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. B$_2$O$_3$@WO$_3$ 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 B$_2$O$_{3-x}$N$_x$@WO$_3$, a certain amount of B$_2$O$_3$@WO$_3$ powder was treated in gaseous NH$_3$ atmosphere with a flow rate of 50 mL/min for 0.5 h at 300 °C.

WO$_3$ reference was synthesized as follows: 1 g of ammonium tungstate hydrate ((NH$_4$)$_{10}$W$_{12}$O$_{41}$·xH$_2$O) was dissolved in 30 mL of 1 M hydrochloric acid (HCl) solution to form tungstic acid (H$_2$WO$_4$) precipitation under stirring, which was recovered by drying at 80 °C. The resultant H$_2$WO$_4$ was heated to obtain WO$_3$ at 600 °C for 2 h in air with a ramping rate of 5 °C/min. The crystal structure and morphology of the WO$_3$ obtained was indicated in Fig. S3.

To prepare B$_2$O$_3$ (5wt%)-loaded WO$_3$, 300 mg of WO$_3$ reference was dispersed in a 25 mL aqueous solution containing 26.6 mg of boric acid (H$_3$BO$_3$). 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 B$_2$O$_3$ (5wt%)-loaded WO$_3$. 
Characterization. X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku diffractometer using Cu irradiation ($\lambda = 1.54056 \text{ Å}$). 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 light of 270 nm with a fluorescence spectrophotometer (Edinburgh Instruments, FLSP-920). Chemical compositions of the modified WO$_3$ samples were analyzed using X-ray photoelectron spectroscopy (Thermo Escalab 250, a monochromatic Al K$_\alpha$ 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 AgNO$_3$ 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 O$_2$ evolved was determined using a Shimadzu gas chromatography system (GC-2014).

Fig. S1 XRD patterns of B$_2$O$_3$@WO$_3$ (a) and B$_2$O$_{3-x}$N$_x$@WO$_3$ (b).

Fig. S2 (A) FT-IR and (B) Raman spectra of B$_2$O$_3$@WO$_3$ (a) and B$_2$O$_{3-x}$N$_x$@WO$_3$ (b).
**Fig. S3** Time course of O$_2$ evolution from water splitting using B$_2$O$_3$@WO$_3$ (black line) and B$_2$O$_{3-x}$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\textsubscript{3} reference before (a) and after (b) the treatment in gaseous ammonia atmosphere.

Fig. S6 (A) UV-visible absorption spectra of bulk B\textsubscript{2}O\textsubscript{3}; (B) Schematic of the relative positions of valence band and conduction band edges of WO\textsubscript{3}, bulk B\textsubscript{2}O\textsubscript{3} and B\textsubscript{2}O\textsubscript{3-x}N\textsubscript{x} nanocluster. The inset in (A) is the plot of transformed Kubelka-Munk function vs the energy of the light absorbed of bulk B\textsubscript{2}O\textsubscript{3}. 

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