## Multifunctional Metasurfaces Empowered by Bound States in the Continuum



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## Multifunctional Metasurfaces Empowered by Bound States in the Continuum

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## Multifunktionale Metaoberflächen basierend auf gebundenen Zuständen im Kontinuum

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Dissertation

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## Contents

	List	of Figu	ires	xi	
	List of Abbreviations			xiii	
	Zus	ammer	ıfassung	XV	
	Abs	tract		xvii	
	List	of Pub	lications	xix	
1	Intr	oductio	on	1	
2	Fun	damen	tals of photonic bound states in the continuum	5	
	2.1	Wave	optics and mechanics	5	
		2.1.1	Maxwell and Helmholtz equations	6	
		2.1.2	Isomorphism of the Schrödinger and Helmholtz equation	8	
		2.1.3	Propagation of electron/photon over a potential and refractive index		
			step	9	
	2.2	Funda	mentals of dielectric metasurfaces	11	
		2.2.1	Mie resonator and optical interactions in nanoscale environments	12	
		2.2.2	Multipole analysis of an isolated scatterer	15	
		2.2.3	Periodic arrangement of scatterers and lattice coupling matrix	18	
	2.3	Photo	nic bound states in the continuum	20	
		2.3.1	Bloch waves and symmetry in photonics periodic structures	20	

		2.3.2	Radiative modes and diffraction channels	21
		2.3.3	Multipolar perspective of BICs	25
		2.3.4	Topological nature of BICs	27
3	Met	hodolo	gу	29
	3.1	Numer	rical simulations	29
	3.2	Nanostructure fabrication		32
		3.2.1	Before lithography	32
		3.2.2	During lithography	34
		3.2.3	After lithography	35
		3.2.4	The marker system	37
	3.3	Optica	l characterization	39
	<b>6</b> (	1		
4	Cata	alytic n	netasurfaces empowered by bound states in the continuum	41
	4.1	Resear	ch background	42
	4.2	Result	s and discussion	46
	4.3	Summ	ary	59
5	Sur	face-en	hanced Raman scattering in BIC-driven semiconductor metasur	-
	face	s	6	61
	5.1	Resear	ch background	62
	5.2	Result	s and dicussion	64
	5.3	Summ	ary	76
6	Env	ironme	ental permittivity-asymmetric BIC metasurfaces	77
	6.1	Resear	ch background	78
	6.2	Result	s and dicussion	80
	6.3	Summ	ary	91

References	Ι
Acknowledgments	XIII

## List of Figures

2.1	Propagation of an electron (left) and an EM wave (right) over a potential step and refractive index step	10
2.2	Schematic representation of a 2D crystal structure and 2D metasurface $\ldots$	11
2.3	Analytical calculation of scattering efficiencies	14
2.4	Schematic representation of a single scatter system with Cartesian coordination	15
2.5	Schematic representation of the lattice effect	18
2.6	Schematic illustration of metasurfaces under incident light and its dispersion relation	22
2.7	Schematic view of the quasi-BIC metasurfaces under the normal incidence of a linearly x-polarized plane wave	25
2.8	Schematic illustration for the polarization vortex and topological charge $\ . \ .$	27
3.1	Workflow of CST Studio simulation	29
3.2	Illustration of <i>S</i> -parameters in two-port network	31
3.3	Schematic illustration of steps before lithography	32
3.4	Schematic illustration of the area modes in eLINE Plus system	34
3.5	Schematic illustration of steps after lithography	35
3.6	Schematic illustration of the marker system	37
3.7	Schematic illustration of the WITec microscopy	39
3.8	Schematic illustration of the transmittance normalization	40
4.1	Catalytic metasurfaces driven by bound states in the continuum $\ldots$	44
4.2	Numerical design of the catalytic metasurfaces	46

4.3	Simulations of the volume loss of the metasurfaces	48
4.4	Simulations of maximum field enhancement of metasurfaces	49
4.5	Experimental metasurface realization and spectral tuning	50
4.6	The experimental quality factors of metasurfaces	51
4.7	Evaluation of catalytic metasurface performance	52
4.8	The dark-field image analysis based on ${\rm TiO_2}\mbox{-}M$ $\hfill \hfill \hf$	53
4.9	Critical light-matter coupling in catalytic metasurfaces	55
5.1	BIC-driven TiO <sub>2</sub> semiconductor SERS metasurface	63
5.2	Numerical design of semiconductor SERS metasurfaces and their far/near	
	field properties	65
5.3	Experimental metasurface fabrication and spectral tuning	67
5.4	The SEM image and Q factors of metasurfaces	68
5.5	Schematic diagram of the unit cell with different scaling factors	68
5.6	Raman spectra of methylene blue on the BIC-assisted semiconductor SERS metasurface	69
5.7	Schematic illustration of algorithm of multi-polynomial fitting for fluores-	71
5.8	Simulated absorption spectrum and corresponding electric field distribution	
	of metasurfaces	72
5.9	Hybrid effect of BIC-assisted semiconductor SERS metasurface	73
6.1	Strong modulation of radiation coupling in permittivity asymmetric <i>quasi</i> -BIC metasurfaces under environment perturbation	80
6.2	Multipole analysis of permittivity-asymmetric BIC metasurfaces	81
6.3	Reconfigurable permittivity-asymmetry BIC metasurfaces demonstration	84
6.4	Numerical simulation of $\varepsilon$ - <i>q</i> BIC metasurfaces with varied $h_{\text{PMMA}}$	85
6.5	Simulated transmittance spectra of $\varepsilon$ -qBICs metasurfaces using different pho-	
	toresists	85
6.6	In-situ coating of conductive polymer on the $\varepsilon$ - <i>q</i> BICs metasurface $\ldots$	86

6.7	Electrical tuning optical properties of $\varepsilon$ - <i>q</i> BICs metasurfaces	88
6.8	Analysis of PANI thickness during the in-situ coating process.	89

## **List of Abbreviations**

AFM	Atomic Force Microscopy
BIC	Bound States in the Continuum
EBL	Electron Beam Lithography
ED	Electric Dipole
EM	Electromagnetic
EQ	Electric Quadrupole
FEM	Finite Element Method
FIT	Finite Integration Technique
FTIR	Fourier-Transform Infrared Spectroscopy
ΙΤΟ	Indium Tin Oxide
LC	Liquid Crystal
MB	Methylene Blue
MD	Magnetic Dipole
MQ	Magnetic Quadrupole
PANI	Polyaniline
PECVD	Plasma-Enhanced Chemical Vapor Deposition
PICT	Photoinduced Charge Transfer
PMMA	Polymethyl Methacrylate
R6G	Rhodamine 6G
RI	Refractive Index
RIE	Reactive Ion Etching
SEM	Scanning Electron Microscopy
SERS	Surface-Enhanced Raman Scattering
UV	Ultraviolet

## Zusammenfassung

Metaoberflächen, bestehend aus zweidimensionalen Arrays von Nanostrukturen, haben die Photonik erheblich vorangebracht, indem sie eine präzise Kontrolle über Licht-Materie-Wechselwirkungen in kompakten Designs ermöglichen. Gebundene Zustände im Kontinuum (engl. bound states in the continuum, BIC) haben zunehmende Aufmerksamkeit als zentraler Mechanismus für die Leistungsfähigkeit von Metasurfaces erlangt, da sie spektrale Selektivität, starke Lichtkonzentration und eine signifikante Verstärkung elektromagnetischer Felder bieten. Diese Arbeit untersucht BIC-Metaoberflächen als vielseitige Plattform zur Bewältigung von Herausforderungen in verschiedenen Anwendungsbereichen und schlägt eine Brücke zwischen grundlegenden Prinzipien und praktischen Anwendungen.

Die grundlegenden Kapitel bieten einen theoretischen Rahmen für das Verständnis von BICs, einschließlich ihrer symmetriegetriebenen Mechanismen der Lichtkonfinierung und topologischen Eigenschaften, und skizzieren fortschrittliche Methoden für deren Design, Herstellung und optische Charakterisierung. Aufbauend auf diesem Fundament demonstrieren die anwendungsorientierten Kapitel das transformative Potenzial von BIC-Metaoberflächen. Im Bereich der Photokatalyse verbessern BIC-Metaoberflächen die Lichtabsorption und Energielokalisierung erheblich, was zu einer deutlich gesteigerten Katalyseeffizienz führt. Für die oberflächenverstärkte Raman-Spektroskopie (SERS) bieten sie eine abstimmbare, reproduzierbare Alternative zu herkömmlichen plasmonischen Plattformen und ermöglichen eine hochempfindliche molekulare Detektion. Im Bereich der dynamischen elektrischen Abstimmung bieten rekonfigurierbare BIC-Metaoberflächen beispiellose Kontrolle über optische Reaktionen und eröffnen neue Möglichkeiten in der adaptiven Optik und Sensortechnologie.

Die in dieser Dissertation vorgestellte multidisziplinäre Forschung zeigt das Potenzial BICgetriebener Metasurfaces als multifunktionale photonische Bauelemente, die Energieumwandlung, Sensorik und rekonfigurierbare Funktionalitäten integrieren.

### Abstract

Metasurfaces, consisting of two-dimensional arrays of nanostructures, have significantly advanced photonics by enabling precise control over light-matter interactions in compact designs. Bound states in the continuum (BICs) have garnered increasing attention as a key mechanism underpinning recent performance advances of metasurfaces, offering spectral selectivity, strong light confinement, and significant enhancement of electromagnetic fields. This thesis explores BIC metasurfaces as a versatile platform across diverse domains, bridging fundamental principles with practical applications.

The foundational chapters provide a theoretical framework for understanding BICs, including their symmetry-driven confinement mechanisms and topological properties, and outline advanced methodologies for their design, fabrication, and optical characterization. Building on this foundation, the application-focused chapters demonstrate the transformative potential of BIC metasurfaces. In photocatalysis, BIC metasurfaces enhance light absorption and energy localization, significantly improving catalytic efficiency. For surface-enhanced Raman spectroscopy (SERS), they provide a tunable, reproducible alternative to conventional plasmonic platforms, enabling high-sensitivity molecular detection. In dynamic electrical tunability, reconfigurable BIC metasurfaces offer unprecedented control over optical responses, unlocking new possibilities in adaptive optics and sensing technologies.

The multidisciplinary research presented in this thesis presented the potential of BIC-driven metasurfaces as multifunctional photonic devices, integrating energy conversion, sensing, and reconfigurable functionalities.

## **List of Publications**

- H. Hu, T. Weber, O. Bienek, A. Wester, L. Hüttenhofer, I. D. Sharp, S. A. Maier, A. Tittl, E. Cortés, *Catalytic metasurfaces empowered by bound states in the continuum*. ACS Nano 16(8), 13057–13068 (2022).
- H. Hu, A. K. Pal, A. Berestennikov, T. Weber, A. Stefancu, E. Cortés, S. A. Maier, A. Tittl, *Surface-Enhanced Raman Scattering in BIC-Driven Semiconductor Metasurfaces.* Advanced Optical Materials, 2302812 (2024).
- H. Hu, W. Lu, A. Antonov, R. Berté, S. A. Maier, A. Tittl, *Environmental permittivity-asymmetric BIC metasurfaces with electrical reconfigurability*. Nature Communications 15(1), 7050 (2024).
- H. Zheng, H. Hu, T. Weber, J. Wang, L. Nan, B. Zou, S. A. Maier, A. Tittl, All-dielectric structural coloration empowered by bound states in the continuum. Nanophotonics 13(23), 4327–4335 (2024).

## 1 Introduction

Metasurfaces, comprising two-dimensional arrays of nanostructures, have emerged as a transformative platform in photonics, offering precise control over light-matter interactions in highly compact designs. Among the mechanisms that underpin the performance of metasurfaces, bound states in the continuum (BICs) have seen surging interest due to their spectral selectivity, strong light confinement, and giant enhancement of electromagnetic fields.<sup>1-9</sup> BICs are unique optical states that remain localized within the energy continuum of radiating modes, allowing for exceptional control over light confinement and scattering.<sup>10</sup> These distinctive properties make BICs an attractive foundation for a wide range of applications such as nanoscale lasing,<sup>11–17</sup> biomolecular sensing,<sup>18–21</sup> and nonlinear photonics.<sup>22–25</sup> While metasurfaces have already demonstrated significant potential in specific areas, the exploration of BICs opens opportunities to tackle even broader challenges. Building on this foundation, this thesis aims to advance BIC metasurfaces as a versatile platform, exploring their potential to drive innovation across diverse functional domains.

The structure of this thesis is outlined as follows: Chapters 2 and 3 establish the foundational concepts and methodologies, setting the stage for the application-focused core chapters (Chapters 4, 5, and 6), with Chapter 7 providing the concluding insights and future perspectives. The research presented in Chapters 4, 5, and 6 explores specific use cases where BIC-driven metasurfaces offer transformative solutions, specifically catalytic reactions, Raman spectroscopy, and dynamic electrical tunability. Each chapter focuses on leveraging the inherent advantages of BICs to overcome limitations in these fields.

**Chapter 2** explores the fundamental principles of wave optics and their relationship to photonic systems, starting with Maxwell's equations and the Helmholtz equation, which form the basis for analyzing electromagnetic wave behavior. The chapter draws analogies between classical electromagnetism and quantum mechanics, highlighting their shared mathematical structures. Building on these concepts, the properties of dielectric metasurfaces are introduced, focusing on their periodic arrangement of subwavelength resonators and the interactions dictated by lattice symmetries. The formation of bound states in the continuum is then

explored, emphasizing the role of symmetry, destructive interference, and geometric tuning in achieving these unique optical states. A multipolar perspective is presented to analyze the electromagnetic field distributions, shedding light on the confinement mechanisms and symmetry protection of BICs. Finally, the chapter discusses the topological features of BICs, particularly their manifestation as polarization vortices, connecting these states to broader principles in topological physics. This theoretical framework provides a comprehensive understanding of BICs and their operation within metasurfaces, paving the way for practical exploration in later chapters.

**Chapter 3** focuses on the practical methodologies used for the design, fabrication, and optical characterization of BIC metasurfaces. The chapter begins by detailing numerical simulation techniques to predict the optical behavior of metasurfaces, including the use of frequency domain solvers and finite element methods to optimize resonance conditions and field confinement. The fabrication processes are then introduced, highlighting advanced nanofabrication techniques such as electron beam lithography (EBL). Following fabrication, the chapter discusses the suite of optical characterization techniques used to evaluate the metasurfaces' performance. This includes dark-field microscopy, transmittance and reflectance measurements to assess spectral responses, and Raman spectroscopy. These methodologies bridge the gap between theoretical design and experimental realization, ensuring that the BIC metasurfaces meet the functional requirements for their intended applications. Together, the tools and techniques outlined in Chapter 3 collectively provide a robust framework for translating conceptual metasurface designs into tangible, high-performance devices.

**Chapter 4** presents the application of BIC metasurfaces for photocatalysis. Photocatalysis plays a pivotal role in chemical and energy industries, where efficient light-driven reactions are increasingly sought after for processes such as hydrogen generation, pollutant decomposition, and carbon dioxide reduction. Traditional catalytic systems often struggle with inefficiencies stemming from inadequate light absorption, poor energy localization, or suboptimal reaction rates.<sup>26,27</sup> Photonic metasurfaces, when integrated with catalytic materials, have shown the potential to address these challenges by enhancing the interaction between light and the catalytic surface.<sup>28,29</sup> However, conventional metasurfaces typically lack the spectral and spatial control necessary to optimize catalytic efficiency. BIC-driven metasurfaces offer a novel solution by providing extreme light confinement and precise energy manipulation at specific wavelengths, significantly enhancing reaction rates. The integration of BICs with catalytic platforms represents a breakthrough, enabling energy concentration at nanoscale hotspots where catalytic activity occurs. This chapter investigates how these properties can be exploited to create more efficient and selective catalytic systems, advancing light-driven catalytic applications.

**Chapter 5** presents the application of BIC metasurfaces in the surface-enhanced Raman spectroscopy. Raman spectroscopy is a powerful analytical technique for chemical and biological sensing, valued for its ability to provide molecular fingerprints with high specificity. However, its inherent weakness lies in the low cross-section of Raman scattering, which results in weak signal intensities.<sup>30–34</sup> Surface-enhanced Raman scattering (SERS) addresses this limitation by using plasmonic structures to amplify electromagnetic fields near the surface, but these structures often suffer from low tunability, poor reproducibility, and limited stability.<sup>35–37</sup> TiO<sub>2</sub> BIC-driven metasurfaces provide a promising alternative by offering high-Q resonances and enhanced field localization without relying on plasmonic materials. These metasurfaces can be engineered to achieve highly tunable and reproducible Raman enhancement, overcoming key limitations of traditional SERS platforms. This chapter explores how BIC metasurfaces can be used to amplify Raman signals, enabling high-sensitivity detection for applications in chemical sensing, and environmental monitoring.

**Chapter 6** presents the design of permittivity asymmetric BIC metasurface and its application of dynamic electrical tunability. The ability to dynamically adapt to environmental changes is crucial for photonic systems used in applications such as reconfigurable optics, adaptive sensors, and tunable filters.<sup>38–40</sup> Geometry-driven *q*BICs (g-*q*BICs) are defined by fixed asymmetry parameters. These parameters are often determined by geometrical differences between two resonators within the unit cell. Changes in the surrounding refractive index (RI) can modulate g-*q*BICs, causing shifts in the resonance position. However, such changes do not provide direct control over over the *Q* factor. Therefore, although useful in certain contexts, this mechanism does not fully exploit the potential for dynamic interaction with the surrounding environment. Alternatively, our reconfigurable  $\varepsilon$ -*q*BICs metasurfaces platform unlocks a new degree of freedom in manipulating radiation couple of BIC systems, which is unachievable with static geometry symmetry-breaking BIC metasurfaces. This active response to environmental changes leverages the integration of optics and electrolyte fluidics on a single chip, particularly in the visible spectral range. This approach can significantly advance the development of on-demand flat optics and sensing technologies.<sup>41–44</sup>

The applications of BIC-driven metasurfaces explored in this thesis share a unifying theme: leveraging the unique optical properties of BICs to precisely control light-matter interactions at the nanoscale. This thesis demonstrates how BICs can serve as a versatile framework for designing metasurfaces that address application-specific needs while maintaining a unified underlying principle of high-*Q* resonance engineering. Through multidisciplinary research, this thesis establishes BIC-driven metasurfaces as a transformative approach to solving diverse challenges and demonstrates how BICs can act as a cornerstone for the next generation of multifunctional photonic devices for energy conversion, sensing, and adaptive optics.

## 2

# Fundamentals of photonic bound states in the continuum

The following chapter presents the theoretical framework underlying metasurfaces empowered by photonic bound states in the continuum (BICs), grounded in classical electromagnetic theory. Prior to introducing the concept of BICs, this chapter outlines fundamental definitions relevant to nanophotonics and optical metasurfaces, establishing a solid foundation for understanding the subsequent design of optical BICs. While comprehensive theoretical details are available in textbooks,<sup>45,46</sup> this chapter focuses on providing a conceptual overview and the logical progression of key ideas.

### 2.1 Wave optics and mechanics

Maxwell's equations form the cornerstone of classical electromagnetic (EM) theory, concisely summarizing the fundamental principles of electricity and magnetism. They provide a unified framework for understanding a wide range of electromagnetic phenomena, from wave propagation in free space to complex interactions within materials. In the context of metasurface research, the emphasis shifts from electromagnetic fields alone to their intricate interactions with the geometrically tailored nanostructures of the materials, highlighting the critical role of these patterns in shaping and manipulating electromagnetic responses.

To delve deeper into the theoretical foundation, it is essential to consider the Helmholtz equation, which is derived from Maxwell's equations under the assumption of time-harmonic fields. The Helmholtz equation describes the spatial distribution of the electric (or magnetic) field within a given medium, providing insight into how EM waves propagate, scatter, and resonate under various boundary conditions. Specifically, it reduces the complexity of Maxwell's equations by decoupling the electric and magnetic fields, enabling a more tractable analysis of wave behavior in homogeneous or structured media.

This analytical approach is particularly valuable in metasurface research, where the primary goal is to engineer subwavelength structures that control light at the nanoscale. By solving the Helmholtz equation within these engineered media, one can predict how metasurfaces manipulate electromagnetic waves through phenomena such as refraction, diffraction, and resonance.

#### 2.1.1 Maxwell and Helmholtz equations

For general time-dependent EM fields, Maxwell's equations in differential form are given by,

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t},\tag{2.1}$$

$$\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J}, \qquad (2.2)$$

$$\nabla \cdot \mathbf{D} = \rho, \tag{2.3}$$

$$\nabla \cdot \mathbf{B} = 0, \tag{2.4}$$

where **E** is the electric field intensity, and **H** is the magnetic field intensity, which are independent vectors. **J** is the electric current density, and  $\rho$  is the electric charge density. Based on the material equations, through introducing the material property of matter, we can obtain the relation of **D** (the electric flux density), and **B** (the magnetic flux density), to these two independent vectors (**E** and **H**) for a linear medium.

$$\mathbf{D} = \varepsilon \varepsilon_0 \mathbf{E}, \tag{2.5}$$

$$\mathbf{B} = \mu \mu_0 \mathbf{H}.$$
 (2.6)

The material equations play a critical role in understanding the interaction between light and matter, as they encapsulate how the electric permittivity  $\varepsilon$ , and magnetic permeability  $\mu$ of a medium influence electromagnetic wave propagation. Through spatially engineering the distribution of the material at the subwavelength scale, metasurfaces can achieve unique electromagnetic responses, such as anisotropy, nonlinearity, and dispersion, enabling tailored light-matter interactions that are not possible with conventional natural materials.

In a medium without charges and currents, the solution of Maxwell's equations leads to a form of plane waves,

$$\psi = e^{i(\omega t - \boldsymbol{k} \cdot \boldsymbol{r})}, \qquad (2.7)$$

which give us a very useful property as a plane monochromatic wave with frequency  $\omega$ , and time-dependent part is well defined as (electric field for example),

$$\mathbf{E}(\mathbf{r}, \mathbf{t}) = \mathbf{E}(\mathbf{r})\mathbf{e}^{i\omega \mathbf{t}},\tag{2.8}$$

Therefore, the Maxwell's equation of electric field (similar for magnetic field),

$$\nabla^{2}\mathbf{E} - \frac{\mathbf{n}^{2}}{\mathbf{c}^{2}}\frac{\partial^{2}\mathbf{E}}{\partial \mathbf{t}^{2}} = \mathbf{0},$$
(2.9)

can be simplified for the time-independent function,

$$\nabla^2 \mathbf{E}(\mathbf{r}) + \frac{n^2}{c^2} \omega^2 \mathbf{E}(\mathbf{r}) = 0$$
(2.10)

or

$$\nabla^2 \mathbf{E}(\mathbf{r}) + \mathbf{k}^2 \mathbf{E}(\mathbf{r}) = 0, \quad \mathbf{k}^2 = \frac{n^2}{c^2} \omega^2,$$
 (2.11)

which is known as the Helmholtz equation. It describes the spatial distribution of an electric field when an EM wave with frequency  $\omega$  propagates in the matter with the refractive index of n(**r**). The wavevector **k** can take on either real or complex values, depending on whether the medium is lossless or lossy, respectively. The relationship between the wavevector **k** and  $\omega$  is defined by the dispersion relation, which is inherently influenced by the refractive index  $n(\mathbf{r})$  of the medium. By carefully engineering the spatial distribution of the refractive index, it is possible to precisely control the propagation characteristics of photons within the medium. This control is achieved by introducing variations in  $n(\mathbf{r})$ . Such manipulation of photon behavior is analogous to the way electron propagation can be influenced by engineering the potential landscape in solid-state systems. In both cases, tailoring the material properties allows for the creation of band structures, energy gaps, and localized states, leading to the emergence of novel wave phenomena. For instance, periodic variations in the refractive index can produce photonic bandgaps that restrict certain frequencies of light from propagating, similar to how periodic potentials in a crystal lattice give rise to electronic bandgaps that control electron flow.

