Ultrathin Broadband Metasurface Superabsorbers from a van der Waals Semimetal

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Metamaterials and metasurfaces operating in the visible and near-infrared (NIR) offer a promising route towards next-generation photodetectors and devices for solar energy harvesting. While numerous metamaterials and metasurfaces using metals and semiconductors have been demonstrated, semimetallic-based metasurfaces in the vis-NIR range are notably missing. This work experimentally demonstrates a broadband metasurface superabsorber based on large area, semimetallic, van der Waals platinum diselenide (PtSe2) thin films in agreement with electromagnetic simulations. The results show that PtSe₂ is an ultrathin and scalable semimetal that concurrently possesses high index and high extinction across the vis-NIR range. Consequently, the thin-film PtSe₂ on a reflector separated by a dielectric spacer can absorb >85% for the unpatterned case and ≈97% for the optimized 2D metasurface in the 400–900 nm range making it one of the strongest and thinnest broadband perfect absorbers to date. The results present a scalable approach to photodetection and solar energy harvesting, demonstrating the practical utility of high index, high extinction semimetals for nanoscale optics.

1. Introduction

Optical metamaterials and their planar counterpart, metasurfaces, are artificial materials engineered using subwavelength features to exhibit a desired response to electromagnetic (EM) fields unachievable with natural materials.[1,2] Metamaterial perfect absorbers (MMPAs) have been designed for frequencies ranging from the visible to microwave.[3] Narrow-bandwidth MMPAs are typically based on a frequency-dependent resonant response and have applications in spectral filtering[4] and sensing.[5] In the visible to near infrared (NIR), broadband MMPAs are important for photodetection and solar energy harvesting.[6,7]

Broadband solar absorption has been achieved using antireflectance effects in superlattices of dielectrics and lossy metals,[8] nanostructuring the surface of thick semiconductor wafers,[9] light trapping in vertically aligned nanowire or nanotube arrays,[10–13] and by light trapping in metamaterials with tapered geometries.[14,15] While effective, these approaches require relatively thick structures and/or complicated fabrication processes, limiting their practicality. Additionally, it is desirable for certain applications—such as photoelectrocatalysis (PEC)—to localize EM waves at or near the surface.[7] Ultrathin metasurfaces exhibiting near-unity absorption and deep subwavelength field confinement are therefore ideal as electromagnetic energy is concentrated at the surface while the thin structure enables lightweight, low-cost devices.

A common approach to metasurface absorbers is using a patterned metal film on top of a lossless dielectric spacer layer on a metal reflector.[5,6,16,17] The dielectric layer recirculates...
light or can be chosen to produce a Fabry–Perot (FP) cavity resonance.\[^5\] Periodic patterning of the top metal layer in metal–insulator–metal (MIM) structures results in gap surface plasmons (GSPs) between the metal resonators and the back metal film.\[^{18,19}\] Plasmons—collective excitations of electrons at the interface between a metal and dielectric—enhance light absorption/emission and can localize electromagnetic fields to deep subwavelength mode volumes.\[^{20,21}\] Further, hot electrons created by plasmons are particularly useful for PEC,\[^{22}\] photodetection,\[^{23,24}\] and plasmonic solar cells.\[^{25}\] However, purely plasmonic absorption modes are highly dependent on the structure geometry and the polarization and incident angle of the incident light. Moreover, plasmonic responses tend to be narrowband\[^{6,26}\] and do not absorb off-resonance light. The polarization dependence can be significantly reduced by patterning elaborate nanoantenna structures\[^{27,28}\] and broadband absorption can be achieved by resonance multiplexing\[^{6,16,29,30}\] or by incorporating epsilon-near-zero materials in the dielectric spacer.\[^{31}\] However, achieving polarization independent broadband absorption in purely plasmonic absorbers requires intricate geometries that make design and fabrication challenging. Using lossy plasmonic metals such as chromium, titanium nitride, and tungsten has been shown to improve broadband absorption,\[^{32–39}\] but the inability to generate photocurrents in a metal limits potential applications.

Lossy, high refractive index dielectrics offer another approach to broadband absorption. In the complex refractive index, $\bar{n} = n + ik$, $k$ is directly related to absorptivity/extinction while $n$ is related to propagation and power localization. Power absorption in a non-magnetic medium is given by:

$$P_{abs} = \frac{1}{2} \omega m (\epsilon | E|^2$$

where $\Im(\epsilon) = 2nk$ is the imaginary part of the permittivity, $\omega$ is the radial frequency, and $|E|$ is the magnitude of the electric field. $P_{abs}$ can therefore be maximized by choosing a material that has a large value of both $n$ and $k$ while simultaneously maximizing the electric field in the material (which is facilitated by a large $n$ value). It has been shown that ultrathin films of high index, highly absorbing semiconductors on a back reflector can exhibit strong absorption due to such interference effects.\[^{40}\] However, semiconductors tend to have relatively small values of $k$ or are otherwise limited by their bandgap. Moreover, conventional bulk semiconductors (Si, Ge, III-V’s, etc.) are impractical in ultrathin layers with high surface-to-volume ratios due to oxidation and the effects of surface states and dangling bonds on electrical transport and recombination.

