

# Tailoring optical absorption via metasurfaces

*Fundamentals of Plasmonics and Metaphotonics IV, Fall MRS 2022*

Stefan A Maier

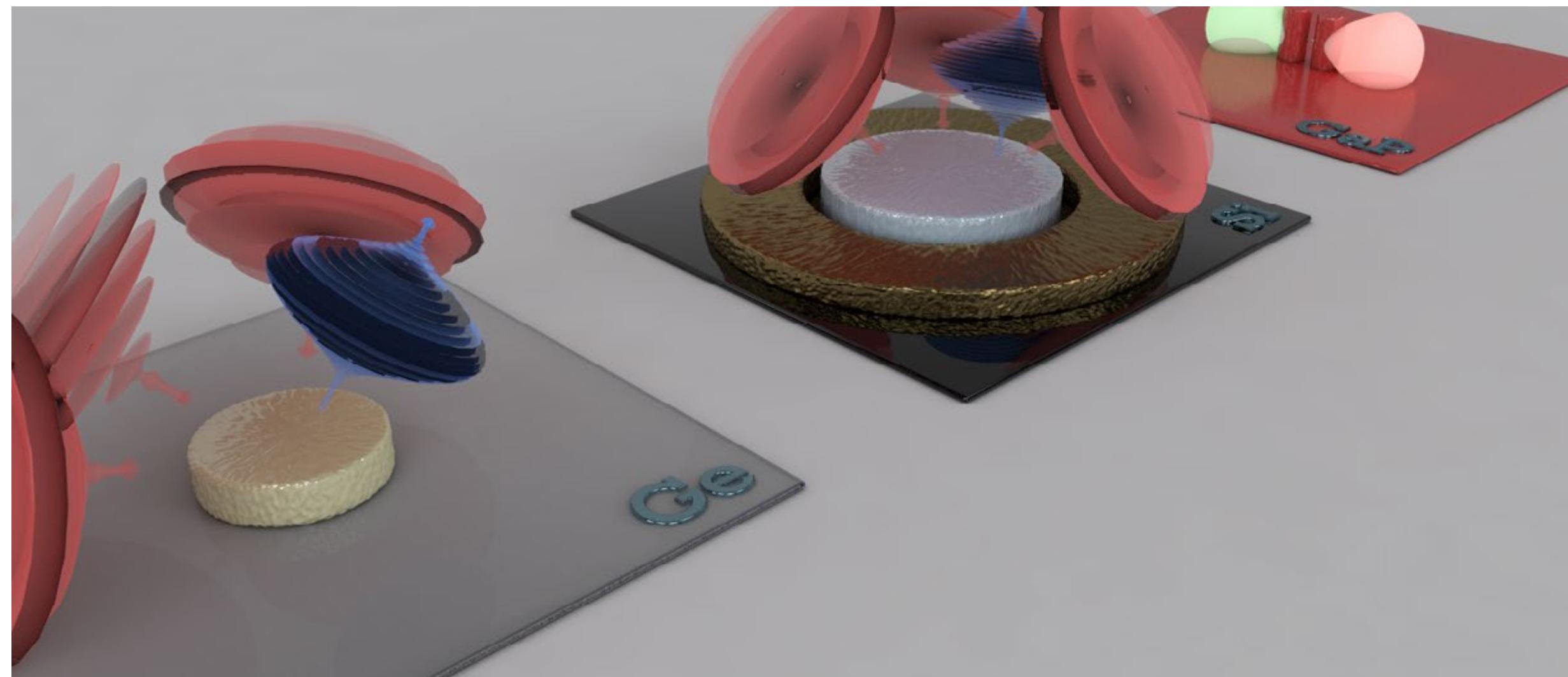
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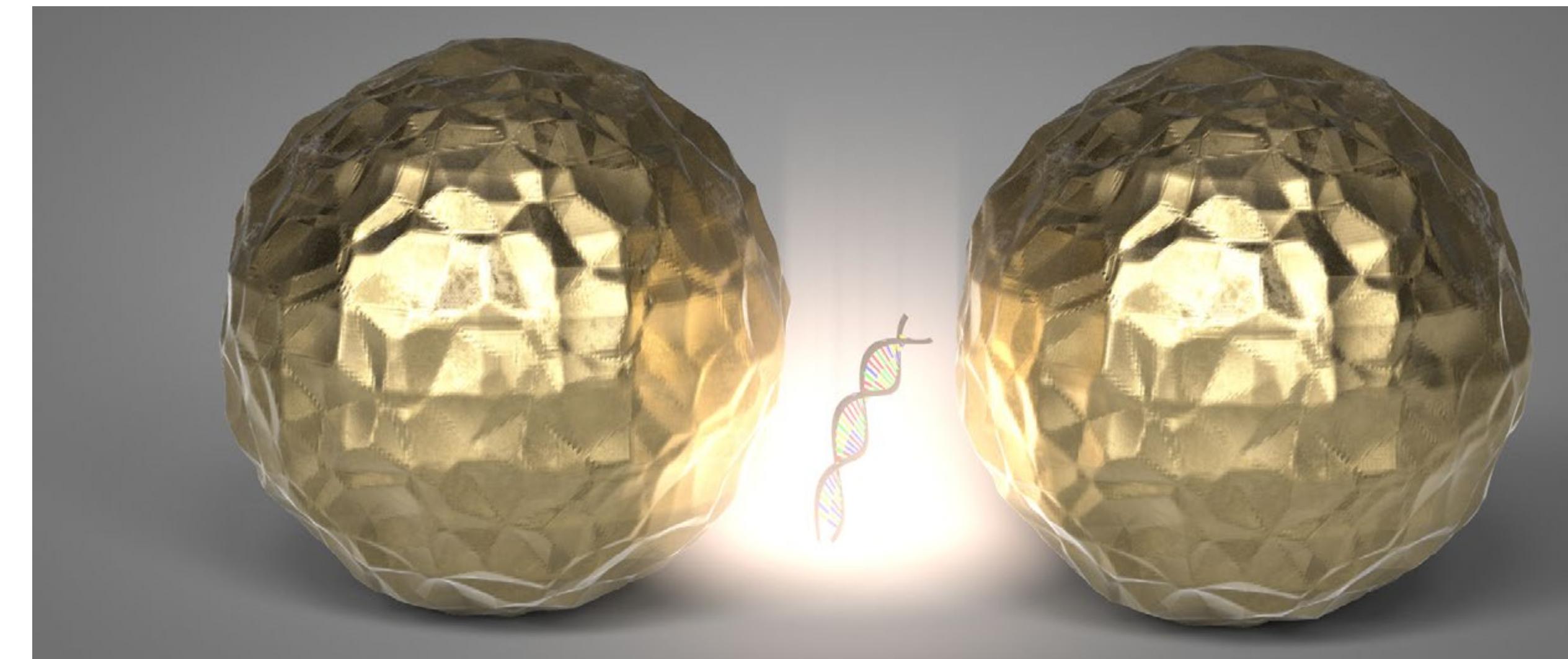
[Stefan.Maier@monash.edu](mailto:Stefan.Maier@monash.edu)

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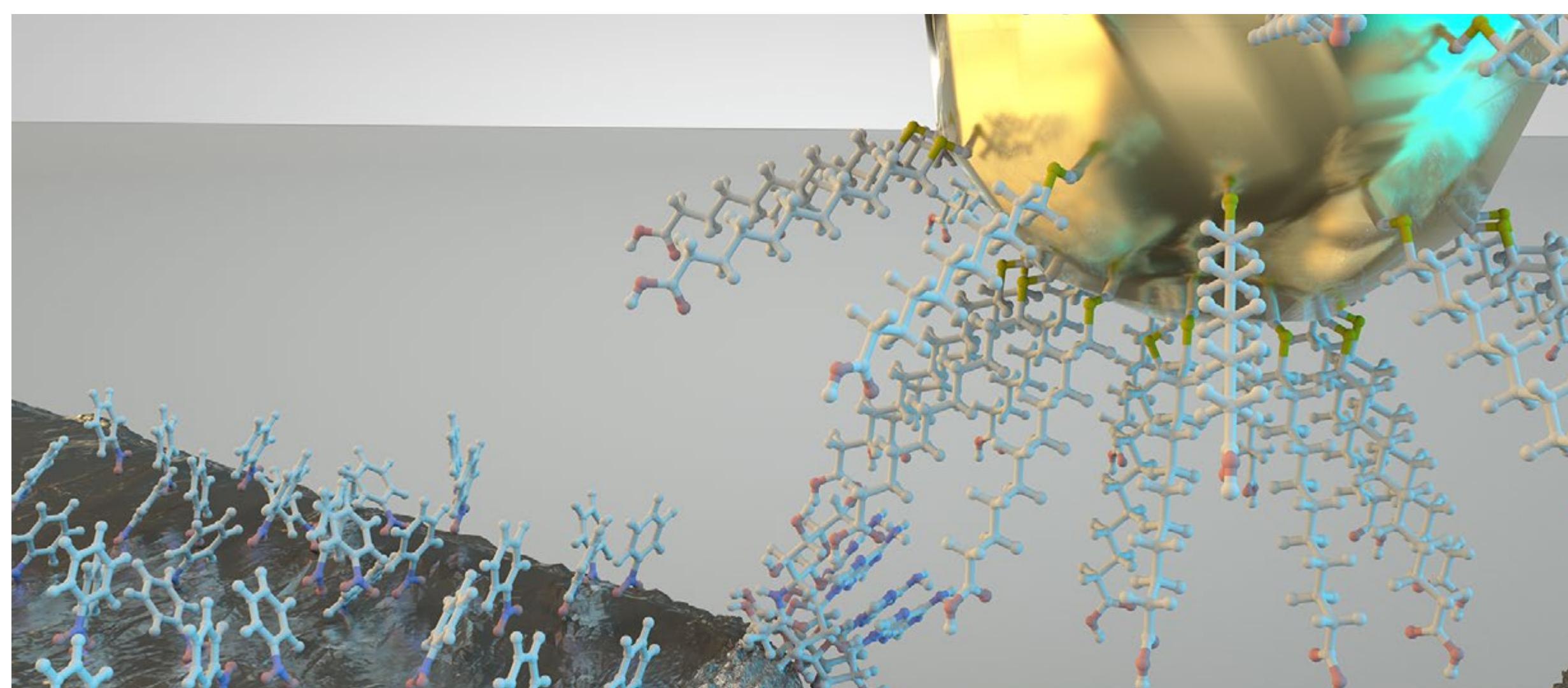
# Nanophotonics for control of light-matter coupling



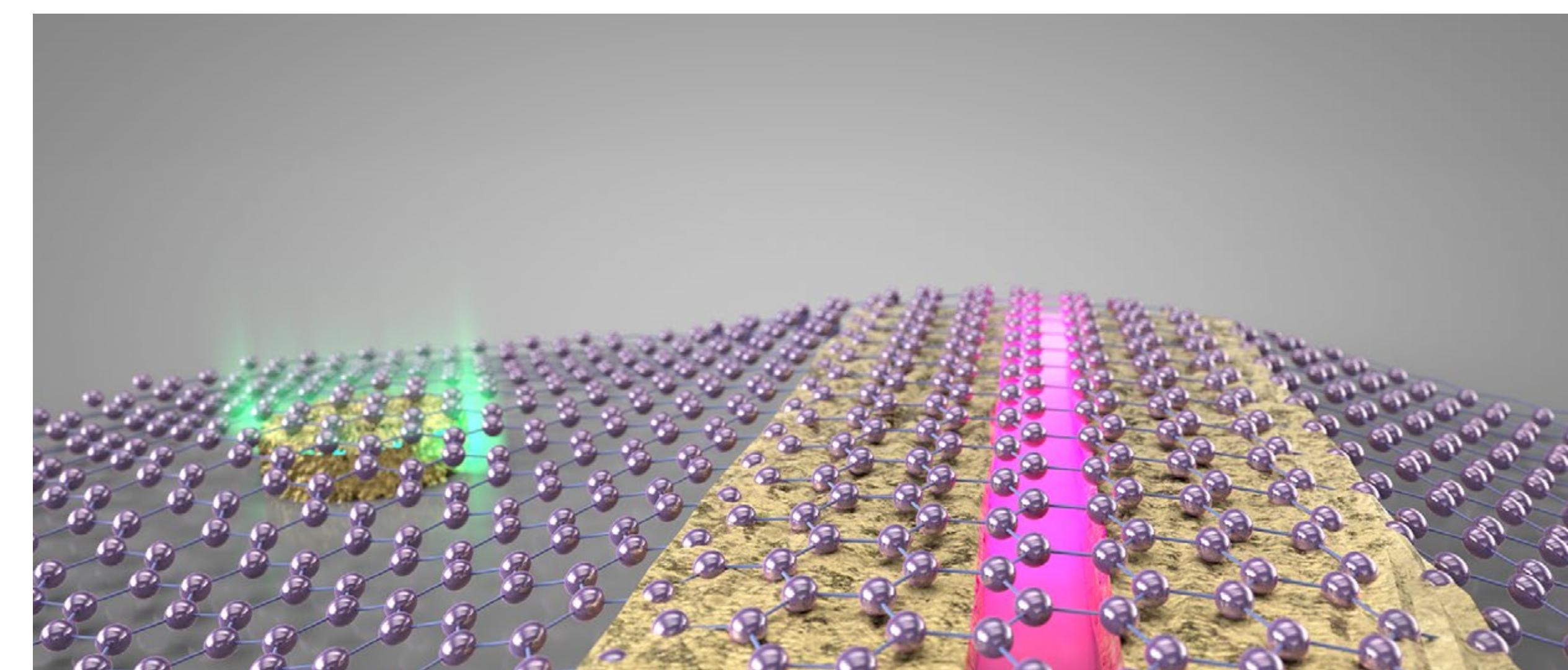
Non-linear interactions and emission control



Surface-enhanced sensing and spectroscopy

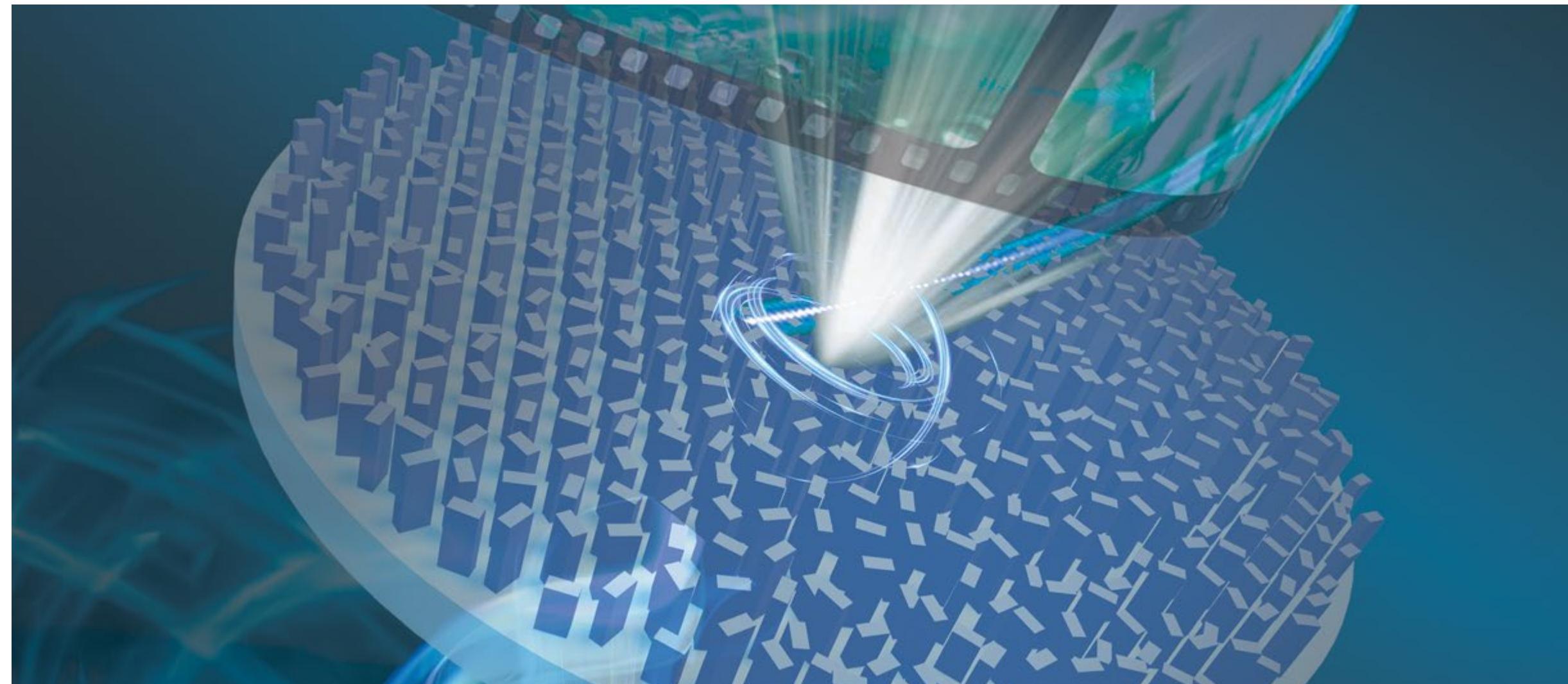


Energy conversion and plasmonic chemistry

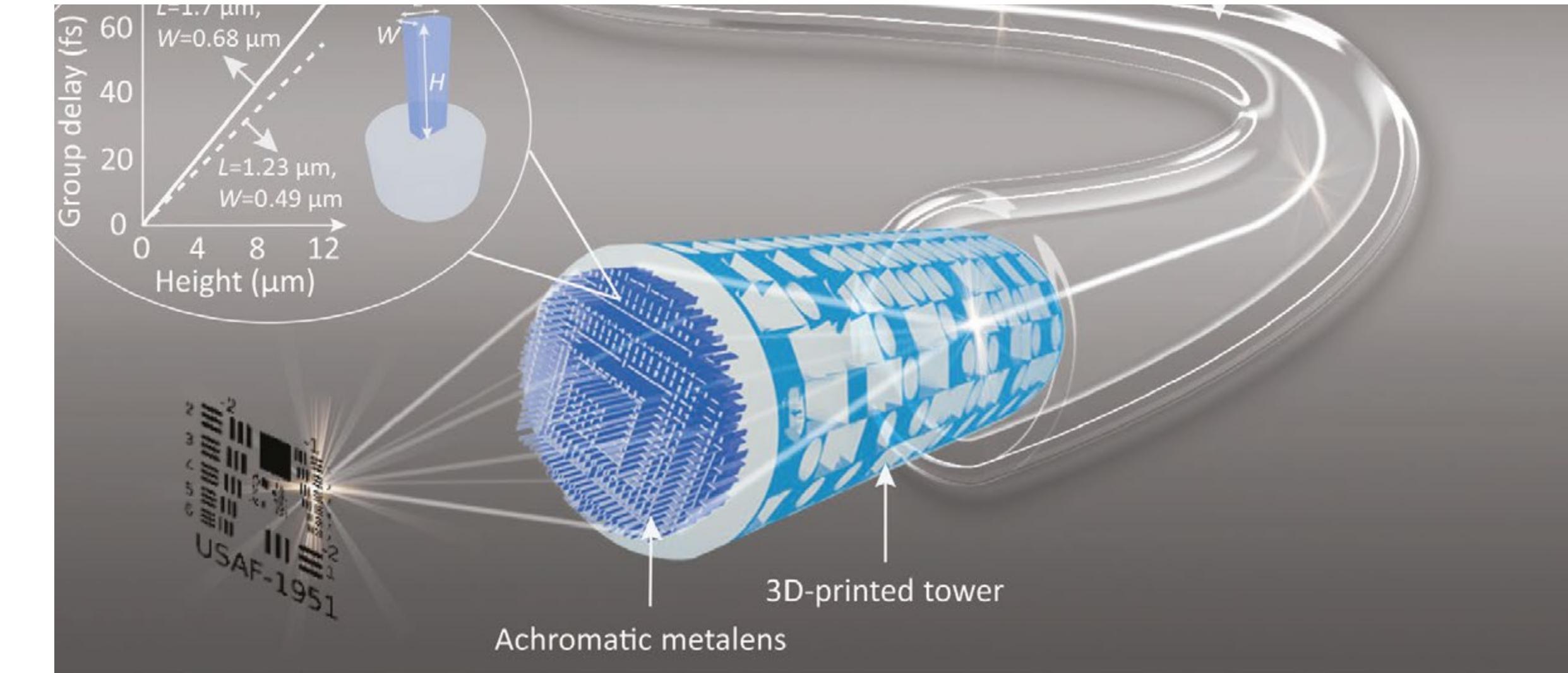


Coupling to low-dimensional materials and devices

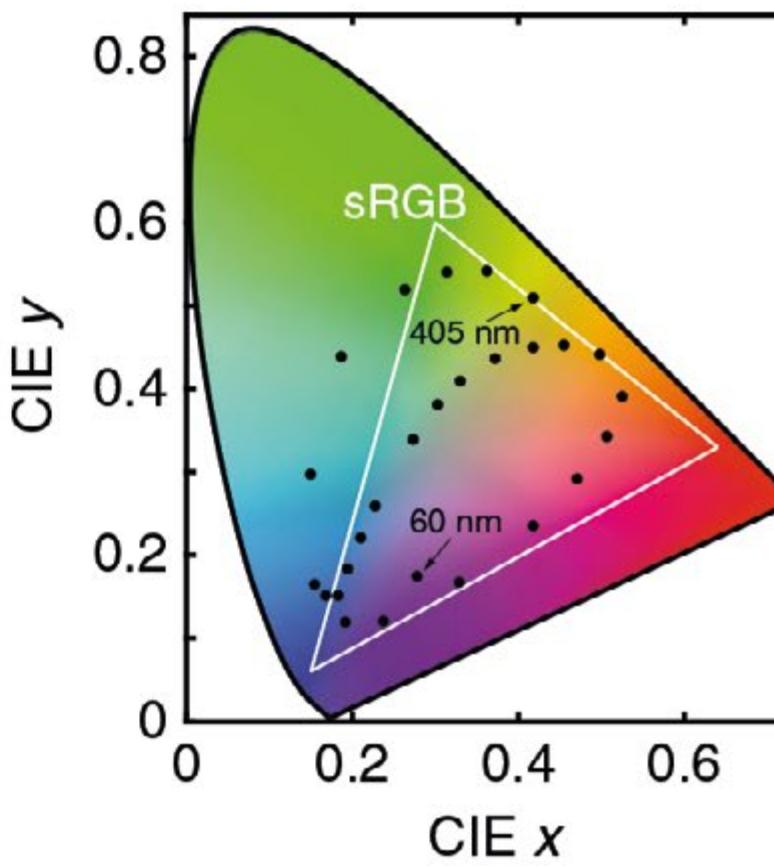
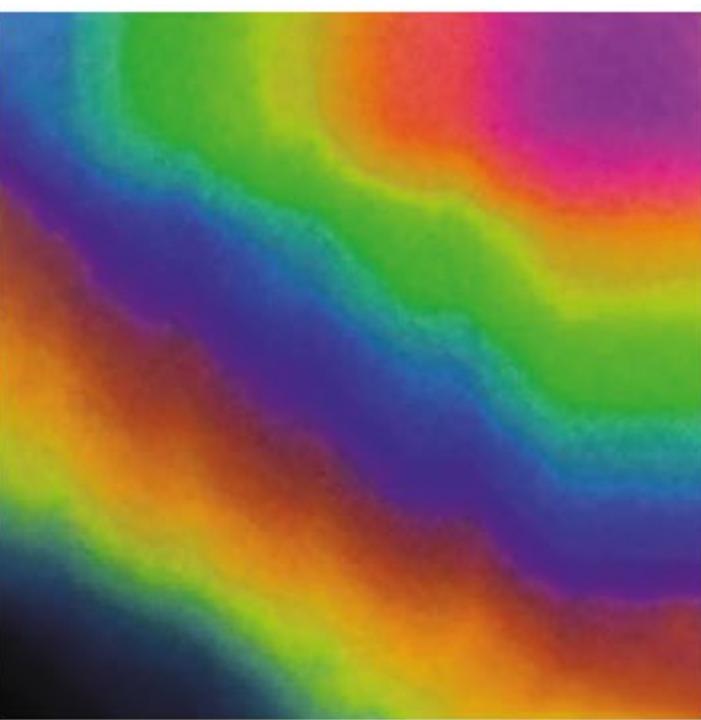
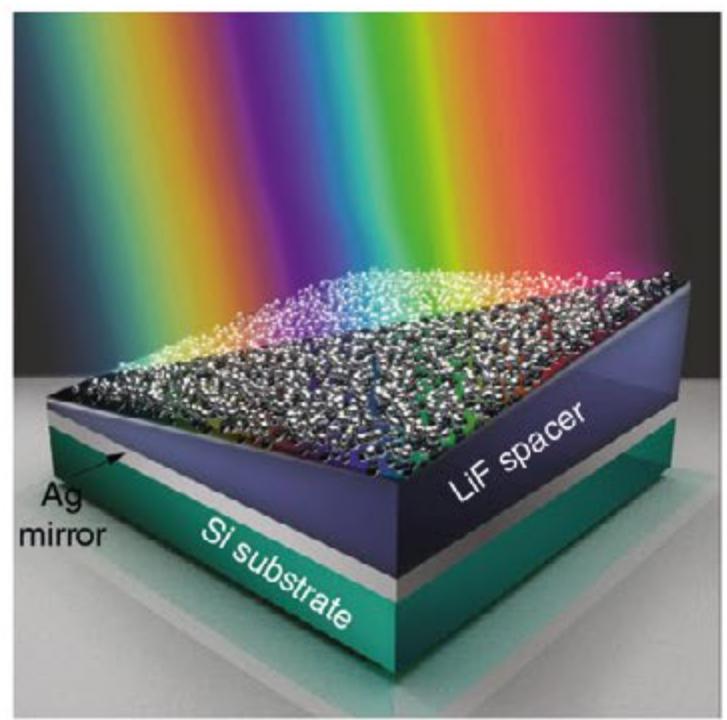
# Meta-optics: Metasurfaces and metafibers



