

Supplementary Information

FDTD simulations.

The distance between the excitation plane and the observation plane for reflection was 500 nm. The distance between the excitation plane and the observation plane was 500 nm. The distance between the bottom of the model and the observation plane for transmission was 100 nm. The mesh size of the simulation space was 20 nm X 20 nm X 20 nm. The number of APML layers was 20, the theoretical reflection coefficient was 1e-18. Real APML tensor parameter was 5 and the power of the grading polynomial was 3.5. Time step was 4.4 e-17 s. A simulation took 20000 equal time steps, with 4.4 e-17 s per step. Simulations were performed under normal incident light. Refractive index of the chitin/melanin composites for the upper layer was set to be 1.76 and the extinction coefficient was 0.7, and parameters for the bottom layer were 1.6 & 0.1. These parameters yielded satisfactory results which are consistent with the original reflectance/transmission spectra.

Synthesizing Procedure.

Pretreatment : Original butterfly wings were submerged in a 7% NaOH solution for 3 hours following a few minutes' pre-soakage in ethanol, after that they were rinsed three times with pure water.

Dipping: The pre-treated wings were put in a 5% TiCl_3 solution for a 40 hours dipping, and then rinsed again with pure water for three times.

Desiccation and sintering: Desiccated the dipped sample in a blast oven for 8 hours at the temperature of 80 degree centigrade, then sintered in a process of calcination at 220 degree centigrade for 2 hours and at 500 degree centigrade for 2 hours with a calefaction rate of 1°C /min. The process which not only maintains the structure but also gets rid of original organism can crystallize TiO_2 .

The TiO_2 nanoparticles were synthesized by hydrolyzing TiCl_3 solution in air for 40h and calcined under the same conditions. Pt nanoparticles were grown on the surface of TiO_2 by irradiating TiO_2 in 2 wt % $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ aqueous solution for 15 minutes. The product was collected by centrifugation, washed 3 times with 50 mL aliquots of water, and dried in air at 80°C.

Characterization.

FESEM observation: original butterfly wings were cut into tiny pieces (~2mm×2mm) and fixed onto specimen stage, while ABWA-TiO₂ were grinded in an agate mortar and then stuck onto the specimen stage by conductive tapes. Au nano particles were deposited on the surface for better conductivity. They were observed on field emission scanning electron microscope (FESEM; FEI SIRION 200) operated at 5Kv.

TEM observation: original wings were treated in a 5% NaOH solution for 5 hours, rinsed in pure water for several times, dried in air at 80°C, and grinded in an agate mortar. ABWA-TiO₂ were grinded in an agate mortar too. Both samples were then suspended in EtOH with ultrasonic treatment for about 5 minutes and dropped onto the copper grids after that. They were examined with a transmission electron microscope (TEM; JEM-2010) equipped with energy dispersive x-ray spectroscopy (EDS; INCA OXFORD) at an applied voltage of 200 kV.

UV-Vis absorption for TiO₂: Using Lambda 750S UV-Vis-NIR to record the ultraviolet-visible spectrum with a detecting range from 200 nm to 800 nm. Equal quantity samples were tested each time.

XRD: With a range from 20 degrees to 90 degrees, 5 degrees/min. The average grain size was obtained by the method proposed by W. H. Hall in order to distinguish the crystalline-size broadening and microstrain broadening. Hall suggested that broadening functions due to small crystalline size and microstrain are Cauchy curves (of the form $1/(1+k^2x^2)$), which is expressed by:

$$\beta_i(\cos \theta_i)/\lambda = K/D + 4\varepsilon(\sin \theta_i)/\lambda$$

Where, β_i is the integral breadth of the i th Bragg reflection peak positioned at $2\theta_i$. K is a constant which equals 0.89. λ is the wavelength of the X-rays with the value of 0.154nm. ε is the microstrain with isotropic distribution and D is the mean size of the crystallites, which were calculated through a least-square fit.