Alternatively, two-dimensional metal dichalcogenides exhibit strong interaction with light despite ultrathin thicknesses.\[^{41–43}\] Among them, noble metal dichalcogenides (NMDs) of form $\text{MX}_2$ (M = Pt, Pd; X = S, Se, Te) have only been recently explored.\[^{44–53}\] PtSe$_2$ is an indirect-gap semiconductor in the monolayer limit but becomes a type-II Dirac semimetal beyond a few layers in thickness.\[^{52–54}\] PtSe$_2$ has attracted the attention of researchers due to its broadband optical properties,\[^{35,56}\] saturable absorption,\[^{37}\] air stability,\[^{49}\] low temperature synthesis compatible with CMOS back end of line (BEOL) processing,\[^{58}\] and high mobilities in single crystalline flakes and films.\[^{59}\]

Further, unlike metals, photocurrents can easily be generated in PtSe$_2$.\[^{60}\] The high mobility and strong absorption have made PtSe$_2$ promising for broadband photodetector applications.\[^{61–63}\] Additionally, PtSe$_2$ has demonstrated immense promise as a photoelectrocatalytic material.\[^{64–69}\] Broadband absorption and strong catalytic properties make PtSe$_2$ an exciting material for broadband metasurface solar absorbers with direct applications in photodetection and solar PEC.

In this work, we demonstrate the scalable synthesis of PtSe$_2$ thin films with extraordinarily large refractive index and extinction, dominated by interband optical transitions, throughout the visible–NIR range. We then replace the commonly used top metal film in the MIM metasurface structure with a semimetallic PtSe$_2$ film. We show that use of the dielectric spacer and back reflector are sufficient to achieve broadband absorption even in unpatterned films. By patterning the PtSe$_2$ to produce plasmons from the Ag and dielectric modes in the PtSe$_2$ broadband near unity absorption (97.0%) is achieved from 400 to 900 nm. Remarkably, our PtSe$_2$-based approach stands out as simultaneously among the most strongly absorbing and thinnest broadband absorbers known to date, exemplifying the broader value of taking a materials-first approach to nanophotonics: simple designs with emerging high-index materials can outperform more complex designs using conventional materials.

2. Results and Discussion

2.1. Synthesis and Characterization

PtSe$_2$ films were synthesized via thermally assisted conversion (TAC) of a sputtered Pt film by annealing in H$_2$Se at 550 °C (Experimental Section). The initial Pt film thickness is approximately 5–6 nm (Section S1.1.1, Supporting Information). Upon selenization, the film thickness increases to ~14 nm due to the added Se atoms and decreased density of PtSe$_2$ compared to Pt. The minimum PtSe$_2$ thickness is therefore determined by the minimum achievable thickness of a continuous Pt film, which for a pulsed DC sputtering process is about ~5 nm. In principle, both Pt and PtSe$_2$ thin films at smaller thickness can be grown via vapor phase epitaxial methods such as Molecular Beam Epitaxy,\[^{59,71–73}\] which is beyond the scope of this work. A picture of a large area PtSe$_2$ film grown by TAC on sapphire is shown in Figure 1a. Raman spectra (Figure 1b) collected at five spots on the sample, corresponding to locations at the center and at each edge, and Raman mapping (S1.1.2, Supporting Information) confirm the formation of PtSe$_2$ with high uniformity across the sample. The peaks observed at 178, 206, and ~237 cm$^{-1}$ correspond to the $E_g$, $A_g$, and longitudinal optical (LO) modes of PtSe$_2$.\[^{76}\] Cross-sectional transmission electron micrographs confirm the horizontally aligned, well-layered structure, and high angle annular dark field (HAADF) elemental mapping verifies the complete selenization of the film (Section S1.1.3, Supporting Information). We synthesized PtSe$_2$ at temperatures ranging from 375 °C to 650 °C (Section S1.1.4, Supporting Information) and found that annealing at 550 °C produced films with the largest optical constants (Section S1.2.1, Supporting Information), but the ability to selenize PtSe$_2$ at
The large area films can then be transferred to arbitrary substrates using the well-established PMMA-assisted wet transfer process (Experimental Section). The transfer process causes the film thickness to increase to approximately 18 nm (S1.1.1, Supporting Information). The RMS roughness of the overall PtSe₂/Al₂O₃/Ag multilayer structure is approximately 3.13 nm (S1.1.1, Supporting Information). This roughness value is two orders of magnitude smaller than the wavelengths of light considered, so it is expected to have negligible effect on optical performance.

