Supplementary Information

Coupling Effects in 3D Plasmonic Structures Templated by *Morpho* Butterfly Wings

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Method

Preparation of the 3D biotemplated plasmonic structure: The *Morpho sulkowskyi* butterflies were purchased from Shanghai Qiuyu Biotechnology Co., Ltd (Shanghai, China). The butterfly wings were cut into 2.5 x 2.5 cm, which were attached to the Si wafers for the deposition of gold (Au) layer. After depositing 2-nm titanium as the adhesion layer, the Au was deposited onto the butterfly wings via physical vapor deposition (PVD) using a thermal evaporator. The deposition thicknesses of Au were controlled by the deposition time at a deposition rate of 0.5 $nm \cdot s^{-1}$.

Structural characterization: The optical microscope images of butterfly wings were acquired with a VHX-1000 digital microscope (Keyence, Japan). Scanning Electron Microscopy (SEM) images were taken with a Quanta 250 SEM (FEI, USA). For the cross-sectional Transmission Electron Microscope (TEM) sample preparation, the butterfly wings were embedded in the epoxy resin and then cut into ultra-thin sections. Prior to the embedding procedure, the butterfly wings were coated with 2 nm Al_2O_3 using atomic layer deposition (ALD) in the Savannah 100 ALD system (Cambridge NanoTech, Inc., USA), in order to enhance the boundary contrast between chitin and epoxy resin. TEM images were obtained using Tecnai G2 Spirit Biotwin microscope (FEI, USA).

Transmittance and SERS measurement: The transmittance spectra were recorded on a Lambda 750S UV/VIS spectrometer (Perkin Elmer, Inc., USA). Raman scattering spectra were recorded using a Senterra R200-L Dispersive Raman Microscope (Bruker Optics, Germany). A 633 nm laser with a power of 0.2 mW was used to excite the sample through a 50× objective (N.A. = 0.5, Olympus). The integration time was 10 s. Methylene blue (MB) was adopted as the Raman probe. The butterfly wings with Au nanostrips were immersed in a MB ethanol solution (10^{-4} M) for 2h, followed by rinsing several times with ethanol, and then dried in air. For measuring the SERS spectra of refractive index (RI) matched specimens, the

butterfly wings with Au coating were immersed in a RI matching fluid (Cargille Laboratories, Inc., USA) after the above MB treatment. The RI matching fluid was a mixture of aliphatic/alicyclic hydrocarbons and hydrogenated terphenyl, which has an index of 1.56.

Optical simulation: The near-field coupling of the Au nanostrips was calculated using the finite-difference time-domain (FDTD) approach. The geometries and relative gaps of nanostrips were acquired from the TEM data. For simplification, the cross-sectional shape of the nanostrip was assumed to be rectangle. Only the upper three layers of Au nanostrips on the butterfly ridge were utilized in the simulation due to the relatively large contribution from these layers. A simulation region of 4 × 4 μm, which contained five butterfly ridges and the corresponding nanostrips, was used in the model. The simulation boundaries were set as perfect matched layers (PML) and the mesh size was adopted to be 1 nm. The refractive index of the Au was obtained from the work of Johnson and Christy.[1] For the surrounding media that consisted of butterfly wing and matching fluid, the effective refractive index was assumed as 1.56 + 0.02i.[2, 3] In order to calculate the transmittance spectra and near-field electric field distribution, the modeled structures were illuminated at normal incidence by a plane wave polarized perpendicular to the longitudinal direction of Au nanostrips.

