Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Activation of Kagome lattice structured $Cu_3V_2O_7(OH)_2 \cdot 2H_2O$ volborthite via hydrothermal crystallization for boosting visible light-driven water oxidation

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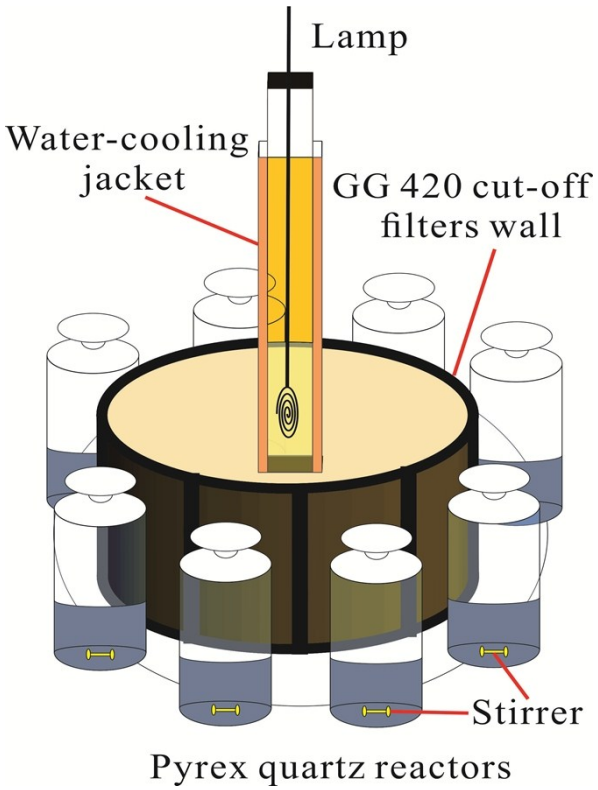
Reaction setup



Scheme S1. Schematic diagram of home-bulit multizone photocatalytic reaction testing system consisting of eight air-tight quartz reactors and a 500 W mid-pressure Hg lamp. Notably, a relative low-power Hg lamp was irradiated on each reactor. The performance measurements of samples prepared in different batches were reproducibly conducted at least three times.

