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Biologically inspired flexible quasi-single-mode random laser: An integration of *Pieris canidia* butterfly wing and semiconductors

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Quasi-periodic structures of natural biomaterial membranes have great potentials to serve as resonance cavities to generate ecological friendly optoelectronic devices with low cost. To achieve the first attempt for the illustration of the underlying principle, the *Pieris canidia* butterfly wing was embedded with ZnO nanoparticles. Quite interestingly, it is found that the bio-inspired quasi-single-mode random laser can be achieved by the assistance of the skeleton of the membrane, in which ZnO nanoparticles act as emitting gain media. Such unique characteristics can be interpreted well by the Fabry-Perot resonance existing in the window-like quasi-periodic structure of butterfly wing. Due to the inherently promising flexibility of butterfly wing membrane, the laser action can still be maintained during the bending process. Our demonstrated approach not only indicates that the natural biological structures can provide effective scattering feedbacks but also pave a new avenue towards designing bio-controlled photonic devices.

Over the past decade, lasers have made a tremendous impact on modern science and technology. Medical applications, sensing, and diagnosis all benefited greatly by related work^{1–4}. As an active photonic device, lasers are composed of a pumped gain medium placed within an optical resonator⁴. Traditionally, most laser works rely on artificial micro- to nanostructures made by semiconductors or doped crystals^{5–10}. Although the solid-state functional devices can be well built and show excellent stable optical characteristics, the lack of biocompatibility still remains as a challenging hurdle. The growing interest for developing future technologies is now motivated towards the realization of biodegradable, biocompatible and implantable photonic components integrated on flexible substrates. Inspired from nature materials, lasers have started to be realized in few types of biological structures, such as cancerous tissue, bone tissue, cicada wing and eukaryotic cell^{11–14}. Up to date, based on the biological structures, the derived lasers are mostly attributed to random lasing (RL). Random lasers are made from disordered highly scattering materials that enable to amplify light when pumped externally, and the scattering strength is nearly constant within the gain spectrum of the active medium^{5,15}. The randomly distributed biological structures are thus feasible to sustain the existence of random lasing. However, considering further practical applications, random lasing suffers the drawback of unpredictable multi-modes. Therefore, how to reduce the lasing peaks and lead to mode-control or single-mode laser is desirable^{15–17}; it is especially quite challenging for the devices based on biological materials.

Nature provides abundant selections of micro- to nanostructures that can be used as templates leading to interesting, and sometimes unexpected physical phenomena^{18–21}. Among alternative biological systems, butterfly wings have attracted great attention because of their quasi-periodically arranged small scales, which contain both regular and irregular photonic structures, thus lead to fruitful optical effects such as interference, diffraction, and scattering²². It therefore provides an excellent alternative to serve as resonant cavities to generate ecological friendly optoelectronic devices. To demonstrate our proof of concept, in this work, we make the first attempt of a quasi-single-mode random laser by using the butterfly (*Pieris Canidia*) wing embedded with ZnO nanoparticles (NPs). ZnO is a promising functional material with a wide direct bandgap ($E_g = 3.37$ eV) and large exciton binding energy (60 meV); it is biocompatible, highly chemical stable, and has excellent UV emission properties²³. In this newly designed composite, the butterfly wing plays the role as an effective biological resonance cavity, and the ZnO NPs act as high gain emitting media. In addition to the distinguished lasing feature,



we also strategically exploit the butterfly wing's inherited nature of soft, which provides excellent flexibility, resulting in the realization of flexible bio-laser.

Results

Morphology and reflectance characterization of butterfly wing. A picture of the *Pieris canidia* butterfly is shown in Fig. 1(a). Figure 1(b) shows the low magnification SEM image of the wing scales. It can be obviously seen that each wing scale has a dimension of about $60 \times 90 \mu\text{m}$, with nearly smooth edges. Under higher magnification, a clear microstructure of a single wing scale can be observed in Fig. 1(c). Between the wing lamellae, there exists a reticular porous network structure, which is made by an organic material called chitin^{21,22}. The reticular porous network, or “window-like structure” is of an average pore size of around $1 \mu\text{m}$. Figure 1(d) shows the reflectance spectrum of the butterfly wing. Since the spectrum shows a good reflection for the whole visible range, and reduces at UV range, it can fairly sustain the as-seen white color of wing scales.