Reflection and transmission spectrums of the original wing scales:

Reflection and transmission spectrums were obtained from Varian Cary 500 infrared-visible-ultraviolet spectrometer under normal incident light. The spectrometer was calibrated by a white diffuse reflection standard before conducting reflection measurements. The white diffuse reflection standard was purchased from the National Institute of Metrology of China. The transmission spectrum was obtained by double optical path method.

Butterflies wings were cleaned in deionized water. Ventral scales were all carefully removed from the wings to leave only the substrate and dorsal scales for reflection spectrum

experiments, and the samples were then examined under an optical microscope to make sure that the dorsal scales and the substrate were sound and intact. Optical properties of the substrate were also investigated separately by removing both sides of the scales. Then the averaged reflection and transmission properties of a single cover scale were obtained through a special algorithm:

suppose transmission of the substrate and the cover scales together is α ;
transmission of the substrate which is obtained by removing both the cover scales and the ground scales is β ;

then, transmission of the cover scales lone is $\gamma = \alpha/\beta$.

Considering the overlap integer equals to the ratio of the overlapped area to the surface area of the sample, here it is 0.5 by calculating the areas in the microscopic images, then the average true transmission for a single scale is $\theta = [(1+8*\gamma)^{1/2} - 1]/2$.

Photocatalytic H₂ Evolution Experiments.

Irradiation was performed at 25°C using a Xe arc lamp (2000 mW/cm²). The flask was filled with 80 mL aqueous solutions including a sacrificial reagent(10% methanol solution) and 80 mg of the respective catalysts and connected to a gas chromatography system. Calcined samples with film-like appearances were put in the quartz flask for reactions. Inevitably, the integrated films broke into tiny pieces under stirring. Even though, the hierarchical architectures could still be observed by FESEM and TEM after the experiments. The flask was evacuated and purged ten times with argon gas, and the stirred mixture was then irradiated for 5 h with periodic removal of gas samples. Gas samples were analyzed with a Varian gas chromatograph employing a Supelco molecular 60/80 sieve 5A column with Ar as the carrier gas and a thermal conductivity detector (TCD).

