

Metasurface Photoelectrodes for Enhanced Solar Fuel Generation

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Tailoring optical properties in photocatalysts by nanostructuring them can help increase solar light harvesting efficiencies in a wide range of materials. Whereas plasmon resonances are widely employed in metallic catalysts for this purpose, latest advances of nonradiative, dielectric nanophotonics also enable light confinement and enhanced visible light absorption in semiconductors. Here, a design procedure for large-scale nanofabrication of semiconductor photoelectrodes using imprint lithography is developed. Anapole excitations and metasurface lattice resonances are combined to enhance the absorption of the model material, amorphous gallium phosphide (a-GaP), over the visible spectrum. It is shown that cost-effective, high sample throughput is achieved while retaining the precise signature of the engineered photonic states. Photoelectrochemical measurements under hydrogen evolution reaction conditions and sunlight illumination reveal the contributions of the respective resonances and demonstrate an overall photocurrent enhancement of 5.7, compared to a planar film. These results are supported by optical and numerical analysis of single nanodisks and of the upscaled metasurface.

1. Introduction

Broadband visible-near-infrared (NIR) light absorption is a key requirement for efficient solar energy harvesting by photocatalysts. The excitation of Mie-resonances in nanostructured photocatalysts is a promising route for trapping light in high aspect-ratio nanoparticles and provides three major advantages:^[1–6] First, Mie-resonances facilitate spectral enhancement of light absorption beyond the bulk property of the material. Second, in a sub-micrometer-sized particle, most absorption

volume is close to the surface, thereby reducing charge carrier recombination because the diffusion length from their excitation site to the catalyst-electrolyte interface is minimized.^[7] Third, nanostructuring of photocatalysts increases the surface area compared to a planar film, enabling denser loading of active sites per geometric area. Whereas dissipation losses in metals limit the efficiencies of plasmonic resonances, high refractive index semiconductor photocatalyst nanoresonators are capable of also supporting Mie-resonances in the form of electric and magnetic multipoles with negligible dissipation losses compared to metals.^[8–10]

Of particular interest are nonradiative excitations, such as the anapole, which lead to light confinement into the resonator and therefore high electromagnetic field strengths within the material.^[11–13] In this type of excitation, far-field scattering is minimized and

near-field energy inside the material reaches its maximum, making it particularly attractive, e.g., for photocatalytic applications. In a previous study, we demonstrated on the single particle level that resonant coupling of the anapole excitation wavelength to electronic transitions in substoichiometric TiO_{2-x} leads to enhanced electron-hole pair generation rates and catalytic yields under sub-bandgap excitation.^[14] The upscaling from single particles to periodic arrays is accompanied by the emergence of lattice resonances, regardless of their metallic or dielectric character.^[15–17] These effects are

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caused by the in-phase coupling of dipolar modes of closely spaced resonators and can be spectrally tuned by the array periodicity.^[18–21] These new collective resonances can be employed, e.g., to enhance the light harvesting and photocatalytic properties of materials. Indeed, this artificially engineered phenomenon gives rise to a new class of material—known as metamaterial or metasurface—in which the optical properties are derived by the periodic micro and nanostructuring more than the chemical nature of the material itself.^[22–24]

As a notable example, Deng et al. showed for a 2D array of metallic particles that the electric field enhancement of the lattice resonance provides a twofold catalytic activity improvement compared to the single-particle-localized surface plasmon resonance.^[25] Our group recently demonstrated for 2D arrays of dielectric resonators that the placement of the lattice resonance in the spectral vicinity of a single-particle anapole excitation causes a strong enhancement of the internal electric fields and thus, of the power absorbed by the material.^[26] This strategy for spectrally tunable light trapping facilitates the increase of the optical absorption range in semiconductor photocatalysts, which are typically characterized by weak absorption onsets in the visible and NIR range. However, quantification of the energy conversion enhancement associated with these photonic effects under realistic catalytic conditions remains a challenge due to the requirement of large active surfaces that provide measurable photocatalytic yields.

Here, we present photonically engineered, large-scale photoelectrodes with dielectric nanoresonators that exhibit a lattice resonance (LR) at 550 nm and an anapole excitation (AE) at 640 nm. As the photocatalytic material, we employ the high-index semiconductor amorphous gallium phosphide (a-GaP). This material was already subject of previous studies by our group, with ellipsometric and XRD characterization reported in references.^[26,27] For electrical contact, the a-GaP is deposited onto a 100 nm thick layer of indium tin oxide (ITO) on an a-SiO₂ substrate. We first demonstrate the spectral tuning of the AE and LR on single particles and 20 × 20 rectangular arrays, both fabricated by electron beam lithography. In a next step, we upscale the optimized array to a 5 × 5 mm² metasurface using nanoimprint lithography, which facilitates cost-effective, high throughput, and large-scale nanofabrication. The functional characteristics of the metasurface are then investigated in a three-electrode photoelectrochemical (PEC) reactor by measuring the enhanced photocurrent density in comparison to a planar a-GaP film under hydrogen evolution reaction (HER) conditions. By illuminating the metasurface with light within different spectral ranges, the AE and LR are independently excited, thus allowing quantification of their individual contributions to the overall photocurrent enhancement under AM 1.5G solar light illumination conditions.