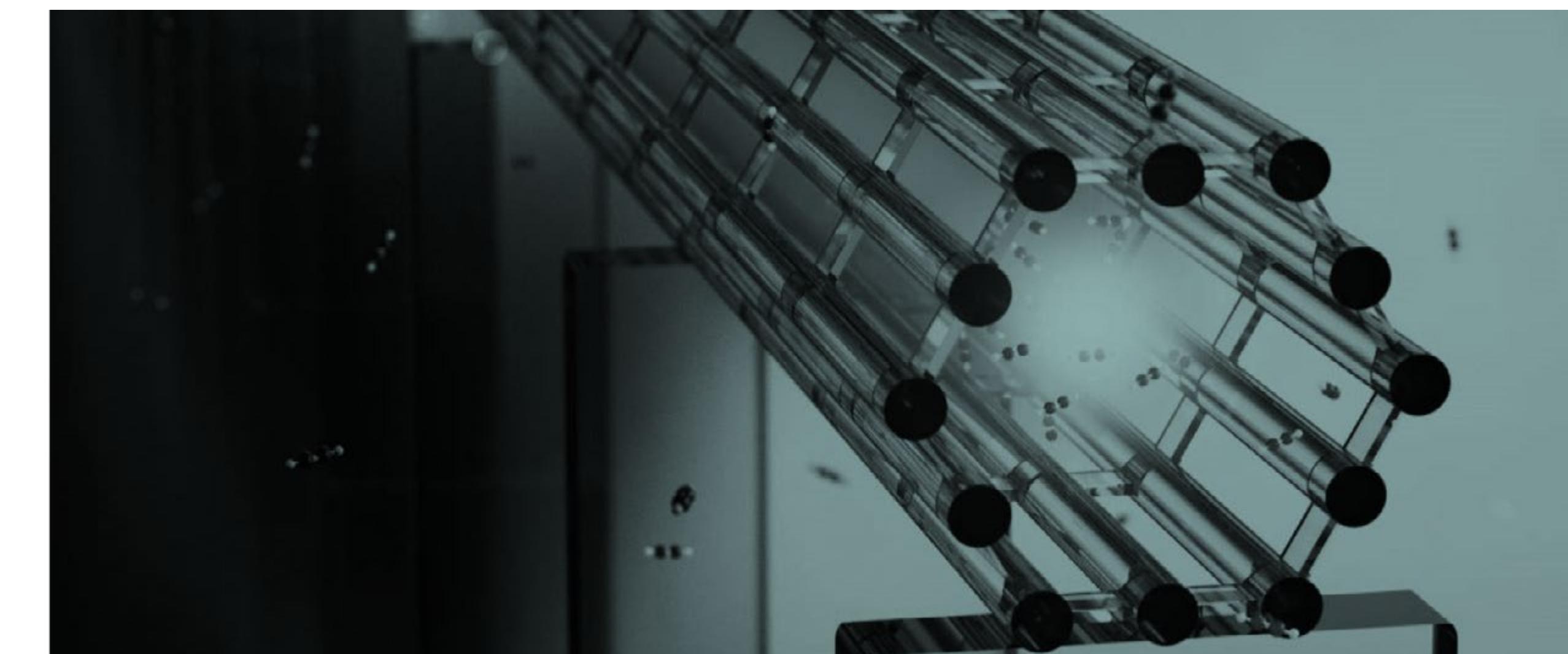
Holography



Telecommunications and fiber optics

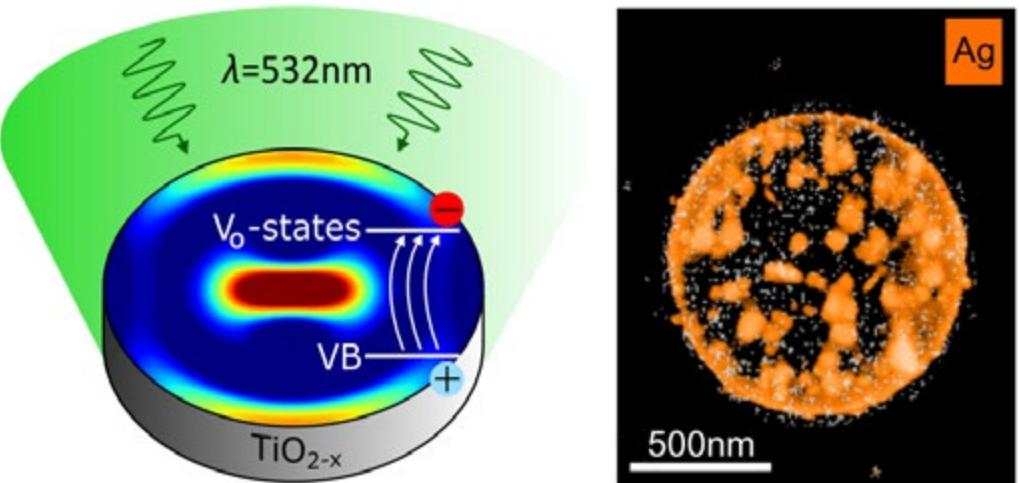


Light harvesting with disordered systems



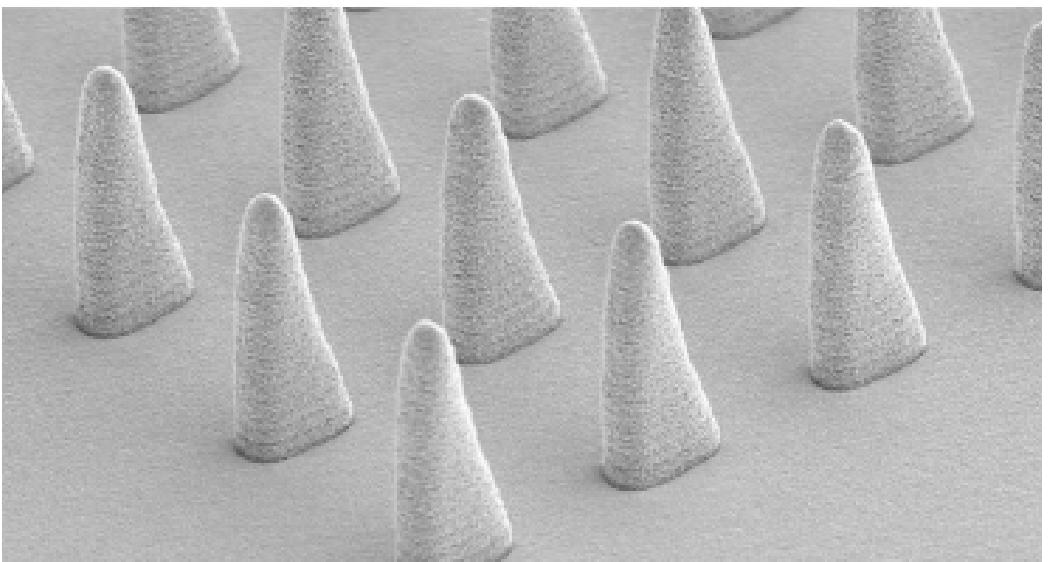
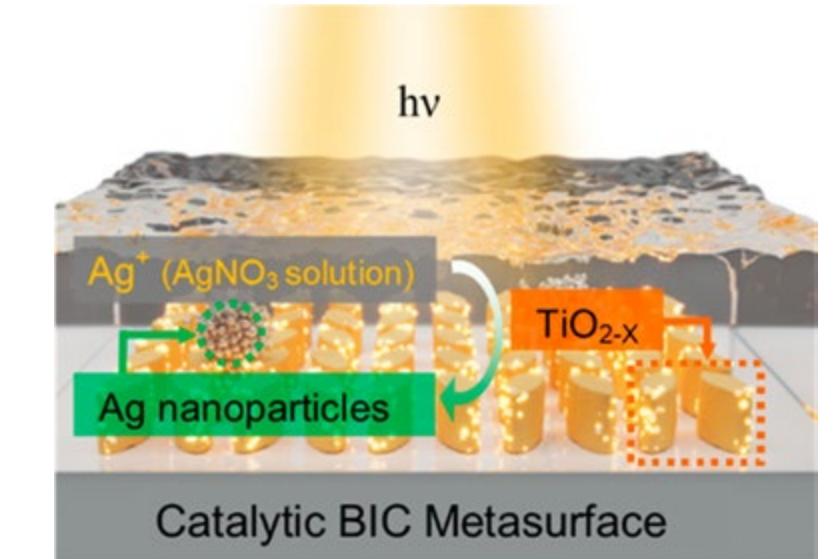
Light cages for sensing and spectroscopy

# Outline



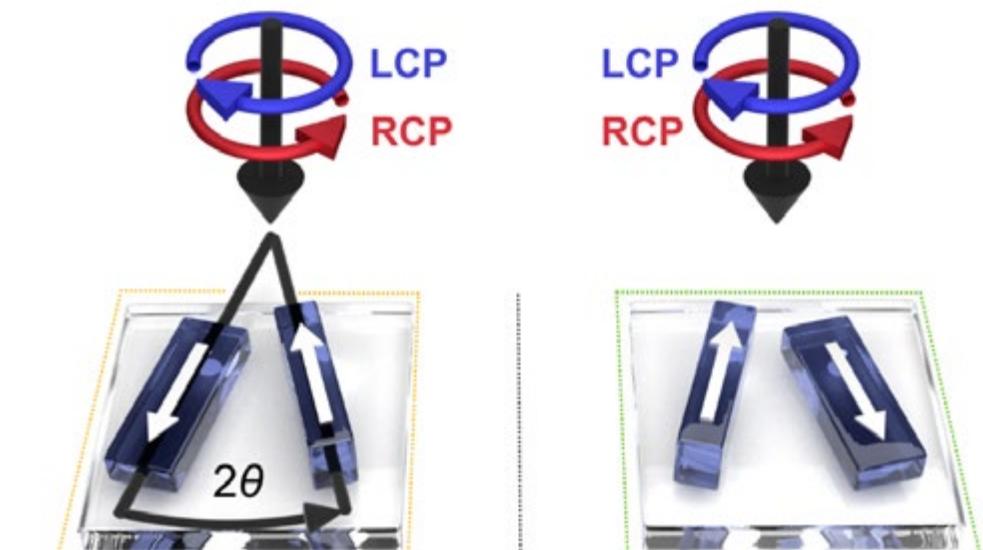
## Anapoles and BICs for energy conversion

*ACS Nano* **16**, 13057 (2022)  
*Adv Energy Mater* **11**, 2102877 (2021)  
*ACS Photonics* **8**, 1469 (2021)  
*ACS Nano* **14**, 2456 (2020)



## BICs for infrared absorption and chirality

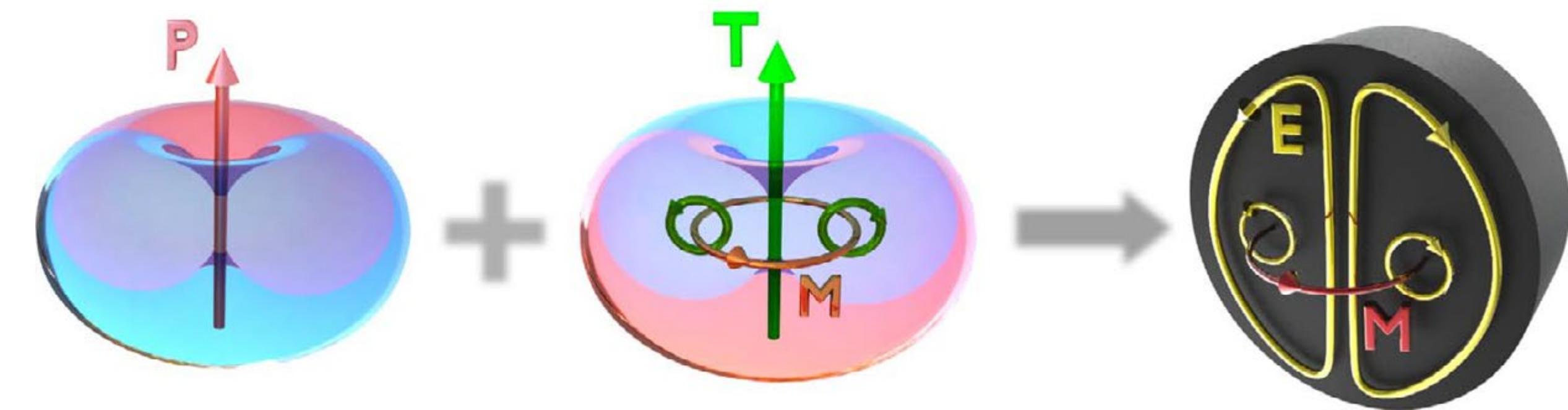
*arXiv:2210.05339*



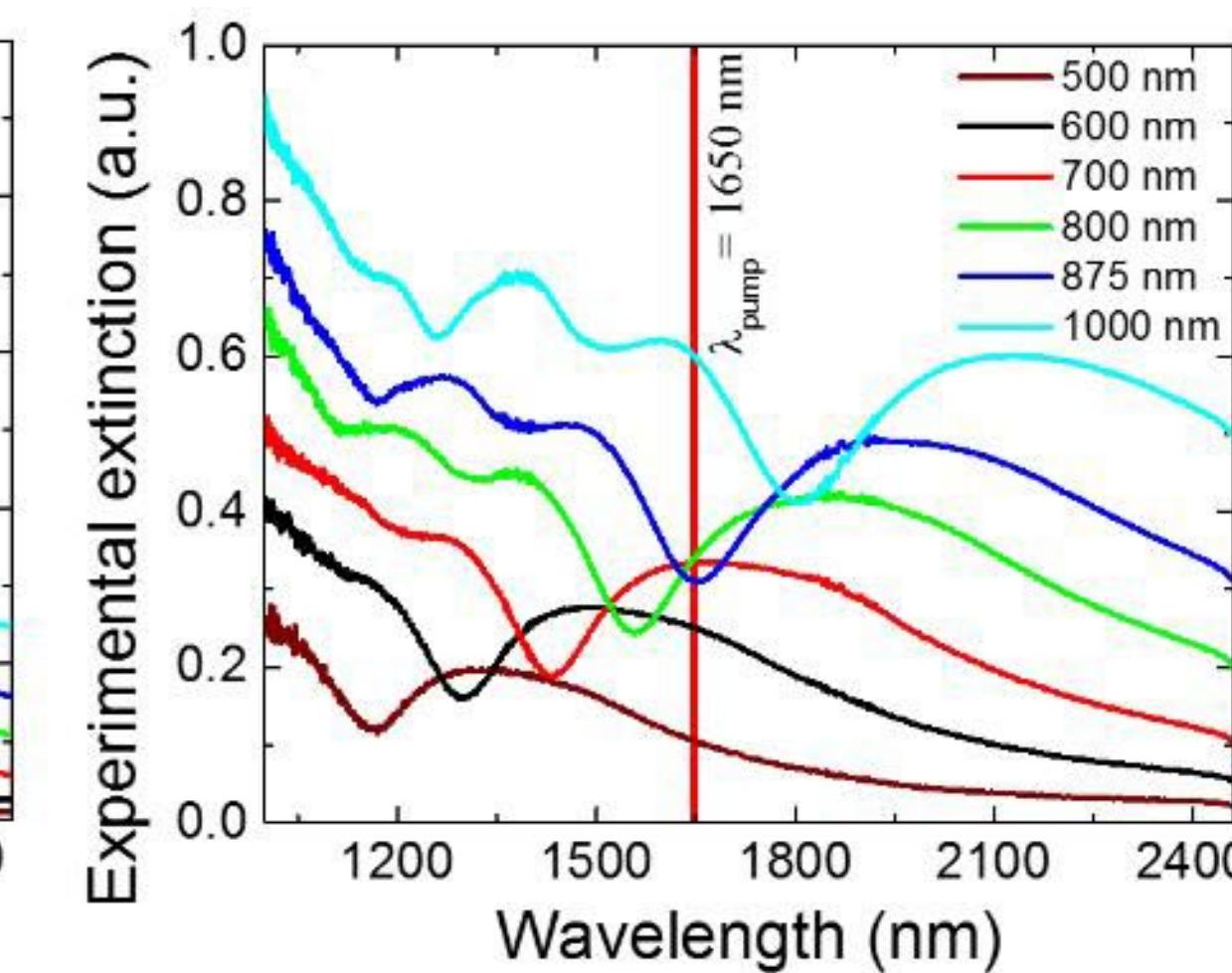
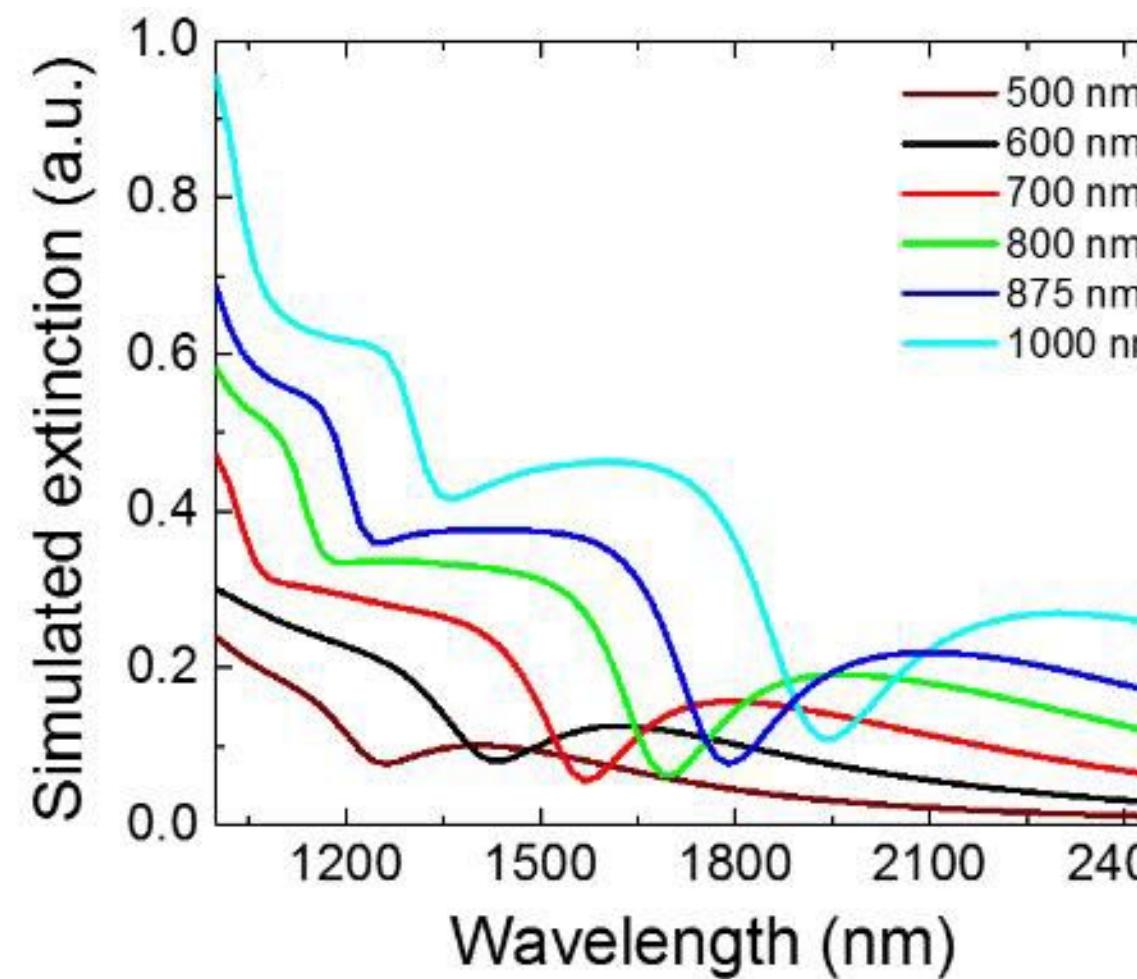
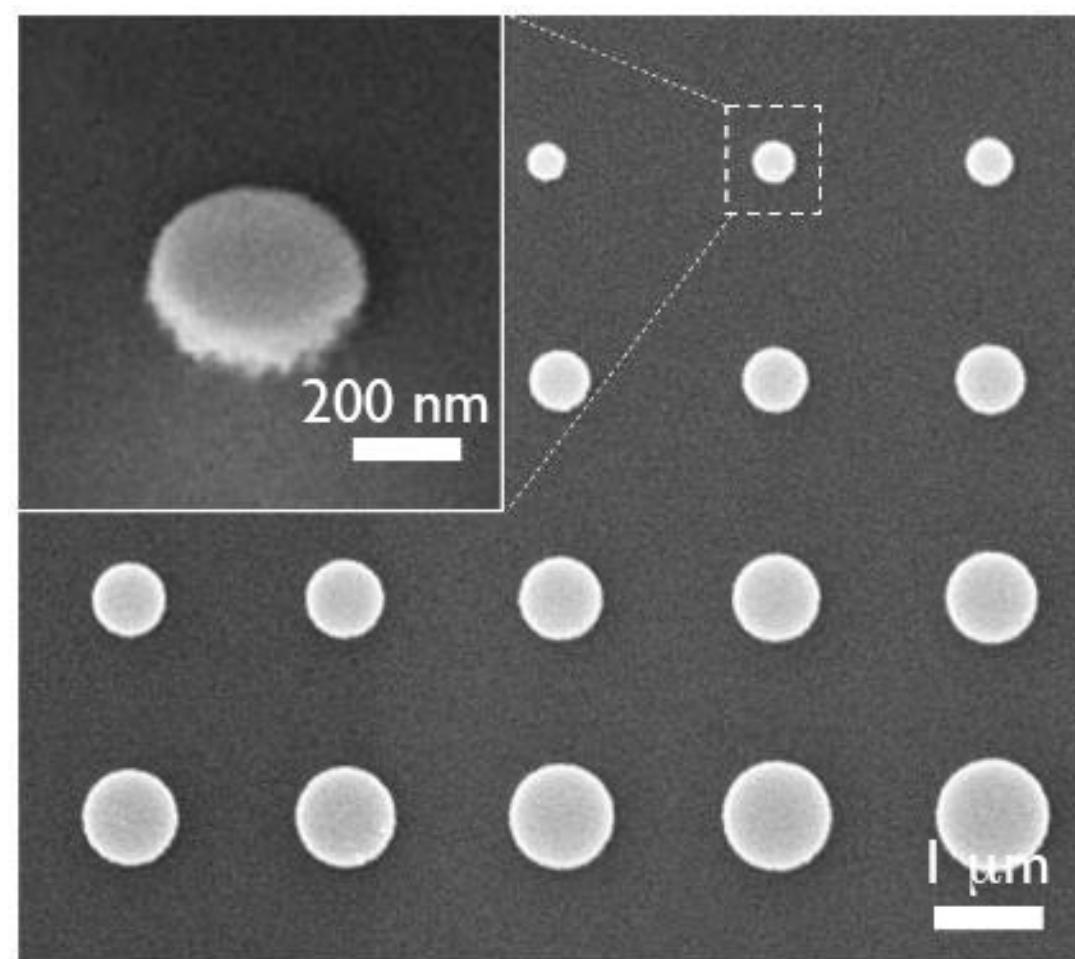
# Maximizing field intensity within dielectric nanostructures

Nano Letters 16, 4635 (2016)

- Anapole excitations, composed of electric and toroidal dipole moments, show a pronounced valley in the scattering cross section due to destructive interference between their similar radiation patterns.
- cf toroidal metamaterial work by Zheludev group (Science 330, 1510 (2010))
- These excitations can occur in thin dielectric nanostructures, in our example 100 nm thick Ge nanodisks of an aspect ratio < 0.4.
- This provides a route to maximizing the electric field energy inside the particle.



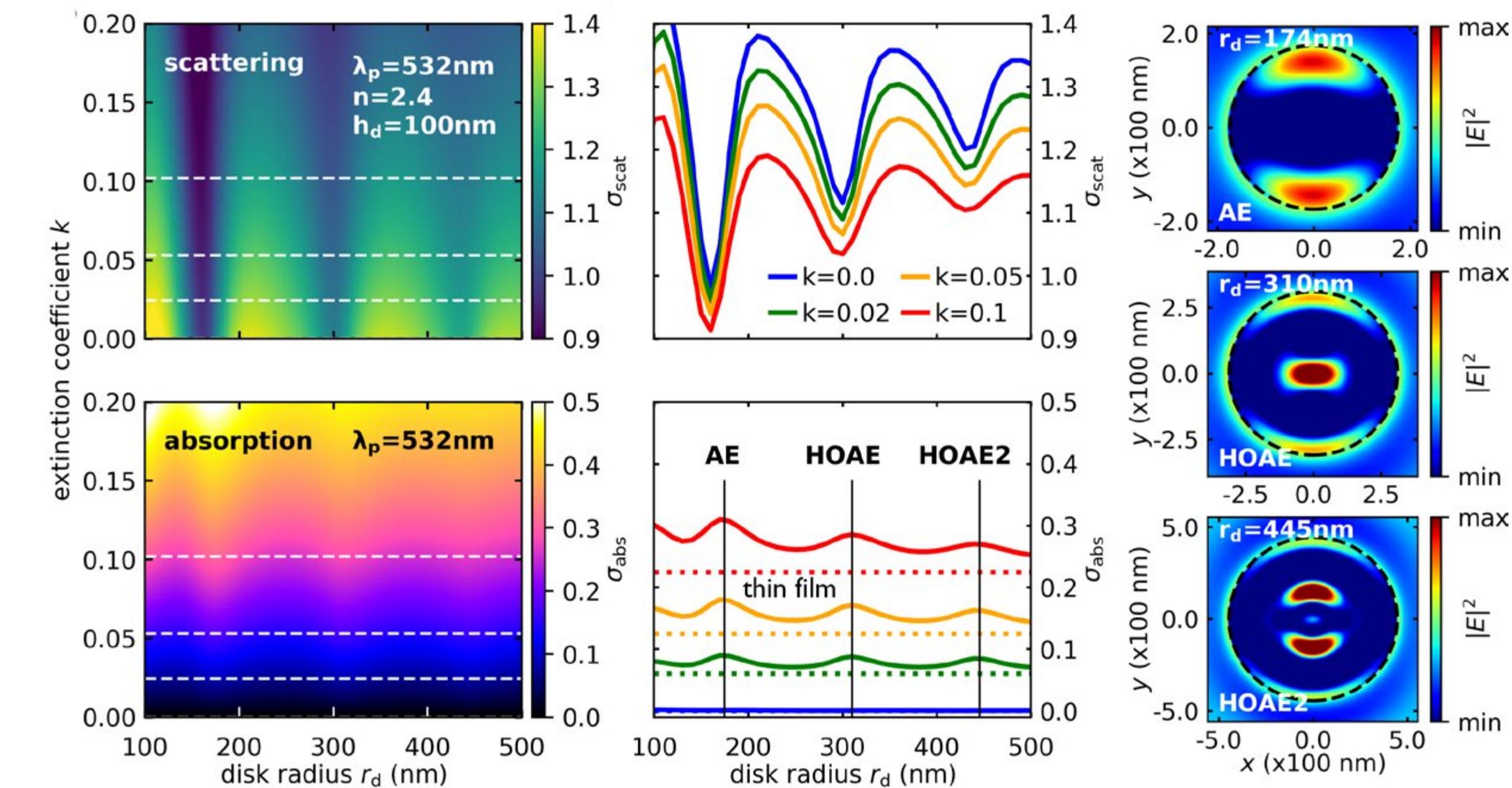
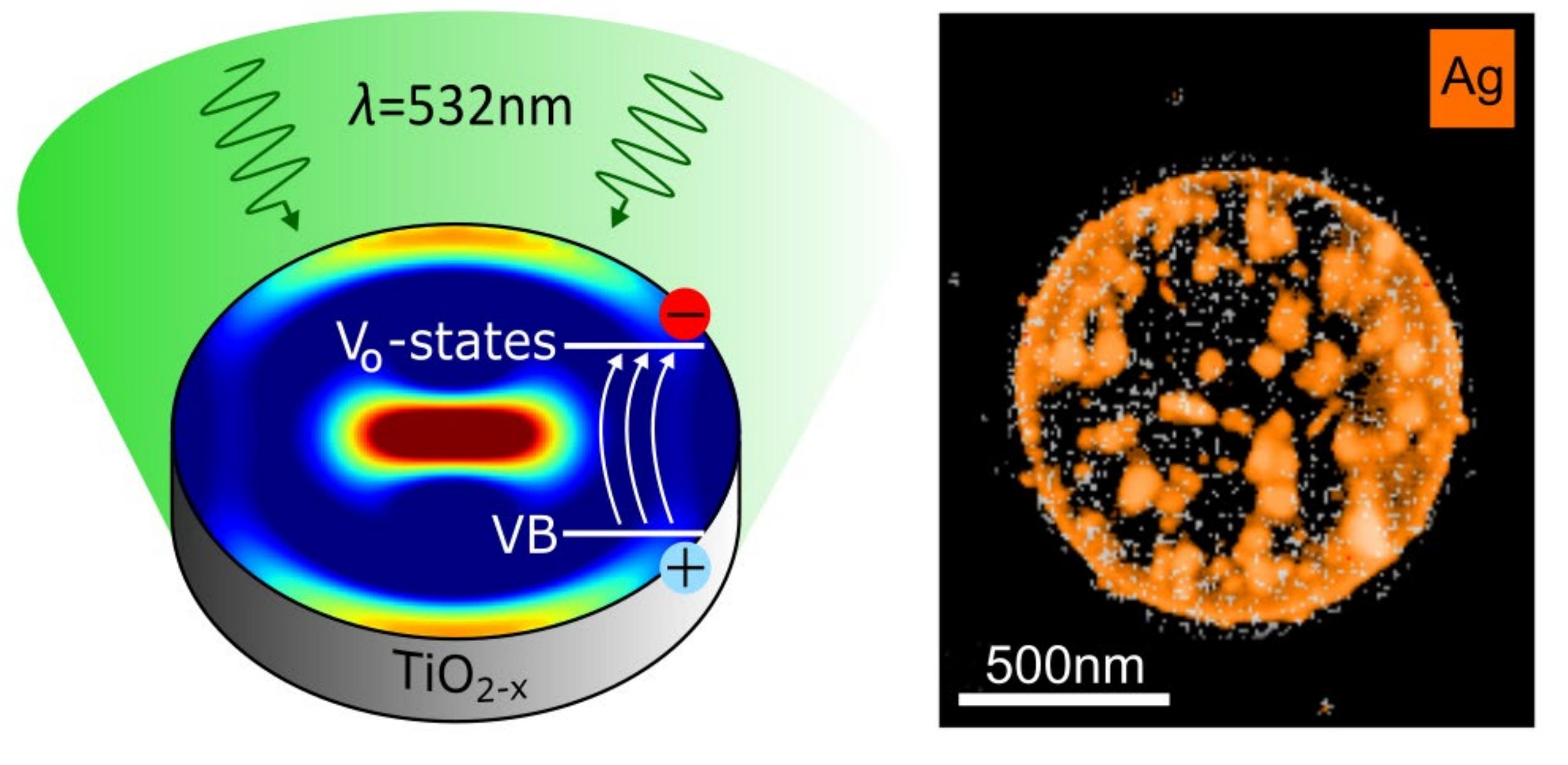
Nature Communications 6, 8069 (2015), Kivshar group