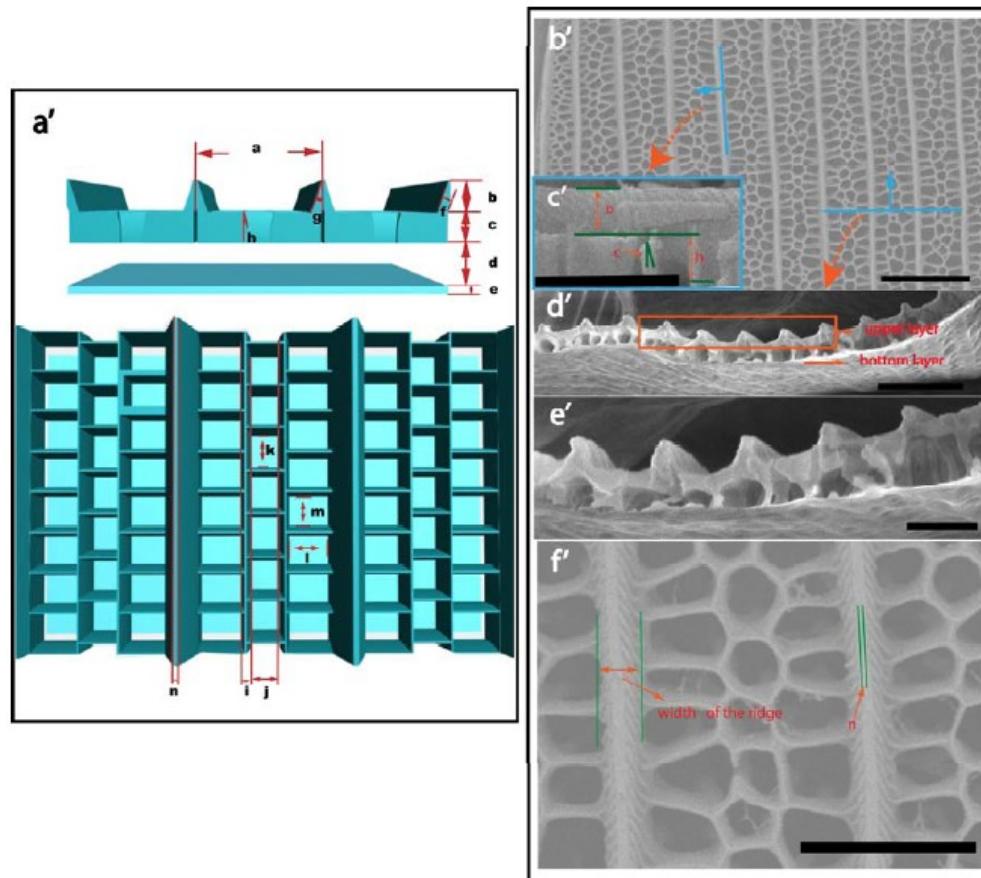


Fig. S1.1. Model and supplementary FESEM photos of *Papilio helenus Linnaeus*. **a'**, Dimensions of the 3D FDTD model of *Papilio helenus Linnaeus*. with *a* being the distance between two ridges; *b* the height of ridges; *c* the depth of the holes; *d* the distance between the bottom of the ridges and the base slab; *e* the thickness of the base slab; *f* the thickness of the ridge walls; *g* the half vertex angle of the ridges; *h* the half vertex angle of the ribs; *i* the width of the ribs; *j* and *k* the width the length of the middle holes; *l* and *m* the length and width of the side holes; and *n* the width of the flat top of the ridge. **b' ~ f'**, Supplementary images for corresponding parameters in **a'**: **b'**, Top view of a scale; **c'**, Side view of the ridge and holes in **b'**; **d' & e'**, Cross - sectional view of the scales; **f'**, Top view of the scale. Sale bars: **b' & d'**, 5 μ m. **c', e' & f'**, 2 μ m. Note that a degree of irregularity exists in the original scales, while our simulation model is idealized by employing the mean dimensions of the real structure.

Table S1. Dimensions for the models of *Papilio helenus Linnaeus*

Dimensions	Model 1	Model 2	Model 3	Model 4
<i>a</i> (μ m)	2.89	2.89	2.89	2.89
<i>b</i> (μ m)	0.64	0.64	0.64	0.64
<i>c</i> (μ m)	0.6	0.6	0.6	0.6
<i>d</i> (μ m)	1	1	$+\infty$	1
<i>e</i> (μ m)	0.22	0.22	0	0.22
<i>f</i> (μ m)	0.2	0.2	0.2	0.2
<i>g</i> (deg)	18	18	18	20.5
<i>h</i> (deg)	13.1	19.3	13.1	13.1

i(μm)	0.14	0.14	0.14	0.14
j(μm)	0.575	0.575	0.575	0.575
k(μm)	0.64	0.64	0.64	0.64
l(μm)	0.68	0.68	0.68	0.68
m(μm)	0.45	0.45	0.45	0.45
n(μm)	0.1	0.1	0.1	0

* a ~ n are defined in Fig. S3.1. Model 1 was built according to the dimensions of original scales and model 2 ~ 4 were contrast models