We demonstrate that photonic engineering by itself can remarkably enhance—by more than five times—the photon-to-electron conversion efficiency in semiconductors. Our study presents an approach for bridging the gap between single-particle photonics and nanoengineering for upscaled solar energy conversion devices by merging concepts of nonradiative nanophotonic metasurfaces and state-of-the-art large-scale nanofabrication techniques. We demonstrate that nanophotonic engineering can enhance the solar light-harvesting possibilities of a broad range of

semiconductors and can be easily coupled to other optimization strategies to significantly improve photoelectrodes efficiencies.

2. Results and Discussion

2.1. Tuning of Single Particle and Lattice Excitations

The AE is a nonradiative state of optical excitation typically observed in flat nanodisks of high index dielectrics.^[28] Its characteristic features are a minimum in far-field scattering and maximum of electrical energy density inside the resonator at the excitation wavelength, λ_{AE} , which is why it has been intensively studied for higher harmonic generation.^[12,29,30] To employ the AE for absorption enhancement, λ_{AE} needs to be within the lossy regime of the resonator material.^[14] For identification of the AE in single particles, an ensemble of nanodisks with height $h = 100$ nm and increasing radius r was fabricated from an a-GaP film on SiO₂ by electron beam lithography (Section S1, Supporting Information), a scanning electron microscope (SEM) image of which is shown in **Figure 1a**. The disks, which are separated by 2 μm to avoid interparticle coupling, are optically characterized by dark-field spectroscopy and corresponding finite-difference time-domain (FDTD) simulations, as shown in **Figure 1b**. A detailed description of experimental conditions and simulation is provided in the Supporting Information Sections S2 and S3. The AE-related scattering minimum redshifts as the disk radius is increased from 130 to 145 nm. The agreement of this trend with the simulations motivates further analysis of the internal fields of the resonator at λ_{AE} . **Figure 1c** (left panel) shows the characteristic intensity profile of the AE at $z = h/2$ under x -polarized illumination for a disk with height $h = 100$ nm and radius $r = 130$ nm. By depolarizing the illumination $|E|_{\text{depol}}^2 = \frac{1}{2}(|E|_{x\text{-pol}}^2 + |E|_{y\text{-pol}}^2)$ to create an illumination condition resembling realistic device operating conditions, the light confinement into the resonator manifests in an even more obvious manner through the intensity maximum in the center (middle panel). Because the AE is driven in the lossy regime of the a-GaP $\text{Im}\{\tilde{n}(\lambda = \lambda_{\text{AE}})\} > 0$, the intensity profile can be recalculated to quantify the absorbed power profile $a(\lambda_{\text{AE}}, x, y, z = 50 \text{ nm})$ using the equations given in reference^[26] with the boundary conditions of zero absorbed power outside of the disk and maximum absorbed power at the center of the disk. Integrating $a(\lambda, x, y, z)$ over the disk volume results in absorbed power spectra $A(\lambda)$, which are plotted together with the simulated scattering in **Figure 1b**. This presentation reveals that the scattering minimum at λ_{AE} is coincident with an absorption maximum due to coupling of the AE to the amorphous tail states in the a-GaP, effectively creating a strong edge over an extended spectral range.

The single-particle analysis highlights that the AE-assisted absorption enhancement within the spectral regime of weak losses of the employed material can be tuned by varying the disk radius r . On the road to upscaling and to guide the choice of the nanoimprint stamp design, a multitude of rectangular arrays of 20 × 20 a-GaP nanodisks with similar r to the single particles discussed above but with varying center-to-center distance p (pitch) was investigated. The nanodisk arrays were fabricated by electron beam lithography from a

