Supplementary Information

Integrating Plasmonic Nanostructures with Natural Photonic Architectures in Pd-Modified *Morpho* Butterfly Wings for Sensitive Hydrogen Gas Sensing

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Materials and Methods

Fabrication of the 3D heterogeneous structure

The *Morhpo sulkowskyi* butterfly was supplied by Shanghai Qiuyu Biotechnology Co., Ltd (Shanghai, China). Small pieces with size of 2.0 × 2.0 cm were cut from the wings and attached to the Si wafers. Then, the samples were deposited with 2 nm titanium adhesion layer and 15 nm Pd layer via thermal evaporation at a deposition rate of 0.5 $nm \cdot s^{-1}$.

Structure characterization

The optical microscope image of *Morpho* butterfly wing was taken with a VHX-1000 digital microscope (Keyence, Japan). The detailed morphologies of *Morpho* butterfly scales were characterized by a field-emission scanning electron microscope (NOVA Nano SEM 230, FEI, USA). To prepare cross-sectional transmission electron microscope (TEM) specimens, the butterfly wings were embedded in the epoxy resin and then cut into ultra-thin sections by room temperature microtomy (Leica Ultracut UC6, Germany). In order to obtain a high boundary contrast between butterfly and epoxy resin, the butterfly wings were pre-coated with 2 nm Al_2O_3 using atomic layer deposition (ALD) in the Savannah 100 ALD system (Cambridge Nanotech Inc., USA) before the embedding procedure. TEM images were taken using Tecnai G2 Spirit Biotwin microscope (FEI, USA).

Measurements of optical response

To measure the optical response of the Pd-modified *Morpho* butterfly scales, the reflectance spectra were recorded using an optical spectrometer (QE65Pro, Ocean Optics, USA). A 20W tungsten-halogen light source (HL-2000, Ocean Optics, USA) was coupled to a bifurcated optical

fiber (QR400-7-Vis-NIR fiber, Ocean Optics, USA) reflection probe. The probe was oriented normal to the sample surface, and the other end of the bifurcated fiber was coupled with the spectrometer. A white panel (WS-1-SL Spectralon Reference Standard, Ocean Optics, USA) was used as the reference. The H_2 sensing studies were performed in a glass chamber equipped with the optical fiber. H_2 was diluted with nitrogen (N_2), and the H_2 concentration was adjusted through mass flow controllers (Alicat Scientific, Inc., AZ, USA). The mixture of N_2 and H_2 were then introduced into the chamber with a constant flow rate of 400 $ml \cdot min^{-1}$ to test the dynamic optical response of the sensor.

Optical simulation

The reflectance spectra of the butterfly wing scales before and after Pd modification were calculated using finite-difference time-domain (FDTD) approach. The structural parameters of the ridges and the Pd nanostrips were acquired from the TEM data. For simplification, the cross-sectional shape of the Pd nanostrip was assumed to be rectangle. A simulation region of 4.5 × 4.5 μm containing five butterfly ridges and the corresponding Pd nanostrips was utilized in the model. In the modeling, a plane wave propagated perpendicular to the ridges was used as the light source. The mesh size was adopted to be 1 nm, and the simulation boundaries were set as perfectly matched layers. The refractive index of the butterfly ridges was assumed as 1.56+0.02i.[1] The dielectric constants of Pd and PdHx were taken from the data reported by Yamada et al.[2] In order to calculate the absorption cross-section of Pd nanostrip, a normal incident plane wave combined with the total field scattering-filed (TFSF) boundary conditions was used in the simulations.

