Supporting Information

Visible-light-responsive Copper (II) Borate Photocatalysts with Intrinsic Midgap States for Water Splitting

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Synthesis method:

All chemicals, including boric acid (Acros, 99+%), boron oxide (City Chemical, 99.9%), copper ( ) nitrate trihydrate (Acros, for analysis), copper (II) oxide (Sigma-Aldrich, 99.99%), iron (III) oxide (Alfa Aesar, 99.5%), sodium nitrate (Alfa Aesar, 99%) were used as received without any further purification.

A typical synthetic procedure of CuB_2O_4 can refer to a previous report.[1] First, H_3BO_3, $Cu(NO_3)_2 \cdot 3H_2O$, and $NaNO_3$ at a molar ratio of 1:10:0.02 were dissolved in distilled water. The solution was slowly evaporated to dryness on a hot plate with constant stirring. The dry mixture was heated at 500 °C for 5 h. The resultant mixture was ground thoroughly and heated at 800 °C for 12 h. The product was washed with a large amount of warm distilled water to remove excess B_2O_3 and then dry at 70 °C overnight. The final product was ground before characterization and property measurements.

A typical synthetic procedure of $Cu_3B_2O_6$ can refer to a previous report[2] with minor changes. A nearly stoichiometric mixture of CuO and B_2O_3 (3% excess B_2O_3) was heated in air at 900 °C for 36 h, with two intermediate grindings. The product was washed with a large amount of warm distilled water and then dried at 70 °C overnight. The final product was ground before characterization and property measurements.

Instrumental characterization:

Powder X-ray diffraction data were collected using a Bruker D8-Advance powder diffractometer operating at 40kV, 40mA for Cu Kα radiation (λ=1.5406 Å). The pure Al_2O_3 was used as the internal standard to allow for accurate measurement of the peak positions (i.e. 2θ values) which might be shifted due to various experimental or instrumental factors such as the height of the sample surface.

The UV-visible absorption spectra were recorded on a Shimadzu UV-3101PC UV-Vis-NIR spectrophotometer operating in the diffuse mode with application of Kubelka-Munk equation.

SEM pictures were recorded on a Philips XL30 scanning electron microscope. A thin layer of Au/Pd was sprayed onto the sample before measurement.

The specific surface area was calculated using the BET (Brunauer-Emmett-Teller) method from the nitrogen adsorption data in the relative range (P/P_0) of 0.04-0.20.

The ESR spectra were obtained on a JES-FA 200 ESR spectrometer at room temperature.

The X-ray photoelectron spectroscopy (XPS) characterization was carried out by using a Kratos AXIS ULTRADLD XPS system equipped with an Al K monochromated X-ray source and a 165-mm electron energy hemispherical analyzer to examine the surface properties and composition of the sample. All the binding energies were calibrated by using the contaminant carbon (C 1s) 284.6 eV as a reference.

Photocatalysis experiments:

Photocatalytic H_2 and O_2 production experiments were conducted in a sealed circulation system. For H_2 evolution, 1 wt% Pt was loaded as cocatalysts by UV irradiation of $PtCl_4$ aqueous solution. In a typical run, 0.100 g of sample was suspended in 120 mL 25% methanol aqueous solution (containing 0.0017 g $PtCl_4$) under magnetic stirring. Then a 300 W Xe lamp was applied to this mixture for 30 minutes, in that case, Pt nanoparticles would be loaded to the surface of CuB_2O_4 as cocatalysts. After degassing the system for about half an hour, this

300 W Xe lamp with a 400 nm cut-on filter (Newport Corp.) was applied to execute the photocatalytic reaction. For O_2 evolution, 1 wt% RuO_2 was loaded by impregnation from a carbonyl complex, $Ru_3(CO)_{12}$ (Aldrich, 99.0%), in acetone solution according to the method reported previously.[3] In a typical run, 0.100 g RuO_2-photocatalysts was suspended in 120 mL 0.05 M $AgNO_3$ aqueous solution containing 0.2 g La_2O_3 as a base buffer to maintain the pH at ~8.08. After degassing the system for about half an hour, the 300 W Xe lamp with a 400 nm cut-on filter was applied to execute the photocatalytic reaction. The products of H_2 and O_2 were analyzed by gas chromatography (Shimadzu GC-8A) equipped with a thermal conductivity detector (TCD). All the photocatalysis experiments were repeated for three times at least.