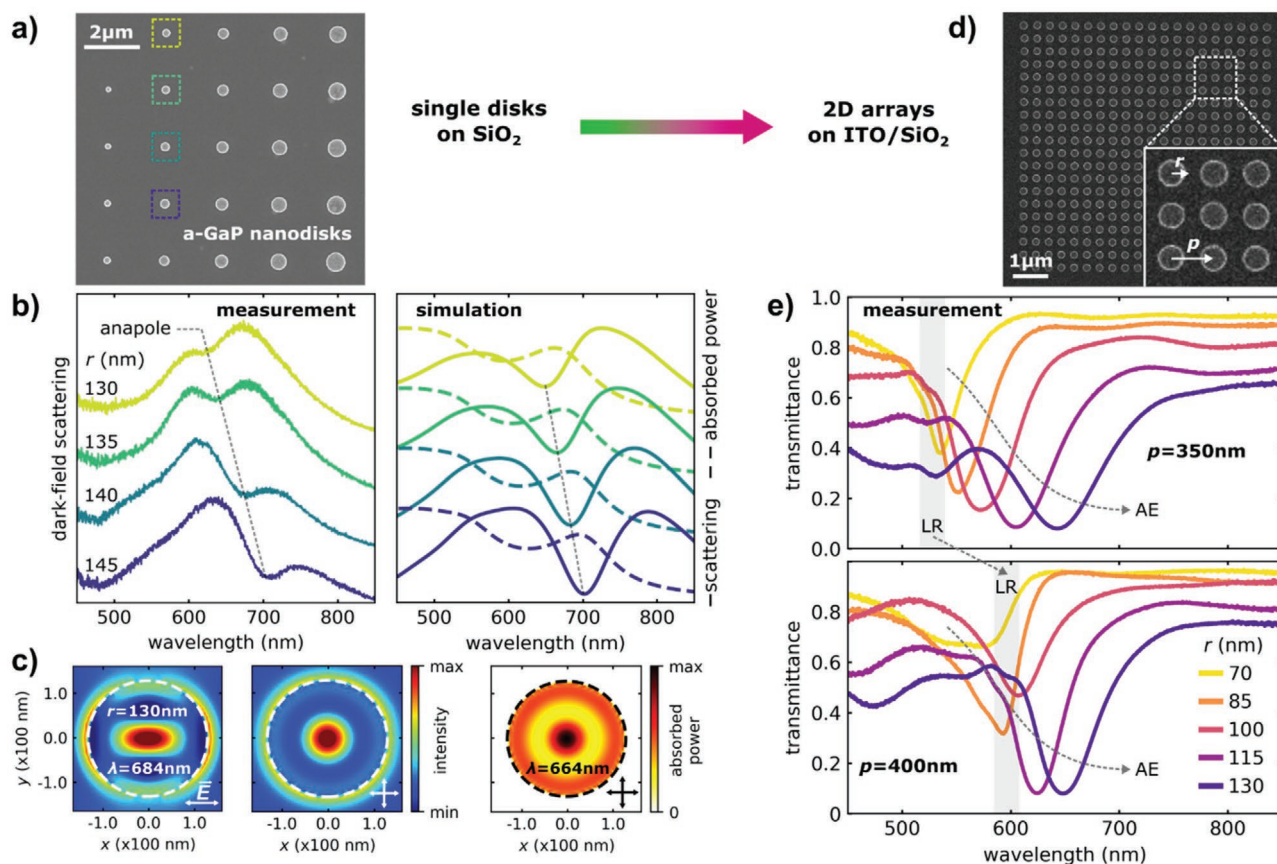


Figure 1. a) SEM image of single, uncoupled a-GaP nanodisks with increasing radius from top to bottom and left to right. b) Comparison between dark-field scattering of single disks, indicated by the dashed boxes in (a), with FDTD simulations of scattering and absorbed power represented by solid and dashed lines, respectively. c) Near-field analysis of a nanodisk with radius $r = 130$ nm. Typical electric near-field profile of the AE with x-polarized light (left) changes under light depolarization (middle) and converted to the absorbed power profile (right). Most light is absorbed in the center of the disk. d) Rectangular array of nanodisks with $r = 130$ nm and pitch $p = 400$ nm. e) Series of transmission spectra of arrays with $p = 350$ nm and 400 nm with several different values of r . The anapole excitation (AE) is tunable by r and the lattice resonance (LR) by p .

sputtered film stack of 100 nm thick a-GaP on 100 nm thick ITO on an a-SiO₂ substrate (Section S1, Supporting Information). An SEM image of an exemplary array is presented in Figure 1d. The array sizes are sufficiently large to show clear signatures of collective interaction effects of the single particles, which are observed in the optical transmission measurements displayed in Figure 1e. The upper panel shows the series of spectra from five individual arrays with different r , each having the same $p = 350$ nm. As explained above, the AE-related transmission minimum (i.e., absorption maximum) redshifts with increasing r , but with lower total absorption at smaller r due to decreased areal coverage (i.e., filling factor) by a-GaP within the array. In addition, a radius-independent transmission minimum arises at 525 nm, which we assign to the emergence of a lattice resonance (LR). The lower panel of Figure 1e) shows transmission spectra of arrays with the same variation of r , but $p = 400$ nm. The LR redshifts to 600 nm, whereas the positions of the AE-related transmission minima remain nearly unchanged.