Exploring the similarities between photon and electron dynamics in carefully designed structures—such as photonic crystals and electronic superlattices—provides valuable insights into the nature of wave propagation across different physical domains. This interdisciplinary perspective deepens our understanding of wave behavior in metasurfaces.

#### 2.1.2 Isomorphism of the Schrödinger and Helmholtz equation

In the study of wave phenomena, it is notable to observe how seemingly disparate physical systems can be governed by mathematically analogous equations. This becomes particularly evident when comparing the quantum mechanical description of electron dynamics with the classical description of electromagnetic wave propagation. Despite originating from distinct physical principles—quantum mechanics for electrons and classical electromagnetism for light—the Schrödinger equation and the Helmholtz equation exhibit a mathematical isomorphism. This isomorphism highlights an underlying symmetry in the behavior of wave functions and electromagnetic fields, suggesting a fundamental connection between different wave phenomena.

To gain a deeper understanding of this connection, it is instructive to first consider the basic form of these equations under time-harmonic conditions, where time dependence is eliminated. This simplification enables a clearer comparison of the spatial distributions of the respective wave functions and fields. In this context, both equations reduce to eigenvalue problems, revealing similarities in their solutions.

Let's start with the basic description of electrons and EM waves under a time-harmonic situation (eliminating time dependence). For electrons, the time-independent Schrödinger equation is given by:

$$\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + [E - U(\mathbf{r})]\psi(\mathbf{r}) = 0, \qquad (2.12)$$

where the wave function of electrons,  $\psi(\mathbf{r})$ , is influenced by the potential field U( $\mathbf{r}$ ). The term *E* represents the eigenvalue of the electron, and  $\hbar$  is the reduced Planck constant. For electromagnetic waves, the time-independent Helmholtz equation as discussed previously (2.10) is given by:

$$\nabla^2 \mathbf{A}(\mathbf{r}) + \frac{\mathbf{n}^2(\mathbf{r})}{\mathbf{c}^2} \omega^2 \mathbf{A}(\mathbf{r}) = 0.$$
 (2.13)

Here, using notation A to represent electric and magnetic fields (E and B).

It can be found that these pair of equations are mathematically identical, which underscores the profound symmetry between quantum mechanical wave functions and classical electromagnetic wave fields, revealing a deep conceptual parallel between the two domains. In both equations, the spatial variation of the potential  $U(\mathbf{r})$  or the refractive index  $n(\mathbf{r})$  gives rise to an eigenvalue problem. In the Schrödinger equation, solving for the eigenvalues *E* provides the discrete energy levels of an electron in a potential well or periodic potential (e.g., a crystal lattice). Similarly, solving the Helmholtz equation for a periodic  $n(\mathbf{r})$ , such as in a photonic crystal, yields the allowed and forbidden frequency bands for light propagation.

This correspondence implies that concepts like Brillouin zones, band gaps, and Bloch waves, which are fundamental in solid-state physics, have direct analogs in photonic systems. For example, in a periodic medium, the refractive index profile  $n(\mathbf{r})$  creates Bragg scattering conditions, resulting in photonic band gaps that prevent certain wavelengths from propagating. This behavior mirrors the formation of electronic band gaps in semiconductors due to the periodic potential  $U(\mathbf{r})$ .

The deep mathematical symmetry between the Schrödinger and Helmholtz equations reveals that principles from quantum mechanics can be translated into the field of classical electromagnetism, providing a powerful toolset for manipulating wave behavior across different physical contexts. This cross-disciplinary approach not only enhances our understanding of wave dynamics but also enables the development of novel photonic devices and materials with tailored electromagnetic responses, leveraging insights from solid-state physics and quantum mechanics.

## 2.1.3 Propagation of electron/photon over a potential and refractive index step

Before delving into the periodic configuration, it is instructive to first consider the most fundamental case: the one-dimensional potential and refractive index step. For the sake of conciseness, the detailed derivation provided in textbook references will not be repeated here.<sup>45</sup> Instead, the corresponding reflectance and transmittance functions for both electrons and photons are presented below (Fig. 2.1).

For the electron,

$$R = r^{2} = \frac{\left(\sqrt{E} - \sqrt{E - U_{0}}\right)^{2}}{\left(\sqrt{E} + \sqrt{E - U_{0}}\right)^{2}},$$
(2.14)

$$T = 1 - R = \frac{4\sqrt{E(E - U_0)}}{\left(\sqrt{E} + \sqrt{E - U_0}\right)^2},$$
(2.15)

and for the EM waves,

$$\mathbf{R} = \mathbf{r}^2 = \frac{(n_1 - n_2)^2}{(n_1 + n_2)^2},$$
(2.16)

$$T = 1 - R = \frac{4n_1n_2}{(n_1 + n_2)^2}.$$
(2.17)

This pair of functions highlights the parallel behavior of electrons and photons when encountering a step configuration. For electrons, the reflectance and transmittance are governed by the potential step  $U_0$ ) and the energy E. In contrast, for electromagnetic waves, these quantities are determined by the refractive indices  $n_1$  and  $n_2$ . This analogy illustrates a fundamental correspondence between the wave properties of particles and electromagnetic fields, despite their distinct natures (quantum vs. classical).



**Figure 2.1: Propagation of an electron (left) and an EM wave (right) over a potential step and refractive index step.** Graphs for the wave function and amplitude are just for illustration without accounting for the partial decrease in amplitude of transmitted waves.<sup>45</sup>

This similarity is instrumental in understanding Bloch waves in periodic metasurfaces. Bloch waves describe the wave-like behavior of particles in a periodic potential, which is a cornerstone concept in solid-state physics, explaining phenomena such as band structure and electron conduction in crystals. Similarly, in photonics, periodic metasurfaces can manipulate light in ways analogous to electronic band structures, leading to novel optical properties and applications, such as photonic band gaps and negative refraction.

Recognizing these analogies enables a deeper understanding of how periodic structures influence wave propagation, whether in the context of electron waves within a crystal lattice or light waves in a metasurface. This understanding bridges fundamental concepts from quantum mechanics and classical electromagnetism, thereby fostering advancements in both fields.

### 2.2 Fundamentals of dielectric metasurfaces

In the previous section, we analyzed the propagation of electrons and photons across potential and refractive index steps, respectively. By introducing periodicity in two dimensions, we can construct two-dimensional metasurfaces, consisting of a two-dimensional array of sub-wavelength resonant elements—often referred to as "meta-atoms"—which manipulate light at the nanoscale.



**Figure 2.2: Schematic representation of a 2D crystal structure and 2D metasurface.** In this crystal structure, basis are periodically arranged, analogous to the periodic arrangement of unit cells in a metasurface.

In 2D metasurfaces the behavior of light is governed not only by the lattice periodicity but also by the intricate geometries of the individual meta-atoms. These meta-atoms, with dimensions much smaller than the wavelength of light, can be modeled as Mie resonators, whose scattering behavior is described by Mie theory. The geometry, size, and material composition of each meta-atom determine the resonant modes of these Mie resonators, enabling strong light-matter interactions that are not achievable with macroscopic materials.

From a solid-state physics perspective, the structure of metasurfaces can be analyzed using the same principles used to describe crystalline solids. Just as a crystal lattice is defined by its periodic arrangement and basis (the repeating unit that defines the crystal structure), a metasurface can be viewed as a 2D lattice with a basis consisting of Mie resonators. This analogy enables the application of concepts such as Bloch's theorem, reciprocal space, and Brillouin zones to describe the propagation of electromagnetic waves in metasurfaces, drawing a direct parallel to the propagation of electron wavefunctions in a periodic potential.

The manipulation of electromagnetic wave propagation in metasurfaces can be further enhanced by tuning the geometry of the meta-atoms to achieve specific phase and amplitude responses. This level of control enables the realization of a wide range of optical phenomena, such as anomalous refraction and reflection, perfect absorption, and even topological light confinement, where light can propagate along the edges of a metasurface without scattering—a behavior analogous to the edge states in topological insulators.

### 2.2.1 Mie resonator and optical interactions in nanoscale environments

Before exploring complex periodic systems, let's start with the individual constituting particle, which can be considered a Mie resonator. The scattering properties of a Mie resonator are well described by Mie theory<sup>47</sup>, which is a solution to Maxwell's equations for the interaction of an electromagnetic wave with a sphere. It provides an exact solution for the scattering, absorption, and extinction of light by spherical particles. The solution involves decomposing the incident, scattered, and internal fields into multipole components-electric and magnetic dipoles, quadrupoles, and higher-order modes. These multipole components are described using scattering coefficients. And the scattering efficiencies of a sphere can by expressed as,

with,

$$a_{n} = \frac{m^{2} j_{n}(mx) \left[x j_{n}(x)\right]' - \mu_{1} j_{n}(x) \left[mx j_{n}(mx)\right]'}{m^{2} j_{n}(mx) \left[x h_{n}^{(1)}(x)\right]' - \mu_{1} h_{n}^{(1)}(x) \left[mx j_{n}(mx)\right]'},$$
(2.18)

$$b_{n} = \frac{\mu_{1} j_{n}(mx) \left[x j_{n}(x)\right]' - j_{n}(x) \left[mx j_{n}(mx)\right]'}{\mu_{1} j_{n}(mx) \left[x h_{n}^{(1)}(x)\right]' - h_{n}^{(1)}(x) \left[mx j_{n}(mx)\right]'}.$$
(2.19)

Here,  $a_n$ , and  $b_n$  are Mie coefficients for n-th order electric and magnetic modes respectively. The size parameter, x = ka, is a function of the sphere's radius a and host medium wavenumber. m is the permittivity contrast parameter ( $m = \frac{\sqrt{\varepsilon_1 \mu_1}}{\sqrt{\varepsilon_0 \mu_0}}$ ), where  $\varepsilon_0$ ,  $\mu_0$ ,  $\varepsilon_1$ , and  $\mu_1$  are vacuum's, and material's (sphere) permittivity and permeability.  $j_n$  is the spherical Bessel functions of the first kind, and  $h_n^{(1)}$  is the spherical Hankel function of the first kind.<sup>47</sup>

However, if the permittivity environment of this sphere changes from a vacuum to other media, the scattering efficiencies will also change accordingly, and the original sphere model may no longer be applicable. Instead, a core-shell model can be used, where the surrounding medium is simplified as a shell with a different refractive index covering the sphere. The scattering efficiency for this core-shell model will then be modified as follows:

$$a_{n} = \frac{j_{n}(y) \left[ j_{n}'(m_{2}y) - A_{n}\chi_{n}'(m_{2}y) \right] - m_{2}j_{n}'(y) \left[ j_{n}(m_{2}y) - A_{n}\chi_{n}(m_{2}y) \right]}{h_{n}^{(1)}(y) \left[ j_{n}'(m_{2}y) - A_{n}\chi_{n}'(m_{2}y) \right] - m_{2}h_{n}^{(1)'}(y) \left[ j_{n}(m_{2}y) - A_{n}\chi_{n}(m_{2}y) \right]},$$
(2.20)

$$b_{n} = \frac{m_{2}j_{n}(y)\left[j_{n}'(m_{2}y) - B_{n}\chi_{n}'(m_{2}y)\right] - j_{n}'(y)\left[j_{n}(m_{2}y) - B_{n}\chi_{n}(m_{2}y)\right]}{m_{2}h_{n}^{(1)}(y)\left[j_{n}'(m_{2}y) - B_{n}\xi_{n}'(m_{2}y)\right] - h_{n}^{(1)'}(y)\left[j_{n}(m_{2}y) - A_{n}\chi_{n}(m_{2}y)\right]},$$
(2.21)

with,

$$A_{n} = \frac{m_{2}j_{n}(m_{2}x)j_{n}'(m_{1}x) - m_{1}j_{n}'(m_{2}x)j_{n}(m_{1}x)}{m_{2}h_{n}^{(1)}(m_{2}x)j_{n}'(m_{1}x) - m_{1}h_{n}^{(1)'}(m_{2}x)j_{n}(m_{1}x)},$$
(2.22)

$$B_{\rm n} = \frac{m_2 j_{\rm n}(m_1 x) j_{\rm n}'(m_2 x) - m_1 j_{\rm n}(m_2 x) j_{\rm n}'(m_1 x)}{m_2 \chi_{\rm n}'(m_2 x) j_{\rm n}(m_1 x) - m_1 j_{\rm n}'(m_1 x) \chi_{\rm n}(m_2 x)},$$
(2.23)

and,

$$x = \frac{2\pi R_{\text{core}}}{\lambda}, \quad y = \frac{2\pi R_{\text{shell}}}{\lambda},$$
 (2.24)

$$m_1 = \frac{n_{core}}{n_{medium}}, \quad m_2 = \frac{n_{shell}}{n_{medium}}$$
 (2.25)

$$\chi_{\rm n}({\rm x}) = -x \sqrt{\frac{\pi}{2x}} N_{n+\frac{1}{2}}(x),$$
 (2.26)

The effect of varying the surrounding medium on the scattering efficiencies of a single Mie scatterer can be quantitatively analyzed by solving the above equations using a customized model. In this model, TiO<sub>2</sub> is employed as the core material ( $n_{core} = 2.5$ ) with a radius of 200 nm ( $R_{core}$ ), while PMMA serves as the shell material ( $n_{shell} = 1.5$ ) with a thickness of 80 nm  $R_{shell}$ .



**Figure 2.3:** Analytical calculation of scattering efficiencies. a. Scattering efficiency across wavelengths ranging from 500 to 900 nm for a standalone  $TiO_2$  sphere with a radius of 200 nm (left) based on the Mie sphere model, and a  $TiO_2$  sphere (same size) embedded in a PMMA (80 nm) with the core-shell model (right). The contributions from the electric dipole (ED), magnetic dipole (MD), electric quadrupole (EQ), and magnetic quadrupole (MQ) are shown (dash lines), along with the total scattering efficiency. **b.** Individual mode coefficients, including the electric dipole a1, magnetic dipole b1, electric quadrupole a2, and electric quadrupole b2, corresponding to the respective resonances observed in the scattering efficiency spectra, which highlights the influence of the surrounding medium on the optical resonances of the  $TiO_2$  spheres.

As shown in Fig.2.3, the scattering efficiencies of  $TiO_2$  nanospheres embedded in different surrounding media (vacuum and PMMA, respectively) are different. This highlights the significant influence of the surrounding environment on the behavior of the Mie resonator.
We will discuss these models in the later section regarding the environmental permittivityasymmetric bound states in the continuum (BIC) metasurfaces.

It is worth noting that, the scattering efficiencies of the sphere can be decomposed into different orders of electric and magnetic modes, which is the fundamental concept in the Mie theory. Specifically, the scattering and extinction of the incident EM waves by the sphere result from contributions of electric and magnetic eigenmodes of various orders.<sup>47</sup> Moreover, these eigenmodes can also be identified in arbitrary subwavelength scatters using multipole expansion.

### 2.2.2 Multipole analysis of an isolated scatterer

This section presents a detailed derivation of the multipole modes that characterize the scattering field of a single isolated scatterer. The derivation includes several critical steps, such as the far-field approximation of Green's function, the expansion of the Dirac delta function as a Taylor series, and the multipole representation of the induced polarization.



Figure 2.4: Schematic representation of a single scatter system with Cartesian coordination.  $\mathbf{r}_0$  is the point contribution to the scattering to the observation point of A.  $\mathbf{r}_c$  is the scatterer's center of mass.

The scattered electric field from a single scatter (taken as source current distribution) initially is in the form of,

$$\mathbf{E}_{\text{scat}}(\mathbf{r}) = i\omega\mu_0 \int d^3\mathbf{r}_0 \,\hat{\mathbf{G}}(\mathbf{r} - \mathbf{r}_0) \mathbf{J}(\mathbf{r}_0), \qquad (2.27)$$

with  $\mu_0$  as the magnetic permeability of free space (vacuum),  $\omega$  as the angular frequency of the incident wave, and current density  $\mathbf{J}(\mathbf{r}_0)$  at the position of  $\mathbf{r}_0$  (Fig. 2.4). Here the dyadic Green's function  $\hat{\mathbf{G}}(\mathbf{r} - \mathbf{r}_0)$  is applied to describe the response at position  $\mathbf{r}$  due to a unit source at position  $\mathbf{r}_0$ .

The dyadic Green's function is a matrix-like function used to represent the response of a vector field to a point source. It extends the concept of a scalar Green's function to vector fields by incorporating both the direction and magnitude of the fields and sources. Mathematically,

the dyadic Green's function  $\hat{G}(\mathbf{r} - \mathbf{r}_0)$  is defined as the solution to Maxwell's equations for a unit vector point source:

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{G}}(\mathbf{r}, \mathbf{r}_0) = \hat{\mathbf{I}}\delta(\mathbf{r} - \mathbf{r}_0), \qquad (2.28)$$

where the term  $\hat{L}$  represents the linear differential operator corresponding to Maxwell's equations, such as the Helmholtz operator. The dyadic Green's function  $\hat{G}(\mathbf{r}, \mathbf{r}_0)$  is a 3 × 3 matrix that characterizes the vector field response at a point  $\mathbf{r}$  due to a point source located at  $\mathbf{r}_0$ . The identity dyadic  $\hat{I}$ , analogous to the identity matrix in linear algebra, is used in the definition of the dyadic Green's function. Finally,  $\delta(\mathbf{r} - \mathbf{r}_0)$  is the Dirac delta function, which describes a point source positioned at  $\mathbf{r}_0$ .

The dyadic Green's function has several key properties that make it valuable for solving electromagnetic problems. It often exhibits symmetry with respect to its source and observation points, meaning that  $\hat{G}(\mathbf{r}, \mathbf{r}_0) = \hat{G}(\mathbf{r}_0, \mathbf{r})$  in many cases. Secondly, it satisfies the principle of reciprocity, as stated by the reciprocity theorem in electromagnetics, which ensures that the Green's function obeys the condition  $\hat{G}(\mathbf{r}, \mathbf{r}_0) \cdot \mathbf{J} = \hat{G}(\mathbf{r}_0, \mathbf{r}) \cdot \mathbf{J}$ . For time-dependent problems, the dyadic Green's function adheres to the principle of causality, ensuring that the response at the observation point occurs only after the excitation at the source point. Finally, the dyadic Green's function can be constructed to satisfy specific boundary conditions, such as perfectly conducting surfaces or dielectric interfaces, depending on the geometry and properties of the medium.

Calculating the full Green's function for electromagnetic problems can be inherently complex, particularly in scenarios involving intricate geometries and boundary conditions. Certain approximations are often applied to simplify the analysis. When the primary focus is on the radiation component of the field—specifically the behavior of the electromagnetic wave at large distances from the source—the far-field approximation becomes particularly useful. This approximation not only reduces computational complexity but also highlights the dominant radiation characteristics, such as the angular distribution and intensity of the scattered field.

It is important to note that the Green's function for electromagnetic waves is fundamentally derived from the Helmholtz equation, as discussed in the previous section. The Helmholtz equation, which governs the propagation of electromagnetic waves in homogeneous media, naturally leads to a form of the Green's function that satisfies both the wave equation and the appropriate boundary conditions. In the far-field region, the Green's function simplifies to represent spherical waves radiating outward, thereby providing an effective way to analyze the radiation properties without needing to consider near-field interactions or complex internal field distributions. The original expression for this Green's function is given by:

$$\hat{\mathbf{G}}(\mathbf{r} - \mathbf{r}_0) = \left(\hat{\mathbf{I}} + \frac{\nabla \nabla}{k^2}\right) \mathbf{G}(\mathbf{r} - \mathbf{r}_0), \qquad (2.29)$$

$$G(\mathbf{r} - \mathbf{r}_0) = \frac{e^{\mathbf{i}k|\mathbf{r} - \mathbf{r}_0|}}{4\pi|\mathbf{r} - \mathbf{r}_0|}.$$
(2.30)

In the far-field approximation,  $|\mathbf{r} - \mathbf{r_0}| \approx r - \hat{\mathbf{n}} \cdot \mathbf{r_0}$  (where  $r = |\mathbf{r}|$  and  $\hat{\mathbf{n}} = \frac{\mathbf{r}}{\mathbf{r}}$ ), the Green's function simplifies to:

$$\hat{G}(\mathbf{r}-\mathbf{r}_0) \approx \frac{e^{ikr}}{4\pi r} e^{-ik\hat{\mathbf{n}}\cdot\mathbf{r}_0} \left(\hat{\mathbf{I}}-\hat{\mathbf{n}}\otimes\hat{\mathbf{n}}\right),$$
 (2.31)

which results in the simplified scattered electric field:

$$\mathbf{E}_{\text{scat}}(\mathbf{r}) = i\omega\mu_0 \frac{e^{ik\mathbf{r}}}{4\pi\mathbf{r}} \left(\hat{\mathbf{I}} - \hat{\mathbf{n}} \otimes \hat{\mathbf{n}}\right) \int d^3\mathbf{r}_0 \, e^{-ik\hat{\mathbf{n}}\cdot\mathbf{r}_0} \mathbf{J}(\mathbf{r}_0) \tag{2.32}$$

By applying the far-field approximation, the mathematical integration over a single scatterer is significantly simplified, as it focuses only on the asymptotic behavior of the scattered field at large distances. However, this approximation inherently neglects the near-field components, leading to the loss of detailed information about the electromagnetic field distribution in the vicinity of the scatterer. This limitation should be considered when analyzing systems where near-field interactions play a crucial role.