Optical properties of ZnO NPs. We first examined the emission from ZnO NPs solution. In fact, ZnO cannot be chemically dissolved in ethanol solution; however, the ZnO NPs are dispersed well in the solution. In order to provide a firm evidence, a laser light with the wavelength of 325 nm was used to inject into a bottle of ZnO NPs solution. From Fig. 2(c), a continuous green trajectory made by 325 nm laser can be clearly observed, which does support the good dispersion of ZnO NPs in the solution. It is worth noting that the emitted green light can be attributed to the oxygen defect luminescence of ZnO NPs generated by the excitation of 325 nm laser pulse²⁴. A 20 μL ZnO NPs solution was dripped onto a clean silicon substrate for the study of PL measurement. After drying in air, the SEM image was performed and shown in Fig. 2(a). The average diameter of the ZnO NPs ranges from 200 nm to 400 nm. To obtain the PL spectra, Nd: YAG 266 nm pulsed laser was used as the excitation source. In Fig. 2(b), the PL spectrum shows a linear dependence (inset) with the increasing laser power, and no laser action can be detected from the prepared sample. The UV emission is due to the bandgap transition of ZnO NPs^{1,24}.

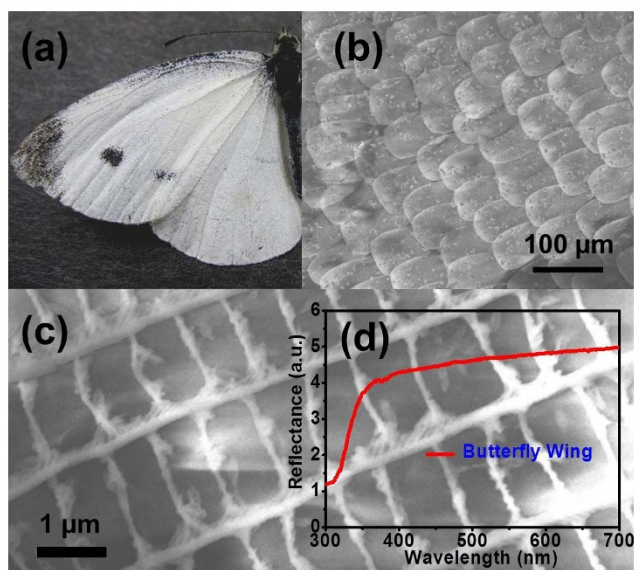


Figure 1 | (a) Picture of a *Pieris canidia* butterfly; (b) low magnification scanning electron microscope (SEM) image of the wing scales; (c) high magnification SEM image of the wing scales; (d) reflectance spectrum of butterfly wing. (The photograph of the *Pieris canidia* butterfly was taken by the first author Cih-Su Wang.).

Characterization of quasi-single-mode laser emission. Let us now demonstrate the emission properties for the ZnO NPs/butterfly wing composite as shown in Fig. 3(a). At a low excitation energy such as 61 μJ , only a single broad emission peak centered at around 386 nm can be observed. However, when the excitation exceeds a specific threshold of 65 μJ , a single sharp lasing peak with the line width less than 1 nm starts to emerge and superpose on the background broad emission peak. The single sharp lasing peak tends to grow stronger and narrower as the excitation increases. The dependence of the emission line width (FWHM) versus pumping energy is shown in Fig. 3(c). Although a quasi-single-mode laser can be successfully derived from the composite sample, the lasing mode is not strictly fixed; however, it shows random fluctuations. The dependence of emission peak position versus excitation energy is shown in Fig. 3(b). It is worth noting that the spectrum under the 85 μJ pumping contains quasi-single-mode random lasing peaks, the most pronounced peak locates at 384.4 nm, and the other weak peaks are at the positions around 386 nm. Since the lasing mode slightly fluctuates at every different pumping, it reflects the characteristics of random laser behavior.

