Optical Properties of Nanostructures: from Random to Periodic

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ABSTRACT

Optical Properties of Nanostructures: from Random to Periodic

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Nanostructures can change optical properties of materials such as optical dispersion and transmission and reflection via scattering and interference. By engineering the degree of order in various dielectric and metallic nanostructures, I demonstrate that light propagation, spontaneous emission, localization and lasing can be controlled.

In the first part of this thesis (chapter 1), the basic concepts of optical scattering and emission in nanostructures are introduced. Fundamental properties of photonic crystals are presented including photonic bandgaps and dispersion of light. Physical properties of surface plasmons are also briefly described.

In the second part of the thesis (from chapter 2 to chapter 5), I describe experimental investigations and theoretically analyze optical properties of photonic crystals, quasi-ordered dielectric structures in avian feathers and random metal structures. We demonstrate,

• room temperature lasing in the near-ultraviolet (UV) frequency in ZnO inverse opal photonic crystals
• spontaneous emission enhancement caused by the frozen mode at a stationary inflection point of a dispersion curve in ZnO inverse opal photonic crystals
• structure color creation by single and double scattering from the quasi-ordered structures of avian feathers
• propagation and localization of surface plasmons in semi continuous metal films

The last part of the thesis (chapter 6), is the conclusion.
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Introduction

1.1. Light Scattering

Light Scattering is a physical process where light is forced to deviate from a straight trajectory by heterogeneity in the medium through which they pass. Everything except a vacuum is heterogeneous in some sense. Even in media that we usually consider to be homogeneous, it is possible to distinguish the individual heterogeneities on the nanometer scale. Therefore, all media scatter light. In fact, many phenomena that are not usually referred to as scattering phenomena such as specular reflection and refraction at optically smooth interfaces, are ultimately the result of scattering.

1.1.1. Single Particle Scattering

The simplest scattering is the interaction of light with a single particle which is embedded in an otherwise homogeneous medium. By homogeneous it is meant that the atomic or molecular heterogeneity is small compared with the wavelength of the incident light.

1.1.1.1. scattering cross section. In light scattering, the concept of a cross section is used to express the likelihood of interaction between a particle and light. Differential scattering cross section and total scattering cross section are most commonly used.
A differential scattering cross section is defined by power radiated in the observation direction per unit solid angle per unit incident flux.

\[
\frac{d\sigma}{d\Omega} = \frac{\text{radiated power}}{\text{incident flux} \times \text{solid angle}}.
\]

A total scattering cross section is the integral of the differential cross section on the whole sphere of observation.

\[
\sigma = \int d\Omega \frac{d\sigma}{d\Omega}.
\]

1.1.1.2. Rayleigh Scattering. Rayleigh scattering is the elastic scattering of light or other electromagnetic radiation by particles much smaller than the wavelength \(\lambda\) of the light [1]. Thus, scattering has an electric dipole-like character. In Rayleigh scattering the scattered field has the same polarization as the incident wave.

Total scattering cross section is given by,

\[
\sigma = \frac{8\pi}{3} k^4 a^6 \left(\frac{m^2 - 1}{m^2 + 2}\right)^2,
\]

where \(m\) is the refractive index, \(k = 2\pi/\lambda\), and \(a\) is the radius of a particle.

The \(k^4\) dependence of the scattering is a characteristic in the long-wavelength limit of scattering. This dependence on frequency is known as Rayleigh’s law. Blue sky is caused by Rayleigh scattering off the molecules in the atmosphere [2].

1.1.1.3. Mie Scattering. Mie theory is an exact analytical solution of Maxwell’s equations for an isotropic, homogeneous, dielectric sphere. It is equally applicable to spheres
of all sizes, refractive indices and for scattering at all wavelengths \[3\]. The total Mie scattering cross section is given by \[4\],

\[
\sigma = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n + 1)(|a_n|^2 + |b_n|^2)
\]

where \( \psi_n \) and \( \eta_n \) are related to spherical Bessel functions. The prime indicates the first derivative with respect to \( r \). The majority of the effort in carrying out Mie calculations is in determining the coefficients \( a_n \) and \( b_n \).

Mie scattering can be used for a spherical particle whose size is comparable with the wavelength. In Mie scattering, the scattering phase function has local maxima in several specific scattering directions. The main scattering direction is the forward direction (with a narrow forward scattering angle). The laws describing the total scattered intensity as a function of the incident wavelength and particles properties are more complex than for Rayleigh scattering. The \( 1/\lambda^4 \) dependence of the total scattered intensity in the Rayleigh case is not true in the general case for the Mie theory. These laws depend on the radius, the refractive index and the absorption of the particle. This complexity is due to resonances with the cavity modes inside the sphere. For a linear incident wave, the polarization of the scattered wave is not necessarily linear as in the Rayleigh case. It will depend on the direction and will be elliptic in the general case.
1.1.2. Multiparticle Scattering

Particles in a collection are electromagnetically coupled: each particle is excited by the external field and the resultant field scattered by all the other particles, but the field scattered by a particle depends on the total field to which it is exposed. There are two types of scattering.

- Independent scattering: If there is no interference between the wave scattered by each particle, scattering is independent. The global scattered intensity is the sum of the intensities scattered by each particle. As an approximative criterium, it can be considered that independent scattering occurs when the distance between particles is more than 3 times larger than the radius of one particle (for few-wavelength radius particles). [6][7]

- Dependent scattering: If the scattering particles are close together, scattering is dependent. Scattered waves interfere. [6] The global scattered intensity must be computed as the square of the sum of electric fields.

1.1.2.1. Scattering Mean Free Path. A mean free path is a characteristic length scale describing the scattering process. For instance, the scattering mean free path $\ell_s$ is defined as the average distance between two successive scattering events. For a random system composed of monodisperse scatters with density $\rho$, the scattering mean free path is [5],

\[
\ell_s = \frac{1}{\rho \sigma},
\]  

(1.5)

when scattering of individual particles is independent of each other. By the size of the system $L$ and $\ell_s$, we can separate scattering regimes.
1.1.2.2. **Single Scattering.** If \( \ell_s > L \), single scattering is dominant. The number of particles are linearly proportional to scattered intensity. This simple proportionality to the number of particles holds only if the radiation to which each particle is exposed is essentially incident light.

1.1.2.3. **Multiple scattering.** If \( \ell_s < L \), multiple scattering will be dominant. In this case, each particle scatters not only the incident light but also the light scattered by the others. Resonances between particles can affect the scattered light profiles. Several criteria can be used to identify multiple scattering processes. There is multiple scattering when an increase in the number of particles does not induce the same increase of the scattered intensity. Multiple scattering also often causes a decrease in the degree of polarization.

### 1.2. Structural Characterization

The differential scattering cross section for elastic scattering is given by [8],

\[
\frac{d\sigma}{d\Omega} = N|f(\vec{q})|^2 S(\vec{q})
\]

where \( N \) is the number of particles, \( \vec{q} \) is the spatial wave vector, \( f(\vec{q}) \) is the form factor which depends only on the properties of individual particles, and \( S(\vec{q}) \) is the structure factor which can be determined solely by particle positions.

An expression of \( S(\vec{q}) \) can be obtained in terms of the particle density function \( \rho(\vec{r}) = \sum_j \delta(\vec{r} - \vec{r}_j) \) where \( \vec{r}_j \) is the position vector of individual particles.

\[
S(\vec{q}) = \frac{1}{N} |\rho(\vec{q})|^2
\]
where $\rho(q)$ is the Fourier transform of the density function $\rho(r)$. $|\rho(q)|^2$ becomes the Fourier transform of the density-density correlation function $C_\rho(\Delta r) = \int \rho(r)\rho(r+\Delta r) d^3r$. Thus $S(q)$ can be expressed in terms of the density-density correlation function.

There are several classes of structures in solids.

- **Periodic structure**: Particle positions have translational periodicity: positions repeat in space in a regular array. One example is a crystal at $0^\circ K$.

- **Short-range ordered structure**: Translational periodicity is absent. However, particles are not randomly distributed in space. The distance between nearest-neighbor particles is the same. One example is liquid.

- **Long-range ordered structure**: Particles are located within a certain range of translational periodicity. One example is a crystal at room temperature.

- **Random structure**: There is no short or long range order. Particles are randomly distributed. One example is gas.
1.3. Photonic Crystals

Photonic crystals are periodic dielectric structures that have a band gap that forbids propagation of light within a certain frequency range. This property enables one to control light with amazing facility and produce effects that are impossible with conventional optics.

![Figure 1.1. Photonic Crystals: (a) 1d, (b) 2d, (c) 3d.](image)

Research on photonic crystals began in 1987 when Yablonovitch first suggested that a three-dimensional periodic dielectric structure could be made to possess a completely forbidden frequency gap in all directions. His idea was to use the photonic crystal to inhibit the spontaneous emission of atoms by overlapping the frequency band gap with the atomic emission frequency. [9] In the same year, John independently suggested that a three-dimensional dielectric superlattice array could induce strong localization of photons. [10]

1.3.1. Bragg Diffraction

The fundamental mechanism determining the properties of photonic crystals is due to interference, and is called Bragg diffraction.
When a monochromatic light is incident on the surface of a photonic crystal, it is partially reflected at each of these planes, which act as mirrors. The reflected rays interfere (Fig. 1.2). The interference is constructive only if the difference between the paths of any two consecutive rays is an integral multiple of the wavelength. That is,

\[ 2d \cos \theta = n\lambda \]

Figure 1.2. Constructive interference of a wave scattered by a family of planes with lattice spacing \( d \) occurs at angle \( \theta \) when the difference of path lengths of successive reflections \( (2d \cos \theta) \) is equal to an integer number of wavelengths \( \lambda \).
1.3.2. Band Structure

The photonic band gap (PBG) is essentially the gap between the air-line and the dielectric-line in the dispersion relation of a photonic crystal (PhC). To design PhCs, it is essential to engineer the location and size of the bandgap. This is done by computational modeling, e.g. via the plane wave expansion method and the Layer KKR method.

1.3.2.1. Plane Wave Expansion Method. The plane wave expansion method is a direct adaptation of electronic band structure methods, and allows optimal account of the crystal lattice symmetry in determining the electromagnetic properties of a photonic crystal. We start from Maxwell’s equations for an inhomogeneous linear dielectric medium without charges or currents

\[
\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}, \quad \vec{\nabla} \cdot \vec{D} = 0
\]

\[
\vec{\nabla} \times \vec{H} = \frac{\partial \vec{D}}{\partial t}, \quad \vec{\nabla} \cdot \vec{B} = 0
\]

(1.9)

together with the constitutive relations for an isotropic and non-magnetic dielectric composite.

\[
\vec{D} = \varepsilon_0 \varepsilon(\vec{r}) \vec{E}
\]

\[
\vec{B} = \mu_0 \vec{H}
\]

(1.10)

The master equation describing photonic crystals can be easily obtained from Maxwell’s equations.
\begin{equation}
\vec{\nabla} \times \left( \frac{1}{\varepsilon(\vec{r})} \vec{\nabla} \times \vec{H}(\vec{r}) \right) = \left( \frac{\omega}{c} \right)^2 \vec{H}(\vec{r})
\end{equation}

Where $\vec{H}(\vec{r})$ is the magnetic field and $\varepsilon(\vec{r})$ the dielectric constant \[11\].

The master equation can also be expressed in terms of electric field. However, the dielectric constant has a periodic modulation which is absent for magnetic permeability. Thus, equation with $\vec{H}$ field has an advantage when we solve the master equation. Another advantage is that the operator $\vec{\nabla} \times \frac{1}{\varepsilon(\vec{r})} \vec{\nabla} \times$ is Hermitian \[12\]. Hermitian operators have real eigenvalues and orthogonal eigenfunctions. Thus it is clear that eigenvalues $\omega^2/c^2$ are real.

In a periodic structure, $\varepsilon(\vec{r})$ has translational symmetry. If we define the lattice constant $\vec{G}$, then $\varepsilon$ becomes a periodic function with period $\vec{G}$

$$\varepsilon(\vec{r} + \vec{G}) = \varepsilon(\vec{r})$$

The eigenfunction of the periodic potential becomes a Bloch function. In Eq. \[11\], $\varepsilon(\vec{r})$ acts like a potential. Since $\varepsilon(\vec{r})$ is periodic, eigenfunctions of the master equation become Bloch functions \[13\],[14],[15\].

$$\vec{H}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} \vec{h}(\vec{r}),$$

where $\vec{h}(\vec{r} + \vec{G}) = \vec{h}(\vec{r})$.

One way to solve Eq. \[11\] is to use plane wave expansion. One can expand the dielectric constant and $\vec{H}$ field with a sum of plane waves \[16],[17\].
\[ \eta(\vec{r}) = \frac{1}{\varepsilon(\vec{r})} = \sum_G \eta_G e^{i\vec{G} \cdot \vec{r}} \]

\[ \vec{H}_{n,\vec{k}}(\vec{r}) = \sum_G \vec{h}_{n,\vec{k}}^{G} e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} \]

where \( n \) is the band index. At the edge of the Brillouin zone, the dispersion relation \( \omega_n(\vec{k}) \) folds back. Thus, the dispersion relation has bands.

The master equation becomes,

\[ \sum_G \eta_{G-G'}(\vec{k} + \vec{G}) \times [(\vec{k} + \vec{G}) \times \vec{h}_{n,\vec{k}}^{G}] = \frac{\omega_n(\vec{k})^2}{c^2} \vec{h}_{n,\vec{k}}^{G'} \]

Eq. 1.13 is an infinite set of linear eigenvalue equations. In a numerical calculation of the eigenvalues \( \omega_n(\vec{k})^2 / c^2 \), the infinite matrix is reduced to a finite size since a numerical calculation of infinite size is impossible. The matrix dimension may be further reduced by using the constraint \( \vec{\nabla} \cdot \vec{H} = 0 \) [18].

Figure 1.3(b) shows the dispersion relation of a square lattice. The dispersion is modified by a periodic structure. At about \( \omega a/2\pi c = 0.3 \), a bandgap is created.

The gap width is determined by the strength of interaction between the incident and Bragg scattered waves. The center frequency of the gap for the lowest order diffraction can be well approximated using Bragg’s law.

\[ \omega_c = \frac{\pi c}{d\sqrt{\varepsilon_{eff}}} \]

where \( d \) is the distance between adjacent layers of scatterers, \( \varepsilon_{eff} \) is the effective dielectric constant, and \( c \) is the speed of light.
Figure 1.3. Dispersion relation of a square lattice structure. Dispersion is calculated for TE mode ($H_z$ is parallel to cylinder axis). A band gap is created at $\omega a/2\pi c = 0.8$, where $a$ is lattice constant. $c$ is speed of light. (a) square lattice structure (b) dispersion relation.