In this context, the electric current density **J** in the integration can be expressed in terms of the polarization **P** using the relation  $\mathbf{J} = -i\omega \mathbf{P}$  for time-harmonic fields. This substitution is particularly useful in dielectric materials, where the electromagnetic response is primarily characterized by the polarization **P**. Using **P** instead of **J** simplifies the calculation, as **P** is directly related to intrinsic material properties, such as permittivity and susceptibility, thereby providing a clearer physical interpretation of the scattering process. In order to obtain the multipole decomposition of the polarization, the **P** can be expressed as follows,<sup>48</sup>

$$\mathbf{P}(\mathbf{r}) = \int \mathbf{P}(\mathbf{r}_0) \delta(\mathbf{r} - \mathbf{r}_0) \, \mathrm{d}^3 \mathbf{r}_0 \tag{2.33}$$

Here we can apply Taylor expansion to the Dirac delta function around the point at the scatterer's center of mass  $r_c$ (Fig. 2.4).<sup>48</sup>

$$\delta(\mathbf{r} - \mathbf{r}_0 - \Delta \mathbf{r}) \simeq \delta(\mathbf{r} - \mathbf{r}_0) - (\Delta \mathbf{r} \cdot \nabla)\delta(\mathbf{r} - \mathbf{r}_0) + \frac{1}{2}(\Delta \mathbf{r} \cdot \nabla)^2\delta(\mathbf{r} - \mathbf{r}_0) - \cdots, \qquad (2.34)$$

where  $\Delta \mathbf{r} = \mathbf{r}_0 - \mathbf{r}_c$ , and  $\nabla$  is the gradient operator. According to the definitions of the multipole moments,<sup>48</sup> the total polarization can be discomposed into several terms as follows,

$$\mathbf{P}(\mathbf{r}) \simeq \mathbf{p}\delta(\mathbf{r}-\mathbf{r}_{c}) - \frac{1}{6}\mathbf{Q}^{e}\nabla\delta(\mathbf{r}-\mathbf{r}_{c}) + \frac{\mathbf{i}}{\omega}[\nabla\times\mathbf{m}\delta(\mathbf{r}-\mathbf{r}_{c})] + \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})) - \frac{\mathbf{i}}{2\omega}[\nabla\times\mathbf{Q}^{m}\nabla\delta(\mathbf{r}-\mathbf{r}_{c})] + \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})) - \frac{\mathbf{i}}{2\omega}[\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})] + \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})) - \frac{\mathbf{i}}{2\omega}[\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})] + \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})) - \frac{\mathbf{i}}{2\omega}[\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})] + \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})] + \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})) - \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})) - \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})) - \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})] + \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c}) + \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})] + \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c}) + \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})) - \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})) + \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})) + \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})) - \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})) - \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})) - \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})) - \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})) - \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})) - \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c}) - \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})) - \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c}) - \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})) - \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c}) - \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c})) - \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}_{c}) - \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r})) - \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla\delta(\mathbf{r}-\mathbf{r}) - \frac{1}{6}\mathbf{O}^{e}(\nabla\nabla$$

Here, we can find the contribution of different modes to the polarization, as  $\mathbf{p}$  is the electric dipole moment.  $\mathbf{Q}^{e}$ ,  $\mathbf{m}$ ,  $\mathbf{O}^{e}$ , and  $\mathbf{Q}^{m}$  are the electric quadrupole tensor, the magnetic dipole moment, the electric octupole tensor, and the magnetic quadrupole tensor, respectively. Once we insert this polarization  $\mathbf{P}$  back into the integration Eq.2.32, we can obtain the contribution of all modes to the scattered electric field by this single scatterer.<sup>49</sup>

# 2.2.3 Periodic arrangement of scatterers and lattice coupling matrix

It is important to note that, when analyzing a single scatterer, its multipole moments are primarily determined by the external field, which, in this case, is simply the incident illumination. However, for metasurfaces consisting of multiple scatterers arranged in a 2D array, the external field experienced by each scatterer is more complex. It is influenced not only by the incident field but also by the scattered fields from all neighboring scatterers in the array. To address this complexity, a theoretical framework has been developed that analytically examines the optical properties of a resonator both as an isolated entity and as part of a 2D array.<sup>49</sup> This framework introduces a lattice coupling matrix that captures the interactions between resonators, enabling a more accurate and detailed understanding of the collective optical response of the metasurface.<sup>49</sup>



**Figure 2.5: Schematic representation of the lattice effect.** Schematic representation of an isolated scatterer (**a**), and the scatterers in 2D lattice (**b**), with the lattice coupling tensor (**c**).

Specifically, in the model of spherical scatterers in Cartesian coordinates, the polarizability matrix of each scatterer is derived from the polarizability matrix of an isolated scatterer, which can be analytically solved using Mie theory. This initial polarizability matrix is then converted into an effective polarizability matrix that accounts for the interactions between particles in the lattice.

$$\bar{\bar{\alpha}}_{\text{eff}} = \left[\bar{I} - \bar{\bar{\alpha}}_{0}(\lambda)\bar{\bar{C}}\left(\hat{k}_{\text{inc}}, \frac{\Lambda_{1}}{\lambda}, \frac{\Lambda_{2}}{\lambda}\right)\right]^{-1}\bar{\bar{\alpha}}_{0}(\lambda), \qquad (2.36)$$

where  $\overline{\tilde{\alpha}}_0$  is the normalized polarizability matrix of the isolated particle.  $\Lambda_1$  and  $\Lambda_2$  are the periodicities.  $\overline{C}$  is the lattice coupling matrix in Cartesian coordinates with the same dimensions as the polarizability, which can be obtained by various summation methods for dyadic Green's functions.<sup>49</sup> Building on this theoretical foundation, we emphasize the crucial concept of polarizability in metasurfaces, which plays a key role in understanding and designing permittivity-asymmetric BIC metasurfaces.

# 2.3 Photonic bound states in the continuum

#### 2.3.1 Bloch waves and symmetry in photonics periodic structures

Periodic structures, such as photonic crystals or metasurfaces, consist of a repeated arrangement of materials with different refractive indices on a subwavelength scale. These structures have the ability to control and manipulate electromagnetic waves in ways that conventional materials cannot. By introducing periodicity, these structures create photonic bands and band gaps, much like how periodic atomic lattices give rise to electronic band structures in solid-state physics. According to Bloch's theorem, the electromagnetic waves in such periodic structures can be expressed as Bloch waves. Mathematically, Bloch waves are written as:

$$\mathbf{E}(\mathbf{r}) = \mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r}),\tag{2.37}$$

where  $e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$  is the plane wave part, which describes how the wave propagates through the structure, with the spatial variation controlled by the wave vector  $\boldsymbol{k}$ . The wave vector determines the wavelength, and thus how fast the phase of the wave oscillates over space, and when the wave vector changes, the interference between the propagating wave and the periodic structure also changes, which can affect how efficiently the wave couples to radiative channels.  $u(\boldsymbol{r})$  is a periodic function that has the same periodicity as the lattice of the structure. This means that the plane wave part of the Bloch mode controls the spatial variation of the wave's phase and amplitude. The periodic function modulates this plane wave, adding the influence of the periodic lattice on the wave, resulting the modified dispersion relation of electromagnetic waves. The key outcome of this modification is the appearance of band gaps in the dispersion curve at specific points in the wave vector space.

In a periodic structure, waves experience Bragg reflection when the wavelength of the wave matches certain multiples of the period of the structure. This happens when the following condition is satisfied:

$$2d\sin\theta = N\lambda,\tag{2.38}$$

For normal incidence, and with the periodicity of d, this simplifies to  $\lambda = 2d/N$ . At these wavelengths (or corresponding wave numbers,  $k_N = N\pi/d$ ), namely at the Brillouin zone boundaries, the waves reflect from the periodic boundaries in such a way that they constructively interfere, leading to the formation of standing waves. In standing waves, the energy is not propagating through the structure, instead, it is oscillating in place. This leads to the creation of a band gap, which is a range of frequencies where no wave propagation is allowed.

In periodic structures, symmetry plays a crucial role in determining the propagation characteristics of Bloch waves. The symmetries of the structure-whether they are reflectional, rotational, or translational-directly influence which modes are allowed or forbidden at different points in reciprocal space. The modes must respect the symmetries of the structure, and this leads to the classification of modes into different symmetry classes. A symmetry class is a group of modes that share the same symmetry properties. The modes in a particular symmetry class respond in the same way to certain symmetry operations, such as reflection, rotation, or inversion. In periodic structures, high-symmetry points in the Brillouin zone are locations where the spatial symmetry of the structure is at its strongest. These points include locations such as:  $\Gamma$ -point (k = 0), no wave vector in the plane of the structure, indicating that the field distribution is uniform across the lattice. X-point, M-point, etc. These points correspond to specific locations along the boundaries of the Brillouin zone, where the wave vector aligns with specific symmetry directions in the lattice. At these high-symmetry points, the structure exhibits special symmetries, and these symmetries impose strict constraints on the field distributions and modes that can exist. This means the mode must behave in a way that is compatible with the symmetry of the structure at the high-symmetry point. For example, at the  $\Gamma$ -point, which is a high-symmetry point where the wave vector is zero, meaning there is no spatial variation of the wave across the structure. The symmetry of the periodic structure imposes strict conditions on the modes that can exist. For instance, if the structure has mirror symmetry, only modes that are even or odd with respect to that mirror plane are allowed to exist at the  $\Gamma$ -point.

#### 2.3.2 Radiative modes and diffraction channels

2D metasurfaces are composed of subwavelength resonators arranged in a periodic manner to manipulate light. The periodic modulation of the refractive index in these metasurfaces alters the dispersion relation of the electromagnetic waves, resulting in the formation of photonic bands that are analogous to the electronic bands in solid-state crystals (Fig. 2.6). While the photonic band structure provides insight into the propagation characteristics of light within these metasurfaces, the formation of optical bound states in the continuum (BICs) requires additional considerations. BICs arise due to specific conditions that prevent certain photonic modes from radiating, despite existing at frequencies within the continuum of radiative states. These conditions can include symmetry-induced decoupling from the radiation channels, destructive interference between different scattering pathways, or careful geometric tuning of the metasurface. As a result, BICs represent a unique interplay between the photonic band structure and the underlying symmetry and interference properties of the metasurface, leading to confined modes that remain trapped without any radiative loss.<sup>50,51</sup>



**Figure 2.6: Schematic illustration of metasurfaces under incident light and its dispersion relation a.** Schematic representation of 2D metasurfaces with external incident field. **b.** The dispersion relation of the light in the vacuum. Here, *k* represents the wave vector's magnitude.

In general, for light with in-plane wavevectors  $k_{\parallel}$  within the plane of periodic structures, the confinement condition depends on whether the frequency is above or below the light line. When the frequency of a mode  $\omega'$  is below the light line, the mode remains confined within the metasurface due to total internal reflection or waveguiding effects. This confinement occurs because the mode becomes evanescent and cannot couple to radiative modes in free space. Mathematically, this condition is given by:

$$\omega' < \omega, \quad \omega = \mathbf{c} \cdot k_{\parallel}, \quad \omega' < \mathbf{c} \cdot k_{\parallel}, \quad (2.39)$$

where  $\omega'$  is the frequency of the confined mode, and  $\omega$  is the frequency of light in vacuum, following the free-space dispersion relation (Fig. 2.6).

For the mode with frequency  $\omega'$  to couple to the far field, it must satisfy the free-space propagation dispersion relation:

$$k_{\parallel}^2 + k_z^2 = \left(\frac{\omega'}{c}\right)^2, \quad k_z = \sqrt{\left(\frac{\omega'}{c}\right)^2 - k_{\parallel}^2}$$
 (2.40)

However, given the condition in Eq. 2.39, the out -of-plane wavevector component  $k_z$  becomes an imaginary number. This implies that the mode cannot propagate as a real wave in the *z*direction but instead decays exponentially, indicating total internal reflection. Consequently, the light is confined within the plane of the metasurface and does not radiate into the far field.<sup>51</sup> Conversely, modes with frequencies above the light line can couple to free-space radiation, resulting in radiative losses and manifesting as resonances with limited lifetimes.<sup>50</sup> A diffraction channel in the context of a metasurface refers to a specific propagation path or mode through which light can escape from the periodic structure and propagate into the surrounding medium. These diffraction channels correspond to specific wave vectors (directions and magnitudes) that allow the wave to diffract (or scatter) out of the metasurface. In periodic structures like metasurfaces, the incident electromagnetic wave interacts with the periodic elements (the meta-atom) and can scatter or diffract into discrete diffraction orders, which are the diffraction channels. Each diffraction channel corresponds to a specific angle and direction of the diffracted wave based on the wave's interaction with the periodic structure.

For a 2D periodic metasurface Fig. 2.6, the structure exhibits periodicity in the in-plane directions. According to Bloch's theorem, the electric field can be written as,

$$\mathbf{E}(\mathbf{r}) = \mathrm{e}^{i\mathbf{k}_{\parallel}\cdot\mathbf{r}}u(\mathbf{r}), \qquad (2.41)$$

where the in-plane periodic function u(r) can be expanded as a Fourier series as,

$$u(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}} \mathrm{e}^{i\mathbf{G}\cdot\mathbf{r}},\tag{2.42}$$

with reciprocal lattice vectors **G**, and Fourier coefficients  $c_{\mathbf{G}}$ .

The total field can be written as,

$$\mathbf{E}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}} e^{i(\mathbf{k}_{\parallel} + \mathbf{G}) \cdot \mathbf{r}},$$
(2.43)

where the in-plane wave vector  $\mathbf{k}_{\parallel} + \mathbf{G}$  represents the total in-plane wave vector, combining the Bloch wave vector  $\mathbf{k}_{\parallel}$  and the reciprocal lattice vector  $\mathbf{G}$ . Each term in the sum corresponds to a different order (or diffraction channel), and the corresponding Fourier coefficient  $c_{\mathbf{G}}$ represents how strongly the field couples to that particular diffraction order. The Fourier expansion of the fields allows us to determine which diffraction channels are open and how much energy is coupled into each channel. For example, at specific in-plane wave vector (e.g., near the  $\Gamma$ -point, where  $\mathbf{k}_{\parallel} = 0$ ), some diffraction channels may be closed due to symmetry, and the mode may remain confined. If the symmetry of the mode does not match the symmetry of the diffraction channel, the mode's Fourier coefficient for that channel can be forced to zero, meaning the mode will not couple to the channel and therefore cannot radiate.

Additionally, for the periodic metasurfaces, for frequencies below the diffraction limit, namely, when the incident light has a wavelength larger than the periodicity of the structure (or equivalently, when the frequency is low), higher-order diffraction modes (those corresponding

to  $\mathbf{G} \neq 0$ ) are evanescent. They cannot propagate into the far field and decay rapidly near the surface. Only the zeroth-order diffraction mode contributes to the far field. Here the diffraction limit refers to the point at which higher-order diffraction (i.e., diffraction orders higher than the zeroth order) becomes possible. Below this limit, only the zeroth-order diffraction can propagate. In reflection, the zeroth-order beam corresponds to the light that is reflected at the same angle as the incident light. And in transmission, it corresponds to the light that passes straight through the structure without being scattered into other directions.<sup>51</sup>

In optical systems, decoupling the resonant mode from the radiative spectrum is the basic idea of bound states in the continuum (BICs),<sup>52</sup> which represent a unique class of confined modes that do not radiate energy into the far field, even though they exist at frequencies where radiation would normally occur. These BICs are typically observed in structures with periodicity in certain directions, which was previously shown to produce both confined and radiative modes based on the relationship between frequency and wave vector. The periodic nature of these structures imposes translational symmetry, resulting in specific in-plane wave vectors  $k_{\parallel}$ . BICs are unique optical modes that occur at particular values of  $k_{\parallel}$  and are characterized by their inability to radiate light in the directions outside the plane of periodicity. This means that even though BICs exist within the continuum of free-space modes, they remain confined within the structure due to symmetry constraints or destructive interference, preventing them from coupling to radiative channels. In contrast, other optical modes near the BICs lack these special conditions and are prone to radiative leakage, resulting in the emission of light into the far field.

Bound states in the continuum (BICs) in periodic structures can be classified into three distinct types: original Friedrich-Wintgen (FW) BICs, accidental BICs, and symmetry-protected BICs. Extensive literature provides detailed introductions and analyses of the unique characteristics of these three types.<sup>53,54</sup>

In this research, we focus primarily on symmetry-protected BICs, which arise due to specific structural symmetries that prevent these modes from coupling to the continuum of radiative modes, thereby confining the light within the structure. Alternatively, it can also be explained as vanishing of Fourier coefficients corresponding to open diffraction channels due to the symmetry of the photonic structure.<sup>52</sup> By leveraging the multipole analysis introduced earlier, we aim to gain deeper insights into the mechanisms underlying the formation and behavior of symmetry-protected BICs.

In symmetry-protected BIC metasurfaces, the overall optical behavior is governed by the interference of radiation emitted from each unit cell within the periodic structure. Each unit cell radiates fields that can be decomposed into a series of multipole components, such

as electric and magnetic dipoles and quadrupoles. The multipole decomposition method is particularly advantageous as it simplifies the complex field distribution by representing it as a combination of these fundamental multipole fields. This technique is essential for analyzing and understanding the intricate radiation patterns and light confinement characteristics unique to symmetry-protected BICs in metasurfaces.<sup>52</sup> Unlike the case of a single nanoparticle, where each multipole independently contributes to far-field radiation, the optical response of a 2D metasurface arises from the collective interference of multipoles generated by all the meta-atoms in the array. As a result, the radiation from different multipoles can interfere with each other in such a way that, in certain directions, their contributions cancel out completely, leading to zero net radiation. This destructive interference is what allows symmetry-protected BICs to exist, effectively confining light within the metasurface despite being in the continuum of radiative modes.

#### 2.3.3 Multipolar perspective of BICs



Figure 2.7: Schematic view of the quasi-BIC metasurfaces under the normal incidence of a linearly x-polarized plane wave. Arrows show excited dipole moments:  $\mathbf{p}_0$  is the dipole moment of a single rod, and  $\mathbf{p}_x$  is the net dipole moment of the unit cell.

Similar to the multipole analysis of an isolated scatterer, we can express the scattered field of a 2D metasurface with isotropic dielectric permittivity as follows:<sup>55</sup>

$$\mathbf{E}_{\rm sc}(\mathbf{r}) = -k^2 \int d^3 \mathbf{r}' \left[ \varepsilon(k, \mathbf{r}') - 1 \right] \hat{\mathbf{G}}_0(k, \mathbf{r}, \mathbf{r}') \cdot \left[ \mathbf{E}_{\rm inc}(k, \mathbf{r}') + \mathbf{E}_{\rm sc}(\mathbf{r}') \right]$$
(2.44)

Here,  $\hat{G}_0(k, \mathbf{r}, \mathbf{r}')$  is the free space dyadic Green's function. As we mentioned before, the external field,  $[\mathbf{E}_{inc}(k, \mathbf{r}') + \mathbf{E}_{sc}(\mathbf{r}')]$ , for each meta-atom is a combination of the incident field  $\mathbf{E}_{inc}(k, \mathbf{r}')$  and the scattered fields from all other meta-atoms  $\mathbf{E}_{sc}(\mathbf{r}')$ . Through quite cumbersome mathematical treatment like the far-field approximation and expansion of the dyadic Green's function over the eigenmodes (the resonant states), the transmittance

coefficient can be expressed as,<sup>55</sup>

$$t(k) = B(k) - i \frac{A(k)}{\Omega + i},$$
 (2.45)

with the coefficients as follows,

$$A(k) = \frac{(-1)^{p_0} \left[ D_{j_0, \mathbf{X}}(k) \right]^2}{\gamma/c}$$
(2.46)

$$B(k) = 1 + \Delta t(k) + \frac{ik}{2S_0} \left[ \varepsilon(k) - 1 \right] V_0 - i \sum_{j \neq j_0} \frac{(-1)^p \left[ D_{j,x}(k) \right]^2}{2(k - k_j)},$$
(2.47)

$$\Omega = \frac{2(\omega - \omega_0)}{\gamma}.$$
(2.48)

Here A(k) is related to the strength of the coupling of the mode to the far-field radiation, with  $D_{j_0,x}(k)$  representing the coupling amplitude associated with a particular mode  $j_0$  in the *x*-direction. For a known resonance mode, the coupling amplitude  $D_x$  is defined as,

$$D_{x} = -\frac{\omega_{0}}{\sqrt{2S_{0}c}} \int d^{3}\mathbf{r}' \left[\varepsilon(\omega_{0},\mathbf{r}')-1\right] E_{\mathbf{r}S,x}(\mathbf{r}')e^{ik_{0}z'}.$$
(2.49)

Here, we can apply a Taylor expansion on  $e^{ik_0z'}$  around z' = 0:

$$e^{ik_0z'} \approx 1 + ik_0z' - \frac{k_0^2z'^2}{2!} + \cdots$$
 (2.50)

And multipole moments, like the electric dipole ( $\mathbf{p}_i$ ), magnetic dipole ( $\mathbf{m}_i$ ), and electric quadrupole ( $\mathbf{Q}_{zi}$ ) can be expressed accordingly as follows for a unit cell of 2D metasurfaces:

$$\mathbf{p}_{i} = \int d^{3}\mathbf{r}' \left[ \varepsilon(\omega_{0}, \mathbf{r}') - 1 \right] \mathbf{E}_{\mathrm{rs}, i}(\mathbf{r}'), \quad i = x, y, \qquad (2.51)$$

$$\mathbf{m}_{i} = \frac{1}{2} \int d^{3}\mathbf{r}' \left[ \varepsilon(\omega_{0}, \mathbf{r}') - 1 \right] \left( \mathbf{r}' \times \mathbf{E}_{rs}(\mathbf{r}') \right)_{i}, \quad i = x, y, \qquad (2.52)$$

$$\mathbf{Q}_{zi} = \int \mathrm{d}^3 \mathbf{r}' \left[ \varepsilon(\omega_0, \mathbf{r}') - 1 \right] z' \mathbf{r}'_i, \quad i = x, y.$$
(2.53)

Thus, the coupling amplitudes  $D_x$  can be defined as,

$$D_x \propto \left[ \mathbf{p}_x - \frac{\mathbf{m}_y}{c} + \frac{ik_0}{6} \mathbf{Q}_{zx} \right].$$
 (2.54)

In each unit cell, maintaining  $C_2$  symmetry ensures that the contributions from different parts of the cell cancel out, resulting in zero net multipole moments. This leads to no coupling to the far field, which is characteristic of a true Bound State in the Continuum (BIC). However, when the symmetry of the system is broken in certain ways, some net modes can emerge, allowing coupling into radiation channels. These states are known as *quasi*-BICs. For example, as shown in Fig.2.7, introducing asymmetric rods in the unit cell generates a net electric dipole moment. This results in a non-zero quasi-BIC resonance, as the symmetry breaking enables partial coupling to the far field.

#### 2.3.4 Topological nature of BICs

Bound States in the Continuum (BICs) are not only remarkable for their unique ability to confine waves without radiating energy but also for their intrinsic connection to topological physics. This section delves into their topological characteristics, their role as polarization vortices, and their links to broader topological phenomena.



**Figure 2.8: Schematic illustration for the polarization vortex and topological charge.** The BIC is found at the nodal line crossing where the direction of vector becomes undefined. The polarization vector can either rotate by angle  $2\pi$  or  $-2\pi$ , which are corresponding to topological charge of +1 and -1, respectively.<sup>51</sup>

As we discussed previously, for the periodic metasurfaces with frequencies below the diffraction limit, only the zero-order Fourier coefficients ( $c_G$ ) describe the amplitude and the direction of the far-field radiation (Eq.2.42). And for the 2D metasurface, this coefficient can be projected onto *x*-direction, and *y*-direction as  $c_x$ , and  $c_y$  respectively, which can also be called the polarization vector. This vector describes the amplitude and direction of outgoing light in the far field for a given in-plane wave vector. For resonances in general, the  $c_x$ , and  $c_y$  are nonzero,

leading to radiation escaping into the far field. When viewed in k-space, the polarization field  $c(\mathbf{k})$  forms a continuous map. In the k-space, varying  $k_x$  and  $k_y$  can't guarantee that the nodal lines of  $c_x$  and  $c_y$  will intersect, unless some underlying symmetry constraints force their alignment. Under the  $C_z^2$  and time-reversal symmetry for the nodal lines must be invariant under  $C_z^2 T$  operation, which imposes that the system's permittivity satisfies,  $\epsilon(x, y, z) = \epsilon^*(-x, -y, z)$ . This constrains the placement and orientation of the nodal lines in *k*-space, forcing them to respect the symmetry of the system. And such symmetry also ensures that  $c_x$  and  $c_y$  can be treated as the real-valued along certain symmetry directions, which makes the nodal intersections more predictable and robust. A resonance turns into a BIC when the radiation power is zero, which means the polarization vector is also zero  $(c_x = c_y = 0)$ . A polarization vortex (Fig.2.8) forms at a BIC due to the singular behavior of the polarization vector field in the vicinity of BIC. As one traverses a closed loop in k-space encircling the BIC, the direction of c(k) rotates continuously, reflecting the topological nature of the field. At the exact location of the BIC, the polarization vector  $c(\mathbf{k})$  becomes undefined, creating a vortex center that is a hallmark of the BIC's presence and its robust topological characteristics.

