Electronic Supplementary Information (ESI)

Boron oxynitride nanoclusters on tungsten trioxide as a metal-free cocatalyst for oxygen evolution from photocatalytic water splitting

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Sample preparation procedure. B₂O₃@WO₃ was synthesized by simply treating tungsten boride (WB, Aldrich, 99.9%) powder at 700 °C for 2 h in air with a ramping rate of 2 °C/min. To prepare B₂O_{3-x}N_x@WO₃, a certain amount of B₂O₃@WO₃ powder was treated in gaseous NH₃ atmosphere with a flow rate of 50 mL/min for 0.5 h at 300 °C.

WO₃ reference was synthesized as follows: 1 g of ammonium tungstate hydrate $((NH_4)_{10}W_{12}O_{41}\cdot xH_2O)$ was dissolved in 30 mL of 1 M hydrochloric acid (HCl) solution to form tungstic acid (H₂WO₄) precipitation under stirring, which was recovered by drying at 80 °C. The resultant H₂WO₄ was heated to obtain WO₃ at 600 °C for 2h in air with a ramping rate of 5 °C/min. The crystal structure and morphology of the WO₃ obtained was indicated in Fig. S3.

To prepare B₂O₃ (5wt%)-loaded WO₃, 300 mg of WO₃ reference was dispersed in a 25 mL aqueous solution containing 26.6 mg of boric acid (H₃BO₃). After a 30 min ultrasonic treatment, the suspension was recovered by evaporating at 120 °C under stirring. The mixture was finally heated at 500 °C for 2 h in air with a ramping rate of 5 °C/min to obtain B₂O₃ (5wt%)-loaded WO₃.

Characterization. X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku diffractometer using Cu irradiation ($\lambda = 1.54056$ Å). Their morphology was determined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) performed on Nova NanoSEM 430 and JEOL 2010 electron microscopy, respectively. Fourier transform infrared spectra (FT-IR) were recorded on Bruker TENSOR 27 (MCT detector). Raman spectra were collected on LabRam HR 800. The optical absorbance spectra of the samples were recorded in a UV-Visible spectrophotometer (JACSCO-550). Fluorescence emission spectrum was recorded at room temperature excited by incident light of 270 nm with a fluorescence spectrophotometer (Edinburgh Instruments, FLSP-920). Chemical compositions of the modified WO₃ samples were analyzed using X-ray photoelectron spectroscopy (Thermo Escalab 250, a monochromatic Al K_a X-ray source). All binding energies were referenced to the C 1s peak (284.6 eV) arising from adventitious carbon.

Oxygen evolution. Photocatalytic water splitting reactions were carried out in a top-irradiation vessel connected to a glass closed gas circulation system. The detailed schematic of water splitting measurement equipment can be found in reference [1]. 100 mg of the photocatalyst powder was dispersed in 270 mL aqueous solution containing 0.85 g AgNO₃ as the sacrificial reagent. The light source was a 300 W Xe lamp (Beijing Trusttech Co. Ltd, PLS-SXE-300UV). A cutoff filter of 400 nm was employed for the visible-light irradiation. The reaction temperature was maintained below 20 °C. The amount of O₂ evolved was determined using a Shimadzu gas chromatography system (GC-2014).

[1] X. Wang, G. Liu, Z. G. Chen, F. Li, L. Wang, G. Q. Lu and H. M. Cheng, *Chem. Commun.*, 2009, 3452.



Fig. S1 XRD patterns of $B_2O_3@WO_3(a)$ and $B_2O_{3-x}N_x@WO_3(b)$.



Fig. S2 (A) FT-IR and (B) Raman spectra of $B_2O_3@WO_3$ (a) and $B_2O_{3-x}N_x@WO_3$ (b).



Fig. S3 Time course of O₂ evolution from water splitting using $B_2O_3@WO_3$ (black line) and $B_2O_{3-x}N_x@WO_3$ (red line) samples under $\lambda > 400$ nm irradiation.



Fig. S4 (A) XRD pattern and (B) SEM image of WO_3 reference.



Fig. S5 UV-visible absorption spectra of WO_3 reference before (a) and after (b) the treatment in gaseous ammonia atmosphere.



Fig. S6 (A) UV-visible absorption spectra of bulk B_2O_3 ; (B) Schematic of the relative positions of valence band and conduction band edges of WO₃, bulk B_2O_3 and $B_2O_{3-x}N_x$ nanocluster. The inset in (A) is the plot of transformed Kubelka-Munk function *vs* the energy of the light absorbed of bulk B_2O_3 .