Supporting Information

Unique Homo-Heterojunction Synergistic Systems Consisting of Stacking BiOCl Nanoplates/Zn-Cr Layered Double Hydroxide Nanosheets Promoting Photocatalytic Conversion of CO_2 into Solar Fuels

Lanqin Tang,[†,‡,§,ξ] Ruotian Chen,[ǁ] Xianguang Meng,[Δ] Bihu Lv,[ξ] Fengtao Fan,[ǁ] Jinhua Ye,[Δ] Xiaoyong Wang,[ξ] Yong Zhou, *[†,§,ξ] Can Li,[ǁ] and Zhigang Zou[†,§]*

[†] *Key Laboratory of Modern Acoustics (MOE), Institute of Acoustics, Department of Physics, Nanjing University, Nanjing 210093, China*

[‡] *College of Chemistry and Chemical Engineering, Yancheng Institute of Technology, Yancheng 224051, P. R. China*

[§] *Eco-Materials and Renewable Energy Research Center (ERERC), Jiangsu Key Laboratory for Nano Technology, Nanjing University, Nanjing 210093, China*

[ξ] *National Laboratory of Solid State Microstructures, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, P. R. China*

[Δ] *Environmental of Remediation Materials Unit and International Center for Materials Nanoarchitectures (WPI-MANA), 1-1 Namiki, Tsukua, Ibaraki 305-004, Japan*

[ǁ] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China*

Lanqin Tang and Ruotian Chen contributed equally to the work.

E-mail: zhouyong1999@nju.edu.cn; ftfan@dicp.ac.cn

Synthesis. All the raw materials used here were of analytical grade purity and used without further purification. The homo-heterojunctions of two-dimensional BiOCl/Zn-Cr layered double hydroxides (Zn-Cr LDH) were synthesized via a facile electrostatic interaction based method. First, BiOCl nanoplates exposed with {001} and {110} facets were synthesized via a hydrothermal rout proposed by Xiong et al.[1] The aqueous suspension of BiOCl nanoplates was freeze-dried and re-dispersed in formamide. The Zn-Cr LDH used in this study was synthesized by direct coprecipitation at room temperature as reported previously.[2] The exfoliation of Zn-Cr LDH was achieved using a simple liquid exfoliation technique.[3] In a typical synthesis, an amount of 0.1g of the Zn-Cr LDH sample was dispersed in a conical beaker with 100 cm^3 of formamide and treated by a 6-mm diameter probe sonic tip at 250W for 180 min. Then, the BiOCl/Zn-Cr LDH homo-heterojunctions were synthesized by mixing of the formamide suspensions of BiOCl nanoplates and exfoliated Zn-Cr LDH nanosheets under a constant stirring at room temperature. A series of homo-heterojunctions were formed with well-controlled weight ratio of Zn-Cr LDH in the BiOCl/Zn-Cr LDH being 0.05, 0.10 and 0.20, and the obtained nanocomposites are denoted as $S_{5wt.\%}$, $S_{10wt.\%}$, and $S_{20wt.\%}$.

Characterization. The crystallinity phase of the prepared samples was studied by X-ray diffraction (XRD) on a CuKα (λ = 0.15418 nm) Bruker D8 X-ray diffractometer. Field emission scanning electron microscopy (FE-SEM) images were obtained on a Hitachi S-4800 field emission scanning electron microscope operated at 10.0 kV. HR-TEM was collected in TEM mode using an Orius SC1000 CCD camera. Element mapping was performed in STEM mode using an Oxford XMax-80T EDS detector. The diffuse reflection spectra were recorded on a UV-visible spectrophotometer (UV-2550, Shimadzu, Japan) and then converted into absorption spectra via Kubelka-Munk transformation. Tapping-mode atomic force microscopy (AFM) images were obtained on DI Innova Multimode SPM platform. The photocurrent response spectra were measured at -0.4 V under a 100 W Xe lamp illumination. The KPFM and AFM images were taken on a Bruker Dimension V SPM system equipped with Pt/Ir coated tips (resonant frequency 72 kHz). Images were acquired at scan rates of 0.5 Hz and tip lift height was set to100 nm at tapping mode for potential mapping. The surface potential of each sample was measured with the same tip in the dark and light illumination. The monochromatic light source was obtained for Zolixmonochromotor with a 500 W Xe lamp light source. The products

of photoreduction CO_2 were measured by using a gas chromatograph (GC-2014, Shimadzu Co., Japan) equipped with a flame ionization detector (FID) according to the standard curves. The transient time-resolved photoluminescence decay measurements were recorded on a fluorescence spectrometer (FLS920, Edinburgh Instruments Ltd, UK). The zeta potential was examined by a zetaPALS zeta potential analyzer (Brookhaven instruments Co., U.S.A.). The isotope analysis of ^{13}C was analyzed by using a gas chromatographmass spectrum (JEOL-GCQMS, JMS-K9 and 6890N Network GC system, Agilent Technologies).