To confirm the H_2 is coming from the photocatalytic reaction, the amount of H_2 we actually collected must exceed the amount of photocatalysts we used in the experiment (Turnover number > 1). To facilitate the measurements, H_2 was collected by illuminating the reaction under UV irradiation.[4] For CuB_2O_4, we collected 702.4 μmol of H_2 under UV irradiation (0.13 W/cm^2) for 116 hours, which exceeds the amount of CuB_2O_4 (0.1 g, 670.4 μmol) used in the experiment. During 116 hours irradiation under UV light, H_2 was steadily produced, which actually further verifies the photostability of the compound. Since $Cu_3B_2O_6$ appears much slower H_2 evolution rate than CuB_2O_4, in order to shorten the measurement period, we increased the light intensity to 1.66 W/cm^2 when performing its turnover number measurement. After 52 hours irradiation, we collected 3781.4 μmol of H_2, which exceeds the amount of $Cu_3B_2O_6$ (0.1 g, 324.39 μmol) used in the experiment. H_2 was steadily produced during the measurement which also further indicates the photostability of the compound.

The apparent quantum yield (AQY) was calculated based on the following equations: AQY of H_2 evolution = 100% × [(number of evolved H_2 molecules) × 2] / (number of incident photons); AQY of O_2 evolution = 100%×[(number of evolved O_2 molecules) ×4] / (number of incident photons). A bandpass filter (Newport Corp.) with various wavelengths from 300 nm to 700 nm was applied. The number of the incident photons was determined using a radiant power energy meter (Newport Corp., Model 70260 with a Thermopile Detector).

Table S1. Apparent Quantum Yield of CuB_2O_4 at different wavelengths

Wavelength	300 nm	420 nm	500 nm	600 nm	700 nm
AQY of H_2	0.67%	0.06%	0.045%	0.034%	0%
AQY of O_2	10.6%	6.39%	3.74%	1.3%	0%

Control photocatalysis experiments:

First, set up a H_2 evolution trial according to the above experimental conditions for H_2 evolution measurement and wrap the reactor with aluminum foils thoroughly. Sample the system every two hours, re-vacuum the system and sample it again in a two hours interval. Second, set up an O_2 evolution trial according to the above experimental conditions for O_2 evolution measurement and wrap the reactor with aluminum foils thoroughly. Sample the system in the same interval as it is used for O_2 evolution experiment above. In control experiments, only trace amount of H_2 or O_2 were observed, indicating the H_2 and O_2 obtained under visible light irradiation were not from the mechano-catalytic water splitting.

To further verify the copper borates do perform photocatalytic water splitting, we illuminated 25% aqueous methanol solution and 0.05 M $AgNO_3$ aqueous solution containing 0.2 g La_2O_3

respectively without adding any copper borates. No H_2 or O_2 was tested.

Density of states (DOS) calculation:

The DOS calculations were performed using the plane-wave-based DFT code, VASP,[5] via the projector-augmented wave method to describe core electrons.[6] The unit cells were sampled with an 8 x 8 x 16 k-point for CuB_2O_4 and an 18 x 2 x 2 k-point for $Cu_3B_2O_6$. Wave functions were expanded by the plane waves up to a cutoff energy of 400 eV. We performed the calculations using the LSDA functional of Ceperley and Alder, parameterized by Perdew and Zunger, and the LSDA+U method implemented by Dudarev and co-workers.[7] We chose the parameters of U(Cu)=7.5 eV, J(Cu)=0.98 eV for CuB_2O_4 and U(Cu)=6.0 eV, J(Cu)=0.98 eV for $Cu_3B_2O_6$ respectively. The first set has been used on similar copper compounds previously (see Reference 5 in the main article), and the predicted population maximum of the midgap state in CuB_2O_4 agrees well with the experimental d-d transition peak maximum. The $Cu_3B_2O_6$ parameters were chosen to shift the midgap state population maximum to the energy corresponding to the experimental d-d transition peak maximum in that material as well.