Anapole excitations as a route towards strong light/matter interactions

# Anapole excitations to increase absorption

ACS Nano 14, 2456 (2020)

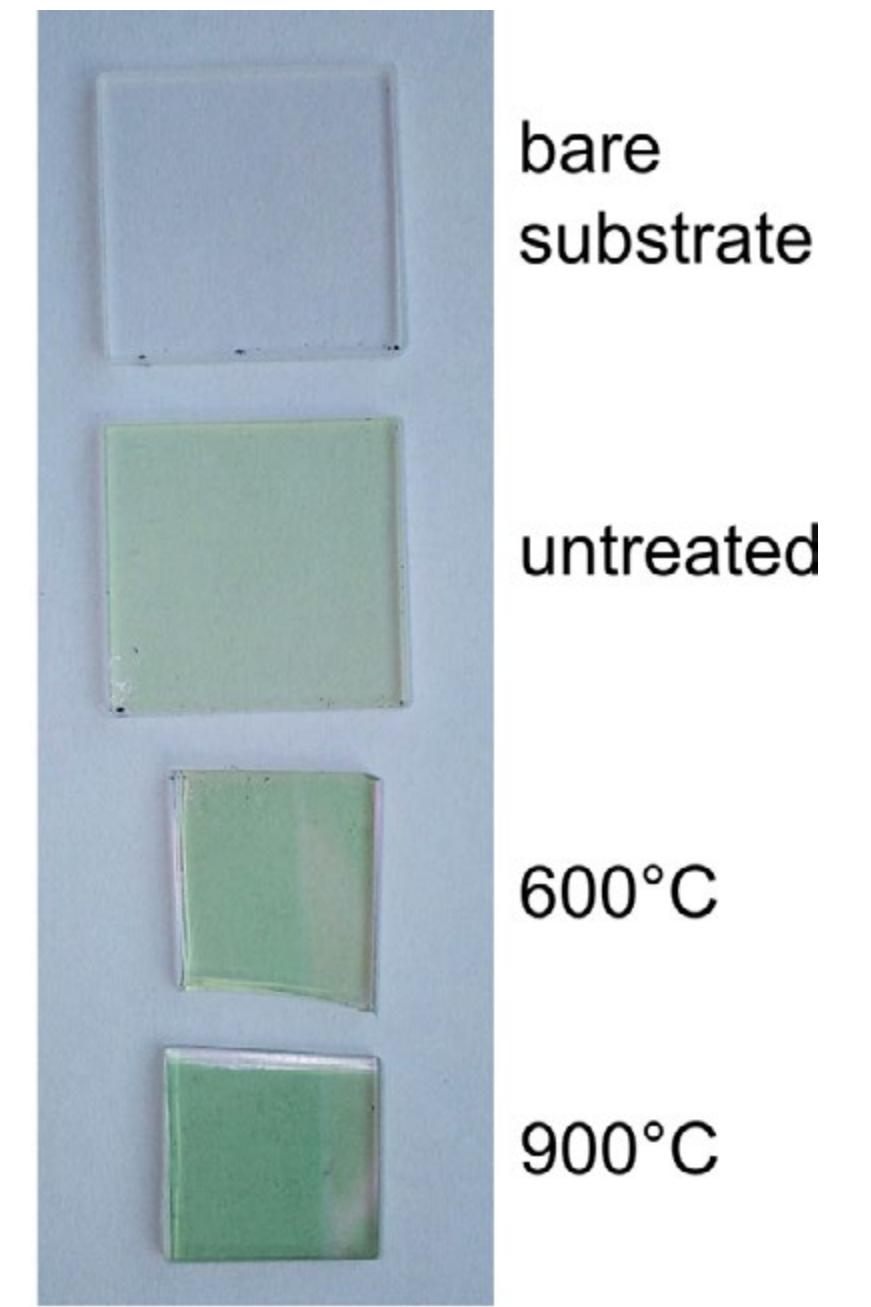
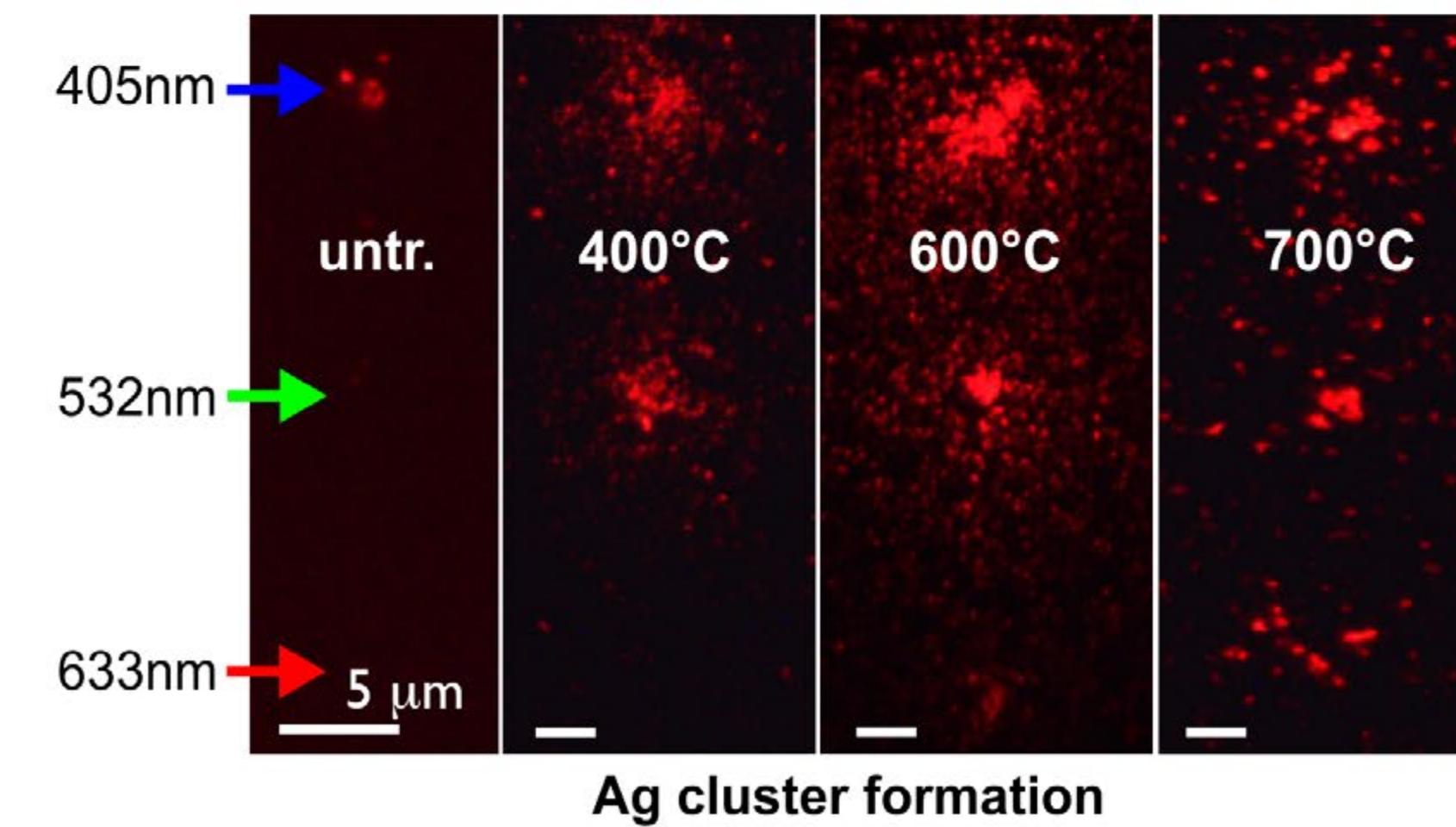
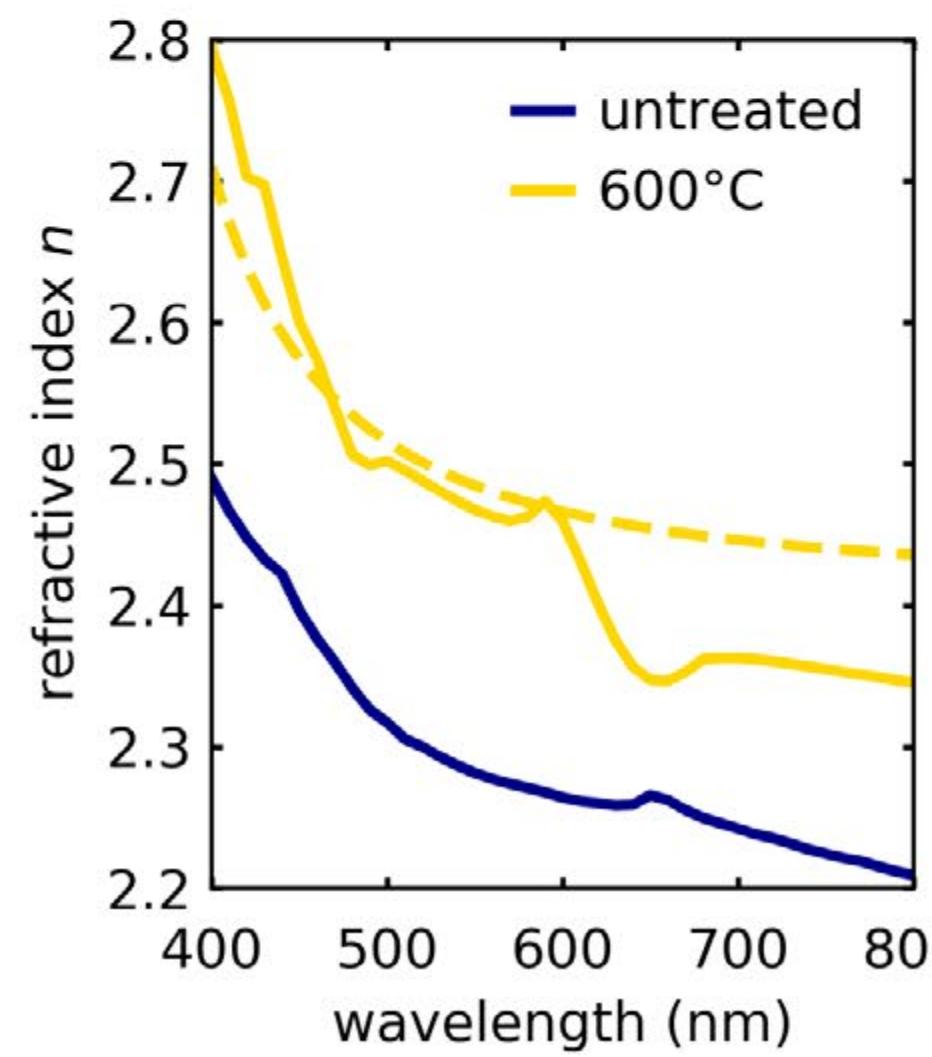
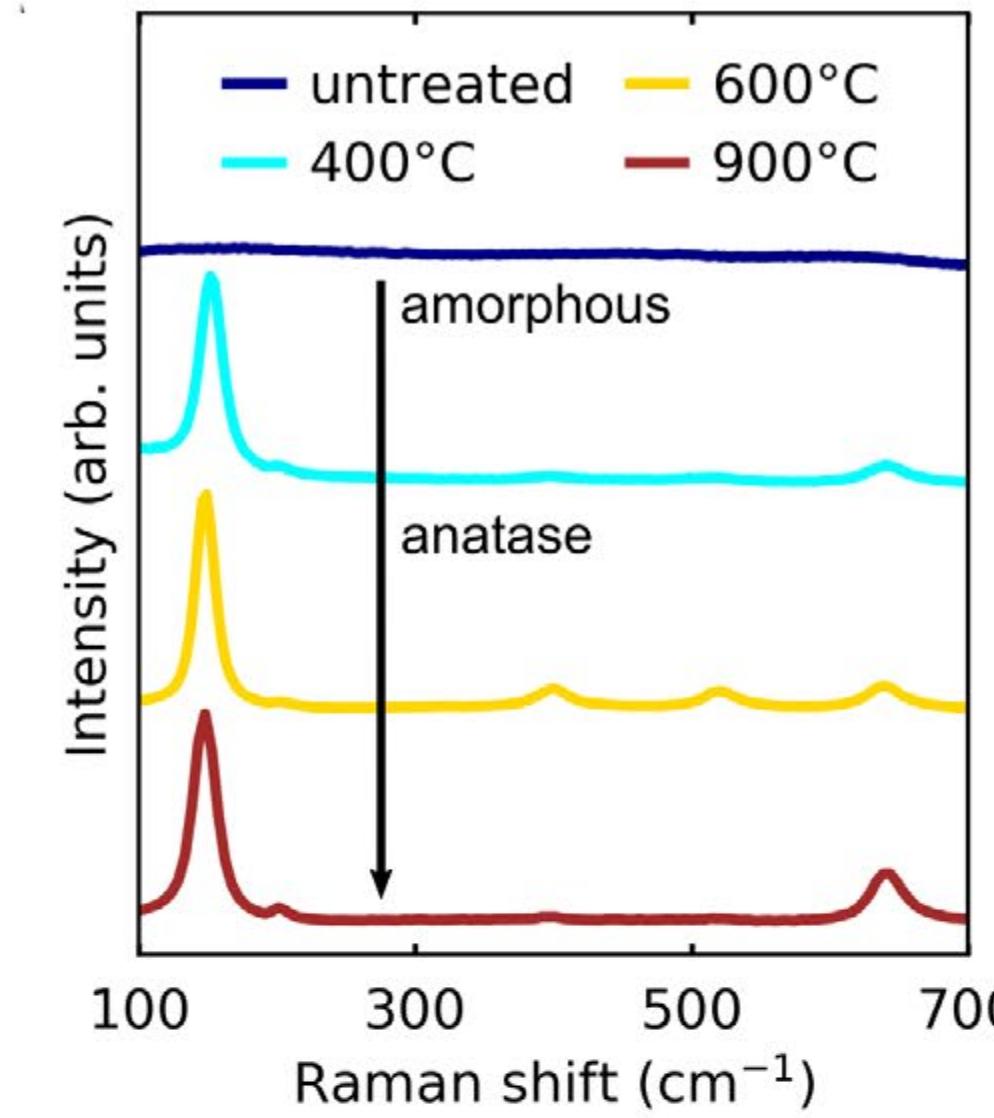
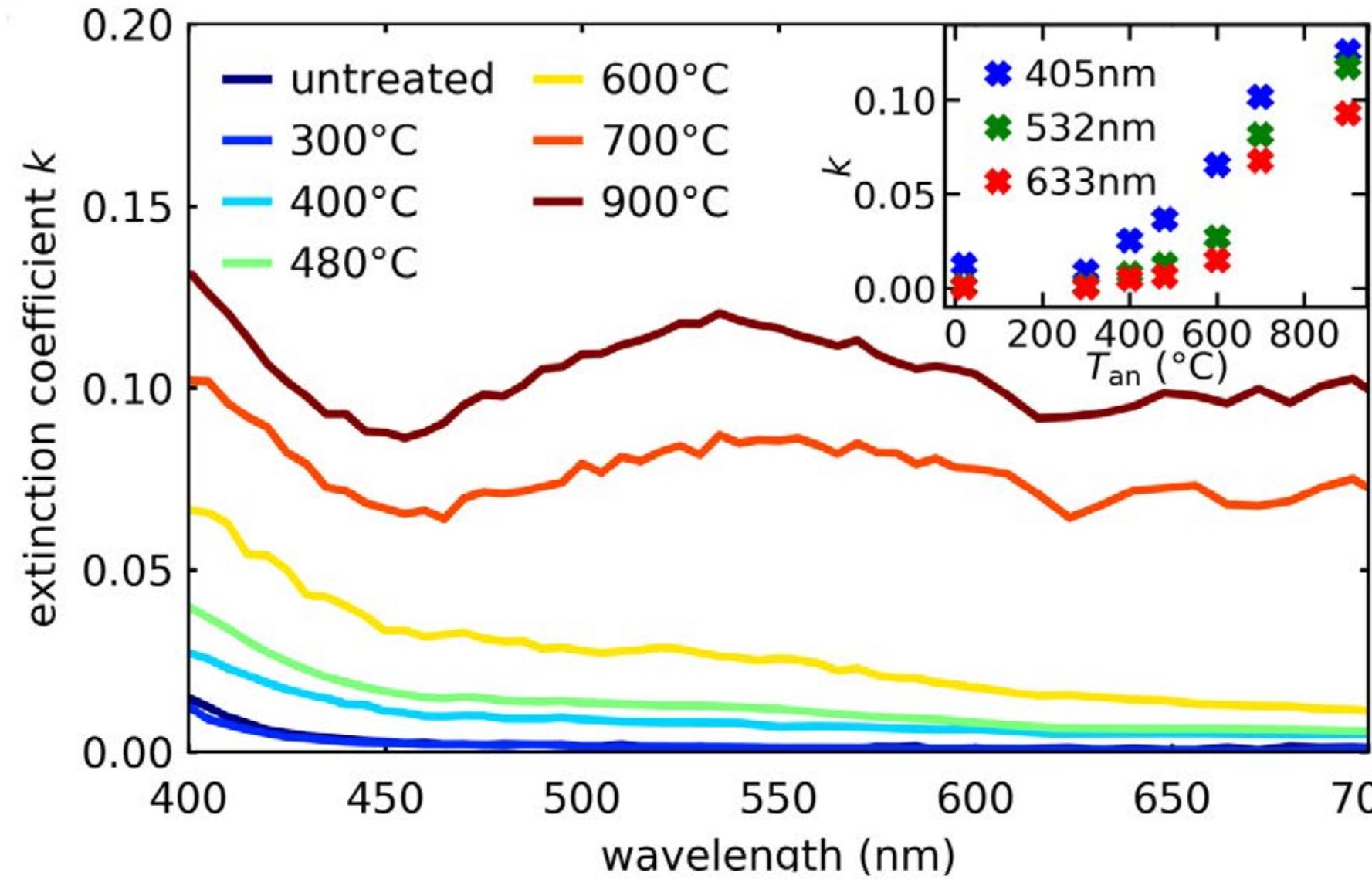


- goal: utilize anapole excitations to directly increase absorption for photo-generation of charge carriers in solar photocatalysis
- $\text{TiO}_2$  as a model system as it allows control of material absorption via oxygen vacancy generation
- photocatalytic activity monitored via  $\text{Ag}^+$  reduction

- however  $\text{TiO}_2$  not ideal due to relatively low refractive index compared to previous demonstrations of anapole modes (in Si, Ge, GaP, ...)
- determine optimum extinction coefficient  $k$  for nanophotonic engineering
- low but non-zero extinction coefficient leads to reasonably high contrast between disk-engineered and bare film absorption in water

# Oxygen vacancy creation via thermal annealing

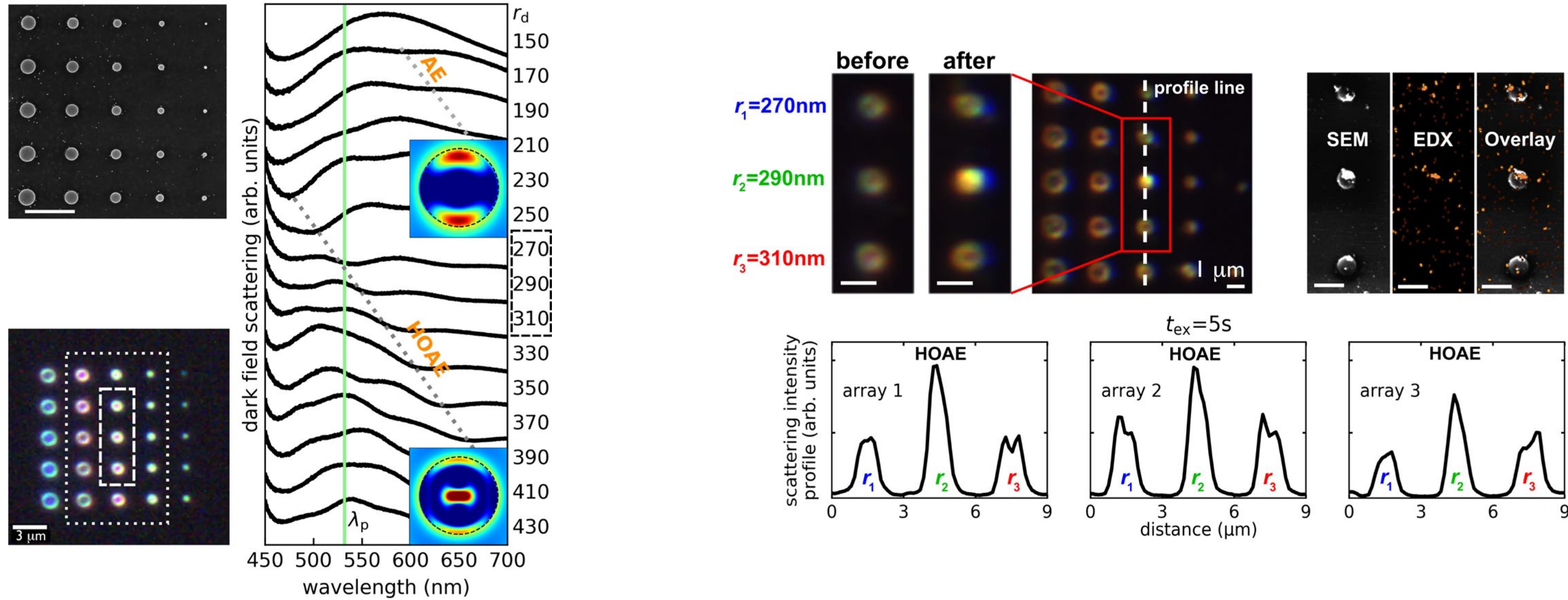
ACS Nano 14, 2456 (2020)



- vacancy centre creation via thermal annealing of 160 nm films; absorption increase monitored via photothermal deflection spectroscopy
- $k \approx 0.03$  @ 532 nm chosen ( $T = 600^\circ\text{C}$ ) in order not to lower  $n$  too significantly; additional problem of crack formation
- surface-activity of generated oxygen vacancy centres monitored via  $\text{Ag}^+$  photoreduction of  $\text{AgNO}_3$  salt
- for vacancy centre creation and monitoring via photoreduction cf Wu et al, *Science Advances* 5, eaax0939 (2019)