Traditional random lasers contain unpredictable multi-modes and are commonly realized in randomly distributed semiconductor micro- to nanostructures^{6,25,26}. As a comparison, we also performed ZnO nanorod (NR) random lasers as shown in Fig. 4. The ZnO NRs were grown on sapphire substrate via vapor-solid (VS) method. Figure 4(a) shows the SEM image of the as-grown ZnO NRs, the diameter of each NR is around 100 nm. To confirm the existence of ZnO product, X-ray diffraction (XRD) spectra were performed and shown by the inset of Fig. 4(a). The diffraction peaks can be well indexed to the hexagonal ZnO crystal structure¹. Figure 4(b) shows the classic random lasers obtaining from the as-grown ZnO NRs. Multiple lasing peaks exist and vary under different pumping and excitation energy. The threshold (72 μJ) behavior is shown by the inset of Fig. 4(b). In Figs. 5(a) and (b), we compared the laser actions between ZnO NPs/butterfly wing composite and ZnO NRs. Unlike the conventional random laser with multiple components, the quasi-single-mode lasing derived from ZnO NPs/butterfly wing composite exhibits a very unique feature.

Discussion

To further understand the quasi-single-mode laser action derived from ZnO NPs/butterfly wing composite, let us examine the underlying structure of butterfly wing. The insets of Figs. 5(a) and (b) show the SEM images of butterfly wing and ZnO NRs, respectively. It is seen that the skeleton of butterfly wing shows a quasi-periodic structure. We further consider the Fabry-Perot (FP) resonance due to the window-like quasi-periodic structure of butterfly wing as the dominant factor to assist the achievement of quasi-single-mode laser action. Each single pore, or “micro window” of butterfly wing provides well-organized two-end facets for the formation of the FP resonance. The FP effect can be described by the following equation²⁷:

$$\frac{\lambda}{2n}M = L, \quad (1)$$

where λ is the resonant wavelength ($\sim 385 \text{ nm}$), n is the refractive index (~ 1), L is the resonant cavity length, and M is a positive integer. After calculating with the M integer of 5, the resultant L is of about $0.96 \mu\text{m}$, which is in good agreement with the size scale of each micro window of the butterfly wing. Furthermore, the resonant mode spacing can be derived by the formula^{27,28}:

$$\Delta\lambda = \frac{\lambda^2}{2nL}. \quad (2)$$

Considering the cavity length of around $1 \mu\text{m}$, the resonant mode spacing is estimated to have the magnitude of about 74 nm. As a consequence, only one single Fabry-Perot mode can be observed in

