Supporting Information

Bio-Templated *Morpho* Butterfly Wings for Tunable Structurally Colored Photocatalysts

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Experimental Details

A custom built, flow-type thermal Atomic Layer Deposition (ALD) system was used for ALD processing. The ALD reaction chamber was set to 150ºC, with an argon carrier gas flow rate of 10 sccm, and the base pressure of the system was ~600 mTorr. An ALD cycle for depositing ZnO films consists of a 0.05 s pulse of diethylzinc (DEZ) and a 30 s argon purge time, and then followed by a 0.1 s pulse of water and 30 s Argon purge. ZnO films of 10 nm, 15 nm, 20 nm, 25 nm, 35 nm, and 50 nm thickness were deposited onto the *Morpho* butterfly wings and glass substrates, based on a growth rate of 2.0 Å/cycle. Five samples of each set of thickness and each substrate were made for this study.

The glass substrates were prepared by dicing them to the desired dimensions and cleaned by rinsing them with acetone, isopropyl alcohol, and deionized water. The glass substrates were then coated with ZnO by ALD. The butterfly samples were pre-baked at 100ºC for 2 hours and then coated with ZnO.

After ALD, a working area of $1cm^2$ area was defined for each sample. The edges of the samples outside of the predefined $1cm^2$ area were covered with a polymethyl methacrylate (PMMA) blocking film to define the wetted area, therefore controlling the area of photocatalytic reaction. The same PMMA was used to help adhere the butterfly wing samples to a clean glass slide to make handling of the butterfly samples easier. The sides and bottom of the samples were also coated with PMMA so that only the active $1cm^2$ area was exposed to water.

A 15 W fluorescent UV (365nm) lamp (UVP Blak-Ray XX-15BLB UV Bench Lamp) was used as the illumination source. The height and position of the sample with respect to the UV light is critical to ensure consistent UV light intensity for all dye degradation experiments. For this, we first assembled the test setup without the dye solution and measured the light intensity at the position where the sample would be placed. A power meter was used to measure the light intensity at the exact position relative to the light source where the samples would be placed. The light intensity was measured to be 15 W/m^2 . The samples were placed at the same position so that the light intensity on the intact butterfly surface was identical for all experiments. This planar geometry provides a much more consistent light illumination at the photocatlyst surface than using powder photocatalysts, allowing for quantitative measurement of reaction-rate kinetics at a uniform intensity.

Prior to illumination of the photocatalyst samples, a 20 μM methylene blue solution was prepared, and all wetted components were pre-rinsed with this methylene blue solution (i.e. inside walls of the beaker, stir bar, and sample). After rinsing, 10 ml of 20 μM methylene blue dye solution were added to the beaker. The beaker was then left stirring in the dark for 30 minutes until adsorption of dye on the sample came to equilibrium with the solution. Next, an aliquot of the dye solution was taken to measure the light absorbance utilizing a UV-vis spectrophotometer (Shimazdu UV-2600). Absorption intensity was recorded at the peak absorption wavelength for Methylene Blue of 664nm to quantify dye-concentration. Aliquot samples of the dye-solution were measured for every 2-hour intervals until the 12th hour, and the entire methods described above were repeated for each sample.

The percentage of dye degraded (%D) was calculated as follows:

$$\%D = \left(\frac{C(o) - C(t)}{C(o)}\right) \times 100 \ = \left(1 - \frac{C(t)}{C(o)}\right) \times 100$$

Where $C(o)$ is the initial concentration as measured by absorption and $C(t)$ is the concentration after an amount of time illuminated by UV-light (t) as measured by absorption. The percentage of the remaining dye concentration (R%) was also calculated such that:

$$\%R = 100 - \%D \ = \left(\frac{C(t)}{C(o)}\right) \times 100$$

To measure the reflectance spectra of butterfly wings with varying ZnO film thicknesses, all the samples were cut into about 1cm*1cm in size and attached to the silica glass with their iridescent sides facing up. The wavelength range was set from 300 nm to 800 nm during the measurement. Reflection spectra were recorded using a Lambda 750S UV/VIS/NIR spectrophotometer (Perkin Elmer, Inc., USA). Five sample replicas were tested for each to observe if the results were reproducible. The error bars on Figure 3a are the standard deviation from the averages of the five replica samples. The reaction rate coefficient was calculated by utilizing the average concentration after time C(t) at each time interval. For example, the concentration for all 5 samples of the 10 nm coated butterfly were averaged at each time interval (the 2nd, 4th, 6th, 8th, 10th, and 12th hour) of light illumination. Then this was plotted in a graph similar to Figure S4 and a regression was fit to that averaged data points. The slope of the graph is our reaction rate coefficient (k). The y-intercept of the graph is 1.098 nanometers and the coefficient of determination

(R2) is 99.97%. All data points including the two thinnest coatings being studied (10nm and 15 nm) traced the fitted line with negligible error. From this, we deduce that nucleation delay effects are trivial within the range of the ALD coatings being studied.