The winding number (*q*) is a topological invariant that characterizes the behavior of the polarization vector  $c(\mathbf{k})$  around a BIC. It measures how many times  $c(\mathbf{k})$  rotates as one makes a full counterclockwise loop around the BIC in the *k*-space,

$$q = \frac{1}{2\pi} \oint_{\mathcal{C}} \nabla_{\boldsymbol{k}} \phi(\boldsymbol{k}) \cdot d\boldsymbol{k}, \qquad (2.55)$$

where,  $\phi(\mathbf{k}) = \arg \left[ c_x(k_x) + i c_y(k_y) \right]$  is the angle of the polarization vector.  $\mathbf{C}$  is a closed path in k-space encircling the BIC. The winding number is always an integer due to the nature of  $\phi(\mathbf{k})$ , meaning  $\phi(\mathbf{k})$  must return to its initial value after a full loop. When q is +1 means polarization rotates counterclockwise once, and -1 means clockwise once. Higher-order charges can occur in more complex systems with higher symmetry.<sup>51</sup>

# **3** Methodology

# 3.1 Numerical simulations



**Figure 3.1: Workflow of CST Studio simulation.** Generally, it includes four steps such as, choosing the simulation type, creating the model and mesh, setting boundary conditions and excitations, and post-processing analysis

The frequency-domain solver serves as the main approach employed in this work for simulation purposes. Frequency-domain solvers are designed to determine the steady-state response of a system to a sinusoidal excitation at a given frequency, making them particularly effective for analyzing narrowband systems and resonant structures. Additionally, it can accurately model frequency-dependent material properties (dispersion relation), which is essential for simulating realistic materials at specific frequencies.

Traditional frequency-domain simulations involve solving an equation system for every frequency sample, which can be computationally expensive if many frequencies are required. The frequency domain solver in CST uses the broadband frequency sweep method. To address this challenge, the frequency-domain solver in CST employs a broadband frequency sweep method. Instead of solving for every frequency point, the solver selects a few initial frequency samples across the desired range and evaluates electromagnetic field distributions, S-parameters, and other relevant quantities at these points.

The solver then applies an adaptive sampling technique to identify regions where the system's response varies significantly with frequency. Additional frequency points are adaptively selected in these regions to capture the system's detailed behavior. Once the key frequency points are identified, Maxwell's equations are solved at each of these frequencies, which involves the computationally intensive process of solving a linear system of equations.

The initial distribution of frequency samples can be customized by the user, with options such as equidistant or logarithmic spacing, depending on the specific requirements of the analysis. This adaptive approach significantly improves computational efficiency while maintaining high accuracy in characterizing the system's frequency response.

The time-domain solvers are capable of analyzing how electromagnetic fields evolve over time, making them ideal for studying transient phenomena like pulse propagation, and time-varying signals. The eigenmode solver can be used to calculate the frequencies and the corresponding electromagnetic field patterns (eigenmodes) without applying external excitation.

During the model-building process, the dielectric properties of the materials can be sourced from the standard material library in CST Studio Suite or imported from external databases. Alternatively, for simplicity, constant values for the refractive index (n) and extinction coefficient (k) can be used for specific materials, provided the wavelength range under consideration does not involve significant variations in the material's dielectric properties.

Once the model is constructed, mesh generation becomes a critical step in accurately simulating electromagnetic fields. In CST Studio Suite, the mesh divides the geometry of the structure into small, discrete elements, enabling the software to compute electromagnetic behavior using numerical methods such as the Finite Element Method (FEM) or the Finite Integration Technique (FIT). The quality and refinement of the mesh significantly affect both the accuracy of the simulation and the computational efficiency.

Tetrahedral meshes, commonly used in this research, are particularly effective for handling complex structures and adapting to irregular geometries. While mesh refinement can enhance simulation accuracy, it inevitably increases computational costs. To balance accuracy and efficiency, the mesh can be selectively refined. For instance, critical components such as resonators can be assigned a finer mesh, while less critical elements, such as the substrate, can use a coarser mesh. This approach optimizes computational resources while maintaining the accuracy required for key aspects of the design.

Before initiating the simulation, it is essential to define the boundary conditions for the unit cell. Periodic boundary conditions are applied along the x- and y- axes to account for the periodic nature of the metasurfaces, while open boundary conditions are set along the z-axis

to simulate free-space propagation. The excitation source can be introduced from the top of the unit cell, and its mode can be tailored based on specific requirements, such as linearly or circularly polarized light. For simulations of BIC metasurfaces, the polarization direction of the linear light source plays a critical role, as the system's response is highly sensitive to this parameter. Therefore, selecting the appropriate excitation mode to align with the geometric configuration of the design is crucial to ensure accurate results.



Figure 3.2: Illustration of S-parameters in two-port network

In the frequency-domain solver, scattering parameters (*S*-parameters) are essential for analyzing the behavior of electromagnetic waves in multi-port systems. *S*-parameters characterize the response of an electrical network to signal inputs and outputs at its ports, providing information about power transmitted, reflected, or absorbed by the system across different frequencies. Each *S*-parameter ( $S_{ij}$ ) represents the ratio of the output signal at port "*i*" to the input signal at port "*j*", accounting for both reflection and transmission between the ports. As shown in Fig. 3.2, the reflectance and transmittance of the system can be evaluated using  $S_{22}$  ( $S_{11}$ ) and  $S_{21}$  ( $S_{12}$ ). These parameters can be calculated within CST Studio Suite through post-processing analysis, enabling precise characterization of the electromagnetic properties of the system.

In addition to the 1D results like *S*-parameters, the solver also provides two-dimensional results, such as field distributions, by defining field monitors (electric or magnetic) at specific frequencies. These 2D visualizations are particularly useful for examining the spatial characteristics of modes of interest, offering deeper insights into their behavior and interactions within the system.

# 3.2 Nanostructure fabrication

# 3.2.1 Before lithography



**Figure 3.3: Schematic illustration of steps before lithography.** There are mainly three steps: cleaning, material deposition, and resist spin coating

Before initiating any fabrication process, the fused silica substrate must undergo thorough cleaning to ensure the removal of contaminants. The substrate is initially rinsed with acetone and isopropanol (IPA) to eliminate surface impurities. Following this, oxygen plasma cleaning is performed for 5 minutes at 100% power. This step effectively removes any remaining organic contaminants by breaking down carbon-based bonds and converting them into volatile compounds, such as  $CO_2$  and  $H_2O$ , which are subsequently evacuated from the chamber.

Additionally, oxygen plasma treatment enhances the surface properties of the substrate. By introducing polar oxygen-containing functional groups, such as hydroxyl groups, the treatment increases the surface energy of the substrate. This renders the surface hydrophilic, thereby significantly improving the adhesion of materials in subsequent processing steps, such as photoresist application or thin-film deposition. This enhanced adhesion is crucial for ensuring the reliability and precision of the fabrication process (Fig. 3.3).

In this thesis, TiO<sub>2</sub> and Si are utilized as all-dielectric resonator components, deposited using three different techniques. For TiO<sub>2</sub> films, two deposition methods are employed: atomic layer deposition (ALD) and sputter deposition (Angstrom). ALD offers a significant advantage in that the oxygen vacancy concentration can be precisely controlled during the deposition process by varying the precursors and process parameters. This enables the tailoring of the extinction coefficient (*k*), allowing for the fabrication of oxygen-vacancy-rich TiO<sub>2</sub> or TiO<sub>2-x</sub>.

In Chapter 4, we detail the preparation of  $\text{TiO}_{2-x}$  films with three different oxygen vacancy concentrations and tailored extinction coefficients (*k*). The  $\text{TiO}_{2-x}$  film with lowest oxygen vacancy concentration was prepared through plasma enhanced ALD (PE-ALD) with the

precursor tetrakis(dimethylamino) titanium (TDMAT, 99.999%, Sigma-Aldrich, kept at 75 °C) and remote oxygen plasma (300W, 99.9999%, Linde). Ar (99.9999%, Linde) was used as purge and carrier gas creating a background pressure of 0.1 mbar throughout the process. The  $TiO_{2-x}$  films with moderate and highest oxygen vacancy concentration were prepared through thermal ALD with precursors of titanium isopropoxide (TTIP, 99.999%, Sigma-Aldrich, kept at 65°C) and TDMAT, respectively, using water as oxidant. The background pressures were 0.2 and 0.3 mbar for the processes with TTIP and TDMAT. All films were deposited in a hot wall reactor (Fiji G2, Veeco) at a substrate temperature of 200°C.

Alternatively, the amorphous  $TiO_2$  can also be deposited via reactive sputtering, using titanium (Ti) as the target material and introducing a reactive gas oxygen (O<sub>2</sub>) into the sputtering chamber. During the deposition process, Ti atoms ejected from the target react with oxygen as they reach the substrate, forming  $TiO_2$ . These  $TiO_2$  molecules accumulate on the substrate, forming a thin film. The thickness of the film is precisely controlled by adjusting the deposition time, sputtering power, and gas flow rates. Additionally, substrate rotation can be employed to enhance the uniformity and density of the deposited film, ensuring consistent material quality across the substrate.

Si films are prepared by plasma-enhanced chemical vapor deposition (PECVD, PlasmaPro 100, Oxford Instruments). PECVD allows precise control over film composition, thickness, and other properties. The plasma enhances surface reactions, improving uniformity and adhesion. The deposition process can be divided into four main steps: gas introduction, plasma generation, reaction, and deposition. Here, for Si deposition, silan (SH<sub>4</sub>) acts as the reactant gas, maintained at a constant flow of 500 sccm. The gas is then ionized into a plasma, initiating chemical reactions on the surface of the substrate. Silicon is gradually produced as a reaction product, condensing and depositing onto the substrate to form a uniform thin film.

After the target film is obtained, the following step is spin-coating of an electron beam resist, the polymethyl methacrylate (PMMA). PMMA resists are available in various molecular weight formulations, which influence their sensitivity and resolution. Lower molecular weight PMMA (e.g., 495k PMMA) is typically used for thicker films or as an underlayer in bilayer resist systems, while higher molecular weight PMMA (e.g., 950k PMMA) is preferred for high-resolution patterning due to its ability to define finer features. The thickness of PMMA films can be controlled by adjusting the concentration of the solution and spin-coating speed, as described in the spin speed curves. In this work, PMMA 950k A4 is used as a single-layer resist. The spin-coating process is performed at 3000 rpm for one minute, followed by hard baking at 180 °C for three minutes to improve the film's mechanical stability and adhesion. To prevent electron charge accumulation during the lithography process, an electrically conductive polymer (Espacer 300Z) is subsequently deposited on the substrate.

#### 3.2.2 During lithography

The prepared sample is loaded into the electron beam lithography machine (eLINE Plus, Raith) for nano-structure patterning. Several factors influence patterning accuracy during exposure. Firstly, the acceleration voltage and the aperture size are critical in determining the resolution and precision of the patterns. A higher acceleration voltage increases electron energy, reducing Coulomb interactions between electrons and enabling a smaller beam spot size, thereby improving resolution and allowing for finer feature patterning. Additionally, higher voltage facilitates deeper electron penetration into the resist and substrate, reducing backscattering and the proximity effect. The aperture size controls the electron beam's diameter and current. A smaller aperture produces a smaller beam spot, enhancing resolution, but at the cost of reduced current, which increases the exposure time needed to achieve the required dose. In this thesis, an acceleration voltage of 20 kV and an aperture size of 15  $\mu$ m are employed. This combination achieves a balance between high patterning accuracy and reasonable exposure times, ensuring efficient and precise nanostructure fabrication.

The area step size in the eLINE Plus settings is another critical parameter that affects the quality of the patterned structures. A smaller step size allows for the resolution of finer features, as it increases the density of exposure points. However, this also leads to an increase in the beam speed. If the electron beam moves too quickly, several issues may arise, including insufficient exposure, reduced resolution, and non-uniform exposure across the pattern. To balance these factors, the area step size in this thesis is carefully selected based on the specific design requirements. The step size ranges from 7 nm to 10 nm, providing a compromise between achieving high-resolution patterns and ensuring consistent and accurate exposure.



**Figure 3.4: Schematic illustration of the area modes in eLINE Plus system.** The left side is the geometrical design, and on the right illustrating the electron beam scan lines for each polygon under the longitudinal mode, and transversal mode.

The area mode is used for exposing larger areas such as polygons or other complex geometries. There are different modes for scanning the electron beam over the area to be exposed. Each mode optimizes how the beam moves across the pattern to achieve the desired resolution, exposure efficiency, and uniformity. For example, as shown in Fig. 3.4, for longitudinal mode, the electron beam scans parallel to the longest dimension of the polygon or feature being exposed. This can reduce the number of passes needed to expose long structures, which can improve the speed of exposure. While in transversal mode, the beam scans perpendicular to the longest dimension of the polygon, which provides more uniform exposure for wide polygons or larger features where scanning across the shorter axis ensures that the entire area receives consistent exposure. If polygons are rotated, the angle mode can be used as the beam will scan the polygon at a specific angle, allowing for exposure of the feature from a non-orthogonal direction, which can minimize edge roughness and ensure consistent feature definition. Each of these modes offers a different scanning strategy, allowing the electron beam to efficiently and accurately expose polygons and other complex geometries. The choice of mode depends on the shape, size, orientation, and desired resolution of the pattern, as well as the need for speed and uniformity in exposure.



## 3.2.3 After lithography

**Figure 3.5: Schematic illustration of steps after lithography.** Including developing, hard mask deposition, lift-off, RIE etching, and wet etching

After lithography, five steps remain to complete the fabrication process (Fig. 3.5). Firstly, the development process will dissolve the exposed area (positive resist). The first step is the development process, which removes the exposed areas of the resist in the case of positive resists. For the PMMA resist used in this thesis, the developer solution consists of a 1:3 mixture of methyl isobutyl ketone (MIBK) and isopropyl alcohol (IPA). MIBK dissolves the exposed areas of the resist, while IPA acts as a stop solution to halt the development process and rinses the resist surface. Depending on the resist thickness and exposure dose, the development

time is set between 1 and 2 minutes. After development, the substrate is thoroughly rinsed in IPA to ensure the process is stopped and to remove any residual developer from the surface.

After development, a metallic hard mask is deposited onto the sample. Common hard mask materials include chromium (Cr), gold (Au), and aluminum (Al), with the choice depending on the resist type and pattern design. For the design with a very high filling factor and small feature sizes of around 10 nm, Au is typically unsuitable due to its softness, which complicates the lift-off process. In this thesis, chromium (Cr) is extensively used as the hard mask material due to its advantages, including ease of lift-off, good adhesion to the substrate, and high durability.

The Cr hard mask is deposited using an electron beam (e-beam) evaporator. During e-beam evaporation, an electron beam bombards the surface of the source material, causing it to heat up rapidly. As a result, the source material melts and eventually vaporizes, forming a vapor cloud. The vaporized atoms travel through the vacuum and condense onto the substrate, forming a thin film. Since the process occurs in a high vacuum, the vaporized atoms experience minimal collisions with gas molecules, enabling clean deposition with minimal contamination. Controlling the deposition rate at approximately 0.7 Å/s improves the lift-off quality.

After lift-off, the sample is transferred to reactive ion etching (RIE). RIE enables the etching of features with vertical sidewalls, allowing for the fabrication of precise patterns and deep trenches. Additionally, RIE provides good selectivity between different materials. Before proceeding, it is essential to conduct etching tests to optimize the recipe and ensure adequate selectivity between the hard mask material and the functional layer. Once the dry etching process is complete, the final step is the wet etching of the hard mask. During wet etching, the substrate is immersed in a chemical etchant that reacts with the hard mask material, selectively removing it. This step completes the fabrication process, leaving the desired pattern etched into the functional layer beneath the hard mask.

#### 3.2.4 The marker system



**Figure 3.6: Schematic illustration of the marker system.** There are two marker groups: global markers, and local markers.

To achieve multilevel lithography, a marker system must be prepared before patterning on the target material. As illustrated in Fig.3.6, the marker system consists of global and local markers, each serving specific alignment purposes. Global markers are used for 3point alignment, enabling the system to accurately determine the substrate's position and orientation. These reference points allow the lithography system to compensate for any rotation, translation, or scaling discrepancies, ensuring a precise overlay of new patterns onto previously fabricated layers. This step is crucial for maintaining alignment accuracy across multiple fabrication steps. Local markers, on the other hand, are utilized for writing field alignment. They measure the relative positions of the writing fields to correct for shifts, rotations, or distortions between adjacent fields. Proper alignment of local markers minimizes stitching errors, which is critical for applications that require precise, continuous structures spanning multiple writing fields.

Markers are typically fabricated from gold (Au) due to its stability, durability, and compatibility with multiple fabrication steps. Au markers can withstand processes such as resist coating, development, and etching without significant degradation. Additionally, gold's high atomic number provides strong contrast in scanning electron microscopy (SEM) imaging, facilitating easier identification during alignment and improving the precision of marker detection. In

this thesis, Au markers were fabricated using the standard electron beam lithography (EBL) process discussed earlier. Each marker comprises a 3 nm titanium (Ti) adhesion layer and a 45 nm gold layer. It is important to note that when Au markers are used, the hard mask material for the target layer must be a different material to prevent damage to the marker system during subsequent fabrication steps. This ensures the integrity and functionality of the marker system throughout the entire lithography process.

# 3.3 Optical characterization

The optical characterization and measurement of the photonic metasurfaces were conducted with several setups. The dark field imaging, transmittance, and Raman measurements were performed using the WITec microscopy system, which offers versatile modules with various functionalities to accommodate different experimental requirements. The refractive index of the materials was determined through ellipsometry using an advanced ellipsometer equipped with dual-rotating compensators and a spectrometer (J.A. Woollam, M2000XI-210). This setup enabled precise measurements of the refractive index and film thickness across a broad spectral range, providing critical material parameters for further analysis.



**Figure 3.7: Schematic illustration of the WITec microscopy.** There are two ports for light incidence, and two output ports for spectra and image results. The different configurations of the optical components can give different optical measurement results

To measure the transmittance and reflectance spectra, the light source can be configured to provide different incident light settings, as illustrated in Fig. 3.7. By selecting either Module 1 or Module 2, the incident light can be set to linear polarization with the desired orientation. This flexibility allows precise control over the polarization state of the incoming light, which

is essential for characterizing the optical response of photonic metasurfaces under specific polarization conditions.

The transmitted or reflected light from the metasurfaces is collected by an objective lens, with the magnification of the objective selected based on the pattern size of the metasurfaces—smaller pattern sizes require objectives with higher magnifications. The collected light is guided into the spectrometer via a multi-mode fiber. Inside the spectrometer, an inserted grating disperses the light onto a silicon CCD chip, which records the photon intensity across the selected optical range.



**Figure 3.8: Schematic illustration of transmittance normalization.** The left panel shows the background transmission spectrum of the  $SiO_2$  substrate, while the middle panel presents the transmission spectrum of the metasurface. The right panel displays the resulting normalized transmittance spectrum, revealing the characteristic resonance dip of the metasurface.

To obtain absolute transmittance spectra, the measured signal must be normalized against the background signal of a bare  $SiO_2$  substrate (Fig. 3.8). For reflectance spectra, a silver mirror is used as a reference to achieve accurate high-reflectance calibration.

The setup also facilitates Raman spectroscopy measurements. Before measuring Raman spectra, system alignment must be carefully checked, as the Raman signal is significantly weaker compared to transmittance and reflectance signals. Once alignment is complete, the excitation laser is configured in light source 2 (Fig. 3.7). A matching edge filter is installed in Module 2 to effectively block the signal from the incident light source, allowing only the Raman signal to be detected. This configuration ensures accurate characterization of both transmittance, reflectance, and Raman spectra of the metasurfaces.

Dark-field images can be captured by incorporating a dark-field condenser into Module 1. To enhance the imaging quality, a small drop of immersion oil is applied to the top of the condenser. The immersion oil allows more oblique rays to enter the sample, improving the overall brightness and contrast of the dark-field images. This setup is particularly effective for highlighting fine structural details and detecting features with low reflectance.

# 4 Catalytic metasurfaces empowered by bound states in the continuum

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# 4.1 Research background

Photocatalytic platforms and devices based on ultrathin films are highly desirable because they offer dramatic enhancements to photocarrier excitation and enable facile short-range carrier transport, but are often limited by insufficient light absorption.<sup>26,27</sup> Increasing the thickness of the semiconductor above the penetration depth of light ensures maximum optical absorption, but can hinder the efficient utilization of the captured energy due to bulk recombination. Hence, obtaining strong light absorption in ultrathin semiconductors has been of great scientific and technological interest for many years, making it one of the essential aspects for the efficient generation of photocarriers, as well as the development of ultrafast optoelectronic devices<sup>57–59</sup> and surface-active photocatalysts.<sup>60,61</sup> However, ultrathin films of many naturally occurring semiconductor materials provide only limited freedom for controlling the spectral location and magnitude of light absorption, since their intrinsic optical properties are fixed.<sup>27</sup> In contrast, ultrathin metasurfaces constructed from twodimensional subwavelength arrays of semiconductor structures have shown tremendous potential for concentrating and controlling light on the nanoscale, positioning them as an ideal toolkit for engineering the light absorption in catalytic materials.<sup>28,29,62–72</sup> Indeed, recent examples have shown that such artificial materials can increase the internal quantum efficiency of semiconductors and metals when shaping them into catalytic metasurfaces.<sup>28,29</sup>

All-dielectric metasurfaces underpinned by the physics of bound states in the continuum (BIC) have seen surging interest due to their spectral selectivity, strong light confinement, and giant enhancement of electromagnetic fields,<sup>1-9</sup> sparking applications in diverse fields including nanoscale lasing,<sup>11–17</sup> biomolecular sensing,<sup>18–21</sup> and nonlinear photonics.<sup>22–25</sup> However, to the best of our knowledge, BICs have not yet been tailored for photocatalytic applications. Conceptually, a BIC is a localized state existing at the same energy level as a continuum of radiation modes.<sup>10</sup> This phenomenon originally appeared in quantum mechanics and has later been applied to many other areas of physics.<sup>73</sup> A true BIC with an infinite value of the quality factor (Q factor, defined as the resonance position divided by the linewidth) can only exist as a mathematical object and can be explained by vanishing coupling constants with all radiation channels. One way of making BICs usable for practical nanophotonics systems is to leverage symmetry-protected metasurfaces, where the coupling constants are tailored using structural asymmetry within the metasurface unit cell, leading to the formation of quasi-BIC modes accessible from the far-field.<sup>1</sup> A central advantage of symmetry-protected BICs is their ability to provide precise control over the resonance properties - and, specifically, the Q factor - through a straightforward geometrical tuning parameter, making them ideal for tailoring light-matter interactions. However, extending these ideas into the field of photocatalysis, where they could enable ways of triggering chemical transformations with light, has so far not been investigated.

Established BIC-based metasurface demonstrations have utilized high refractive index materials like Si,<sup>74,75</sup> where pushing the operating range towards the blue part of the visible spectrum is still challenging due to significant dielectric losses associated with the inter-band transitions.<sup>76</sup> The blue side of the optical regime is particularly interesting for catalysis because the bandgap and band alignment of many relevant semiconductors lies in the 2 to 3 eV region and the energy of (hot) electron-hole pairs in metals is in most cases high enough for promoting hydrogen generation or oxygen evolution, among other important chemical transformations. In particular, TiO<sub>2</sub> is a promising alternative to Si because of its extremely low losses throughout the visible wavelength range (400 to 750 nm), but has, so far, not been employed in the context of two-dimensional BIC-based systems. In addition, TiO<sub>2</sub> is an ideal photocatalyst with advantages like chemical stability, band alignment with the water-splitting reaction, nontoxicity, and long-term durability, enabling the efficient conversion of solar into chemical energy.  $^{77}$  The photocatalytic properties of  $\rm TiO_2$  are derived from photogenerated charge carriers (holes and electrons), which transfer to the surface and participate in reduction or oxidation processes.<sup>78</sup> In this way, the energy of photons can be stored in chemical bonds, which has stimulated many TiO<sub>2</sub>-based photocatalytic applications like hydrogen fuel production and pollutant degradation.<sup>78</sup> Importantly, the extinction coefficient k of TiO<sub>2</sub> can be tuned throughout the visible spectrum by introducing oxygen vacancies (leading to the formation of oxygen-vacancy-rich  $TiO_2$  or  $TiO_{2-x}$ ),<sup>67,79–83</sup> which provides strong potential for absorption engineering when combined with nanophotonic concepts such as BICs.