TEM/HRTEM images

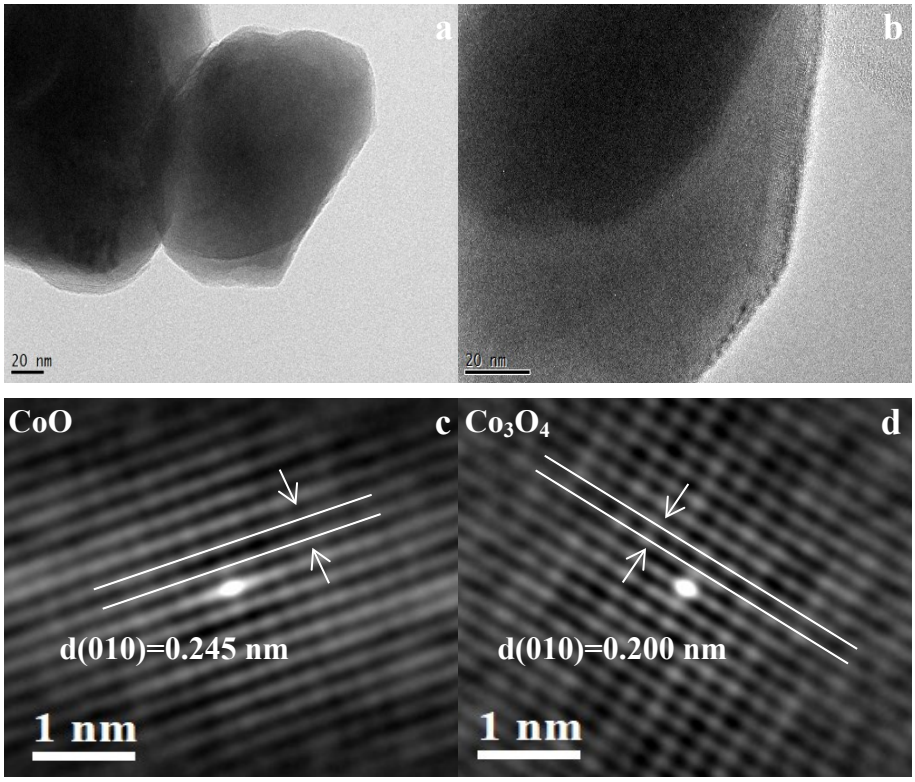


Figure S1. TEM images of the HT volborthite sample (a, b), the auto-correlated HRTEM images of CoO (c) and Co_3O_4 (d) obtained from the corresponding rectangles in the HRTEM image of 2 wt.% CoO_x/HT in Figure 3.

UV-Vis DRS spectra

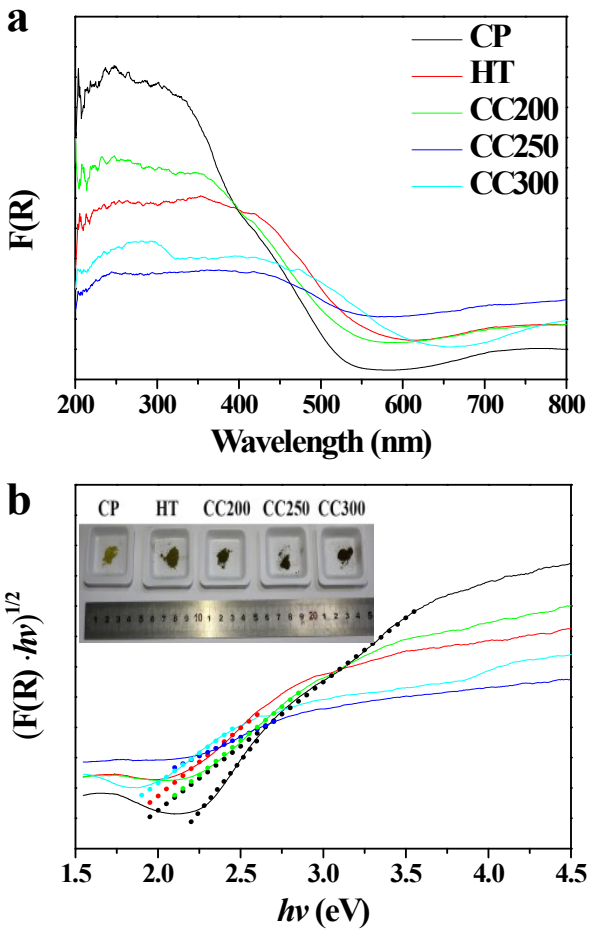


Figure S2. (a) Kubelka–Munk transformation of UV-Vis diffuse reflection (UV-Vis DRS) spectra of the volborthites; (b) Tauc plots calculated from the Kubelka-Munk transformation. Top-left inset: photograph for the as-synthesized volborthites taken by an ordinary camera.

High resolution XPS spectra

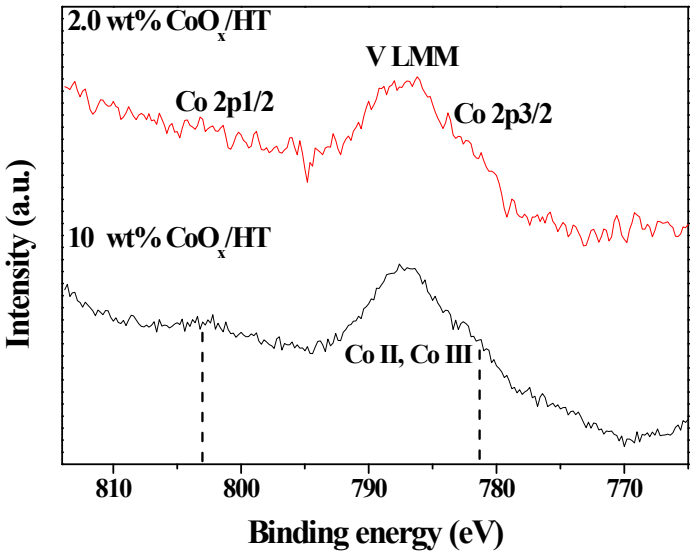


Figure S3. High resolution XPS spectra of Co 2p on the recycled 2.0 wt% and 10 wt% Co/HT volborthite sample, respectively.