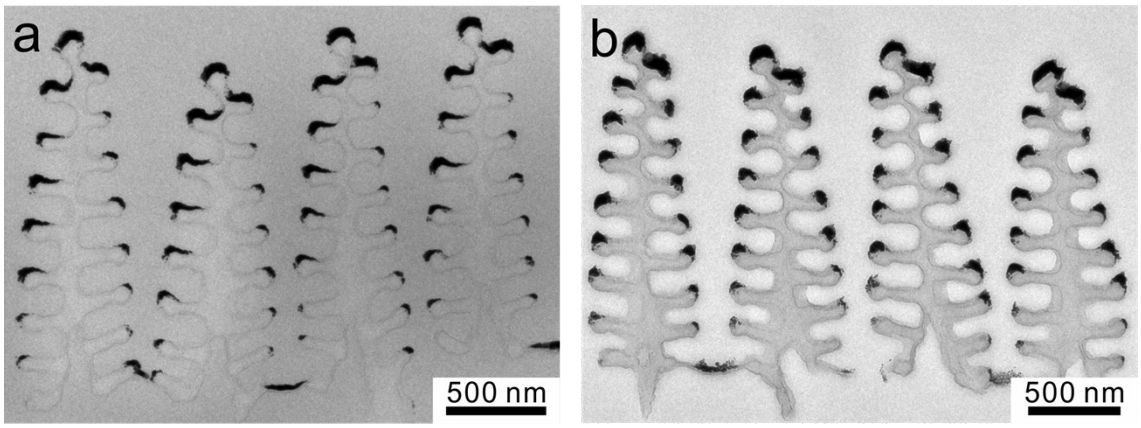

Fig. S1 Morphology of the *Morpho* butterfly wings with Au nanostrips. (a) TEM image showing the Au structures located on the lamellae structures with deposition thickness of 50 nm; (b) TEM image of the sample with deposition thickness of 70 nm.

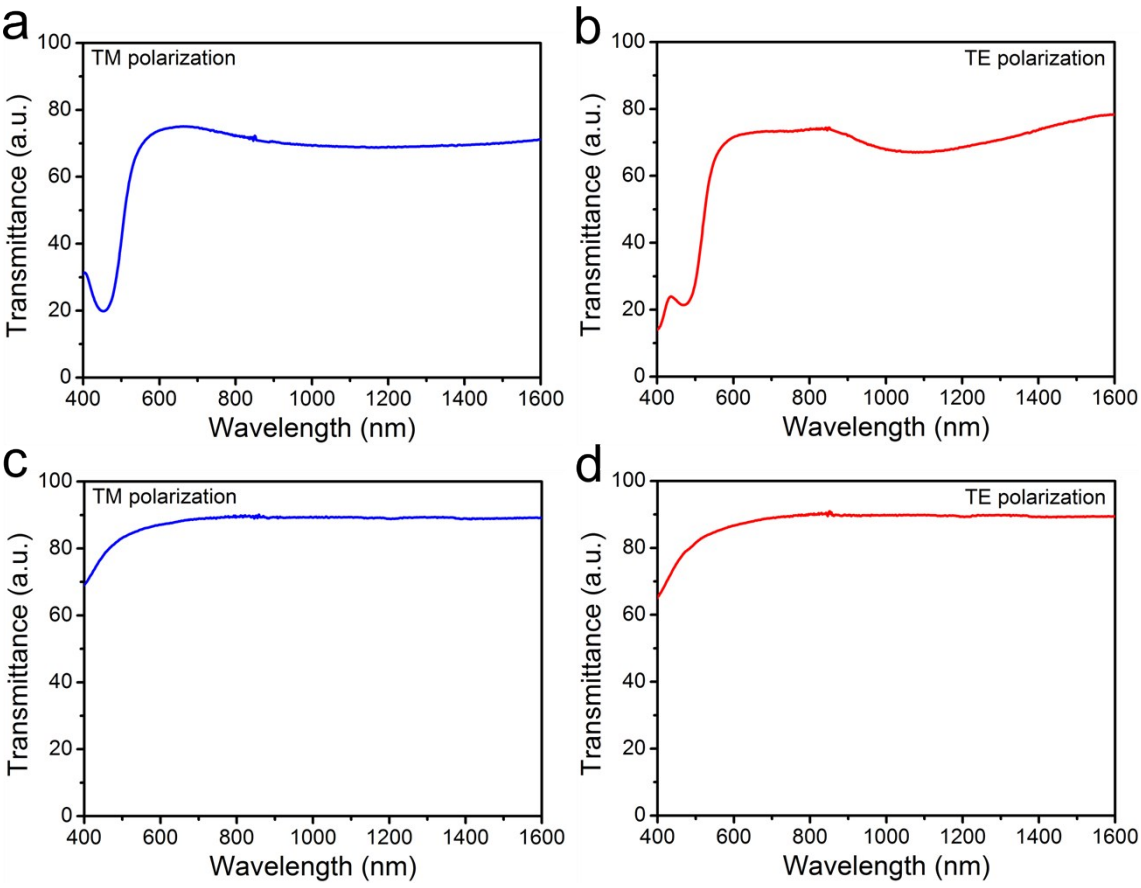

Fig. S2 Transmittance of the *Morpho* butterfly wings. (a, b) Transmittance of butterfly wings in air measured with the TM and TE polarized incident light; (c, d) Transmittance of butterfly wings immersed in RI matching fluid measured with the TM and TE polarized incident light.