**Figure 4.1: Catalytic metasurfaces driven by bound states in the continuum. a.** Schematic of the  $TiO_{2-x}$ -based BIC metasurface platform for the photoreduction of silver ions, where reduced silver particles aggregate on the surface, revealing the active sites and overall functionality of the platform. **b.** Schematic of oxygen vacancies acting as the defect energy level between the conduction band and valence band, which extends the light absorption to the visible region. The photo-excited electron exhibits strong reducing reactivity, resulting in the reduction of Ag<sup>+</sup> ions. **c.** The reduction rate of Ag<sup>+</sup> is increased via metasurface-enhanced light absorption at a given excitation wavelength. Spectral tunability of the catalytic metasurfaces is achieved by adjusting the scaling factor of the unit cell, which enables versatile control over the resonance position throughout the visible spectrum (left). Strong nanoscale light confinement and enhancement of the local electromagnetic fields of the catalytic metasurface are provided by the BIC concept (right). This idea can be extended to other materials.

Here, we engineer catalytic  $TiO_{2-x}$  based BIC metasurfaces to provide strong light confinement and flexible absorption control for visible light photocatalysis (Fig.4.1). We use a standard Ag reduction reaction<sup>67,79</sup> to reveal the active sites on the metasurface and find a significant increase in the reduction rate of a factor 7 compared to non-resonant structures. This finding highlights the potential of this strategy to circumvent the intrinsic tradeoff between light absorption and photocarrier recombination on ultra-thin photocatalytic films. We show that strong electromagnetic near fields within the semiconductor material are crucial for the enhancement of such processes, providing guidelines for boosting light-matter interactions and photocatalytic activity.<sup>28,67,80,81</sup> Furthermore, we find that strong near fields are readily achieved in metasurfaces composed of  $TiO_{2-x}$  with low extinction coefficient through precise matching of intrinsic and radiative losses (i.e., by utilizing BICs with narrow linewidths). This brings another dimension for the field of photocatalysis, where the use of semiconductors with high extinction coefficients is usually preferred. Additionally, we extend the understanding of light-matter coupling in our BIC-enabled systems to materials with different extinction coefficients based on temporal coupled-mode theory, which provides a general framework for maximizing light-matter interactions in diverse heavily used photocatalytic materials like ZnO, SnO<sub>2</sub>, SiC, and others. BIC-based metasurfaces can thus efficiently utilize typically poor light-absorbing materials, and enable their use for the realization of versatile and selectively absorbing nanophotonic systems.



# 4.2 Results and discussion

**Figure 4.2: Numerical design of the catalytic metasurfaces. a.** Sketch of a TiO<sub>2-x</sub> BIC unit cell (scaling factor S = 1) with tunable extinction coefficient *k* and tilting angle  $\theta$ . **b.** Photographs and spectrally resolved extinction coefficients of TiO<sub>2-x</sub> films (deposited on SiO<sub>2</sub>) with different extinction coefficients k prepared by atomic layer deposition (ALD). **c.** Simulated absorbance spectra of BIC metasurfaces with S = 1 composed of different TiO<sub>2-x</sub> materials (TiO<sub>2</sub>-L, TiO<sub>2</sub>-M, and TiO<sub>2</sub>-H) with a tilting angle of  $\theta = 6^{\circ}$ . **d.** Color-coded simulated absorbance maps of the different catalytic metasurfaces as a function of tilting angle  $\theta$  and wavelength  $\lambda$ . **e.** Electric near fields (taken at h = 0) of individual unit cells of the different TiO<sub>2</sub>-L, TiO<sub>2</sub>-M, and TiO<sub>2</sub>-H metasurfaces with the respective optimal tilting angles ( $\theta = 6^{\circ}$ , 18°, 20°) corresponding to maximum absorption enhancement.

Numerical design of catalytic BIC metasurfaces. As a basis for our  $TiO_{2-x}$ -based BIC metasurface platform, we utilize a unit cell composed of two elliptical resonators on a silicon

dioxide substrate (Fig.4.2a). Compared to other BIC unit cell geometries, the two ellipse structure exhibits the strongest fabrication robustness<sup>84</sup> and maintains its volume when breaking the symmetry using the ellipse tilting angle, which is important for comparing of photo reduction rate between metasurfaces with different asymmetry factors.

As introduced above, a true bound state in the continuum (BIC) is a mathematical concept with an infinite quality factor and vanishing spectral linewidth. In practice, BICs can be converted to quasi-BICs with finite resonance width once the in-plane inversion symmetry of the unit cell is broken, enabling the excitation of the resonant mode from the far field. In our case, this symmetry breaking is induced by tilting the ellipses under an angle  $\theta$  with respect to each other. We implement titanium oxide layers with three different concentrations of oxygen vacancies, characterized by varying extinction coefficients *k*(in the visible region), which are denoted as TiO<sub>2</sub>-L (k = 0.003), TiO<sub>2</sub>-M (k = 0.022), and TiO<sub>2</sub>-H (k = 0.110) for the lowest, moderate, and the highest V<sub>0</sub> concentration, respectively (Fig.4.2b). Exact dielectric functions for the three films were determined with spectral ellipsometry and used as input for our numerical metasurface design process. The tunable defect concentration can be realized during atomic layer deposition (ALD) by choosing different precursors (see Methods). Such defects can influence both the electromagnetic properties of the material (by regulating the losses and absorption) and the reactivity (by altering the dynamics of the photogenerated electron-hole pairs).<sup>85–89</sup> In order to identify the optimal TiO<sub>2-x</sub>-based BIC metasurface design for photocatalysis, we will consider both the optical and catalytic properties of the system.

Based on our simulations, for the low-defect case (TiO<sub>2</sub>-L), a sharp quasi-BIC resonance can be obtained in the metasurface absorbance spectrum (A = 1 - R- T), where maximum visible light absorption at a wavelength of 530 nm occurs for an asymmetry parameter of  $\theta = 6^{\circ}$  (Fig.4.2c). With the same meta-unit geometry and asymmetry parameter, metasurfaces realized with TiO<sub>2</sub>-M and TiO<sub>2</sub>-H show reduced resonance-assisted absorption and exhibit significantly broadened resonance line shapes. This absorption reduction originates from the damping of the metasurface resonance by the intrinsic loss of the materials, as quantified by the extinction coefficient (*k*), and contrasts with the behavior in unstructured thin films, where increased absorption is expected for higher defect concentrations. The complex interplay between material loss and resonant absorption highlights the need for tailoring the metasurface design to specific material parameters.

To provide a deeper understanding of the metasurface-enhanced light-matter interaction, we have examined the variation of the resonant absorption with the asymmetry parameter  $\theta$  for all given values of the intrinsic material loss *k* (Fig. 4.2d). As discussed above, we find that the absorption in regions of the parameter space away from the resonance (where

no metasurface-based enhancement occurs) increases with the extinction coefficient (*k*), as illustrated by the overall darker color in simulated absorbance maps of the TiO<sub>2</sub>-M and TiO<sub>2</sub>-H metasurfaces compared to TiO<sub>2</sub>-L. Introduction of the quasi-BIC resonance greatly boosts light confinement and optical absorption compared to the off-resonant case. For the low-defect material (TiO<sub>2</sub>-L), a clear region of the parameter space with optimal absorption can be identified, with a maximum for  $\theta = 6^{\circ}$ . Similar regions of optimal absorption are present for the medium- and high-defect cases as well, but show broader linewidths and are found for higher asymmetry parameters ( $\theta = 18^{\circ}$  and  $\theta = 20^{\circ}$  for TiO<sub>2</sub>-M and TiO<sub>2</sub>-L, respectively), indicating a systematic connection between the metasurface and material properties. In addition to the absorbance spectrum, the total optical power absorbed by the TiO<sub>2-x</sub> ellipses (i.e., the volume loss) exhibits the same trend (Fig.4.3). To describe the coupling of incident light with the catalytic metasurfaces from an analytical perspective, we will provide a detailed discussion based on temporal coupled-mode theory (TCMT) in following part.



Figure 4.3: Simulations of the volume loss of the metasurfaces. a. Simulation results of the volume loss of the metasurfaces with different  $\theta$  based on TiO<sub>2</sub>-L. The volume loss is calculated as Volume loss =  $\pi \cdot f \cdot \tan(\delta) \cdot \varepsilon_0 \cdot \varepsilon_r \int |\vec{E}|^2 dV$ , where  $\tan(\delta)$  is given as the ratio between the imaginary and real parts of the complex permittivity. **b.** Volume loss values at the resonance wavelength ( $\omega = \omega_0$ ) of the metasurfaces with different  $\theta$  based on TiO<sub>2</sub>-L are evaluated, and the maximum volume loss is obtained when  $\theta = 6^\circ$ .

Even though the metasurface designs for the different materials share similar values of maximum absorption for their optimum asymmetry parameters, their electromagnetic near-field patterns differ greatly. Specifically, the maximum electric field enhancement ( $|E/E_0|_{max}$ ) in the hot spots of the TiO<sub>2</sub>-L metasurface (i.e., at the tips of the ellipsoids) is around 3 times higher than that of TiO<sub>2</sub>-M and 6 times higher than that of TiO<sub>2</sub>-H (Fig.4.2e), which means that the light-matter interaction is much more intense in TiO<sub>2</sub>-L than in the other cases, demonstrating the importance of efficient resonant enhancement for obtaining maximum absorption. Advantageously, the near-field enhancement of our structures does not strongly depend on the resonator height (Fig.4.4). Our simulations highlight the capabilities of BIC-based metasurfaces for engineering visible light absorption and strong nanoscale light confinement at the catalytic  $TiO_{2-x}$  interface.



**Figure 4.4: Simulations of maximum field enhancement of metasurfaces.** Simulations of the maximum field enhancement of metasurfaces ( $\theta = 5^{\circ}$ ) with different extinction coefficients (k = 0.003, and k = 0.022) as a function of TiO<sub>2-x</sub> thickness.

**Experimental realization of TiO**<sub>2-x</sub>-based metasurfaces. The TiO<sub>2-x</sub>-based metasurfaces were realized using a top-down nanofabrication process based on high-resolution electronbeam lithography and anisotropic reactive ion etching (see Methods). Intentionally lossy TiO<sub>2-x</sub> thin films with a thickness of 100 nm were fabricated by atomic layer deposition (ALD), and their extinction coefficients were engineered by choosing different metalorganic precursors, tetrakis(dimethylamino) titanium (TDMAT) and titanium isopropoxide (TTIP), combined with either thermal (H<sub>2</sub>O) or plasma-enhanced (O<sub>2</sub>) oxidation steps (see Methods). We experimentally realized metasurface designs with asymmetry parameters of  $\theta = 5^{\circ}$ , 10°, and 15° for all three defect concentrations (TiO<sub>2</sub>-L, TiO<sub>2</sub>-M, TiO<sub>2</sub>-H), and verified their accurate reproduction using scanning electron microscopy (SEM, see Fig.4.5a). The specific values of the asymmetry parameters, though slightly different from the numerically predicted optimum values, were chosen for better reproducibility and stability within the constraints of our nanofabrication processes. Nevertheless, it is important to note that the experimentally realized asymmetry values span a sufficient range to clearly elucidate the different light-matter coupling regimes.

The presence of quasi-BIC resonances for the TiO<sub>2</sub>-L and TiO<sub>2</sub>-M cases was confirmed through white light transmittance measurements and a clear blueshift of the resonance wavelength with increasing  $\theta$  was observed, consistent with the numerical predictions (Fig.4.5b). Notably,



**Figure 4.5: Experimental metasurface realization and spectral tuning. a.** SEM images of exemplary two ellipse metasurface unit cells (scaling factor S = 1) with different tilting angle values of 5°, 10°, and 15°. **b.** Measured 1-Transmittance spectra for metasurfaces with different tilting angles ( $\theta = 5^{\circ}, 10^{\circ}, 15^{\circ}$ ) and different defect concentrations of the TiO<sub>2</sub> films (TiO<sub>2</sub>-L, TiO<sub>2</sub>-M, TiO<sub>2</sub>-H). **c.** Measured 1-Transmittance spectra for low-defect TiO<sub>2</sub>-L metasurfaces with unit cells of different scaling factors S and tilting angles  $\theta$ .

no resonance was observed for the highest defect concentration  $TiO_2$ -H, which we attribute to the signal-to-noise characteristics of our optical spectroscopy setup considering the already very weak resonance expected from simulations (compare Fig.4.2c). We find that the quality factor of the metasurfaces is clearly correlated with the asymmetry parameter, showing a gradual decrease with increasing  $\theta$ . As expected, the Q factors of the TiO<sub>2</sub>-L metasurfaces are much higher than those composed of TiO<sub>2</sub>-M with the same  $\theta$  (Fig.4.6). Because of the extremely weak and broad resonances observed for TiO<sub>2</sub>-H, we focus our catalytic experiments on metasurfaces fabricated from TiO<sub>2</sub>-L and TiO<sub>2</sub>-M, which nevertheless provide a broad range of resonance Q factors and absorption efficiencies for analysis.


**Figure 4.6: The experimental quality factors of metasurfaces.** The experimental quality factors of metasurfaces (scaling factor = 1) with different tilting angles ( $\theta = 5^{\circ}$ ,  $10^{\circ}$ ,  $15^{\circ}$ ) are based on TiO<sub>2</sub>-L and TiO<sub>2</sub>-M.

We experimentally demonstrate the spectral tunability of the catalytic metasurfaces through tuning the scaling factor S of the unit cell, which enables versatile control over the resonance position throughout the visible spectrum. Transmittance measurements confirm that the positions of quasi-BIC resonances can be precisely placed at a given excitation wavelength through tailoring the scaling factors (Fig.4.5c), providing flexibility to create BIC-induced absorption enhancement at any desired wavelength in the visible region.

Metasurface-enhanced photocatalysis. We use a standard Ag reduction reaction<sup>67,79</sup> to investigate the potential of TiO<sub>2-x</sub>-based BIC metasurfaces as a functional photocatalysis platform. A red CW laser source with an emission wavelength of 633 nm was used to trigger the photoreduction process. Fine tuning of the scaling factor of the unit cell was carried out to place the quasi-BIC resonance at the target excitation wavelength of 633 nm for all asymmetry parameters, taking into account the slight resonance shifts caused by a variation of  $\theta$  (see Fig.4.2d). Transmittance spectra measured in an aqueous environment confirm that the resonances of different  $TiO_2$ -L and  $TiO_2$ -M metasurfaces can be excited at 633 nm (Fig.4.7, 4.8). To investigate the visible light photocatalytic performance of our BIC-based metasurfaces, photoreduction of silver ions was conducted for samples with different asymmetry parameters  $(\theta = 0^{\circ}, 5^{\circ}, 10^{\circ}, \text{ and } 15^{\circ})$ . The metasurface samples were immersed in a 50 mM silver nitrate (AgNO<sub>3</sub>) aqueous solution, and a CW laser (633 nm, 50 mW) was used to illuminate the target metasurface area. Upon illumination, excited electrons generated in the TiO<sub>2-x</sub> transfer to Ag<sup>+</sup>, resulting in the formation of Ag nanoparticles on the metasurfaces.<sup>67,79</sup> Additionally, the metasurface resonance significantly enhances light absorption at the electric field hotspots, boosting charge carrier excitation and, consequently, the reduction rate. The photogenerated holes are consumed by hydroxide ions, leading to the generation of oxygen and water, which ensures that the reduction reaction can continue.<sup>90,91</sup>



Figure 4.7: Evaluation of catalytic metasurface performance. a. 1-Transmittance spectrum measured in an aqueous environment for metasurfaces with tilting angles  $\theta$  =  $0^{\circ}, 5^{\circ}, 10^{\circ}, 15^{\circ}$  based on TiO<sub>2</sub>-L, where the scaling factors of unit cells are finely adjusted to place the quasi-BIC resonances at the target wavelength position (633 nm). b. Darkfield images (top) illustrate different visible light photocatalytic reduction rates on the metasurfaces with different tilting angles ( $\theta = 0^{\circ}, 5^{\circ}, 10^{\circ}, 15^{\circ}$ ) based on TiO<sub>2</sub>-L. The non-resonant metasurface pattern ( $\theta = 0^{\circ}$ ) is used for comparison because it maintains the same volume, material mass, and activated surface area as the BIC-driven systems. The photocatalytic experiments were performed in AgNO<sub>3</sub> solution (50 mM), illuminated with the focused CW laser from the top (633 nm, 50 mW). To enable observation of the reduction process, an additional broadband light source was used for darkfield illumination. To avoid the excitation of TiO<sub>2</sub> by UV light from the broadband source, a long-pass filter (590 nm) was applied, causing the reddish appearance of the darkfield images. The bright red spots are reduced Ag particles aggregated on the metasurfaces. Signal locations and intensities associated with Ag nanoparticles on planar images are visualized in 3D models (bottom), where the intensity of red pixels is represented by the height as a function of the spatial position. c. On the basis of digital image analysis in panel b for each metasurface, the sum of red light intensity enables direct comparison of the different Ag<sup>+</sup> reduction rates on metasurfaces as a function of their tilting angles.

Visible light photocatalysis can be monitored through dark-field microscopy by tracking the amount of Ag particles created on the surface, which manifest as distinct bright red spots accumulating in the dark-field images over time (Fig.4.7b). Therefore, through analysis of the brightness and size of these characteristic spots, we can provide an estimation of the amount of reduced Ag nanoparticles, which is related to the photocatalytic rate on the different metasurface fields. We note that the Ag particles are not generated evenly on the metasurface, because the growth is influenced by the local surface environment, including effects such as the local availability of active sites, adsorption energy, and initial Ag seed deposition. Similar distributions of Ag particles on  $TiO_2$  nanostructures have been reported before.<sup>67,79</sup>



**Figure 4.8: The dark-field image analysis based on TiO**<sub>2</sub>-**M a.** Transmittance spectra measured in an aqueous environment for metasurfaces with tilting angles  $\theta = 0^{\circ}$ , 5°, 10°, and 15° based on TiO<sub>2</sub>-M, where the scaling factors of unit cells are finely adjusted to place the quasi-BICs resonances at the target wavelength position (633 nm). **b.** Darkfield images (top) illustrate different visible-light photocatalytic reduction rates on the metasurfaces with different tilting angles ( $\theta = 0^{\circ}$ , 5°, 10°, and 15°) based on TiO<sub>2</sub>-M. The photocatalytic experiments were performed in AgNO<sub>3</sub> solution (50 mM), illuminated with the focused CW laser (633 nm, 50 mW). The red spots are reduced Ag particles aggregating on the metasurfaces. Signal locations and intensity of Ag nanoparticles on planar images are visualized in 3D models (bottom), where the intensity of red pixels is represented by the height of the peaks as a function of spatial position.

To quantify the amount of Ag reduced at the metasurface, a statistical approach was employed based on the distribution and brightness of the red pixels in the captured dark-field images. The locations and intensity of the signals induced by the Ag particles are visualized in three dimensions in Fig.4.7b, where the intensity of the red pixels is represented by the height of the peaks. By applying thresholding, the signals of the Ag particles can be separated from the background, and a sum of pixel intensities can be calculated to estimate the photoreduction rate. The results of the numerical image analysis for different metasurfaces are shown in Fig.4.7c for metasurface structures composed of  $TiO_2$ -L and  $TiO_2$ -M.

The BIC metasurface concept allows us to completely turn off the resonant enhancement by moving to a fully symmetric unit cell design, which provides an ideal reference case for our analysis of the photocatalytic rates. For a symmetric metasurface ( $\theta = 0^{\circ}$ ) composed of TiO<sub>2</sub>-L, we find an extremely low Ag+ photoreduction rate at 633 nm, which we attribute to the low intrinsic absorption of the material caused by a small number of defects. The non-resonant reduction rate of TiO<sub>2</sub>-M is around 2 times higher (Fig.4.7c) than that of TiO<sub>2</sub>-L, which is expected considering the difference in extinction coefficient between the two materials (see Fig.4.2b).

This picture changes drastically when moving to the resonantly enhanced case. Notably, for the TiO<sub>2</sub>-L metasurface with an asymmetry parameter of  $\theta = 5^{\circ}$ , the reduction rate (as evaluated by our image processing approach) is boosted by a factor of 7, providing the greatest enhancement of quasi-BIC assisted light absorption compared to the other metasurface geometries ( $\theta = 10^{\circ}$  and  $\theta = 15^{\circ}$ ), as predicted by our simulations. The quantities of deposited Ag and therefore the reduction rates are closely related to the capability of the different metasurfaces samples to absorb visible light.<sup>67</sup>

Notably, the metasurface-enhanced reduction rate on TiO<sub>2</sub>-M is lower than that of TiO<sub>2</sub>-L for all asymmetries ( $\theta = 5^{\circ}$ , 10°, 15°), which is due to the weaker resonances in TiO<sub>2</sub>-M as well as the associated lower quality factors and electric field enhancements. This resonance attenuation is driven by the higher extinction coefficient of TiO<sub>2</sub>-M compared to TiO<sub>2</sub>-L and leads to overall weaker light-matter interaction in the photoreduction process. Nevertheless, the TiO<sub>2</sub>-M metasurface geometries still allow an asymmetry dependent assessment of the BIC-enhanced photoreduction rate, which shows a maximum for  $\theta = 15^{\circ}$ , consistent with the numerical simulations. In order to understand why maximum absorption occurs at markedly different asymmetry parameters for the different materials ( $\theta = 5^{\circ}$  for TiO<sub>2</sub>-L and  $\theta = 15^{\circ}$  for TiO<sub>2</sub>-M), a fundamental model for light-matter interactions in BIC-based metasurfaces is necessary, which we develop in the following section.

Strikingly and in contrast to typical photocatalysis platforms where materials with high extinction coefficient are preferred, BIC-based metasurfaces incorporating low-defect  $TiO_2$ -L exhibit much higher catalytic performance as well as greater flexibility for optical absorption engineering through tuning of the asymmetry factor of the unit cell, enabling the simultaneous optimization of visible light absorption and near-field enhancement. Therefore, our approach can enhance visible light photocatalysis on ultra-thin films, especially when utilizing weakly absorbing materials.

**BIC-enabled critical light-matter coupling.** Our numerical simulations (Fig.4.2d) and photoreduction experiments (Fig.4.7c) clearly demonstrate that to obtain maximum absorption and the highest photoreduction performance,  $\text{TiO}_{2-x}$  films with different extinction coefficients *k* require metasurface designs with different optimized asymmetry parameters  $\theta$ . To deepen our understanding of this phenomenon, we analyze the absorption and field enhancement over a wide parameter space of extinction coefficients *k* and asymmetry parameters  $\theta$  using temporal coupled-mode theory (TCMT).<sup>92–94</sup>

The BIC-enabled catalytic metasurface platform can be described as a single-mode cavity with two mirror-symmetric ports (Port 1 and Port 2, see Fig.4.9), which is illuminated from

one side with a time harmonic excitation  $(s_1^+)$  and allows for reflected  $(s_1^-)$  and transmitted  $(s_2^-)$  waves.