Photocatalytic CO_2 Reduction Experiment. The gas phase photoreduction reaction was carried out in a closed circulation system equipped with a vacuum line. 0.1 g of photocatalyst was dispersed uniformly on a quartz reaction cell with the area of 4 cm^2. 0.4 mL of ultrapure water was injected into the system as reducer. The system was vacuumed and then 710 Torr of CO_2 was introduced. A 300 W Xe lamp was employed as a light source.

REFERENCES

(1) Jinyan Xiong, Gang Cheng, Guangfang Li, Fan Qin, Rong Chen, Well-crystallized square-like 2D BiOCl nanoplates: mannitol-assisted hydrothermal synthesis and improved visible-light-driven photocatalytic performance, *RSC Advances*, **2011**, 1, 1542-1553.

(2) Prevot, V.; Forano, C.; Besse, J. P. Syntheses and thermal and chemical behaviors of tartrate and succinate intercalated Zn3Al and Zn2Cr layered double hydroxides, *Inorg. Chem.* **1998**, 37, 4293-4301.

(3) Li, L.; Ma, R. Z.; Ebina, Y.; Iyi, N.; Sasaki, T. Positively charged nanosheets derived via total delamination of layered double hydroxides, *Chem. Mater.* **2005**, 17, 4386-4391.

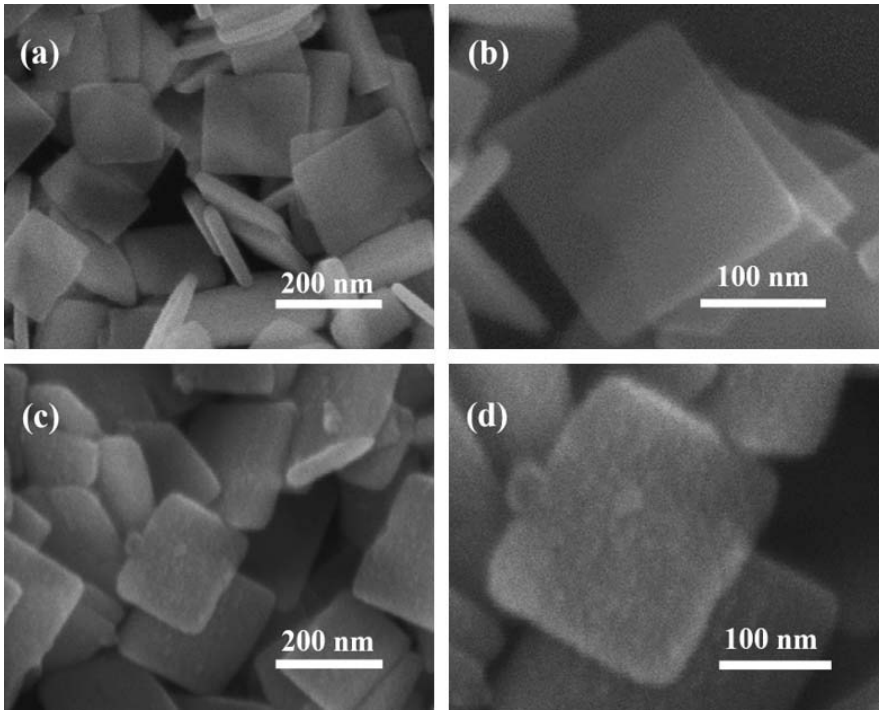

Figure S1. FE-SEM images of (a, b) pristine BiOCl and (c, d) $S_{10wt.\%}$.

