Naturally occurring order-disorder duality in photonic structures of the *Haliotis fulgens* abalone shell

SEUNG HO CHOI¹,²,⁴ and KYUNG MIN BYUN³,⁵

¹School of Electrical Engineering, University of Ulsan, 93 Daehak-ro, Nam-gu, Ulsan 44610, South Korea
²Department of Biomedical Engineering, Yonsei University, 1 Yonsei-dae-gil, Wonju, Gangwon-do 26493, South Korea
³Department of Biomedical Engineering, Kyung Hee University, 1732 Deogyeong-daero, Giheung-gu, Yongin 17104, South Korea
⁴chltmdghlove@hotmail.com
⁵kmbyun@khu.ac.kr

**Abstract:** We experimentally realize the ordered and disordered photonic structures in a single system by taking advantage of the nacre structures in the *Haliotis fulgens* abalone shell. The nacre layers naturally contain different degrees of disorder in thickness, ranging from quasi-order to strong disorder. Using optical characterization, numerical simulation, and SEM image analysis, we show that such wide range of disorder strength affords a full account of the transformation of periodicity-induced wave transport into disorder-induced wave transport. We believe this unique biophotonic platform will be an object of interest for both fundamental and applied photonic researches in the field of disordered photonics.

© 2019 Optical Society of America under the terms of the OSA Open Access Publishing Agreement

1. Introduction

Periodic structures and disordered structures are considered as completely opposite optical systems. Wave transport in periodic structures is described by Bragg scattering, while wave transport in disordered structures is described by light localization. If a dielectric function of material is periodic, an incident wave is partially reflected at each interface and multiple reflections constructively or destructively interfere with each other according to the Bragg’s law. When the photonic band gap is created, forward propagating wave is eliminated by destructively interfering multiple reflections; away from the spectral range of the photonic band gap, such structure becomes totally transparent [1,2]. In contrast, if the dielectric functions of material become disorder, incident wave undergoes multiple scattering in random directions. Once the randomly scattered waves yield an identical phase delay, the scattered wave can interfere with each other that gives rise to light localization. In this case, the outgoing waves are forbidden and the waves entering the materials are confined with localized mode. Consequently, light localization elimimates most of transmitted light in the whole spectral range, while occasionally allows resonant tunneling through localized modes with a small number of spectral peaks [3,4].

Given the sharply divided nature of wave transport in ordered and disordered systems, an interplay between Bragg scattering and disorder-induced scattering (e.g. Anderson localization) is of particular interest. The physics underlying this relationship is rich, yet not fully discovered. Generally, disorder degrades the Bragg band, while periodicity suppresses Anderson localization [5–10]. In certain cases, the disorder can induce Fano resonance, and this resonance is associated with a link between Bragg scattering and disorder-induced scattering [11]. However, such mechanismic study of the interplay between the order and disorder mostly relying on numerical studies and analytical theory. This is partly because photonic structures with different degrees of disorder are rare in nature and challenging to fabricate.
In this regard, it is good to have an immediately exploitable system that allows us to experimentally study the interplay between the order and disorder. In search of such photonic platform, we find a clue from a wondrous nanostructure in nacre of the abalone shell. Native nacre is well known for its captivating color. As mother-of-pearl, native nacre is biologically synthesized to have an extremely large number of parallel layers by a few orders of magnitude [12]. Due to its layer structure, coherent scattering can be created, and this give rise to the interference phenomena including structural color [13–16], random lasing [17], and light localization [18]. It is common experience that native nacre appears mildly iridescent, and one may assume that all of the layers are fully periodic creating structural colors [13–16]. However, we recently found that deproteinized nacre has a diffuse white color and such white color is mediated by random variation in thicknesses of individual layers for random lasing and light localization [17,18]. Thus, we speculate that nacre might possess both ordered and disordered structures in a single abalone shell.

In this article, we investigate that a single *Haliotis fulgens* abalone shell has both ordered and disordered nacre structures. First, we deproteinize the pigment of the organic materials in native nacre to make a light propagation in nacre is dominated by the dielectric functions of the aragonite layers. Second, using the deproteinized nacre sample, we optically characterize ordered and disordered photonic structures in nacre, and study the interplay between the order and disorder. For optical characterization, we measure reflection in space and wavelength using hyperspectral imaging system, which is customized to measure light-matter interaction from the deep inside of the nacre layer. Third, based on the transfer matrix method (TMM), we explain the effect of disorder on the reflection spectrum by simulating different degrees of disorder in thickness of the nacre layers. Fourth, analyzing scanning electron microscope (SEM) images, we confirm the existence of order-disorder duality in the photonic structures of the abalone shell. From a set of SEM images, we identify that the degree of disorder in thickness changes by nacre’s relative location in the shell; the nacre layer is nearly ordered when it is close to the outer surface of abalone shell, while the nacre layer is strongly disordered when it is close to the inner surface of abalone shell. Overall, optical characterization, numerical simulation, and SEM image analysis allow us to unveil the coexistence of ordered and disordered nanostructures in a single abalone shell.