When there is a small perturbation $\Delta \varepsilon$ of the dielectric function, the frequency shift is [19],

(1.15) \[ \Delta \omega \approx -\frac{\omega}{2} \frac{\int d^3\vec{r} \Delta \varepsilon(\vec{r}) |\vec{E}(\vec{r})|^2}{\int d^3\vec{r} \varepsilon(\vec{r}) |\vec{E}(\vec{r})|^2} \]

The band gap width $\psi$ is,

(1.16) \[ \psi = \frac{\Delta \omega}{\omega_c} \approx \frac{1}{2\varepsilon_{eff}} \left( \frac{\int d^3\vec{r} \Delta \varepsilon(\vec{r}) |\vec{E}_{top}(\vec{r})|^2}{\int d^3\vec{r} |\vec{E}_{top}(\vec{r})|^2} - \frac{\int d^3\vec{r} \Delta \varepsilon(\vec{r}) |\vec{E}_{bot}(\vec{r})|^2}{\int d^3\vec{r} |\vec{E}_{bot}(\vec{r})|^2} \right) \]
where \( \Delta\varepsilon(\vec{r}) = \varepsilon(\vec{r}) - \varepsilon_{\text{eff}}, \) \( \vec{E}_{\text{top}}(\vec{r}) \) is the electric field distribution of the top band edge mode, and \( \vec{E}_{\text{bot}}(\vec{r}) \) is the distribution of the bottom band edge mode.

For dielectric structures, the photonic strength can be increased in three ways according to Eq. 1.16

1. increasing the difference in dielectric constant \( \Delta\varepsilon. \)
2. decreasing the volume averaged dielectric constant \( \varepsilon_{\text{eff}}. \)
3. highly concentrating \( \vec{E}_{\text{bot}}(\vec{r}) \) in the dielectric of larger \( \varepsilon \) (high index material), and/or \( \vec{E}_{\text{top}} \) in the dielectric of smaller \( \varepsilon \) (low index material).

In figure 1.4 and figure 1.5 all the parameters are exactly the same. The refractive index of the high index material is 2.0. That of the low-index material is 1.0. A face-centered cubic (FCC) structure (opal structure) is used. In figure 1.4 low index material forms spheres. In figure 1.5 high index material forms spheres. This difference gives different \( \varepsilon_{\text{eff}}. \) According to Eq. 1.16 the band gap is wider for lower \( \varepsilon_{\text{eff}}. \)
Figure 1.4. (a) Inverse opal structure. FCC array of air spheres in dielectric with $n = 2$. (b) Band structure. Since refractive index contrast is less than 2.8, there is no full band gap. Only pseudo gap exists. Its relative width is 14.7%.
Figure 1.5. (a) Opal structure. FCC array of dielectric spheres in air. (b) band structure. All structure parameters are the same as those in Fig. 1.4. The fundamental gap is a pseudogap of relative width is 7.4%.
1.3.2.2. Layer KKR method. The Layer KKR (Korringa-Kohn-Rostoker) method is different from the plane wave expansion method. In the Layer KKR method, a frequency is selected and one obtains the eigenmodes of the crystal for this frequency. Therefore, these methods are ideally suited for photonic crystals consisting of strongly dispersive materials. [20][21]

The crystal is considered as a succession of layers (slices) parallel to a given crystallographic plane of the crystal. Each layer has the same two-dimensional (2D) periodicity (that of the chosen crystallographic plane) described by a 2D lattice

\[ \vec{R}_n = n_1 \vec{a}_1 + n_2 \vec{a}_2, \]  

where \( \vec{a}_1 \) and \( \vec{a}_2 \) are primitive vectors of the 2d lattice, \( n_1 \) and \( n_2 \) are integer numbers.

We may number the sequence of layers which constitute the infinite crystal, extending from \( z = -\infty \) to \( z = +\infty \). The \((N + 1)\)th layer is obtained from the \(N\)th layer by a primitive translation to be denoted by \( \vec{a}_3 \). Obviously, \( \vec{a}_1, \vec{a}_2, \) and \( \vec{a}_3 \) constitute a basis for the 3D lattice of the infinite crystal.

A 2D reciprocal lattice corresponding to \( \vec{a}_1, \vec{a}_2 \) is described by

\[ \vec{g} = m_1 \vec{b}_1 + m_2 \vec{b}_2, \]  

where \( m_1 \) and \( m_2 \) are integers. The reduced \((k_x, k_y)\)-zone associated with the above, which has the full symmetry of the given crystallographic plane is known as the surface Brillouin
We define a corresponding 3D reduced $\vec{k}$-zone as follows

\begin{equation}
\vec{k}_\parallel = (k_x, k_y) \text{ within the SBZ}
\end{equation}

\begin{equation}
-|\vec{b}_3|/2 \leq k_z \leq |\vec{b}_3|/2
\end{equation}

where $\vec{b}_3 = 2\pi \vec{a}_1 \times \vec{a}_2 / (|\vec{a}_1| \cdot (\vec{a}_2 \times \vec{a}_3))$ is normal to the chosen crystallographic plane. The reduced $k$-zone defined by Eq. (1.19) is of course completely equivalent to the commonly used more symmetrical Brillouin zone (BZ), in the sense that a point in one of them lies also in the other by a vector of the 3D reciprocal lattice. Let us now assume that we have a photonic crystal consisting of nonoverlapping spherical scatterers in a host medium of a different dielectric constant and let us look at the structure as a sequence of layers of spheres with the 2D periodicity of Eq. (1.17). A Bloch wave solution, of given frequency $\omega$ and given $k_\parallel$, of Maxwell’s equations for the given system has the following form in the space between the $N$th and the $(N + 1)$th layers (we write down only the electric-field component of the EM wave):

\begin{equation}
\vec{E}(\vec{r}) = \sum_{\vec{g}} \{ \vec{E}_{\vec{g}}^+(N) \exp[i\vec{K}_{\vec{g}}^+ \cdot (\vec{r} - \vec{A}_N)] + \vec{E}_{\vec{g}}^-(N) \exp[i\vec{K}_{\vec{g}}^- \cdot (\vec{r} - \vec{A}_N)] \},
\end{equation}

with

\begin{equation}
K_{\vec{g}}^\pm = \left( k_\parallel + \vec{g}, \pm q^2 - (k_\parallel + \vec{g})^2 \right)^{1/2},
\end{equation}

where $q$ is the wavenumber, and $A_N$ is an appropriate origin of coordinates in the host region between the $N$th and the $(N + 1)$th layers. A similar expression (with $N$ replaced
by \(N+1\) gives the electric field between the \((N+1)\)th and the \((N+2)\)th layers. Naturally the coefficients \(\vec{E}^-_{g}(N+1)\) are related to the \(\vec{E}^\pm_{g}(N)\) coefficients through the scattering matrices of the \(N\)th layer of spheres. We have:

\[
\begin{align*}
E^-_{gi}(N) &= \sum_{g'g''} Q^IV_{gi,g'i'j'} E^-_{g'i'}(N+1) + \sum_{g'g''} Q^II_{gi,g'i'} E^+_{g'i'}(N) \\
E^+_{gi}(N+1) &= \sum_{g'g''} Q^I_{gi,g'i'} E^+_{g'i'}(N) + \sum_{g'g''} Q^II_{gi,g'i'} E^-_{g'i'}(N+1)
\end{align*}
\]

where \(i = x, y, z\), and \(Q\) are appropriately constructed transmission/reflection matrices for the layer. [23][24][25]

A generalized Bloch wave, by definition, has the property

\[
\begin{align*}
\vec{E}^\pm_{g}(N+1) &= \exp(ik \cdot \vec{a}_3) \vec{E}^\pm_{g}(N) \\
k = (k||, k_z(\omega, k||))
\end{align*}
\]

where \(k_z\) may be real or complex. Substituting equation 1.23 into equation 1.22 we obtain,

\[
(1.24)
\begin{pmatrix}
Q^I & Q^II \\
-[Q^IV]^{-1}Q^IIIQ^I & [Q^IV]^{-1}[I - Q^IIIQ^II]
\end{pmatrix}
\begin{pmatrix}
\vec{E}^+(N) \\
\vec{E}^-(N+1)
\end{pmatrix}
= \exp(ik \cdot \vec{a}_3)
\begin{pmatrix}
\vec{E}^+(N) \\
\vec{E}^-(N+1)
\end{pmatrix},
\]

where \(\vec{E}^\pm\) are column matrices with elements: \(\vec{E}^\pm_{g_1x}, \vec{E}^\pm_{g_1y}, \vec{E}^\pm_{g_1z}, \vec{E}^\pm_{g_2x}, \vec{E}^\pm_{g_2y}, \ldots\).

Equation 1.24 constitutes a typical eigenvalue problem; because the matrix on the left-hand side of equation 1.24 is not Hermitian, its eigenvalues are in general complex numbers. We remember that \(\omega\) and \(k||\) are given quantities and therefore the eigenvalues
of the matrix on the left-hand side of equation [1.24] determine \( k_z \); depending on the number of \( \vec{\gamma} \)-vectors we keep in the calculation, we obtain a corresponding number of \( k_z \)-eigenvalues for the given \( \omega \) and \( \vec{k}_\parallel \). For given \( \vec{k}_\parallel \) and \( \omega \), out of the many eigenvalues of \( k_z \) none or at most, a few are real; the Bloch waves corresponding to them represent propagating modes of the EM field in the given crystal. The remaining eigenvalues of \( k_z \) are complex and the corresponding Bloch waves are evanescent waves; they have an amplitude which increases exponentially in the positive or negative \( z \)-direction and, unlike the propagating waves, do not exist as physical entities in the infinite crystal. They are however very useful in the understanding of the optical properties of finite slabs of the crystal. For example, the attenuation of a wave of given \( \vec{k}_\parallel \), incident on a slab of material with thickness \( d \) having a frequency within a region over which no propagating solution exists for the given \( \vec{k}_\parallel \), is determined by that evanescent wave.
1.3.3. Equifrequency Surface

Light propagation in photonic crystals is represented by Bloch waves. Bloch waves have a definite propagation direction in spite of strong scattering by the periodic structure. This character leads us to consider a geometric optics approach to understand the propagation in photonic crystals. In uniform materials, the propagation direction is calculated using Snell’s Law whereas in photonic crystals, the propagation direction depends on the band structure. In general, the propagation direction after any interface is determined by a boundary condition which requires the tangential component of the wave vector $\vec{k}$ to remain constant. Since the phase velocity is related to the $\vec{k}$ through $v_p = \omega |\vec{k}|$, while the group velocity is related through derivative, the phase velocity directly determines the behavior of light at the boundary.

A convenient way to analyze the directional dependence of the $\vec{k}$ within the photonic crystal is by calculating and plotting an equifrequency surface. The equifrequency surface maps out the allowed $\vec{k}$-vectors for all orientations within a structure for a constant frequency. In a uniform isotropic material, where the phase and group velocities are independent of orientation, the equifrequency surface is a circle. The radius of the circle is the magnitude of the $\vec{k}$-vector, which scales with the phase velocity, and the group velocity points away from the circle in the direction normal to the surface. However, in photonic crystals, due to the periodicity in the refractive index, neither the phase velocity nor group velocity are constant and depend on direction. Hence, the equifrequency surface is no longer circular. [26]

Several important properties of photonic crystals can be analyzed using the equifrequency surface:
First, conservation of momentum for light coupling from a homogeneous medium (e.g. air) into the photonic crystal across a given surface dictates that $k_1^\parallel = k_2^\parallel + G^\parallel$, where $G$ is any reciprocal lattice vector. Secondly, it is clearly possible that several Bloch modes fulfill the above condition simultaneously and therefore more than one refracted (or diffracted) wave can exist in the photonic crystal. Thirdly in a photonic crystal, the direction of energy transfer does not generally coincide with the direction of the Bloch wave vector which specifies the mode. This simply follows from the fact that along the direction of the Bloch wave vector the refractive index is not constant and therefore the spatial configuration of the electric field can be very irregular. The direction of energy transport in a photonic crystal is given by the group velocity vector.

\begin{equation}
\vec{v}_q = \vec{\nabla}_k \omega'(\vec{k})
\end{equation}

These properties are illustrated in Figure 1.6 for the case of an incoming beam $\vec{k}_i$ incident on a 2-D lattice. The direction of the Bloch and group velocity vectors for the reflected and refracted beams are analyzed by applying momentum conservation. The strongly distorted dispersion surfaces can lead to a number of interesting phenomena in photonic crystals, such as the superprism effect [27,28,29] and negative refraction [26,30].
Figure 1.6. Refraction of light in a 2D photonic crystal. For clarity, only the transmitted beams are shown. The dispersion in air and the incident wave vector are shown on top. The dashed green line shows the condition of conservation of $\vec{k}_\parallel$. (a) At a frequency below the photonic bandgap, the equifrequency surface is only slightly deformed, $\vec{k}_t$ and $\vec{v}_g$ are almost collinear. (b) In this case a band gap has opened at the M point. Waves propagating with $\vec{k}_{i1}$ cannot propagate in the periodic structure. For waves with $\vec{k}_{i2}$, the direction of energy flux is different from the transmitted wave vector $\vec{k}_{t2}$. 
1.4. Emission and Lasing

1.4.1. Spontaneous Emission

When materials such as atoms, molecules or nanocrystals decay from an excited state to the ground state by vacuum fluctuations, light is emitted whose frequency is the same as the energy difference between the excited state and ground state. This emission is called spontaneous emission. It has been realized that spontaneous emission depends not only on properties of atoms or molecules but also on the electromagnetic mode structure around the emitters. Light can be emitted when there is an electromagnetic mode available for photon radiation. The number of electromagnetic modes per unit frequency is called the photonic density of states. Yablonovitch first proposed the photonic crystal structure because it has the ability to inhibit spontaneous emission via a photonic band gap where the photonic density of states is zero \([9]\).