Optimized crystal geometry compared with experimental results (in parentheses)

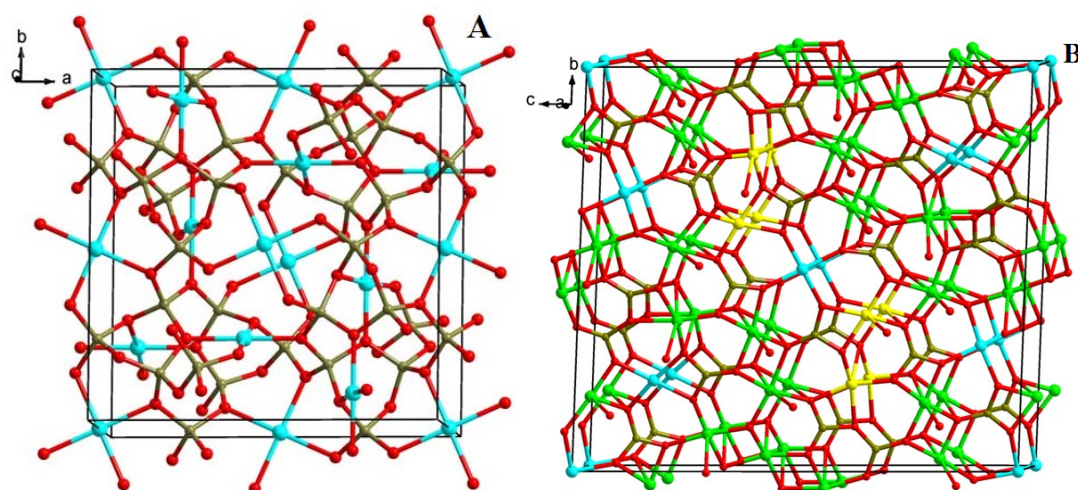|	CuB_2O_4	$Cu_3B_2O_6$
a (Å)	11.499(11.480)	3.30397(3.35300)
b (Å)	11.499 (11.480)	19.7983(19.6650)
c (Å)	5.6049(5.6200)	19.7672(19.6270)
α (degree)	90.000 (90.000)	88.9970(88.7700)
β (degree)	90.000 (90.000)	69.6042(69.7100)
γ (degree)	90.000 (90.000)	69.3382(69.2400)
V	741.158 (741.178)	1125.44(1127.41)
density	4.01031(4.01020)	4.54812(4.54019)