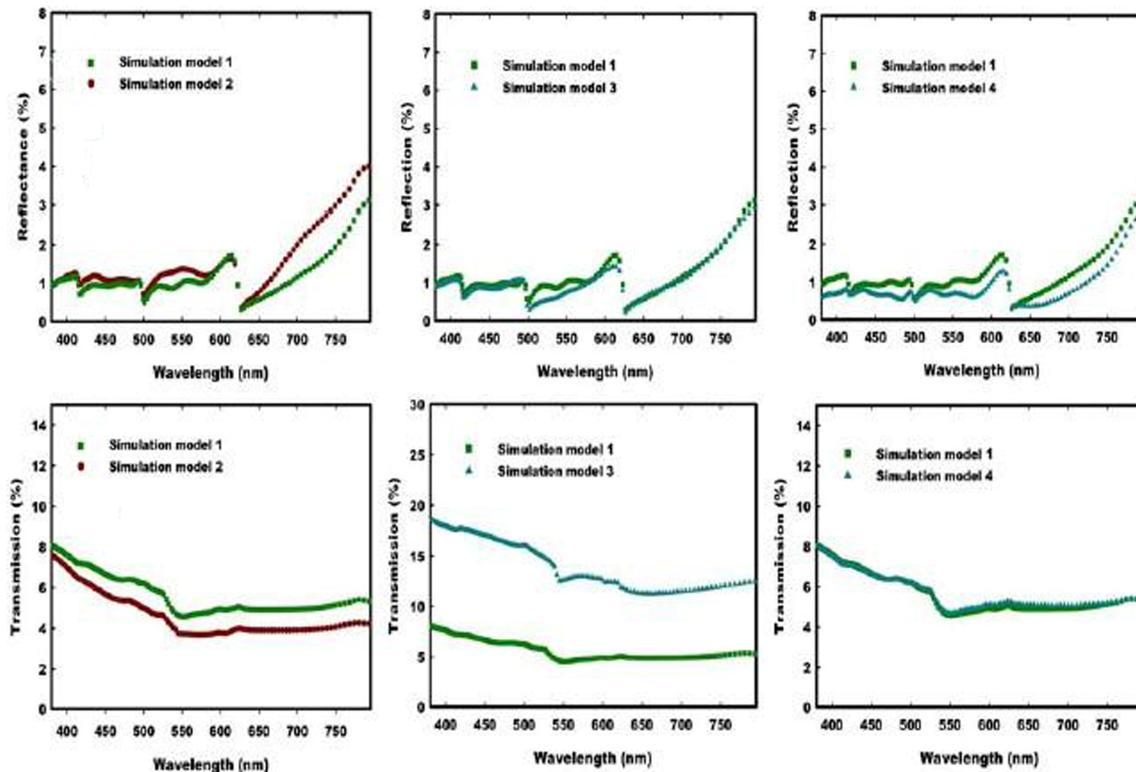


Fig. S1.2. Reflection and transmission spectra of different models of *Papilio helenus Linnaeus*.