**Figure 4.9: Critical light-matter coupling in catalytic metasurfaces. a.** Model of a metasurface with two radiative decay channels. **b.** Simulations of maximum absorbance  $(\omega = \omega_0)$  of metasurfaces as a function of extinction coefficient (*k*) and tilting angle ( $\theta$ ). **c.** CST simulations with TCMT fits: the absorbance at resonance ( $\omega = \omega_0$ ) of metasurfaces with different tilting angles ( $\theta = 1^\circ - 20^\circ$ ) based on the TiO<sub>2-x</sub> film with different extinction coefficients (*k* = 0.003 and *k* = 0.022, respectively). **d.** Top: Simulations of maximum field enhancement of metasurfaces as a function of extinction coefficient (**k**) and tilting angle ( $\theta$ ). Bottom: Simulation of the electric field enhancement in one unit cell ( $\theta = 5^\circ$  and 15°) based on TiO<sub>2-x</sub> films with different extinction coefficients. **e.** SEM images of the TiO<sub>2</sub>-L metasurface ( $\theta = 5^\circ$ ) after Ag<sup>+</sup> reduction. The yellow patterns are the reduced Ag particles aggregating together. **f.** The normalized reduction rate (( $R_{\theta,k} - R_{\theta=0,k}$ )/ $R_{\theta=0,k}$ ,  $\theta = 0^\circ$ , 5°, 10°, 15°), based on the sum of pixel intensities shown in TCMT fits. **g.** Dark field images illustrating different photocatalytic reduction rates on the TiO<sub>2</sub>-L metasurface ( $\theta = 5^\circ$ ) and TiO<sub>2</sub>-M metasurface ( $\theta = 15^\circ$ ).

The interaction between the far field and the cavity mode at each port is determined by a coupling rate  $\kappa$ , which can be calculated from the radiative decay rate  $\gamma_{rad}$  via  $\kappa = \sqrt{\gamma_{rad}}$ . Additionally, an intrinsic decay rate  $\gamma_{int}$  describes the energy loss through material absorption. The far-field absorbance can then be calculated according to.

$$A = \frac{2\gamma_{int}\gamma_{rad}}{(\gamma_{int} + \gamma_{rad})^2}.$$
(4.1)

Which has its maximum value for  $\gamma_{int} = \gamma_{rad}$ , referred to as the critical coupling condition.<sup>25</sup> A similar critical coupling condition can be derived for the near fields, where the electric near-field enhancement  $|E/E_0|^2$  can be related to the total quality factor  $Q = \omega_0/2(\gamma_{int} + \gamma_{rad})$  and the far-field absorbance A via,

$$\left|\frac{\mathrm{E}}{\mathrm{E}_{0}}\right|^{2} \sim \frac{\gamma_{\mathrm{rad}}}{\left(\gamma_{\mathrm{int}} + \gamma_{\mathrm{rad}}\right)^{2}} = \frac{4\gamma_{\mathrm{rad}}}{\omega_{0}^{2}} \cdot \mathrm{Q}^{2} = \frac{\mathrm{A}}{2\gamma_{\mathrm{int}}}$$
(4.2)

A central advantage of BIC-based metasurface approaches is the precise control over the radiative decay rate via the asymmetry factor of the specific BIC unit cell design, where the relationship between  $\gamma_{\rm rad}$  and  $\alpha$  follows the characteristic quadratic relationship.<sup>2</sup>

$$\gamma_{\rm rad} \sim \alpha^2 = \sin^2 \theta \tag{4.3}$$

Additionally, the intrinsic decay rate  $\gamma_{int}$  follows a linear relation to k. To reveal the correlation between k,  $\theta$ , and the efficiency of light-matter coupling, we simulate the far-field absorbance at resonance for different values of the extinction coefficient (k=0.001) to (k=0.13)) and tilting angle ( $\theta = 1^{\circ}$  to  $\theta = 20^{\circ}$ ). Notably, the maximum absorbance of A=0.5 is reached at the critical coupling condition, indicated by a dotted line in Fig.4.9b. Furthermore, we fit the absorbance data corresponding to the two extinction values of our experimental TiO<sub>2</sub>-L and TiO<sub>2</sub>-M films (i.e., k=0.003 and k=0.022) with Equation 4.2, which shows excellent agreement between our model and the full-wave numerical simulations (Fig.4.9c).

Even though the far-field absorbance remains high for all parameter values where the critical coupling condition is satisfied, our experimental results for the TiO<sub>2</sub>-M metasurface with medium defect concentration clearly showed reduced catalytic activity compared to the TiO<sub>2</sub>-L metasurface. To resolve this apparent discrepancy, we additionally simulate the electric near-field amplitudes (normalized to the incident electric field) around the resonant metasurface elements for varying k and  $\theta$  (Fig.4.9d). As predicted from our theory, the parameter combinations where critical coupling occurs are identical to the far-field absorbance case. However, we observe a strong decrease in the near-field amplitudes with increasing

extinction coefficient (Fig.4.9d, bottom), which matches the reduced reduction rates for TiO<sub>2</sub>-M in our experiments. This behavior can be explained by the greatly increased light-matter coupling efficiency provided by the enhanced near-fields.<sup>83</sup> Crucially, the effects of resonant absorption for low-loss materials outweigh the benefits of higher intrinsic material losses, and simultaneously deliver flexible spectral and spatial control over the absorption. This may provide an alternative way to tackle the intrinsic low absorption in the optical regime of many semiconductor materials that could be tested for sunlight-driven photocatalysis. Also, it points to the nanoscale spatial locations in which co-catalysts should be located to maximize light-matter interactions.

Comparing Fig.4.9d and Fig.4.7c, we find that the trends agree qualitatively for both defect concentrations TiO<sub>2</sub>-L and TiO<sub>2</sub>-M. To provide a more quantitative perspective, we combine Equations 4.2 and 4.3 to define an effective Ag coverage ratio (ECR) based on the relative deviation of the sum of pixel intensities  $R_{\theta,k}$  in our dark-field images from the unenhanced case (compare, e.g., Fig.4.7b), which is related to the overall photocatalytic reduction rate, and is given by:

$$ECR(\theta, \mathbf{k}) = \frac{\mathbf{R}_{\theta, \mathbf{k}} - \mathbf{R}_{\theta=0, \mathbf{k}}}{\mathbf{R}_{\theta=0, \mathbf{k}}} = \beta(\mathbf{k}) \cdot \left| \frac{\mathbf{E}}{\mathbf{E}_0} \right|^2 (\theta, \mathbf{k}).$$
(4.4)

Experimentally, the reduction of silver ions can be further confirmed through SEM (Fig. 4.9e). We first fix the parameters  $\gamma_{rad}$  and  $\gamma_{int}$  of the electric field enhancement  $|E/E_0|^2(\theta, k)$  by fitting Equation 4.4 with  $\beta(k) = 1$  to numerical simulations, and then fit Equation 4.4 to the rescaled experimental data via a scaling approach, by varying  $\beta$ , which yields  $\beta(k = 0.003) = 39 \pm 1$  for the Ti<sub>2</sub>-L material and  $\beta(k = 0.022) = 24 \pm 2$  for the TiO<sub>2</sub>-M material, respectively (Fig. 4.9f).

The excellent agreement of the fit further supports the importance of resonant-enhanced light-matter interaction in photocatalytic processes. While the enhancement of the ECR is mainly governed by the 6-fold increase of electric near-field intensity,  $\beta$  increases by 63% when comparing TiO<sub>2</sub>-M with TiO<sub>2</sub>-L. This highlights that the reduction rate does not scale linearly with electric near-field intensity, but rather favors low defect concentrations even more strongly. The functional dependence of  $\beta(\mathbf{k})$  has the potential to give insights into the reduction reaction mechanism and will be the subject of further research.

Overall, the results of this analysis offer a clear design strategy for highly efficient catalytic metasurfaces. The precise determination of scaling behavior and power dependence of the reaction is highly dependent on the exact reaction conditions, the surface structure of the materials, and the determination of the concentration of reaction products. Nevertheless, our BIC-enabled critical coupling approach provides a general framework for maximizing light-matter interactions in diverse materials, enabling us to tackle the challenges faced

by many semiconductor-based ultrathin films applied in photocatalysis, such as poor light confinement and limited absorption manipulation.

#### 4.3 Summary

In this research, based on TiO<sub>2-x</sub> materials with controllable extinction coefficients, we have designed ultrathin semiconductor metasurfaces leveraging bound states in the continuum (BIC) to demonstrate enhancements of visible light absorption with spectral tunability and selectivity. Our multi-method analysis shows that visible light absorption in catalytic metasurfaces can be precisely tuned for maximum enhancement through the radiative loss engineering characteristics of the BIC concept, leveraging the in-plane asymmetry of the individual unit cells to reach a critical coupling regime with balanced rates of radiative and material loss. Ultrahigh values of BIC-assisted electric field enhancement and strong light confinement have been achieved, which was shown to produce optimal light absorption for the TiO<sub>2-x</sub> film with the lowest defect concentration and therefore extinction coefficient. This could provide an alternative way for tuning absorption in the optical regime in a broad range of materials. Furthermore, we demonstrated that the BIC-enabled resonant absorption can be tailored for any desired spectral position throughout the whole visible wavelength range by finely tuning the scaling factor of the metasurface unit cell. Importantly, as a versatile catalytic platform, we explore opportunities of these ultrathin TiO<sub>2-x</sub>-based BIC metasurfaces for visible light photocatalysis. Typically, semiconductors with high extinction coefficient k are preferred in the field of photocatalysis due to their overall higher intrinsic absorption. Our catalytic metasurface platform challenges this preconception by showing optimum resonantly enhanced light absorption for  $TiO_{2-x}$  with low *k*, which enables more freedom for optical engineering of the metasurface, and achieves a stronger field enhancement which makes the light-matter interaction much more intense. Finally, our catalytic TiO<sub>2-x</sub>-based BIC metasurface platform enables us to circumvent long-standing drawbacks of many semiconductor-based ultrathin films applied in catalytic processes, such as poor light confinement and limited absorption manipulation, which brings perspectives in other fields including solar-to-electric energy conversion, where our approach can help to address the longstanding trade-off in photovoltaics between optical absorption and thickness of the active layer.

# 5

### Surface-enhanced Raman scattering in BIC-driven semiconductor metasurfaces

The content of this chapter has been published in the scientific journal Advanced Optical Materials (H. Hu, A. K. Pal et al. Surface-enhanced Raman scattering in BIC-driven semiconductor metasurfaces. Adv. Opt. Mater., 2024: 2302812).<sup>95</sup> This chapter is based on the peer-reviewed manuscript, with text elements—including words, sentences, full paragraphs—as well as graphic content and figures, directly sourced from the publication. The reuse of this material complies with the open-access Wiley-VCH publication guidelines, which permit the inclusion of an author's own contributions in theses, in accordance with the terms of the CC-BY Creative Commons Attribution 4.0 International license http://creativecommons.org/licenses/by/4.0/.

#### 5.1 Research background

Surface-enhanced Raman spectroscopy (SERS) is a highly sensitive, chemically specific, and non-destructive analytical technique that has garnered significant attention in the fields of biophysics, chemistry, and medical diagnostics.<sup>30-34</sup> The SERS substrate is at the core of SERS-based technologies, providing large Raman enhancement factors through two independent mechanisms: electromagnetic (EM) and chemical (CM).<sup>31,96–98</sup> So far, noble metals such as Au, Ag, and Cu have played a dominant role in SERS applications due to their ability to quench fluorescence and enhance the EM fields through plasmon resonances, achieving ultrasensitive and even single-molecule-level SERS detection.<sup>35,99–102</sup> However, there are some disadvantages for noble metal SERS substrates such as high cost, poor chemical and thermal stability, lack of uniformity and biocompatibility, low SERS signal reproducibility, and poor selective recognition ability for probe molecules.<sup>35–37</sup> Semiconductor SERS substrates are a promising alternative to metals due to their better chemical stability and biocompatibility.<sup>103</sup> Semiconductor materials are capable of manipulating light at the nanoscale (using optical absorption engineering, light trapping by total internal reflection, etc.),<sup>104,105</sup> and they allow for straightforward surface modification with a diverse range of functional groups (-NH<sub>2</sub>, -COO<sup>-</sup>, -PO<sub>4</sub><sup>3-</sup>, -SH, etc.),<sup>31</sup> which have significantly broadened SERS applications across various fields.<sup>33,35,37,88,106</sup> In particular, semiconductor SERS substrates benefiting from photoinduced charge transfer (PICT),<sup>35,37,107</sup> have also demonstrated great potential for detecting target molecules in complex environments and monitoring interfacial chemical reactions with high sensitivity, making them valuable tools in the fields of biophysics, chemistry, and medical diagnostics research.<sup>108</sup>

However, compared to noble metals, semiconductor substrates generally have a poorer limit of detection, which can be attributed to weaker EM field enhancement and light-matter interactions.<sup>36,109–111</sup> Therefore, it is crucial to explore strategies to improve the SERS performance of semiconductor substrates.<sup>112</sup> To this end, several methods have been reported to enhance the EM field and light-matter interaction. Common approaches based on Mie resonances are to synthesize semiconductor nanospheres to trap light,<sup>113</sup> or assemble homogeneous spheres to form two-dimensional arrays or three-dimensional colloidal crystals.<sup>114</sup> Alternatively, semiconductor doping has also been applied to generate surface plasmon resonance (SPR), which inevitably introduces enormous optical loss.<sup>31,115</sup> However, these methods have not fully harnessed one of the most distinctive advantages of semiconductors: their optical engineering capabilities.<sup>31,116</sup>

Metasurfaces constructed from two-dimensional subwavelength arrays of semiconductor nanostructures have shown tremendous potential for enhancing light-matter interaction at



**Figure 5.1: BIC-driven TiO**<sub>2</sub> **semiconductor SERS metasurface. a.** Schematic of the TiO<sub>2</sub>-based BIC metasurface platform for SERS applications. **b.** Illustration of BIC-assisted absorption enhancement and spectral tunability. The simulated absorbance spectra for the pure TiO<sub>2</sub> film (top), BIC-assisted TiO<sub>2</sub> metasurfaces with the symmetrical geometry (middle), and asymmetrical geometry ( $\theta = 10^{\circ}$ ) as an example (bottom). The absorbance of the metasurface can be enhanced with the excitation of quasi-BIC resonances in asymmetrical geometry. This can be further spectrally tailored through the *S* (scaling factor), and the amplitudes can additionally be tuned by adjusting the degree of asymmetry factor ( $\theta$ ).

the nanoscale.<sup>29,31,117–120</sup> In particular, metasurfaces underpinned by the physics of bound states in the continuum (BIC) have seen a surging interest due to their strong light confinement and remarkable enhancement of electromagnetic fields,<sup>1,6</sup> stimulating applications across diverse fields, including nanoscale lasing,<sup>11,121</sup> biomolecular sensing,<sup>21,122,123</sup> and nonlinear photonics.<sup>22,124</sup> Hence, BIC-assisted metasurfaces serve as an ideal toolkit for light manipulation in semiconductor SERS substrates (Fig. 5.1a), which, to the best of our knowledge, have not yet been realized.

Here, we demonstrate BIC-driven semiconductor metasurfaces as a new platform for highsensitivity SERS. Through precise nanophotonic engineering of quasi-BIC resonances in the TiO<sub>2</sub> BIC system, we successfully enhance both the PICT effect (chemical mechanism) and the EM field confinement (physical mechanism) of SERS. Significantly, the integration of metasurface nano-engineering techniques with BIC physics offers a versatile approach applicable to a wide range of semiconductor SERS substrate materials (with low intrinsic losses), which can be adapted to diverse molecules like methylene blue (MB), Rhodamine 6G, and adenine.<sup>35,37,125</sup> This synergistic combination leverages the benefits of nanoscale light manipulation (metasurface) and the remarkable chemical effects empowered by photoinduced charge transfer (semiconductor), thereby optimizing the SERS performance of these substrates.

#### 5.2 **Results and dicussion**

Conceptually, a BIC is a localized state existing in a continuum of radiative modes.<sup>1,126</sup> This phenomenon originally appeared in quantum mechanics and has later been applied to many other areas of physics where resonant behavior is prevalent.<sup>73</sup> A true BIC, with an infinite value of the quality factor (Q factor, defined as the resonance position divided by the line width), can be explained by vanishing coupling constants with all radiation channels.

One way of making BICs usable in practical nanophotonic systems is to design symmetryprotected metasurfaces, where the coupling constants to the radiation continuum are tailored using structural asymmetry within the metasurface unit cell, leading to the formation of quasi-BIC modes accessible from the far field.<sup>1</sup> The narrow quasi-BIC could be a drawback from the perspective of scaling the EM enhancement of the Stokes-shifted field, however, it offers several advantages for the SERS application. A key advantage of symmetry-protected BICs is their ability to accurately control the resonance position (Fig. 5.1b). This attribute is particularly crucial for semiconductor SERS platforms, since matching the quasi-BIC resonance to the laser wavelength can significantly enhance the SERS sensitivity.

Numerical Investigation of  $TiO_2$  BIC metasurfaces. We implemented metasurfaces with two different geometries (two ellipses and hole-in-disk) for our BIC metasurfaces designs (Fig. 5.2a,b). As introduced previously, for semiconductor SERS applications, both the enhanced absorption of the incident light source leading to the substrate-molecule PICT effect, and the inherent strong electric field enhancement of the nanomaterial are vital to the amplification of the Raman signal. Hence, in our simulation, we evaluate the absorption and electric field enhancement for the these two metasurface geometries.

As mentioned above, a true BIC is a mathematical concept characterized by infinite quality factor and vanishing spectral line width. In practice, true BICs can be converted to quasi-BICs with finite resonance width by breaking the in-plane inversion symmetry within the unit cell, allowing the resonant mode to be excited from the far field. For the unit cell with two ellipses, the symmetry breaking can be achieved by tilting the ellipses at an angle  $\theta$  with respect to each other. In the hole-in-disk geometry, the symmetry is broken by shifting the hole from the center along the y-axis by a specific value ( $\beta$ ).

Through the quasi-BIC resonance, we can achieve a significant enhancement in absorption after breaking the  $C_2^z$  symmetry in the metasurfaces. The absorbance spectrum is calculated from the simulated reflectance (R) and transmittance (T) spectra (A = 1 – R – T). Here, we emphasize one of the most important advantages of BIC metasurfaces in SERS applications,

namely that the light confinement at the interface (characterized by absorbance) can be maximized through tuning the asymmetry parameter.



**Figure 5.2: Numerical design of semiconductor SERS metasurfaces and their far/near field properties. a.** Top: Sketch of a BIC unit cell with the two ellipses geometry (A, B,  $P_x$ , and  $P_y$  will scale linearly according to scaling factor *S*. Bottom: Color-coded simulated absorbance maps of TiO<sub>2</sub> metasurfaces as a function of tilting angle  $\theta$  and wavelength. **b.** Top: Sketch of the unit cell with hole-in-disk geometry (D<sub>i</sub>, D<sub>o</sub>, P<sub>x</sub>, and P<sub>y</sub> will scale linearly according to scaling factor S). Bottom: Color-coded simulated absorbance maps of metasurfaces as a function of offset value ( $\beta$ ) and wavelength. **c.** The simulated electric field enhancement of metasurfaces with different geometries (two ellipses, and hole-in-disk) under different asymmetry factors. Inset: The electric near field at the resonance frequency for unit cells (two ellipses, and hole-in-disk) of TiO<sub>2</sub> metasurfaces, corresponding to maximum absorption, and field enhancement.

Specifically, we used numerical simulations for calculating absorbance maps of TiO<sub>2</sub> metasurfaces with different geometries (two ellipses and hole-in-disk) as a function of the asymmetry parameters  $\theta$  and  $\beta$ . The absorbance enhancement of the quasi-BIC resonances is found to be strongly dependent on the asymmetry parameter, reaching maximum magnitudes at specific values ( $\theta = 10^{\circ}$ , and  $\beta = 30$  nm, respectively), as determined by the critical coupling condition explained by the temporal coupled-mode theory. In brief, the BIC-enabled semiconductor SERS metasurface platform can be described as a single-mode cavity with two mirror-symmetric ports, where the interaction between the far-field and the cavity mode at each port is determined by the coupling rate  $\kappa$ , which can be derived from the radiative decay rate  $\gamma_{rad}$ . Additionally, an intrinsic decay rate  $\gamma_{int}$  accounts for the energy loss through material absorption, and the far-field absorbance can be calculated according to:

$$A = \frac{2\gamma_{\text{int}}\gamma_{\text{rad}}}{(\gamma_{\text{int}} + \gamma_{\text{rad}})^2},$$
(5.1)

which reaches its maximum value when the intrinsic decay rate  $\gamma_{int}$  is equal to the radiative decay rate  $\gamma_{rad}$ , referring to the critical coupling condition.<sup>127</sup> Although both geometries can achieve the maximum absorbance magnitude (A = 0.5) under the critical coupling condition, they present different near-field EM enhancements, which is also an important aspect for SERS.<sup>128</sup> It can be clearly seen that the unit cell with two ellipses geometry exhibited stronger electric field enhancement ( $|E/E_0| = 32$ ) than the hole-in-disk geometry ( $|E/E_0| = 12$ ) even though both of them operate at the critical coupling condition (Fig. 5.2c). It's worth noting that semiconductor SERS substrates typically rely on the chemical mechanism (PICT) to amplify the Raman signal, but often suffer from extremely weak EM enhancement.<sup>36,109,110</sup> Here, our semiconductor metasurfaces, empowered by the BIC resonances, allow for strong electric field enhancement. Conducting the SERS experiment on these metasurfaces of different geometries could deepen our understanding of how the BIC metasurface geometry affects SERS performance.

**Experimental fabrication of TiO**<sub>2</sub>**-Based metasurfaces.** While bottom-up methods can provide scalable production and produce a wide variety of nanostructures, considering the importance of precise control over the shape and spatial distribution of all metasurface elements, we employed top-down nanofabrication. TiO<sub>2</sub> thin films with a thickness of 140 nm were fabricated by sputter deposition, followed by high-resolution electron beam lithography and anisotropic reactive ion etching (see Chapter 3).

We experimentally implemented the metasurfaces designs composed of two ellipses (Fig. 5.3a) and hole-in-disk geometries (Fig. 5.4). Here, we took two ellipses metasurfaces as an example to confirm their fabrication quality using electron microscopy (Fig. 5.3a). We performed



**Figure 5.3: Experimental metasurface fabrication and spectral tuning. a.** SEM images of experimental metasurfaces with two ellipse geometry (scaling factor *S*). **b.** Statistical measurements of the length of long and short axes (A and B) of the ellipses in different unit cells (100 in counting). The surface area of a single unit cell (S<sub>metasurface</sub>) is calculated based on these values according to the proximate formula shown in the figure. **c.** Measured transmittance spectra for metasurfaces with different scaling factors (0.994 to 1.006 for fine tuning). Both the dashed and solid lines are measured spectra.

statistical measurements on the long and short axes (A and B) of 100 unit cells, obtaining average values of ±294 and ±144 nm, respectively (Fig. 5.3b). We increased the effective surface area of semiconductor metasurfaces by approximately 2 times compared to the nonstructured pure TiO<sub>2</sub> film, which provides a greater active contact surface area for analyte molecules to form surface complexes and generate stronger Raman signal.<sup>125</sup>

The presence of quasi-BIC resonances has been confirmed through white light transmittance measurements (see Chapter 3). We experimentally demonstrate broad spectral tunability of the semiconductor BIC metasurfaces by scaling the size of the unit cell (*S*, Fig. 5.5), which enabled us to control the position of the quasi-BIC resonance throughout the whole visible



**Figure 5.4:** The SEM image and Q factor of metasurfaces. a. SEM images of experimental hole-in-disk metasurfaces (scaling factor S = 1). b. Quality factor (Q factor) of the quasi-BIC resonance with different geometries (two ellipses, and hole-disk) extracted from the experimental transmittance spectra with different scaling factors.

spectrum (Fig. 5.3c), and cover several widely used Raman laser sources (532, 633, 785 nm). Fine-tuning the *S* factor around the target laser wavelength (633nm here) ensured that we could precisely excite the quasi-BIC resonance. We applied the temporal coupled-mode theory (TCMT) model to fit the experimental transmittance spectrum,<sup>92</sup> which characterizes the spectral mode energy density and is directly related to the enhancement of light-matter interaction.<sup>129</sup>



**Figure 5.5: Schematic diagram of the unit cell with different scaling factors.** Here it shows the scaling down and up of the unit cell

Matching the excitation wavelength to the semiconductor substrate absorption has been a long-standing challenge for SERS semiconductor substrates,<sup>32</sup> which has now been experimentally achieved in our semiconductor BIC metasurfaces. Additionally, when the laser wavelength matches the molecular absorption resonance, the Raman signal can be amplified



by several orders of magnitude due to the resonant Raman effect (as discussed in the following section).<sup>128</sup>

Figure 5.6: Raman spectra of methylene blue on the BIC-assisted semiconductor SERS metasurface. a. Schematic layout of the laser illuminating on the  $TiO_2$  BIC metasurfaces (two ellipses, and hole-in-disk geometries), and the pure  $TiO_2$  film. b. Raman spectra for MB were measured on the BIC metasurfaces with different geometries (two ellipses, and a hole-in-disk), and on the pure  $TiO_2$  film. c. The Raman spectra for MB at different concentrations ( $10^{-5}$  to  $10^{-9}$  M) on the BIC-assisted  $TiO_2$  semiconductor SERS substrate with two ellipses geometry. d. The maximum Raman signal of MB (at 1624 cm<sup>-1</sup>) at different concentrations measured on the metasurfaces with two ellipses geometry, and the analysis of the signal-to-noise ratio (inset).