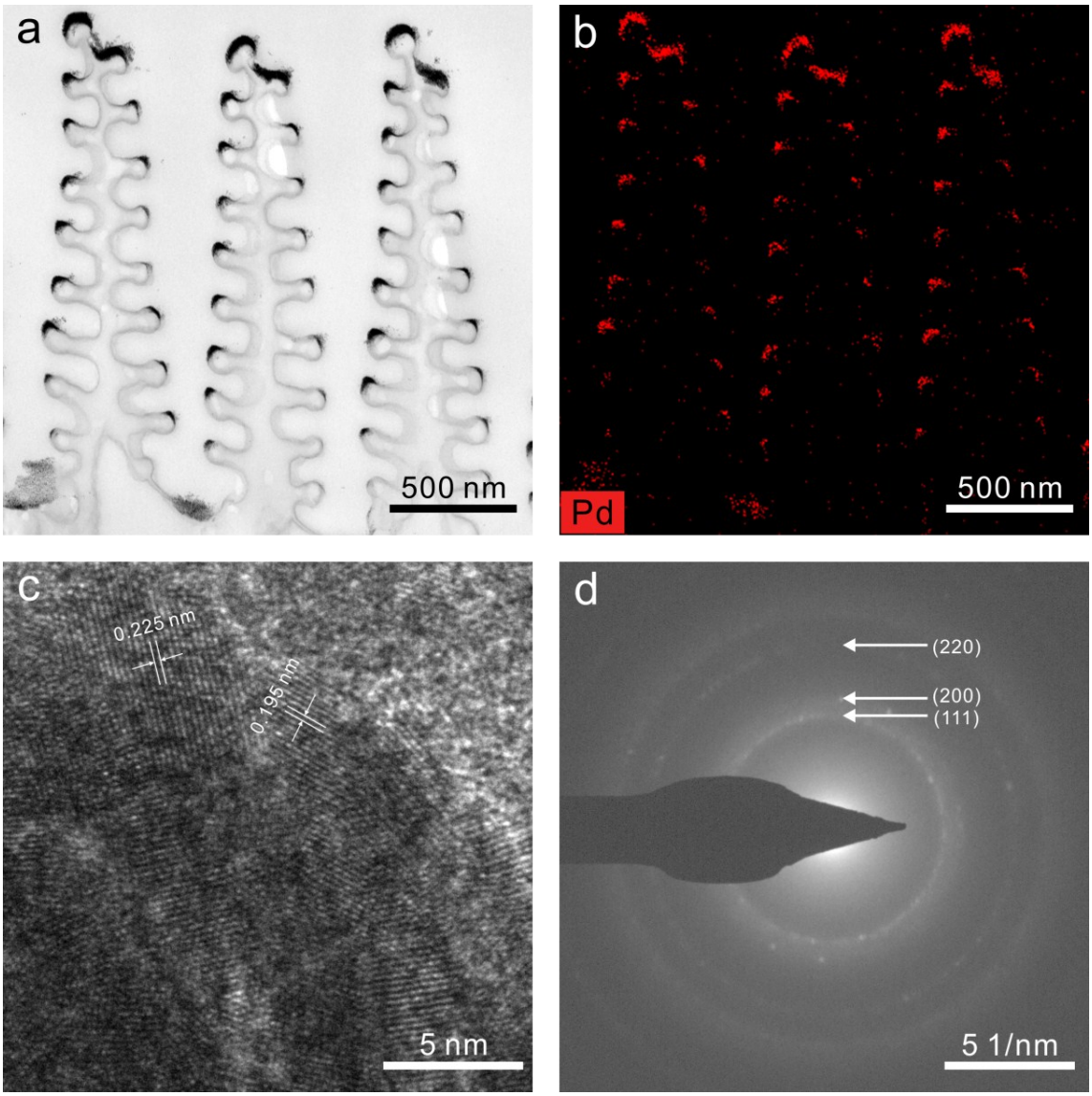

Fig. S1 Characterization of Pd-modified *Morpho* butterfly wing scales. (a) The cross-sectional TEM image; (b) Elemental map of the Pd-modified *Morpho* butterfly wing scale for Pd; (c) HRTEM image of the Pd nanostrips; (d) Corresponding SAED pattern.