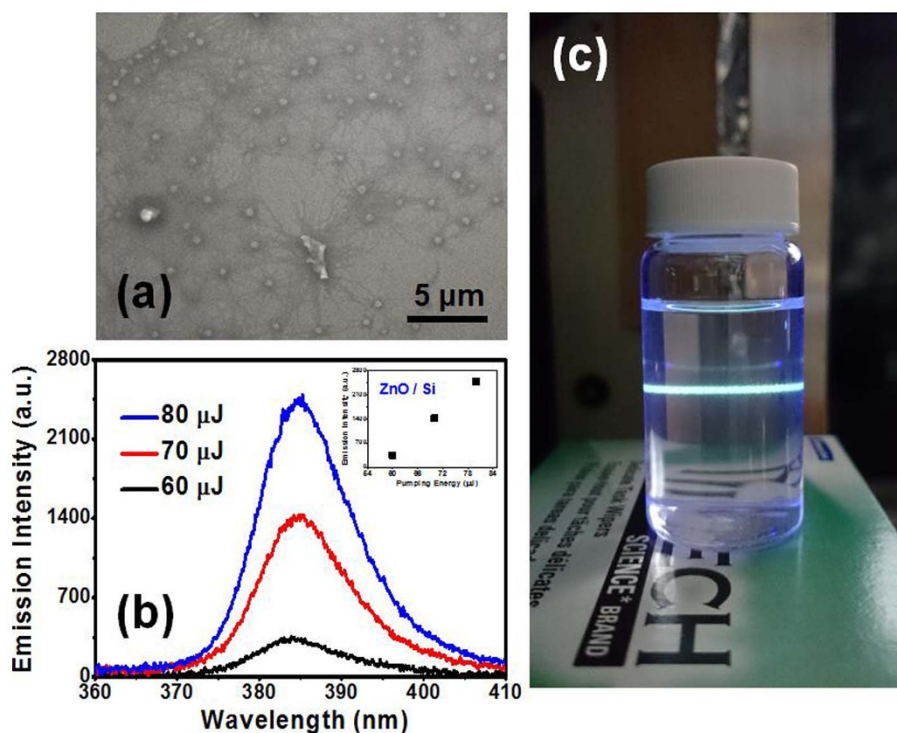


Figure 2 | (a) Scanning electron microscope (SEM) image of ZnO nanoparticles (NPs) on silicon substrate; (b) photoluminescence (PL) of ZnO NPs under various excitation energy. Inset: emission peak intensity versus pumping energy. (c) Bottle of ZnO solution with the ethanol as solvent, the green light (defect emission of ZnO) denotes the trajectory produced by 325 nm He-Cd laser.

the UV emission range of ZnO NPs. In addition to the dominant single-mode laser, the rest peaks can be attributed to the mechanism of random lasing generated by multiple light scattering in random cavities formed by ZnO NPs and butterfly wing microstructure. By using the information of the wavelength difference ($\Delta\lambda$) derived from

the two nearest lasing peaks, the transport mean free path (L) of a light in the composite system can be further calculated by $L = \lambda^2 / 2n\Delta\lambda$ ²⁹, and the approximate value is about 82.3 μm . In Figs. 3(a) and (b), it is seen that the lasing peak positions slightly fluctuate under different pumping and excitation energy. The underlying reason