# Photoreduction in $\text{TiO}_2$ anapole disks

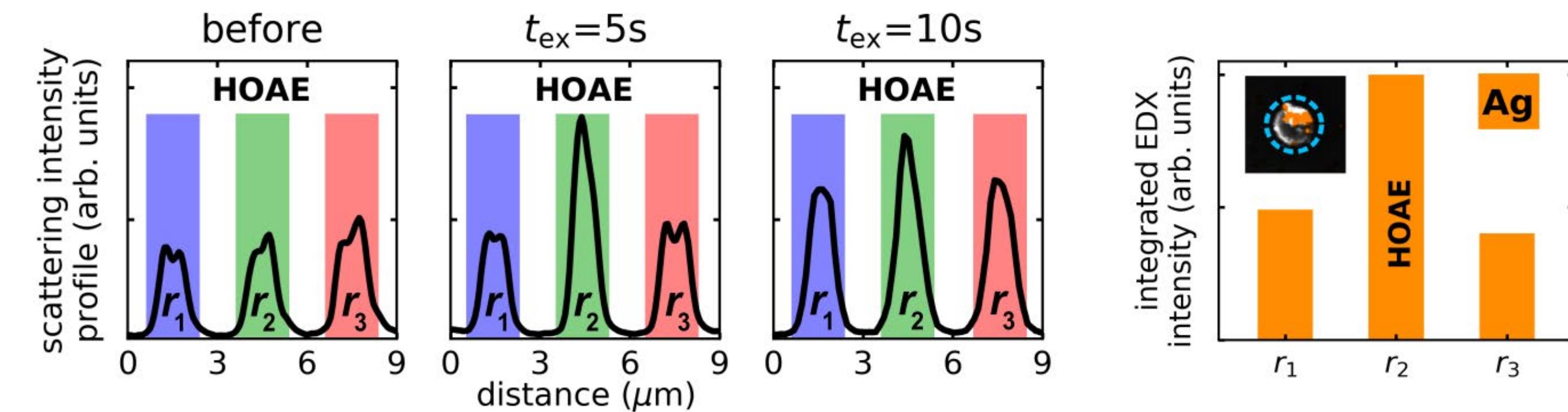
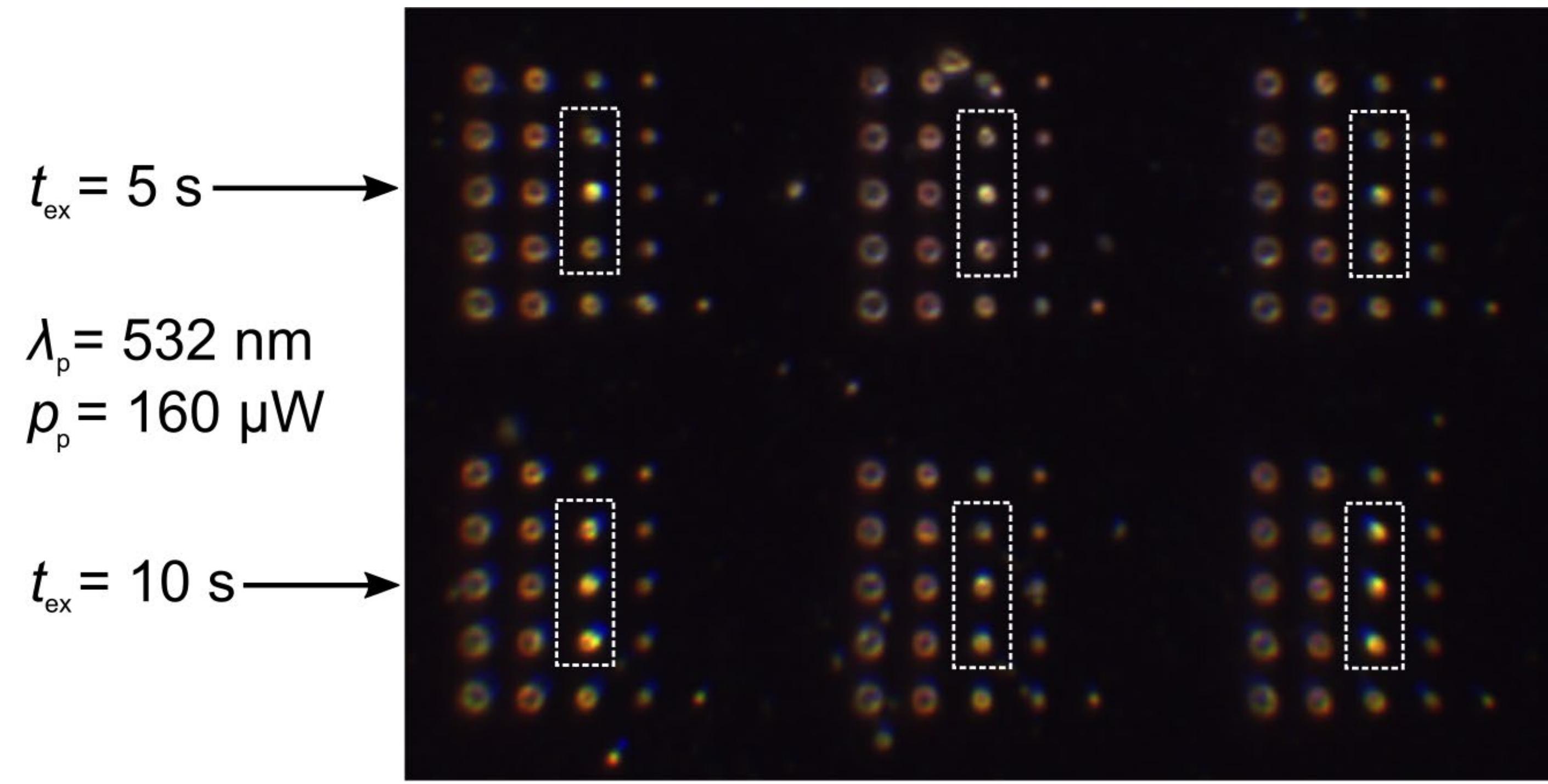
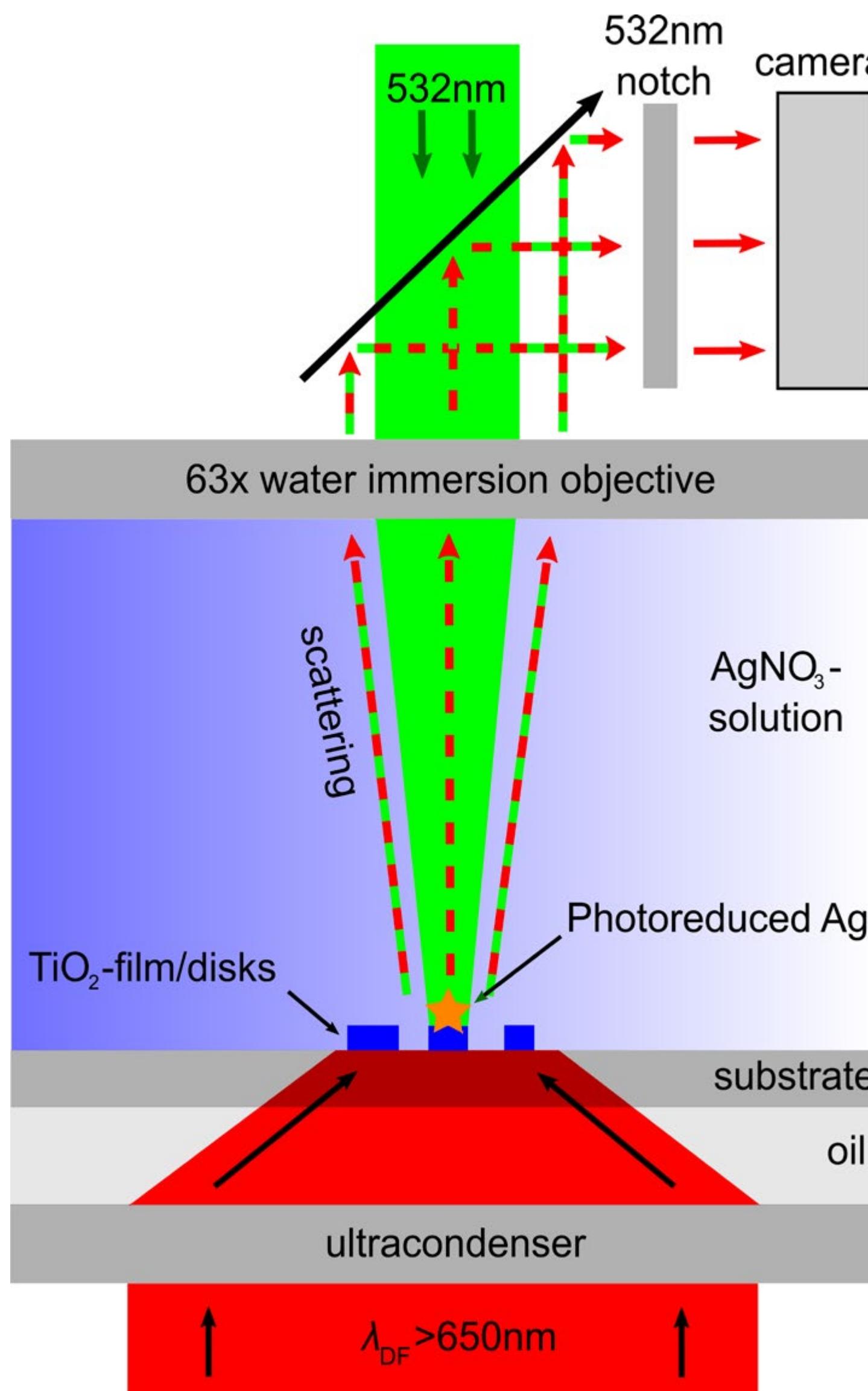
ACS Nano 14, 2456 (2020)



- utilization of higher-order anapole mode for demonstration of confinement-enhanced charge-carrier generation via  $\text{Ag}^+$  photoreduction in 1mM  $\text{AgNO}_3$  aqueous solution
- simulations predict 25 nm blue-shift of absorption maximum with respect to scattering minimum  $\Rightarrow$  290 nm disk
- excitation at 532 nm with 160 mW for 5s
- Ag cluster formation confirmed via EDX, quantitative assessment difficult
- lower bound of photocatalytic enhancement given by geometrical cross section ratio of 1.14 (310 and 290 nm diameter disks)

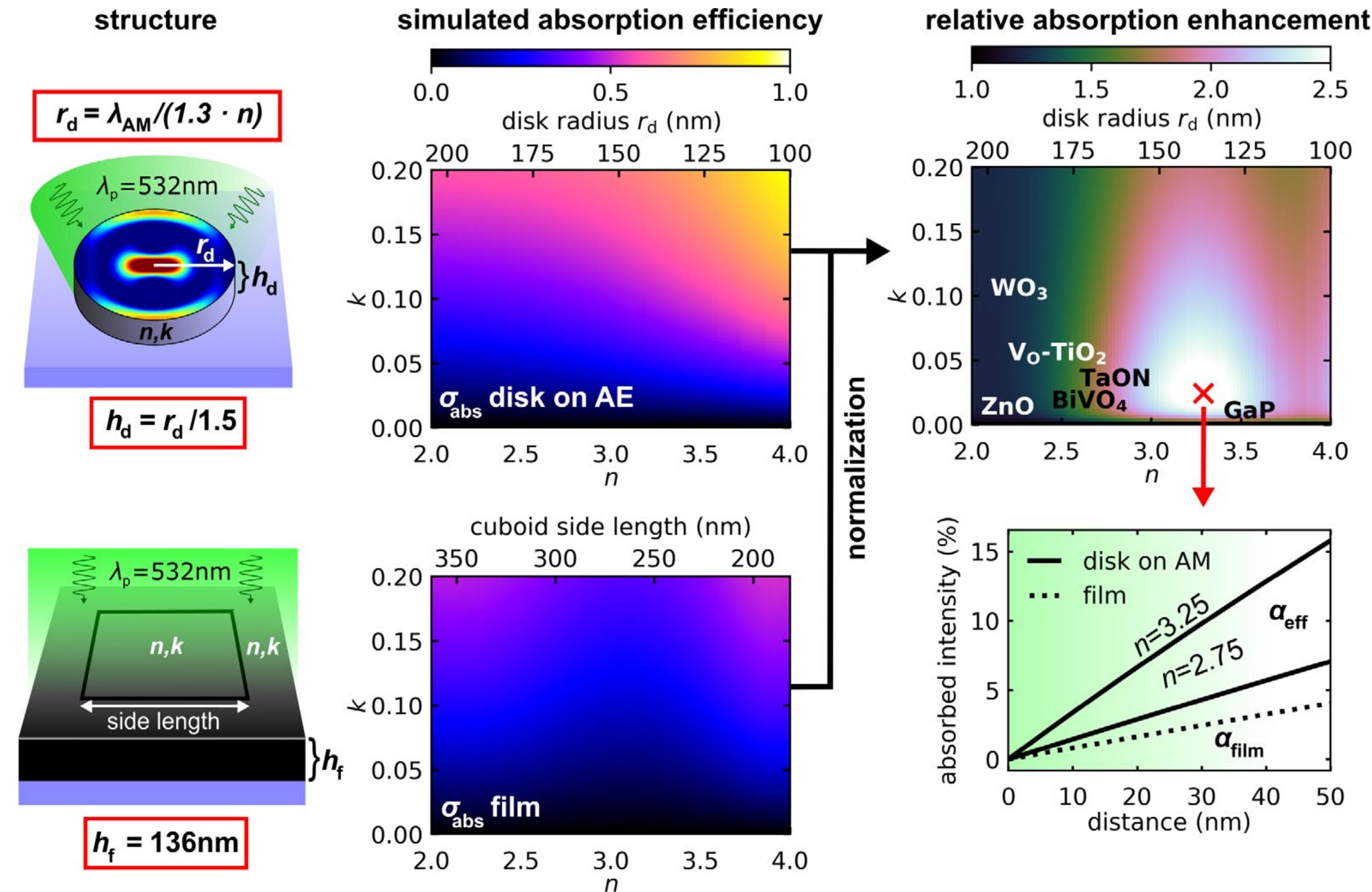
# Additional photoreduction statistics

ACS Nano 14, 2456 (2020)



# Generalization to higher-index dielectrics

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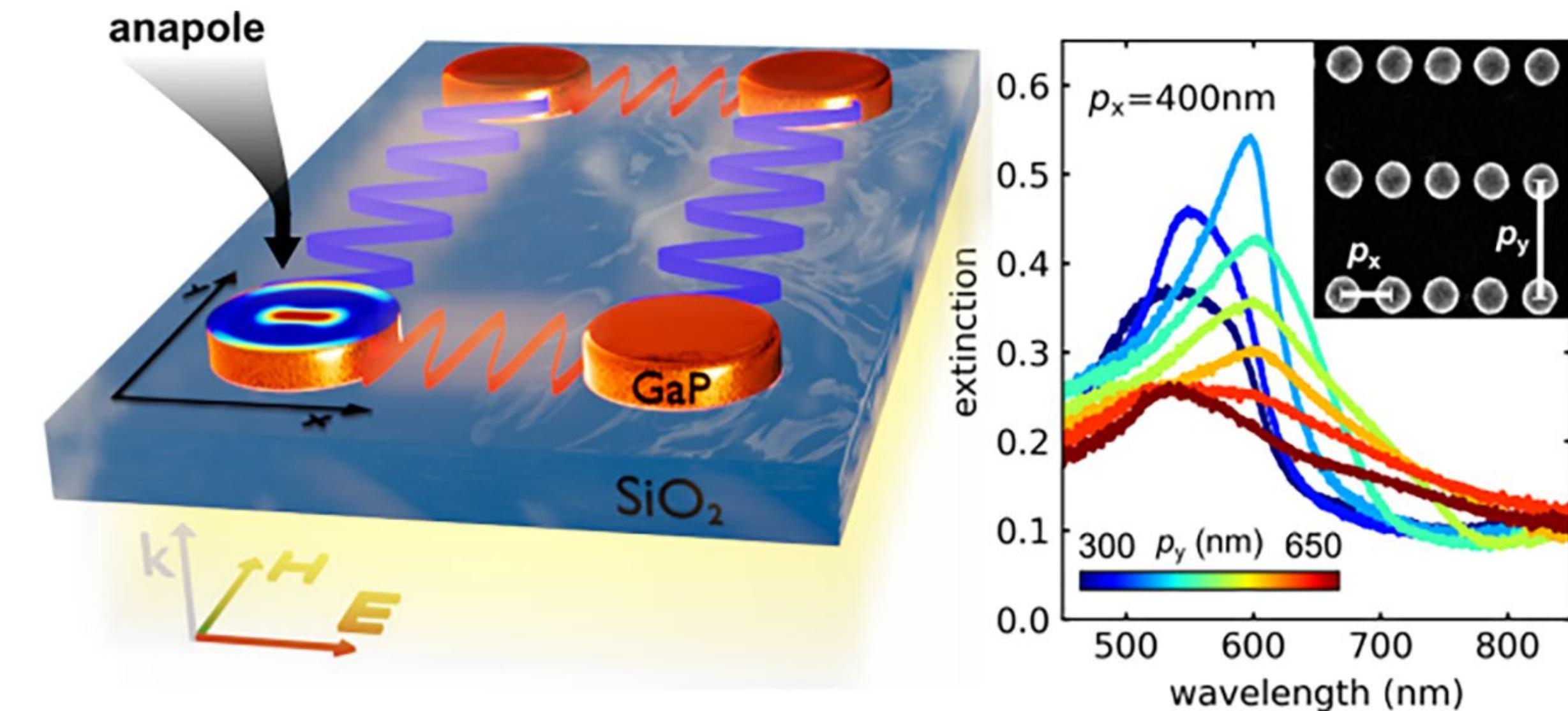
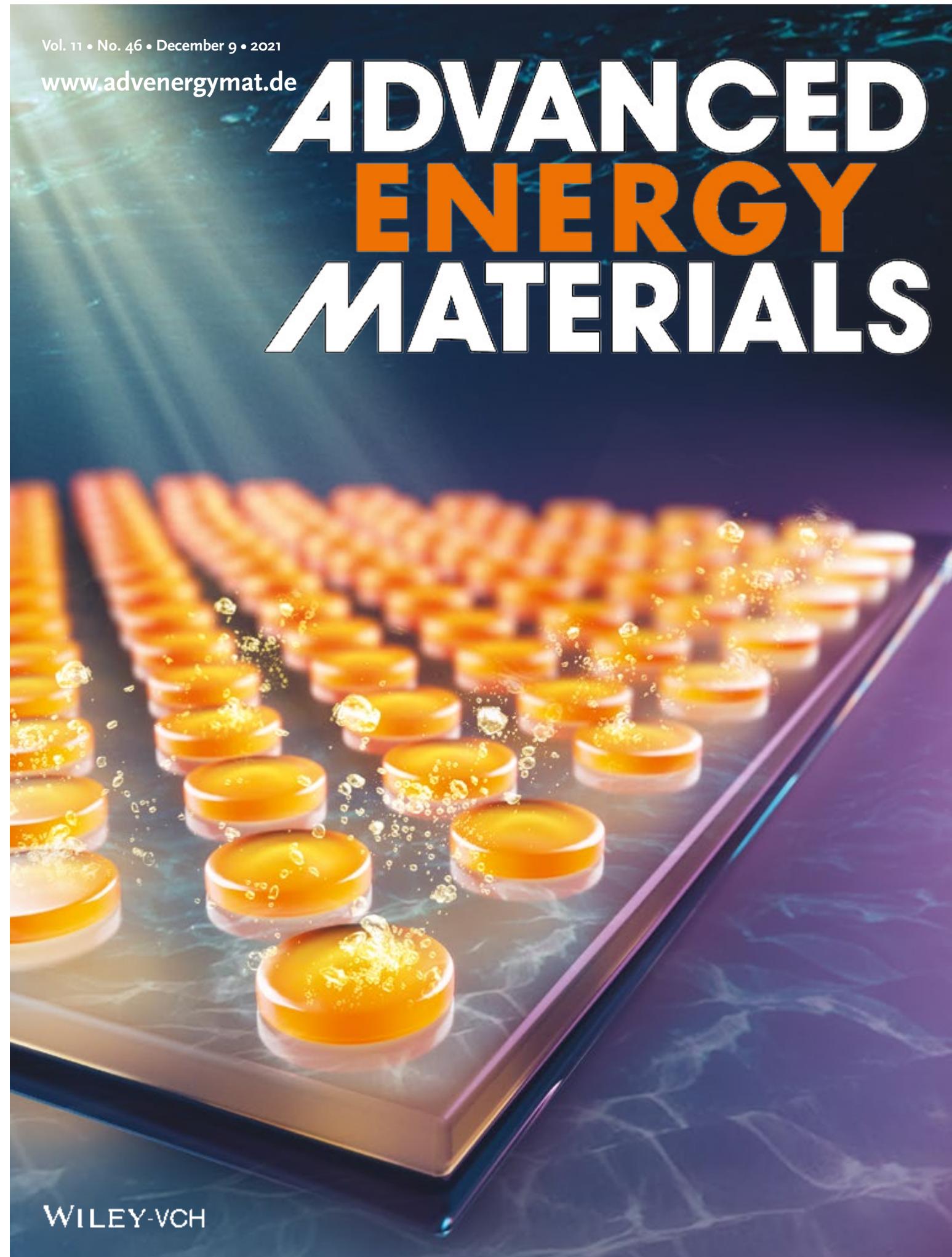


Engineered absorption enhancement favourable for higher-index materials such as GaP

# Towards large-area light harvesting in a reactor

Adv Energy Mater 11, 2102877 (2021)

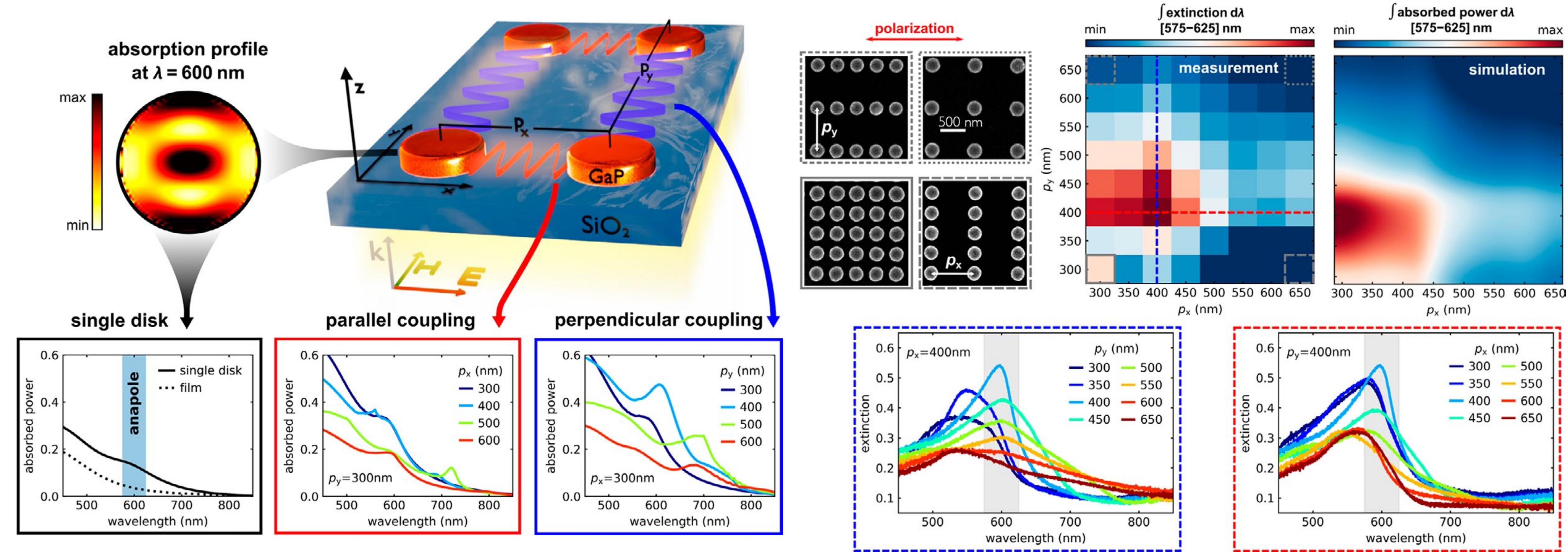
ACS Photonics 8, 1469 (2021)



Large-area patterning necessitates study of anapole-anapole interactions in a 2D grating

# Asymmetry in coupling mediated via lattice resonances

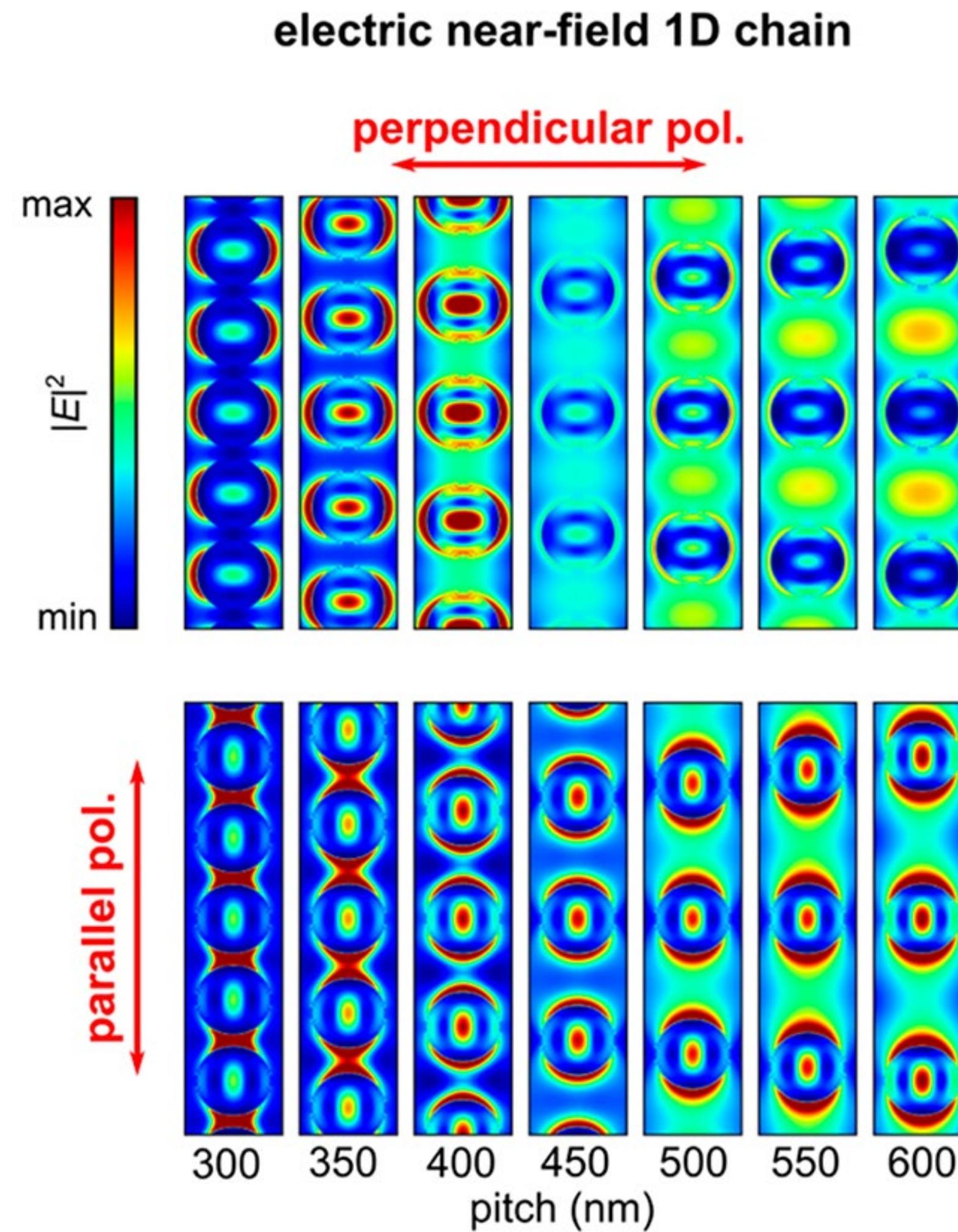
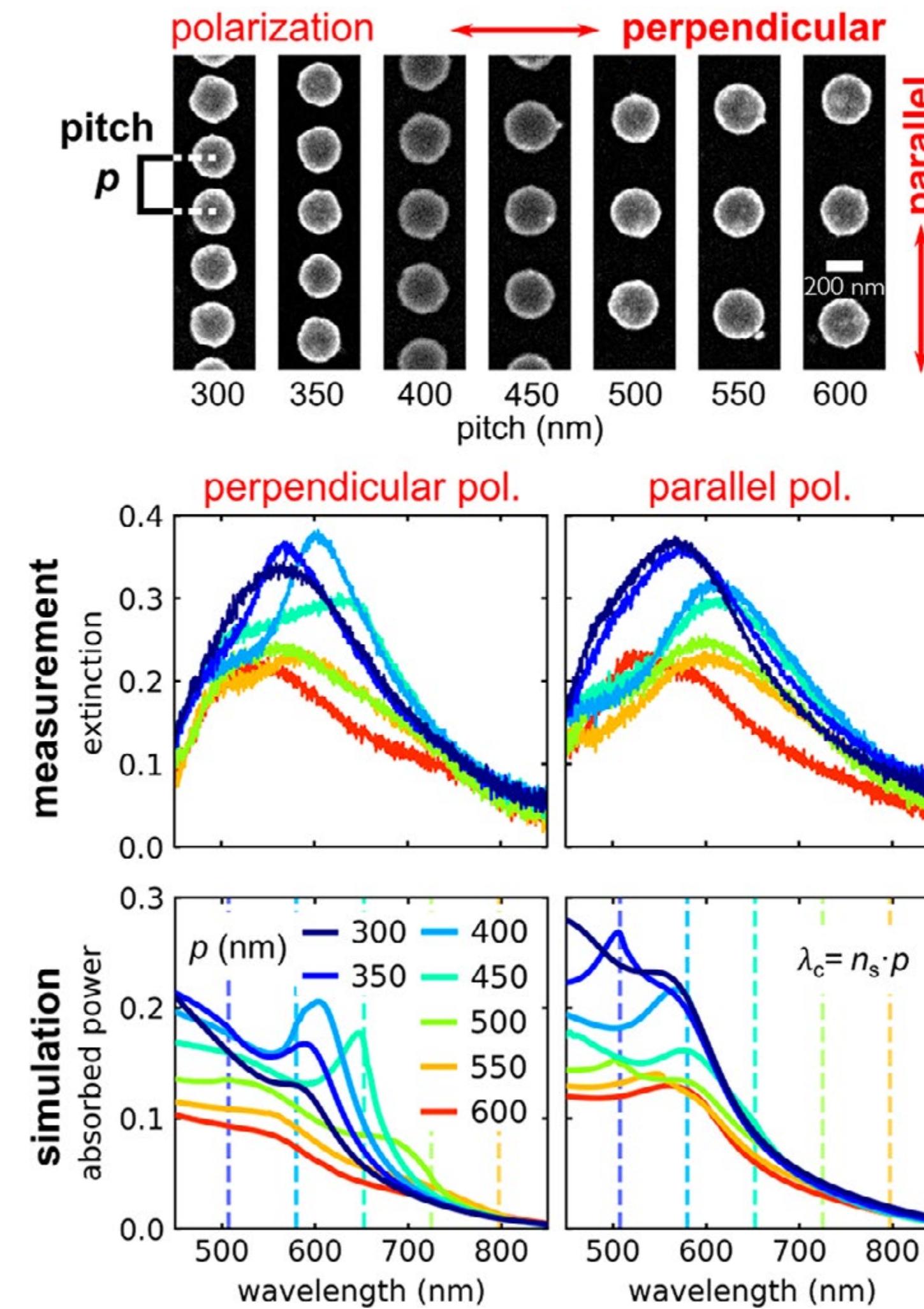
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Highest absorption enhancement (300%) not achieved for densest packing but for optimum spacing