2. Materials and methods

2.1. Nanoscale structure and optical property of nacre

As an inner shell layer, the structure of nacre is composed of nanoscale hexagonal aragonite platelets (Fig. 1(a)), which are firmly assembled into the aragonite layers. These aragonite layers are separated by the organic interlayers, which are sheets of biopolymers matrixes (i.e., lustrin and chitin). Arrangement of such platelets induce strength and resilience in organic-inorganic composite of nacre. Such excellent mechanical properties of nacre have received considerable attention, whereas nacre has not much been used as a photonic material. From an optical standpoint, nacre can be one of option for cost-effective photonic material. Aragonite is one of crystal forms of calcium carbonate CaCO$_3$ and biologically synthesized by precipitation from freshwater environment. It has pseudohexagonal crystal structures and this induce transparency in aragonite crystals. Due to the transparency, aragonite shows minimal light absorption and large refractive index $n_A$ such that (inset in Fig. 1(a)) [19]:

$$n_A^2 - 1 = 0.733 + \frac{0.964\lambda^2}{\lambda^2 - 1.943 \times 10^{-2}} + \frac{1.828\lambda^2}{\lambda^2 - 120} \quad (1)$$

Because such optical property is favorable for photonic material, nacre will be one of option for cost-effective photonic materials (i.e. the cost of abalone shell is $\sim$ $0.05cm^{-2}$).
2.2. Clearing protein pigments in nacre

Biopolymer interlayers are located at between the aragonite layers and reside in entire area of the shell. The appearance (or original color) of native abalone shell is ascribed to both optical effects of the aragonite layers and pigments of the organic materials. The biopolymer interlayer contains pigments that absorb light. Such absorption changes the structural color, which originates from the elastic light scattering in the aragonite layers. In other words, absorption of the organic materials largely attenuate light along scattering paths and thus the natural state of abalone shell is not ideal to induce optical resonance. Thus, light absorption of native nacre should be removed [17,18], to induce optical resonance, or to explore the effect of δ-disorder on optical resonance in nacre. Once the refractive index contrast of the alternating layers becomes sufficiently high and the light absorption of materials becomes low (i.e. removal of the protein pigments), all of the boundary can produce the consistent optical phenomena for resonance.

To remove the protein pigments, we mechanically and chemically process native abalone shell as follow (Fig. 2): (i) Remove the external layers (i.e. periostracum, prismatic calcite, and nacreous growth surface [12]) using a bench grinder. Do not inhale the dust created by grinder, as these particles can penetrate into the lower respiratory tree and cause respiratory irritation responses. (ii) Slice the polished nacre into small pieces using a tile saw. (iii) Immerse the sliced nacre into the sodium hypochlorite (NaOCl) solution (6%) and slowly stir for ~ 7 days at 27 °C to effectively remove biopolymer matrices including protein pigments. Avoid high shear during stirring that may cause dismantle of the nacre layer.

After removal of the protein pigments, the deproteinized nacre shows a diffuse white color (right panel of Fig. 2). We note that deproteinization minimally affects the aragonite structure, because of the excellent mechanical properties of nacre. The aragonite platelets are strongly assembled in the x–y plane (Fig. 1(a)) by the “brickwork” arrangement; such arrangement inhibit transverse crack and deformation of the aragonite layers [15,20]. In other words, the excellent mechanical properties of the aragonite layers enable to maintain the original aragonite structure, while NaOCl solution removes biopolymers matrixes. Although the aragonite platelets are strongly assembled in the x–y plane, the aragonite layers can easily be disassembled in the z-direction as the biopolymer interlayers are removed (right panel of Fig. 2). Using such mechanical properties of the deproteinized nacre, we can easily select and detach the nacre layers at different locations in the shell. This allow us to compare the optical characteristics of the nacre layer at different locations of abalone shell (Fig. 3(b)).
Fig. 2. Schematic of the protein pigments clearing procedure. Going from native abalone shell to the final deproteinized nacre takes 7 days. The aragonite platelets are strongly assembled in the x–y plane, while the aragonite layers can be disassembled in the z-direction as the biopolymer interlayers are removed (right).