The reflection properties and electric field intensity distribution of the *Morpho* wings with different ZnO thicknesses were simulated by finite-difference time-domain (FDTD) methods. ZnO films were assumed to be deposited on the butterfly wings uniformly, consistent with the SEM analysis. In the modeling, the refractive index of chitin was set to be 1.56 and the wavelength-dependent refractive index of ZnO was input.[1] A plane wave was used as the light source and the incident direction was perpendicular to the surface of butterfly wings. The boundary condition was set based on the assumptions that the light was absorbed (perfectly matched layer, PML) in the vertical direction and the nanostructures were periodic (periodic boundary condition, PBC) in the horizontal direction. The mesh size was 2 nm×2 nm. The structural parameters were set based on SEM image of Morpho butterfly wings, including the lamella thickness (~ 60 nm), the lamella length (~ 200 nm), the inter-lamella spacing (~ 150 nm), the height of the ridge (~ 1900 nm), the width of the ridge (~ 70 nm), and the separation between ridges (~ 770 nm), as shown in Figure S5.

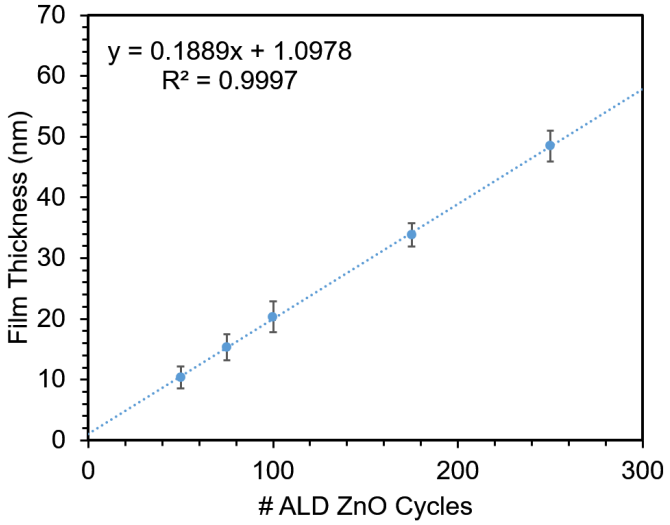

Figure S1: Film thickness of the ZnO coated *Morpho* butterflies (measured using image processing software) as a function of ALD cycles. A linear regression that fit the set of film thickness data is included.

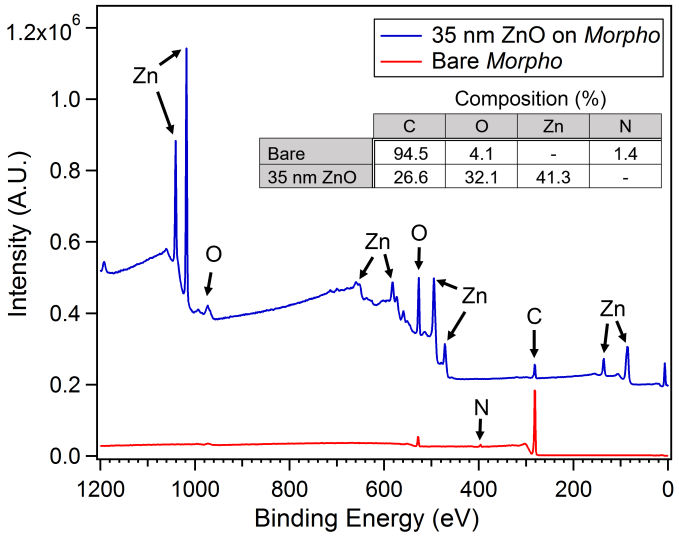

Figure S2: X-ray photoelectron spectroscopy of a bare *Morpho* wing sample and a *Morpho* wing coated with 35 nm of ZnO.

