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Supplementary Material

Insight into the origin of photoreactivity of various well-defined Bi₂WO₆ crystals:

exposed heterojunction-like surface and oxygen defect

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Sample	Х	$E_{g}(eV)$	$E_{CB} (eV)$	$E_{VB} (eV)$
Nanosheet-assembled microspheres	6.36	2.51	0.61	3.12
Nanoparticle-assembled microspheres	6.36	2.41	0.66	3.07
Single-crystalline nanosheets	6.36	2.51	0.61	3.12

Table S1 The valence band (VB) edge and the conduction band (CB) edge positions of Bi_2WO_6 .

The valence band (VB) edge and the conduction band (CB) edge positions of the prepared Bi_2WO_6 can be calculated from the following formula:

$$E_{VB} = X - E^e + 0.5E_g \qquad (1)$$

$$E_{CB} = E_{VB} - E_g \qquad (2)$$

where E_{VB} is the VB edge potential, E_{CB} is the CB edge potential, E_g is the band gap energy of the semiconductor, X is the electronegativity of the semiconductor that is the geometric mean of the electroegativity of the constituent atoms, E^e is the energy of free electrons on the hydrogen scale (about 4.5 eV). The X values of Bi_2WO_6 is 6.36 eV¹.



Fig. S1 Emission spectrum of the 300W Xe lamp with a 420 nm cutoff filter.



Fig. S2 TEM images of as-prepared Bi_2WO_6 samples: (a-b) nanosheet-assembled microspheres, (c-d) nanoparticle-assembled microspheres and (e) single-crystalline nanosheets.



Fig. S3 (a) Schematic illustration of the crystal orientation of the nanosheets with exposed (020) facets. (b) The crystal structure of orthorhombic Bi_2WO_6 . Atomic structure of the (020) facets: (c) side view and (d) top view. W, O and Bi atoms are represented as blue, red and yarrow spheres, respectively.



Fig. S4 Enlarged profile of the XRD patterns of the prepared Bi_2WO_6 samples between angles 10-30 °: (a) nanosheet-assembled microspheres, (b) nanoparticleassembled microspheres and (c) single-crystalline nanosheets.



Fig. S5 Photocatalytic degradation of MO under visible light irradiation over various Bi₂WO₆ samples: (a) nanosheet-assembled microspheres, (b) nanoparticle-assembled microspheres and (c) single-crystalline nanosheets.



Fig. S6 N₂ absorption-desorption isotherms of the prepared Bi₂WO₆ samples: (a) nanosheet-assembled microspheres, (b) nanoparticle-assembled microspheres and (c) single-crystalline nanosheets.

Fig. S6 describes typical N₂ adsorption-desorption isotherms of the prepared samples. Both Bi_2WO_6 nanosheet-built microspheres and nanosheets showed a typical II adsorption-desoprtion isotherms. In addition, the weak adsorption-desoprtion hysteresis demonstrated monolayer absorption. However, the nanoparticle-assembled microspheres displayed IV-type isotherm character, indicating the existence of mesopores. The specific surface areas of nanosheet-assembled microspheres, nanoparticle-assembled micropsheres and single-crystalline nanosheets are 26.97±1, 40.72±1 and 13.56±1 m² g⁻¹, respectively.

Supplementary reference

1. L. Chen, H. Hua, Q. Yang and C. Hu, Appl. Surf. Sci., 2015, 327, 62-67.