Fig. 3. Hyperspectral imaging of nacre. (a) Schematic of the hyperspectral imaging system that enhances imaging depth by back-directional gating. (b) Typical reflectance spectra for the nacre layers close to the outer surface of abalone shell (left) and for the nacre layers close to the inner surface of abalone shell (right). When the nacre layers are close to the outer surface of abalone shell, the reflectance shows the second, third, and fourth order Bragg bands, $h = 2,3,4$.

2.3. Quantification of disorder in nacre

1D disordered photonic systems can possess disorder, either in thickness $\delta$ and in refractive index $n$ [11,21]. In nacre, the refractive indices of the aragonite layers $n_A$ and the biopolymer layers $n_B$ are relatively consistent over positions, while the thicknesses of the aragonite layers $\delta_A$ and the biopolymer layers $\delta_B$ are fluctuating [18,22]. Thus, we consider the effect of thickness disorder, namely $\delta$-disorder (Fig. 1(b)). In this case, it is important to define the degree of $\delta$-disorder. To
quantify the degree of \( \delta \)-disorder, we use an averaged fractional standard deviation \( \sigma \) such that:

\[
\sigma = \sqrt{\frac{s_A^2 + s_B^2}{\delta_A + \delta_B}}
\]

where \( \delta_A \) and \( \delta_B \) are the average thicknesses of the aragonite and gap layers, \( s_A \) and \( s_B \) are their standard deviations. To obtain \( \sigma \) of nacre, we analyze the structures revealed in the SEM images (Figs. 5(a) and 5(d)). To quantify \( \sigma \) of relatively ordered structures, we use highly magnified images to precisely capture small variations in thicknesses.

2.4. Hyperspectral imaging of nacre

We measure reflection in space and wavelength from the nacre sample using a hyperspectral imaging system that enhances imaging depth and area (Fig. 3(a)); this allow us to detect light-matter interaction from the deep inside of the nacre layer. Hyperspectral imaging system is combined with diffuse-light-suppression technique that suppresses unwanted diffuse light to improve penetration depth of imaging system (\( \sim 1 \text{ mm} \)) [23,24]. To suppress diffuse light, we collect the scattered light with a small angular cone of \( \sim 5^\circ \) using a 4-focal length (4-f) lens system in the back direction, namely back-directional gating. This fixed detection geometry allows us to measure light-matter interaction from the deep inside of the nacre layer. Also, the hyperspectral imaging system is designed to consistently obtain reflectance signals in a large area of 15 mm \( \times \) 15 mm (i.e. mesoscopic scale). The large field of view provides a \((300 \times 300)\)-matrix of reflectance spectra with a pixel size of 50 \( \mu \text{m} \) \( \times \) 50 \( \mu \text{m} \). Each reflectance contains a full spectral information at all of the wavelengths in the visible to near-infra-red (NIR) regions (350 \( \sim \) 950 nm). Such mesoscopic imaging system allow us to easily assess the degree of disorder over a large area of the nacre sample, which otherwise would be investigated destructively.

Figure 3(b) shows typical reflectance spectra from the nacre samples. One can observe the photonic band gap at one side of the deproteinized sample; this further confirms that deproteinization minimally affects the aragonite structure, otherwise both sides of the sample should appear diffusive by enhanced disorder.

3. Results and discussions

To optically assess the ordered and disordered nanostructures in nacre, we measure reflection in space and wavelength using hyperspectral imaging system. The nacre sample is placed in water and water fills the gap that produced from deproteinization. A beam from a xenon arc lamp is normally incident on the sample to induce light-matter interactions at the deep inside of the nacre layer. From a set of reflection measurements, we find that the nacre structures produce completely different optical phenomena depends on the relative position of the nacre layers in abalone shell. When the nacre layers are close to the inner surface of abalone shell, the reflectance spectrum becomes relatively flat in the visible and NIR regions (right panel of Fig. 3(b)). However, when the nacre layers are close to the outer surface of abalone shell, the reflectance spectrum shows the second, third, and fourth order Bragg bands, \( h = 2,3,4 \) (left panel of Fig. 3(b)). The wavelengths of the \( h \)-order Bragg bands \( \lambda_h \) are determined by the thicknesses of the aragonite layer \( \delta_A \) and the gap layer \( \delta_B \) such that (Fig. 4(b)):

\[
\lambda_h = \frac{2n_{\text{eff}}(\delta_A + \delta_B)}{h}
\]

where \( n_{\text{eff}} = (n_A \delta_A + n_B \delta_B)/(\delta_A + \delta_B) \). At \( \lambda_h \), the nacre structure is highly reflective, because transmission is suppressed by the Bragg stop-bands (Fig. 4(d)).