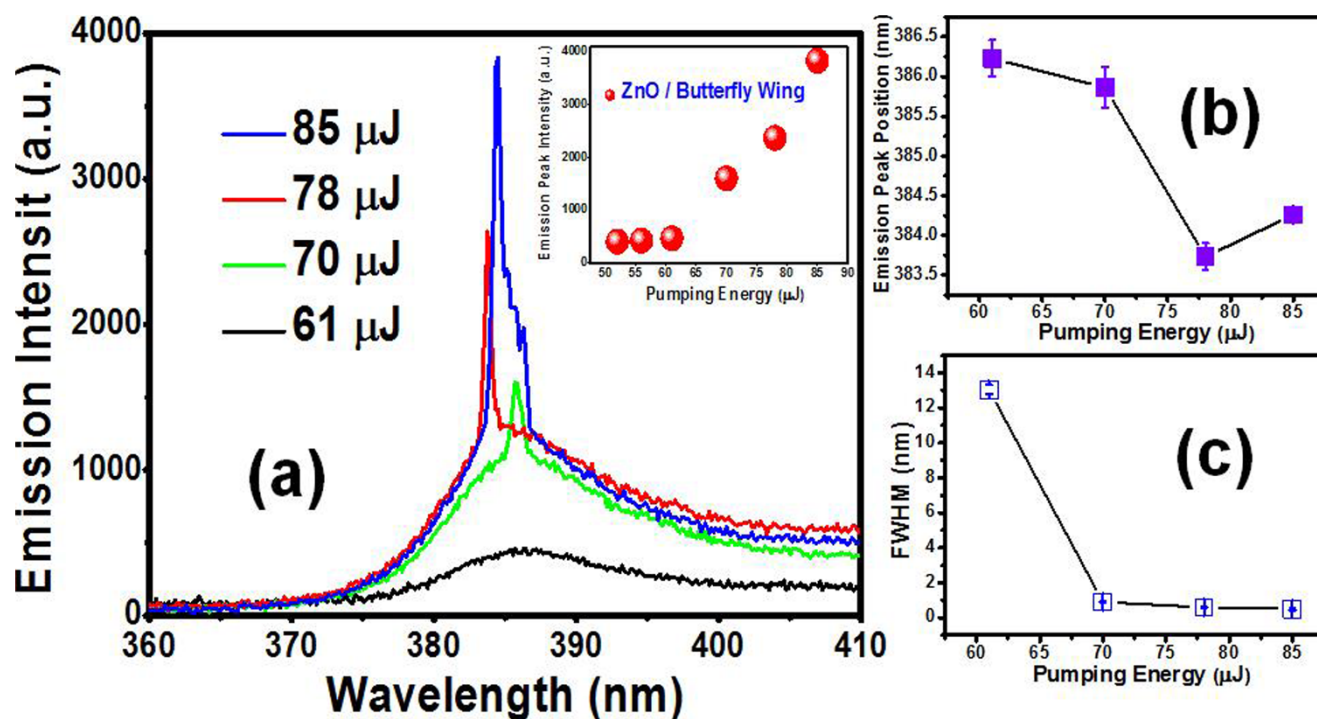


Figure 3 | (a) Lasing spectra of ZnO NPs/butterfly wing composite with increasing excitation energy. Inset: emission peak intensity versus pumping energy. (b) and (c) Emission peak position and FWHM versus pumping energy, respectively.

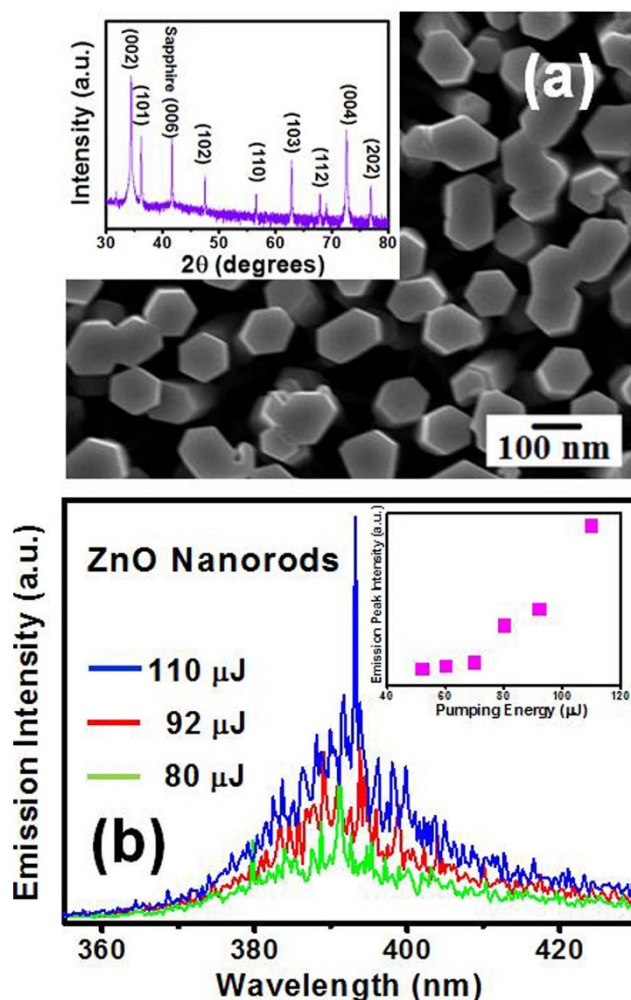


Figure 4 | (a) Scanning electron microscope (SEM) image of ZnO nanorods. Inset: X-ray diffraction pattern of ZnO nanorods. (b) Random lasing spectra under different excitation power. Inset: emission peak intensity versus pumping energy.

might be attributed to the quasi-periodic structure of butterfly wing, in which, each of the micro window between lamellae appears nearly the same but slightly different size. The fluctuating sizes of the micro windows thus result in different FP cavity length L and leads to the unfixed single-mode lasing peak. In Fig. 6, we have performed an enlarged SEM image of the ZnO NPs/butterfly wing composite. The