# Separation of coupling mechanisms

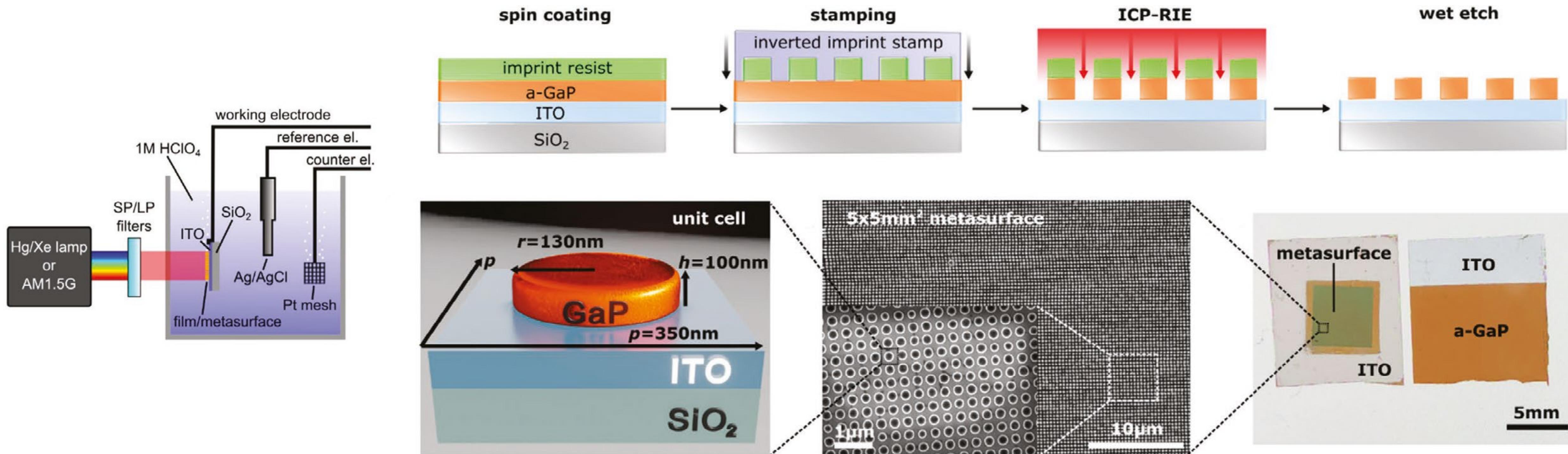
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Highest absorption for optimized lattice coupling while *maintaining the anapole condition*

# Metasurface photoelectrodes via nanoimprint patterning

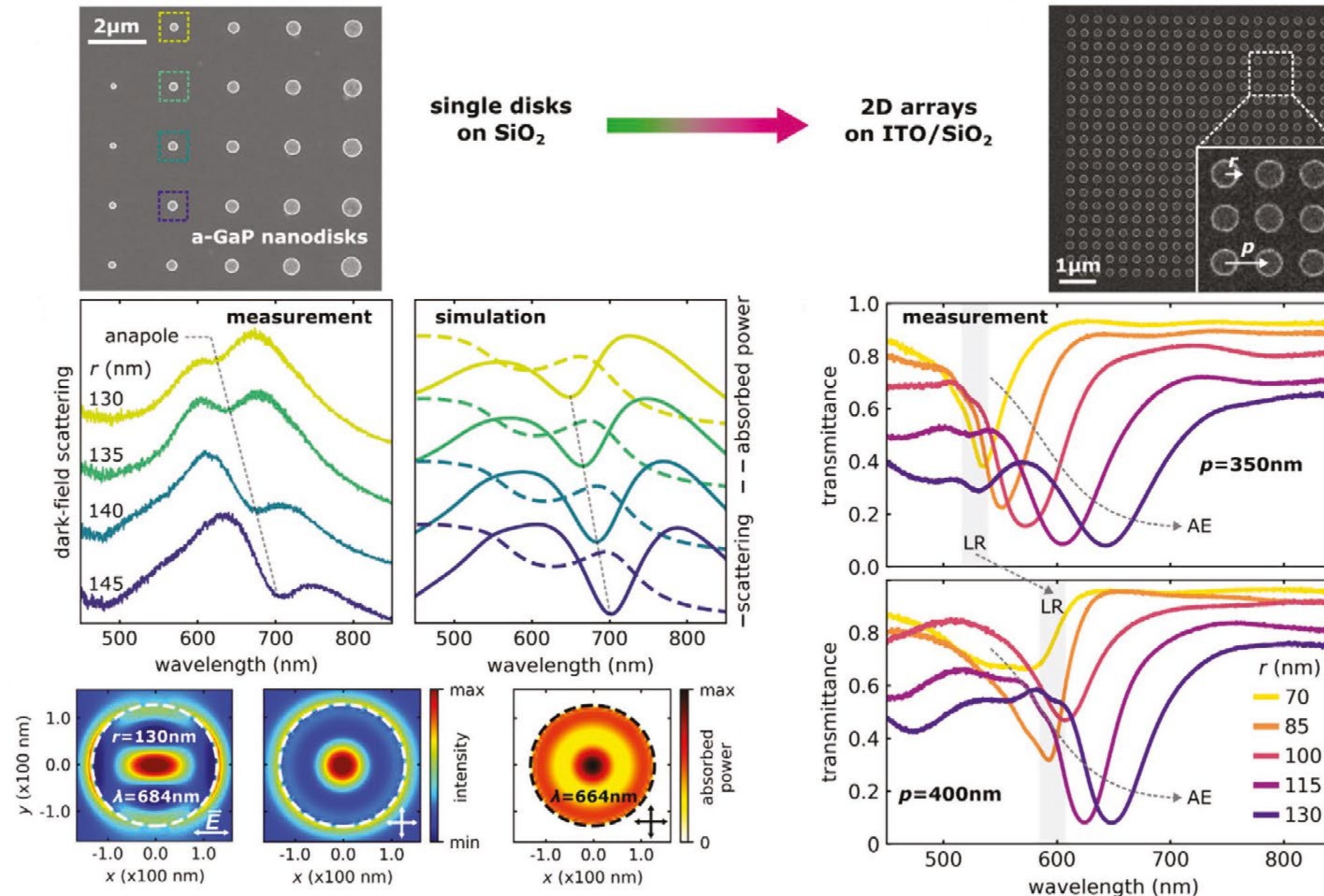
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Study of hydrogen evolution reaction with a-GaP metasurface photoelectrodes

# Spectrally separated lattice resonance and anapole

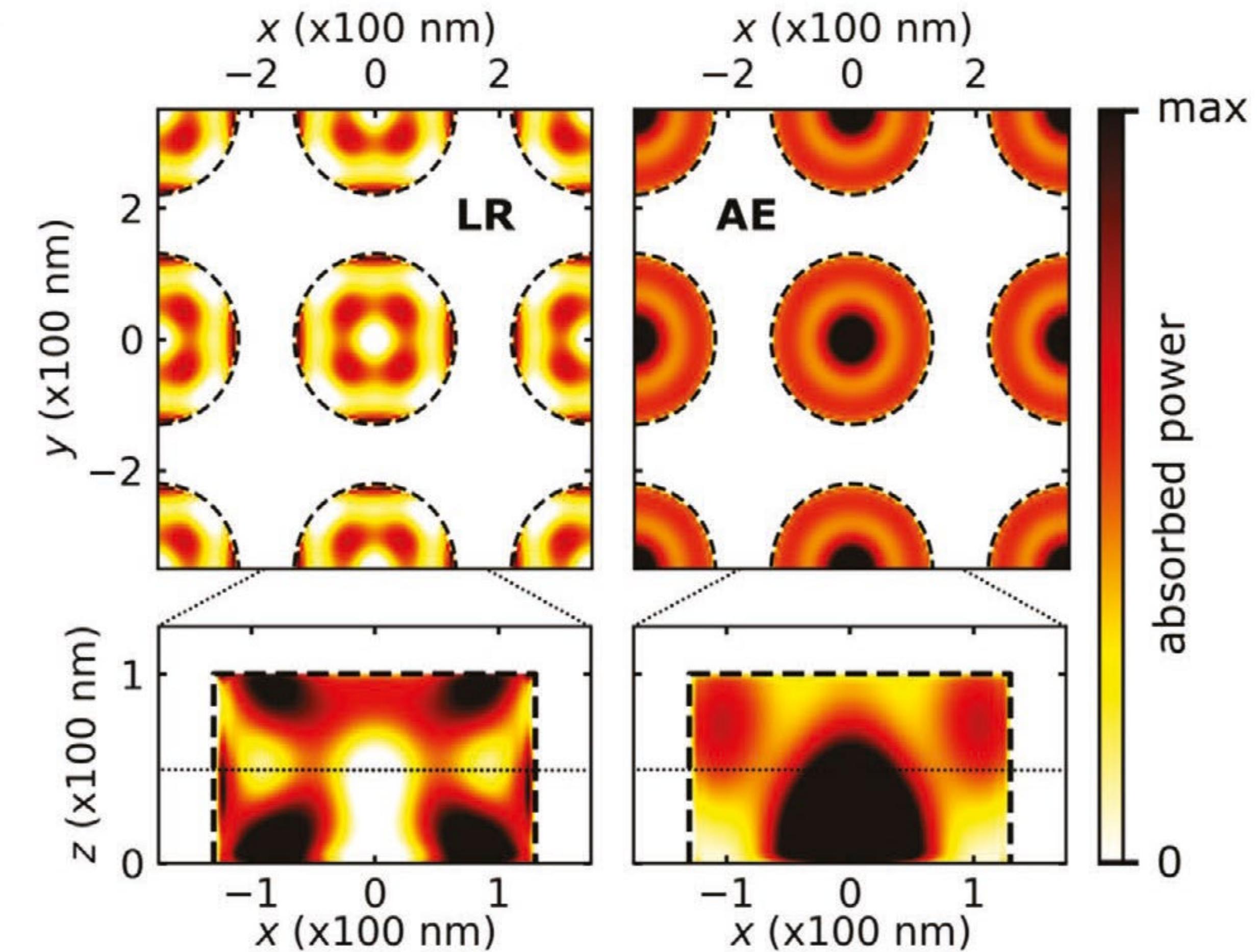
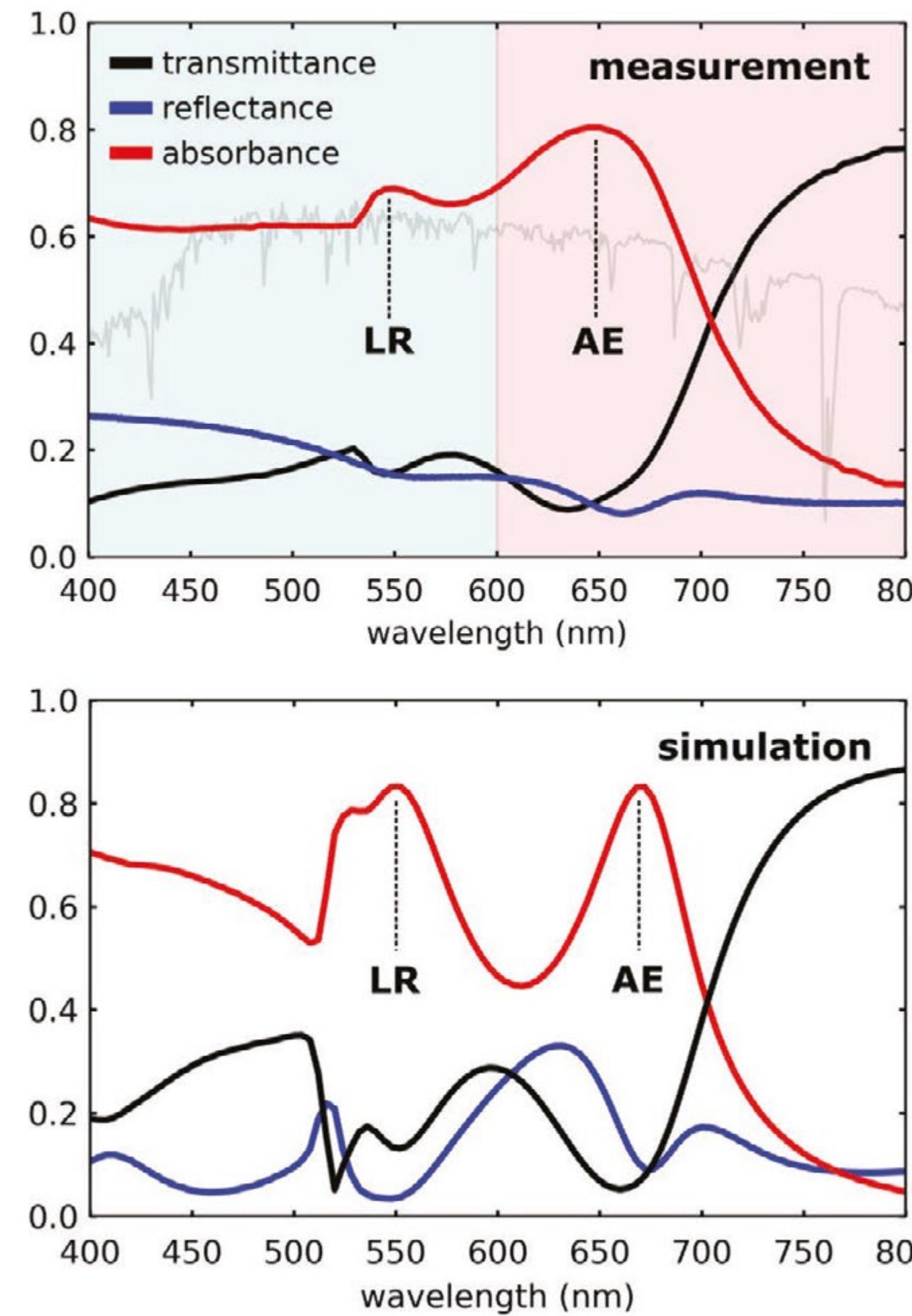
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Spectral separation allows assessment of respective contribution to photocatalytic enhancement

# Field profiles of lattice resonance and anapole excitation

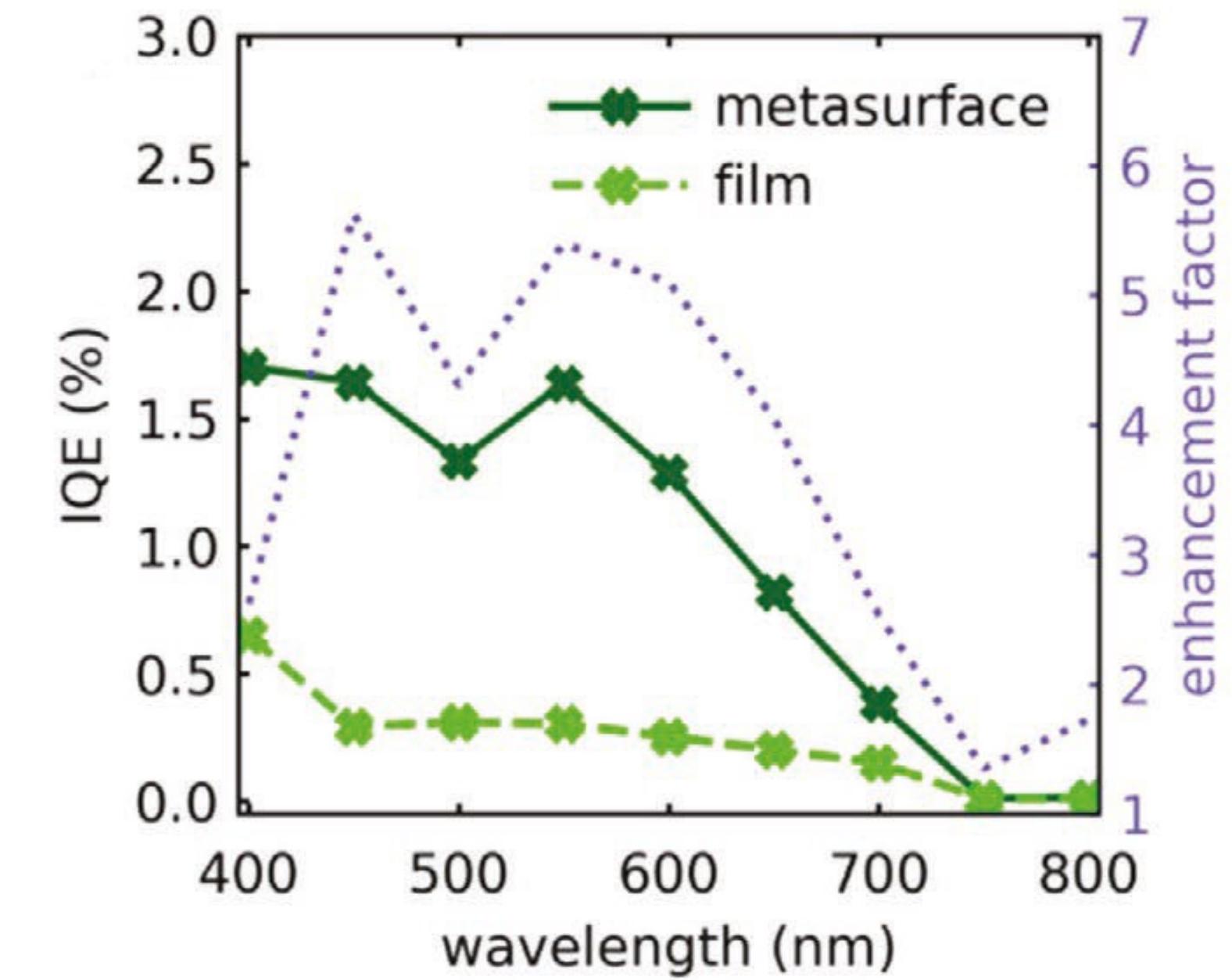
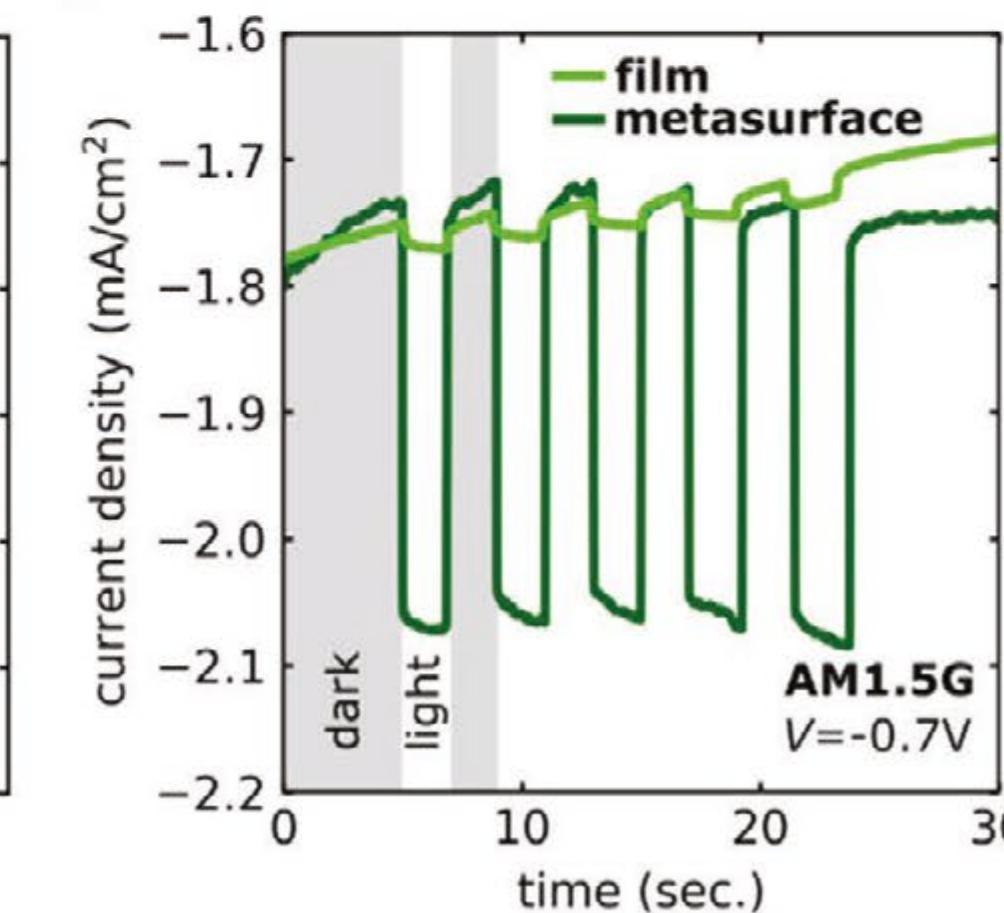
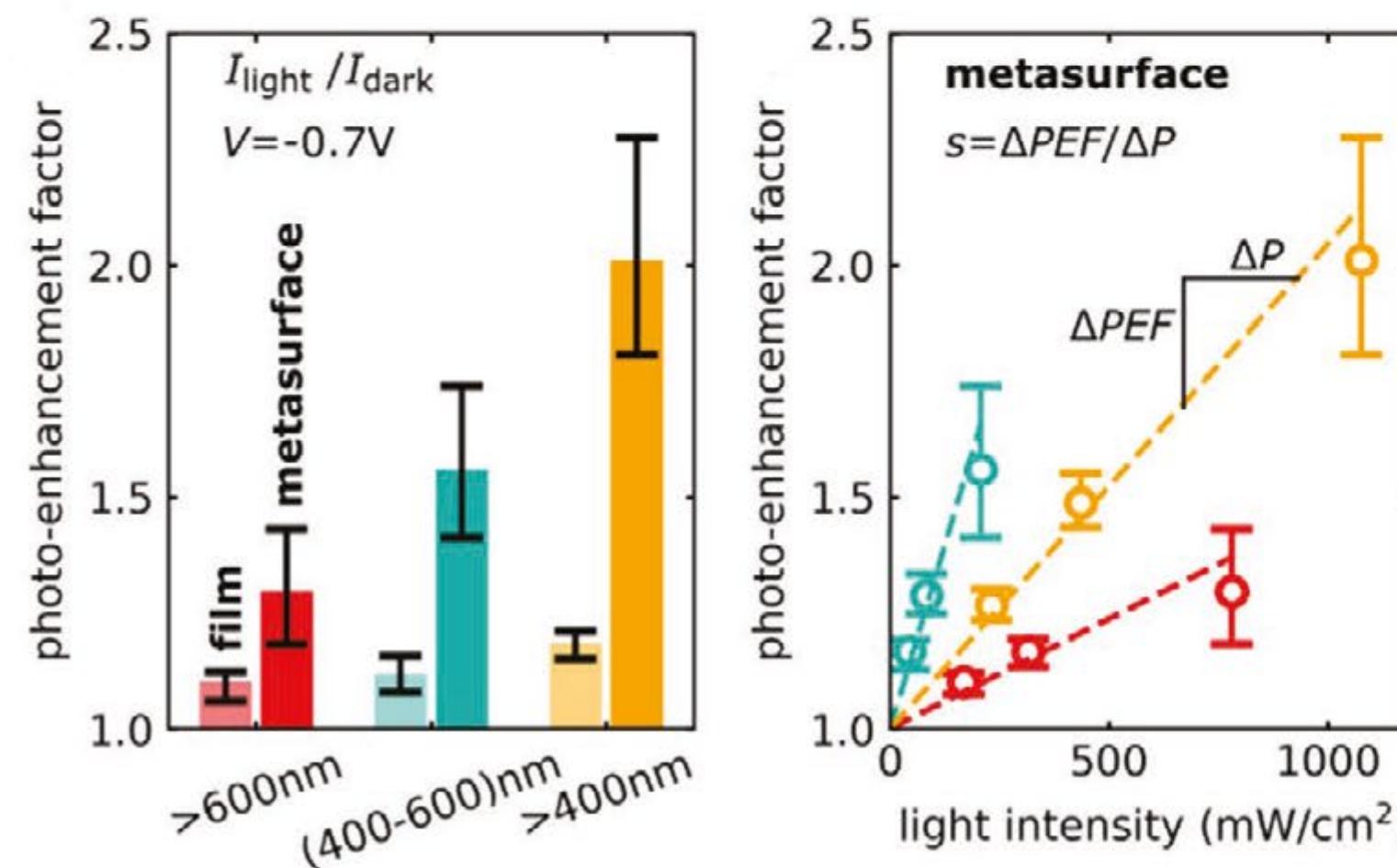
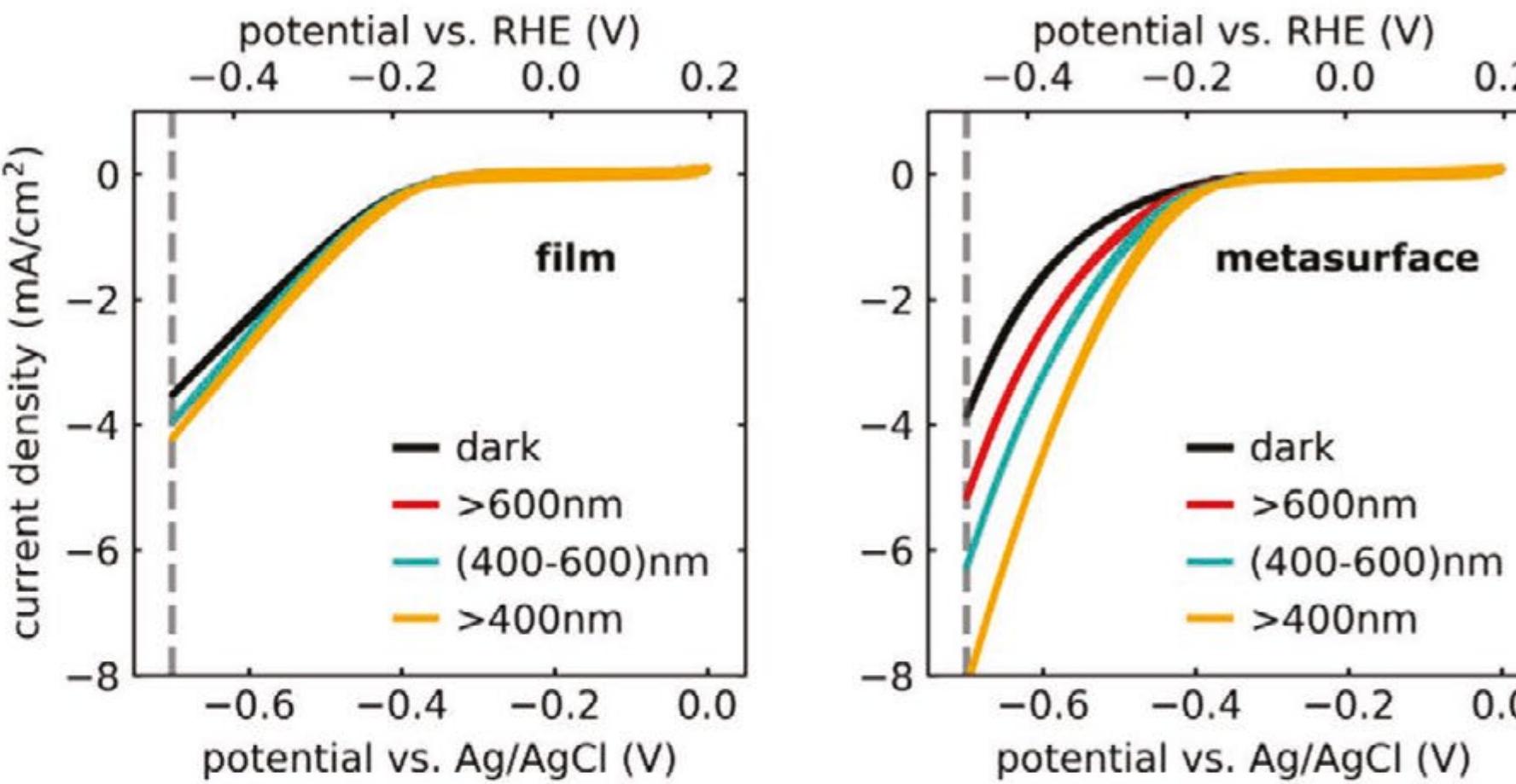
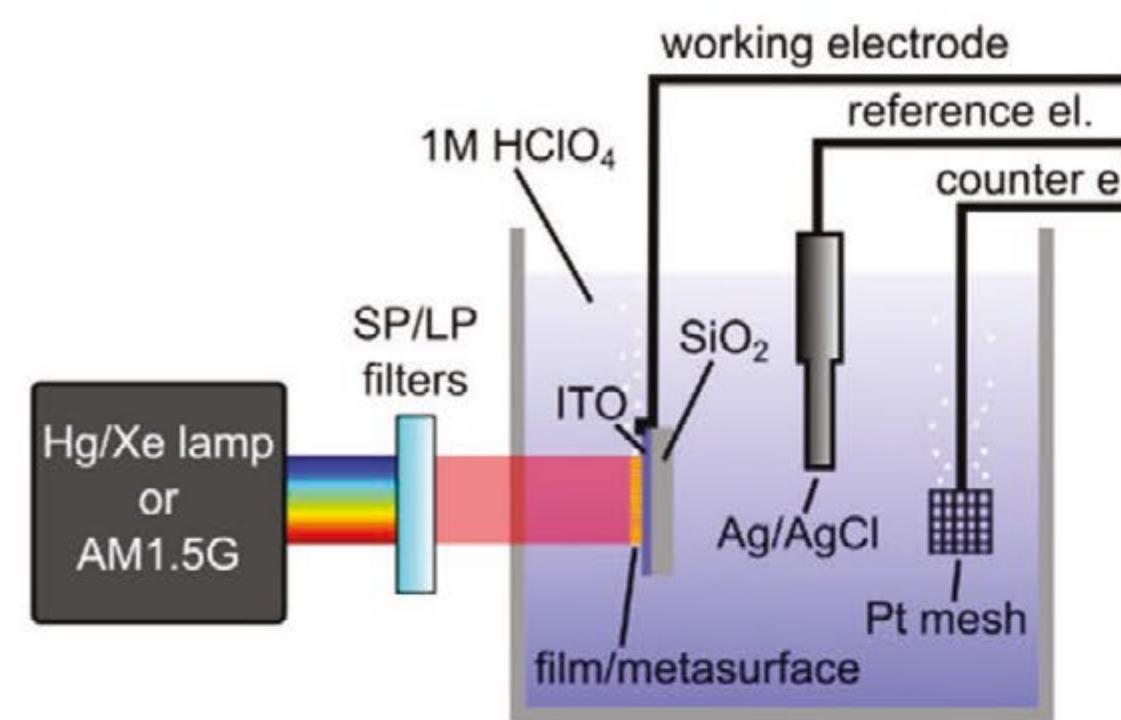
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Lattice resonance promotes absorption hot spots on the surface