We determined the complex refractive index (Figure 1c) of 18 nm PtSe₂ transferred onto 40 nm Al₂O₃/100 nm Ag/300 nm SiO₂/Si by spectroscopic ellipsometry and fitting using Lorentzian oscillators (Experimental Section and Section S1.2.1, Supporting Information). The optical response of PtSe₂ in the UV/Vis regime is dominated by a high density of interband transitions between Se-p and Pt-d bands near the Fermi level, resulting in a large, broadband \( n \). The massive \( n \) and \( k \) in the vis-NIR result in strong broadband absorption. The semimetallic optical behavior of PtSe₂ is evident upon transfer from the growth substrate (sapphire wafers) onto a silver mirror coated with 40 nm Al₂O₃ (Figure 1d, inset), resulting in >85% absorption in the unpatterned case (Figure 1d). The measured absorbance spectrum is well-predicted by the transfer-matrix method (TMM), a robust technique for modeling a multilayered slab with planar interfaces. Broadband >85% absorption in an 18 nm thick semimetallic film using only a back reflector and a lossless dielectric to recirculate light is remarkable, particularly because it presents a scalable lithography-free approach to broadband light-harvesting in ultrathin geometries.

By adding a ≈65 nm Al₂O₃ anti-reflective coating (ARC) on top of the PtSe₂, the total absorption over the measured range exceeds 97% without lithography (Section S1.3, Supporting Information). This result is extraordinary and makes large area PtSe₂ photodetectors promising and scalable, but the ARC adds thickness to the structure and no longer enables the PtSe₂ absorber to be used as a photocathode for catalysis. For the remainder of this study, we explore the enhancement of the optical absorption of the 3-layer PtSe₂/spacer/Ag structure to near unity without an ARC by patterning PtSe₂ nanoresonators that localize the electric field in PtSe₂.

Figure 1. PtSe₂ film structural and optical characterization. a) A large area PtSe₂ film as grown on sapphire. b) Raman characterization of a PtSe₂ film as grown on sapphire, taken at five different spots that are randomly and evenly distributed across the film. c) Real and imaginary parts of the complex refractive index: \( \tilde{n} = n + ik \). d) Experimental and transfer-matrix method (TMM) calculated absorbance spectra of an unpatterned PtSe₂ film transferred onto 40 nm Al₂O₃/100 nm Ag/SiO₂/Si. Inset: a picture of the sample. Optical constants for PtSe₂ were determined by spectroscopic ellipsometry on a transferred film (Experimental Section).
2.2. Nanoribbon Array Metasurfaces

The first structure considered for broadband absorption is a 1D metasurface based on nanoribbons patterned in the 18 nm thick PtSe₂ film by a combination of electron beam lithography and reactive ion etching (further details found in Experimental Section). Patterning periodic nanoresonators in the PtSe₂ creates a nonzero in-plane wavevector for transverse magnetic (TM) polarized light that excites plasmons from the Ag mirror. Simultaneously, patterning high index materials into nanoresonators results in electric dipole (ED) Mie modes oriented with the polarization of incoming light, enabling electric field enhancement and control over the wavefront. Given the ultrathin resonators, we do not expect magnetic Mie modes. The combination and coupling of these modes result in electric field enhancement in and around the PtSe₂, enhancing absorption. Figure 2a shows a schematic of the three-layer structure: the top layer is composed of PtSe₂ nanoribbons with width \( w \) arranged in an array with period \( p \); the middle layer is a 40 nm thick Al₂O₃ film; and the bottom layer is a sputtered 100 nm thick Ag film. The substrate is Si with a 300 nm thick thermal oxide. There is no transmission through the Ag mirror, so the substrate choice is arbitrary as long as it is flat and smooth. Because there is no transmission, we can approximate the absorption of films and metasurfaces from the reflectance spectra as \( A \approx 1 - R \).

We fabricated nanoribbon arrays (NRs) with a fixed period \( p = 300 \text{ nm} \) and widths varying from 110 to 225 nm by patterning 15 × 15 micron pixels in PtSe₂ (Figure 2b,c). The pixels look increasingly dark with increasing width, and the higher fill factor, \( f \), arrays look darker than the unpatterned PtSe₂, which itself absorbs over 85% of visible light. The unpolarized reflectance measurements in Figure 2d confirm the absorbance broadening with increasing nanoribbon width. By patterning the PtSe₂ into a 1D metasurface, the absorption can be enhanced relative to the unpatterned film across the broadband spectral region between 400 and 900 nm.

The absorption mechanisms can be better understood by considering separately the transverse electric (TE) and TM polarized modes of the NR. At normal incidence (propagation along \( \hat{z} \)), we define TE polarized light as linearly polarized plane waves with the electric field component parallel to the nanoribbon length (i.e., \( E_x \)) while TM polarized light has its electric field component orthogonal to the nanoribbon length (i.e., \( E_y \)), respectively.