Based on this analysis, we chose to fabricate the nanoimprint stamp with the parameters $r = 130$ nm and $p = 350$ nm for the following reasons: First, this configuration separates the

AE and the LR, which reduces their spectral overlap and facilitates independent measurement of the respective contribution of each to the photocatalytic enhancement. At the same time, a larger spectral range for solar light harvesting is covered. Second, larger values of p and/or smaller values of r reduce the filling factor of the metasurface, thereby reducing the overall absorption. Third, smaller values of p compromise the nanoimprint stamp fabrication due to proximity effects during electron beam exposure.

2.2. Nanoimprint Fabrication

After determination of the metasurface parameters on small-scale arrays, the nanoimprint stamp was fabricated using a Si wafer and electron beam lithography. Supporting Information Section S4 provides additional details of the stamp fabrication and the imprint procedure. Although electron beam writing for a high-resolution surface with a total area of 5×5 mm² is time consuming, high sample throughput and excellent reproducibility are achieved once the reusable stamp is produced. A scheme of the imprint procedure is shown in Figure 2a.

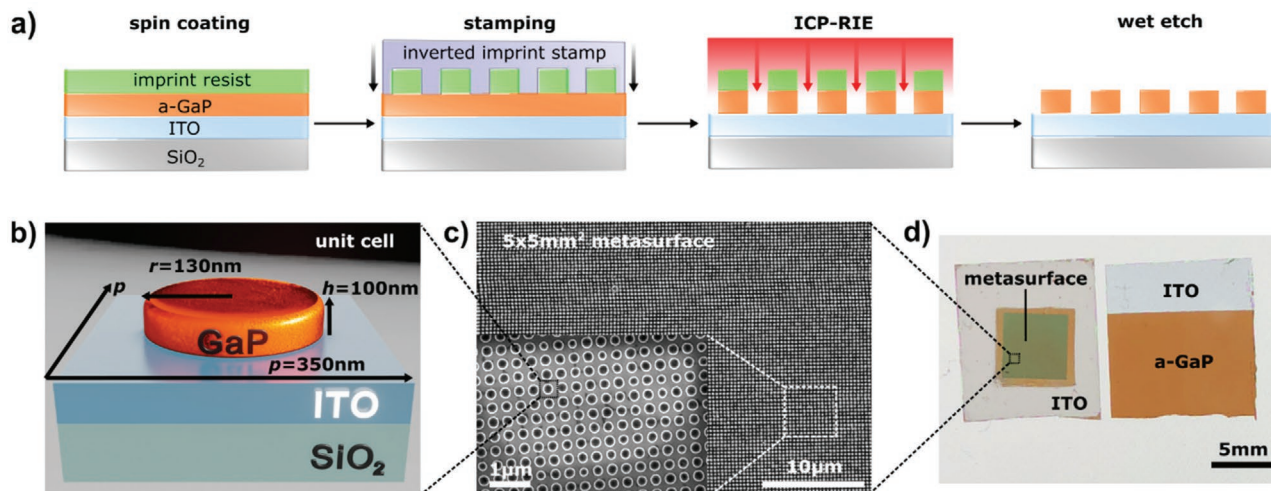


Figure 2. a) Fabrication procedure of a-GaP metasurface with nanoimprint lithography. The imprinted polymer structure is used as the etching mask. b) Scheme of the metasurface unit cell. c) SEM image with different zooms into the large-scale nanostructure. d) Photograph of the photoelectrodes with the imprinted metasurface on the left and a 100 nm thick continuous a-GaP film, both on top of a 100 nm thick layer of ITO.

After spin-coating of the imprint resist, the inverted stamp is pressed onto the sample and leaves a polymer mask with height of ≈ 180 nm. This relatively large thickness enables the use of the polymer itself as etching mask, which significantly reduces the temporal and resource expenditure for the metasurface fabrication. Finally, the residues of the polymer mask are removed in acetone and isopropanol. Figure 2b–d displays a zoom-out series of images from small to large dimensions, beginning with a scheme of the unit cell of the metasurface illustrating the parameters that are critical for its optical properties, i.e., height, radius, and pitch. The SEM images (Figure 2c) demonstrate the high homogeneity of the nanostructure, with only minor fabrication defects. In particular, small variations of r among the disks are caused by irregularities of the stamp itself (Supporting Information Section S4). The photograph in Figure 2d shows the as-fabricated metasurface photoelectrode next to a continuous film of a-GaP. After dry etching, the ITO is exposed around the edges and is used as the back contact for both types of electrodes.

2.3. Mode Analysis of the Metasurface

The metasurface was characterized by optical transmission and reflection spectroscopy (Supporting Information Section S2). Figure 3a shows the transmission, reflection, and absorption spectra of the metasurface on 100 nm thick ITO. The LR and AE signatures are pronounced at 550 and 640 nm, respectively, and provide an enhanced extinction across the terrestrial solar spectrum, which is indicated by the gray line. The LR is within the spectral range of 400–600 nm and the AE is covered by $\lambda > 600$ nm, depicted by the turquoise and red shaded areas, which will be used for the later PEC measurements. Particularly instructive for real device applications, the combination of the LR and AE enables a robust suppression of transmission with variation of the angle of incidence (Supporting Information Section S5). The results verify that the optimized 2D array

was successfully upscaled with excellent reproduction of its optical properties.