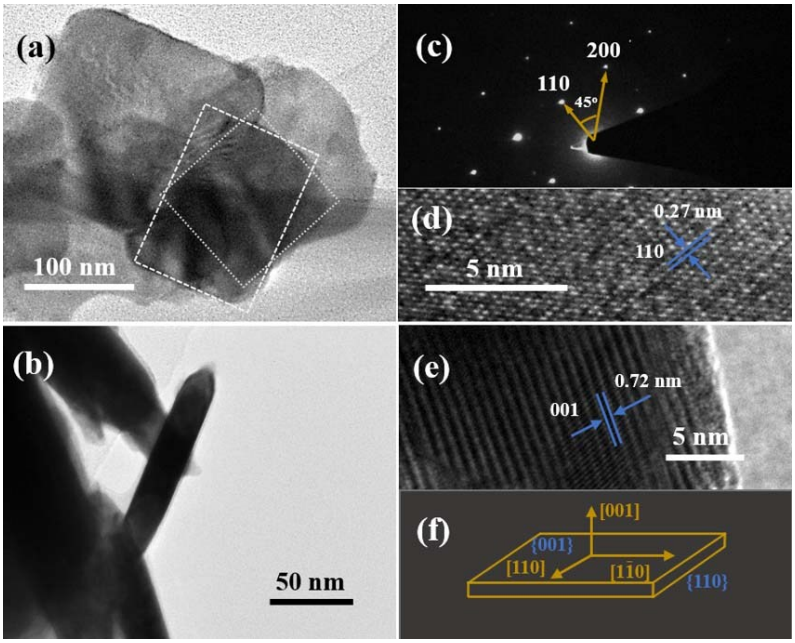

Figure S2. TEM images of the BiOCl nanoplate with (a) title and (b) standing viewing, SAED pattern (c), HRTEM images with (d) title and (e) standing viewing, and (f) Schematic illustration of the crystal orientation.

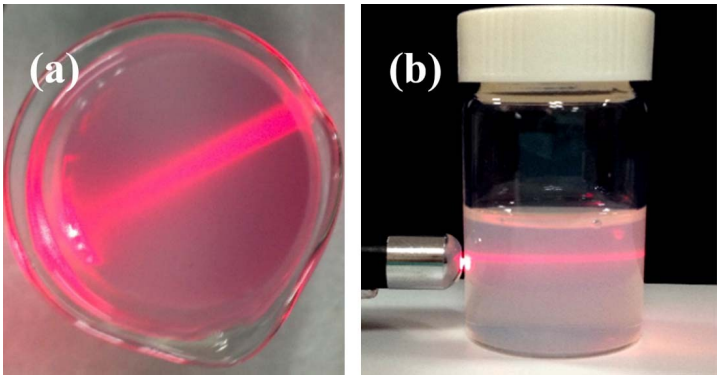

Figure S3. Tydall photos of the exfoliated Zn-Cr LDH nanosheets: (a) top and (b) side view.

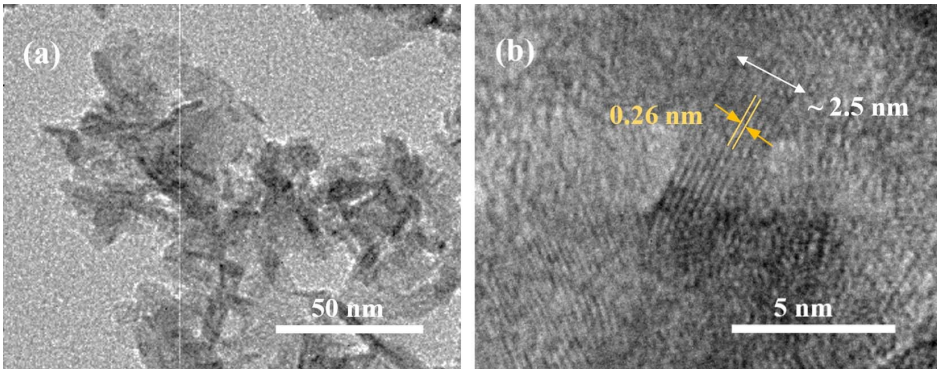

Figure S4. (a) TEM and (b) HRTEM images of the Zn-Cr LDH nanosheet.

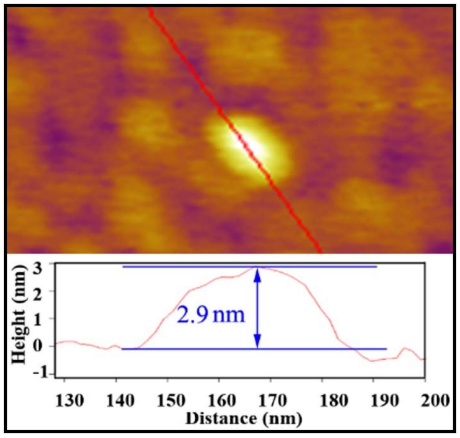

Figure S5. AFM image of the Zn-Cr LDH nanosheet and the corresponding thickness profile.

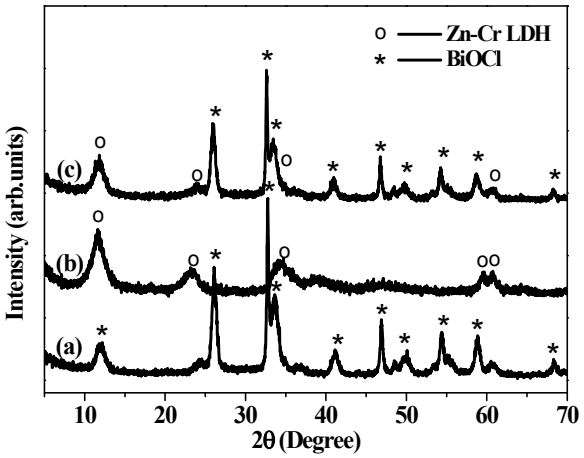

Figure S6. XRD patterns of (a) pristine BiOCl nanoplate, (b) Zn-Cr LDH nanosheet, and (c) $S_{10wt.\%}$.