Adsorption capacity and photodegradation pseudo first-order rates

The adsorption capacity is calculated based on the experimental data and according to the mass balance relationship:

$$Q_e = \frac{(C_o - C_{eq})V}{m} \quad (1)$$

where Q_e is the amount of dye adsorbed onto the volborthite samples, C_o and C_e are the initial and equilibrated dyes concentrations (mg/L), respectively, V is the volume of solution (L), and m is the mass of the volborthite samples (g).

The intra-particle diffusion model is expressed by:

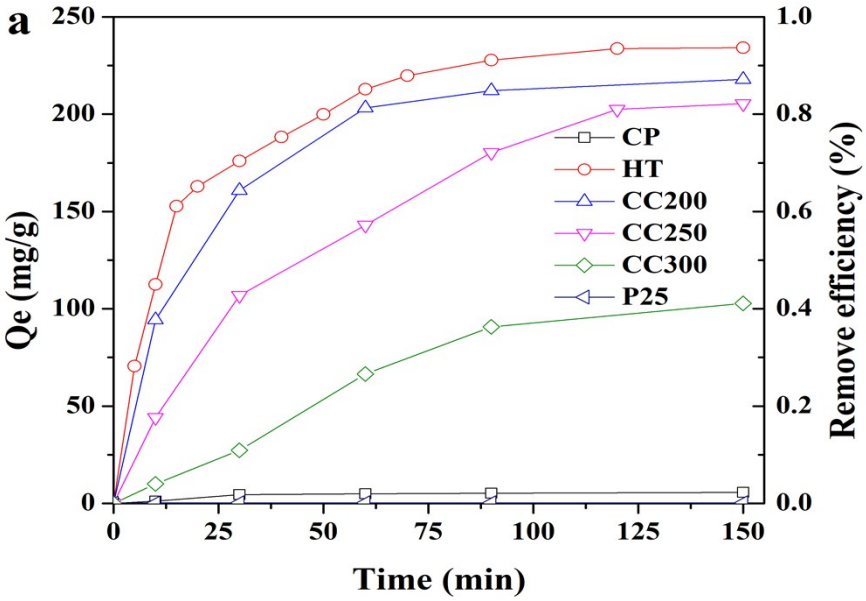
$$Q_e = k_p t^{1/2} + C \quad (2)$$

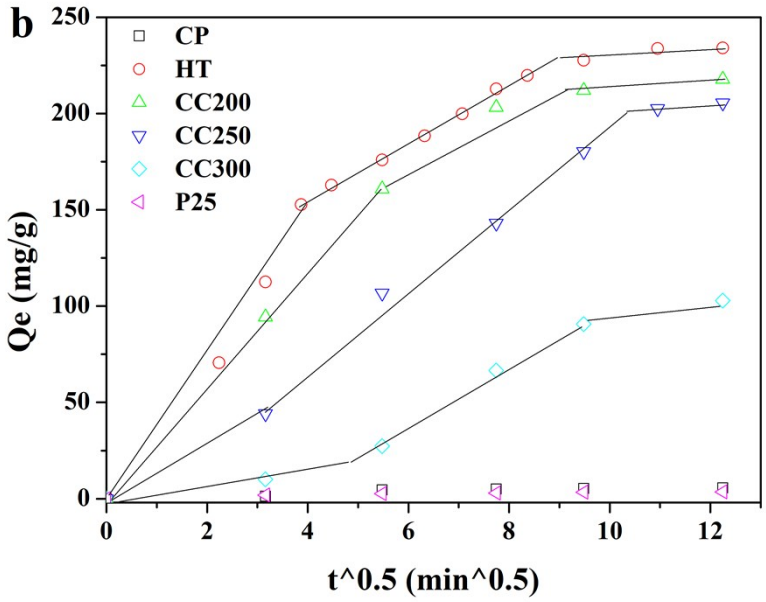
where k_p is the intra-particle diffusion rate constant, C is a constant related to the thickness of the boundary layer.