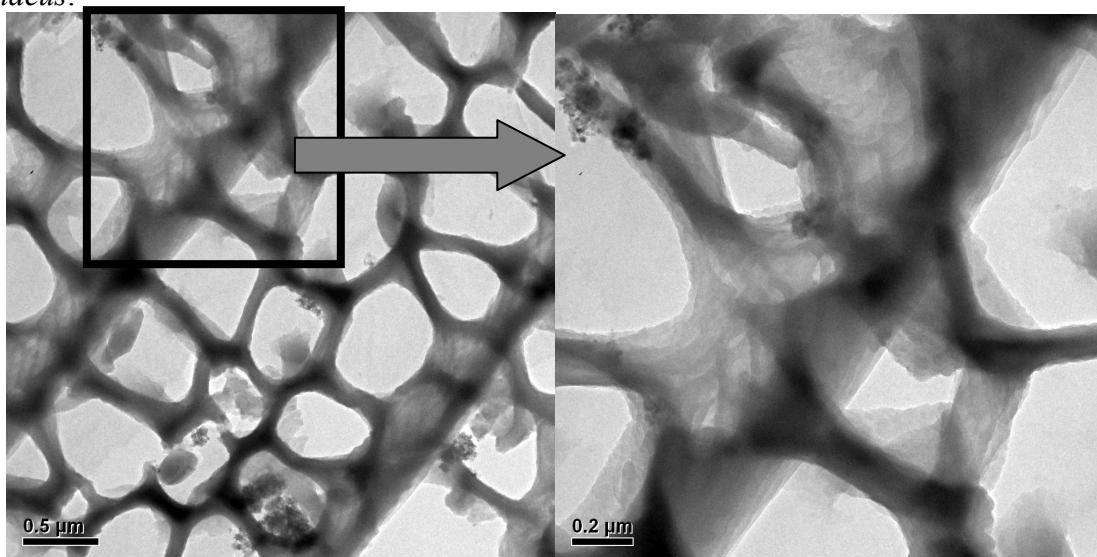


Fig. S2 Transmission electron microscope (TEM) image of the micro structure on a typical wing scale of the black dorsal wing of the male *Papilio helenus Linnaeus*, showing the ultra thin chitin layers.

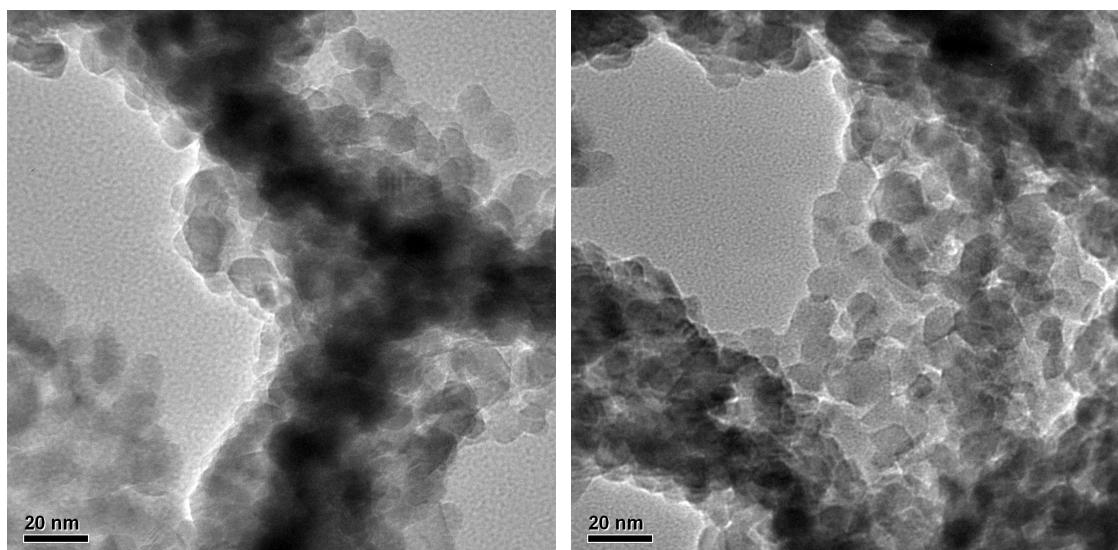


Fig. S3 Transmission electron microscope (TEM) image of the ABWA-TiO₂ showing the homogeneous size distribution of grains and nano pores.

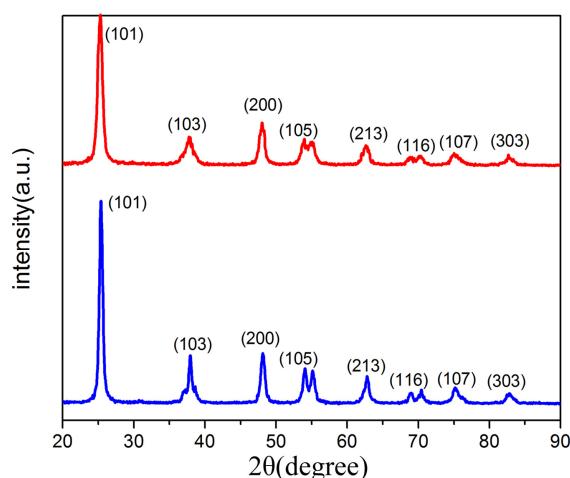


Fig. S4. XRD patterns of the ABWA-TiO₂ (red) and NT-TiO₂ (blue).