The spontaneous emission rate \(\Gamma(\omega)\) in a photonic crystal is directly related to the local density of states of the medium \(\rho_\ell(\vec{r}, \omega)\) \([31]\).

\[
\Gamma(\omega) = \frac{2\pi}{\hbar} \rho_\ell(\vec{r}, \omega)
\]

(1.26)

The local density of states (LDOS) is defined as \([32]\),

\[
\rho_\ell(\vec{r}, \omega) = \frac{1}{(2\pi)^3} \sum_n \int d^3 k |\vec{\mu} \cdot \vec{E}_n(\vec{r})|^2 \delta(\omega - \omega_n)
\]

(1.27)

where \(\omega_n\) are the eigenfrequencies of the electric field modes \(\vec{E}_n\), and \(\vec{\mu}\) is the dipole transition moment of the emitter.
1.4.2. Light Localization and Random Lasing

Localization was first discussed by Philip Anderson who described this phenomenon in the context of electrons and their spins confined in a semiconductor. Light localization is an effect that arises entirely from coherent multiple scattering and interference. In traditional studies of electromagnetic wave propagation in dielectrics, scattering takes place on scales much longer than the wavelength of light. Localization of light occurs when the length scale of coherent multiple scattering is reduced to the wavelength (strong scattering). When scattering is strong, after multiple scattering, light can return to its original position through many different paths forming closed loops. When the optical amplification along the loop exceeds the loss, lasing oscillation occurs in the loop that serves as the cavity. Since all the backscattered waves interfere, the feedback is coherent and phase sensitive. Only at certain frequencies is the interference constructive, making it possible to confine light inside the random system. Lasing occurs at these frequencies, producing discrete peaks in the emission spectrum. Above the lasing threshold, emission intensity increases much more rapidly with pumping intensity. The coherent random laser was first demonstrated for ZnO powders and polycrystalline films. The behavior of a random laser with coherent feedback can thus be very similar to that of a conventional laser, yet there is a significant difference between the two. A random laser does not have directional output, because the disorder-induced scattering is random in direction. Individual lasing modes have multi-directional output which varies from mode to mode.
1.4.3. Photonic Crystal Lasing

The photonic crystal’s ability of tailoring electromagnetic dispersion facilitates new approaches to low threshold micro-lasers. \[39\,40\] Two types of lasers can be realized in photonic crystals: a distributed feedback laser and a defect mode laser.
1.4.3.1. distributed feedback lasing. At a photonic band edge, strong coupling between light emitters and electromagnetic modes results in low group velocity. The effective gain $g_{\text{eff}}$ may be qualitatively estimated by assuming that the small value of $\vec{v}_g$ is due entirely to an increased optical path length $\ell_{\text{eff}}$. Simple estimation leads to diverging $g_{\text{eff}}$ at the band edge since the group velocity approaches zero in an infinitely large sample. Mirrorless, low threshold laser action at photonic band edges has been demonstrated for one dimensional, two dimensional and three dimensional photonic crystals. [41][42]

1.4.3.2. defect lasing. The spontaneous emission can be suppressed when the emission frequency falls in the photonic bandgap. Thus if a small defect is introduced in the photonic crystal, a localized electromagnetic mode can be created within the structure at a bandgap frequency. In this case, the spontaneous emission enters preferentially into this localized mode, making it act as a micro-cavity with a very high quality factor. Such single defect cavities are expected to realize nearly thresholdless lasers, and its volume is confined in the structure defect, which can be on the scale of $\lambda^3$. Laser action in a micro-cavity formed from a single defect in two dimensional photonic crystals has already been demonstrated. [43]
1.5. Surface Plasmon

A plasmon is the collective excitation of free electrons in a solid. Electron plasma effects are the most pronounced in free-electron-like metals. The dielectric constant of such materials can be expressed as $\varepsilon(\omega) = 1 - (\omega_p/\omega)^2$, where $\omega_p$ is the plasma frequency. The electromagnetic properties related to the electron plasma effects are significantly different from ordinary dielectric materials because in the frequency range below the plasma frequency the real part of the dielectric constant is negative. In this frequency range, there is no propagating wave in such a medium.

Surface plasmons are the electron plasma oscillations near a metal surface that originate from the broken translational invariance in the direction perpendicular to the surface. [44]

1.5.1. Surface Plasmon Polariton

![Diagram of propagating surface plasmon with labels](image)

Figure 1.8. Propagating surface plasmon (a) configuration, (b) dispersion.

A combined excitation consisting of a surface plasmon and a photon is called a surface plasmon polariton. Let us consider a metal film with the dielectric constant $\varepsilon_1$ on a substrate whose dielectric constant is $\varepsilon_2$. If a metal film is thick enough, we can neglect
the interaction between surface plasmon polaritons on the different interfaces. The electric field of the surface plasmon polariton propagating on a metal interface \((z = 0)\) can be expressed as [43],

\[
E = E_0 \exp^{i(k_{sp}x - \omega t) - k_z|z|}
\]

The surface polariton dispersion relation on a smooth surface is given by,

\[
k_{sp} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}}
\]

The respective dispersion relation is shown in figure 1.8 together with the photon dispersion relation in dielectric. Since the surface plasmon polariton curve lies on the larger wavevector side of the light dispersion in the adjacent dielectric, surface plasmon polariton can neither radiate light into adjacent dielectric nor be excited with conventional illumination from the adjacent dielectric.

1.5.2. Localized Surface Plasmon

Surface plasmons also can be excited in a bound geometry such as metallic nanoparticles. Such a plasmon is called a localized surface plasmon. Its frequency can be determined using the electrostatic approximation by solving the boundary conditions of Maxwell’s equations since a nanoparticle’s size is very small compared to the wavelength of light. [45][46]
Localized surface plasmons can be resonantly excited with light of the appropriate frequency irrespective of excitation light wavevector. Therefore, localized surface plasmons also effectively decay with light radiation.

Since localized surface plasmons are confined to the particle, this results in a significant electromagnetic field enhancement at small metallic particles due to the small volume of the localized surface plasmon mode.\[47\] This effect contributes to numerous phenomena such as light emission from STM tunnel junctions, enhanced scattering, surface enhanced Raman scattering and enhanced second harmonic generation.\[48,49,50,51,52,53,54\]

1.5.3. Surface Plasmon Localization and Giant Local Field Enhancement (Hot Spot)

In random metal-dielectric films, surface plasmon excitations are localized in nanometer-scale areas and referred to as hot spots. Hot spots are located at the edges of large metal clusters and separated by a distance on the order of the correlation length $\xi_p$.

\[
\xi_p \approx |p - p_c|^{-\nu}
\]

(1.30)

Where $p$ is the metal concentration, $p_c$ is the metal concentration at percolation threshold, and $\nu$ is the critical exponent. $\xi_p$ diverges when the metal volume concentration approaches the percolation threshold where the metal-insulator transition takes place. The localization can be attributed to Anderson localization of surface plasmon polaritons in semicontinuous metal films near a percolation threshold. The electromagnetic energy is accumulated in the hot spots associated with localized plasmons, leading to the local fields that can exceed the intensity of the incident field by four or five orders of magnitude. The
high local fields in the hot spots also result in dramatically enhanced nonlinear optical responses proportional to the local field raised to a power greater than one. [49][55]
UV Lasing in 3D Disordered Photonic Crystals

The pursuit of light localization has led to two alternative approaches to realize mirrorless lasers: random lasers and photonic crystal (PhC) lasers. In a random laser, feedback is provided by strong scattering of light in a disordered medium. Random lasing has been observed in various disordered media. However, the currently achievable thresholds are too high for many practical applications because of incomplete confinement of light. One approach to improve the confinement is to maximize the scattering strength by using Mie resonances. Another approach, first proposed by John, is to reduce the effective momentum of light by introducing periodicity into the system: The Ioffe-Regel criterion for light localization in the presence of periodicity is replaced by \( k_c \ell \leq 1 \), where \( k_c \) is crystal momentum, which is much smaller than the optical wavevector \( k \) at near band edge. Due to the challenges in fabrication, real PhCs possess an unavoidable degree of disorder, and the optical properties of such partially ordered systems must be understood because uncontrolled scattering is very detrimental to passive PhC devices. Theoretical studies of 2D systems have shown that very high quality modes can exist in disordered PhCs, which facilitates lasing action. A recent study illustrates a gradual transition from lasing in a photonic crystal to random lasing behavior. In this chapter we report experimental results on the UV lasing characteristics of ZnO.
inverse opal PhCs. We observe a strong reduction in lasing threshold when the fundamental PBG in the [111] direction is tuned to overlap with the gain spectrum of ZnO. This demonstrates a combination of random lasing with partial PBG confinement.

In 3D PhCs, realizations of gain enhancement, stimulated emission, and lasing so far have relied on light sources infiltrated into a passive PhC. Infiltration complicates fabrication and can lead to a reduction of refractive index contrast and interactions of the emitters with the dielectric walls. In our samples ZnO acts as both the dielectric backbone and the gain medium for lasing. This allows us to study the emission properties without infiltrating quantum dots or dye molecules. However, we need to take into account the frequency-dependence of the refractive index and absorption in the PBG region in our active systems.

2.1. Fabrication of ZnO inverse Opal

Polystyrene opals were prepared by self-assembly onto glass substrates using the vertical deposition technique. The opals are typically ~50 layers thick with single crystal domains of several tens to hundreds of micrometers. The templates were infiltrated with ZnO by atomic layer deposition (ALD) and then removed by firing at 550°C. The remaining structures are face-centered cubic (FCC) arrays of air spheres surrounded by ZnO dielectric shells, with the (111) crystal surface parallel to the substrate [figure 2.1(a)]. All samples were infiltrated and fired together to ensure similar material and optical qualities.

High-quality ZnO inverse opals have been reported with the first PBG in the red and near-IR spectrum. However, the small sphere diameters (< 200nm) necessary to
tune the fundamental gap to the UV spectrum are difficult to grow with good monodispersity and to assemble into defect-free structures. In addition, after infiltration firing at elevated temperatures causes sintering and grain growth of the nanocrystalline ZnO and thereby leads to small scale disorder in the structure due to roughness of the ZnO shell surfaces (Fig. 2.1 (b)). As a result, disorder becomes increasingly important with decreasing sphere size.
Figure 2.1. SEM images of ZnO inverse opals. (a) (111) surface of d=256 nm sample and (b) cross section (cleaved surface) of d=171 nm sample. The rough granular structure is due to crystal growth during firing.

2.2. Optical Experiment

Transmission and reflection spectra of the PhCs were measured with a Cary 500 UV-vis-NIR spectrophotometer. In general, a white light source is passed through a monochromator to select a particular wavelength for observation. For transmission spectroscopy, the monochromatic source is split into two beams. One of these beams is passed through
a reference sample, typically a blank substrate, while the other is passed through the sample. After passing through the samples, the two light beams are collected, and their intensities compared. The obtained value of the transmission (\(\% T\)) corresponds to the ballistic transmission through the PhC along the [111] crystal direction. Reflection spectra were obtained using the diffuse reflectance accessory (DRA) of the spectrophotometer. In this technique both the diffuse and the total (diffuse plus specular) reflection from the sample surface are measured using an integrating sphere in a two-beam setting. The specular component can then be calculated by subtracting the two measured spectra. The angle of incidence of the beam onto the sample surface is 3°, i.e. very close to the normal [111] direction.

The optical setup used to measure lasing and photoluminescence is shown in Figure 2.2. To measure the emission from the samples, the sample surfaces were first imaged by a white-light source and a 20X objective lens onto a CCD camera, and highly reflective areas free of cracks were selected for our experiments. The samples were then pumped by a continuous-wave He-Cd laser of \(\lambda = 325\text{nm}\) in photoluminescence (PL) measurements, or at 10 Hz with 20ps pulses of wavelength \(\lambda = 355\text{nm}\) from a mode-locked Nd:YAG laser in the lasing experiment. The beam had a spot diameter of approximately 20\(\mu\text{m}\) and was incident along the [111] crystal direction. The emission was collected by the objective lens (NA=0.4). All measurements were performed at room temperature.

The angle resolved lasing experiment setup is shown in Figure 2.3. The sample was mounted on a goniometer stage. Only the detection arm moved and the sample did not rotate. The third harmonics of the pulsed Nd:YAG laser was used to pump the ZnO. The pump beam was focused onto the sample focused by a lens (L1) at a fixed angle
Figure 2.2. Schematic of the optical setup used to measure lasing and photoluminescence from the ZnO inverse opal structures. The white light and pump beam are incident normal to the sample surface along the [111] direction, and the emission is collected in the same direction. BS stands for UV beam splitters, L1 is a 20X UV objective lens, M is a flip mirror to select the pump beams.

$\theta_p \sim 30^\circ$. The emission was collected by another lens (L2) and focused to a fiber bundle which was connected to a spectrometer. A linear polarizer (P) was placed in front of the fiber bundle to select $s$- or $p$-polarized light with electric field perpendicular or parallel to the detection plane (consisting of the detection arm and the normal of sample surface). The angular resolution, which was determined mainly by the range of collection angle of lens L2, was about 5$^\circ$. Lasing spectra into different angles $\theta_e$ were measured when the
detection arm was scanned in the horizontal plane. To prevent the reflected pump light from entering the detector, the incident beam was tilted vertically so that the incidence plane deviated from the detection plane. A long pass filter (F) was placed in front of the fiber bundle to block the scattered pump light at wavelength $\lambda = 355\text{nm}$.

Figure 2.3. Schematic of the optical setup used to measure angle resolved lasing. The sample was mounted on a goniometer stage. Only the detection arm moved and the sample did not rotate. Pump beam is focused onto the sample by lens (L1). Emission is collected by another lens (L2) and focused to optical fiber bundle connected to a spectrometer. Polarization was selected by linear polarizer (P). A long pass filter (F) was placed in front of the fiber bundle to block the scattered pump light.
2.3. Results

Figure 2.4 shows specular reflection spectra taken from four samples, with white light incident normal to the sample surface along the [111] crystal direction, and the calculated band structures of the PhCs. The largest sample \(d = 256\, \text{nm}\) shows a main reflection peak at \(\lambda = 525\, \text{nm}\). It corresponds to the fundamental PBG in the (1 1 1) direction. Its wavelength is far from the ZnO absorption/emission edge. Additional reflection features between 390 and 400\,\text{nm} correspond to high order gaps. The narrow width and small amplitude of the reflection peak of the 171\,\text{nm} sample suggest that the fundamental gap is reduced by disorder and overlaps with the absorption edge of ZnO. This means that the observed reflection peak corresponds to the low-frequency part of the PBG and the high-frequency part of the gap is effectively destroyed due to absorption by ZnO. For the smallest sample \(d = 160\, \text{nm}\) the fundamental PBG lies in the absorption region of ZnO and no PBG can be observed. The calculations were performed using the plane-wave-expansion (PWE) method with values for the refractive index \(n(\lambda)\) of ZnO for wavelength \(\lambda > 385\, \text{nm}\). The calculated gap position agrees well with the reflection peak frequency.

The results of photoluminescence measurements are shown in Fig. 2.5. We observe broad spontaneous emission peaks from the ZnO PhCs. For a comparison of spectral shapes and peak positions, the emission spectra have been normalized to a peak value equal to 1. For the \(d = 171\, \text{nm}\) sample the PBG overlaps the emission band and the PL peak is clearly suppressed at the low-frequency edge and the maximum is blue-shifted. A similar modification of the spontaneous emission near the first PBG has been observed.
Figure 2.4. (a) Calculated photonic band structures of the ZnO inverse opals in the vicinity of the first ΓL pseudogap. The dashed line marks the approximate position of the ZnO absorption edge. With decreasing sphere size the fundamental PBG shifts closer to the absorption edge and the 160nm sample has no PBG due to absorption. (b) Specular reflection spectra of ZnO inverse opal PhCs with varying sphere diameters.

for light-sources infiltrated into PhC structures and can be explained by a redistribution of emission from the directions prohibited by the PBG to other allowed directions. [76]

With increasing pump intensity, scattering of light by disorder in the structure causes random lasing in samples with no PBG ($d = 160nm$) or a PBG away from the gain
Figure 2.5. Photoluminescence and lasing spectra of the ZnO inverse opals with varying sphere diameters. The random lasing modes in the $d = 160\text{nm}$, $202\text{nm}$ and $256\text{nm}$ samples overlap with the peak in PL spectrum. In the $d = 171\text{nm}$ sample the PL is suppressed and blue-shifted by the PBG (indicated by the reflection spectrum, dashed line). The main lasing modes are red-shifted into the PBG and do not overlap with the PL maximum.

Similar random lasing behavior has been observed in ZnO powders. The random lasing modes overlap spectrally with the PL peaks.
and have output in many directions. The linewidth of individual lasing peaks is \( \sim 0.5\,\text{nm} \), but often several lasing peaks overlap partially in the spectrum.