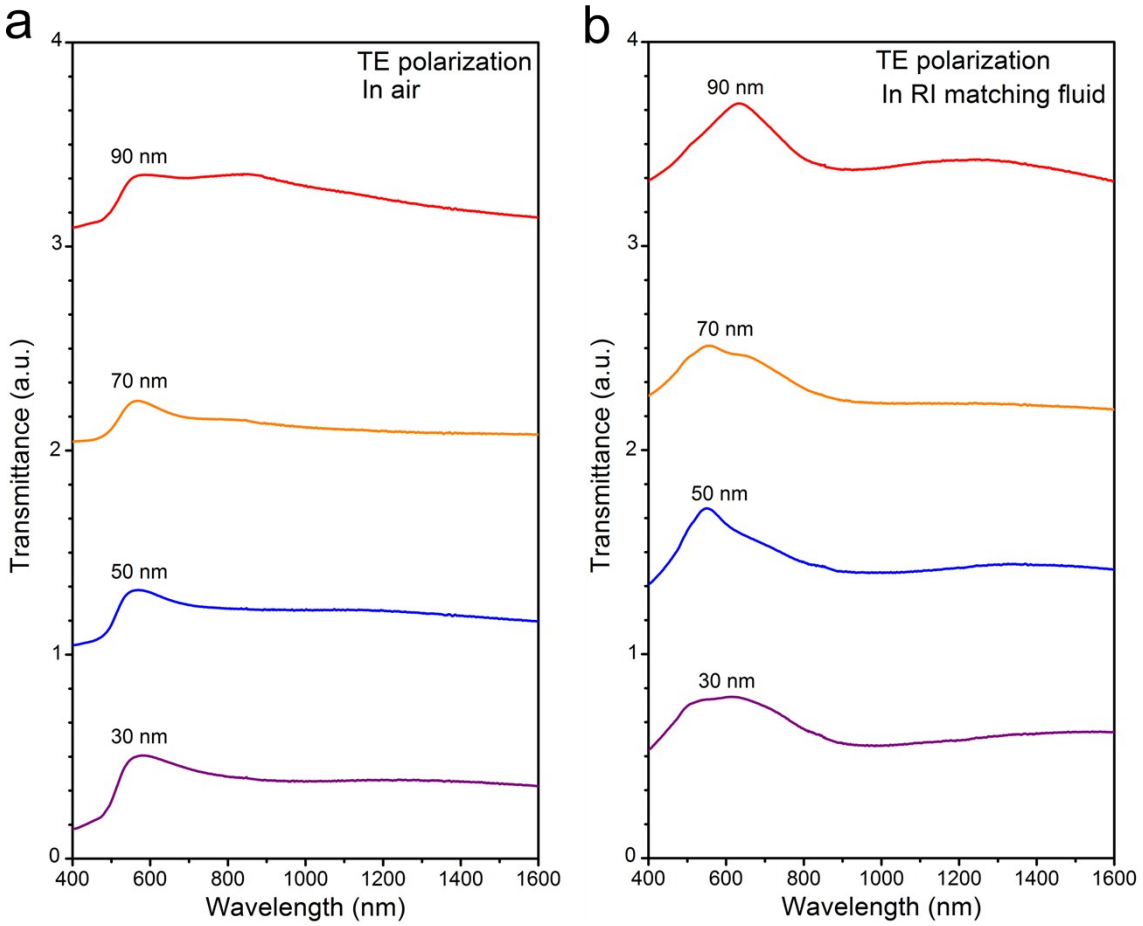

Fig. S3 Transmittance spectra of the 3D Au nanostructures with the butterfly wing templates under the incident light polarized along the longitudinal direction of Au nanostrips (TE polarization). (a) Samples in air; (b) Samples immersed in RI matching fluid.