It is particularly useful to have both ordered and disordered structures in a single system. Such unique photonic platform allows us to study the interplay between the order and disorder. To
Fig. 4. Optical characterization of ordered and disordered nacre structures in the _Haliotis fulgens_ abalone shell. (a) Experimentally measured reflection in space and wavelength for visible light. The key feature of interest is the Bragg bands, which are emphasized by the vertical black lines. At the edge of sample $y = 2.3\, \text{mm}$, the narrow Bragg bands degrade and this indicates that the sample contains more disordered layers. The sample is sliced to contain different ratio of ordered and disordered layers that leads to spatially changing degree of $\delta$-disorder in the $y$-direction. A beam is normally incident on the sample. (b) The wavelengths of the $h$-order Bragg bands $\lambda_h$ as a function of thickness of pair of layers $\delta_A + \delta_B$ (Eq. (3)). (c) Experimentally measured reflection at five representative locations of the sample in (a). (d) Calculated ensemble-averaged reflection (black lines) and reflection for two realizations (red and blue lines). For TMM calculation, we use the refractive index described in Eq. (1) and the layer thicknesses described in Eq. (2).
study this intriguing interplay, we slice the nacre sample with a thickness of 0.5 mm as shown in Fig. 4(a). At the edge of sample ($y = 0$ and 2.3 mm), the sliced sample contains the nacre layers either close to the outer or inner surface of abalone shell. In between edges ($y = 0 < y < 2.3$ mm), the sliced sample contains different ratio of ordered and disordered layers that leads to spatially changing degree of $\delta$-disorder in the $y$-direction. Thus, the averaged degree of $\delta$-disorder depends on the $y$ position, while independent to the $x$ position.

The key results are presented in Fig. 4(a). As the relative location of layer becomes close to the inner surface of abalone shell, the sample contains more disordered layers that leads to gradual degradation of the narrow Bragg bands ($y = 0$ mm) into the flat reflectance spectrum ($y = 2.3$ mm). The measured reflection depends on the ratio of ordered and disordered layers. In other words, we observe that periodicity-induced wave transport is transformed to disorder-induced wave transport by increasing disorder. When disorder is introduced, most of transmissions are suppressed by light localization and this enhances reflection over the entire wavelength range from 350 to 950 nm. As a result, averaged reflection $\int R(\lambda) d\lambda$ is enhanced when the sample includes more disordered layers. This observation is in good agreement with theory of light localization [4,11,25]. Overall, we optically characterize that both ordered and disordered structures are existing in a single abalone shell, and that periodicity-induced wave transport is transformed into disorder-induced wave transport.

In some sense, this finding is contrary to common belief, because one usually sees mild iridescence at the inner surface of abalone shell, and one may assume that periodic structures are located inside of the inner surface of abalone shell. Through removal of light absorption from native abalone shell, we find that, in fact, disorder-induced scattering dominates the optical effect of the nacre layers close to the inner surface of abalone shell, while Bragg scattering dominates optical effect of the nacre layers close to the outer surface of abalone shell. This shows that the hyperspectral imaging system is indirect yet effective method to assess the degree of disorder in the nanostructures of nacre.