![Graph showing lasing threshold versus sphere diameter for ZnO inverse opals.](image)

Figure 2.6. Lasing threshold versus sphere diameter for the ZnO inverse opals. The lasing threshold is strongly reduced when the PBG overlaps the emissionspectrum of ZnO. Inset: L-L curve measured for a \( d = 171\,\text{nm} \) sample, with lasing intensity (in a.u./10\(^5\)) plotted versus pump intensity (in MW/mm\(^2\)). (b) Lasing output intensity versus detection angle for the \( d = 171\,\text{nm} \) sample. Lasing is not confined to the [111] direction. The peak in p-polarized emission around 50\(^\circ\) is attributed to the Brewster angle effect.
We have estimated the scattering mean free path of light $\ell_s$ in our samples from transmission and reflection data:

\[
\frac{T}{(1 - R) \cdot T_{sg} \cdot T_{ga}} = \exp\left(-\frac{L}{\ell_s}\right)
\]

The probe light is incident onto the sample/air interface, $T$ and $R$ are the measured values of ballistic transmission and total reflection (including specular and diffusive reflection), $T_{sg}$ and $T_{ga}$ are the transmission coefficients for the sample/glass and glass/air interfaces, and $L$ is the sample thickness. A comparison of $\ell_s$ values for different samples is only possible at wavelengths away from the ZnO absorption band and the PBGs. Thus we choose $\lambda = 650\,nm$, and obtained values of $\ell_s$ equal to $29.2\mu m$ for $d = 256\,nm$, $21.5\mu m$ for $d = 202\,nm$, $22.8\mu m$ for $d = 171\,nm$, and $23.3\mu m$ for $d = 160\,nm$. These results confirm that disorder slightly increases with decreasing lattice parameters, but also that the degree of disorder is similar for the three smaller sphere samples. Scattering will be significantly stronger at the ZnO emission wavelength due to increased refractive index of ZnO, but should remain comparable in all samples.

Unlike the other samples, lasing peaks from the $d = 171\,nm$ sample are spectrally located not at the position of strongest PL but are red-shifted into the PBG. As shown in Fig.2.6, lasing exhibits a clear threshold and the threshold decreases dramatically when the PBG is tuned to the gain spectrum of ZnO. More specifically, the threshold is reduced by approximately a factor of 5 from $d = 256\,nm$ to $d = 171\,nm$ and a factor of 3 from $d = 160\,nm$ to $d = 171\,nm$. Because the difference in disorder between the samples is small and the optical quality is similar, this suggests that lasing is enhanced by the additional
confinement of light provided by the PBG. However, despite the reduction of the lasing threshold, the lasing output remains non-directional and similar to that of a random laser (Fig. 2.6 b). The absence of directionality of laser emission excludes the possibility of lasing in the defect states within the [111] PBG or band edge lasing in the high symmetry directions of the PhC. \[71,72,75\] Random lasing modes with enhanced confinement in the [111] direction would be expected to emit more strongly in other directions outside the PBG. However, the partial gap in the 171\(nm\) sample is located near the absorption edge and covers only a narrow solid angle relative to directions outside the gap, so the angular redistribution of light is small. An alternative explanation in terms of directional lasing plus subsequent diffusion of laser emission appears unlikely since a short absorption length of the pump light would make lasing occur close to the sample surface. Based on these experimental findings, we believe that what we observe is still random lasing and the spatial confinement of the random lasing modes is improved by reduced \(k_c\) from the Bragg diffraction in the partial PBG. Further experimental and theoretical studies will be needed for a complete description of the complicated physical properties of such optically active, partially disordered photonic structures.

2.4. Conclusion

We have demonstrated UV lasing at room temperature from ZnO inverse opal PhCs. The disorder in the structures, primarily due to imperfections in the opal templates and roughness caused by grain growth during firing, induces optical scattering and leads to random lasing. When the first \(\Gamma L\)-pseudogap of the PhCs is tuned to the ZnO gain spectrum, a pronounced reduction in lasing threshold is observed, indicating enhanced
confinement of light by the incomplete PBG. We believe a fine tuning of the PBG position and a reduction in disorder by improving the sample fabrication will lead to photonic crystal lasing and a further reduction of lasing thresholds and improvement of the output directionality.
Modification of Photoluminescence by Photonic Band Singularity

An opal that is made of dielectric spheres only has partial photonic bandgap (PBG), namely, the PBG exists only within certain angle range instead of all angles. An inverse opal can have a full PBG if the refractive index contrast is high enough (> 2.8). It has been shown \[7,79,76,80,81,82,83,84,85,86,87,88,89,90,91,92,93,94,95,96\] that a partial PBG can affect the spontaneous emission process in an opal or inverse opal by suppressing spontaneous emission into certain directions. Enhancement of spontaneous emission is also observed at the edge of a PBG. Recent studies \[97,98,99,100,101,102,103,104,105,106,107,108,109,110,111,111,112\] show that a high-order photonic band can have abnormal dispersion which leads to many interesting phenomena such as a super prism \[27,28,29\] and a negative refractive index \[26,30\]. In this chapter, we demonstrate that a high-order photonic band with abnormal dispersion can significantly modify the photoluminescence (PL) intensity, directionality and polarization in an inverse opal.

The dispersion of photons in a photonic crystal (PhC) can be dramatically different from that in free space. Let us denote the dispersion of a photonic mode by \(\omega(k)\), where \(\omega\) is the photon frequency and \(k\) is the wave vector. A mode with \(d\omega/dk \simeq 0\) is called a slow mode because the group velocity is nearly zero. There have been many proposals of utilizing the slow modes of a PhC to reduce the speed of light by orders of magnitude. A
serious problem that hinders the slow light application is that a typical slow mode with 
\(d^2\omega/dk^2 \neq 0\) has a large impedance mismatch at the PhC/air interface, thus the conversion
efficiency of incident light into the slow mode is very low. To solve this problem, Figotin
and Vitebskiy proposed to use the photonic mode at the stationary inflection point of a
dispersion curve of a photonic band. [113,114] Such a mode has both \(d\omega/dk \simeq 0\) and 
\(d^2\omega/dk^2 \simeq 0\). It is called a frozen mode. When the incident light is in resonance with
a frozen mode, the vanishing group velocity is offset by the diverging electromagnetic
energy density. The energy flux inside the PhC is finite and comparable to the incident
flux. Hence, the incident light can be completely converted to the frozen mode instead
of being reflected. Our aim is to employ the unique properties of a frozen mode in a 3D
PhC to tailor spontaneous emission. The vanishing group velocity enhances emission into
the frozen mode, while the perfect impedance match at the PhC/air interface leads to
efficient extraction of emission from the PhC.
3.1. Sample fabrication

Monodisperse polystyrene spheres were assembled in a face-centered-cubic (FCC) structure on a glass substrate via a vertical deposition process. The sample thickness could be varied from 20 to 100 layers of spheres. The opal had "domains" with widths of $\sim 50 \, \mu\text{m}$ and lengths of hundreds of microns, separated by cracks. The crystalline arrangement was constant across these cracks which formed after the self-assembly process during drying of the opal. ZnO was infiltrated into the template by atomic layer deposition (ALD). We ensured the exposure times were sufficiently long during ALD growth so that the precursors could be fully diffused into the opal structure and the ZnO thin film grown conformally and uniformly around each polystyrene sphere throughout the sample. The polystyrene spheres were then removed by firing at an elevated temperature. Figure 3.1 shows the scanning electron microscope (SEM) images of the top surface and cleaved edge of a ZnO inverse opal. The sample surface was parallel to the (111) crystallographic plane. Even for a 100-layer-thick sample, ZnO was fully infiltrated into the opal template and the filling was nearly 100%.

A random sample was fabricated to provide reference for optical measurements. Polystyrene spheres of different sizes were mixed and deposited on a glass substrate. The lack of monodispersity prevented the formation of ordered crystal domains. The randomly packed structure was subsequently infiltrated with ZnO and fired at the same temperature as for ZnO inverse opal. The identical fabrication conditions ensured similar microstructure and material properties.
3.2. Optical Setup

We performed the angle- and polarization-resolved reflection measurements to characterize the photonic band structures. Figure 3.2(a) shows the experimental setup. The
sample was mounted on a goniometer stage. The reflection scan was taken in the $\theta - 2\theta$ geometry, namely, when the sample was rotated by an angle $\theta$, the detection arm was rotated by $2\theta$. Collimated white light from a UV enhanced Xe lamp was focused onto the sample by a lens (L1). The beam spot on the sample surface was about 1mm in diameter. The angle of incidence from the surface normal was $\theta$. The reflected light was collected by another lens (L2) and focused to a fiber bundle which was connected to a spectrometer. A linear polarizer (P) was placed in front of the fiber bundle to select s- or p-polarized light with electric field perpendicular or parallel to the detection plane (made of the detection arm and the normal of sample surface). The angular resolution, which was determined mainly by the collection angle of lens L2, was about 5°. The reflection spectra were taken with the incident angle $\theta$ varying from 5° to 50°. The spectral resolution was about 1nm.

In the photoluminescence (PL) experiment, only the detection arm moved and the sample did not rotate. As shown in Figure 3.2(b), white light was replaced with He:Cd laser light which excited the ZnO. The pump beam was focused onto the sample at a fixed angle $\theta_p \sim 30^\circ$. Spectra of emission into different angles $\theta$ were measured when the detection arm was scanned in the horizontal plane. To prevent the reflected pump light from entering the detector, the incident beam is shifted vertically so that the incidence plane deviates from the detection plane. A long pass filter (F) was placed in front of the fiber bundle to block the scattered pump light at wavelength $\lambda = 325nm$. 
3.3. Experimental Results

3.3.1. Reflection spectra

We measured many ZnO inverse opals with different lattice constants. The sample uniformity was checked carefully with scanning electron microscopy and optical spectroscopy. Only the samples that were uniform in crystalline arrangement, thickness, and infiltration over an area much larger than the probe beam spot were used in the reflection and PL measurements. The data presented below were taken from one sample with an air sphere diameter of 400 nm and a lattice constant of 566 nm. The number of layers of air spheres was about 60. Figure 3.3(a) plots the first Brillouin zone (BZ) of ZnO inverse opal. In the reflection and PL measurements, the sample was oriented so that the detector was scanned in the ΓLK plane. Note that in the reflection measurement the UV light from the Xe lamp could excite ZnO and generate PL. The PL intensity, however, was much weaker than the reflected light intensity. Thus, the PL signals can be ignored in the reflection spectra.

Figure 3.4(a) shows the reflection spectra of p-polarized light for θ varying from 5° to 50° with 5° steps. For θ = 5°, there is a primary reflection peak centered at wavelength λ ≃ 800 nm with the peak reflectivity ~ 0.7. It corresponds to the lowest-order photonic band gap in the [111] direction, which is confirmed in the numerical simulation to be presented in the next section. With increasing angle θ, this peak shifts to shorter wavelengths. There are additional reflection peaks at higher frequencies. They are less dispersive and shift to slightly longer wavelengths with increasing θ. The reflection spectra of s-polarized light, shown in Fig. 3.4(b), exhibited significant differences from those for p-polarized light.
There is an additional reflection peak at $\lambda \simeq 510\,nm$ for $\theta = 5^\circ$. It shifts significantly to longer wavelengths with increasing $\theta$. Since the primary reflection peak shifts to the opposite direction, these two peaks exhibit an anti-crossing at $\theta \sim 45^\circ$.  

Figure 3.3. (a) The first Brillouin zone (BZ) for a FCC structure. The symmetry points are marked. (b) Cross section of the first BZ by the $\Gamma L K$ plane.
Figure 3.4. Angle-resolved reflection spectra of a ZnO inverse opal with sphere diameter 400nm. Both the incidence plane and detection plane are parallel to the ΓLK plane. The incidence angle \( \theta \) ranges from 5° to 50°. The values of \( \theta \) are written in the graph. The spectra are offset vertically. (a) \( p \)-polarized light, (b) \( s \)-polarized light.

3.3.2. Photoluminescence data

When pumped by the He:Cd laser at \( \lambda = 325 \text{nm} \), the ZnO inverse opal has PL in both the UV and visible frequencies. The UV emission is ascribed to the electron transition from the conduction band to valence band, and the visible emission is via the defect states within the electronic bandgap. At room temperature the defect emission, which results from various material defects such as oxygen vacancies, zinc interstitials and oxygen interstitials, covers a 300nm wavelength range. Here we
concentrate on the defect emission, whose broad spectral range allows us to observe the effects of many different-order photonic bands on emission.

Figure 3.5 shows the PL spectra of the ZnO inverse opal and the random sample. The spectral shape of PL from the random sample does not change with observation angle $\theta$. The PL of ZnO inverse opal is strongly modified, and the modification is angle-dependent. For comparison, the emission spectra taken at identical $\theta$ are scaled so that they overlap at $\lambda = 880\,nm$, well below the lowest-order PBG. Suppression of emission at longer wavelengths is evident in the ZnO inverse opal. At shorter wavelengths there is significant enhancement of s-polarized emission. This enhancement is not related to stimulated emission, as the emission intensity is confirmed to vary linearly with pump intensity.

We extracted the PL enhancement factor by dividing the PL spectrum of ZnO inverse opal by that of the reference sample for the same $\theta$. If the normalized PL intensity is less (or more) than unity, the spontaneous emission is suppressed (or enhanced). Figure 3.6 shows the normalized PL spectra for both s- and p-polarizations with $\theta$ varying from $0^\circ$ to $50^\circ$. The spectra are vertically shifted with a constant offset of 1.5. The reference line of unity for each spectrum is plotted as a dashed line. For $\theta = 10^\circ$, the dip at $\lambda \sim 800\,nm$ coincides with the primary reflection peak in Fig. 3.4. Its blue-shift with increasing $\theta$ is identical to that of the reflection peak. As mentioned earlier, the primary reflection peak corresponds to the lowest-order PBG. This partial gap suppresses the emission due to the depletion of density of states (DOS) within a certain angle range. The peaks at higher frequencies in the normalized PL spectra reveal the emission enhancement by higher-order photonic band structures. Most enhancement peaks for both polarizations
Figure 3.5. Measured PL spectra of a ZnO inverse opal (sphere diameter = 400 nm) and a random sample (black dotted line). The emission angle $\theta = 20^\circ$ (a), $30^\circ$ (b), and $40^\circ$ (c). The red solid curve and blue dashed curve represent the s and p-polarized emission from the ZnO inverse opal, respectively.
are weakly dispersive with angle, except one for s-polarized PL. This peak red-shifts dramatically with increasing $\theta$. Its amplitude reaches a maximal value of 2.3 at $\theta = 40^\circ$, exceeding all other peaks. It is responsible for strong enhancement of s-polarized PL in Fig. 3.5. We notice that this PL peak has similar dispersion to the reflection peak that exists only for s-polarization in Fig. 3.4. To compare their frequencies, we overlay the normalized PL spectra and reflection spectra in Fig. 3.7 (1st row) for $\theta = 20^\circ - 50^\circ$. It is evident that the two peaks do not overlap spectrally, instead the PL peak is always at the low frequency shoulder of the reflection peak.