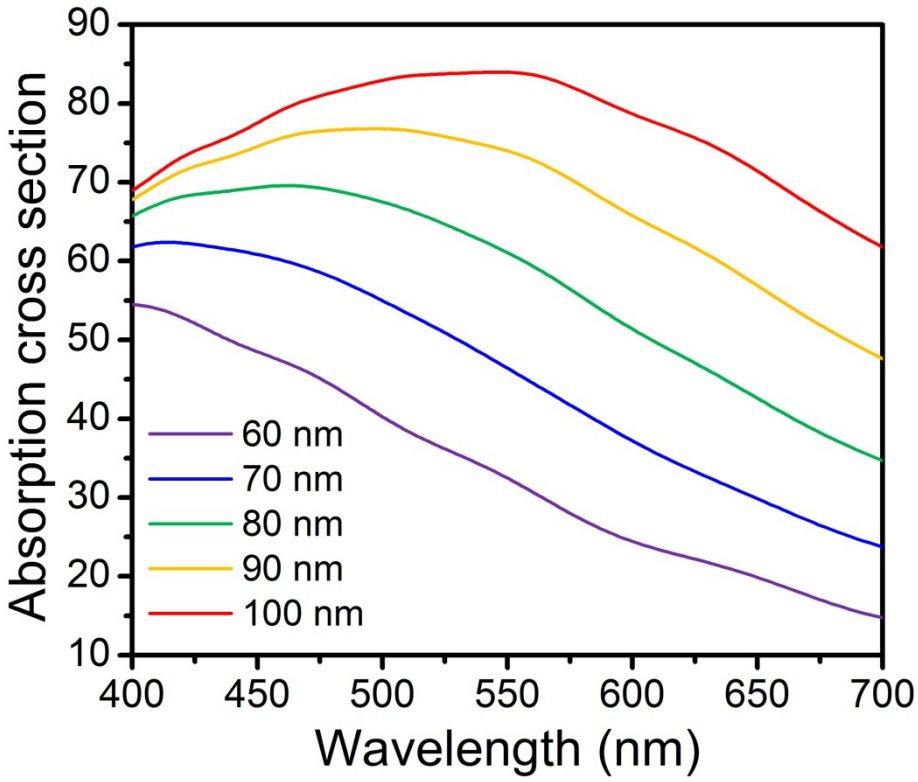

Fig. S2 Simulated absorption spectra for Pd nanostrips with different widths. The thickness of Pd nanostrips was 15 nm.

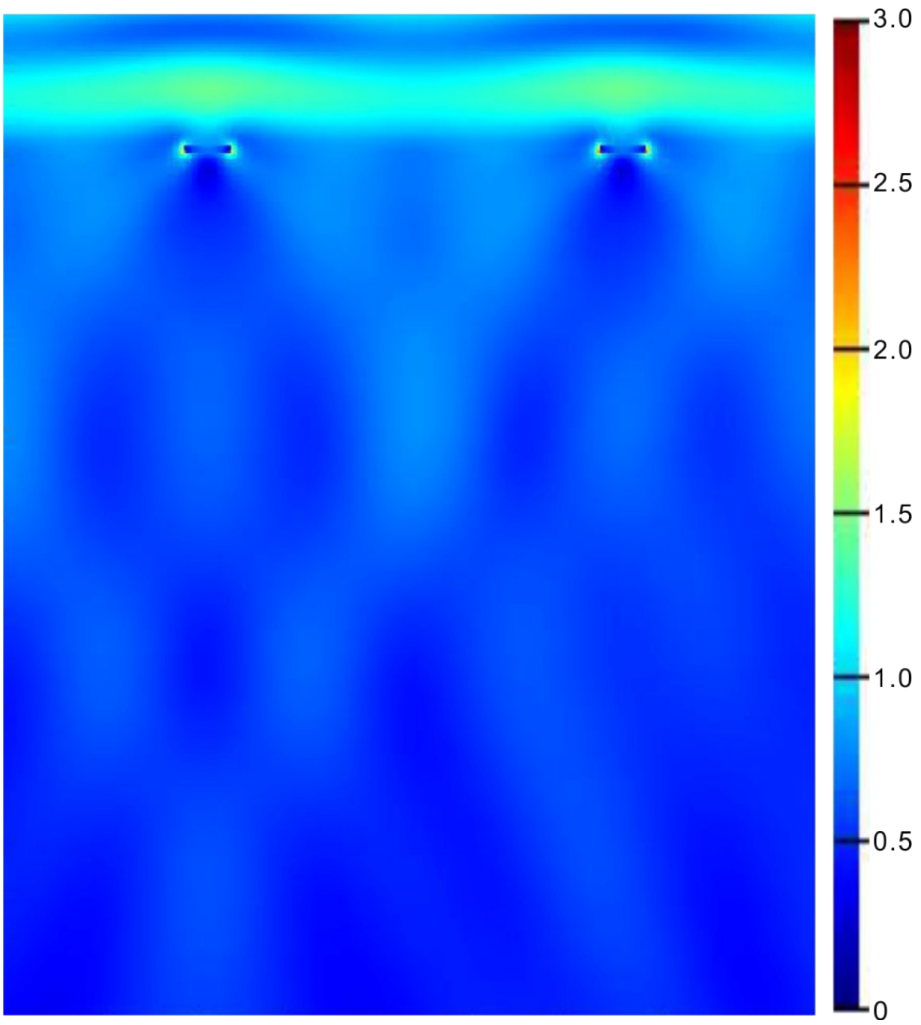

Fig. S3 Calculated electric field distributions of the Pd nanostrips that were placed on a planar dielectric substrate at the wavelength of 500 nm.