2.2.1. Transverse Magnetic Modes of PtSe₂ Nanoribbons

The enhanced absorption of TM light is facilitated by localization of the electric field by hybrid plasmonic and dielectric modes in and around the PtSe₂. The periodicity, \( p \), in the \( \hat{x} \) direction imposes a nonzero in-plane wavevector \( (k_x) \) for TM-polarized light with incident angle \( \theta \) described by:

\[
k_x(\theta, p) = k_0 \sin \theta + \frac{2\pi m}{p}, \quad m = \text{integer}
\]

where \( k_0 \) is the free space wavevector. At normal incidence, Equation (2) becomes \( k_x(\theta = 0, p) = \frac{2\pi m}{p} \). The nonzero \( k_x \) has two effects: (i), plasmonic modes are excited from the Ag film and (ii), light that is diffracted by the grating-like structure and hits the Ag mirror at an angle but does not excite a

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**Figure 2.** PtSe₂ nanoribbon array (NR) structure and unpolarized reflectance. a) Schematic of a PtSe₂ NR. The nanoribbons sit on a 40 nm Al₂O₃ layer on a 100 nm Ag mirror. The nanoribbons have width \( w \) and are arranged in a 1D array with period \( p \). b) Unpolarized optical image of a set of array pixels with widths ranging from \( w = 110-225 \text{ nm} \). All arrays have period \( p = 300 \text{ nm} \). The area surrounding the 15 × 15 µm pixels is the unpatterned PtSe₂ film. c) Scanning electron microscope images of arrays with \( w = 110 \text{ nm} \) (left) and \( w = 225 \text{ nm} \) (right). Both structures have period \( p = 300 \text{ nm} \). Measurements using the scanning electron microscope (SEM) software overlaid on the images confirms the accuracy of the patterning. d) Unpolarized absorbance spectra for the arrays shown in (b) and the unpatterned film area.
plasmon reflects and is collected by the PtSe$_2$. Light with a diffraction order, $m$, of 0 will also have direct absorption similar to planar PtSe$_2$.

Simultaneously, for nanoribbons with dimensions on the order of $\lambda/\eta$, TM polarized light results in dielectric Mie scattering from the PtSe$_2$ resonators. The combination of the plasmon, ED coupling between adjacent nanoribbons, and the interaction between these resonances across the dielectric cavity results in hybrid modes. An important consequence of these hybrid modes is the recirculation and localization of light in the PtSe$_2$, resulting in enhanced overall absorption.

Figure 3a shows the experimentally measured (top) and simulated (bottom) transverse magnetic (TM) polarized absorbance spectra (taken to be $A = 1 - R$) for the arrays shown in Figure 2b with $p = 300$ nm and $w$ ranging from 110 to 225 nm. The label “WG” refers to the waveguide mode that emerges at nonzero incident angles. The linearly polarized spectra in (a) extend only up to 825 nm due to the limited bandwidth of the linear polarizer. b) Electric field profile heat map with overlaid electric field lines (top) and $P_{abs}$ profile (bottom) at the absorption maxima of $\lambda = 595$ nm for a NR with $w = 110$ nm, $p = 300$ nm. c) Same as (b) but at a wavelength of $\lambda = 520$ nm for a NR with $w = 225$ nm, $p = 300$ nm. The field profiles in (b) and (c) were calculated by Numerical finite-difference time-domain (FDTD) simulations.

Figure 3b shows the calculated electric field profile (top) and $P_{abs}$ profile (bottom, calculated using Equation (1)) for an array with $w = 110$ nm, $p = 300$ nm excited by a normal incidence TM-polarized plane wave of wavelength 595 nm, corresponding to the absorbance maximum for this structure. There is an ED between the edges of the nanoribbon that hybridizes with the cavity formed by the spacer in between the PtSe$_2$ and Ag. This results in the electric field being enhanced in the PtSe$_2$ and in the spacer layer underneath the corners of the ribbon. For certain dimensions, this mode has a strong FP cavity character (in Section S2.1.1, Supporting Information).

As $w$ is increased, there becomes stronger interaction between the ED modes of individual resonators. At shorter and intermediate wavelengths, the dielectric mode hybridizes with the plasmon mode in the Ag and the cavity formed by the spacer layer (Figure 3c). At longer wavelengths, direct absorption of incident light, light localization by the inter-ribbon
dipoles, and absorption of off-resonance diffracted light reflected from the Ag mirror are the prominent mechanisms, and power absorption is concentrated in the center of the ribbons. Detailed discussion of the TM modes is provided in Section S2.1 (Supporting Information).

2.2.2. Broadband Absorption of TE Polarized Light in PtSe₂ Nanoribbons

In addition to strong hybrid resonance-enhanced absorption, the PtSe₂ nanoribbons exhibit broadband absorption for TE light. Figure 4a shows the experimental (top) and simulated (bottom) TE-polarized absorbance spectra for the structures in Figure 2b with a fixed \( p = 300 \) nm and varying widths. Like the plot for the TM case, the polarized data is limited from 400 to 825 nm by the polarizer bandwidth. The experimental spectra match up well with the corresponding simulated spectra for most of the measured area. The simulated spectra include the power absorbed by the Ag, which is negligible due to the lack of a plasmon resonance: on average, the \( P_{\text{abs}} \) in the Ag mirror is only 3.8% for the \( w = 225 \) nm structure. Dependence of absorbance on \( f \) is less drastic than for the TM case, and broadband absorption is observed for all ribbon widths. Overall, absorbance is enhanced relative to the unpatterned case for part or all of the measured range, depending on the array dimensions. Here, we observe the benefit of replacing the top metal layer in a MIM broadband metasurface absorber with a high index, high-\( k \) material: there is strong absorption even for polarizations that do not excite the plasmon resonance.