The reaction kinetics of photocatalytic degradation is generally followed the pseudo first-order rate model:[3b]

$$-In\,(C_t/C_o) = kt \quad (3)$$

where C_o and C are the concentrations of MB solution at times 0 and t (mg/L), k is the photodegradation rate, which is equal to the corresponding slope of the fitting line, and t is the illumination time (min).


a
Qe (mg/g)
Remove efficiency (%)
Time (min)
CP
HT
CC200
CC250
CC300
P25


b
Qe (mg/g)
t^0.5 (min^0.5)
CP
HT
CC200
CC250
CC300
P25

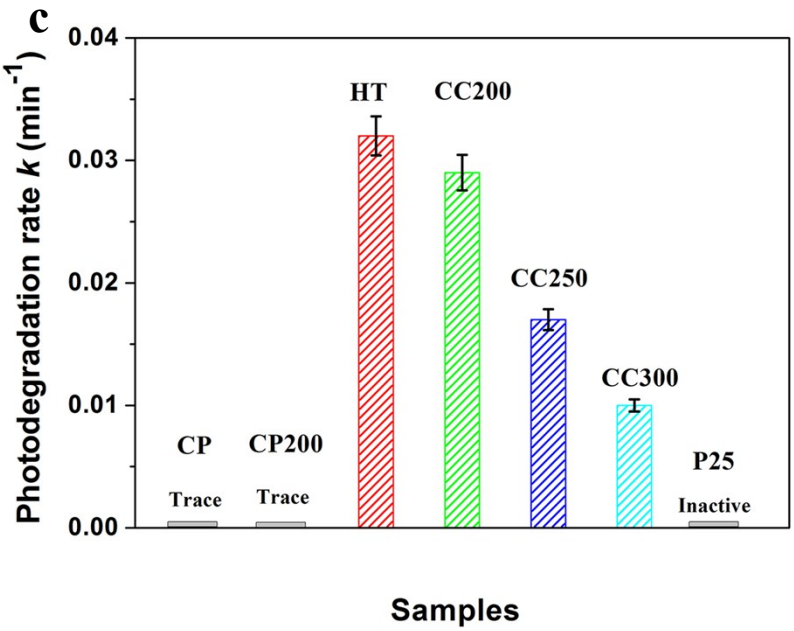


Figure S4. (**a**) Kinetic adsorption capacity of the as-synthesized volborthite samples and the corresponding related removal efficiencies. (b) Kinetic behavior of intra-particle diffusion model for MB adsorption; (c) The estimated photodegradation pseudo first-order rates for MB adsorption. Error bars represent that all the measurements were reproducibly conducted at least three times with deviations less than 5%.