For a thorough analysis of the internal fields of the nanodisks embedded in the metasurface (infinite array), FDTD-simulations were performed (Supporting Information Section S3). The calculated transmission, reflection, and absorption spectra are presented in Figure 3b. The results provide good agreement with the experimental data (Figure 3a). The sharp transmission minimum at 520 nm is attributed to a simulation artifact, which was also previously encountered in infinite array simulations with a plane wave source at normal incidence^[26] and is not present in the measurements. We assign the transmission minima at 550 and 660 nm to the measured signatures of the LR and AE, respectively, and conclude that they are caused by maxima of absorption. Figure 3c shows the absorbed power profiles of a nanodisk embedded in the metasurface at the LR and AE wavelengths in top view ($z = h/2$) and side view ($y = 0$ nm) for depolarized excitation, which reveal distinct characters. Whereas at AE, the absorption region is located in the lower, center part of the disk, the LR promotes absorption hotspots at the top face and the edges, which is beneficial for optical excitation of the near-surface volume of the a-GaP. A deeper analysis to investigate the origin of the absorption enhancement by the LR is given in the Supporting Information Section S6.

2.4. Photoelectrochemical Characterization

Having characterized the fundamental optical characteristics of a-GaP metasurfaces, we prepared photoelectrodes from the nanoimprinted samples and investigated their PEC performance in comparison to flat a-GaP films for the HER. As discussed above, a-GaP is very well suited for photonic engineering of the metasurface. In addition, although crystalline GaP is a well-known photoelectrode material for solar water splitting and carbon dioxide reduction,^[31–34] a-GaP has not been investigated in detail. Prior to the characterization, we thoroughly

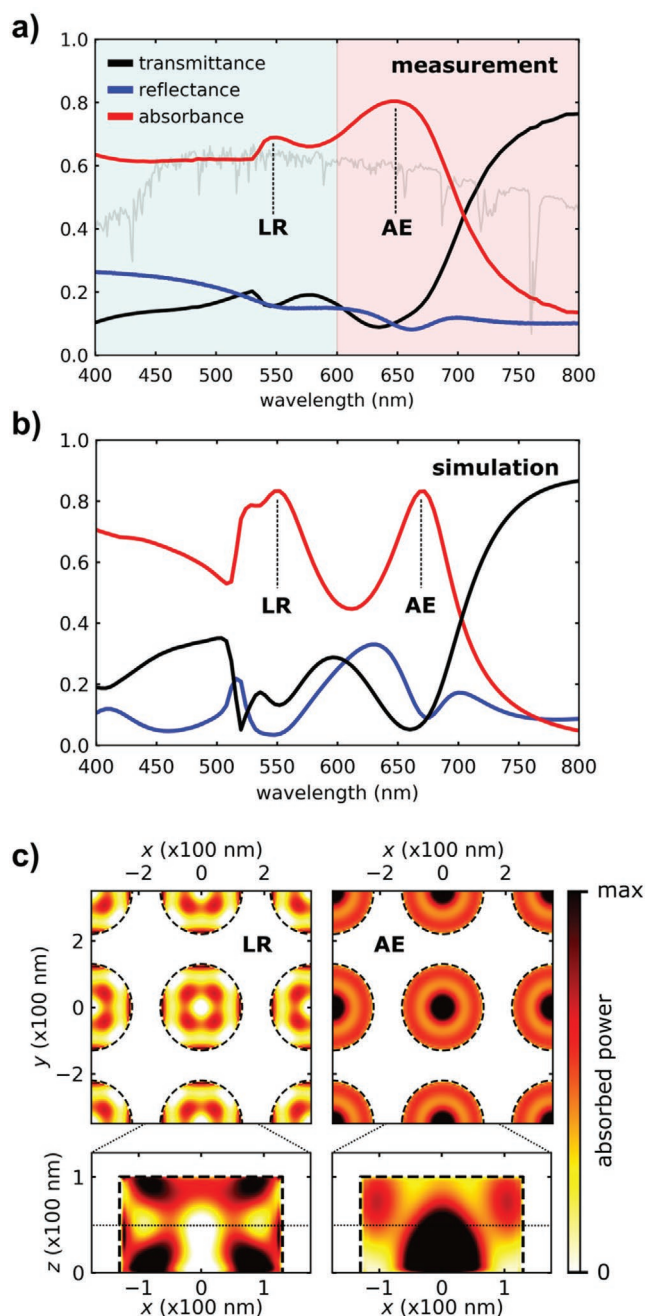


Figure 3. a) Measured transmission, reflection, and absorption spectra of the metasurface. The turquoise and red shaded areas indicate the spectral regions for covering the LR and the AE. The gray curve represents the terrestrial solar spectrum. b) Corresponding simulation of transmission, reflection, and absorption by an infinite array. c) Color maps of the absorbed power profile in the nanodisks as horizontal and vertical cross-sections for the LR (left) and AE (right).