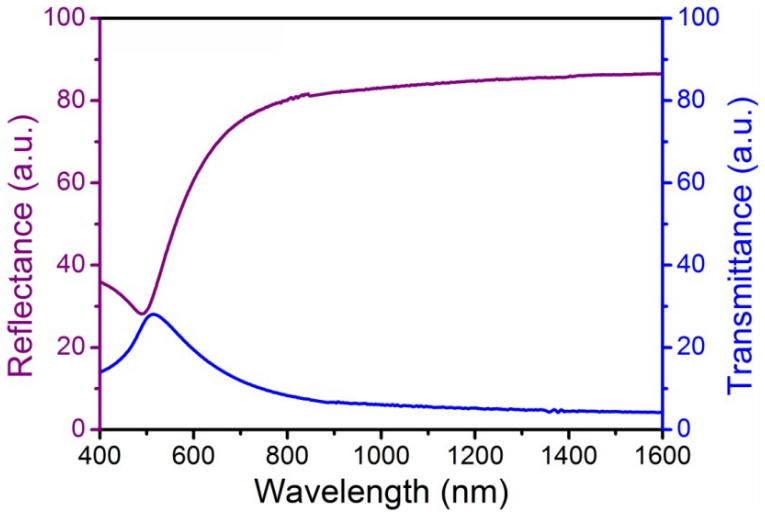

Fig. S4 Reflectance and transmittance of a continuous Au film with thickness of 50 nm.

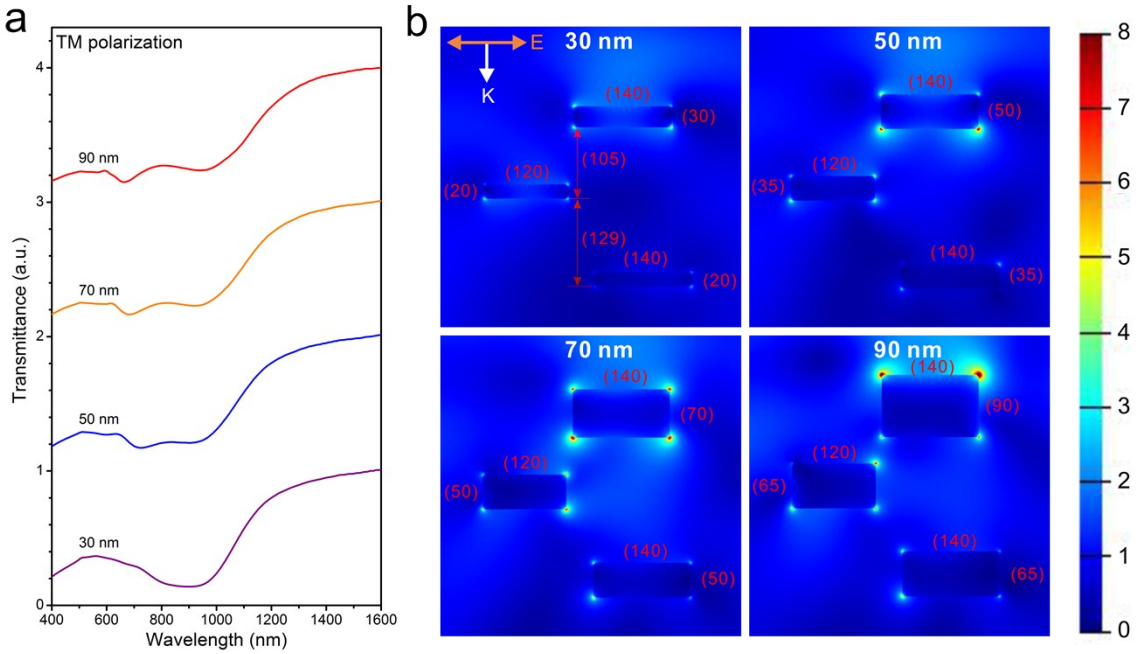

Fig. S5 Simulated results of the plasmonic properties of 3D Au nanostrips in RI matching fluid. (a) Simulated transmittance of the 3D Au nanostrips; (b) Simulated electric field distribution in the vicinity of the 3D Au nanostrips at the wavelength of 633 nm.

References

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2 S. Banerjee and Z. Dong, *Opt. Rev.*, 2007, **14**, 359-361.
3 A. D. Pris, Y. Utturkar, C. Surman, W. G. Morris, A. Vert, S. Zalyubovskiy, T. Deng, H. T. Ghiradella and R. A. Potyrailo, *Nat. Photon.*, 2012, **6**, 195-200.