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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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Supplementary Information

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

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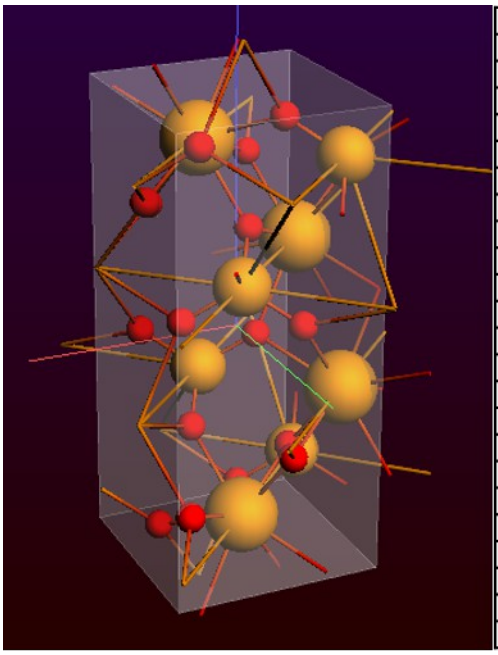
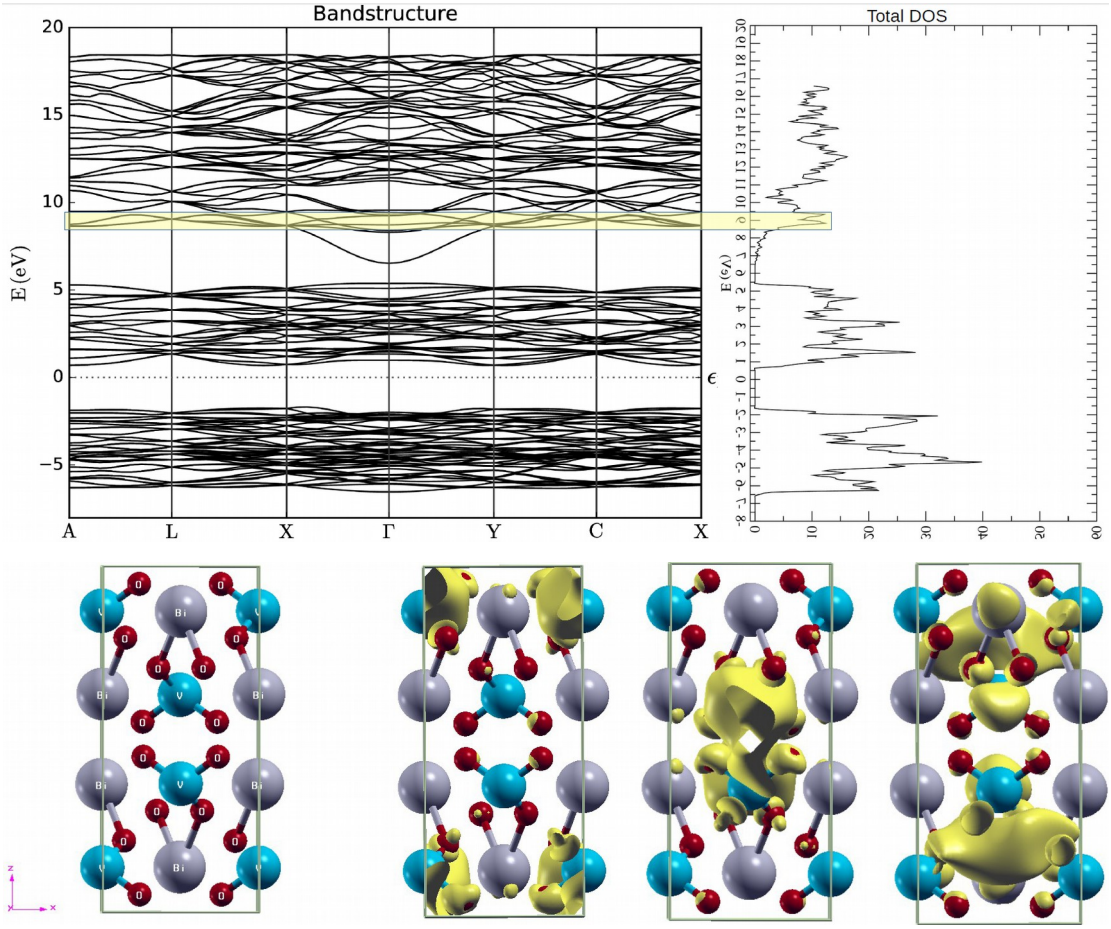