evaluated the suitability of our a-GaP for the oxygen and hydrogen evolution reaction, OER and HER, respectively. Surface photovoltage measurements revealed that the a-GaP shows weak, but measurable upward band bending that is characteristic of unintentional n-type doping (Supporting Information Section S7). Therefore, our a-GaP should be more advantageous

for the OER, since n-doping leads to internal electric fields that drive the drift of electrons (holes) away from (toward) the solid/liquid interface.^[35] However, measurements performed on flat films with alkaline electrolyte (1 M and 0.1 M KOH) under anodic bias lead to rapid dissolution of the a-GaP, whereas the a-GaP remained stable with acidic electrolyte (1 M HClO₄) under cycled cathodic bias for several hours (Supporting Information Sections S8 and S9). Hence, in order to clearly evaluate the contributions of the AE and LR for photocatalytic reactions under stable conditions, we decided to study the HER and compare the photocurrent enhancements relative to a bare a-GaP film grown under the same conditions. Although the unintentional n-doping is not favorable for the HER, the approach can be further adapted to intentionally doped GaP films or other high refractive index semiconductors. Thus, our experiments provide valuable insights for the optimization of photocatalytic reactions by photonic engineering. The PEC characteristics of bare a-GaP films and metasurface are presented in the Supporting Information Section S10. To improve the photoreponse of the material, we additionally use a 15 Å Pt layer as HER catalyst, which has minor effects on the optical properties (Supporting Information Section S11).

Figure 4a shows the three-electrode photoelectrochemical setup comprising a reactor filled with the electrolyte (1 M HClO₄), a Ag/AgCl reference electrode (3 M KCl), and a Pt mesh counter electrode. The working electrode, i.e., either the a-GaP film or the metasurface, was contacted via the ITO, while the ITO exposed to the electrolyte was passivated with a nonconductive lacquer. The working electrode was illuminated by a Hg/Xe lamp with a 400 nm long pass filter to block out the UV spectral region, as well as exchangeable short and long pass filters (Supporting Information Section S12). The respective lamp powers are given in the Supporting Information Section S10. The wavelength ranges cover either the AE ($\lambda > 600$ nm, red) or the LR ($400 \text{ nm} < \lambda < 600$ nm, green) or both ($\lambda > 400$ nm, white). For PEC characterization, we performed cyclic voltammetry with a sweep rate of 0.2 V s^{-1} . The I - V curves of the metasurface and the film in dark and under illumination at highest powers are displayed in Figure 4b. The currents were normalized by the active areas exposed to the electrolyte, i.e., 25 mm^2 in the case of the metasurface. The electrode potential was initially cycled several times in dark until the current stabilized (full measurements in Figure S13, Supporting Information). Compared to the film, the metasurface promotes a clear enhancement of the photocurrent density under all illumination conditions. Potential contributions from the bare ITO between the nanodisks can be neglected due to small dark and photocurrents (Supporting Information Section S14).

For better visualization of the metasurface-related photocurrent enhancement, the ratio $I_{\text{light}}/I_{\text{dark}}$ at $V = -0.7 \text{ V}$ versus Ag/AgCl (photo-enhancement factor, PEF) is plotted in Figure 4c for the film and the metasurface, illuminated by the three different spectral ranges. The presentation illustrates that the PEF is strongly enhanced by the metasurface for all three wavelength ranges. Power-dependent PEC measurements were carried out by defocusing the Hg/Xe lamp and running cyclic voltammetry using the setup illustrated in Figure 4a. The photo-enhancement factors at low, medium, and high lamp