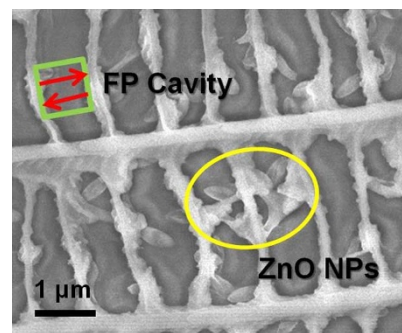


Figure 6 | Scanning electron microscope (SEM) image of the ZnO NPs/butterfly wing composite. The upper inset denotes the schematics illustration of a Fabry-Perot (FP) cavity provided by the butterfly wing microstructure. The yellow-circled region indicates the ZnO nanoparticles lying on and between the porous network of butterfly wing scale.

upper inset denotes the schematics illustration of a Fabry-Perot (FP) cavity provided by the butterfly wing microstructure. Inside the cavity, the emission derived from ZnO NPs can be multiply scattered back and forth (denoted by red arrows), leading to the amplification and generation of the single-mode laser action. And the pictured cavity length is in good agreement with the theoretical calculation ($\sim 0.96 \mu\text{m}$) based on equation (1). The yellow-circled region indicates the ZnO nanoparticles lying on and between the porous network of butterfly wing scale. In addition to the FP mechanism, the randomly distributed ZnO NPs existing among the wing structure can also lead to the occurrence of random lasing²⁶. Furthermore, due to the quasi-periodic structure of butterfly wing, the coupling among FP cavity modes is also efficient to selectively enhance the peak intensity of some particular eigenmodes. Therefore, with the coupling among FP resonances and closed-loop paths arising from scattering caused by ZnO NPs, a quasi-single-mode random laser can be expected and obtained.

Finally, we extended our work to a unique and facile potential practical application by placing the ZnO NPs/butterfly wing composite onto a mechanically flexible PET substrate. The bending measurements were performed and shown in Fig. 7. The device was bended to a curvature radius of around 1.5 cm. The lasing spectra of flat and bending state ($R \sim 1.5 \text{ cm}$) were shown in Figs. 7(a) and (b), respectively. The insets show the illustrations of the flat and bending devices. The excitation is fixed at an energy of 85 μJ. Interestingly, for both of the experimental conditions, the quasi-single-mode laser can be well maintained and clearly observed. However, during the bending process, the bending device exhibits a broadened background spectrum and less lasing efficiency.

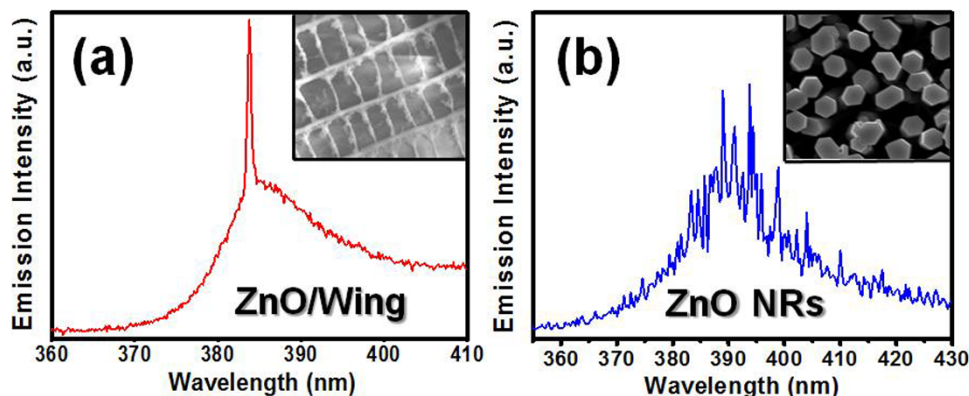


Figure 5 | (a) Single-mode lasing spectrum of ZnO nanoparticles/butterfly wing composite. Inset: Scanning electron microscope (SEM) image of butterfly wing scale. (b) Multi-mode lasing spectrum of ZnO nanorods. Inset: SEM image of ZnO nanorods.