To understand the role of disorder on degradation of the Bragg band, we numerically simulate the experimentally observed transformation of reflection. For calculation of reflection from the multilayered nanostructures of nacre, we use the transfer matrix method (TMM) as described in our previous studies [17,22]. Accounting the sample thickness of 0.5 mm, we model alternating aragonite and gap layers, of which number of pairs is $N = 1000$. We assume that the refractive index of aragonite $n_A$ (Eq. (1)) and gap $n_B$ are homogeneous. We introduce disorder in thicknesses of aragonite $\delta_A$ and gap $\delta_B$ by imposing different values of fractional standard deviation $\sigma$ (Eq. (2)) around the average thicknesses of aragonite $\overline{\delta_A}$ and gap $\overline{\delta_B}$ layers. As reflection is collected over the pixel size of 50 $\mu$m $\times$ 50 $\mu$m, the measured reflection intensity can be considered as ensemble-averaged reflection. To mimic such ensemble-averaged reflection, we average the calculated reflection over 100 different realizations of nacre structures (black lines in Fig. 4(d)). Assuming a perfect disorder-free nanostructure with $\sigma = 0$ in the nacre layers (Fig. 4(d)), reflection $R$ shows the second ($h = 2$), third ($h = 3$), and fourth ($h = 4$) order Bragg bands around $\lambda_h = 755$, 509, 386 nm, respectively. These wavelengths are in good agreement with those of the optical measurement (Fig. 4(c)). When $\delta$-disorder is introduced ($\sigma = 0.02$), the Bragg band shows degradation and the nacre structure becomes reflective outside the Bragg band. Further growth of $\delta$-disorder ($\sigma = 0.04–0.1$) leads to an increment of reflection outside the Bragg band. At $\sigma = 0.14$, the nacre structure becomes highly reflective and the shape of the reflectance spectrum becomes relatively flat in the whole visible and NIR regions. From a set of simulation, we numerically explain how periodicity-induced wave transport is switching to disorder-induced wave transport and predict that the feature of Bragg band almost disappears as the value of $\sigma$ increases to 0.14.

To confirm the existence of such order-disorder duality in photonic structures of abalone shell, we analyze the degree of $\delta$-disorder of the nacre layers directly from the scanning electron microscope (SEM) images. Specifically, we confirm our prediction whether abalone shell
contains both strongly disordered structures ($\sigma = 0.14$) and relatively ordered structures. We image the nacre layers at two locations in the shell; (i) nacre layer close to the outer surface of abalone shell and (ii) nacre layer close to the inner surface of abalone shell.

Figure 5(a) and 5(d) show the nacre layers close to the outer and inner surface of abalone shell, respectively. The nacre layers close to the outer surface of abalone shell appear relatively ordered, while the nacre layers close to the inner surface of abalone shell appear strongly disordered. By measuring the thicknesses of individual layers in the SEM images, we can quantify the degree of $\delta$-disorder to obtain $\sigma$ at different locations in the shell. In Figs. 5(b) and 5(e), we obtain $\sigma = 0.039$ for the nacre layers close to the outer surface of abalone shell and $\sigma = 0.144$ for the nacre layers close to the inner surface of abalone shell. Although the nacre layers in Fig. 5(a) are not a perfect periodic system, the Fourier transform of the SEM image (Fig. 5(c)) shows the presence of periodicity in the nacre layers. As predicted in Fig. 4(d), $\sigma = 0.04$ can induce the narrow Bragg bands (i.e. iridescence) and $\sigma = 0.14$ is sufficiently large to make the nacre structure highly reflective outside the Bragg band (i.e. white color). From a set of SEM images, we confirm that the wide range of degree of $\delta$-disorder is existing in abalone shell; it is a unique photonic platform to investigate the transformation of periodicity-induced wave transport into disorder-induced wave transport in the same system.

![Fig. 5. Quantification of disorder in nacre using the SEM images. (a) SEM showing the nacre layers close to the outer surface of abalone shell. (b) Histogram of thickness of the nacre layers in (a). (c) 2D Fast Fourier transform of (a). (d) SEM showing the nacre layers close to the inner surface of abalone shell. (e) Histogram of thickness of the nacre layers in (d). (f) 2D Fast Fourier transform of (d).](image)

4. Conclusion

Animals can synthesize the layered structures by organizing their biological structures [21] (e.g. guanine crystals, protein platelets, and cytoplasm gaps). A certain degree of $\delta$-disorder is known to govern a formation of the nanostructure either for periodicity-induced optical effect or for
disorder-induced optical effect. However, we found that a single abalone shell can produce both quasi-ordered ($\sigma = 0.039$) and disordered ($\sigma = 0.144$) photonic structures. As a result, we could simultaneously observe two opposite optical phenomena and their transformation in a single system. We can simply control the degree of $\delta$-disorder in the sample by selecting and detaching the nacre layer from different locations in the shell. Nacre is a naturally occurring structure and thus can be a cost-effective platform to study the interplay between the order and disorder. Also, the presented results will enhance our understanding of the structural colors of abalone shell. In fact, the captivating color at the inner surface of abalone shell is ascribed to the pigment of the organic materials in native nacre. Deproteinization shows that disorder structures are located in the inner surface of abalone shell, while periodic structures are located in the outer surface of abalone shell.

**Funding**

University of Ulsan (UOU) (2018 Research Fund).

**Acknowledgments**

This work was supported by the 2018 Research Fund of University of Ulsan.

**References**

