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Probing the coupling of butterfly wing photonic crystals to plasmon resonances with surface-enhanced Raman spectroscopy

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Nanoparticle Characterization

We show the extinction spectrum for the silver nanoparticles used in this work in Figure S1, along with a representative SEM image.



Fig. S1 Extinction spectrum of colloidal silver nanoparticles prior to deposition on butterfly wing substrates. The SEM image of the silver nanoparticles has a scale bar of 200 nm.

Raman Instrumentation

In Figure S2, we show an experimental schematic of the lab-built spontaneous Raman apparatus used for these measurements. We illuminate the sample at three excitation wavelengths in a back-scattering geometry.



Fig. S2 A schematic depiction of the Raman spectrometer with 180 degree back-reflection.

UV-Vis Characterization

As in the main text, all UV-Vis diffuse reflectance measurements were made using a Shimadzu UV-2600 UV-Vis spectrophotometer. Fig. S3 compares the diffuse reflectance of the butterfly wing substrates and filter paper before and after bleaching and addition of the AgNP/pyridine solution. Bleached wings were prepared with the plasma etching process reported in the main text followed by the addition of 10 μ L of 30% bleach. It is apparent that the addition of the AgNPs into the photonic structure slightly modifies the photonic bandgap of the wings, as demonstrated by the blueshift of the peak of reflectance for the teal wings.

To determine the wavelengths influenced by pigment absorption, we calculate differential spectra from those in Fig. S3. Pigments absorb light to reduce reflectance. Therefore, bleaching or degrading the pigments would result in an increase in the diffuse reflectance. Fig. S4A depicts the bleached wing's reflectance subtracted from the unmodified wings. Because bleaching produces higher reflectance, negative peaks in the differential spectra would indicate the presence of pigment absorption at that wavelength. Conversely, positive features in the differential spectra

would indicate damage or changes to the photonic structure of the wings. We repeated this calculation with reflectance measurements of the butterfly wings with silver nanoparticles and pyridine. We notice pigment degradation, modification of the photonic structure, and plasmon absorption after adding the AgNP/pyridine solution (Fig. S4B). Comparing the highlighted lines in Fig. S4, which represent the wavelengths enhanced by Raman scattering, we see that pigment absorption notably influences the reflectance analysis for 547 nm in orange and red wings and for 819 nm in teal wings.

Many photonic structures are iridescent because they act as diffraction gratings. This means that the wavelength of reflectance is dependent on the angle of light incidence. Measuring the angle-resolved diffuse reflectance has been used to measure the location of a photonic bandgap as the bandgap blueshifts at increasing light scattering angles. We produced angle-resolved spectra for normal incidence, 4.8 degrees, and 9.5 degrees (Fig. S5). However, the change in reflectance is largely dominated by the decreasing reflectance from a larger diffusive angle and sample distance, rather than a shift in energetic scattering by the photonic structures. The butterfly wings in this study were also minimally iridescent when compared to species such as the blue morpho.



Fig. S3 UV-Vis reflectance compared on all butterfly wing substrates and filter paper (A) before modification, (B) after adding a silver nanoparticle/pyridine solution, and (C) after bleaching the substrates.



Fig. S4 Subtracted spectra of butterfly wing diffuse reflectance. (A) Diffuse reflectance of the unmodified butterfly wings minus that of the butterfly wings with the silver nanoparticle/pyridine solution. (B) Diffuse reflectance of the unmodified butterfly wings minus that of the bleached butterfly wings. The dashed lines correspond to the averaged wavelength of each excitation source (532, 633, and 785 nm) and the 1001 cm⁻¹ Raman mode. The corresponding wavelengths are 547, 655, and 819 nm.



Fig. S5 Angle-resolved diffuse reflectance of butterfly wings. The hue of the spectra follows from darkest to lightest for incident probed angles of 0, 4.8, and 9.5 degrees.

Raman Characterization

We show the full SER spectra in Figure S5. These spectra exhibit a number of Raman features most likely assigned to chitin and underlying pigments in the 1200 - 1600 cm⁻¹ region, as well as a modest background. We highlight the pyridine vibration at 1008 cm⁻¹ used for analysis in the main text with a vertical dashed line. In Figure S6, we plot the amplitude of the SERS signal as a function of excitation power, which nicely fits a linear trendline.



Fig. S6 Full spectra of butterfly wing SERS samples. The wavelength of excitation for each SER spectrum was (A) 532, (B) 633, and (C) 785 nm.



Fig. S7 Butterfly wing SERS power-dependence. The 633 nm power-dependence of three butterfly wings of colors (A) orange, (B) teal, and (C) yellow is reported. The R^2 -value of each linear trend is 0.9978, 0.9972, and 0.9821, respectfully. The vertical error bars denote the error of the Gaussian fit amplitude.

Plasmonic and Photonic Coupling

A quantitative analysis of plasmonic and photonic coupling effects is hindered by competing optical absorption, a wavelength-dependent localized surface plasmon resonance, heterogenous photonic structure across the butterfly wing, and variable nanoparticle aggregation on each wing. We address the second point in the main text by normalizing the Raman scattering and reflectance to that of the filter paper standard. The third through fifth points can be mitigated by the presenting the standard deviation averaged data. However, it is challenging to circumvent pigment absorption that changes for each butterfly wing. Fig. S8 presents an identical analysis to that of Fig. 5, but it expresses the reflectance ratios of the substrates without the addition of the AgNP/pyridine solution. Coincidentally, the trends in Fig. S8B are much more consistent than those reported in the main text, likely due to of pigment absorption influencing butterfly wing reflectance.



Fig. S8 Plasmonic and photonic coupling analyzed from the perspective of butterfly wings without silver nanoparticles. (A) Reflectance results normalized to the filter paper reference from each data set. (B) The difference between the ratios in (A) for 655 and 547 nm followed by the difference for 819 and 547 nm. Error bars are excluded because the standard deviation of three measurements was less than 5% of the original value.

COMSOL Multiphysics (Wave Optics Module, Version 5.4)

We implemented finite element analysis to compare theoretical and experimental results of photonic-plasmonic coupling. The photonic crystal and coupled system simulations are shown in the main text. Here, Figure S9 shows the wavelength dependent field interactions with the silver nanoparticle dimer, and Figure S10 depicts the geometry for the simulation of the coupled system.



Fig. S9 Simulations of a silver nanoparticle dimer cross section at 530, 635, and 785 nm excitation.



Fig. S10 A labelled depiction of the component configuration in COMSOL Multiphysics simulations.