![Normalized PL spectra of the ZnO inverse opal at various emission angles $\theta$. The values of $\theta$ are written in the graph. The spectra are vertically shifted with a constant offset of 1.5. The reference line of unity for each spectrum is plotted as a horizontal dashed line. (a) p-polarized emission, (b) s-polarized emission.](image-url)
3.4. Numerical simulation

3.4.1. Reduced photonic bands

To interpret the experimental results, we performed numerical simulations of ZnO inverse opals using the experimental values. To account for the angular dependence of reflection and PL, we calculated photonic bands and the density of states (DOS) corresponding to a specific angle of incidence/exit in air. These bands and DOS are called reduced bands and reduced DOS [100], as opposed to angle-integrated bands and DOS. Since the top surface of ZnO inverse opal corresponds to the (111) crystallographic plane, we define a reference frame shown in Fig. 3.3: the origin at the Γ point, z-axis in the ΓL direction normal to (111) surface, xy plane parallel to the surface with x-axis in the LK direction and y-axis in the LW direction. The wavevector of an incident/exit photon in air can be expressed as

\[ \mathbf{k_i} = \frac{\omega}{c} (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \phi) , \]

where \( \omega \) is the frequency, \( \theta \) is the polar angle, and \( \phi \) is the azimuthal angle. It should be noted that \( \theta \) and \( \phi \) denote the direction of light incidence/exit in air, which differs from the direction of light propagation inside the PhC. Even if the incidence/exit direction in air is fixed, the propagation direction inside the PhC may change with frequency \( \omega \).

The reduced photonic band structure is obtained from the full band structure by using two conservation laws: (i) parallel momentum conservation modulo a reciprocal lattice
vector, (ii) energy conservation. They can be written as

\[(3.2)\quad \mathbf{k}_\parallel + \mathbf{G}_\parallel = \frac{\omega_c}{c} (\sin \theta \cos \phi, \sin \theta \sin \phi, 0),\]

and

\[(3.3)\quad \epsilon_n(\mathbf{k}_\parallel, k_z) = \hbar \omega,\]

where \(\mathbf{k}_\parallel\) is the \(\mathbf{k}\)-component parallel to the (111) surface \((xy\text{-plane})\), \(\mathbf{G}_\parallel\) is the parallel component of any reciprocal lattice vector \(\mathbf{G}\), and \(\epsilon_n(\mathbf{k}_\parallel, k_z)\) represents the \(n\)th energy band of the PhC with wavevector \(\mathbf{k} = \mathbf{k}_\parallel + k_z\).

We used the computer program MULTEM, which is based on the layer KKR (Korringa-Kohn-Rostoker) method \[122\], to calculate the reduced band structure. One advantage of this method is that it gives \(k_z\) for given \(\epsilon_n\) and \(\mathbf{k}_\parallel\). Another advantage is that it can calculate angle-resolved reflection and transmission spectra of a PhC with finite thickness, thus allowing direct comparison with the experimental data. The reduced DOS is inversely proportional to the group velocity, which is calculated from the slope of the dispersion curve for an individual reduced band. Since the frequency range of calculation is below the ZnO electronic bandgap, the dispersion of the ZnO refractive index is rather weak. We neglected the frequency dependence of refractive index in the numerical simulation.

To take into account the interstitial tetrahedral pores in the ZnO inverse opals \[73\], we set the value of refractive index at 1.95, which is slightly lower than the actual refractive index of ZnO.

We calculated the reduced photonic bands for \(\mathbf{k}_i\) scanning in the \(\Gamma L K\) plane, namely \(\phi = 0\) and \(\theta\) varying from 0° to 80° with 10° steps. The first BZ has mirror symmetry with
respect to the ΓLK plane [Fig. 3.3(a)]. The s- or p-polarized light, with \( \mathbf{k}_i \) in the ΓLK plane and electric field perpendicular or parallel to the ΓLK plane, has distinct mirror symmetry with respect to the ΓLK plane. Hence, the two polarizations are decoupled and the reduced photonic bands with \( \mathbf{k}_i \) in the ΓLK plane are either s- or p-polarized. We plot the s-polarized bands in Fig. 3.7 (2nd row) and p-polarized bands in Fig. 3.8 (2nd row). The reduced bands with positive \( k_z \) differ from those with negative \( k_z \). This is because the cross section of the first BZ by the ΓLK plane, shown in Fig. 3.3(b), does not have mirror symmetry with respect to the \( x \)-axis.

Comparing the reduced s- and p-polarized bands reveals their significant differences. For example, at \( \theta = 30^\circ \), the second and third s-polarized bands [labeled as 2s and 3s in Fig. 3.7] exhibit frequency anti-crossing around \( k_z a/2\pi = 0.7 \), while the 2p and 3p bands nearly cross in Fig. 3.8. For both polarizations, the second and third reduced bands originate from Bragg diffraction of light by \( (111) \) and \( (\bar{1}11) \) planes for \( k_z > 0 \), and by the \( (111) \) and \( (200) \) planes for \( k_z < 0 \). At their crossing point near \( k_z a/2\pi \sim 0.7 \), simultaneous Bragg diffraction by the \( (111) \) and \( (\bar{1}11) \) planes results in band repulsion. The anti-crossing of 2s and 3s bands indicates strong band coupling via multiple diffraction. The interaction of the 2p and 3p bands, however, is much weaker. Such differences can be explained by the dependence of diffraction efficiency on polarization. It is well known for X-ray diffraction that when the Bragg angle is close to \( 45^\circ \) the intensity of the diffracted beam is extremely weak for a p-polarized wave. The suppression of Bragg diffraction has a formal analogy to the Brewster effect on reflection of p-polarized light by a homogeneous medium. The diffraction efficiency for p-polarized light in a PhC can be greatly reduced if the incident angle approaches the
critical angle. The weak coupling of $2p$ and $3p$ bands is attributed to low efficiency of multiple diffraction of $p$-polarized light at the band crossing point because one of the Bragg angles is close to the critical angle.

Comparison of the calculated band structure to the measured reflection spectra confirms that the primary reflection peak corresponds to the lowest-order gap between the first and second bands for both polarizations. The additional reflection peak, observed only for $s$-polarization, overlaps with the gap opened by anti-crossing of the $2s$ and $3s$ bands. As $\theta$ increases, the gap moves toward lower frequencies, and the reflection peak follows. This reflection peak is not observed for $p$-polarization because the $2p$ and $3p$ bands have little repulsion. In fact, the calculated reflection spectrum for $\theta = 40^\circ$ exhibits a very narrow peak corresponding to the small gap between the $2p$ and $3p$ bands at $k_z a/2\pi \sim 0.7$ [Fig. 3.8]. Such a narrow peak is smeared out experimentally by averaging over a finite collection angle.
Figure 3.7. 1st row: angle-resolved $s$-polarized reflection spectra (black dashed line) of the ZnO inverse opal overlaid with the normalized PL spectra (red solid line) of same polarization and angle $\theta$. 2nd row: calculated $s$-polarized reduced band structure of the ZnO inverse opal for a fixed angle of incidence/exit in air. Lattice constant $a = 566$ nm, the dielectric constant of ZnO is $\varepsilon = 3.8$. 3rd row: calculated reduced density of $s$-polarized states of the ZnO inverse opal. 4th row: calculated reflectivity of $s$-polarized light from a ZnO inverse opal whose thickness is 34 layers of air spheres. $\phi = 0$, and $\theta = 20^\circ$ (1st column), $30^\circ$ (2nd column), $40^\circ$ (3rd column), $50^\circ$ (4th column). For $\theta = 40^\circ$, a stationary inflection point is developed for the $2s$ band at $\omega a/2\pi c = 0.856$.

3.4.2. Stationary inflection point

The dispersion of the $2s$ band is nearly flat in the vicinity of its avoided crossing with the $3s$ band. It produces a peak in the reduced DOS shown in Fig. 3.7. The enhanced PL peak, which is observed only for $s$-polarization, coincides with this DOS peak. It follows the DOS peak as it moves to a lower frequency at higher $\theta$. At $\theta = 40^\circ$, the dispersion
curve for the 2s band has a stationary inflection point at $k_z a/2\pi \simeq 0.6$ where $d\omega/dk_z \simeq 0$ and $d^2\omega/dk_z^2 \simeq 0$.

The existence of a stationary inflection point is verified by tracing the evolution of the 2s band with $\theta$. For $\theta = 50^\circ$, the dispersion curve for the 2s band exhibits a local minima at $k_z a/2\pi \sim 0.5$ and a local maxima at $k_z a/2\pi \sim 0.7$. As $\theta$ decreases, the local minima and local maxima approach each other, eventually they merge at $\theta \simeq 40^\circ$. With a further decrease of $\theta$, e.g. at $\theta = 30^\circ$, the dispersion curve has neither local minima nor local maxima, its slope does not change sign throughout the region of interest. Such band evolution confirms that the 2s band has a stationary inflection point at $\theta = 40^\circ$ where the merging of a local minima and a local maxima gives not only $d\omega/dk_z = 0$ but also $d^2\omega/dk_z^2 = 0$. The evolution of the 2p band with $\theta$, shown in the 2nd row of Fig. 3.8 is
completely different from that of the 2s band. It reveals that the 2p band does not have a stationary inflection point near $\theta = 40^\circ$, possibly due to its tiny anti-crossing with the 3p band.

The DOS at the stationary inflection point diverges in an infinitely large PhC. In a real sample such divergence is avoided because of finite sample size. Nevertheless, the DOS peak has maximal amplitude at $\theta \approx 40^\circ$ where the stationary inflection point is developed. The large DOS enhances the spontaneous emission process. Although the 2p band does not have a stationary inflection point, its dispersion is relatively flat in the neighborhood of $k_z a/2\pi = 0.6$ [Fig. 3.8]. It produces a peak in the reduced DOS, which should enhance emission. Experimentally, the $p$-polarized PL is not enhanced.

The question arises why the DOS peak leads to enhanced PL for $s$-polarization but not for $p$-polarization. The answer lies in the emission extraction efficiency. One unique property of the frozen mode at the stationary inflection point is its efficient coupling to the free photon mode outside the PhC. It leads to vanishing reflectivity at the sample/air interface, which is confirmed by our calculation and measurement of reflectivity from ZnO inverse opal. The calculated reflection spectrum for $\theta = 40^\circ$ [Fig. 3.7] reveals that the reflectivity at the stationary inflection point $\omega a/2\pi c = 0.856$ is almost zero. Experimentally, the measured reflectivity is low but not zero due to averaging over a finite collection angle. To verify that the zero reflectivity is not a result of finite sample thickness, we calculated the reflection spectra of three ZnO inverse opals with different thicknesses (34, 36 and 38 layers of air spheres). Figure 3.9(a) shows that for $\theta = 40^\circ$ the reflectivity reaches zero at multiple frequencies. As the sample thickness varies, all the zero points of reflectivity shift in frequency except the one at $\omega a/2\pi c = 0.856$. Their dependence
on sample thickness suggests those vanishing reflectivities result from interference of light multiply reflected by the two surfaces of the ZnO inverse opal. The fact that the zero reflectivity at $\omega a/2\pi c = 0.856$ is independent of sample thickness confirms that it is caused not by the Fabry-Perot resonance in a finite PhC slab but by the intrinsic property of the photonic band, more specifically, the dispersion of the $2s$ band. This result demonstrates a perfect impedance match for the frozen mode at the interface of ZnO inverse opal and air. The light emitted to the frozen mode experiences little reflection at the sample surface when leaving the sample. Hence, $s$-polarized PL at the stationary inflection point of the $2s$ band can be efficiently extracted from the sample. The reflection of $p$-polarized light does not go to zero in the absence of a frozen mode, thus $p$-polarized PL cannot escape easily from the sample.

Figure 3.9. (a) Calculated reflectivity of $s$-polarized light as a function of normalized frequency $\omega a/2\pi c$. The incidence angle $\theta = 40^\circ$, $\phi = 0$. The thickness of ZnO inverse opal is equal to 34 (red solid line), 36 (blue dashed line) and 38 (black dotted line) layers of air spheres. (b) Calculated reflectivity of $s$-polarized light at the stationary inflection point $\omega a/2\pi c = 0.856$ as a function of the azimuthal angle $\phi$. $\theta$ is fixed at $40^\circ$. 
Therefore, the observed large enhancement peak of \( s \)-polarized PL around \( \theta = 40^\circ \) is attributed to two factors: (i) enhanced emission into the frozen mode due to the large DOS, (ii) efficient extraction of emitted light out of the PhC. As \( \theta \) approaches \( 40^\circ \), the DOS increases and surface reflection decreases. Thus, PL is enhanced in the vicinity of a stationary inflection point. The maximal PL enhancement occurs at the stationary inflection point where the DOS reaches a maximum and the surface reflection a minimum.

The enhanced emission is directional, namely, it exits the ZnO inverse opal to air at the polar angle \( \theta = 40^\circ \). Next we investigate the emission directionality in terms of azimuthal angle \( \phi \). Since the cross section of the first BZ by the \( \Gamma L K \) plane does not have mirror symmetry with respect to the \( z \)-axis (\( \Gamma L \) direction), the reduced band structure for \( k_i \) scanning along the \( LK \) path is different from that along the \( LU \) path. The reflection spectra, however, are the same for the two scanning directions due to reciprocity of reflection. [127] This is confirmed by our calculation and measurement of reflection spectra. Figure 3.9(b) plots the calculated reflectivity for \( s \)-polarized light at the frequency of stationary inflection point versus the azimuthal angle \( \phi \). The reflectivity exhibits six-fold symmetry when \( \phi \) varies from 0° to 360°. In principle, the PL spectra should exhibit differences between the scanning path along \( LK \) and that along \( LU \). Experimentally, the PL spectra for the two scanning paths are similar. This is attributed to the structure disorder, in particular, the twin structure in the ZnO inverse opal. [123] As a result, the enhanced PL can be observed at six azimuthal angles.
3.5. PL enhancement in a different crystal direction

![Graph showing angle-resolved spectra](image)

Figure 3.10. Measured angle-resolved spectra of normalized PL (a) and reflection (b) of a ZnO inverse opal with sphere diameter = 400 nm. The scanning plane is parallel to the ΓLW plane, φ = 90°. θ varies from 10° to 60°. The values of θ are written on the graph. In (a), the normalized PL spectra are shifted vertically with a constant offset of 2. The horizontal dashed lines mark unity for individual spectra. The reflection spectra in (b) are also shifted vertically.

Although the data presented above were taken from the ZnO inverse opal with a sphere diameter of 400nm, we repeated the experiments with several samples of different sphere sizes and obtained similar results. The enhancement of PL by the frozen mode is a common phenomenon because many high-order bands of ZnO inverse opals have stationary inflection points in their dispersion curves. In addition to scanning in the ΓLK path...
plane, we also scanned in the $\Gamma L W$ plane and observed PL enhancement at a different angle $\theta$.

![Graph showing angle-resolved reflection spectra and normalized PL spectra](image)

Figure 3.11. 1st row: angle-resolved reflection spectra (black dashed line) of the ZnO inverse opal overlaid with the normalized PL spectra (red solid line) of same angle $\theta$. 2nd row: calculated reduced band structure of the ZnO inverse opal for a fixed angle of incidence/exit in air. Lattice constant $a = 566$ nm, the dielectric constant of ZnO $\varepsilon = 3.8$. 3rd row: calculated reduced density of states of the ZnO inverse opal. 4th row: calculated reflectivity of a ZnO inverse opal with thickness = 34 layers of air spheres. $\phi = 90^\circ$, and $\theta = 30^\circ$ (1st column), $40^\circ$ (2nd column), $50^\circ$ (3rd column), $60^\circ$ (4th column). For $\theta = 50^\circ$, a stationary inflection point is developed at $\omega a/2\pi c = 0.87$.