The high index of PtSe₂ again results in the excitation of lossy dielectric modes for TE polarizations. Figure 4b shows the TE Re(\( E_y \)) field profile with the magnetic field lines overlaid (top) and the \( P_{\text{abs}} \) profile (bottom) for a NR with \( w = 225 \) nm, \( p = 300 \) nm at a wavelength of 400 nm. At \( \lambda = 400 \) nm, there is an ED mode along the \( \hat{y} \) direction in between adjacent nanoribbons, resulting in field enhancement in the gap and at the edges of the PtSe₂ (Figure 4b). The confinement between ribbons is due to the Re(\( \varepsilon \)) < 0 of PtSe₂ below 470 nm. The corresponding \( P_{\text{abs}} \) profile shows that power absorption primarily occurs toward the edges of the ribbons. In the spectra shown in Figure 4a, the absorption maximum below 470 nm increases and blue shifts with increasing \( w \) as the field is being confined in a narrower area before decreasing for \( w = 225 \) nm.

The TE Re(\( E_y \)) field profile with \( \hat{H} \)-field lines overlaid (top) and \( P_{\text{abs}} \) profile (bottom) are shown in Figure 4c for the same structure and dimensions but at a wavelength of 583 nm. An ED mode along the \( \hat{y} \) direction is once again observed, but Re(\( \varepsilon \)) > 0 at this wavelength, so the dipole mode is confined in the PtSe₂ ribbons. The \( P_{\text{abs}} \) profile is consistent with this, as the

![Figure 4. Nanoribbon array (NR) transverse electric absorption. a) Experimentally measured (top) and simulated (bottom) transverse electric (TE) polarized absorbance spectra for the arrays shown in Figure 2b with \( p = 300 \) nm and \( w \) ranging from 110 to 225 nm. b,c) Re(\( E_y \)) field profiles with \( \hat{H} \)-field lines (top) and corresponding \( P_{\text{abs}} \) (bottom) profiles for a NR (\( w = 225 \) nm, \( p = 300 \) nm) illuminated with TE-polarized plane waves of wavelength b) \( \lambda = 400 \) nm and c) \( \lambda = 583 \) nm.](image-url)
power absorption is evenly distributed across the nanoribbon cross-section instead of being maximized at the edges.

### 2.3. 2D Array PtSe₂ Metasurfaces

Now that we have observed the contributions to absorption of the Ag and PtSe₂ in 1D NRs, we design relatively simple 2D arrays to maximize absorption of unpolarized visible light. We maintain the general three-layer structure of PtSe₂ transferred on 40 nm Al₂O₃/100 nm Ag, but now fabricate 2D arrays. 2D periodicity results in nonzero in-plane wavevectors in both the \( \hat{x} \) and \( \hat{y} \) directions. For any given polarization, we expect the simultaneous presence of TM-like hybrid plasmon-dielectric and TE-like lossy dielectric modes due to the strong \( n \) and \( k \) of PtSe₂. Absorber design is therefore flexible and can be tailored to applications as any well-designed periodic, high PtSe₂ fill factor pattern will exhibit broadband near-unity absorption. We demonstrate this by fabricating structures with simple, inverted patterns: crossed PtSe₂ gratings/nanoribbons (XGs, Figure 5a – top) and a square array of PtSe₂ nanosquares (NSQs, Figure 5a, bottom). The XGs can alternatively be thought of as a square array of square nanoholes.

Dies were fabricated with 3 XGs and 3 NSQ arrays per die. Scanning electron microscope (SEM) images of representative structures are shown in Figure 5b. The XGs have a fixed \( p = 300 \) nm and different \( w \)'s of 100, 150, and 200 nm, respectively. The NSQ arrays have the following dimensions \((w, p)\): (150, 200 nm), (150, 300 nm), and (250, 300 nm). Figure 5c is an unpolarized optical image of a die of metasurface pixels. All pixels, except for NSQ (150, 300 nm), appear dark or even completely black compared to the unpatterned PtSe₂ film, which itself absorbs over 85% of visible light. Unpolarized reflectance measurements (Figure 5d) show broadband near-unity absorption for all metasurfaces except the array of 150 nm NSQs with period 300 nm. Our results are well predicted by finite-difference time-domain (FDTD) simulation of the structures with a broadband plane wave polarized along the \( \hat{x} \) direction (Section S3.1, Supporting Information).

Characteristics of the TM and TE modes in 1D are observed in both the NSQ arrays and the XGs. The XGs exhibit similar field profiles to those observed in the NRs with similar ratios of width to period. At shorter wavelengths (<470 nm) TM-like field localization by coupled dipole modes in the hole between gratings is the dominant absorption mechanism, with strong absorption at the edges of the PtSe₂. A weak plasmon contribution is also observed. At intermediate wavelengths, the FP-like TM modes, ED (TE-like) modes, and diffraction effects are observed. At longer wavelengths, the dielectric ED modes dominate absorption. The XG modes do not exhibit a strong contribution from plasmonic field enhancement above 470 nm.