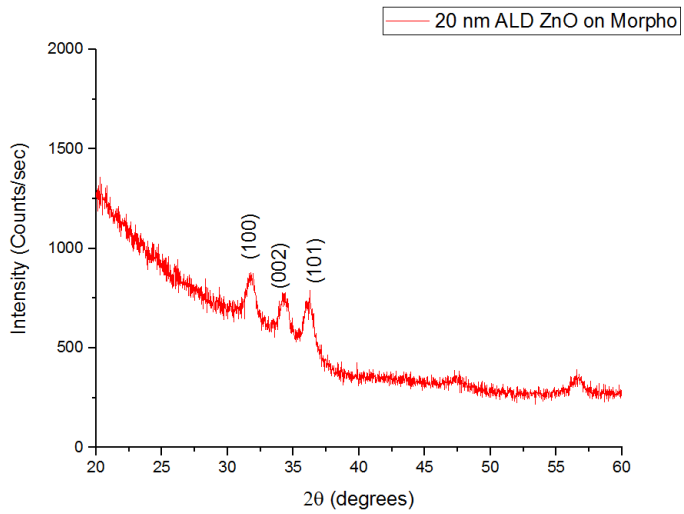

Figure S3: X-Ray Diffraction showing Wurtzite crystal structure of Morpho butterfly coated with 20 nm of as-deposited ALD ZnO.

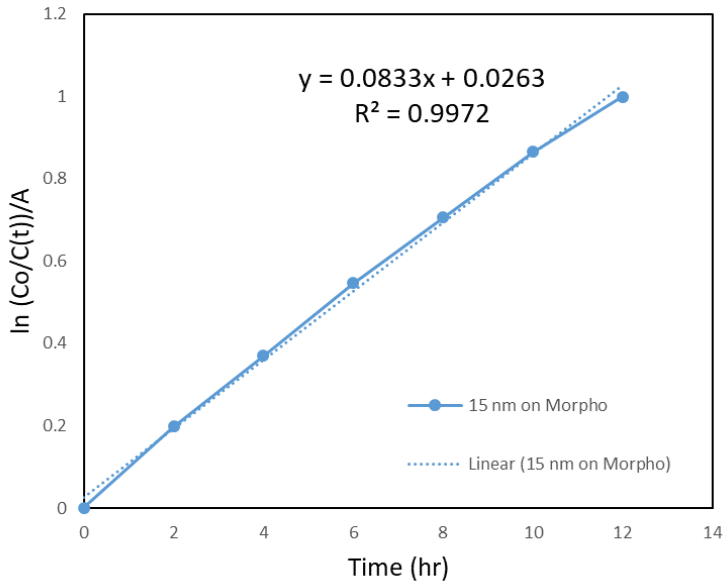

Figure S4: First order kinetics model of the initial concentration per averaged concentration after illumination, per unit area as a function of time. The slope of the regression is the reaction rate constant (k) for a 15 nm ZnO coated *Morpho* butterfly.

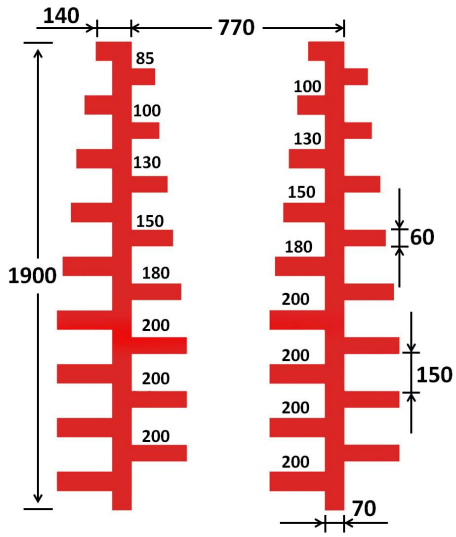

Figure S5: Geometric representation of the branched lamellae structures of the *Morpho* wing utilized for Finite-Difference Time-Domain modeling. Used to simulate the optical properties (Main Text Figure 2) and the electric field intensity (Main Text Figure 4) for different thickness of ZnO coatings (unit: nm).

References

(1) Yoshikawa, H.; Adachi, S. Optical Constants of ZnO. *Jpn. J. Appl. Phys.* **1997**, *36* (Part 1, No. 10), 6237–6243.