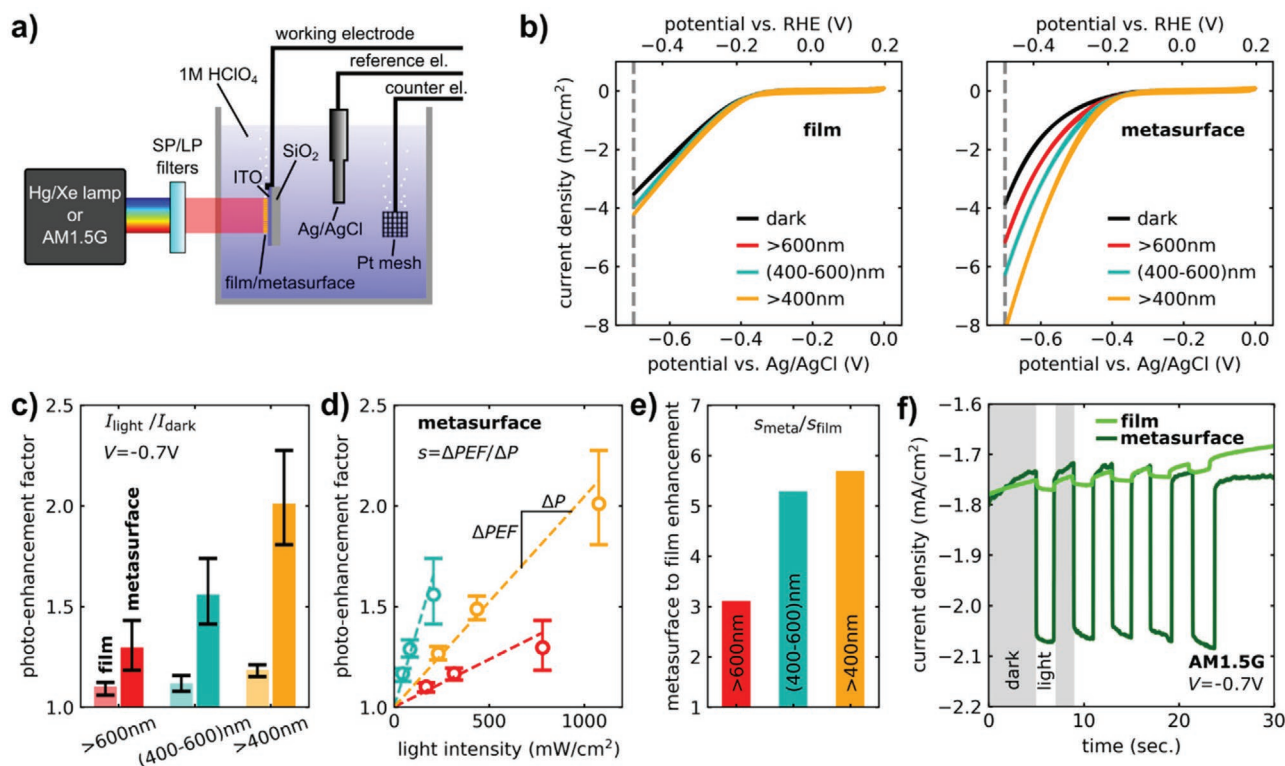


Figure 4. a) Experimental setup for the PEC characterization of the a-GaP film and metasurface. b) Cyclic voltammetry on the photoelectrodes under dark conditions and red, green, and white light illumination. c) Photo-enhancement factor (photo divided by dark currents) for the three different wavelength ranges at $V = -0.7$ V versus Ag/AgCl. d) Linear power dependence of the photo-enhancement factor, with s representing the slope for each of the three investigated illumination conditions. e) Metasurface to film enhancement factors calculated from the data in (d) as the ratio between the slopes of power-dependent photo-enhancement factors from metasurfaces and continuous films (Section S15, Supporting Information). f) Chopped-light chronoamperometry curves for an a-GaP metasurface compared to continuous a-GaP film at a potential of -0.7 V versus Ag/AgCl under simulated AM 1.5G 1 Sun illumination.

powers in Figure 4c reveal a linear power dependence, which is less pronounced for the film at low powers (Supporting Information Section S15). The slopes s of the linear fits to the power-dependent PEF are used to calculate the metasurface to film enhancement (MFE) factor by $MFE = s_{\text{meta}}/s_{\text{film}}$ for each wavelength range. Figure 4e shows the calculated MFE factors of 3.1, 5.3, and 5.7 for red, green, and white light, respectively. These values demonstrate an unexpectedly strong contribution from the LR to the overall photocurrent enhancement, which we attribute to the near-surface absorption hot-spots and energetically higher electronic states populated by the LR-assisted absorption compared to the AE. Finally, we performed chopped light chronoamperometry measurements using a solar light simulator (AM 1.5G, 100 mW cm^{-2}) to mimic the performance of the metasurface with solar illumination at -0.7 V versus Ag/AgCl (Figure 4f). The cyclic voltammograms are shown in the Supporting Information Section S16. We observe a clear photocurrent and a strong enhancement by the metasurface in contrast to the a-GaP film, which exhibited a much weaker photoactivity. Our results show that the judicious photonic engineering of anapole excitations and lattice resonances results in a substantial, relative efficiency enhancement through the superior absorption properties. Considering that the absorber volume of the metasurface is less than half of the film, the

applied metrics for the calculation of the MFE values provide merely lower bounds of enhancement.