The NSQ arrays exhibit more characteristics of the TM modes of nanoribbons but with additional dielectric mode effects at shorter wavelengths. The more absorptive, high \( f \) structures exhibit strong dipole interactions between adjacent NSQs, much like high \( f \) nanoribbons. Both hybrid

![Figure 5. 2D array PtSe₂ broadband metasurface superabsorber structures and experimental results. a) Schematics of single unit cells of the crossed grating (XG) metasurface (top) and the nanosquare (NSQ) metasurface (bottom). b) Scanning electron microscope (SEM) images of an XG metasurface (left) with dimensions \( w = 100 \) nm and \( p = 300 \) nm and NSQ array metasurface (right) with dimensions \( w = 250 \) nm and \( p = 300 \) nm. Measurements of the feature sizes using SEM software are displayed on the images, confirming accurate dimensions. c) An unpolarized optical micrograph of a representative die, consisting of six 20 by 20 µm pixels patterned into PtSe₂—the metasurfaces—and a small white rectangular patch where the PtSe₂ is removed to show the alumina-coated Ag substrate. The top row of pixels is a set of XGs while the bottom row is a set of NSQ arrays. The structure dimensions for each pixel are lithographically patterned into the PtSe₂ film. d) Absorbance spectra of XGs (top) and NSQ arrays (bottom) as determined by normal incidence unpolarized reflectance spectroscopy. The unpatterned PtSe₂ film absorbance spectrum is included for reference. All reflectance spectra are normalized to a baseline spectrum from the substrate and corrected for background noise (Experimental Section).](https://www.advancedsciencenews.com)
plasmonic-dielectric-FP modes and TE-like dielectric modes contribute to absorption for shorter (<470 nm) wavelengths, but the TE-like confinement vanishes as the real permittivity changes sign. Akin to the high f NRs, direct absorption, localization by coupled dipoles, and the diffraction-reflection effect are the primary absorption mechanisms at longer wavelengths in high f NSQ arrays.

The NSQ array response has a greater dependence on f due to effects of interaction between resonators and the lack of uncoupled TE-like ED mode localization at higher f. The NSQ arrays also exhibit greater plasmonic character than the XGs. A detailed explanation and field profiles of the modes are provided in Section S3.2 (Supporting Information).

The average absorbance in the visible range (400–700 nm), $A_{\text{vis}}$, and the average solar-weighted absorbance, $A_{\text{solar}}$, over the measured range (400–900 nm) are calculated as follows:

$$A_{\text{vis}} = \frac{1}{300\text{nm}} \int_{400\text{nm}}^{700\text{nm}} A(\lambda) d\lambda$$

$$A_{\text{solar}} = \frac{\int_{400\text{nm}}^{900\text{nm}} A(\lambda) P_{\text{solar}}(\lambda) d\lambda}{\int_{400\text{nm}}^{900\text{nm}} P_{\text{solar}}(\lambda) d\lambda}$$

$A(\lambda) = 1 - R(\lambda)$ is the measured absorbance spectrum for a given structure (Figure 5d), and $P_{\text{solar}}(\lambda)$ is the solar irradiance spectrum (ASTM G-0173-03 AM1.5 Standard). The results are plotted in Figure 6 for unpatterned films and selected metasurfaces. Up to 97.9% absorption of visible light and 97.0% absorption of solar light (400–900 nm) is achieved, enhanced from 86.4% of visible light and 87.6% of solar light for the case of unpatterned PtSe$_2$ on the dielectric coated silver mirror. We reiterate that the absorption is occurring almost entirely within an 18 nm thick film with <6% power absorbed on average by the Ag mirror from 400 to 900 nm. Near unity solar absorption concentrated in a large area, 18 nm strongly catalytic$^{[46,64–69]}$ layer is therefore a significant step toward ultrathin solar photocathodes for PEC water splitting.

We compare the $A_{\text{vis}}$ of our best structures for visible range absorption (the NSQ array with $w = 150$ nm, $p = 200$ nm) to other broadband absorbers in literature (Figure 7), plotting $A_{\text{vis}}$ as a function of total structure thickness and the thickness of the active layer (i.e., the layer(s) in which most or all light is absorbed). We also include our unpatterned PtSe$_2$ film on the Al$_2$O$_3$/Ag substrate, with and without an ARC. Our PtSe$_2$-based metasurface stands out as simultaneously among the thinnest and strongest absorbing broadband absorbers to date. To our knowledge, the only experimental study that has demonstrated higher average visible absorption in a total thickness less than 700 nm was Wang et al.$^{[37]}$ who achieved 99.6% average visible absorption in a TiN/AlN nanocomposite active layer (126 nm thick) but required a 100 nm thick ARC. With our NSQ metasurface, we demonstrate comparable absorption in a thinner overall structure and in an 18 nm thick active layer that is on the surface—i.e., without the need for an ARC. Further, we achieve comparable or greater absorbance as compared to vertical nanowire arrays exceeding 1 micron in thickness.$^{[10,11]}$