Figure S1: Unit cell portions of the crystal structures of CuB_2O_4 (A) and $Cu_3B_2O_6$ (B). The color code is as follows: oxygen (red); boron (dark yellow); copper in square (cyan), pyramidal (yellow) and octahedral (green) geometry. Some of the Cu atoms in CuB_2O_4 are coordinated as distorted octahedron due to Jahn-Teller effect.
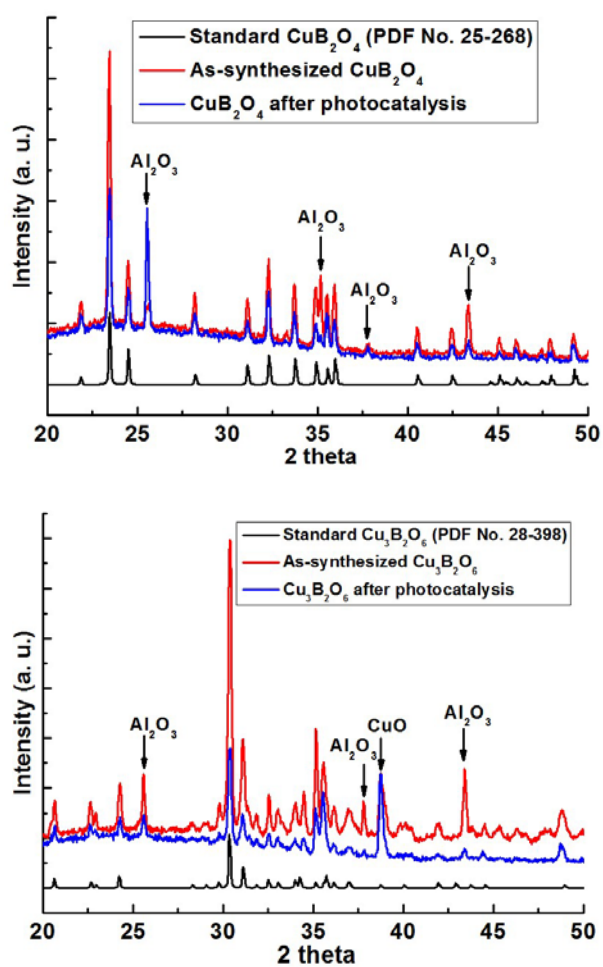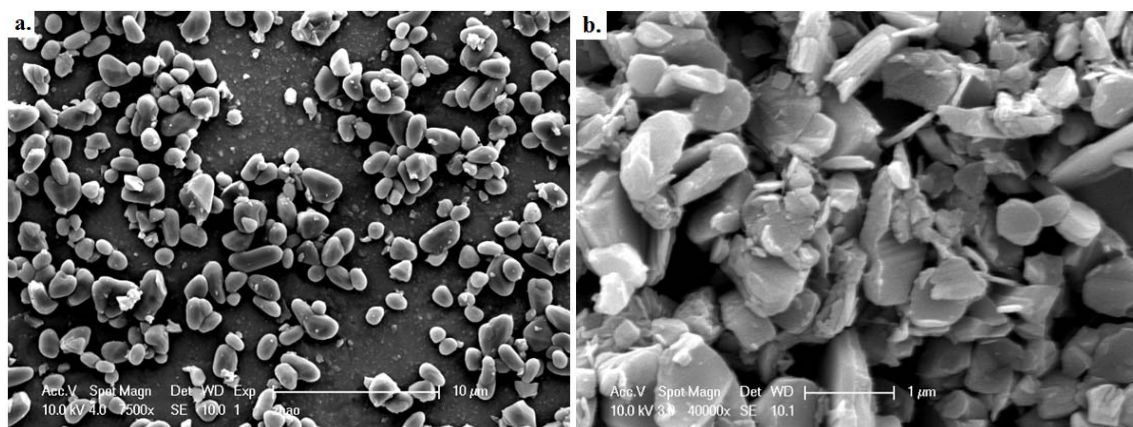
Figure S2: XRD patterns of CuB_2O_4 and $Cu_3B_2O_6$