Photographs for color variations of MB solution

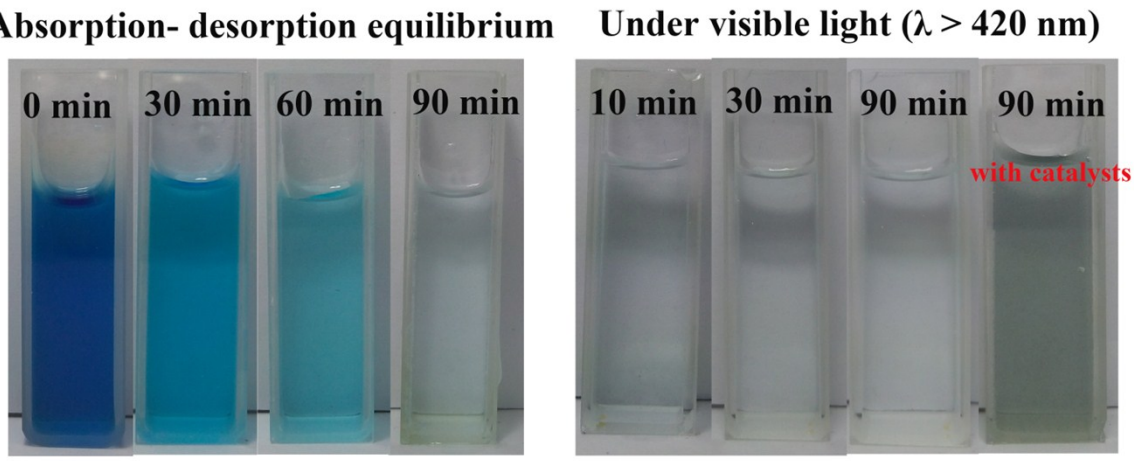


Figure S5. Color variations of MB solution over the absorption-desorption and photodegradation processes over HT volborthite sample.

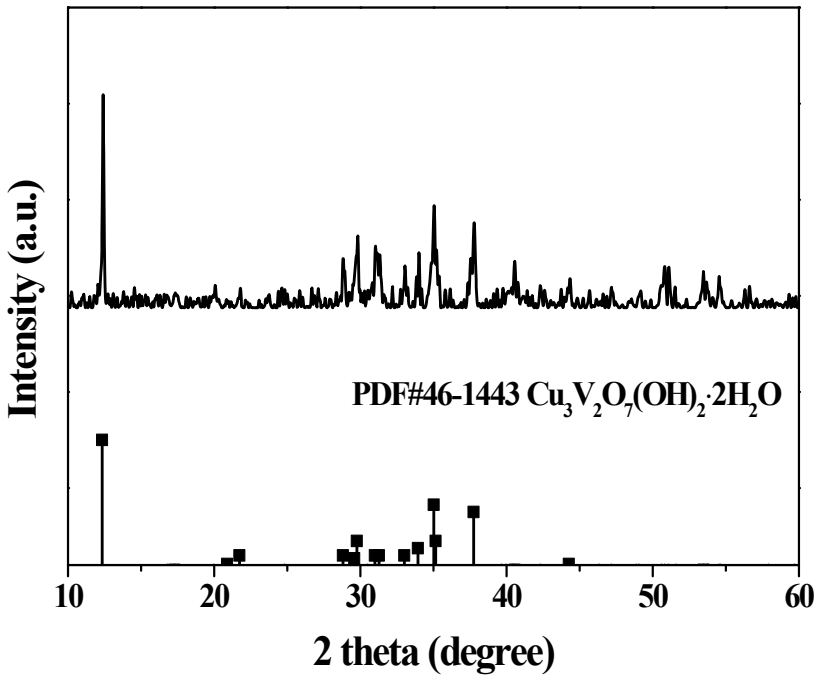


Figure S6. XRD pattern of 2.0 wt.% CoO_x/HT volborthite sample after photocatalytic O_2 evolution reaction for 5h.

Theoretical calculation

The conduction band (E_{CB}) and valence band (E_{VB})positions of $Cu_3V_2O_7(OH)_2 \cdot 2H_2O$ can be estimated according to Butler and Ginley method using the experimental band gap value and the following equation related to Mulliken electronegativity:[1]

$$E_{CB} = \chi - E_e - 0.5E_g \quad (1)$$

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

where χ is the geometric mean value of Mulliken electronegativity of the different atoms of the $Cu_3V_2O_7(OH)_2 \cdot 2H_2O$ material (~5.98 eV), E_e is the free electron energy (E_e = 4.44 ± 0.02 eV) and E_g is the measured band gap of the $Cu_3V_2O_7(OH)_2 \cdot 2H_2O$ (E_g = ~2.1 eV). Thus, the corresponding E_{CB} and E_{VB} of $Cu_3V_2O_7(OH)_2 \cdot 2H_2O$ can be calculated to be about +0.49 eV and +2.59 eV, respectively.

