Supporting Information for

TiO₂ Based Sensor with Butterfly Wing Configurations for Fast Acetone

Detection at Room Temperature

Guiqin Yang,^{a, b} Meng Zhang,^a Decheng Dong,^a Xiaofang Pan,^c Ye Zhou,^d Suting Han,^a Zongxiang Xu, ^e Wanlin Wang,^{*a} Yan Yan^{*a}

^{a.} Institute of Microscale Optoelectronics (IMO), Shenzhen University, Shenzhen 518060, China.

^b. Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong

Province, College of Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China.

^c. College of Electronic and Information Engineering, Shenzhen University, Shenzhen 518060, China.

^{d.} Institute for Advanced Study, Shenzhen University, Shenzhen 518060, China.

^{e.} Department of Chemistry, Southern University of Science and Technology, Shenzhen, Guangdong 518000, China.

Materials

Fore wings of Princeps paris (family Papilionidae) were purchased from Shanghai Qiuyu Biotechnology Co., Ltd.. The material of titanium (\mathbb{N}) sulfate [Ti(SO₄)₂] was obtained from Sinopharm Chemical Reagent Co., Ltd.:, and the ethanol and ethanol anhydrous (CH₃CH₂OH \geq 99.5%) were purchased from Aldrich. All chemicals and solvents were used

without further purification.

Preparation of ANH-TiO₂-BW

The fore wings of Princeps paris were washed with anhydrous ethanol carefully first and then soaked in diluted hydrochloric acid for a half hour to clean impurities away. Then, clean wings were picked out, washed with deionized water and dried at room temperature. Ti(SO₄)₂ lump (7.2 g) was dissolved into ethanol absolute (99.9 %, 50 ml) and stirred for 6 hours to form a transparent Ti-colloid. Then, the pretreated wing templates were dipped flatly into the colloid at room temperature in a breathable vessel (Fig. 1a). The templates with coating of metal ions were taken out after 14 hours, washed thoroughly with deionized water, and then fixed between a pair of clamped quartz glasses to keep the soaked wing flat (Fig. 1b). After then, the coated wings together with quartz glasses were transferred into a clean corundum

boat, and another smaller corundum boat filling with 10 ml Ti-colloid was placed on the top of the quartz glasses in the bigger corundum boat (Fig. 1c). This novel combination was then transferred into the tube furnace and heated to 550 °C at a rate of 1 °C min⁻¹. Original butterfly wings were burnt out after holding at this temperature for 1.5 hours, and the final ANH-TiO₂-BWs were obtained.





Fig. S1. The XRD patterns of the structural evolution from ANH-TiO₂-BW to N-TiO₂-BWP. The XRD patterns of the structural evolution from ANH-TiO₂-BW to N-TIO₂-BWP are shown in Fig. S1. It is observed that the diffraction peak of samples transforms from extremely diffused broad peak to distinguishable one with the extended annealing time, indicating that the amorphous TiO₂ based products can crystallize gradually once the atoms obtained enough thermal energy. In addition, the emerged peaks are excellent consistent with certain low index crystal orientations of anatase (JCPDS21–1272) and rutile (JCPDS87–0920) TiO₂. The observed diffraction peaks of N-TiO₂-BWP are relatively broad, indicating its tiny grain size. There are no notable peaks of impurities, demonstrating that no other phases have been formed during the whole experimental procedure.

Supplementary explanation of TEM images



Fig. S2 The original wing (a) and its partial SEM images (b), the SEM images of fragmentary (c), filled and blocked (d) structures of N-TiO₂-BWP.

The natural Princeps paris wings are covered densely with scales around 60 μ m wide and 150 μ m long. The configurations made of the replicate biomorphic porous metal oxide materials through soaking and following natural sintering are usually loose and brittle and difficult to maintain the original morphology for the duplicate structure, which usually turns into powder during sintering and transfer process (Fig. S2b). The brickle replicates are usually made into pastes and then coated on substrates with patterned electrodes to fabricate gas sensors, therefore the most of micro-holes in these structures are plugged (Fig. S2c).



Fig. S3. TEM images of ANH-TiO₂-BW (a), further enlarged portion (b), the part of nanocrystal regions, (c) and the part of transition regions (d)

Fig. S3 shows the details of the enlarged image of Fig. 3b, the interplanar spacing of anatase TiO_2 nanocrystal is 0.325 nm and the corresponding crystal face index is (110). The transition areas between amorphous and nanocrystal can be clearly observed.



Fig. S4. TEM images and SAD patterns of N-TiO₂-BWP (a-c) and TiO₂-P samples (d-f).

The porous framework of N-TiO₂-BWP is similar to the ANH-TiO₂-BW, but the enlarged portion of N-TiO₂-BWP demonstrates that its structure is fragile polycrystalline, and the rings are indexed as (101), (110), (004), (200), (105), (211) and (204) diffractions, respectively. The morphology and microstructures of TiO₂-P samples are also characterized by TEM and shown in Fig. S4d-S4f. The TEM image of TiO₂-P with a flake-like structure is shown in Fig. S4d, and the enlarged portion in Fig. S4c demonstrates that the TiO₂-P is a typical polycrystalline structure, which is further confirmed by the regularly arranged spots of the selected area diffraction pattern in Fig. S4f.