Broadband near-unity visible light absorption concentrated in an 18 nm thick PtSe$_2$ film is noteworthy result due to its potential for both enhanced photodetection and efficient solar PEC in ultrathin, lightweight devices. While some metals are either good absorbers (Ti, Cr, W) or good catalysts for the hydrogen evolution reaction (Pt, Ir, Rh), they are generally not both.$^{[81]}$ PtSe$_2$ maintains much of the catalytic activity of Pt but is a significantly more efficient absorber as a Dirac semimetal. Further, the Pt film precursors are extremely thin, lowering the cost relative to pure Pt electrodes. Additionally, unlike semiconductors, PtSe$_2$ perfect absorbers can be applied to...

Figure 6. Integrated visible and solar light absorption for selected structures. Average visible range absorbance ($A_{\text{vis}}$) and integrated solar absorbance efficiency ($A_{\text{solar}}$) calculated by (3a) and (3b) for unpatterned structures, a selected nanoribbon array (NR) structure, the three different nanosquare (NSQ) array metasurfaces, and the three different crossed grating metasurfaces (XG). The dimensions in parentheses are the width and period of the structures, respectively.
photo detection.\[^{[82]}\] However, PtSe\(_2\) has significantly larger and more broadband imaginary refractive indices than conventional semiconductors have for most of the visible-NIR range,\[^{[83]}\] and van der Waals PtSe\(_2\) layers have self-passivated bonds and therefore enable much more practical devices from ultrathin absorbers.

### 3. Summary and Outlook

In summary, we have demonstrated the synthesis of 18 nm thick PtSe\(_2\) films with large real and imaginary refractive indices. The large, broadband refractive index and extinction were leveraged to realize strong absorption (>87\%) in the 400–900 nm range for an ultrathin, cm\(^2\) scale absorber (PtSe\(_2\)/spacer (alumina)/reflector (Ag) structure in a lithography-free approach. Upon using lithography to pattern the PtSe\(_2\) into 1D and 2D meta-surfaces of nanoresonator arrays, broadband absorption was further enhanced to 97\% in the most optimized 2D metasurface comprising NSQ resonators. Finally, all our experimental observations were verified with electromagnetic simulations which suggest that the enhanced broadband absorption in PtSe\(_2\) metasurfaces is a consequence of both: 1. the large optical indices intrinsic to the PtSe\(_2\) due to its semimetallic character as well as 2. nanophotonic effects such as plasmonic and dielectric resonances. This work pioneers the use of ultrathin PtSe\(_2\)-based metasurfaces for broadband visible and near infrared light absorption. Our approach presented here can be generalized to other existing and to-be-discovered van der Waals semimetallic and semiconducting materials exhibiting high broadband extinction due to interband transitions, presenting an exciting opportunity to design future metasurfaces for photodetection, photochemistry, and solar energy harvesting. We expect that our metasurfaces will be particularly promising as a photocathode for solar photoelectrolysis given the strong solar absorbance in a catalytically active material, electric field enhancement, and hot electron generation.

### 4. Experimental Section

\textit{PtSe\(_2\) Synthesis:} A total of 100 mm single-side polished c-plane sapphire substrates (UniversityWafer) were diced with a diamond scribe and subsequently cleaned by sonicating in acetone and isopropyl alcohol before being blow-dried with N\(_2\). Samples were then loaded in a custom-built sputtering system with a minimum base pressure of 3 \times 10^{-4} Torr. A 2" Pt sputter target was mounted on a 2" Mak sputter source (MeiVac, Inc) and positioned at an angle of 30° and distance of 8 cm from the substrate. A \(\approx\) 5 nm thick Pt precursor layer was deposited at...
room temperature using a Pinnacle Plus pulsed power supply (Advanced Energy) operated at a nominal power of 90 W, pulse frequency of 65 kHz, and a pulse width of 0.4 μs under argon with a pressure of 15 mTorr and Ar flow rate of 25 sccm. The total deposition time was 8 s.

Formation of PtSe2 was performed via thermally assisted conversion. The samples were loaded in a tube furnace and held under vacuum for 1 h, then pumped under H2 gas (200 sccm) for another hour. The pressure was then increased to 500 Torr under a flow of 10 sccm H2 and 160 sccm N2. The temperature was ramped from room temperature to 550 °C over 20 min then allowed to equilibrate for 5 min before H2Se gas flow (150 sccm) was turned on. The chamber was held under these conditions for 30 min before the tube furnace lid was opened to rapidly cool the chamber. The H2Se flow was turned off once the temperature decreased below 400 °C.

Vibrational Characterization: The room temperature Raman spectroscopy was performed using a Horiba LabRam HR Evolution Confocal Microscope with a 100x objective lens (Olympus) and a 633 nm laser filtered to have an intensity of <1 mW. Calibration of the spectra was done using a Si reference sample.