# Photoelectrochemical characterization

Adv Energy Mater 11, 2102877 (2021)

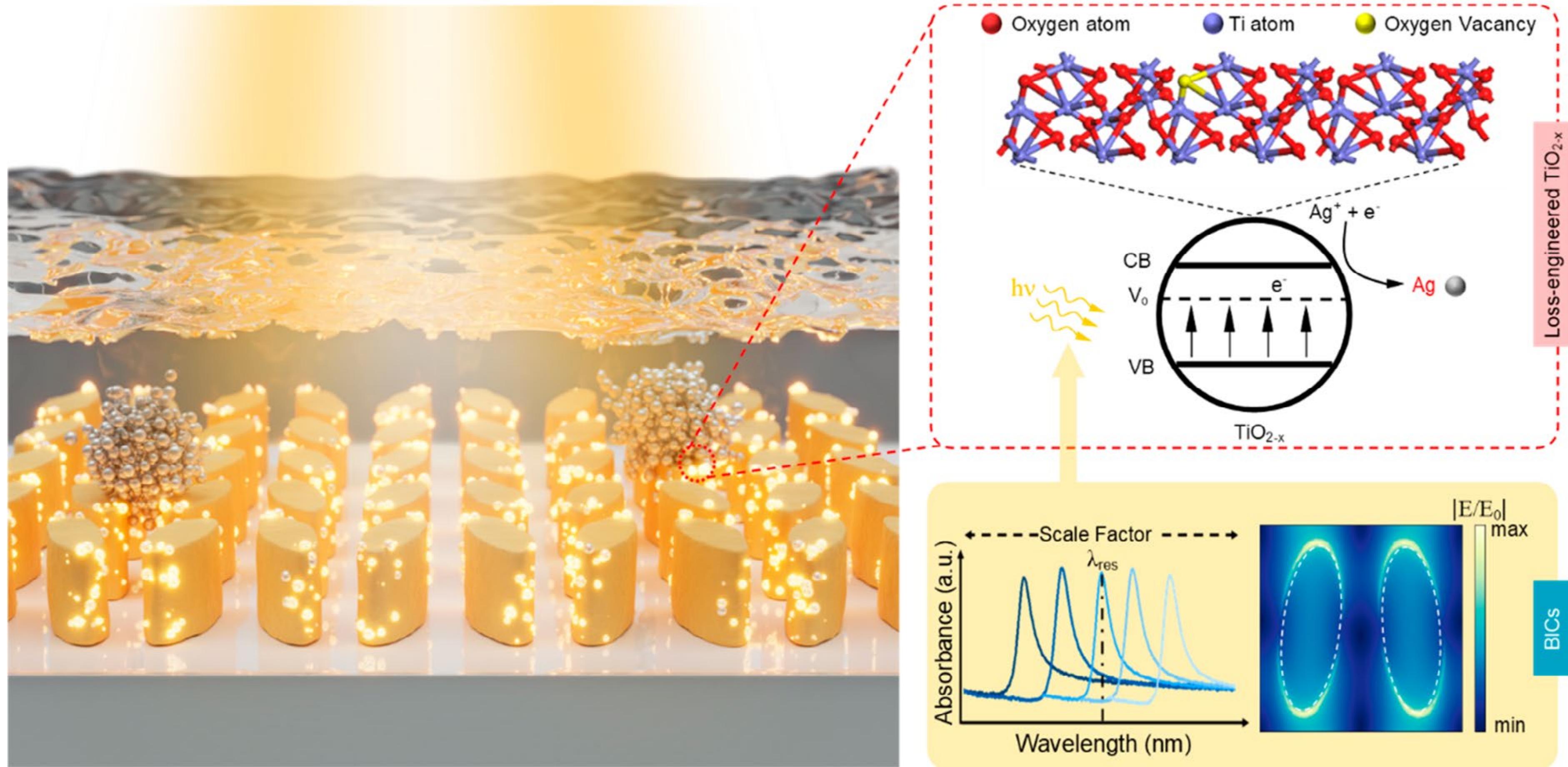


- unintentional n-doping of a-GaP revealed via surface photovoltage measurement  $\Rightarrow$  not ideal for hydrogen evolution reaction
- clear enhancement of photocurrent compared to bare film

- metasurface-to-film enhancement factor  $\sim 5$  for white light
- strongest contribution of lattice resonance to overall enhancement due to near-surface absorption hot spots

# Catalytic metasurfaces via bound states in the continuum

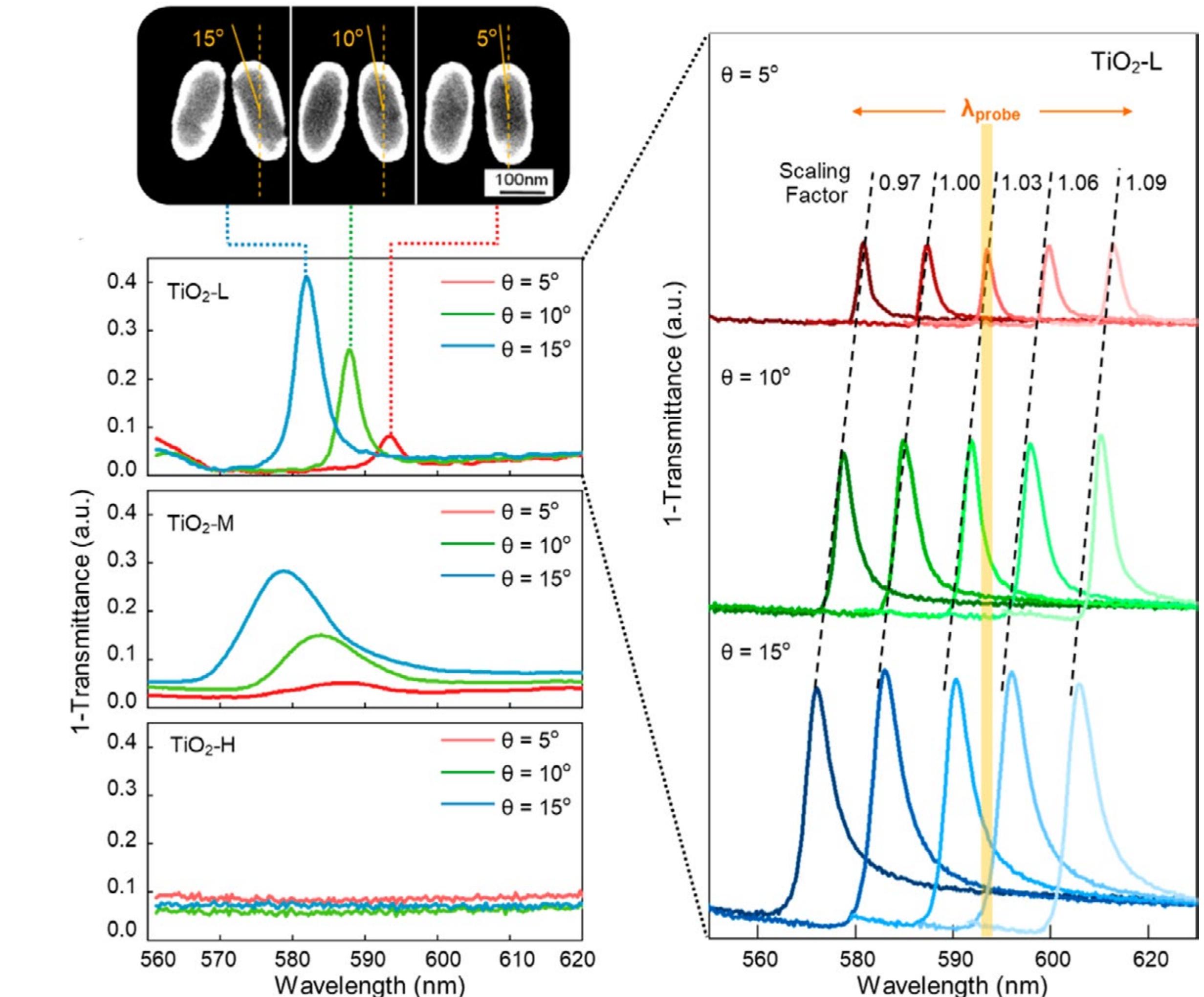
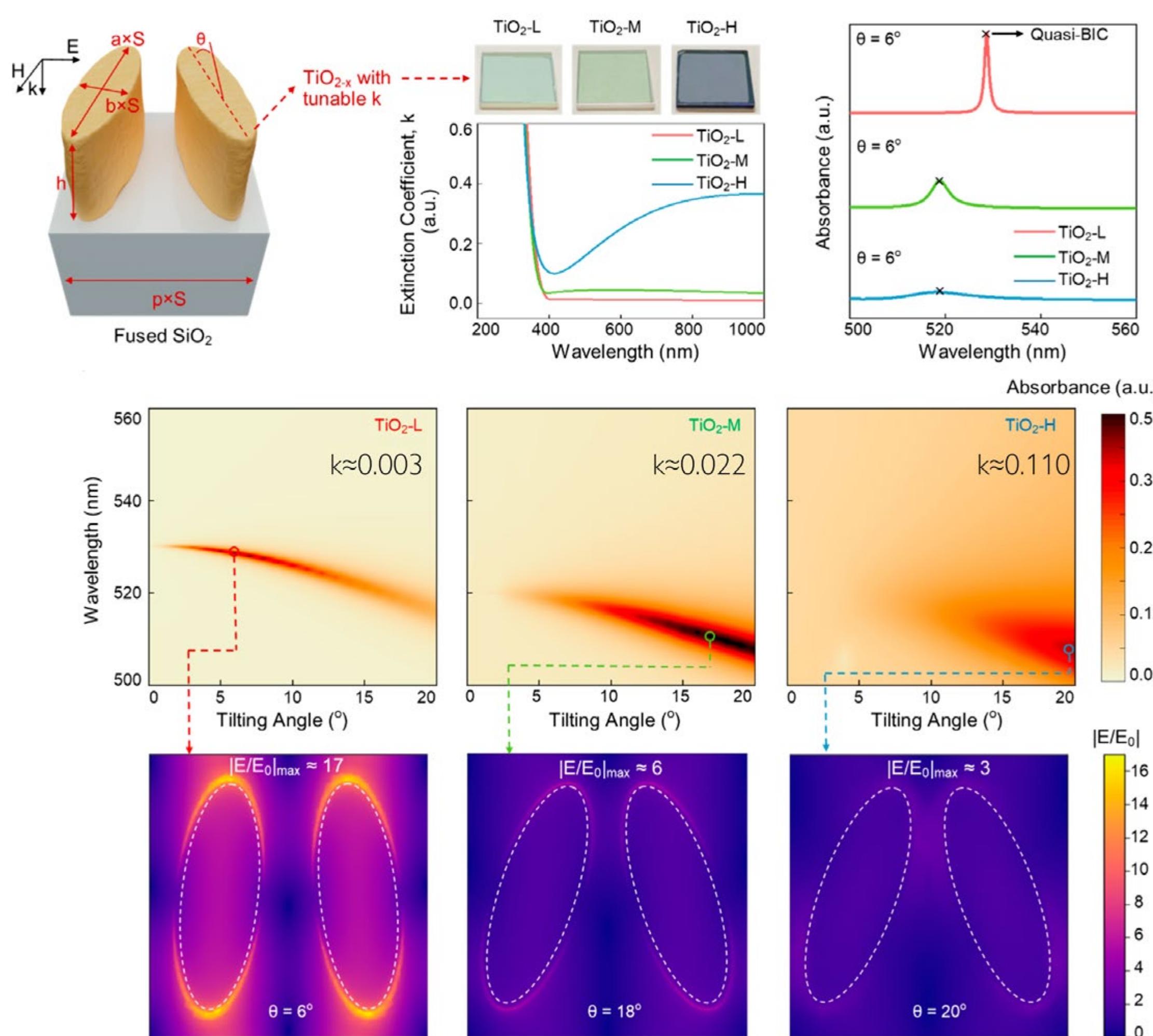
ACS Nano 16, 13057 (2022)



Optical absorption engineering via BICs enables thin, low-materials-loss catalytic metasurfaces

# Tunability of resonance: frequency and field enhancement

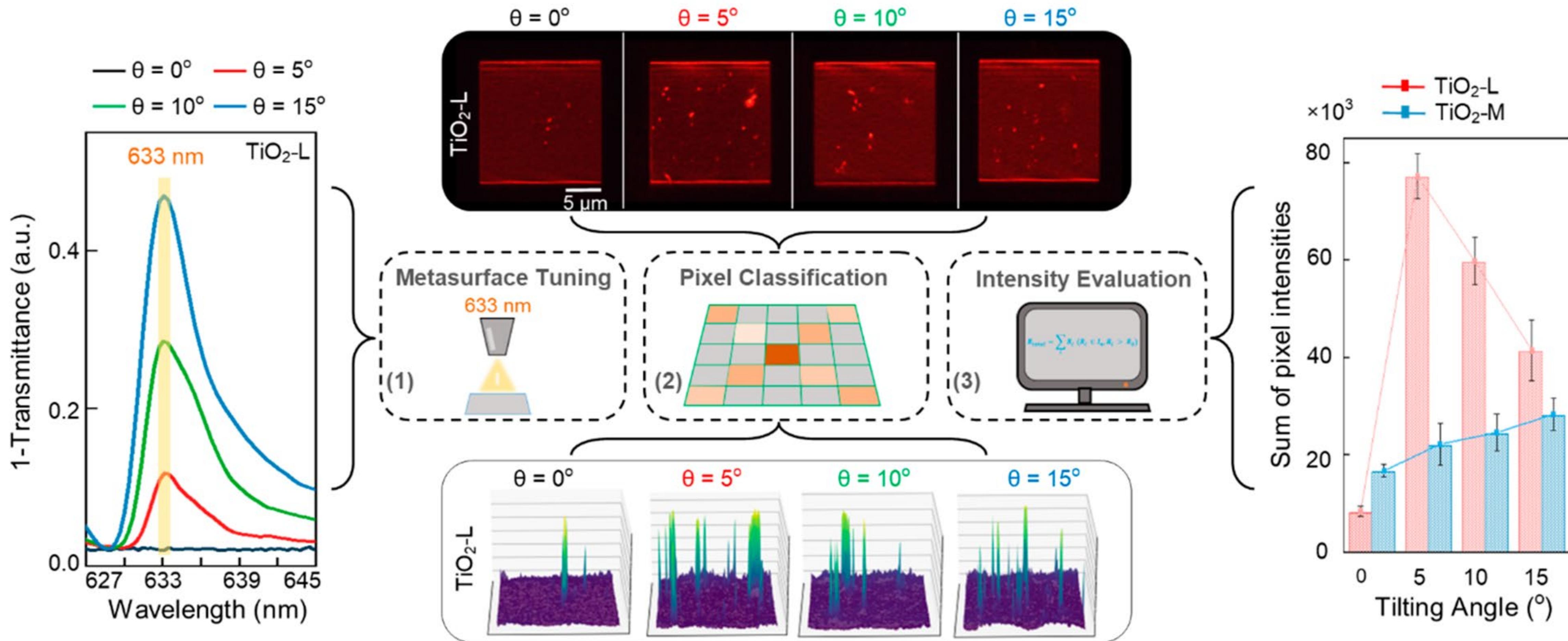
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Bound states in the continuum enable a large amount of design flexibility

# Experimental monitoring of silver reduction

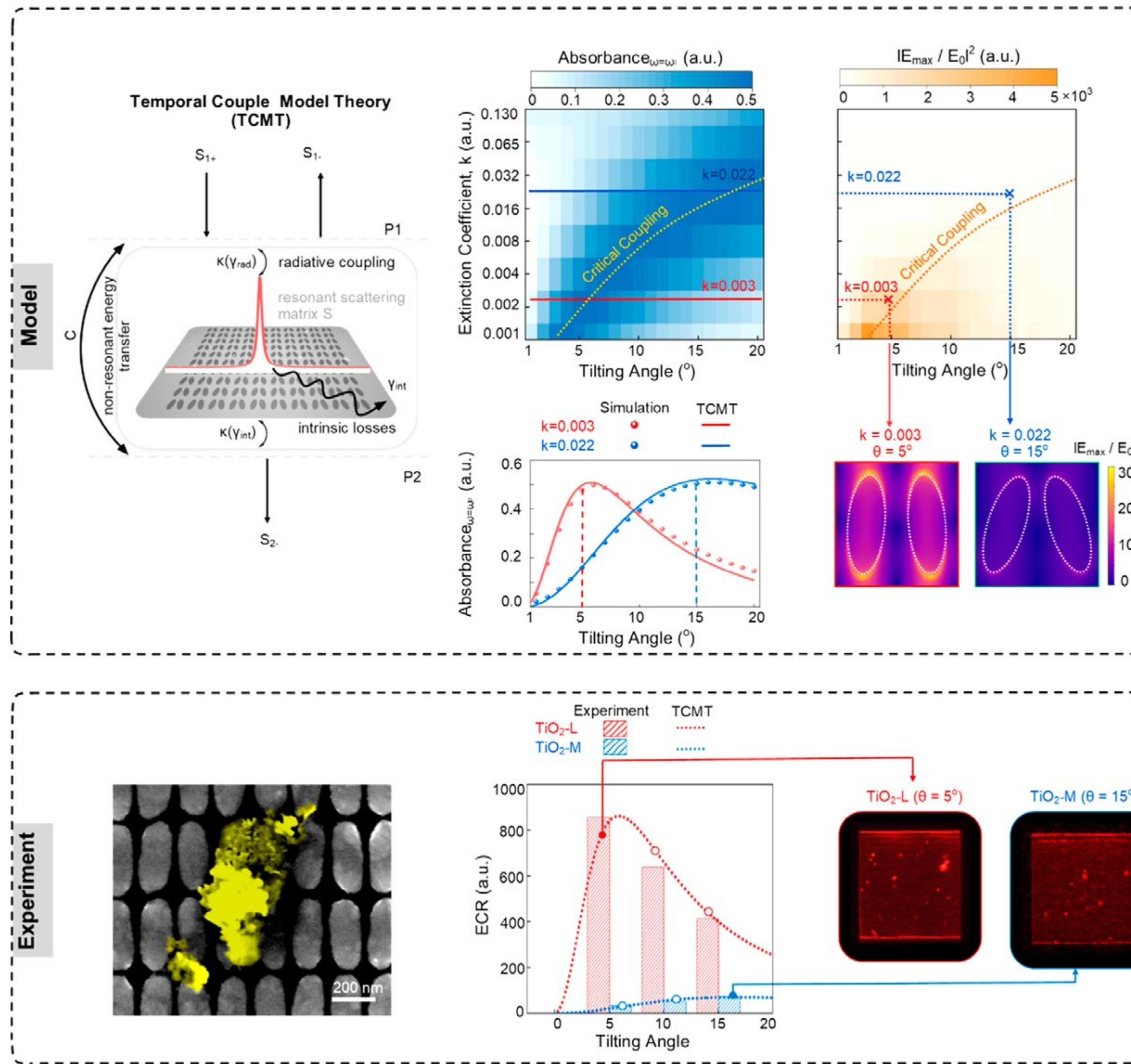
ACS Nano 16, 13057 (2022)



Low-loss TiO<sub>2</sub> outperforms higher-loss TiO<sub>2</sub> due to resonant field enhancement

# Critical coupling model of photocatalytic performance

ACS Nano 16, 13057 (2022)



- intrinsic loss tunability via change in ALD precursors  $\gamma_{\text{int}} \sim k$
- radiative loss tunability via BIC  $\gamma_{\text{rad}} \sim \alpha^2 = \sin^2 \theta$
- effective Ag coverage ratio (ECR) can be related to field-enhancement via fitting parameter  $\beta(k)$
- enhancement of ECR between low-loss and high-loss  $\text{TiO}_2$  mainly driven by six-fold increase of electric near-field intensity
- reduction rate does not scale linearly with electric near-field intensity:  
 $\beta(k \approx 0.003) = 39 \pm 1$ ;  $\beta(k \approx 0.022) = 24 \pm 2$

$$\text{ECR}(\theta, k) = \frac{R_{\theta, k} - R_{\theta=0, k}}{R_{\theta=0, k}} = \beta(k) \cdot |E/E_0|^2(\theta, k)$$

Low defect concentrations, low extinction, are favoured more strongly!

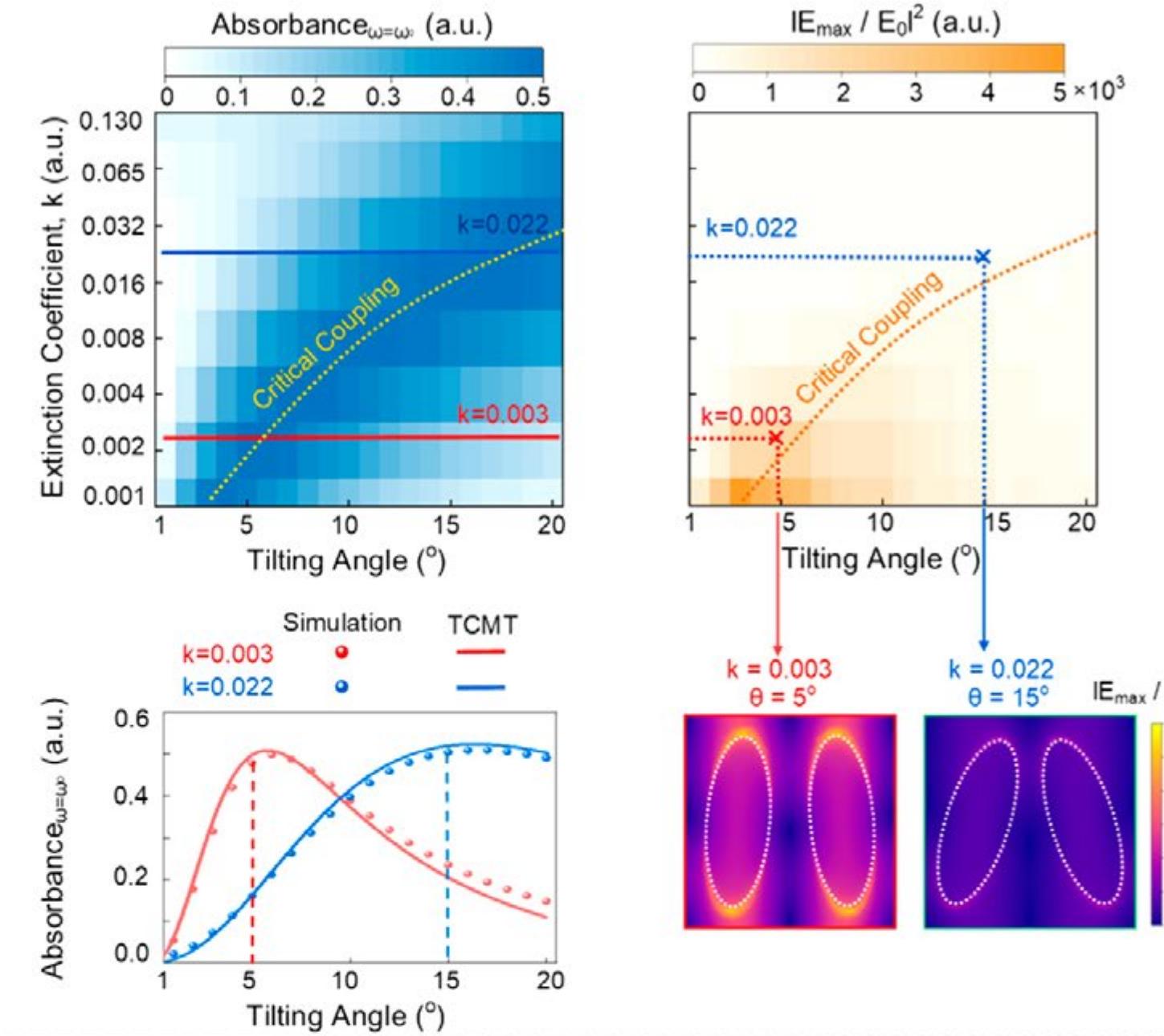
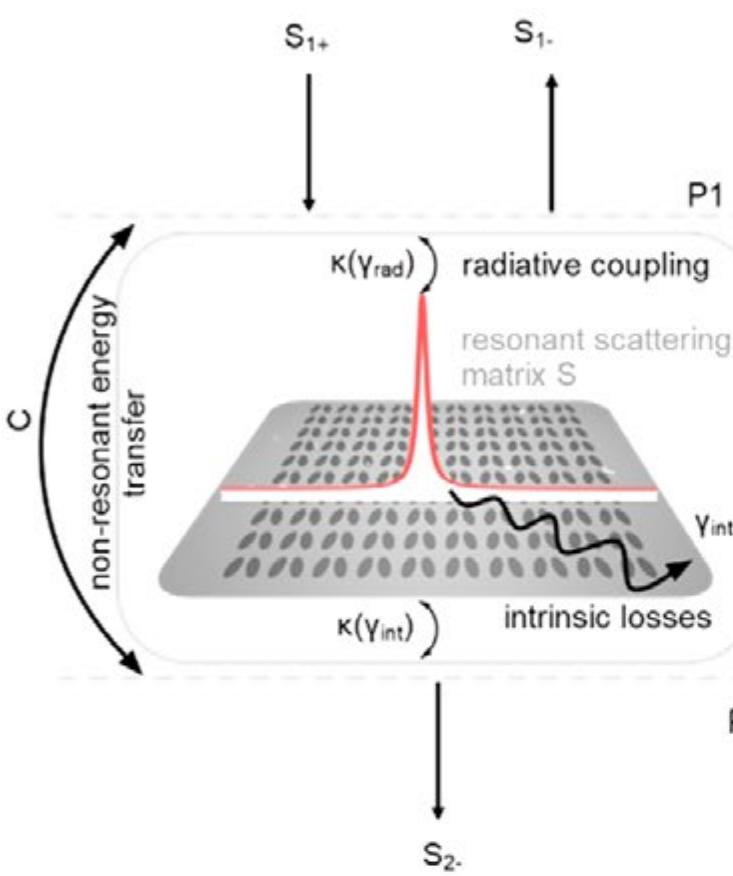
# Metasurfaces: a versatile platform for energy conversion