Figure S3: SEM pictures of prepared (a) CuB_2O_4 and (b) $Cu_3B_2O_6$.
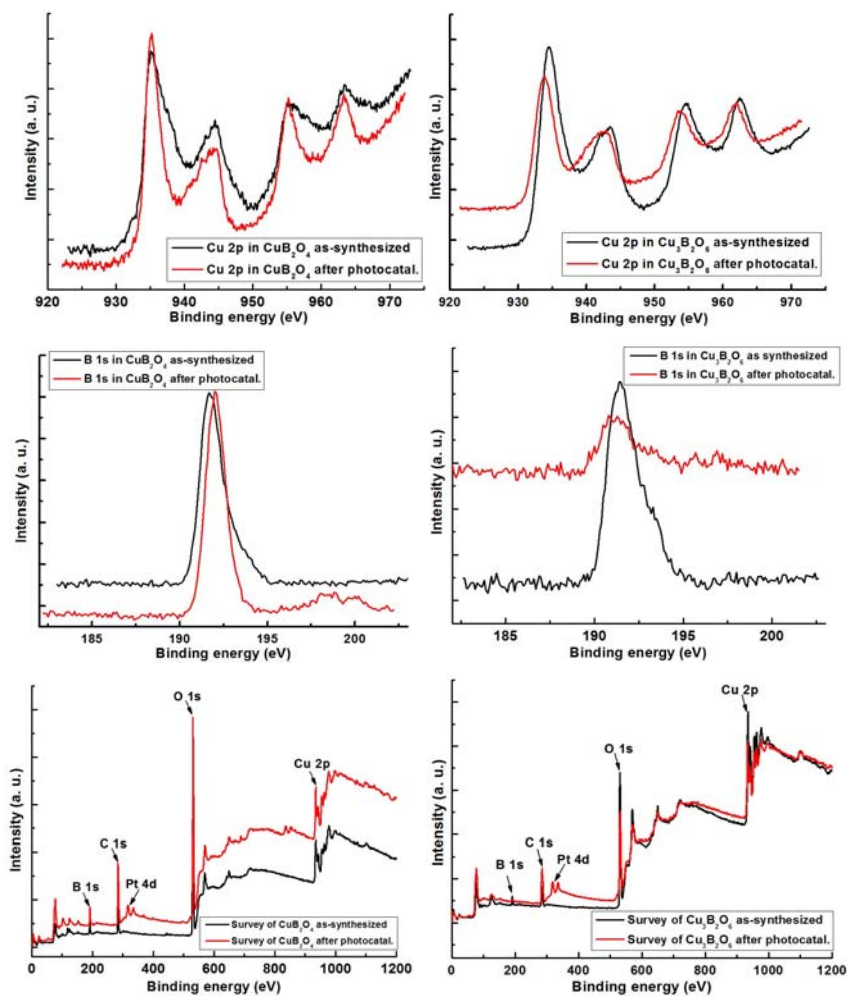
Figure S4: XPS spectra of copper borates before and after H$_2$ evolution reaction
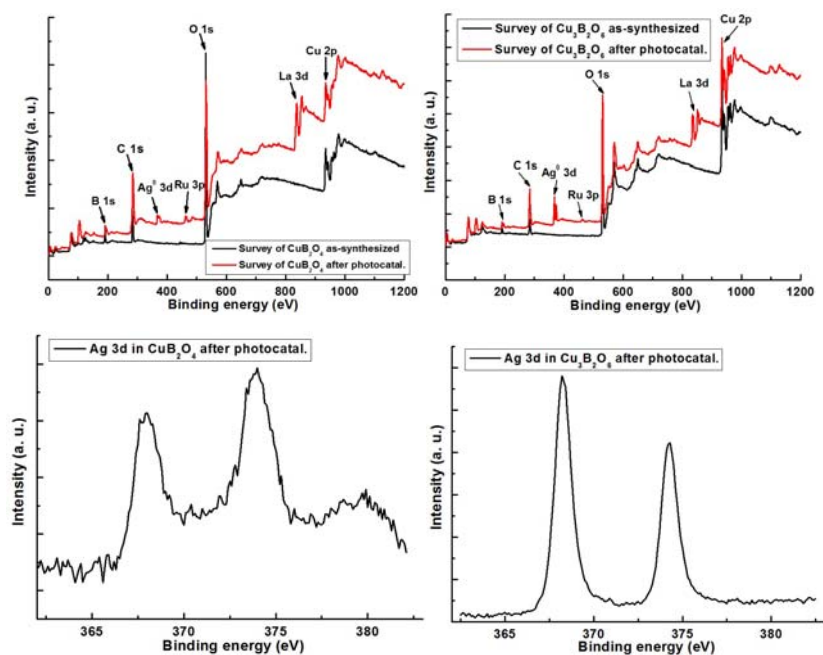