2.5. Incident Photon-to-Current Conversion and Internal Quantum Efficiencies

A detailed spectrally resolved analysis of the photocurrent enhancement was carried out in order to determine the incident photon-to-current conversion efficiency (IPCE) and the internal quantum efficiency (IQE) of the system. Figure 5a shows the measured absorbance spectra of the metasurface and the film with the Pt cocatalyst. The IPCE (Figure 5b) was extracted from a set of chronoamperometry measurements under chopped light with 10 nm bandwidth filters (Supporting Information, Section S17). The results confirm the strong photocurrent enhancement for the metasurface across the visible range, consistent with the optical characterization of the photoelectrodes (shown in the previous section). From these values, the IQE was calculated by the $IPCE/\text{absorbance}$ ratio, shown in Figure 5c. We attribute the significant IQE enhancement by the metasurface to the near-surface absorption hot spots in the nanoresonators created by the engineered photonic states, as elaborated in Figure 3c. We believe that these hot

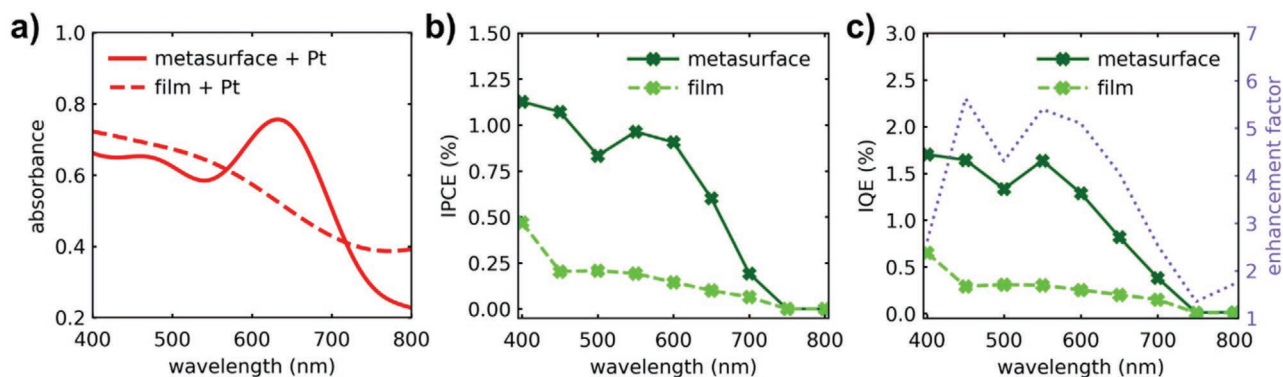


Figure 5. a) Absorbance spectra of the metasurface and film with the platinum cocatalyst. b) Incident photon-to-current conversion efficiency (IPCE) of the photoelectrodes. The metasurface provides a strong conversion enhancement at the maximum of the solar spectrum. c) Internal quantum efficiency (IQE) calculated from the values of (a) and (b).

spots facilitate highly efficient and near-surface generation of electron-hole pairs, thereby reducing their recombination probability during migration on the—now shorter—path to the solid/liquid interface compared with the continuous film counterpart. A comparison of the IQE values reported here with previous studies investigating metallic nanoparticle systems^[36–38] reveals similar to up to two orders of magnitude higher IQE from our electrodes.

3. Conclusion

We have demonstrated a strategy for the design of a nano-disk metasurface that drastically increases the photocurrent of a moderately photoactive material with a thickness of only 100 nm over nearly the full visible spectrum. Specifically, we elaborated the key parameters for spectral tuning of the anapole excitation, as well as the lattice resonance, and discussed the parameter window for optimal solar light harvesting. We proposed a procedure to fabricate the photonically engineered metasurfaces at large-scale and with high-throughput for use as photoelectrodes in solar fuel applications. The optical and numerical analysis of the metasurface photoelectrode connects the nanophotonic effects to the enhanced photocurrent generation. In particular, we quantitatively assigned the respective contributions of the anapole excitation and the lattice resonance to the overall enhancement by calculating wavelength-dependent enhancement factors, which demonstrate an overall photocurrent enhancement factor of 5.7, compared to a continuous planar film, despite the latter possessing a significantly larger absorber volume. Importantly, we note that our concept is not restricted by the use of α -GaP but is readily applicable to further optimize solar light harvesting in intentionally doped, high-performing semiconductor photocatalysts with more positive onset potentials.^[39–41] Furthermore, ITO is used in this study for electrical contact while also facilitating optical characterization by transmission spectroscopy. However, a low refractive index substrate is not required for the support of Mie-resonances in dielectrics.^[42] This makes our study instructive for direct nanoimprinting of crystalline wafers consisting of established semiconductor photocatalysts without the need for material transfer. Large-area roll-to-roll or roll-to-plate nanoimprinting

techniques enable continuous and high-throughput production of large-scale nanopatterned surfaces, thereby providing a viable path from nanophotonic device concept demonstrations to industrially relevant applications.^[43] Finally, we stress that nanophotonic engineering of photoelectrodes can be easily combined with other material-optimization approaches, i.e., for charge transfer, increased stability, etc., to develop a new generation of highly efficient solar meta-electrodes.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

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