**BIC-assisted semiconductor SERS metasurface.** We utilized MB as a test molecule for SERS investigations together with a 633 nm laser as the excitation source. Taking advantage of the high spectral tunability of our semiconductor SERS substrate, we engineered the resonance position of metasurfaces with different meta-units (two ellipses, and a hole-in-disk) to match the pump wavelength (633nm) by finely tuning the *S* factor (discussed in Fig. 5.3). The target BIC metasurfaces pattern with the size of 33 × 33  $\mu$ m<sup>2</sup> is illuminated by the

excitation laser with a spot size around 14  $\mu$ m in diameter passing through a 20 X waterimmersed objective, which ensured the successful excitation of quasi-BIC resonance (Fig. 5.6a). It is well known that in SERS applications, the excited molecules can emit also fluorescence in addition to the Raman emission. This is particularly important in semiconductor SERS substrates which, unlike metals, do not quench the fluorescence emission.<sup>112</sup> Hence, in this research, we employed an automated algorithm for fluorescence removal based on modified multi-polynomial fitting (Fig. 5.7a,b).<sup>130</sup>

To better understand the SERS application of the BIC-assisted semiconductor  $TiO_2$  metasurfaces, we compared the SERS enhancement on the two ellipses and hole-in-disk metasurfaces. Specifically, for the same MB concentration ( $10^{-7}$  M), the semiconductor BIC metasurface with two ellipses exhibited a SERS signal approximately 7 times higher than that of holein-disk geometry, which is attributed to the higher EM field enhancement associated with the two ellipses geometry (discussed in next section) in the vicinity of BIC metasurfaces. Outstanding SERS enhancement by the BIC metasurfaces was observed when we compared it with the non-patterned pure  $TiO_2$  film where no appreciable Raman scattering was detected, thereby proving the fundamental advantages offered by the BIC metasurfaces engineering technique for semiconductor SERS substrates (Fig. 5.6b). Additionally, to confirm that the SERS enhancement is indeed induced by the BIC resonance, we deactivate the resonance by rotating the BIC metasurfaces by 90°, which consequently resulted in no SERS enhancement (Fig. 5.7c), despite having the same surface area (i.e., equal amount of molecules interacting with the platform).

The SERS detection sensitivity of the two ellipses semiconductor BIC metasurfaces was further investigated by performing Raman measurements at different MB concentrations  $(10^{-5} \text{ to } 10^{-9} \text{ M})$ . It can be clearly seen that the Raman signal intensity decreased sharply with decreasing MB concentration (Figure 4c). The detection sensitivity for MB on our BIC-assisted semiconductor SERS metasurfaces was  $10^{-8}$  M, which was evaluated from the signal-to-noise ratio, in accordance with IUPAC recommendations.<sup>131</sup> We estimate the detection sensitivity of our SERS metasurfaces by considering both the processing error induced by mathematically removing the autofluorescence background signals (Fig. 5.7) and the noise level associated with our experiments, which includes detector noise, source stability, and optical alignment.<sup>21</sup> Specifically, we captured a total of n = 5 reference Raman measurements, using BIC metasurfaces that mismatched the excitation laser (633 nm) and proceeded with the same mathematical background noise removal treatment. Based on the obtained Raman spectra, we calculated the standard deviation for each reference Raman spectrum and obtained the average value for the amplitude of the noise background. The signal-to-noise ratio (STN, in dB) was calculated according to the following formula (Equation 5.2), where A<sub>signal</sub> is the



Figure 5.7: Schematic illustration of algorithm of multi-polynomial fitting for fluorescence removal. a. Detailed diagram of the modified multi-polynomial fitting method. b. The fluorescence background fitted by the modified multi-polynomial fitting method, and the extracted Raman spectrum. c. Raman spectrums of the methylene blue  $(10^{-7} \text{ M})$ were measured on the BIC metasurfaces with two ellipses geometry, which were excited by the x, and y polarized light respectively. The quasi-BIC resonance, which corresponds to an excitation laser wavelength of 633 nm, exhibits polarization dependency, specifically requiring the polarization of the incident light to be aligned along the x-axis for its activation for the SERS application. Insert: the original measured spectral lines corresponding to x and y polarized light illumination.

amplitude of the specified Raman signal (1624 cm<sup>-1</sup>) mode, and A<sub>noise</sub> is the amplitude of background noise, which can be obtained as described earlier.

$$STN = 10 \times \log_{10} \left( \frac{A_{signal}}{A_{noise}} \right)$$
(5.2)

The calculated STN of the Raman mode (1624 cm<sup>-1</sup>) with maximum amplitude is approximately 7 dB (Fig. 5.6d), which exceeds the common threshold for minimum acceptable SNR (3 dB).<sup>132</sup>

In summary, we have experimentally demonstrated significant SERS enhancement of MB on our BIC-assisted semiconductor metasurfaces, achieving detection sensitivity of  $10^{-8}$  M which is higher than the reported TiO<sub>2</sub> semiconductor SERS substrates for MB sensing ( $10^{-6}$  M).<sup>109,110</sup> To deepen our understanding of mechanisms underlying the SERS enhancement achieved through BIC-assisted semiconductor metasurfaces, we will discuss the chemical and EM enhancement mechanisms in the following section.

Hybrid effects on BIC-assisted semiconductor SERS metasurface. Enhancing the photoinduced charge transfer (PICT) effect between semiconductors and molecules is an established general strategy for achieving a high enhancement on semiconductor SERS substrates.<sup>133</sup> When the molecules are bound to the semiconductor surface by weak covalent bonds, the charge can be transferred across the interface between the semiconductor and molecule, which can generate strong Raman enhancement if the excitation frequency resonates with the PICT transition.<sup>31,107,109,134,135</sup> Specifically, when the energy levels of the semiconductor are coupled with the absorbed molecules, the charge can be transferred from the valence band states ( $|V\rangle$ ) of the semiconductor to the molecular excited states ( $|K\rangle$ ) via the transition moment,  $\mu_{VK}$ , or from the molecular ground state ( $|I\rangle$ ) to the conduction band states ( $|C\rangle$ ) of the semiconductor via the transition moment,  $\mu_{VC}$  or molecular transitions  $\mu_{IK}$ , through the Herzberg-Teller coupling term ( $h_{CK}$  or  $h_{VI}$ ), as shown in Fig. 5.9a.<sup>107,109</sup>



**Figure 5.8: Simulated absorption spectrum and corresponding electric field distribution of metasurfaces.** Which are based on the two ellipses geometry with different scaling factors

As discussed above, matching the excitation laser with the molecular resonance is pivotal for achieving high PICT rates, and consequently high SERS enhancement factors, typically by 3-4 orders of magnitude.<sup>31</sup> This enhancement can be further amplified by absorption engineering in tailored SERS substrates.



**Figure 5.9: Hybrid effect of BIC-assisted semiconductor SERS metasurface. a.** Schematic PICT transition in the semiconductor-molecule system. **b.** Left: Simulations of absorbance at the resonance ( $\omega = \omega_0$ ) for the TiO<sub>2</sub> BIC metasurfaces (two ellipses geometry) at different tilting angles ( $\theta = 1^{\circ} - 20^{\circ}$ ). Right: Enhanced absorption of TiO<sub>2</sub> BIC metasurfaces ( $\theta = 10^{\circ}$ ), aligned with the absorption of MB ( $10^{-3}$  M). **c.** Simulations of the electric field enhancement in TiO<sub>2</sub> BIC metasurfaces at various tilting angles ( $\theta = 1^{\circ} - 20^{\circ}$ ), where the maximum field enhancement is achieved at  $\theta = 10^{\circ}$ , satisfying the critical coupling condition (radiation loss equals intrinsic loss). **d.** Left: The logarithm of the gradient of the squared electric field enhancement, based on simulation results, which can be used to estimate the optical trapping effect on the MB molecule. Right: Map of the Purcell factor values for a single unit cell to evaluate the enhanced light-matter interaction in the BIC nanocavity.

Due to the diversity of molecular analytes, conventional semiconductor SERS substrates face challenges in maximizing the absorption of the excitation visiable laser source which matches the molecular resonance. To address this limitation, the absorption of the two-ellipse TiO<sub>2</sub> metasurface can be optimized to its maximum value by precisely tailoring the radiation

loss via tuning the asymmetry factor ( $\theta$ ) to match intrinsic losses, thus satisfying the critical coupling condition.<sup>136</sup> Tailoring our BIC resonance to match the molecular resonance in the UV region poses challenges due to the intrinsic loss characteristics of TiO<sub>2</sub> in that range. Therefore, we have strategically targeted the visible region, ensuring alignment with the corresponding molecules and effectively leveraging the advantageous properties of TiO<sub>2</sub> BIC metasurfaces.

We obtained the maximum absorption on the TiO<sub>2</sub> metasurface for  $\theta = 10^{\circ}$  (Fig.5.9b). After successfully achieving the maximum absorption enhancement of TiO<sub>2</sub> metasurface at the molecular resonance position, the charge-transfer resonance and molecular resonance can couple to each other by the Herzberg-Teller coupling constant,<sup>31</sup> which can further boost the PICT effect and provide stronger SERS activity of our BIC-assisted semiconductor SERS metasurface.

Even though the chemical mechanism (PICT) plays an important role in semiconductor SERS technologies, here, we also emphasize the importance of the physical mechanism brought by BIC metasurfaces to the field of semiconductor SERS substrates.

Because the SERS signal is proportional to the enhancement of the EM field,<sup>137</sup> achieving high EM field enhancements has been a long-standing challenge in the semiconductor SERS community. As already described above, strong EM field enhancement can be achieved by engineering the semiconductor TiO<sub>2</sub> substrate into a BIC metasurface, thereby benefiting from strong light localization provided by the BIC resonances. Our BIC-driven TiO<sub>2</sub> substrate produces maximum EM field enhancement at  $\theta = 10^{\circ}$  (Fig. 5.9c), where |E| represents the absolute magnitude of the local electric field with the metasurface, and |E<sub>0</sub>| represents the incident field without the structure. The highest electric field enhancement (|E|/|E<sub>0</sub>|) is found to be around 35 at the resonance frequency. Additionally, the large gradient of the squared electrical field  $F_{grad} \propto \nabla |E(r)|^2$  at the hot spots region (Fig. 5.9d) suggests a possible molecule trapping effect.<sup>138</sup> The contribution of the enhanced EM field to the amplification of radiative spontaneous emission can be explained by the Purcell effect as given below.<sup>129,139</sup>

$$F_{\rm p} = \frac{3}{4\pi^2} \left(\frac{\lambda_{\rm c}}{n_{\rm c}}\right)^3 \left(\frac{\rm Q}{\rm V_{\rm eff}}\right),\tag{5.3}$$

where  $\lambda_c$  is the resonance wavelength,  $n_c$  is the refractive index of the medium, Q is the resonance quality factor, and  $V_{eff}$  is the effective mode volume. This is the classical definition of the Purcell factor; however,  $V_{eff}$  is not straightforward to define and evaluate for open optical systems.<sup>139,140</sup>

Alternatively, the Purcell factor can also be defined as the change of the total radiated power at the frequency of the emitter.<sup>141,142</sup> The method is based on numerical simulations of the power radiated by an active dipole coupled to the resonators ( $P_{rad}$ ) divided by the radiated power of the same emitter in free space ( $P_{0,rad}$ ).

$$F_{\rm p} = \frac{P_{\rm rad}}{P_{0,\rm rad}} \tag{5.4}$$

Fig. 5.9d shows the Purcell factor map in a unit cell at the resonant frequency. Comparing the values of the Purcell factor, one can clearly see that the Purcell factor around the vertices of the ellipses is much higher ( $F_p \sim 20$ ). Hence, through mapping the Purcell factor over the whole unit cell region, we can clearly observe larger Purcell factors around the hot spot region of the BIC resonators, illustrating the strong capability of enhancing the Raman signal in this area, which highlights the active role of BIC resonance in amplifying Raman activity.

#### 5.3 Summary

We have developed TiO<sub>2</sub>-based semiconductor SERS metasurfaces and demonstrated that the synergistic integration of semiconductor materials and BIC-resonant photonic metasurfaces offers tremendous potential for advanced sensing and detection applications. We challenge the preconception that conventional semiconductor SERS substrates suffer from inefficient EM field enhancement, by showing high electric field enhancement ( $|E/E_0|^2 \approx 10^3$ ) on our BIC platform. Additionally, due to the possibility of fine-tuning the BIC resonance across a wide range, it is easy to match it with the absorption wavelength of the analyzed molecule, resulting in the enhanced PICT effect. Based on our BIC-assisted semiconductor SERS metasurface, we demonstrate a detection efficiency for the molecule MB at  $10^{-8}$  M, two-fold higher than the one reported for TiO<sub>2</sub> semiconductor SERS substrates ( $10^{-6}$  M).<sup>109,110</sup> Finally, our BIC-assisted semiconductor SERS metasurface, so f many semiconductor SERS metasurface platform circumvents the long-standing drawbacks of many semiconductor SERS substrates, such as poor spectral tunability of light absorption, weak electromagnetic field enhancement, and lack of strong light-matter interaction, and shows that improved SERS activity can be extended to multiple sensing systems with different semiconductor substrates and analytes.

## 6 Environmental permittivity-asymmetric BIC metasurfaces

The content of this chapter is published in the scientific journal Nature Communications (H. Hu, W. Lu et al. Environmental permittivity-asymmetric BIC metasurfaces with electrical reconfigurability. Nat. Commun., 2024, 15(1):7050).<sup>143</sup> As the foundation of the chapter, the peer-reviewed manuscript is used, and text elements such as words, sentences, full paragraphs, as well as graphic content and figures, are drawn directly from the publication in accordance with the Springer Nature that allows the reprinting of own contributions in theses and in accordance with the terms of the CC-BY Creative Commons Attribution 4.0 International license http://creativecommons.org/licenses/by/4.0/.

#### 6.1 Research background

In modern optical physics, permittivity is one of the principal determinants of light-matter interactions, and constitutes a crucial degree of freedom for designing and engineering optical systems and components.<sup>38–40</sup> The artificial engineering of permittivity at interfaces has led to the development of metasurfaces, revolutionizing nanophotonics by enabling subwavelength light manipulation.<sup>144–146</sup> Among versatile metasurface concepts, bound states in the continuum (BIC) metasurfaces stand out as a powerful platform for realizing high-quality resonance modes,<sup>53,147</sup> demonstrating the transformative potential of permittivity engineering in driving progress in the fields of nonlinear optics,<sup>24,148</sup> sensing,<sup>21,149</sup> and lasing.<sup>150</sup>

BICs have attracted growing attention in nanophotonics due to their strong photon localization at the nanoscale.<sup>53,147</sup> BICs are distinguished into two primary categories, each defined by the distinct mechanism through which the eigenmodes of the structures evade coupling with the radiative continuum. The first category, known as accidental BICs, arises under the Fridrich-Wintgen scenario,<sup>151</sup> where the coupling with radiative waves is suppressed through the tuning of system parameters. The second category, symmetry-protected BICs, results from the preservation of spatial symmetries, such as reflection or rotation, which inherently restrict the coupling between the bound state and the continuum due to symmetry incompatibility.<sup>52,55</sup> True symmetry-protected BICs are theoretical entities of infinitely high-quality factors and vanishing resonance width, which can turn into a *quasi*-BIC (qBIC) through the introduction of a finite coupling to the radiation continuum, resulting in a finite quality (Q) factor and an observable resonance in far-field spectra.<sup>152</sup> Such coupling can be realized through minor geometric perturbations in the symmetry of resonators within the unit cell, for instance, via changes in the length, height, relative angle, or area of the constituent resonators, etc.<sup>21,55,73,148</sup>

The generation of *q*BICs in geometrically modulated systems strongly relies on the geometrical design, and precision of current lithographic techniques.<sup>153,154</sup> Moreover, the fixed geometry of the resonators upon fabrication limits the possibilities of harnessing dynamic *q*BICs for potential applications in optical modulation,<sup>41,155</sup> dynamic sensor,<sup>156</sup> and light guiding.<sup>157,158</sup>

An alternative solution involves leveraging the isotropic permittivity of unit cell constituents to induce qBICs resonances, a strategy that circumvents the need for precise modifications of geometric asymmetry.<sup>159–162</sup> Here, the asymmetry parameter is governed by the difference in the intrinsic permittivity within the unit cell, allowing for the induction of qBIC resonances through perturbations in the permittivity symmetry of resonators.

Compared to the intrinsic permittivity of construction materials for nanostructures, the permittivity of environmental media can be more convinently engineered. In this work, we introduce the design concept that leverages environmental permittivity asymmetry to manipulate qBIC resonances. Conceptually, we can embed identical resonators into surround-ing media with different refractive indexes (RI), effectively introducing an environmental permittivity symmetry breaking to this system.

Practically, we fabricate a metasurface consisting of two identical dielectric nano-rods per unit cell, where one rod is embedded in PMMA with higher RI, contrasting with its counterpart in air. This differential RI surrounding breaks the permittivity symmetry and activates the permittivity-asymmetric *q*BICs ( $\varepsilon$ -*q*BICs), which can respond actively to further changes in RI asymmetry by altering the environment of the uncovered nanorod. The concept of the environmental  $\varepsilon$ -*q*BICs also opens the possibility of engineering dynamic BICs for active narrowband applications, such as tunable modulators, sensors, filters, and lasers.<sup>41</sup>

As an experimental demonstration, we incorporate polyaniline (PANI), an electrically active conductive polymer, which has been widely applied in active metasurfaces<sup>163–166</sup> due to its large RI variation and fast switching speed,<sup>167–170</sup> for the realization of electrically reconfigurable BICs. This integration, achieved through in-situ polymer growth on the metasurface, ensures mechanical and electrical durability, facilitating rapid and reliable switching of  $\varepsilon$ -*q*BICs states.<sup>164</sup> Specifically, we successfully engineer the radiative coupling of the  $\varepsilon$ *q*BICs by leveraging the electro-optical response of PANI, where the *q*BICs resonance in the transmittance spectra can be switched between the "ON" and "OFF" states with a fast switching speed of 18.8 ms within low operation voltage range from -0.2 V to +0.6 V. Moreover, we observe a superior cycling stability of over 1000 switching cycles without noticeable degradation. Our reconfigurable  $\varepsilon$ -*q*BICs metasurfaces platform unlocks a new degree of freedom in manipulating radiation couple of BIC systems, which is unachievable with static geometry symmetry-breaking BIC metasurfaces. This active response to the environmental perturbation exploits the synergy derived from integrating optics and electrolyte fluidics on a single chip, especially in the important visible spectral range, which can be transformative in the development of on-demand flat optics and sensing technologies.<sup>41–44</sup>

#### 6.2 Results and dicussion



Figure 6.1: Strong modulation of radiation coupling in permittivity asymmetric quasi-BIC metasurfaces under environment perturbation. a. Illustration of the transition from symmetry-protected BIC (top) to *q*BICs (middle) via two distinct approaches: conventional geometry symmetry breaking and innovative permittivity symmetry breaking within the unit cell. Schematic of embedding these two kinds of asymmetric BIC metasurfaces into different environments (bottom), where the refractive index (RI) is variable. The changing of RI can be taken as the environmental perturbation for the permittivity asymmetric case, leading to different asymmetry parameters. **b.** Schematic illustration of the BIC coupling mechanism. The symmetric geometry with two identical dielectric rods corresponds to a true BIC state, exhibiting no coupling with the radiation continuum (top). Introducing a symmetry-breaking perturbation enables coupling to the far field and transforms the bound state into qBICs (middle), which present distinct optical responses to the environmental RI changes depending on the type of symmetry breaking (bottom). c. Simulated transmittance spectra reveal that the geometry-induced qBICs only present spectral shifts when environmental RI changes, while permittivity-induced *qBICs* respond dynamically and present a transition between the 'ON' and 'OFF' states.

**Coupling of bound states to the radiation continuum mediated by environmental permittivity.** For the symmetry-protected BIC metasurfaces, the system of two identical rods in an isotropic environment represents an unperturbed, nonradiative bound state (Fig. 6.1a). Breaking the in-plane symmetry of the unit cell can induce coupling of the bound state to the radiation continuum, resulting in a *q*BIC with a finite Q factor (Fig. 6.1b). Conventionally, this coupling channel is opened through breaking the symmetry of the unit cell geometry, for instance by shortening one of the rods, removing one of the original mirror plane symmetries and giving rise to the geometry-asymmetric *quasi*-BICs (g-*q*BICs). The asymmetric factor here is proportional to the volume change of one of the resonators (Fig. 6.1a).



**Figure 6.2: Multipole analysis of permittivity-asymmetric BIC metasurfaces. a.** Simulated electric field distribution in arb.u. over the middle cut of the nanorods at the perfect BIC (without PMMA coverage) and **b.** *q*BIC (with PMMA coverage) resonant wavelengths. **c.** Transmittance spectra of *q*BIC metasurfaces, and contributions of electric dipole  $P_y$ , magnetic dipole  $M_x$ , and electric quadrupole  $Q_{yz}$  moments in arb.u. provided by the rod immersed in the PMMA (red lines), uncovered rod (blue lines), and PMMA itself (gray lines).

Alternatively, changes in environmental permittivity can disrupt the system's symmetry, thereby enabling the coupling of true BIC modes into the radiative continuum (Fig. 6.1a). In this configuration, two identical nano-rods (within the unit cell) are embedded into heterogeneous surrounding media, each in a different refractive index (RI) environment. Specifically, one nano-rod is placed in a medium with an RI of 1.5 (PMMA), while the other is in the air with an RI of 1.0 (Fig. 6.1a). This RI contrast disrupts their original destructive interference, transitioning the system from a true BIC to an  $\varepsilon$ -*q*BIC. This change makes it observable in the far field.