Figure 3.10(a) shows the angle-resolved PL spectra when scanning in the $\Gamma L W$ plane. The normalized PL spectra are shifted vertically with a constant offset of 2. We observed an enhancement peak which shifts to lower frequency with increasing $\theta$. The maximum enhancement occurred around $\theta = 50^\circ$ and reached the value of 3.2. Since the cross section
of the first BZ by the $\Gamma LW$ plane is symmetric with respect to the $y$-axis (parallel to the $\Gamma L$ direction), the photonic mode with $(k_\parallel, k_z)$ is identical to that with $(k_\parallel, -k_z)$. The reduced band structure with positive $k_z$ is the same as that with negative $k_z$. However, the first BZ does not have mirror symmetry with respect to the $\Gamma LW$ plane. The photonic modes with $k_i$ in the $\Gamma LW$ plane contain both electric field components parallel and perpendicular to the $\Gamma LW$ plane. Hence, the reduced photonic bands can no longer be divided into $s$- and $p$-polarized bands. Consequently, the PL spectra as well as the reflection spectra are insensitive to polarization. The angle-resolved reflection spectra in Fig. 3.10(b) exhibit the frequency shift of the first and second reflection peaks with $\theta$. Comparing the reflection spectra to the PL spectra in Fig. 3.11 reveals that the enhanced PL peak overlaps with the reflection dip at the low-frequency side of the second reflection peak. Our calculation of the reduced band structure, the reduced DOS and reflection spectra (Fig. 3.11) illustrates that the maximal PL enhancement peak observed around $\theta = 50^\circ$ results from the stationary inflection point of a high-order band, which produces a peak in the DOS and a dip in reflectivity at $\omega a/2\pi c \simeq 0.87$. Note that the reflectivity at $\theta = 50^\circ$ is not zero, because the exact angle for the stationary inflection point is $47^\circ$. The comparison of numerical results to experimental data confirm that the PL enhancement originates from the frozen modes, similar to that observed when scanning in the $\Gamma LK$. 
3.6. Conclusion

We present a detailed study on the angle- and polarization-resolved photoluminescence and reflection spectra of ZnO inverse opals. The broad ZnO defect emission exhibits multiple enhancement peaks for both polarizations. Our numerical simulation reveals that the largest enhancement peak results from the frozen mode at the stationary inflection point of the dispersion curve for a high-order photonic band. The frozen mode has a well defined propagation direction and may be linearly polarized. At its frequency, the reduced DOS diverges, greatly enhancing the spontaneous emission into the frozen mode. Perfect coupling of the frozen mode to the free photon mode outside the sample leads to efficient extraction of emission from the PhC. The enhanced emission not only has good directionality but also can be linearly polarized. We note that the above mechanism does not work for all the enhanced PL peaks. Many peaks, which overlap spectrally with the high-order photonic bands, remain to be explained. Nevertheless, our results demonstrate that a high-order band of a 3D PhC can strongly modify the spontaneous emission, which offers potential application for a highly efficient light source.
Structural Color

The color of avian feather barbs can be produced by pigments or by structures. Pigments generate color by spectrally selective absorption of incident light by molecules. Structural color is generated by optical scattering of nanostructures. Light of certain wavelength scattered from ordered nanostructures interfere constructively in some directions and destructively in other directions. Thus the color depends on the viewing angle and is iridescent. However the color created by optical scattering from disordered structures is non-iridescent. It is mostly due to Rayleigh scattering or Mie scattering of individual scatterers.

Prum et.al first pointed out that non-iridescent color can be generated by constructive interference from short-range ordered (quasi-ordered) structures. He showed through 2D Fourier analysis of transmission electron microscopy (TEM) images, a quasi ordered nanostructure has a characteristic length scale on the order of visible wavelengths. Although it is perceived that the optical properties are closely related to the underlying nanostructure, the exact mechanisms of light scattering and of color generation are still unknown.

The avian quasi-ordered nanostructures have two types. One consists of air spheres, the other consists of air channels. Such nanostructures were recently studied through small-angle x-ray scattering (SAXS) measurements. The channel-type nanostructures are
similar to structures formed by spinodal decomposition and the sphere-type nanostructures are likely formed by nucleation and growth.

In this chapter, we investigate the intensity of light reflected or scattered by the avian feather barbs as a function of wavelength, scattering angle, polarization, incident angle and the sample orientation. Our data reveal how non-iridescent color is generated by optical scattering of quasi-ordered nanostructures and what the effect of multiple scattering is. We attribute the structural color mostly to single scattering and double scattering.
4.1. Sample Characteristics

Structural colors of avian feather barbs are produced by light scattering from spongy $\beta$-keratin and air nanostructures within the medullary cells of avian feather barb rami.\[129,130,131\] Feathers are composed almost entirely of feather $\beta$-keratins, which are $\beta$-pleat sheet proteins that self-assemble into filaments.\[135,136\]

We measured light scattering from both quasi-ordered sphere type structures shown in Fig. 4.1(a) and quasi-ordered channel-type structures shown in Fig. 4.1(b).

For a control experiment, we also measured a periodic array of spheres in $\beta$-keratin to understand the difference between quasi-ordered and ordered structures (Fig. 4.1(c)).

Table 4.1 lists the birds and their feather colors for each type that we investigated.

<table>
<thead>
<tr>
<th>Structure Type</th>
<th>bird name</th>
<th>color of a feather</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ordered Sphere Type Structure</td>
<td>Lepidothrix iris (Liris)</td>
<td>iridescent</td>
</tr>
<tr>
<td>Quasi Ordered Sphere Type Structure</td>
<td>Cotinga maynana (Cmaynana)</td>
<td>light blue</td>
</tr>
<tr>
<td></td>
<td>Lepidothrix coronata (Lcoronata)</td>
<td>medium blue</td>
</tr>
<tr>
<td></td>
<td>Cotinga cotinga (Ccotinga)</td>
<td>deep purple</td>
</tr>
<tr>
<td>Quasi Ordered Channel Type Structure</td>
<td>Sialia sialis (Ssialis)</td>
<td>medium blue</td>
</tr>
<tr>
<td></td>
<td>Irena puella (Ipuela)</td>
<td>medium blue</td>
</tr>
<tr>
<td></td>
<td>Coracias benghalensis (Cbenghalensis)</td>
<td>turquoise</td>
</tr>
</tbody>
</table>

Table 4.1. bird names and color of feathers in each type

In the following, we show the data Cmaynana as an example of quasi ordered sphere type structure and Cbenghalensis a quasi ordered channel type structure. They have the same effective refractive index $n_{eff} = 1.25$ because both have an air filling fraction of 62\% and the refractive index of $\beta$-keratin is 1.58 [137].

We performed SAXS measurements to characterize structures. SAXS data were collected at Beam line 8-ID at the Advanced Photon Source Argonne National Labs using a
20\(\mu m\) beam width. Figures 4.2(a) and (b) are images of SAXS intensity in transmission mode. (a) is for Cmaynana and (b) is for Cbenghalensis. The center part of the image is blocked to prevent unscattered x-ray from going into the detector. SAXS images show ring patterns confirming isotropic scattering. Since scattering is isotropic, we averaged scattering intensity over the azimuthal angle. Fig 4.2(c), (d) is the plot of angle-averaged intensity vs. spatial frequency \(q\). The main peaks for Cmaynana and Cbenghalensis are at 0.03\(nm^{-1}\), 0.0286\(nm^{-1}\) respectively. The peak of Cbenghalensis is broader than that of Cmaynana. Cmaynana has a minor peak at \(q = 0.05nm^{-1}\), while Cbenghalensis exhibits only a shoulder on the large \(q\) side of the main peak.

The main structures that generate color are located in the barbs of avian feathers. In order to measure scattering from barbs, we mounted the feather in such a way that the probe area was free standing. This eliminates scattering from the sample holder.
Figure 4.2. Images of SAXS patterns for Cmaynana(a) and Cbenghalensis (b). (c) and (d) are angle-averaged SAXS intensity vs. spatial frequency $q$.

4.2. Optical Setup

To probe the dependence of color on the illumination direction, viewing angle and sample orientation, we performed 3 different angle-resolved scattering measurements. Two angles are defined for a clear description of the experimental configuration. $\theta$ is the angle between the incident beam and detector arm. $\phi$ is the angle between the incident light direction and the normal direction of the sample surface.
(1) Method 1 to measure specular reflection: \( \phi \) was changed with the relation \( 2\phi = \theta \) from \( \phi = 10^\circ \) to \( 60^\circ \) with \( 10^\circ \) steps.

(2) Method 2 to measure backward scattering: \( \phi \) was changed from \( 5^\circ \) to \( 55^\circ \) with \( 10^\circ \) steps while \( \phi \) was fixed at \( 10^\circ \).

(3) Method 3 to measure diffusive scattering: \( \theta \) was changed from \( 10^\circ \) to \( 60^\circ \) with \( 10^\circ \) steps while \( \phi \) was fixed at \( 0^\circ \).

We used a goniometer for angle-resolved measurements. A feather was positioned at the rotation center of the goniometer. The orientation of barbs was carefully adjusted so that the barb axis was perpendicular to the rotation axis of the goniometer. A UV enhanced Xe lamp from Oriel was used as a collimated white light source. The spot size on the sample was about \( 1\text{mm} \). Scattered light was collected by a lens and focused to an optical fiber on the rotation arm and spectrum analyzed. We used a spectrometer HR2000+ from Ocean Optics Inc. The angular resolution was \( \sim 5^\circ \). For the polarization dependent measurement, we used two linear polarizers. One was placed in the path of the incident beam, the other was in front of the detector. The spectra of scattered light was normalized by that of the incident light. We also smoothed the spectra by a Gaussian function of full width at half maximum \( 2\text{nm} \).
4.3. Experimental Results

First, we present the control experiment with (Fig. 4.4). In the specular reflection spectra shown in Fig. 4.4 (a), there is a peak at $\lambda = 613 nm$ for $\phi = 10^\circ$. It moves to shorter wavelengths as $\phi$ increases. At $\phi = 60^\circ$ the peak wavelength is $472 nm$. When only the sample is rotated (method 2), the reflection peak appears only at $\phi = 5^\circ$ which is close to the specular reflection direction. For other values of $\phi$, the reflection peak disappears. To check scattering into other directions, we also moved the detector while keeping the sample fixed (method 3). Figure 4.4 (c) shows a result similar to backward scattering. The reflection peak can be observed only at $\theta = 10^\circ$. Therefore the reflection peak can be obtained only in the direction close to that of specular reflection. The reason
Figure 4.4. Scattering spectra of Liris measured by method 1 (a), method 2 (b) and method 3 (c)
that scattering peak can be observed close to the specular direction is because of surface roughness of the avian feather barbs. These results indicate that the color of Liris feather is iridescent.

Figure 4.5 shows the scattering spectra of Cmaynana. In the specular reflection (Fig.4.5(a)), there is a main peak at $\lambda = 525\text{nm}$ for $\phi = 10^\circ$. The peak moves to shorter wavelengths as $\phi$ increases from $10^\circ$ to $60^\circ$. The peak amplitude is maximal at $\phi = 10^\circ$ and decreases as $\phi$ increases. In the backward scattering spectra (Fig.4.5(b)), there is a peak at $\lambda = 533\text{nm}$. The peak position does not change with the angle. There is no significant change in peak amplitude with $\phi$ either. In diffusive scattering (Fig.4.5(c)), the reflection peak wavelength is $533\text{nm}$ at $\theta = 10^\circ$. When $\theta$ increases, the peak moves to shorter wavelengths, and the peak amplitude decreases. The peak wavelength in specular reflection and diffusive scattering becomes coincident when $2\phi = \theta$ (Fig. 4.6(a)). Also the spectral position of the peak in the backward scattering is the same as that of $\theta = 10^\circ$ in diffusive scattering spectra. In all the spectra measured by 3 methods, there is a dip at $600\text{nm}$. This dip results from absorption by pigments because there is no angle dependence of its spectral position. The spectral profile of the scattering peak shape is highly asymmetric and there is a shoulder at $\lambda = 398\text{nm}$ for $\theta \leq 20^\circ$ in specular reflection and diffusive scattering, the shoulder moves to longer wavelengths as $\theta$ or $\phi$ increases. It merges with the main peak and then reappears on the longer wavelength side.

Figure 4.7 shows the scattering spectra of Cbenghalensis. The phenomena are the same as those of Cmaynana.

The summary of results is as follows,
Figure 4.5. Scattering spectra of Cmaynana measured by method 1 (a), method 2 (b) and method 3 (c)
Figure 4.6. Wavelength of main peak measured by method 1 and 3 as a function of angle $\theta$. (a) Cmaynana (b) Cbenghalensis

- The main peak in the scattering spectra shifts in wavelength as the incident angle and/or view angle changes. However the peak wavelength depends only on $\theta$, as shown in Fig. 4.6.
- Peak is the strongest in the backward direction.
- Secondary peak shifts spectrally in the opposite direction from the main peak as $\theta$ increases.

We also studied the dependence of scattering spectra on polarizations of the input beam and scattered light. The scattering spectra taken at $\theta = 10^\circ$ and $\phi = 10^\circ$ for 4 different polarization combinations are presented in Fig. 4.8. In the legend, S is S polarization-electric field vector is perpendicular to the plane of incidence. P is P polarization-electric field vector is parallel to the plane of incidence. The first letter describes polarization of incident light, the second letter polarization of scattered light into the detector. In Fig. 4.8 (a), the co-polarization (SS,PP) spectra for Cmaynana has two peaks at $\lambda = 365nm$ and $\lambda = 534nm$. The cross-polarization(SP,PS) spectra are very different, the main peak
Figure 4.7. Scattering spectra of C. menghalensis measured by method 1 (a), method 2 (b) and method 3 (c)
Figure 4.8. Polarization dependence of scattering peaks. (a) Cmaynana: two peaks at 365\textit{nm} and 534\textit{nm} for copolarization. For cross polarization, the peak at 534\textit{nm} disappears. The peak at 365\textit{nm} has small change in amplitude. (b) Cbenghalensis: for copolarization, there are two peaks at 396\textit{nm} and 568\textit{nm}. In the case of cross polarization, the peak at 568\textit{nm} disappears. The peak amplitude at 396\textit{nm} has small change.

amplitude at 534\textit{nm} disappears, the secondary peak at 365\textit{nm} remains although its amplitude is reduced by 40%. Cbenghalensis is similar.
4.4. Discussion

4.4.1. Single Scattering

The scattering measurements with different polarizations indicate that the main peak is from single scattering because single scattering does not change the polarization of incident light. The secondary peak is from multiple scattering which causes depolarization. For single scattering, there is a relation between the incident light wave vector ($\vec{k}_{\text{in}}$) and scattered light wave vector ($\vec{k}_{\text{out}}$), as illustrated in Fig. 4.9.

\begin{align*}
\vec{k}_{\text{in}} \text{ is scattered into } \vec{k}_{\text{out}} \text{ via structure vector } \vec{q}, \quad \vec{k}_{\text{out}} = \vec{k}_{\text{in}} + \vec{q}. \quad \text{Since the scattering is elastic, } |\vec{k}_{\text{in}}| = |\vec{k}_{\text{out}}| = k. \quad \text{Thus the relation between } k \text{ and } q \text{ is,}
\end{align*}

\begin{equation}
q = 2k \cos(\theta_m/2)
\end{equation}
where $\theta_m$ is the angle between incident and scattered light inside the sample, $k = 2\pi n_{eff}/\lambda$, $\lambda$ is the wavelength in vacuum.