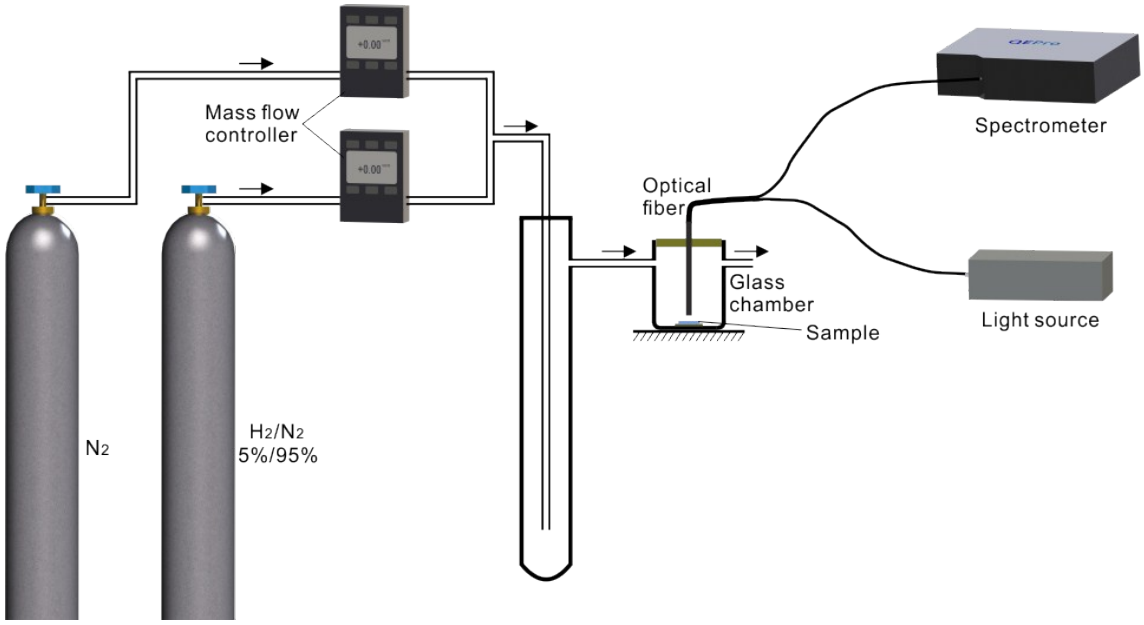

Fig. S4 Schematic representation of the experimental setup for the study of optical response of the Pd-modified butterfly wing sample upon exposure to H_2.

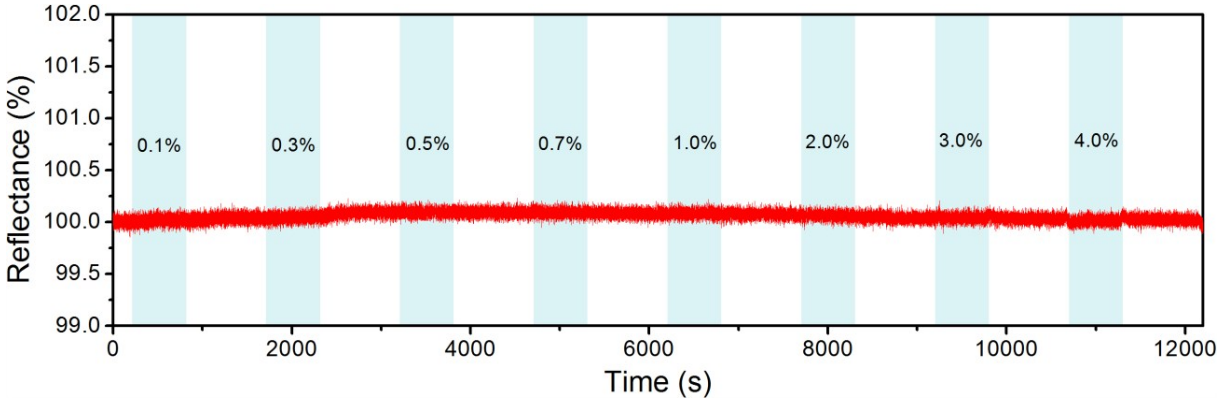

Fig. S5 Response of the original *Morpho* butterfly wing scales to H_2. The normalized reflectance change at the wavelength of 500 nm could be ignored upon exposure to H_2 with different concentrations from 0.1% to 4%.