Figure S5: XPS spectra of copper borates before and after O$_2$ evolution reaction (bottom: highly resolved XPS spectra of Ag 3d after O$_2$ evolution reaction)
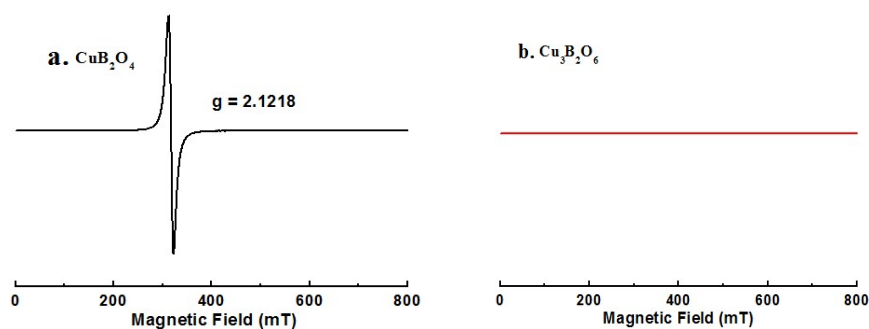
Figure S6: The ESR spectra of (a) CuB_2O_4 and (b) $Cu_3B_2O_6$ at room temperature
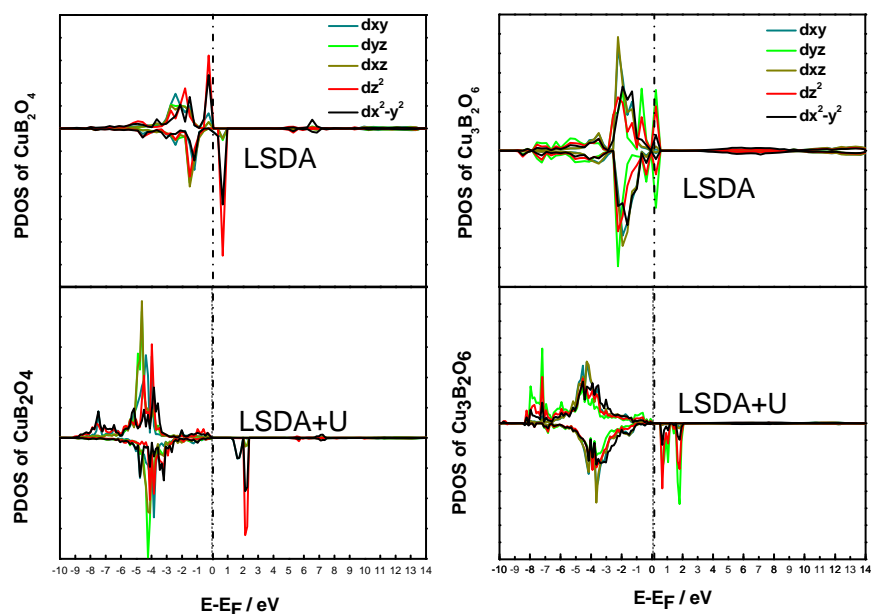

Figure S7: The comparison of the PDOS with LSDA and LSDA+U calculations

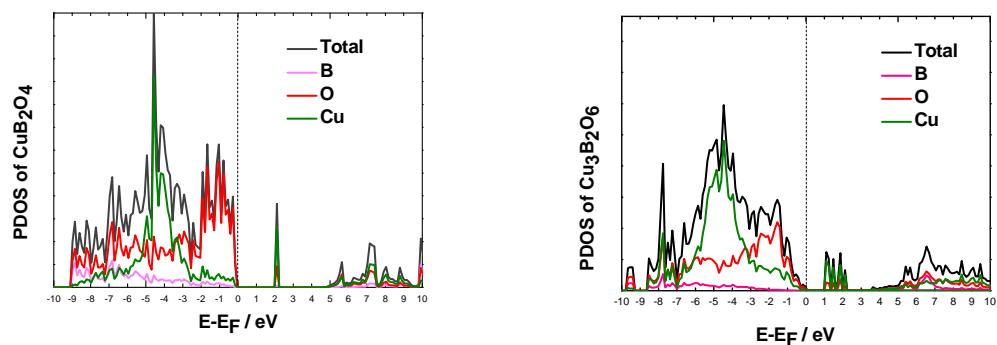**Figure S8:** LSDA+U PDOS in antiferromagnetically ordered ground state. U(Cu)=7.5 eV, J(Cu)=0.98 eV are used for both CuB_2O_4 and $Cu_3B_2O_6$.

References:

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(7)   (a) V. I. Anisimov, J. Zaanen and O. K. Andersen, *Phys. Rev. B* 1991, 44, 943-954; (b) S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys and A. P. Sutton, *Phys. Rev. B* 1998, 57, 1505-1509.