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Atomic-scale understanding of the electronic structure-crystal facets synergy of nanopyramidal CoPi/BiVO₄ hybrid photocatalyst for efficient solar water oxidation

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Authors

Nie, K
Kashtanov, S
Wei, Y
et al.

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Supplementary Information

X-ray Spectroscopy Study of the Electronic Interaction between Bismuth Vanadate Pyramid and Cobalt Phosphate Co-catalysts for Improved Photocatalytic Water Splitting

*Kaiqi Nie^{1,2,§}, Stepan Kashtanov^{1,§}, Yankuan Wei³, Yi-Sheng Liu², Hui Zhang¹, Mukes
Kapilashrami², Yifan Ye², Yujian Xia^{1,2}, Jenn-Min Lee⁴, Per-Anders Glans-Suzuki², Jun
Zhong¹, Lionel Vayssieres³, Xuhui Sun¹, Jinghua Guo^{2,5}*

¹ Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, Suzhou 215123, Jiangsu, China

² Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

³ International Research Center for Renewable Energy, State Key Laboratory of Multiphase Flow in Power Engineering, School of Energy & Power Engineering, Xian Jiaotong University, Xian 710049, China

⁴ National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan.

⁵ Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA 95064, USA.

Supplementary Figure 1 | Crystal structure parameters of optimized unit cell and atomic positions of ms-BiVO₄ bulk for the DFT calculations in this work.

Supplementary Figure 2 | BiVO_4 unit cell. Wave-function electron density distributions for the bands (at G-point) which contribute to highlighted DOS features. High symmetry points labeling is made assuming monoclinic $C2/c$ space group (unique axis c).

The band-structure simulation for BiVO_4 is mapped against computed total DOS profile. DOS features span the range 8.7 - 9.4 eV (assuming Fermi energy E_f is zero). The wave-functions for these bands at G-point was plotted. There are about 3 bands at G-point which contribute to the highlighted features on DOS profile. The electron density is localized on atomic centers which contribute most for selected band and k -vector. According to these plots such atomic centers are V and O for given k -vector point (G).

Supplementary Figure 3 | Scanning electron microscopy images of (a) bare and (b) CoPi apex-capped nano-pyramidal BiVO_4 . (c) TEM images (d) high-resolution TEM images of CoPi apex-capped nano-pyramidal BiVO_4 .

Supplementary Figure 4 | Schematic geometry diagram of normal incident (perpendicular) and glancing incident.

Supplementary Figure 5 | **In-situ Illumination** O K-edge XAS of nano-pyramidal

Supplementary Figure 6 | Linear combination curve fitting.

Supplementary Figure 7 | I–V curve photo-electrochemical responses of CoPi-apex nano-pyramidal BiVO_4 (red) bare nano-pyramidal BiVO_4 (black).

Supplementary Figure 8 | The electron density distribution maps for (004) and (112) facets in mBiVO₄ crystal (001 and 112 crystal planes in the unit cell of BiVO₄). Total electron density distribution for several crystal planes in the unit cell of BiVO₄. Atomic colors: V-small orange ball, Bi-big orange ball, O-red ball; electron density colors: red- lowest values, blue- highest values. First row shows the electron density distribution maps, second row shows the pictures of unit cell and the positions of cutting planes corresponding to the line. The leftmost images (among these three)

shows the electron density distribution maps for (004) and (112) facets. Other images (middle and rightmost) show the electron density distribution maps for cutting planes which are slightly off of the corresponding (004) and (112) facets. Please, note that this is electron density distribution in the 3D bulk.

Table S1 | The contribution ratio from the very top tips of nano-pyramidal BiVO₄

incidence angle	h of	of	r of	R of	volume	volume of	R' of	volume	TEY	Ratio of	log
	tip	bottom	tip	bottom	of tip	bottom	inner bottom	of inner diameter	contributed volume of bottom	tip/bottom	
0	10	130	2.68	34.83	71.824	157706.8	24.83	80148.8	77558.0	0.09%	-3
30	10	91.92	2.68	24.63	71.824	55762.1	14.63	19674.3	36087.8	0.20%	-2.7
60	10	65	2.68	17.42	71.824	19724.7	7.42	3578.7	16146.0	0.44%	-2.4
85	10	11.25	2.68	3.02	71.824	102.6	3.02	102.6	102.6	70.00%	-0.16

Supplementary Note 1:

In-situ illumination measurement

AM 1.5 illumination was applied on this system via solar simulator through the quartz port. As shown in Fig. S6, the intensity can be compared by normalizing all the spectra at 550 eV where far above the O K-edge absorption edge. The overall intensity drops upon illumination, especially obvious (spectra weight decreased by 1.6%) in the spectra by glancing incident which the top tips dominate the spectra. The intensity variety can be interpreted as the photo generated electron was excited into the conduction band which leading to less unoccupied states in the conduction band. Therefore, the lower transition possibility of O 1s electron, the lower the O K-edge XAS intensity will be.^{1,2} Thus, the intensity responds of the in-situ illumination measurement confirmed that the very top tips of this novel pyramid structure is indeed the active site for charge separation which facilitate the overall photo assist reaction.

Supplementary Reference

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