Directionally Controlled Fluorescence Emission in Butterflies

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In synthetic optical emitters such as light-emitting diodes (LEDs), the majority of generated light is trapped internally. Recently developed high-efficiency devices, however, use two-dimensional (2D) photonic-crystal geometries to enhance the extraction efficiency of light, and the devices also use distributed Bragg reflectors (DBRs) to control emission direction. Here we detail the elaborate optical emission system on the wing scales of a small group of butterflies. Their scales comprise a pigment-infused 2D photonic crystal that provides intense directed fluorescence, which is directionally enhanced by a DBR. This biological system shares many design features with high-emission LEDs.

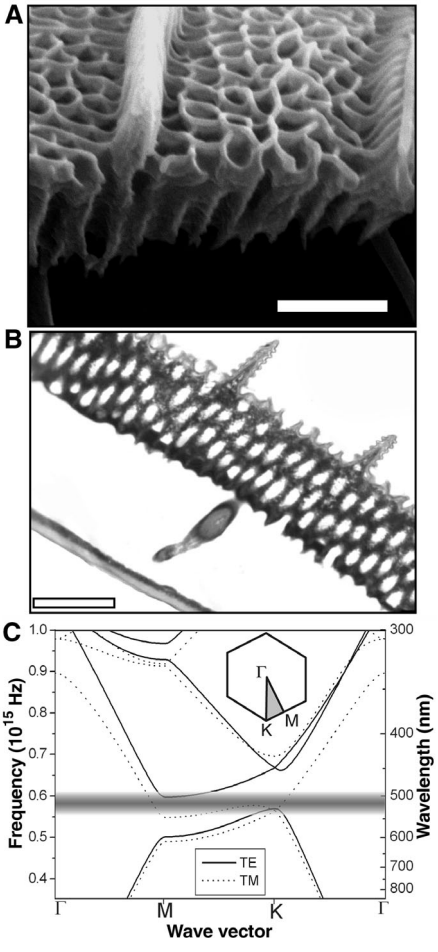

Fig. 1. (**A**) Scanning electron microscope image of the PCS in the *P. nireus* colored scale showing fractured air cylinder edges. Scale bar, 1 μm. (**B**) Transmission electron microscope image of a section through a *P. nireus* colored scale, taken at a small angle to the plane of the PCS. Scale bar, 1 μm. (**C**) Band diagram of *P. nireus* intra-domain PCS structure (the horizontal bar at 505 nm represents fluorescence emission full width at half maximum).

Swallowtail (*Papilio*) butterflies in the *Princeps nireus* group, which are endemic to eastern and central Africa, have dark wings with bright blue or blue-green dorsal wing bands or patches (fig. S1). The wing scales from their colored regions make up a nanostructure that is characterized by a ~2-μm-thick 2D photonic crystal slab (PCS) of hollow air cylinders in a medium of solid cuticle (Fig. 1, A and B). The cylinders have a mean diameter of ~240 nm and a spacing of ~340 nm. The PCS rests parallel to and ~1.5 μm above a three-layer, cuticle-based DBR, which forms the base of the scale (fig. S2). Highly fluorescent pigment is infused exclusively throughout the PCS; its peak emission wavelength is ~505 nm, depending on species, with peak excitation at ~420 nm (fig. S3). The arrangement of air cylinders within the PCS is quasiperiodic, made up of domains of triangular symmetry over a range exceeding several lattice constants (fig. S4A). Two-dimensional Fourier transforms of this structure confirm such quasiperiodicity, revealing a single principal component of spatial variation in refractive index (fig. S4B). This demonstrates the in-plane directional independence with which this PCS scatters light.

Because photonic band diagrams indicate all possible electromagnetic scattering interactions in periodic systems, we calculated the photonic band structure for the idealized intra-domain triangular symmetry in this crystal. We found that the peak fluorescence emission lies across a frequency band in which the density of accessible optical states is significantly depleted, i.e., the pseudo-gap region (Fig. 1C). This finding indicates that the 2D photonic crystal inhibits emission in the crystal plane and thereby increases its out-of-plane emission. To verify this, fluorescence emission was measured both with and without specimen immersion in index-matching fluid (immersion effectively removes the nanostructure's photonic influence). Time-resolved analysis yielded the fluorescence decay rate and the explicit influence of the PCS. Because decay rate depends on the local density of optical states (LDOS) (described by Fermi's Golden Rule), the immersion of a fluorescent photonic crystal in matching fluid will change the LDOS and, subsequently, the fluorescence lifetimes [previously demonstrated in synthetic photonic crystals (*1*)]. We found that immersion in matching fluids considerably modified the decay lifetime of fluorescent emission from the butterfly wing scales, principally around the peak emission wavelength. The primary decay lifetime increased from 0.43 to 0.58 ns in the case of *Papilio nireus* (fig. S5).

As in ultra–high-efficiency LEDs (*2*), these butterflies' DBRs support a spectral stop band that matches the peak emission from the structure above it. The DBRs reflect upwardly the downward-emitted fluorescence concurrently with nonabsorbed longer wavelengths pass through the PCS. The spatial separation between the DBR and PCS minimizes losses via coupling to guided modes in the DBR.

Excitation for this fluorescent material appears to be optimized for the radiance from blue skylight, which peaks around 420 nm. Additionally, because the α-absorbance band of rhodopsin (*3*) dominates the green wavelength photosensitivity of *Papilio* vision, the spectral form of this absorption is ideally placed for stimulation by fluorescence from conspecific wings (fig. S3). As with some shrimps (*4*) and birds (*5*), this enhances signaling, because absorption of visually less-productive short wavelengths leads to the emission of longer wavelengths that trigger photoreception.

References

1. W. L. Vos, A. Polman, *Mater. Res. Soc. Bull.* **26**, 642 (2001).
2. A. Erchak *et al.*, *Appl. Phys. Lett.* **78**, 563 (2001).
3. A. Kelber, C. Thunell, K. Arikawa, *J. Exp. Biol.* **204**, 2469 (2001).
4. C. H. Mazel, T. W. Cronin, R. L. Caldwell, N. J. Marshall, *Science* **303**, 51 (2004).
5. K. E. Arnold, I. P. F. Owens, N. J. Marshall, *Science* **295**, 92 (2002).

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Figs. S1 to S5
References

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