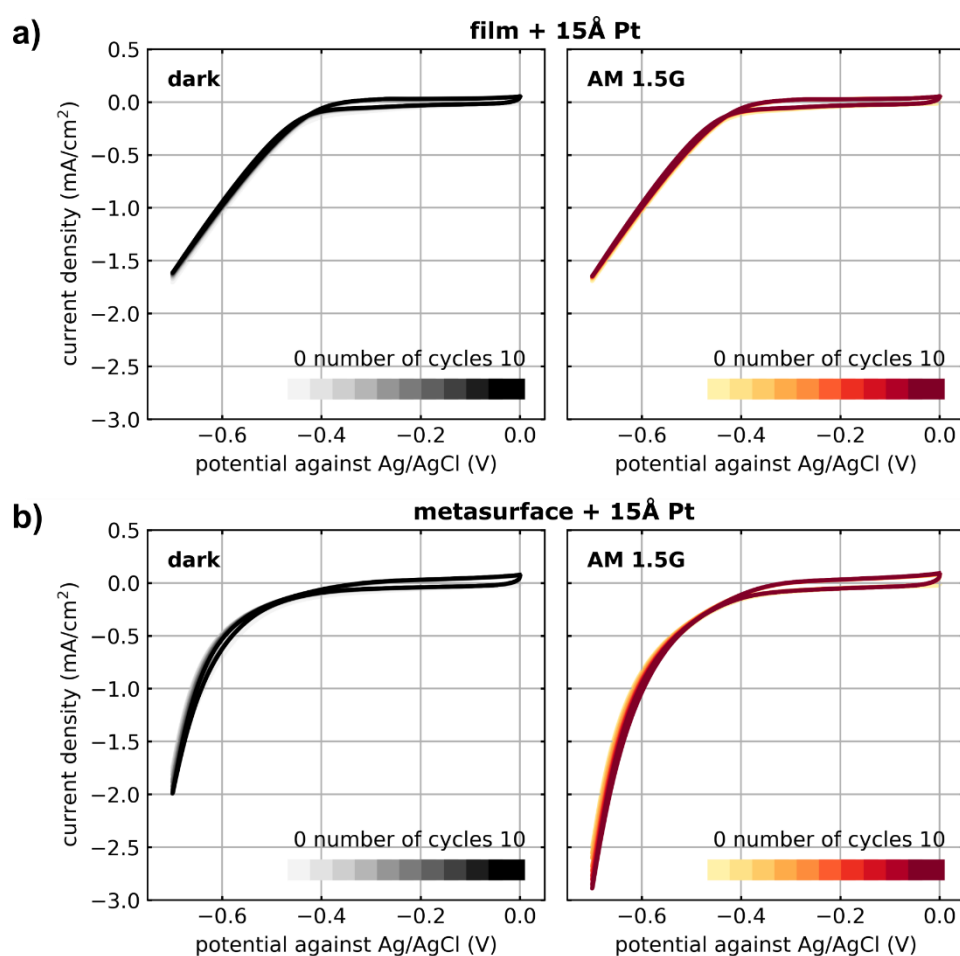


Figure S16. *I-V*-curves of with photoelectrodes with the planar a-GaP film (a) and the metasurface (b) in dark and under AM 1.5G illumination. The nanostructure provides a significant photoresponse by the material.

S17 – Narrow Band Width Chopped Light Chronoamperometry

To determine the incident photon-to-current conversion efficiency (IPCE) the current density of the electrodes with the Pt cocatalyst were measured under applied constant voltage of -0.7 V vs Ag/AgCl and chopped light from a 1000W Xe/Hg lamp with various band pass filters with a bandwidth of 10 nm (Newport 20BPF10). The chronoamperometric curves are shown in

Fig S17 a) for the planar film and b) the metasurface, from which the photocurrents were extracted. The IPCE is calculated by

$$IPCE(\lambda)[\%] = \frac{c \cdot h \cdot I_{ph}(\lambda)}{\lambda \cdot P_{light}(\lambda)} \times 100$$

with c , h , I_{ph} and P_{light} being the speed of light, the Planck constant in eVs, the photocurrent density and the irradiance of photons at the wavelength λ , respectively.^[9] The IQE is calculated by:

$$IQE(\lambda)[\%] = IPCE(\lambda)[\%]/absorbance(\lambda)$$

Since we are looking at the material operated as a cathode, there are only two possible reaction pathways: 1) HER and 2) photocorrosion. We have incorporated Pt catalyst, which overwhelmingly favors HER under the current testing conditions. We observe no evidence of photocorrosion during the short periods of measurement times.

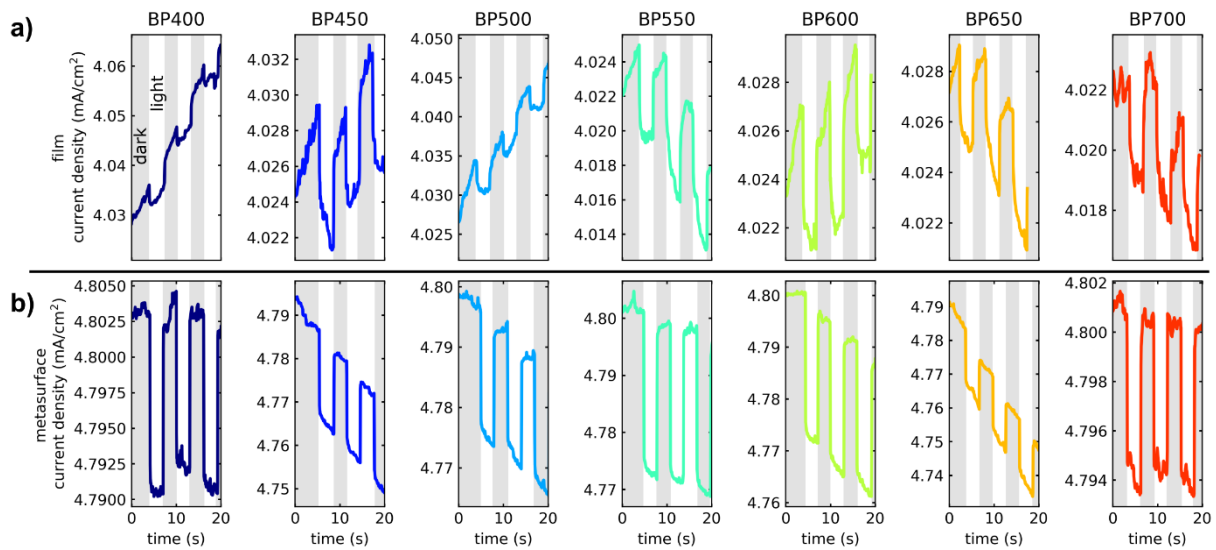


Figure S17. a, b) Chronoamperometric curves of the photoelectrodes (top film, bottom metasurface) under chopped light illumination with 10 nm bandwidth band pass filters (BP).

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