Measurement of Optical Constants: Spectroscopic Ellipsometry on as-grown films was performed with a Woollam RC2 ellipsometer at wavelengths 210–2300 nm and incident angles of 53°, 65°, and 75°. SE of transferred films and bare ALD Al2O3/Ag substrates was later performed with a Woollam UV-Vis VASE ellipsometer from 240–900 nm at an incident angle of 65°. The complex permittivity was extracted from the raw Psi-Delta data by fitting the data in the CompleteEASE software (v6.55) with Lorentzian oscillators (See Supporting Information for details).

Optical Simulation: Absorbance of structures with unpatterned films was calculated using the 1D TMM.37 Because the experimental reflectance results were normalized to the 40 nm alumina on Ag substrate, the TMM results were normalized to TMM calculated reflectance for this substrate as well. Both the 1D and 2D metasurfaces were modeled by FDTD simulation using the Lumerical FDTD solver. Both systems were modeled using a normal incidence, broadband plane wave source composed of wavelengths 300 to 900 nm and collecting reflectance and E/H profiles at 200 (100) wavelength points for 2D (3D) simulations. The optical constants used for Al2O3 were determined using spectroscopic ellipsometry and the constants for Ag are from Palik.38 The Pnm profiles were calculated directly from the E field profiles using the optical constants for the respective media and Equation (1). Additional field profiles monitored only in the Ag and PtSe2 regions were used to determine the fraction of light absorbed in each material by integrating the P nm profiles calculated over the area (volume) for 2D (3D) simulations of the respective regions. For the 1D NRs, the percent absorption is calculated for TM and TE polarizations. The 2DMSs are both square lattices, so the percent absorption is only calculated for light polarized in the x direction.

Metasurface Fabrication: A 1 x 1 cm p-Si substrate with a 290 nm thermal oxide was cleaned by sonication in acetone and isopropyl alcohol, followed by blow-drying with N2. A 100 nm Ag film was deposited by DC sputtering (Kurt J. Lesker PSG). The 40 nm thick Al2O3 layer was deposited by atomic layer deposition (Cambridge Nanotech) at 150 °C at a rate of 0.9 Å per cycle for 444 cycles. The precursors for Al and O were trimethyl aluminum (TMA) and H2O, respectively.

The PtSe2 films were transferred onto the dielectric/Ag substrates using a wet transfer method. The PtSe2 films were spin-coated with PMMA A4 (2k rpm, 60 s; left to dry overnight) before being removed from the sapphire growth substrate using a n~2 molar potassium hydroxide/water solution. The film was thoroughly cleaned with DI H2O to remove potassium ions before being transferred to the target substrate. The PMMA was removed by soaking the samples in Remover 1165 on a hot plate set to 80 °C for 30 min, leaving in room temperature acetone overnight, and then placing the samples in fresh acetone and isopropyl alcohol for 5 min each before blow-drying with N2.

The PtSe2 films were patterned by electron beam lithography (Elionix ELS-75) and a subsequent dry etch (Oxford RIE 80). ZEP520A E-beam resist diluted with anisole (1:1 by weight) was spin coated at 2K rpm for 60 s and baked at 120 °C for 3 min. Proximty effect correction with a base dose of 225 μC cm−2 was used for the NRs while the 2D metasurfaces used proximity effect correction with a base dose of 190 μC cm−2. The samples were then developed using ~10 °C o-Xylene for 90 s before rinsing in room temperature isopropyl alcohol and DI water for 30 s each. The film was then etched using reactive ion etching (Oxford RIE 80; 200 W RF power, 25 mTorr pressure, 20 sccm CF4 flow, room temperature) for 28 s. Finally, the resist was removed by leaving the samples in Remover 1165 on a hot plate set to 80 °C for 2 h, rinsing with acetone and isopropyl alcohol, and blow-drying with N2.

Reflectance Measurements: Reflectance measurements were performed at normal incidence with a 50x objective lens (Olympus SLMPL50X N.A. = 0.35) in ambient conditions using a confocal microscope (Horiba LabRam HR Evolution) and an external white light source (AvLab-HAL). The spot size was approximately 4 μm in diameter. For linearly polarized reflectance measurements, a linear polarizer (Edmund Linear Glass Polarizing Filter #43-783) was inserted between the and the sample. Measurements with the linear polarizer were limited to the spectral range of 400–825 nm due to polarizer bandwidth. Measurements were performed in the dark to minimize noise and the spectra were normalized to a baseline scan taken from the Al2O3/Ag and incident substrate. A background scan was also collected during which the white light source was turned off. The background was subtracted from each scan:

$$R = \frac{R_{\text{sample}} - R_{\text{background}}}{R_{\text{substrate}} - R_{\text{background}}}$$

(4)

Scanning Electron Microscope (SEM) Characterization: SEM images of metasurfaces were taken using a FEI Quanta 600 ESEM at an accelerating voltage of 10 kV and with a spot size of 2.0.

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

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

2D materials, dirac semimetals, metasurfaces, perfect absorbers, PtSe2

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