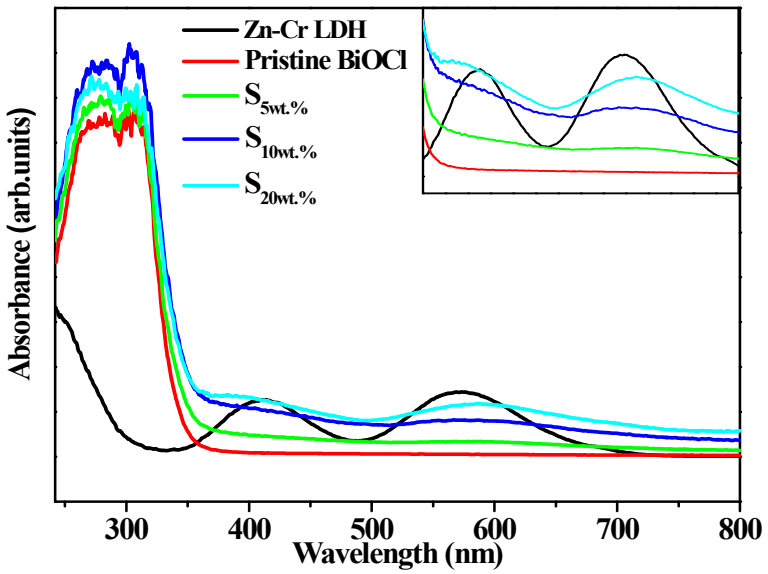

Figure S7. UV-vis absorption spectra of the BiOCl, Zn-Cr LDH, $S_{5wt.\%}$, $S_{10wt.\%}$ and $S_{20wt.\%}$ and the inset is the enlarged region from 350~700 nm.

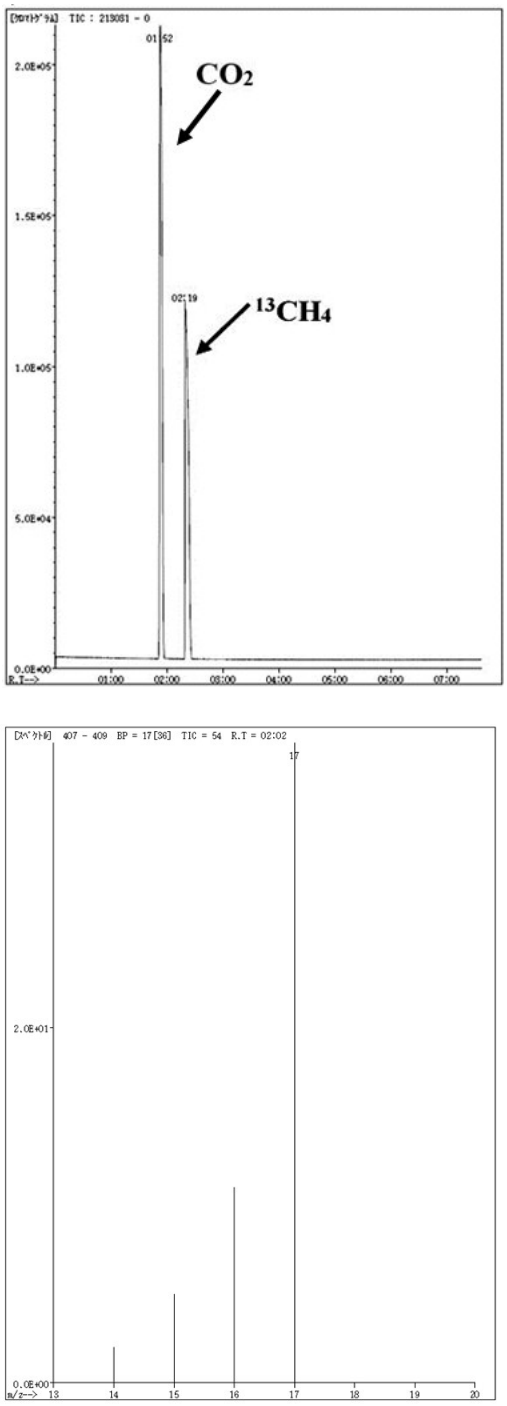

Figure S8. Gas chromatogram (top) and mass spectra of $^{13}CH_4$ (down) produced over $S_{10wt.\%}$. Carbon dioxide $^{13}CO_2$ was used.