Here, each meta-atom acts as a Mie-resonant nanoparticle that supports various multipole modes, including electric and magnetic dipoles, as well as higher-order multipole modes.<sup>52,171</sup> The scattering efficiency of each meta-atom is influenced by the characteristics of its surrounding medium.<sup>172,173</sup> Through applying multipole analysis, we can gain more insight into the origin of qBIC in this design. The coupling coefficient of the eigenstate with the normally incident light along the z-direction with a wave vector  $k = \omega/c$  and polarization along **e** is proportional to an overlap integral.<sup>55</sup>

$$m_{\mathbf{e}} \propto \int_{\mathrm{V}_1}^{\mathrm{V}_2} \mathbf{J}(\mathbf{r}) \cdot \mathbf{e} \, \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \, \mathrm{dV},$$
 (6.1)

where  $\mathbf{J}(\mathbf{r})$  is the displacement current density,  $V_1$  and  $V_2$  are the volumes of the dielectric nanorods. In the case of symmetry-protected BIC, the resonance of the system is described by a pair of antiparallel dipole moments  $\mathbf{p}_1 = -\mathbf{p}_2$ , which obviously eliminates the coupling:  $\mathbf{m}_e \propto \mathbf{p}_1 \cdot \mathbf{e} + \mathbf{p}_2 \cdot \mathbf{e} = 0$ . Then, by introducing PMMA cladding, which breaks one of the mirror plane symmetries along the y direction, and performing multipole expansion of the coupling coefficient, one can easily obtain:

$$m_y \propto P_y - \frac{1}{c}M_x - \frac{i\omega}{6c}Q_{yz},$$
 (6.2)

where the components of electric dipole, magnetic dipole, and electric quadrupole moments are introduced. Consequently, we employ numerical simulation by COMSOL Multiphysics to compare the contributions of all terms to the coupling coefficient for the PMMA-covered model. We integrate the calculated fields separately over both nanorods and PMMA according to Supplementary Equations (3)-(5). As shown in Fig. 6.2c, the main contribution comes from nanorods due to electric dipole moments  $P_y$ . However, the role of the magnetic dipole  $M_x$ and electric quadrupole  $Q_{yz}$  moments cannot be neglected: their corresponding absolute value at *quasi*-BIC resonance is only 3 times less than the value of  $P_y$ . Regarding the PMMA coverage, its predominant contribution arises from electric dipole moments  $P_y$ . Although its peak value is almost 5 times less than that of the rods, it is enough to transform non-radiative BIC into a well-pronounced *q*BIC.

Geometry-driven *q*BICs (g-*q*BICs) with fixed asymmetry parameters after fabrication, as, e.g., determined by the geometrical differences between two resonators within the unit cell, can naturally also be modulated by surrounding RI changes, which leads only to shifts of the resonance position without direct control over the Q factor (Fig. 6.1c). Therefore, although useful in certain contexts, this mechanism does not fully exploit the potential for dynamic interaction with the surrounding environment. Alternatively, our  $\varepsilon$ -*q*BICs metasurface design directly and strongly responds to perturbations in the surrounding RI, providing significant advantages over traditional g-*q*BICs metasurfaces. Simulation spectra provide clear evidence that, as the environmental RI transitions from 1.3 to 1.7, the  $\varepsilon$ -*q*BICs metasurfaces not only exhibit a pronounced shift in the optical response but also demonstrate a unique ability to turn the qBIC resonance 'ON' and 'OFF' in the transmission spectrum (Fig. 6.1c). This behavior is directly correlated with the RI contrast between the environments of the different rods, highlighting the superior adaptability of  $\varepsilon$ -*q*BICs over traditional g-*q*BICs metasurfaces.

**Experimental realization of reconfigurable environmental**  $\varepsilon$ -*q***BICs.** To construct such  $\varepsilon$ -*q***BICs** metasurfaces, we demonstrate a multi-step nanofabrication approach to obtain a metasurface with the unit cell consisting of two identical rods embedded in distinct surrounding mediums. As shown in Fig. 6.3a, the procedure begins with the spin-coating of PMMA onto pre-fabricated symmetry-protected BIC metasurfaces. The crucial step of our fabrication strategy occurs from the second step, where the aim is to construct  $\varepsilon$ -*q*BICs metasurfaces characterized by alternating rows of TiO<sub>2</sub> nano-rods. These rows are distinctively configured, with one set embedded in PMMA and the other exposed to air, thereby introducing a deliberate permittivity asymmetry essential for  $\varepsilon$ -*q*BICs functionality. To achieve that, a well-defined lithographic marker system is applied to provide precise spatial alignment.

Subsequent development of the exposed PMMA regions results in the formation of metasurfaces where each unit cell hosts two identical nano-rods, each within a distinct medium: either PMMA or air. The successful fabrication of PMMA-based  $\varepsilon$ -*q*BICs metasurfaces is confirmed by scanning electron microscopy (SEM) in Fig. 6.3b. The precise spatial alignment between the two lithographic steps is evidenced by a distinct visual contrast in each unit cell. Specifically, the rod exposed to air displays markedly different features compared to its counterpart encased in PMMA. Here, the PMMA layer is applied with a thickness of 200 nm, sufficient to completely encase the nano-resonators which are 140 nm in height. Fig. 6.4 illustrates the influences of PMMA thickness on  $\varepsilon$ -*q*BICs in transmittance spectra, indicating that saturation gradually occurs after 140nm. Beyond PMMA, this approach is applicable to a variety of resists that offer different RI contrasts (Fig. 6.5), offering on-demand design flexibility.



**Figure 6.3: Reconfigurable permittivity-asymmetry BIC metasurfaces demonstration. a.** Workflow for the fabrication and post-fabrication tuning of the  $\varepsilon$ -*q*BIC metasurfaces. The geometrical parameters of the unit cell are: L = 321 nm, D = 107 nm, H = 140 nm, T<sub>x</sub> = T<sub>y</sub> = 403 nm. The thickness of ITO is 50 nm. **b.** SEM images of the fabricated metasurfaces corresponding to the true BICs without permittivity symmetry breaking (before PMMA coating), and the *q*BICs stemming from a permittivity asymmetry (after PMMA coating). **c.** Experimental and numerical transmittance spectra confirm the high reconfigurability of  $\varepsilon$ -*q*BICs metasurfaces through customized refilling of different environmental media (air, water, or PMMA) for tuning the refractive index contrast ( $\Delta n$ ) surrounding the media of the two rods. **d.** Color-coded simulated transmittance map of different  $\varepsilon$ -*q*BICs metasurfaces as a function of  $\Delta n$  and the wavelength. Inserts depict schematic illustrations of unit cells with two rods embedded into different materials. The orange shadowed region showcases the wide tunability of  $\Delta n$  provided by the conductive polymer PANI as a surrounding medium. The asymmetric factor of this PMMA-based  $\varepsilon$ -*q*BICs metasurface, the RI contrast ( $\Delta n$ ), can be actively reconfigured by immersing it in different environmental media, such as air ( $\Delta n = -0.5$ ), water ( $\Delta n = -0.17$ ), and PMMA ( $\Delta n = 0$ ), resulting in different optical responses as depicted in Fig. 2c. Specifically, a pronounced  $\varepsilon$ -*q*BIC was observed in the transmittance spectra with the largest asymmetric factor ( $\Delta n = -0.5$ ). When the asymmetric factor returns to zero (PMMA environment), the *quasi*-BIC transitions to the true BIC state, evidenced by the disappearance of the signal in the transmittance spectra.



**Figure 6.4:** Numerical simulation of  $\varepsilon$ -*q*BIC metasurfaces with varied *h*<sub>PMMA</sub>. a. Color-coded maps for transmittance spectra of  $\varepsilon$ -*q*BICs metasurfaces as a function of wavelength and PMMA thickness (*h*<sub>PMMA</sub>). Inserted schematic shows the unit cell of the  $\varepsilon$ -*q*BIC metasurfaces, where *h*<sub>PMMA</sub> is varied. The PMMA covers on one rod in the unit cell, while the other rod is exposed to air. **b.** Analysis of the Q factor (top) and the modulation (bottom) of the *q*BICs resonances, derived from transmittance spectra across PMMA coating thicknesses, presented as upward and downward trends.



Figure 6.5: Simulated transmittance spectra of  $\varepsilon$ -*q*BICs metasurfaces using different photoresists.a. Simulated transmittance spectra of the  $\varepsilon$ -*q*BICs metasurfaces, where one rod in the unit cell is covered by different photoresists with the thickness of 200 nm. b. The refractive indices of the e-beam photoresists with linear interpolation used in the simulation.

In contrast to static alterations of the surrounding medium, the conductive polymer (PANI) enables dynamic tailoring of the optical response of this system (Fig. 6.3d). Its RI can be electrically tailored between 1.3 (oxidized state) and 1.7 (reduced state).<sup>164</sup>



**Figure 6.6:** In-situ coating of conductive polymer on the  $\varepsilon$ -*q*BICs metasurface. **a.** Schematics of the in-situ polymer growing on the  $\varepsilon$ -*q*BICs metasurfaces in an electrochemical cell. The polymer is grown over a conductive ITO layer without PMMA covering around the rod exposed to the aqueous environment (bottom inset). A scanning voltage from -0.2 to +0.8 V with a total of 60 cycles is applied to polymerize PANI and coat on the nano-rods (right). **b.** SEM images of the  $\varepsilon$ -*q*BICs metasurfaces before (left) and after (right) in-situ polymer coating (60 cycles). Scale bar: 500 nm. **c.** The experimental in-situ transmittance measurement of  $\varepsilon$ -*q*BICs metasurfaces with different coating cycles (0, 36, 42, 48, 54, 60) of the PANI at the reduced state (left). The simulated transmittance spectra of  $\varepsilon$ -*q*BICs metasurfaces with increasing thickness (0, 40, 80, 120, 160, 200 nm) of the PANI (right). **d.** Simulated electric near-fields of individual unit cells with 200-nm thick polymer covering on one of the nano-rods. Top: the side view (yz-plane) of the electric field distribution. Bottom: the sliced planer electric field distribution (xy-plane) at different heights (0 nm, 70 nm, 140 nm) corresponding to the two-rod resonators unit cell.

**Conductive polymer in-situ coating on the**  $\varepsilon$ -*q***BICs metasurface.** As a proof of concept, an electrochemical method was utilized to in-situ grow PANI on the bare resonators, while monitoring the optical transmission response in real-time (Fig. 6.6a). The PANI coating process was initiated through electrochemical polymerization utilizing an aqueous electrolyte. Here, the pre-deposited ITO layer underneath the metasurface functioned as the working electrode, complemented by an Ag/AgCl reference electrode and a Pt wire as the counter electrode,
respectively. The polymerization was precisely controlled via a linear scanning voltage from -0.2 V to 0.8 V at a rate of a scanning rate of 25 mV/s. As PMMA covers every second row (odd rows) of the nano-rod resonators, blocking the electrolyte access, resonators in the complementary (even) rows remain exposed to the aniline electrolyte and accessible for a row-selective PANI coating. After 60 cycles of coating, the as-coated PANI achieved a thickness comparable to that of the PMMA (200 nm). The successful integration of PANI onto the metasurface was confirmed through SEM in Fig. 6.6b, which indicates the preferential PANI coating on the even rows of resonators, while the PMMA remains covered on the odd rows.

This in-situ polymer coating approach allows for the real-time observation of the metasurfaces' optical response under continuous environmental perturbation throughout the PANI coating process. As shown in Fig. 6.6c, increasing PANI thickness on the PMMA-based  $\varepsilon$ -qBICs metasurfaces induces a red shift in the *q*BICs resonance alongside a reduction in modulation depth. Additionally, the asymmetry factor,  $\Delta n$ , changes from -0.16 (between  $n_{\text{electrolyte}}$  = 1.34 and  $n_{\text{PMMA}} = 1.5$ ) to 0.2 (between  $n_{\text{PANI}} = 1.70$  and  $n_{\text{PMMA}} = 1.5$ ), and the intrinsic loss of PANI reduces the Q factor of quasi-BIC resonance. These trends agree well with the numerical simulation, indicating a consistent optical response to the polymer's accretion. Deviations from simulated transmittance spectra primarily stem from the inhomogeneity in the morphology of the coated PANI, which can act as a limit for such configurations. After completion of the PANI coating process, the system maintains its *q*BICs state, as evidenced by the  $\Delta n$  (asymmetric factor) of 0.2 between PANI (n = 1.7 in the reduced state) and PMMA (n = 1.5). Simulated electric field distribution reveals the asymmetric mode distribution across the two TiO<sub>2</sub> nano-rods within each unit cell (Fig. 6.6d). By analyzing Q factors derived from the transmittance spectra of simulations with increasing thickness of PANI, and correlating these with data from experimental in-situ PANI coating cycles, we explore the potential relationship between PANI thickness and its growth cycles (Fig. 6.8).

After integrating PANI into PMMA-based  $\varepsilon$ -*q*BICs metasurfaces, the system's dynamic reconfigurability can be further explored by electrically adjusting PANI's refractive index.

Electrically reconfigurable  $\varepsilon$ -*q*BICs based on polymer states switching. Leveraging the advanced electrochemical tunability of PANI, this conductive polymer stands out for its ability to undergo reversible transitions between its reduced and oxidized states (Fig. 6.7a) with large-scale variation in RI.<sup>164</sup> Different RI contrasts between PANI and PMMA ( $n_{PMMA} = 1.5$ ) can control the radiation loss of this system. The extinction coefficient of PANI increases with the applied voltages,<sup>164</sup> which will also interact with  $\varepsilon$ -*q*BICs resonance as the intrinsic loss channel.



**Figure 6.7: Electrical tuning optical properties of**  $\varepsilon$ -*q***BICs metasurfaces. a.** Schematics illustrating the electrical tuning of the optical response of the  $\varepsilon$ -*q***BICs.** The inset shows the voltage-time profile for tuning the intermediate states of the PANI. **b.** Transmittance spectra at various applied voltages demonstrate the transition of  $\varepsilon$ -*q***BICs** between high (ON) and low (OFF) transmittance modulation. **c.** Time-resolved normalized modulation response of the electrical switching of the  $\varepsilon$ -*q***BICs. d.** Durability analysis of the electrical switching of the  $\varepsilon$ -*q***BICs.** The upper graph presents the normalized modulation maintenance of the ON/OFF states for over 1000 switching cycles. The lower graphs quantify the variations in the Q factor and modulation of the  $\varepsilon$ -*q***BICs** at the ON state for every 10 switching cycles in the 1000-cycle test.

The  $\varepsilon$ -*q*BICs resonance modulation strength can be effectively tailored by applying various voltages from -0.2 V to +0.6 V (Fig. 6.7b). Specifically, the  $\varepsilon$ -*q*BIC resonance modulation strength decreases together with slight blueshifts in wavelength, which is in agreement with our design predictions. We define the  $\varepsilon$ -*q*BICs with the highest and lowest transmittance

modulation as ON and OFF states, corresponding to the applied voltages of -0.2 V and +0.6 V, respectively. We evaluate the switching speed of our  $\varepsilon$ -*q*BICs metasurfaces by measuring the time-resolved transmittance response while modulating the applied voltages between the ON (-0.2 V) and OFF (+0.6 V) states, as presented in Fig. 6.7c.



**Figure 6.8: Analysis of PANI thickness during the in-situ coating process.a.** Q factor analysis for the PANI thickness in the simulation and the PANI coating cycle in the experiment. **b.** The fitted PANI thickness for different coating cycles. The polymer thickness fitting is based on the Q factors obtained in the simulation. **c.** Electrochemical current-voltage diagram recorded during the in-situ PANI coating process. **d.** Electrochemical integral current for different coating cycles during the in-situ coating process. **e.** Comparison of the fitted PANI thickness and the integral current at different coating cycles. Inserted figure shows the analysis of the discrepancy between the *Q*-factor-based fitted PANI thickness and the integral current.

The rise time and fall time are defined as the time required for the *q*BIC modulated intensity to rise or fall between the 10% and 90% switching window for switch-on and switch-off processes, respectively, where the modulated intensity is defined as the normalized amplitude of the qBIC resonances. The rise time and fall time are measured to be 12.2 ms and 18 ms, respectively, which are mainly limited by the intrinsic material property of the PANI electro-optical dynamics.<sup>164</sup> To demonstrate the durability and repeatability of the electrical switching, we monitor the reconfigurable  $\varepsilon$ -*q*BICs on our system for 1000 switching cycles. It is clearly observed that the  $\varepsilon$ -*q*BICs at the ON and OFF states remain fully reversible even after 1000 switching cycles (Fig. 6.7d). The stable switching performance can be potentially further extended to 10<sup>7</sup> switching cycles.<sup>174</sup> The key characteristic supporting excellent durability is that, when electron injection or extraction takes place by voltage application, the highly conductive PANI can redistribute delocalized  $\pi$ -electrons along the polymer chain without structural degradation.<sup>175,176</sup> We further statistically confirm the consistency of the Q-factor and modulation of the  $\varepsilon$ -*q*BICs at the ON states of 100 cycles evenly sampling from the total 1000 switching cycles. Both plots show that the bulk of the data is concentrated around the median, indicating the stability and consistency of the  $\varepsilon$ -*q*BIC metasurfaces during the electrical switching processes.

#### 6.3 Summary

Our research introduces a new approach for engineering BIC metasurfaces via permittivityinduced symmetry breaking in the surrounding environment of the resonators, a significant departure from traditional, geometry-reliant methods. This strategy not only overcomes the inherent constraints of geometric asymmetry manipulation but also unlocks the flexibility of post-fabrication control over the coupling to the radiation continuum, a governing aspect of BIC physics. Additionally, our  $\varepsilon$ -*q*BICs metasurface design showcases enhanced optical response to the refractive index perturbations of the surrounding medium. In contrast to straightforward spectral shifts, our  $\varepsilon$ -qBICs metasurface concept opens possibilities to finely modulate between quasi and true BIC states. We have experimentally demonstrated the generation of the  $\varepsilon$ -*q*BICs from specifically designed metasurfaces, where the coupling channel of BIC to continuum radiation is established by the embedding of two identical TiO<sub>2</sub> nano-rods into surrounding media with different permittivity (such as PMMA and air). The ε*q*BICs concept is further exploited for realizing electrically reconfigurable BICs by integrating a conductive polymer into our metasurfaces. The advantageous electro-optical properties of PANI endow the  $\varepsilon$ -*q*BICs with excellent electrical reconfigurability. By tuning the optical properties of PANI, the ε-*q*BICs can be dynamically switchable, exhibiting fully reconfigurable *q*BICs with high modulation contrast. Additionally, we have demonstrated the electrical switching performance of the reconfigurable  $\varepsilon$ -*q*BICs, with fast switching speed (12.2 ms and 18 ms for switch-on and switch-off processes, respectively), and excellent switching durability even after 1000 cycles. Our design is compatible with a range of active materials beyond PANI, including liquid crystals, phase change materials, and transparent conducting oxides. The permittivity-induced BIC metasurfaces unlock an additional degree of freedom for manipulating and engineering BIC states, thereby laying the groundwork for on-demand integrated electro-optical devices.

# 7

### **Conclusion and Outlook**

This thesis has explored and demonstrated the multifunctionality of metasurfaces empowered by Bound States in the Continuum (BICs), establishing their transformative potential across three key application areas: photocatalysis, surface-enhanced Raman spectroscopy (SERS), and dynamic electrical tunability. Through a combination of theoretical insights, advanced fabrication techniques, and rigorous optical characterization, the research has successfully shown how BIC metasurfaces can address long-standing challenges in these fields.

**Photocatalytic metasurfaces.** In this research, we demonstrate how semiconductor  $TiO_{2-x}$  metasurfaces, leveraging BICs, address critical limitations in photocatalytic applications. Through precise radiative loss engineering, these metasurfaces achieved optimized light absorption and strong electric field enhancement, significantly enhancing visible light photocatalysis. Notably, the work introduced a novel paradigm by achieving optimal absorption for materials with low extinction coefficients, countering traditional preferences for highly absorptive semiconductors. These advances open pathways for applications in solar-to-electric energy conversion, where traditional trade-offs between thickness and absorption efficiency are overcome.

**SERS metasurfaces.** Challenges associated with traditional plasmonic surface-enhanced Raman spectroscopy (SERS) platforms, such as low reproducibility and poor thermal stability, have been addressed in this work through the use of TiO<sub>2</sub>-based BIC-driven semiconductor metasurfaces. By leveraging the tunability of BIC resonances over a wide spectral range, this approach achieved an enhanced photoinduced charge transfer (PICT) effect, resulting in a detection efficiency for the molecule MB at  $10^{-8}$  M, two-fold higher than the one reported for TiO<sub>2</sub> semiconductor SERS substrates ( $10^{-6}$  M).<sup>109,110</sup> More importantly, this BIC-assisted semiconductor SERS metasurface platform circumvents the long-standing drawbacks of many semiconductor SERS substrates, such as poor spectral tunability of light absorption, weak electromagnetic field enhancement, and lack of strong light-matter interaction, and shows that improved SERS activity can be extended to multiple sensing systems with different semiconductor substrates and analytes.

Active metasurfaces. Here we introduce a novel concept of permittivity-induced quasi-BICs ( $\varepsilon$ -*q*BICs). The study demonstrated that these metasurfaces enable precise modulation between quasi and true BIC states, achieved through symmetry-breaking strategies involving surrounding refractive index perturbations. Furthermore, the integration of conductive polymers such as PANI imparts fast switching speeds, with 12.2 ms for switch-on and 18 ms for switch-off processes, alongside exceptional durability, maintaining performance even after 1,000 switching cycles. Importantly, the design is compatible with a wide range of active materials beyond PANI, including liquid crystals, phase-change materials, and transparent conducting oxides. By unlocking an additional degree of freedom for manipulating and engineering BIC states, permittivity-induced BIC metasurfaces establish a robust foundation for the development of on-demand integrated electro-optical devices.

Despite the advancements made in this thesis, certain limitations remain. For photocatalysis applications, future studies can explore the coupling between BIC modes and interband transitions in photocatalytic semiconductors, which could further improve charge carrier dynamics and reaction efficiencies. Additionally, extending BIC-enhanced light absorption to novel materials such as perovskites or 2D materials could enable highly efficient photocatalytic systems with tailored absorption spectra. From a technological perspective, large-area BIC metasurfaces can be utilized for water splitting and other fundamental photocatalytic reactions, enabling the production of valuable chemical compounds.

For SERS applications, exploring dual-BIC resonance metasurfaces that simultaneously enhance both the incident laser excitation and the target Raman emission wavelengths could further amplify the SERS signal. This approach would optimize light-matter interactions at both key spectral regions, significantly improving detection sensitivity. On the application side, these BIC-driven metasurfaces could be integrated into microfluidic platforms, transforming them into portable, lab-on-a-chip sensors for highly sensitive molecular diagnostics in healthcare, environmental monitoring, and chemical analysis.

Based on the permittivity asymmetric BIC metasurfaces, further exploration of permittivitydriven BIC tunability in nonlinear and quantum optical systems could lead to new regimes of strong light-matter interaction, potentially enabling low-threshold optical bistability or ultrafast all-optical switching. Additionally, studying the coupling between  $\varepsilon$ -qBICs and excitonic materials could open new opportunities in exciton-polariton physics. From a technological standpoint, the demonstrated fast and durable tuning capabilities of  $\varepsilon$ -qBIC metasurfaces make them promising candidates for integration into high-speed optical modulators and tunable filters for next-generation telecommunication systems. Moreover, extending this concept to mid-infrared and terahertz frequencies could enable dynamic infrared imaging and sensing applications, such as adaptive thermal camouflage or smart windows that regulate infrared radiation in real time.

Overall, this thesis has established BIC-driven metasurfaces as a cornerstone for the next generation of photonic devices, highlighting their potential future innovations in multifunctional metasurface technologies in fields ranging from energy and healthcare to information processing and beyond.

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