ACS Nano 16, 13057 (2022)

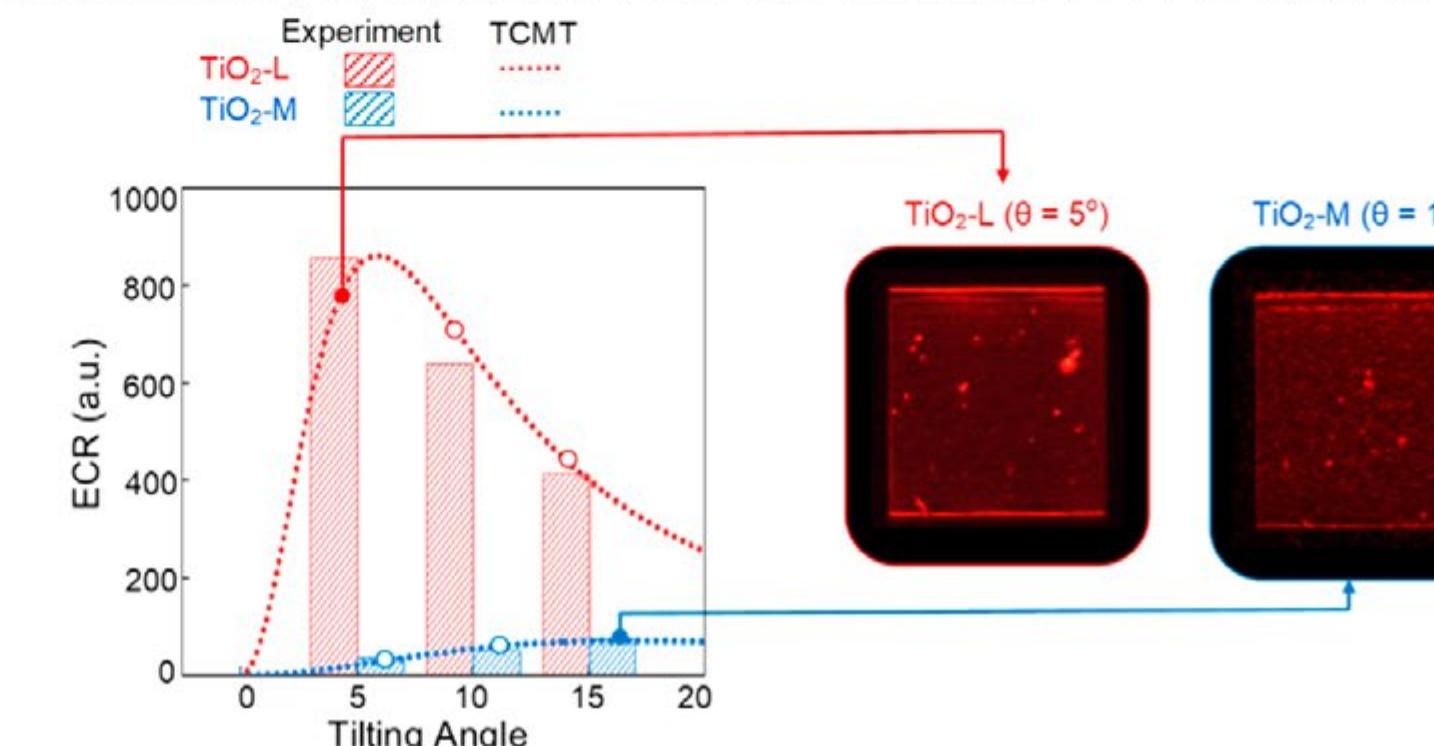
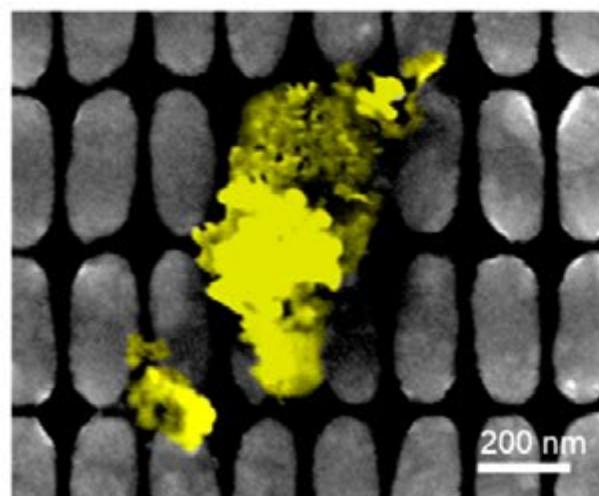
Chemical Reviews 122, 15082 (2022)

## Model

### Temporal Couple Model Theory (TCMT)



## Experiment



# CHEMICAL REVIEWS

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Review

## Optical Metasurfaces for Energy Conversion

Emiliano Cortés,\*# Fedja J. Wendisch,# Luca Sortino,# Andrea Mancini, Simone Ezendam, Seryio Saris, Leonardo de S. Menezes, Andreas Tittl, Haoran Ren, and Stefan A. Maier\*

Cite This: <https://doi.org/10.1021/acs.chemrev.2c00078> Read Online

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**ABSTRACT:** Nanostructured surfaces with designed optical functionalities, such as metasurfaces, allow efficient harvesting of light at the nanoscale, enhancing light–matter interactions for a wide variety of material combinations. Exploiting light-driven matter excitations in these artificial materials opens up a new dimension in the conversion and management of energy at the nanoscale. In this review, we outline the impact, opportunities, applications, and challenges of optical metasurfaces in converting the energy of incoming photons into frequency-shifted photons, phonons, and energetic charge carriers. A myriad of opportunities await for the utilization of the converted energy. Here we cover the most pertinent aspects from a fundamental nanoscopic viewpoint all the way to applications.



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Special Issue: Chemistry of Metamaterials

Received: January 31, 2022

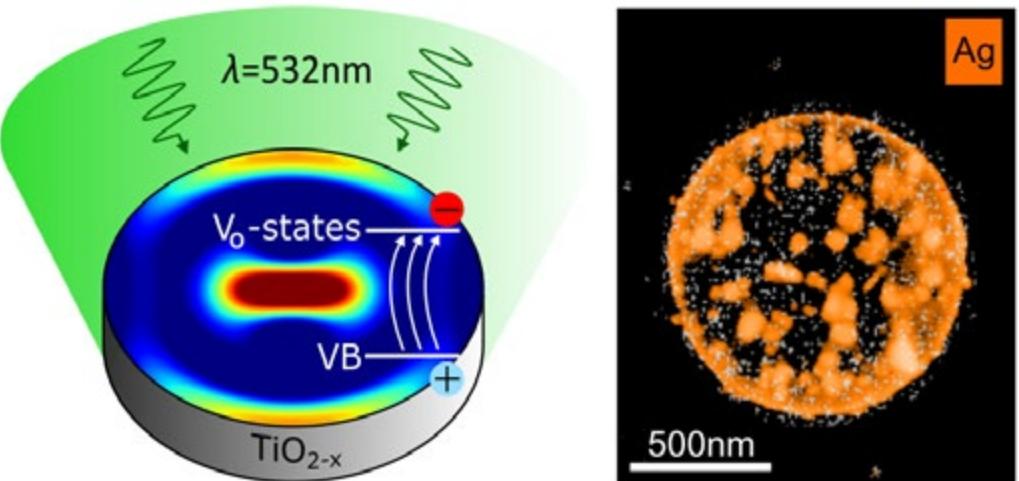
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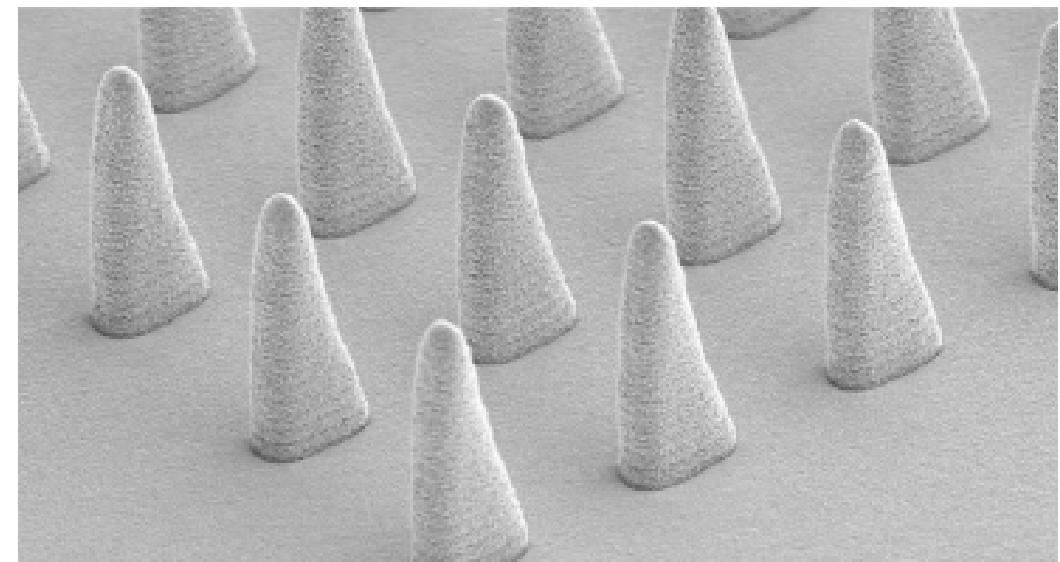
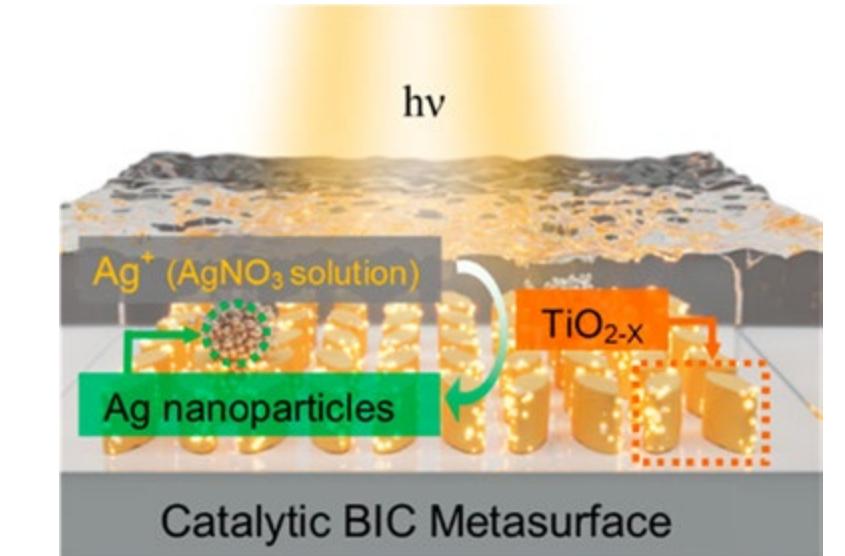
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Chem. Rev. XXXX, XXX, XXX–XXX

# Outline



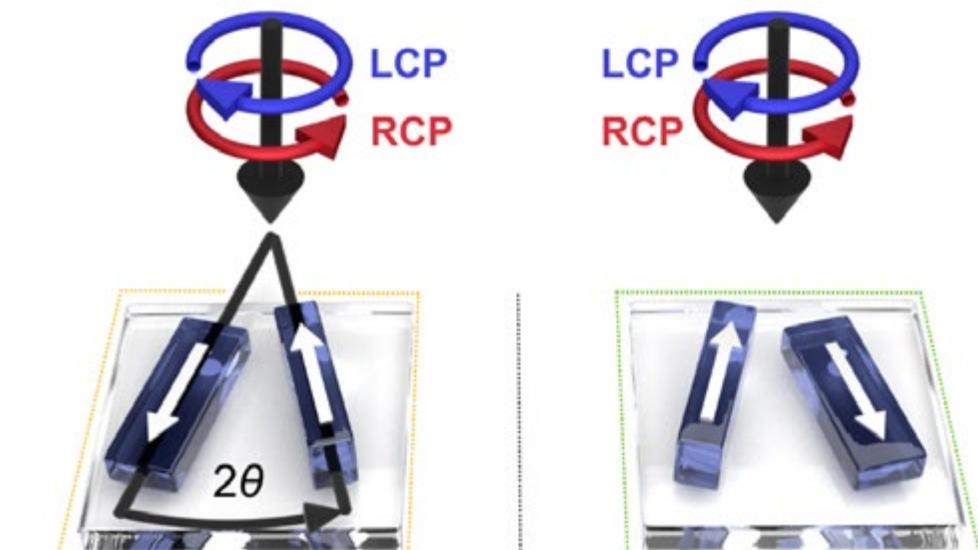
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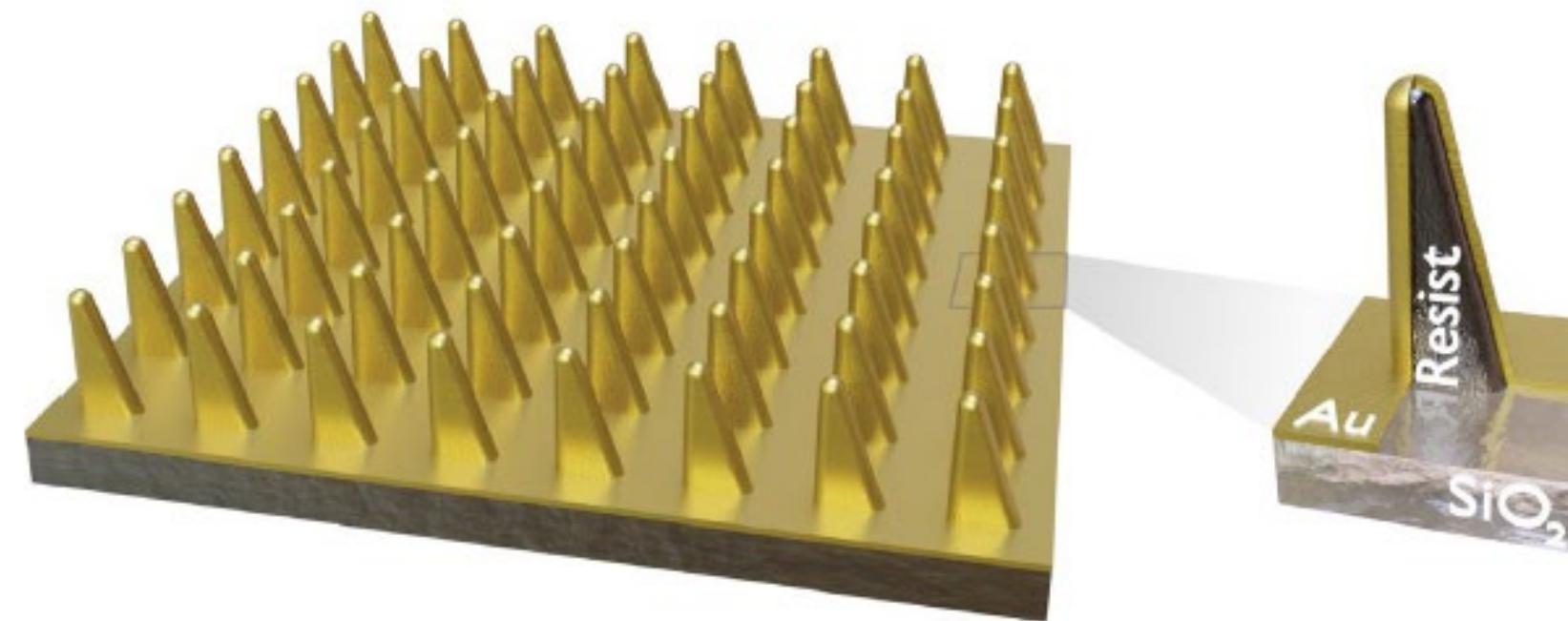


## BICs for infrared absorption and chirality

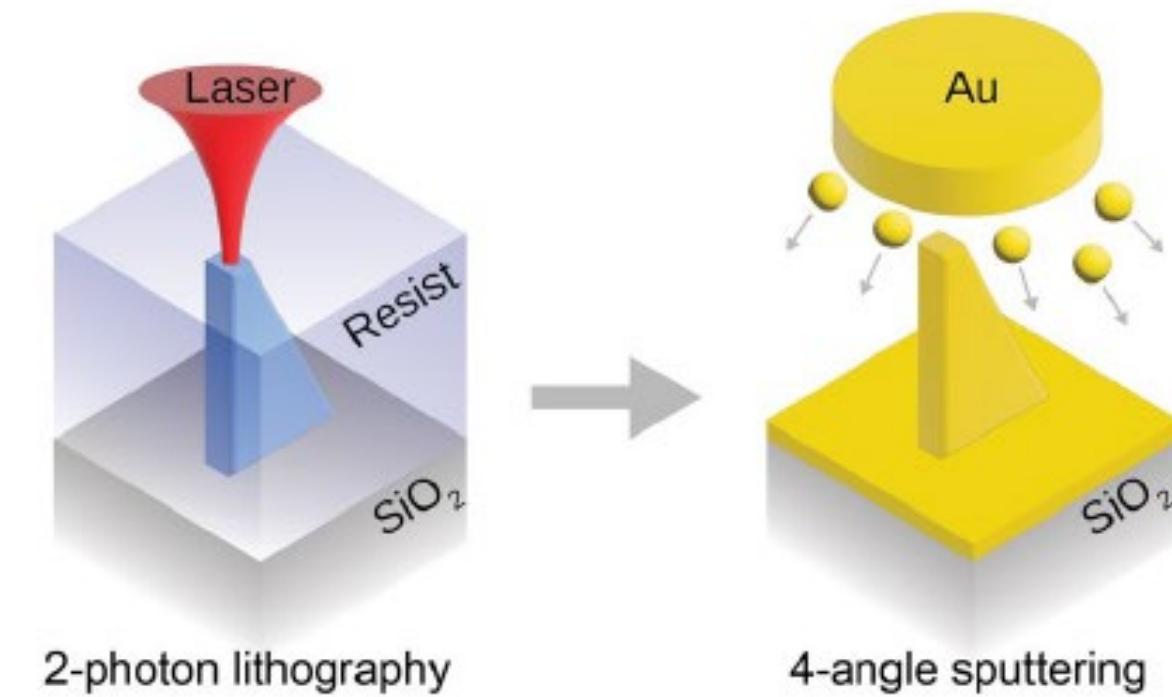
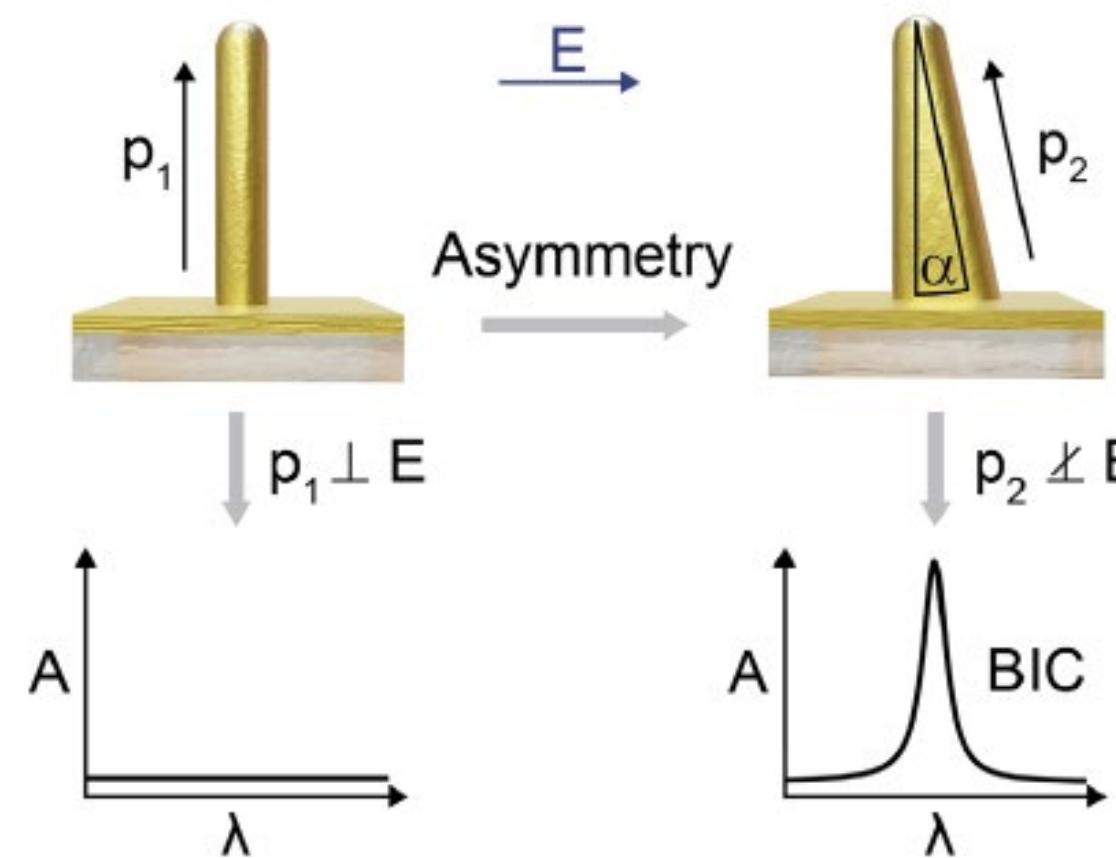
*arXiv:2210.05339*



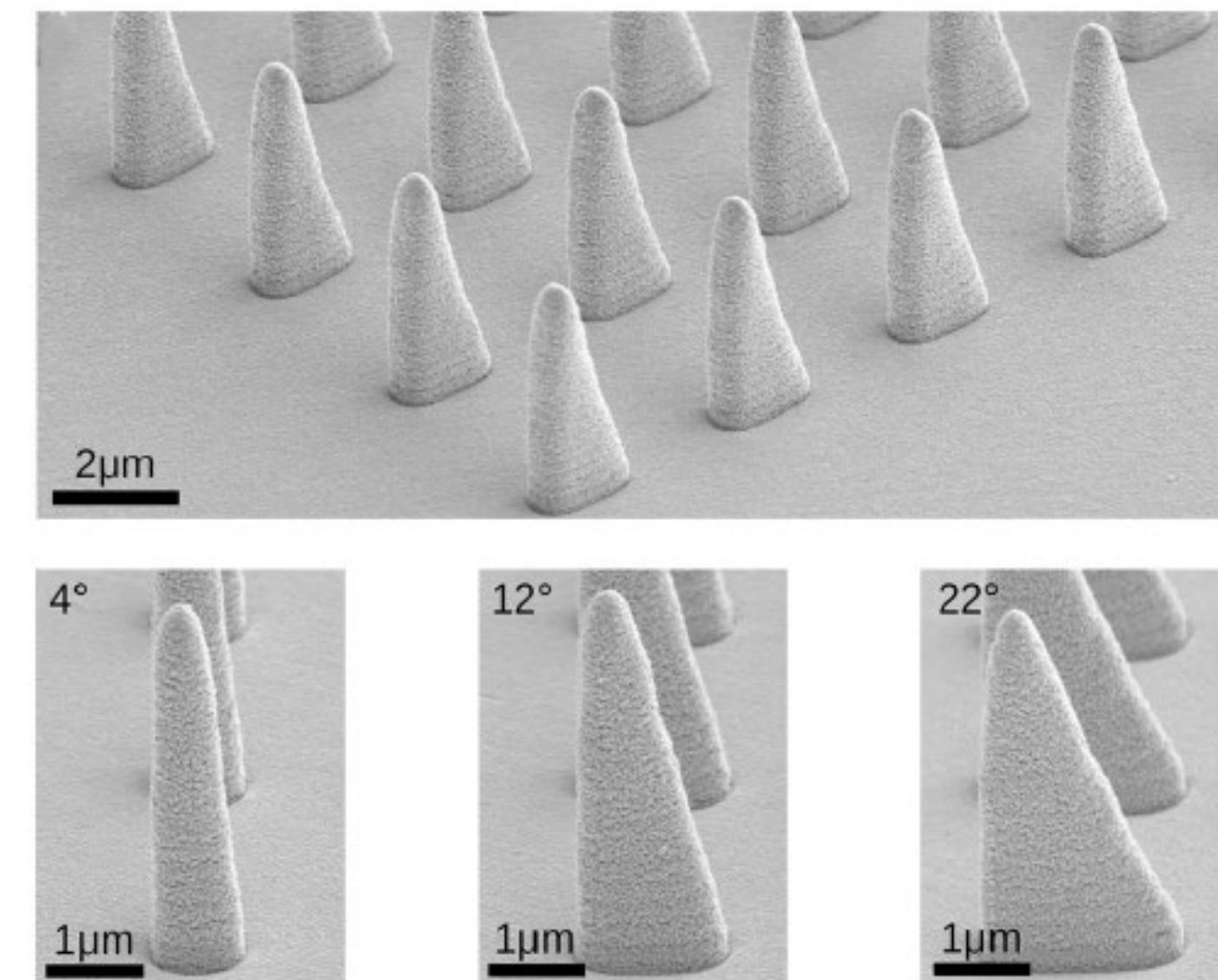
# Mid-IR metasurfaces based on nanoantenna engineering