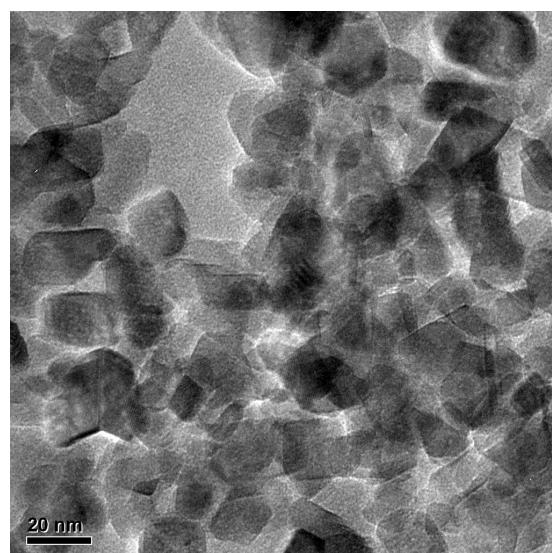


Fig. S5 Transmission electron microscope (TEM) image of NT-TiO₂, showing larger grain size and pore size than ABWA-TiO₂.

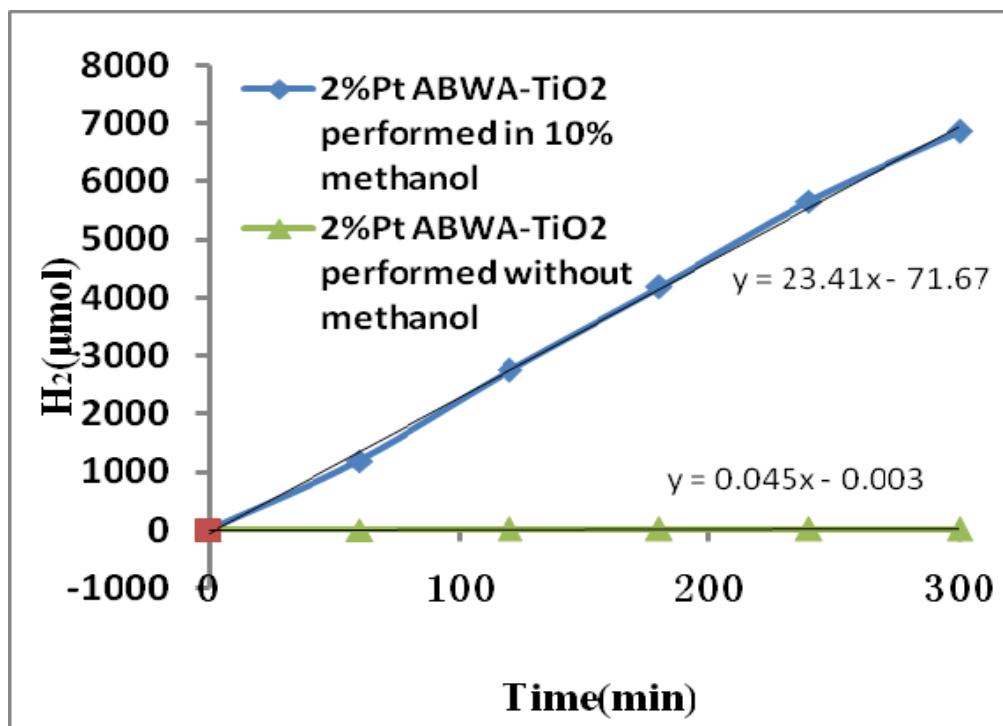


Fig. S6. Hydrogen evolution of 2% Pt loaded ABWA-TiO₂ performed in and without 10% methanol. The former has a rate 500 hundred times larger than the later.