Due to surface refraction, $\theta$ outside the sample differs from $\theta_m$, which can be calculated with $n_{eff}$. For the three measurement methods,

$$\theta_m = 2 \sin^{-1}(\phi/n_{eff}) \text{ for specular reflection}$$

(4.2) $$\theta_m = \sin^{-1}(\sin(\phi)/n_{eff}) - \sin^{-1}(\sin(\phi - 10)/n_{eff}) \text{ for backward scattering}$$

$$\theta_m = \sin^{-1}(\sin(\theta)/n_{eff}) \text{ for diffusive scattering}$$

Figure 4.10. $q$ vs. $\theta$ for Cmaynana (a) Cbenghalensis (b). $q$ is obtained by method 1 and 3.

Using Eq. 4.1 we calculated $q$ for the main peaks in the specular reflection and diffusive reflection spectra. Figure 4.10 shows the result for Cmaynana and Cbenghalensis. The horizontal axis is angle $\theta$. $q$ is constant for all $\theta$ and $q$ obtained from specular reflection and diffusive scattering is the same. This result also confirms that the main spectral peak originates from single scattering. The colors of Cmaynana and Cbenghalensis feathers are
created mostly by single scattering. Because their structures are isotropic $S(\vec{q}) = S(q)$, the color has no dependence on feather orientation.

The scattering peak has a larger amplitude for smaller angle $\theta_m$. The main reason for the peak amplitude change with angle is that the relation between $q$ and $k$ is not linear. They are related by $\cos(\theta_m/2)$. Thus, $\frac{dq}{d\theta_m} = -k\sin(\theta_m/2)$. The rate what $q$ changes with $\theta_m$ is very small near the backward scattering direction where $\theta_m$ is close to zero.

In the measurements, we have an average angle $\sim 5^\circ$. As a result, the angle-averaged $\theta_m$ peak intensity becomes maximal for $\theta_m = 0$. Figure 4.9 (b) plots the calculated single scattering intensity vs. frequency ($1/\lambda$) for various $\theta_m$. As $\theta_m$ increases, the scattering peak shifts faster in $q$. The peak height remains constant due to isotropic $S(\vec{q})$.

### 4.4.2. Double Scattering

The scattering peaks at $\lambda = 365nm$ for Cmaynana and $\lambda = 396nm$ for Cbenghalensis in Fig 4.8 originate from multiple scattering since the peak amplitude difference between co-polarization and cross-polarization is small. We first consider double scattering, and calculate the scattering intensity using $S(q)$ from SAXS measurements.

Figure 4.11 is a schematic diagram of double scattering. In double scattering, the incident light is scattered twice successively before exiting the sample. The wavevector $\vec{k}_m$ changes to $\vec{k}_m$ and then to $\vec{k}_{out}$. $\vec{k}_m$ is the wave vector before second scattering and after first scattering. We assume the two consecutive scattering events are independent, and each can be described by single scattering. $\alpha_1$ and $\alpha_2$ denote the angles for each single scattering. Since scattering is elastic, $|\vec{k}_m| = |\vec{k}_m| = |\vec{k}_{out}| = k$. 
Figure 4.11. Schematic diagram of double scattering. Close to backward scattering gives peak at long wavelength (a) and close to forward scattering gives peak at short wavelength (b).

Even when the directions of $\vec{k}_{\text{in}}$ and $\vec{k}_{\text{out}}$ are fixed, $k_m$ can be in multiple directions. Figure 4.11 shows two scattering diagrams for the same $\vec{k}_{\text{in}}$ and $\vec{k}_{\text{out}}$ but different $\vec{k}_m$. When each scattering event is closer to backward scattering (Fig. 4.11 (a)), $k$ has a smaller amplitude. Let us consider a special case $|\vec{q}_1| = |\vec{q}_2| = q_0$, where $S(q)$ reaches the maximum at $q_0$. As $\alpha_1$ and $\alpha_2$ increase, the amplitude of $k$ decreases. This means the wavelength of double scattered light increases when each scattering gets closer to the backward direction.

We calculated double scattering intensity for 1000 different $\vec{k}_m$ whose directions are uniformly distributed over $4\pi$ solid angle. To compare with experimental results, we took into account surface refraction and averaged over $5^\circ$ collection angle of double scattering spectra.

Figure 4.12 shows the calculated diffusive scattering spectra for single scattering (a) and double scattering (b). The single scattering peak position has good agreement with
experimental results for various angles $\theta$. In double scattering spectra, the scattering peak is broadened as $\theta$ increases. The maximum peak intensity of double scattering is located on the longer wavelength side of the broad peak, and it shifts to longer wavelengths at larger $\theta$.

The reason for the broadening of the double scattering peak is as follows. If we assume $S(q)$ is a delta function at $q_0$, when the angle $\theta$ is zero, $\alpha_1 = \alpha_2=90^{\circ}$. Thus only single scattering into $90^{\circ}$ is allowed for $\theta = 0^{\circ}$. The allowed range of scattering angles $\alpha_1$ and $\alpha_2$ increases as $\theta$ increases, which broadens the double scattering peak. The maximal intensity of double scattering at longer $\lambda$ also can be understood from single scattering intensity. According to Eq.4.11, the single scattering peak position changes little when angle $\alpha_1$ and $\alpha_2$ are small. Thus, when all possible values of $\alpha_1$ and $\alpha_2$ are included in double scattering for each $\theta$, the intensity of double scattering involving smaller $\alpha_1$ and $\alpha_2$ is higher and located at longer $\lambda$.

Figure 4.13 compares the measured $q$ values of the single scattering peak ($q_{\text{single}}$) and the double scattering peak ($q_{\text{double}}$) to the calculated one for Cmaynana (a) and Cbenghalensis (b). Due to low efficiency of our detector at $\lambda \leq 300\text{nm}$, we can only extract the position $q_{\text{double}}$ of the double scattering intensity maximum at larger $\lambda$. Both $q_{\text{single}}$ and $q_{\text{double}}$ values were obtained from angle-resolved copolarization measurements. The double scattering peak position is more clear in co-polarization measurements because it can suppress higher order scattering efficiently. We used double peak fitting of the co-polarized scattering spectrum to obtain $q_{\text{single}}$ and $q_{\text{double}}$. As shown in Fig.4.13, $q_{\text{double}}$ decreases as $\theta$ increases. Calculated and measured $q_{\text{double}}$ shows the same trend as $\theta$ changes. This indicates the secondary peak in the scattering spectrum originates mostly
from double scattering. A small offset in $q_{\text{double}}$ may be due to inaccuracy of determining $q_{\text{double}}$ from curve fitting since the double scattering peak is rather broad.

Figure 4.12. (a) single scattering (b) double scattering spectra calculated based on SAXS data of Cmaynana for different $\theta$
Figure 4.13. Comparison of $q$ values of single and double scattering peaks between calculation (lines) and experiment data (symbols). (a) Cmaynana (b) Cbenghalensis

4.5. Conclusion

We studied the structural color produced by quasi-ordered nanostructures in avian feathers. One is quasi-ordered air spheres in protein, the other is quasi-ordered channel structure. Both show non-iridescent color. The angle- and polarization- resolved scattering measurements show that color is produced mostly by single scattering. However there are additional contributions from multiple scattering especially double scattering, which is confirmed by numerical simulation and polarization-dependent measurements.
Propagation and Localization of Optical Excitations in Random Metal Films

Spatial correlations of field and intensity have been widely studied in the context of electromagnetic (EM) wave propagation in disordered systems and are indicative of the nature of wave transport in random media. In dielectric random systems, the enhancement of nonlocal intensity correlations due to localization effects has been theoretically and experimentally investigated. In disordered metallic nanostructures, surface plasmon (SP) modes are governed by structural inhomogeneities and may be strongly localized. Localization of surface plasmon polaritons (SPPs) has been observed in rough and semi-continuous metal films. The near-field intensity distribution across a semicontinuous metal film near the “percolation threshold” is extremely inhomogeneous with giant local field maxima (hot spots). The hot spots not only vary in size by orders of magnitude from subwavelength to multiple wavelength (λ), but also vary strongly in intensity. These properties are very different from those in a dielectric random system where the speckle pattern is relatively more homogeneous with an average speckle size of the order of λ. Moreover, the accumulation and subsequent dissipation of EM energy in localized SP modes result in anomalous absorption in semicontinuous metal films. These fundamental differences between metallic and dielectric
random systems suggest that the near-field intensity correlation functions in these two systems can be dramatically different.

In this chapter, we present the experimental study of near-field intensity correlations in semicontinuous metal films. The concentration $p$ of metal particles on a dielectric surface is varied over a wide range to control the scattering strength. When $p$ is far from the “percolation threshold” $p_c$, scattering is weak and the impinging light mostly excites extended SP modes. These propagating EM surface waves correlate the near-field intensity over large distances. When $p$ is near $p_c$, substantial structural inhomogeneities result in strong scattering. The incident wave couples predominately to localized SP modes, and the near-field intensity correlation becomes short ranged. We compare the spatial intensity correlation functions in metal-dielectric and purely dielectric random systems to illustrate their differences.
5.1. Fabrication of Semi Continuous Metal Film

Silver was used for these experiments because at optical frequencies its dielectric constant has a large negative real part and a relatively small imaginary part compared to transition metals so that resonant effects are expected to be large. Similar behavior is expected for gold and other coinage metals.

The random metal-dielectric films used in our experimental study were synthesized by laser ablation of a solid silver target under argon gas pressure of 0.3 mTorr (0.04 Pa). A nanosecond Nd:YAG laser (Quanta-Ray DCR-02A) provided pulses with an energy of 100 mJ/pulse, a repetition rate of 10Hz, and a wavelength of 532 nm. The spot size of the laserbeam at the target was approximately 1mm. Silver was deposited on glass substrates for optical study on Formvar-coated copper grids for characterization by transmission electron microscopy (TEM), and on silicon substrates for scanning electron microscopy (SEM) analysis under identical conditions.

TEM images reveal that the samples are composed of individual silver grains of average size 20 ~ 30nm. An increase in deposition time (surface concentration of silver) induces a structural transition from isolated metal grains ($p \leq 0.4$) to interconnected metal clusters ($p \approx 0.6$) and finally to a nearly continuous metal film with dielectric voids ($p \geq 0.8$) (Fig.5.1(a)-(e)).

The two-dimensional (2D) Fourier transforms of the structures, obtained from TEM micrographs, exhibit isotropic distributions in k space for all samples (Fig.5.4(f)-(j)).
Figure 5.1. Transmission electron microscopy images (1×1 \( \mu m^2 \)) of silver films at various metal concentrations \( p \) show a transition from individual metal grains to interconnected clusters. (a) \( p=0.36 \) (b) \( p=0.45 \) (c) \( p=0.65 \) (d) \( p=0.73 \) (e) \( p=0.83 \). (f)-(j) corresponding 2d Fourier spectra.
5.2. Percolation Threshold

The percolation threshold can be found from the electrical resistance measurement. The effective electric resistance of a metal-dielectric film, \( \rho \), decreases as metal filling fraction or deposition time increases. The largest changes occur in the vicinity of the percolation threshold \( p_c \), i.e., \( |p - p_c| \ll \Delta p \), where the effective electric resistance \( \rho \), obeys the power laws

\[
\rho \approx \begin{cases} 
\rho_d(p - p_c)^{1.3} & \text{for } \Delta p < p_c - p < < 1 \\
\rho_m(p_c - p)^{-1.3} & \text{for } \Delta p < p - p_c < < 1 
\end{cases}
\]

where \( \rho_m \) is metal resistance, \( \rho_d \) is tunneling resistance which is associated with the tunneling of electrons between metal components across the dielectric area of the film.

The percolation threshold was found at \( p_c = 0.65 \) (Fig.5.2).
Figure 5.2. Electrical resistance vs filling fraction. The theoretical curves are plotted in accordance with Eq. 5.1.

5.3. Near Field Scanning Optical Microscopy

Figure 5.3. Schematic of experimental NSOM apparatus
In the near-field experiment, samples were illuminated by the evanescent field (in the total internal reflection geometry) of He-Ne lasers operating at 543 and 633nm (p polarized). The local optical signal was collected by a tapered, uncoated optical fiber of tip radius \( \sim 50 \text{nm} \). The tip-to-sample distance, controlled by shear-force feedback, was \( \sim 10 \text{nm} \). The tip resolution was estimated to be \( \sim 150 \text{nm} \) from the smallest features in the near-field images.

Figure 5.4 shows near-field scanning optical microscopy (NSOM) images for samples of \( p = 0.36, 0.45, 0.65, 0.75, 0.83 \) at a probe wavelength of 543nm. The projection of the incident beam’s \( k \) vector on the film plane (x-y plane), \( k_\parallel \), is along the vertical \( y \) axis. At \( p = 0.36 \), there is a clear indication of interference fringes parallel to the horizontal \( x \) axis, which are weakened at \( p = 0.45 \) and completely lost at \( p = 0.65 \). The NSOM images at \( p = 0.65 \) exhibit inhomogeneous intensity distributions with hot spots of various sizes. The interference fringes start to reappear at \( p = 0.75 \) and are clearly visible at \( p = 0.83 \).

To identify the spatial frequencies or \( k \) vectors of excitations in a sample, 2D Fourier transforms of the near-field intensity distribution \( I(x, y) \) were obtained. The beating of waves of different spatial frequencies results in intensity modulations, thus allowing the extraction of \( k \) vectors from the Fourier transform of the intensity distribution. In Fig. 5.4, the spatial Fourier spectra exhibit significant elongation of the \( k \)-vector distribution along the incident direction at low and high \( p \), whereas the distribution is nearly isotropic at \( p_c \approx 0.65 \). This reflects changes in the scattering strength in the samples. At low densities of metal particles, both elastic and inelastic scattering are weak. Because of the small grain size, scattering by single metal particles occurs mainly in the forward and backward directions. Hence, the in-plane \( k \) vectors are predominately parallel or
Figure 5.4. Near-Field Scanning Optical Microscopy images (4×4 μm²) of silver films at various metal concentrations p (a) p=0.36 (b) p=0.45 (c) p=0.65 (d) p=0.73 (e) p=0.83
antiparallel to the incident wave vector $k_\|$. As $p$ increases, scattering becomes stronger and the impinging wave is more strongly scattered into other directions until the memory of the incident $k$ vector is completely lost at $p_c$. With a further increase in $p$, the structure approaches that of a continuous metal film and scattering, now caused by dielectric voids, decreases again leading to a nonisotropic $k$ distribution. Similar phenomena were also observed at the other probe wavelength of 633 nm. These data thus reveal that both weak and strong scattering regimes can be accessed by varying metal concentration.