Mott-Schottky plots

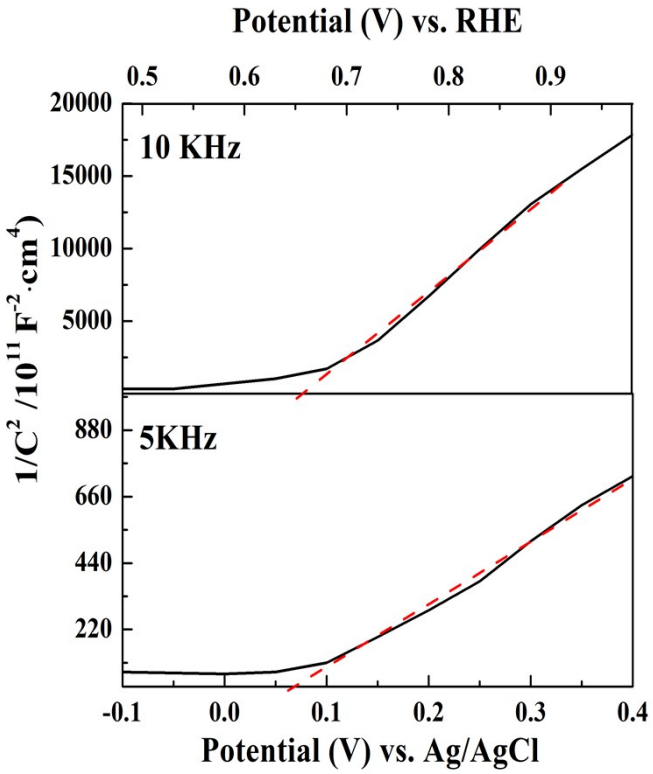


Figure S7. Mott-Schottky plots of the HT volborthite in dark at 5 KHz and 10 KHz and an AC current of 5 mV with a three-electrode system in a 0.5M Na_2SO_4 solution (pH 6.5).

Comparasion of band gaps and positions

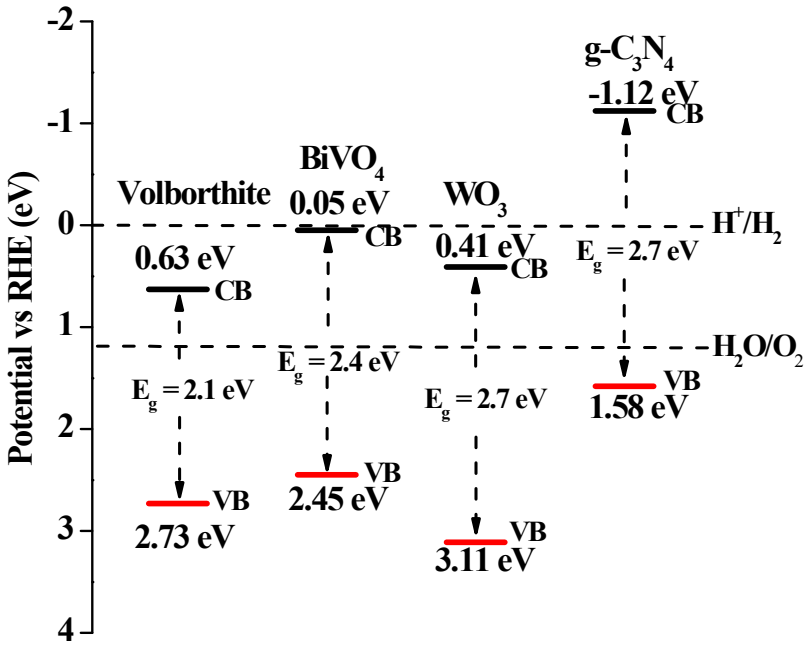


Figure S8. Schematic diagram of the band gaps and positions of the volborthite, $BiVO_4$, WO_3 and g-C_3N_4.

Reference

(1) Butler, M. A.; Ginley, D. S. *J. Electrochem. Soc.* **1978**, 125, 228-232.