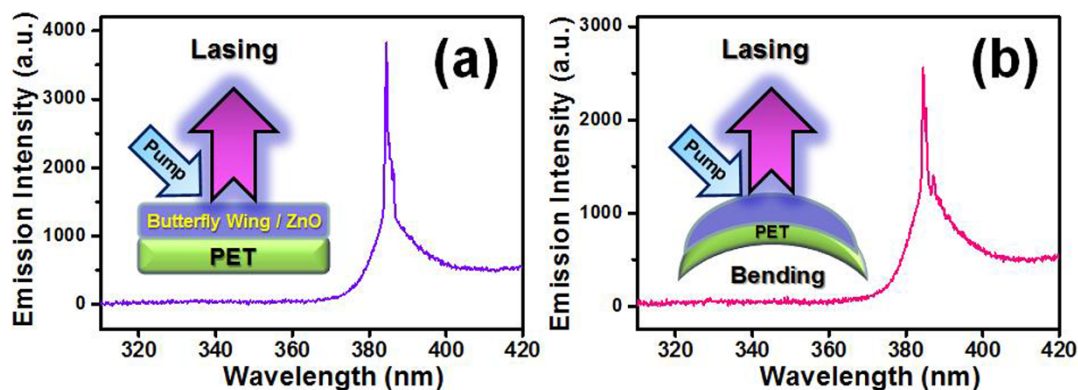


Figure 7 | (a) Single-mode lasing derived from flat ZnO/wing/PET device. Inset: illustration of the device. (b) Single-mode lasing derived from bending ZnO/wing/PET device. Inset: illustration of the device.

In summary, we have successfully made the first demonstration of a flexible quasi-single-mode random laser based on ZnO NPs/butterfly wing composite. Such unique lasing properties can be well interpreted in terms of both of the random lasing mechanism and Fabry-Perot resonance existing in the window-like quasi-periodic structure of *Pieris canidia* butterfly wing scales and ZnO NPs. In addition, the inherited soft of butterfly wings can provide excellent flexibility and the laser action can be sustained even under the bending state. Our results not only indicate that the natural butterfly wing can be an attractive candidate to realize bio-inspired photonic lasing properties, but also motivate the research towards studying various types of biological materials and structures for ecological friendly optoelectronic devices with low cost.

Methods

Sample fabrication. The *Pieris canidia* butterflies were captured on the meadow of National Taiwan University, Taipei, Taiwan. Before fabrication, the wings were cut into small slices with a diameter of about 1.5 cm by using the scissor. The wing scales were then dipped in ethanol solution at room temperature for 6 h to remove impurities adhering to the surface of original butterfly wings. After cleaning, the wing scales were picked up by a glass slide, carefully washed by deionized water and subsequently dried in air for 3 h. During the drying process, a ZnO solution was prepared by mixing the high-purity ZnO NPs (99.99%) with ethanol solution (99.8%). The density was set to be 0.05 mg/ml because if the concentration is too high, it leads to the aggregation of ZnO NPs, which results ZnO clusters instead of NPs. On the contrary, if the concentration is too low, there will not be sufficient ZnO NPs in solution to play the role as emitting materials. The cleaned and well dried wing scales were then infiltrated with ZnO NPs solution and placed onto a bendable PET (poly ethylene terephthalate) substrate. Ethanol was chosen as the solvent since the butterfly wings are naturally hydrophobic, meanwhile, it helps the ZnO NPs solution infiltrate well into the small interstitial spaces of the wing structures.

Morphology characterization and optical measurements. The morphologies of ZnO NPs and butterfly wings were characterized by scanning electron microscope (SEM; JEOL JSM6500). The crystal characteristics were carried out by X-ray diffraction (XRD; Panalytical X'pert PRO). The reflectance spectrum was detected by a spectrophotometer (Jobin-Yvon H10). To study the lasing behavior, the samples were optically excited by a Q-switched 4th harmonic Nd:YAG laser (266 nm, 3–5 ns pulse, 10 Hz) and measured with a Jobin Yvon iHR550 imaging spectrometer system. The laser beam was focused to a diameter of about 500 μm . All the experiments were performed at room temperature.

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Author contributions

C.S.W., T.Y.L. and Y.F.C. designed the experiment. T.Y.C. reviewed the manuscript. C.S.W.



performed the data measurements and wrote the manuscript. All authors contributed to the analysis and commend of the manuscript.

Additional information

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