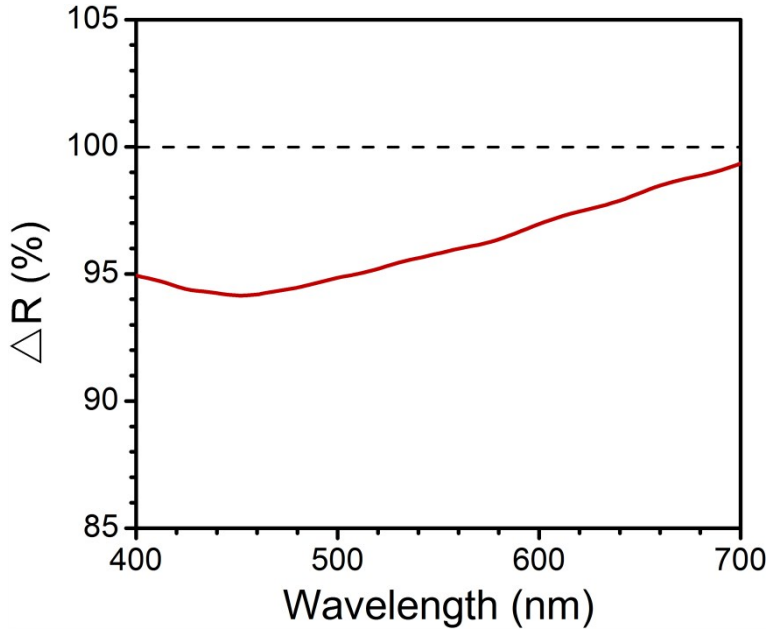

Fig. S6 Simulated relative reflectance of the Pd nanostrips on a planar dielectric substrate when Pd is converted into β-PdHx.

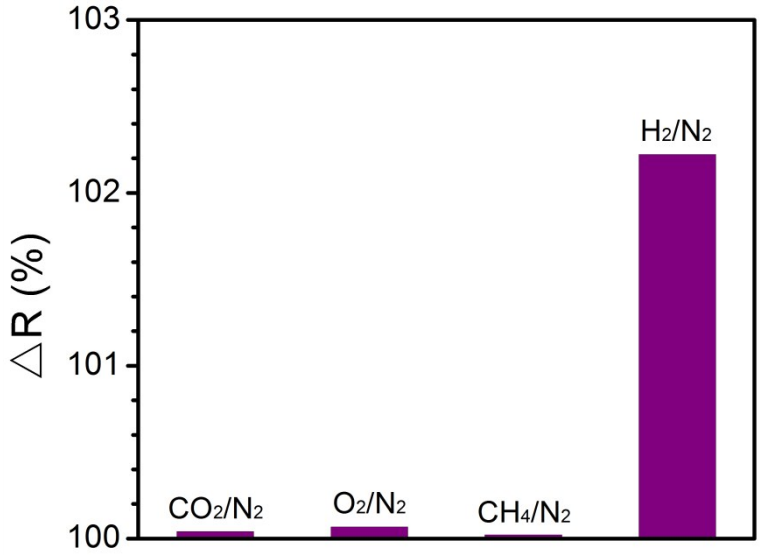

Fig. S7 Response of the Pd-modified *Morpho* butterfly wing scales to CO_2, O_2, CH_4, and H_2. The concentration of CO_2/N_2, O_2/N_2, CH_4/N_2, and H_2/N_2 was 5000 ppm.

Reference

1 A. D. Pris, Y. Utturkar, C. Surman, W. G. Morris, A. Vert, S. Zalyubovskiy, T. Deng, H. T. Ghiradella and R. A. Potyrailo, *Nat. Photonics*, 2012, **6**, 195-200.

2 Y. Yamada, K. Tajima, S. Bao, M. Okada, A. Roos and K. Yoshimura, *J. Appl. Phys.*, 2009, **106**, 013523.