Arrays of gold coated standing triangles

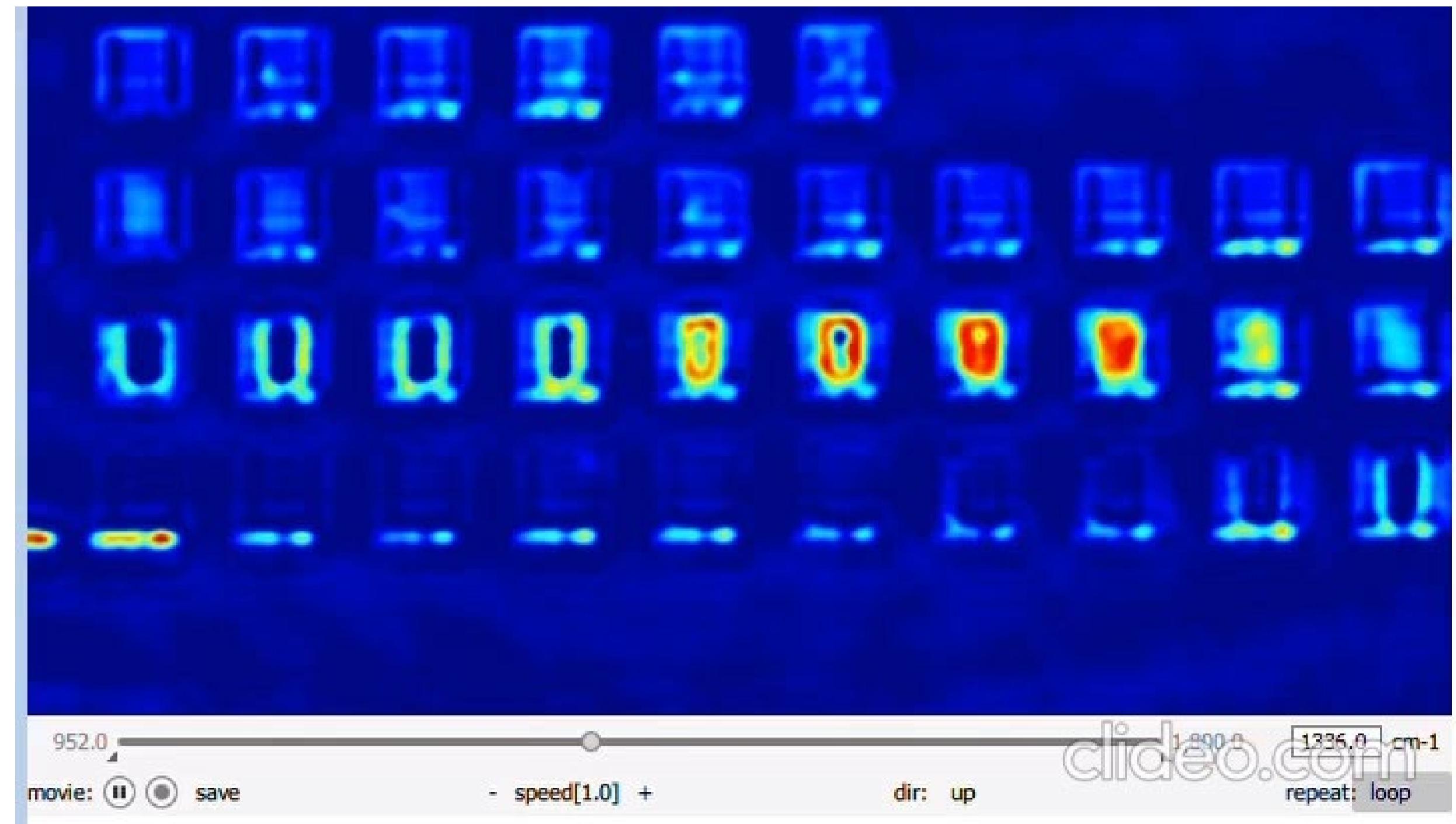
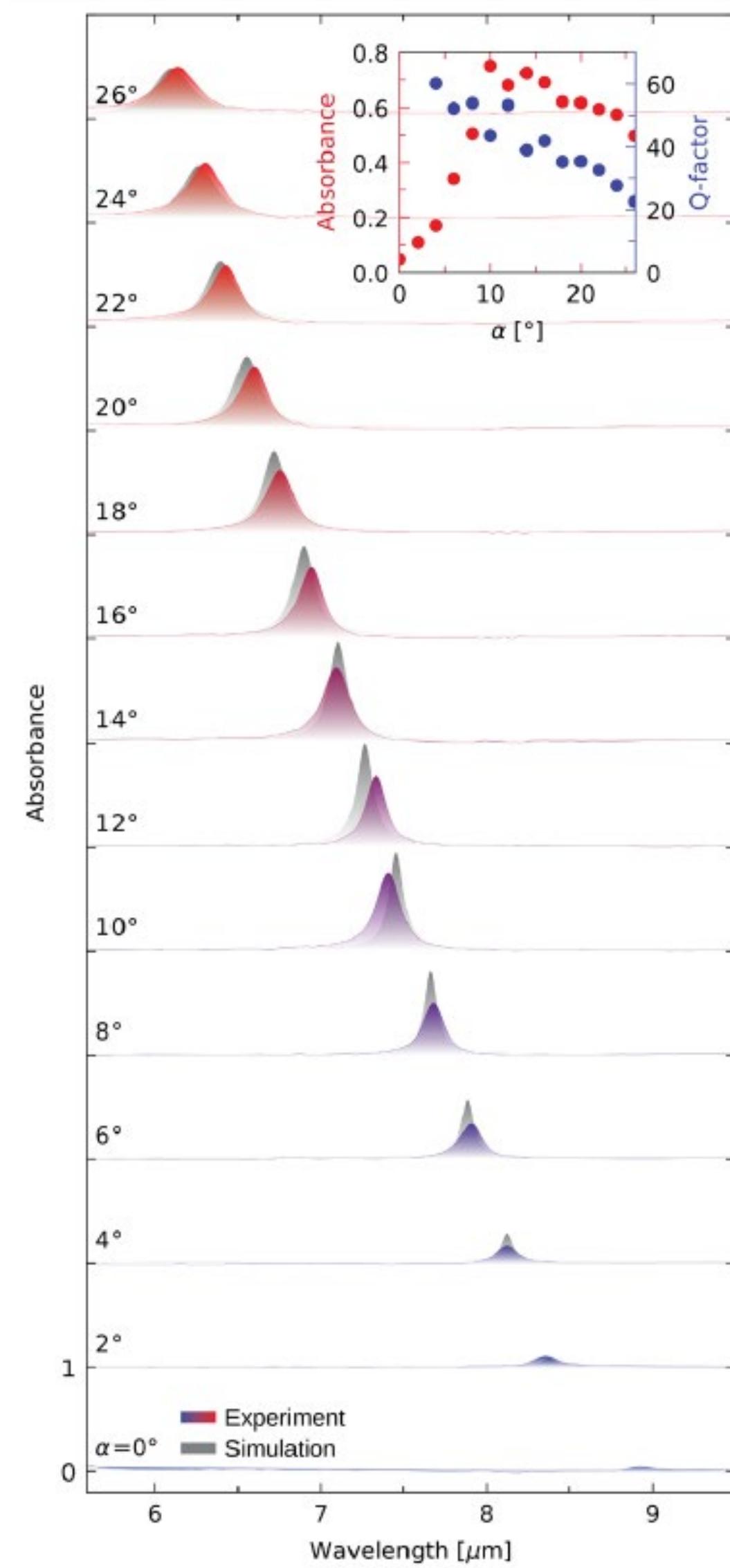


2-photon lithography      4-angle sputtering



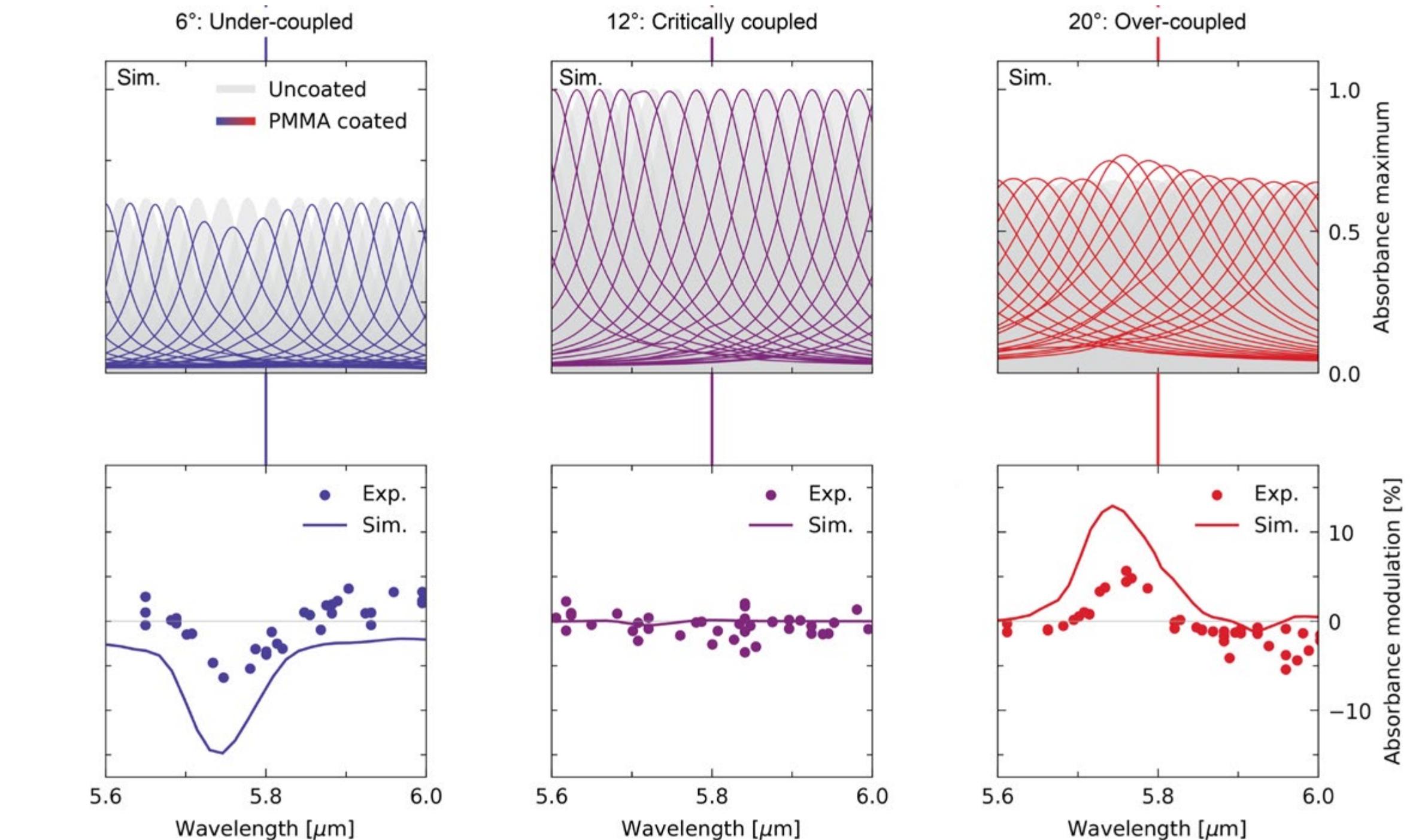
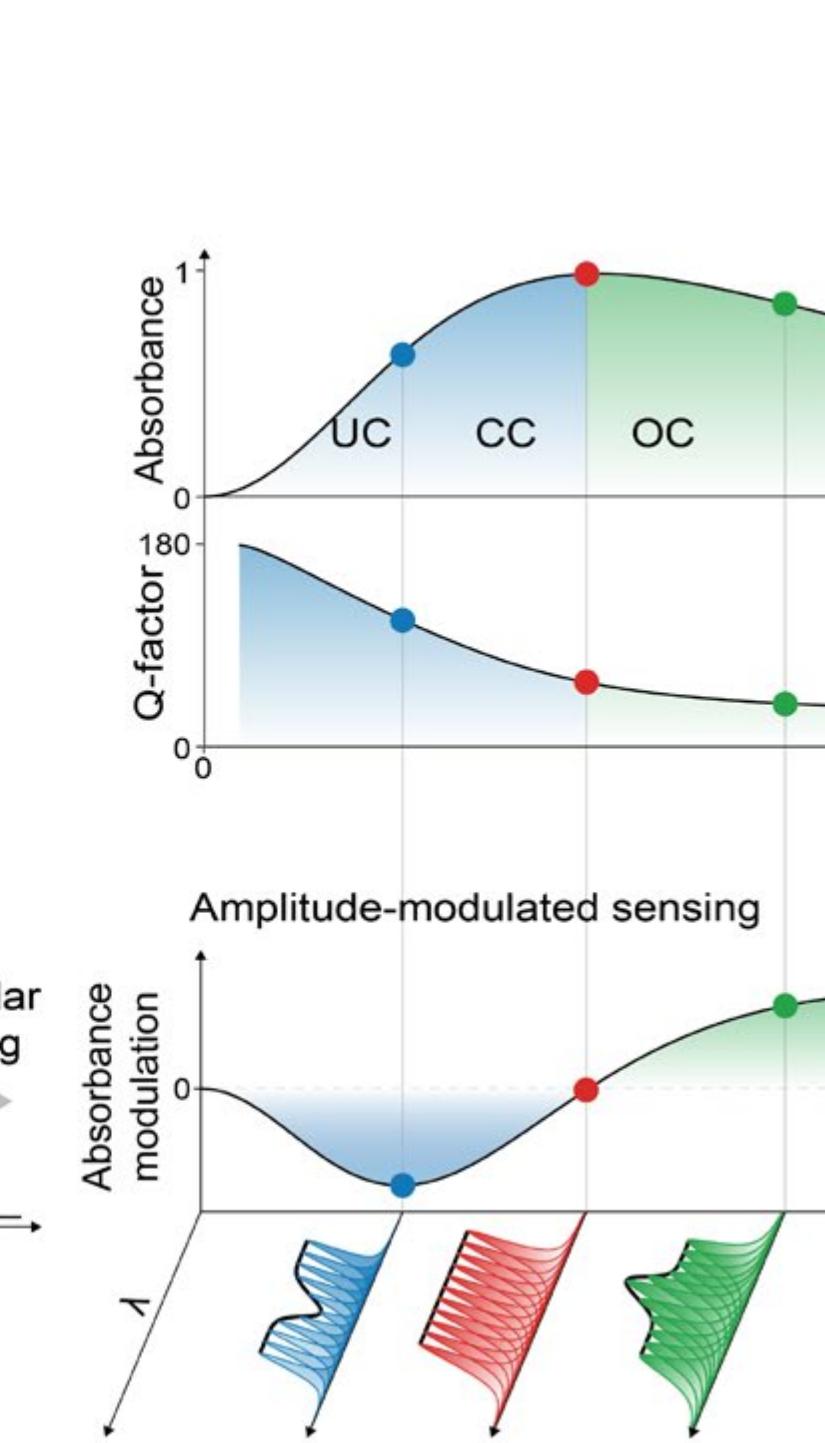
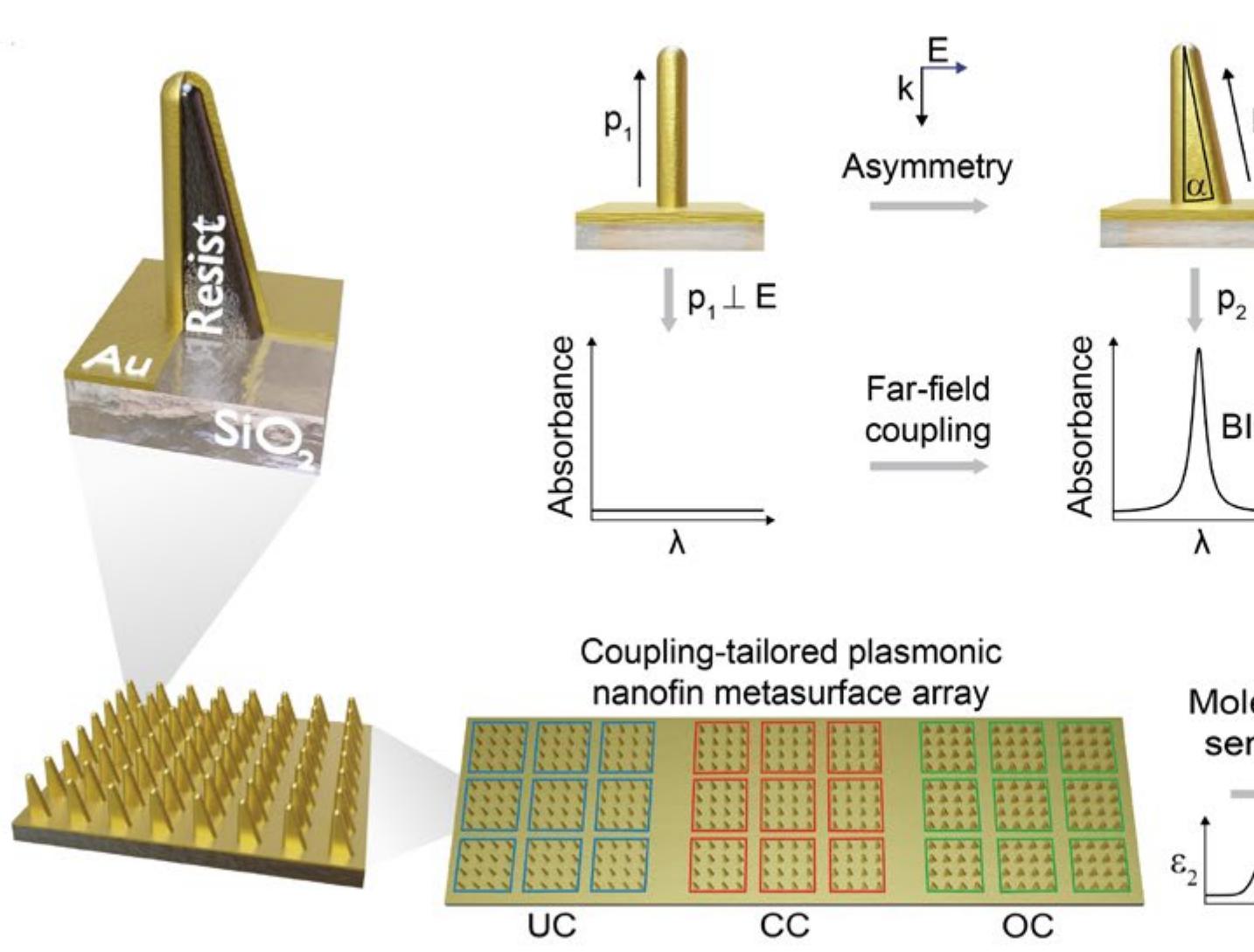
Example of a symmetry-broken “nanofin” bound states in the continuum metasurface

# Bound states in the continuum generate sharp resonances



Pixelated sensing arrays

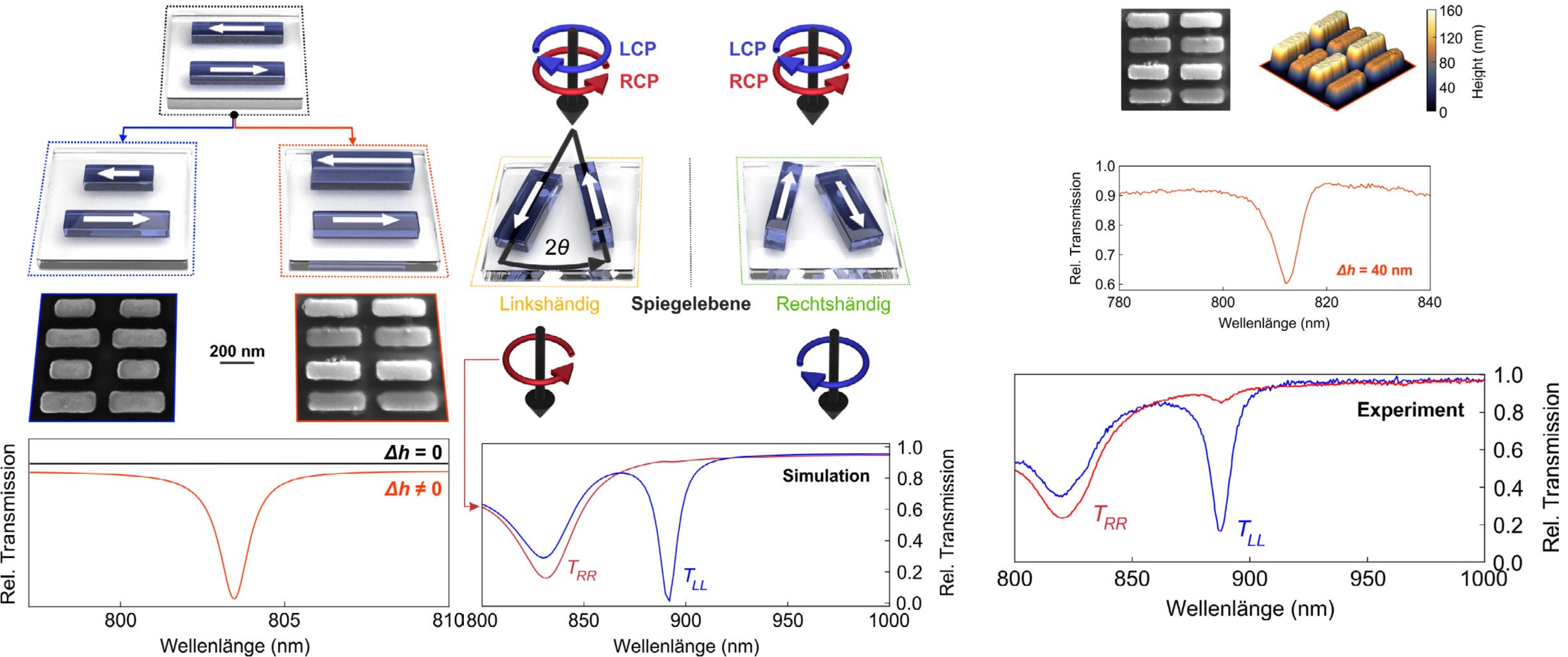
# Coupling-tailored molecular sensing in the mid-IR



Symmetry-breaking tunes ratio of radiative to intrinsic losses  
Surface-enhanced infrared absorption spectroscopy (SEIRA) in different coupling regimes

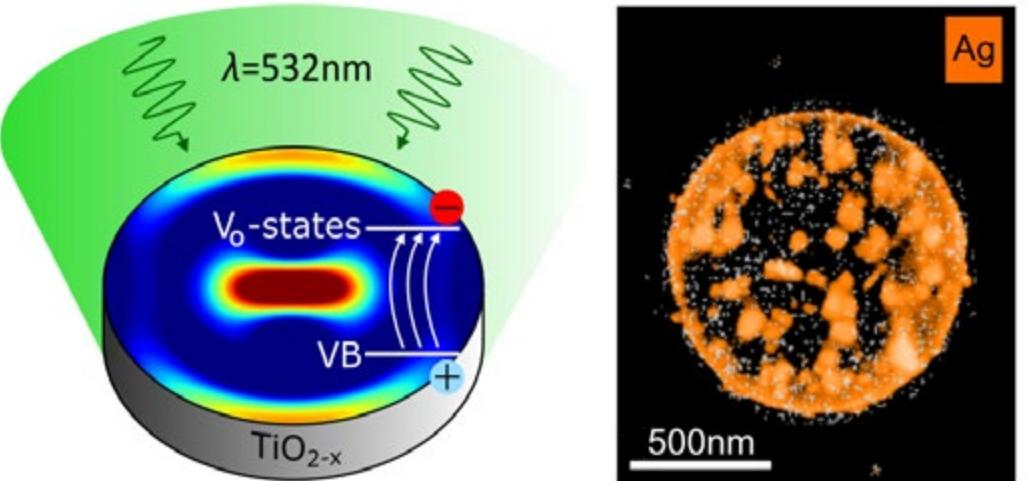
# Chiral BIC Metasurfaces

arXiv:2210.05339

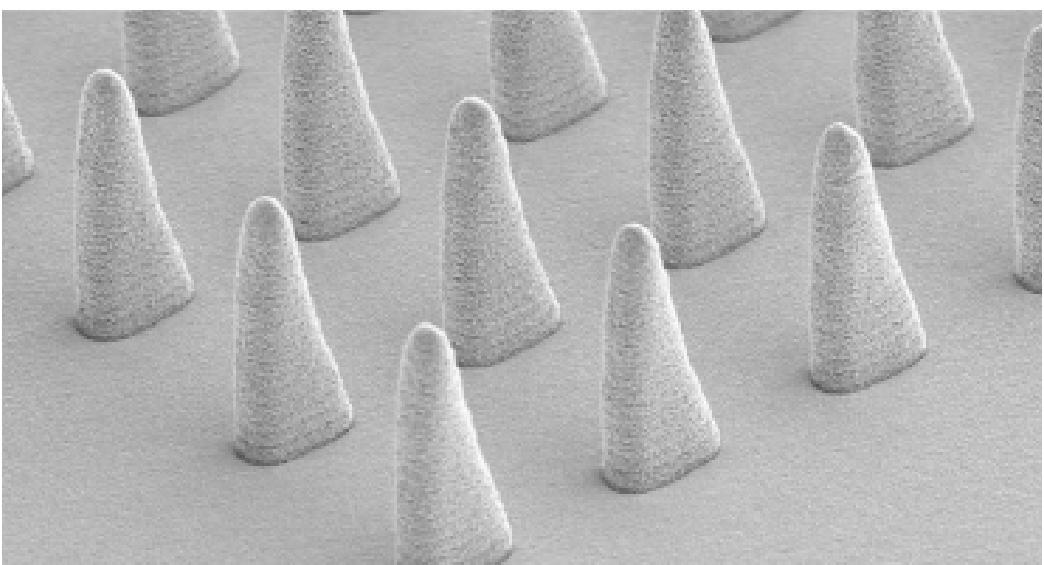


Height degree of freedom enables new chiral BIC designs

# Closing credits

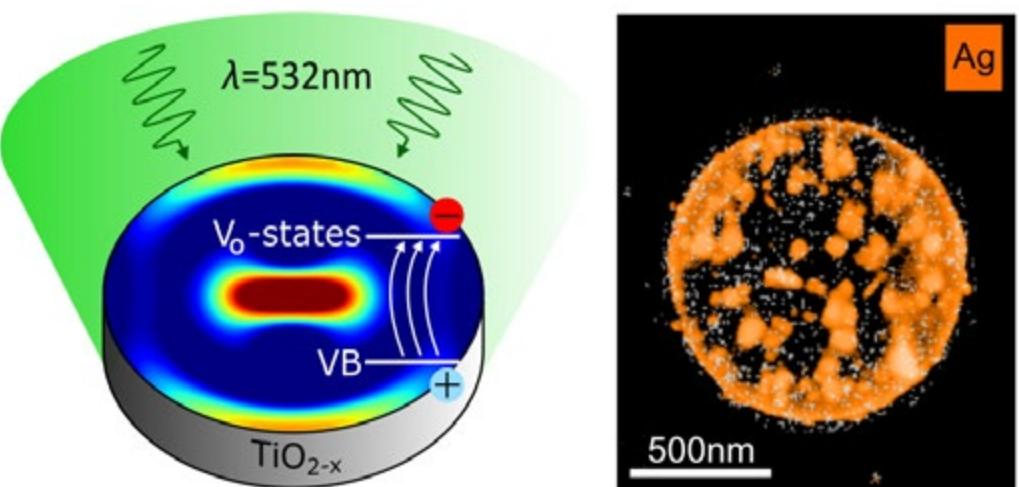


Emiliano Cortés  
Andreas Tittl  
Ian Sharp  
Markus Becherer



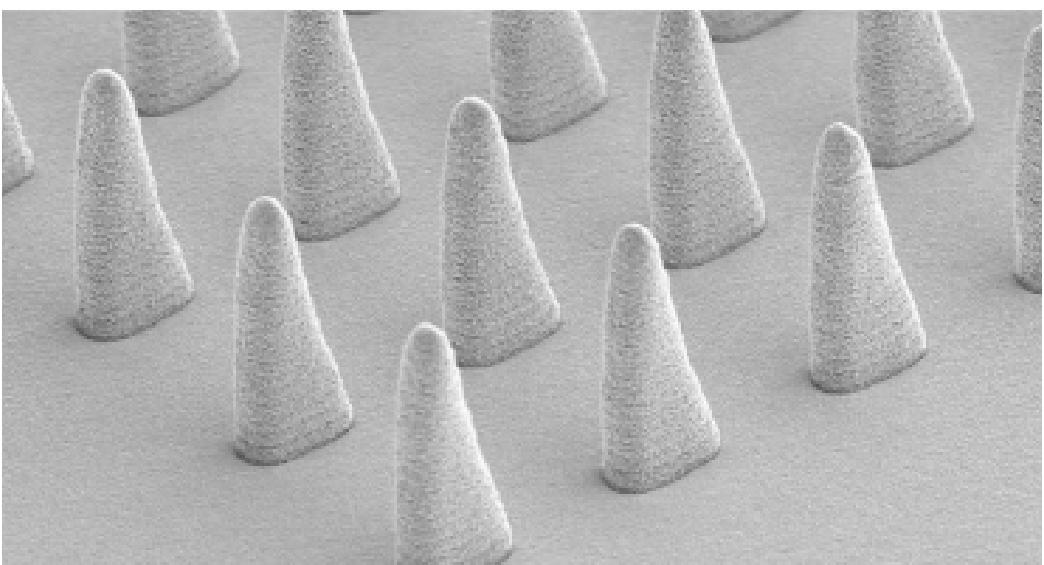
Andreas Tittl  
Haoran Ren  
Yuri Kivshar

# Thanks for your attention :-)



## Anapoles and BICs for energy conversion

*ACS Nano* **16**, 13057 (2022)  
*Adv Energy Mater* **11**, 2102877 (2021)  
*ACS Photonics* **8**, 1469 (2021)  
*ACS Nano* **14**, 2456 (2020)



## BICs for infrared absorption and chirality

*arXiv:2210.05339*