![Figure 5.5](image)

Figure 5.5. The 2D intensity correlation functions $C(\Delta x, \Delta y)$ at $p=0.36$, 0.65, and 0.83. The incident wave is along the $y$ axis.

From near-field images, the 2D correlation functions for near-field intensities were computed:

\[
C(\Delta x, \Delta y) =< \delta I(x, y) \delta I(x + \Delta x, y + \Delta y) >
\]

(5.2)

Where, $\delta I(x, y) = (I(x, y) - <I(x, y)>)/<I(x, y)>$. Figure 5.5 shows the spatial dependence of $C(\Delta x, \Delta y)$ for samples with $p = 0.36$, 0.65, and 0.83 at $\lambda = 633\text{nm}$. Fringes are present along the direction of the incident wave for $p = 0.36$ and 0.83, but disappear at $p = 0.65$. Figures 5.6 and 5.7 are plots of the correlation functions in the directions
parallel and perpendicular to the incident wave vector $k_{\parallel}$, i.e., $C(0, \Delta y)$ and $C(\Delta x, 0)$. Along $k_{\parallel}$, $C(0, \Delta y)$ exhibits oscillatory behavior at $p = 0.36$ with a period of 870 nm. The oscillation is replaced by a monotonic decay at $p = 0.65$. The inset of Fig. 3.6, a log-linear plot of $C(0, \Delta y)$ at $p = 0.65$, indicates an exponential reduction in correlation for a $\Delta y$ range of 50 nm to 0.9 µm (beyond 0.9 µm its value reduces to the noise level). At $p = 0.83$, the oscillations reappear with a smaller period of 690 nm. Oscillations are also observed for $p = 0.45$ and 0.75 (not shown here for figure clarity), but their amplitudes are damped quickly. The presence of oscillations in $C(0, \Delta y)$ indicates the excitation of propagating surface waves with well-defined wave vectors along the $y$ axis. Note that oscillations have been reported in near-field correlations of thermal emission from a smooth surface of bulk metal, as a result of excitation of propagating SPPs [156]. Although all our samples are semicontinuous films, scattering due to structural inhomogeneities is rather weak at low and high $p$, as seen in Fig. 3.1. Hence, the incident wave is subjected to the effective medium properties, and coupled predominately to propagating EM modes. A detailed explanation of the propagating surface waves is given later. When $p$ is near $p_c$, large structural inhomogeneities result in strong scattering. The disappearance of oscillations in the intensity correlation functions reveals the suppression of propagating surface waves with well-defined wave vectors. The impinging light is coupled mostly to localized SP modes. The local field fluctuations occur on the length scale of microscopic structures. Because of the wide range of structural scales in a semicontinuous metal film near $p_c$, no single length scale prevails. As a result, the intensity correlation function exhibits a monotonic decay. Therefore, the existence, suppression, and revival of the oscillations in the near-field intensity correlation function with increasing $p$ reflect the variation in the
coupling strength between the incident light and microscopic structural inhomogeneities of semi-continuous metal films.

It is clear from Fig. 5.6 that $C(\Delta x, 0)$ shows no oscillations at any metal concentration. Hence, there is no wave propagation in the direction perpendicular to the incident wave vector. At $p = 0.36$, $C(\Delta x, 0)$ decreases gradually with $\Delta x$, but does not reduce to zero even at large $\Delta x$. The drop is much sharper at $p = 0.65$, and $C(\Delta x, 0)$ is almost zero when $\Delta x > 0.5 \mu m$. At $p = 0.83$, the decrease becomes gradual again and $C(\Delta x, 0)$ remains well above zero even for $\Delta x > 3 \mu m$. The long tail of $C(\Delta x, 0)$ suggests the existence of long-range correlation at low and high $p$, which results from a delocalized field. In the intermediate regime of metal concentration, the rapid decay of $C(\Delta x, 0)$ to zero indicates that the intensity correlation becomes short ranged because of strong scattering and anomalous absorption [153, 154, 155]. The correlation radius $R_c$ [HWHM of $C(\Delta x, 0)$] allows a quantitative comparison between different samples and is plotted in the inset of Fig. 5.6 as a function of $p$ for both probe wavelengths. $R_c$ decreases from 500 nm at $p = 0.36$ to about 250 nm at $p = 0.45$, where it remains almost constant till $p = 0.75$. At $p = 0.83$, $R_c$ increases to about 350 nm. This type of analysis was not attempted for $C(0, \Delta y)$ as the oscillations make it difficult to extract $R_c$. Nevertheless, the variation of correlation radius with $p$ is consistent with the change in scattering strength exhibited in Fig. 5.4.

Near-field intensity correlations in disordered metal-dielectric structures appear to be very different from those in purely dielectric random media. In the latter, $C(\Delta \vec{r})$ is dominated by short-range correlation in the delocalization regime, whereas in the localization
regime long-range correlation is greatly enhanced [140][141][142]. However, in the former, the intensity correlation becomes short ranged; i.e., \(C(\Delta \vec{r})\) decays quickly to zero at \(p = p_c\), where localization of SPPs is expected. In addition, \(C(\Delta \vec{r})\) exhibits damped oscillations with a period of \(\lambda/2\) in a dielectric random medium. In contrast, in a metallic random system, when scattering is weak, \(C(\Delta \vec{r})\) oscillates with a period longer than \(\lambda/2\) and the damping of the oscillations is much slower than in dielectric systems. As shown next, the oscillation period is determined by the characteristic length scales of collective excitations in the system.

Since a single propagating wave cannot induce oscillations in the intensity correlation function, the oscillations observed at low and high \(p\) indicate the existence of at least two propagating surface waves. To identify these waves, we calculated the wave vectors of the SPPs excited by the impinging light. At \(p \geq 0.8\), the system consists of a continuous network of silver clusters and can be treated as a continuous metal film with a random array of dielectric voids. SPPs may exist at both silver-air and silver-glass interfaces. The high metal concentration allows the use of the effective medium approximation to calculate the effective dielectric constant, which varies with \(p\). The film permittivity is anisotropic: its value \(\varepsilon_e\) in the \(x\)-\(y\) plane differs from \(\varepsilon_z\) in the \(z\) direction. At our probe wavelengths, \(|\varepsilon_z| >> |\varepsilon_e|\). Thus, the dispersion relation for SPP propagation ascribes the form

\[
(5.3) \quad \varepsilon_d \times (1 - D\sqrt{-1 + x^2\sqrt{-\varepsilon_e}}) - \sqrt{x^2 - \varepsilon_d} \times (D\sqrt{-\varepsilon_e} + \sqrt{-1 + x^2\varepsilon_e}) = 0
\]
where \( x = \frac{c}{\omega}k_{sp} \), \( k_{sp} \) is the SPP wave vector, \( D = \coth(\omega d \sqrt{-\varepsilon_d}/c) \), \( d \) is the film thickness, and \( \varepsilon_d \) is the dielectric constant of the glass substrate. Equation (5.3), a third-order equation in \( x^2 \), has only two physical solutions with values \( k_1 \) and \( k_2 \) for SPP at the silver-air \((z = -d/2)\) and silver-glass \((z = d/2)\) interfaces, respectively.

The conditions for the existence of SPPs in a semi-continuous metal film are as follows: (i) sufficiently small losses, i.e., \( \text{Re}[k_1,2] \gg \text{Im}[k_1,2] \) (ii) \( \text{Re}[k_1] > \omega/c, \text{Re}[k_2] > \sqrt{\varepsilon_d}\omega/c \). These conditions can be fulfilled at sufficiently large metal concentrations \((p \geq 0.8)\). In a continuous silver film on glass \((p = 1)\), SPPs cannot be excited at the silver-glass interface as the incident \( k \) vector is less than \( \text{Re}[k_2] \). However, for semicontinuous films used in the current experiment, SPPs are effectively excited due to the structural randomness and associated giant local field fluctuations. The spatial beating between the fields of the two SPP waves results in a stationary intensity modulation with period \( \lambda_s = 2\pi/|k_1 - k_2| \). At \( p = 0.83 \), we estimate \( \lambda_s = 640\,\text{nm} \) from Eq. (5.3) for incident light at 633\,\text{nm}. \( \lambda_s \) should be equal to the oscillation period of the correlation function which, from Fig. 5.6, is about 690\,\text{nm} and agrees well with the estimated value. Note that from our calculations, for \( p < 0.7 \), the total loss in the system given by \( \text{Im}[k_2] \), is comparable to \( \text{Re}[k_2] \). Thus, \( \text{Im}[k_2] \) is large despite small intrinsic losses in the metal \((\text{Im}[\varepsilon_m] \ll \text{Re}[\varepsilon_m])\), which substantiates the anomalous absorption due to the localization of SPPs near \( p_c \).

The oscillations of intensity correlation functions at low metal coverage \( p \leq 0.4 \) once more indicate the interference of two propagating waves. These oscillations cannot be explained solely by interference of the incident evanescent wave \((\lambda_\parallel = 2\pi/k_\parallel \approx 610\,\text{nm})\) with the wave elastically backscattered by the metal particles, as the observed oscillation period \((870\,\text{nm})\) is considerably larger than \( \lambda_\parallel/2 \). Therefore, there must exist another
Figure 5.6. $C(0, \Delta y)$ at $p=0.36$ (solid line), 0.65 (dashed line), and 0.83 (dotted line) for incident wavelength 633nm. Inset: log-linear plot of $C(0, \Delta y)$ at $p = 0.65$. For comparison, all $C(0, \Delta y)$ curves are divided by $C(0,0)$.

Figure 5.7. $C(\Delta x, 0)$, again divided by $C(0,0)$, at $p = 0.36$ (solid line), 0.65 (dashed line), and 0.83 (dotted line), for incident wavelength 633nm. Inset: correlation radius $R_c$ vs $p$ for probe wavelengths at 633nm (dashed line) and 543nm (solid line).
propagating wave with a different $k$ vector. At $p \leq 0.4$, the sample consists of individually separated metal grains of nearly uniform shape. When collectively excited by incident light, these grains can be treated as oscillating dipoles with identical resonances and strong coupling between them [157,158]. For $p < p_c$, the semicontinuous silver film is in a dielectric state; its effective dielectric constant $\varepsilon_{\text{eff}} = \varepsilon' + i\varepsilon''$ satisfies $\varepsilon' > 0$ and $\varepsilon' \gg \varepsilon''$. Using the Maxwell Garnet equation to estimate $\varepsilon_{\text{eff}}$, we find that as $p$ increases towards $p_c$, $\varepsilon'$ increases and becomes significantly larger than the dielectric constants of the surrounding media (glass and air). A thin dielectric waveguide is thus formed at the surface of the glass substrate. The incident light excites mainly the lowest-order guided mode of this waveguide, leading to propagating surface waves. At $p = 0.36$ and $\lambda = 633nm$, we estimate the wavelength of the lowest-order guided mode $\lambda_s = 383nm$. The beating between the incident evanescent wave ($\lambda_{\parallel} \sim 610nm$) and the propagating guided wave results in oscillations in the intensity correlation function with a period $\lambda_c \sim 1\mu m$. From Fig. 5.6 the experimentally obtained $\lambda_c = 870nm$ is close to the estimated value.
5.4. Conclusion

In conclusion, the nature of the spatial intensity correlation functions show that as $p$ increases, the semicontinuous metal film transitions from a dielectric waveguide at $p < p_c$ to a metallic waveguide at $p > p_c$. In between at $p \approx p_c$, the propagation of surface waves with well-defined wave vectors is greatly suppressed by strong scattering. At $p$ below $p_c$, the intensity correlation function oscillates due to beating between the incident wave and propagating guided wave in the film. As $p$ approaches $p_c$, scattering increases significantly and the oscillations in the correlation function disappear. We attribute this phenomenon to the localization of SPs. Finally, for $p$ much above $p_c$, oscillations reappear in the correlation function due to beating between SPPs propagating along the top and bottom interfaces of the film. Unlike dielectric random media, localized and delocalized modes are believed to coexist in metallic random systems [159]. Our experimental observations illustrate that at low and high metal coverages, delocalized modes dominate the transport, leading to the propagation of guided surface waves, while in the intermediate regime of metal content where structural inhomogeneities are substantial, localized modes take over, resulting in the localization of near-field energy. Both propagation and localization regimes have important applications. In the former, EM energy and information can be transferred over long distances, whereas the localization of EM fields in subwavelength scales can enhance various linear and nonlinear optical processes [146, 147].
Conclusion

In this thesis, I present experimental and numerical studies on optical properties in dielectric and metallic nanostructures with various degrees of order/disorder. In particular, I investigate light scattering and localization, spontaneous emission and lasing in photonic crystals, quasi-ordered and random media.

In photonic crystals, I have showed UV lasing at room temperature from ZnO inverse opals. The disorder in the structures, primarily due to imperfections in the opal templates and roughness caused by grain growth during firing, induces optical scattering and leads to random lasing. When the fundamental photonic bandgap is tuned to the ZnO gain spectrum, a pronounced reduction in lasing threshold is observed, indicating enhanced confinement of light by the incomplete PBG.

In the angle- and polarization-resolved photoluminescence measurement of ZnO inverse opals, the broad ZnO defect emission exhibits multiple enhancement peaks for both polarizations. Our numerical simulation reveals that the largest enhancement peak results from the frozen mode at the stationary inflection point of the dispersion curve for a high-order photonic band. The frozen mode has a well defined propagation direction and may be linearly polarized. At its frequency, the reduced DOS diverges, greatly enhancing the spontaneous emission into the frozen mode. Perfect coupling of the frozen mode to the free photon mode outside the sample leads to efficient extraction of emission from the
PhC. The enhanced emission not only has good directionality but also can be linearly polarized.

I studied the structural color of bird feathers with quasi-ordered nanostructures. One is quasi-ordered spheres in protein, the other is quasi-ordered channel structure. Both show non-iridescent color. The angle- and polarization-resolved scattering measurements show that color is produced mostly by single scattering. However, there are additional contributions from multiple scattering, especially double scattering, which is confirmed by numerical simulation and polarization dependent measurements.

The near field intensity correlation functions of metal semicontinuous films show that as metal density \( p \) increases, the semicontinuous metal films go through a transition from a dielectric waveguide at \( p < p_c \) to a metallic waveguide at \( p > p_c \). In between at \( p \approx p_c \), the propagation of surface waves with well-defined wave vectors is greatly suppressed by strong scattering. At \( p \) below \( p_c \), the intensity correlation function oscillates due to beating between the incident wave and propagating guided wave in the film. As \( p \) approaches \( p_c \), scattering increases significantly and the oscillations in the correlation function disappear. We attribute this phenomenon to surface plasmon localization. Finally, for \( p \) well above \( p_c \), oscillations reappear in the correlation function due to beating between surface plasmon polaritons propagating along the top and bottom interfaces of the metal film. Unlike dielectric random media, localized and delocalized modes are believed to coexist in metallic random systems. Our experimental observations illustrate that at low and high metal coverages, delocalized modes dominate the transport, leading to the propagation of guided surface waves, while in the intermediate regime of metal content where structural
inhomogeneities are substantial, localized modes take over, resulting in the localization of near-field energy.
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