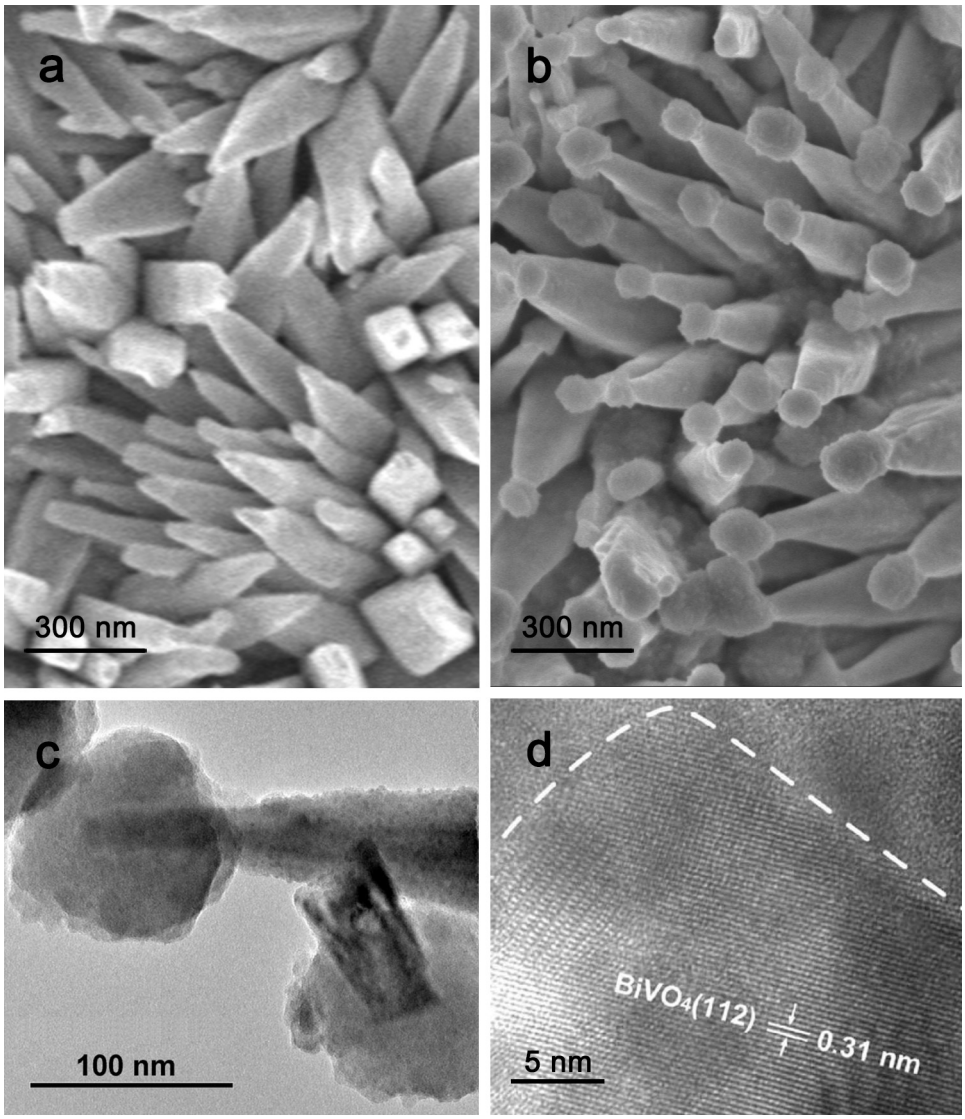
Bi(1)	**0**	**0.25**	**0.62770101**
Bi(2)	0.5	0.75	0.12770101
Bi(3)	0	0.75	0.37229899
Bi(4)	0.5	0.25	0.87229899
V(5)	0	0.25	0.129839657
V(6)	0.5	0.75	0.629839657
V(7)	0	0.75	0.870160343
V(8)	0.5	0.25	0.370160343
O(9)	0.144195583	0.503941234	0.207194945
O(10)	0.644195583	0.003941234	0.707194945
O(11)	0.855804417	0.996058766	0.207194945
O(12)	0.355804417	0.496058766	0.707194945
O(13)	0.144195583	0.003941234	0.792805055
O(14)	0.644195583	0.503941234	0.292805055
O(15)	0.855804417	0.496058766	0.792805055
O(16)	0.355804417	0.996058766	0.292805055
O(17)	0.260730331	0.380610769	0.449506436
O(18)	0.760730331	0.880610769	0.949506436
O(19)	0.739269669	0.119389231	0.449506436
O(20)	0.239269669	0.619389231	0.949506436
O(21)	0.260730331	0.880610769	0.550493564
O(22)	0.760730331	0.380610769	0.050493564
O(23)	0.739269669	0.619389231	0.550493564
O(24)	0.239269669	0.119389231	0.050493564

Supplementary Figure 1│ Crystal structure parameters of optimized unit cell and atomic positions of ms-$BiVO_4$ bulk for the DFT calculations in this work.

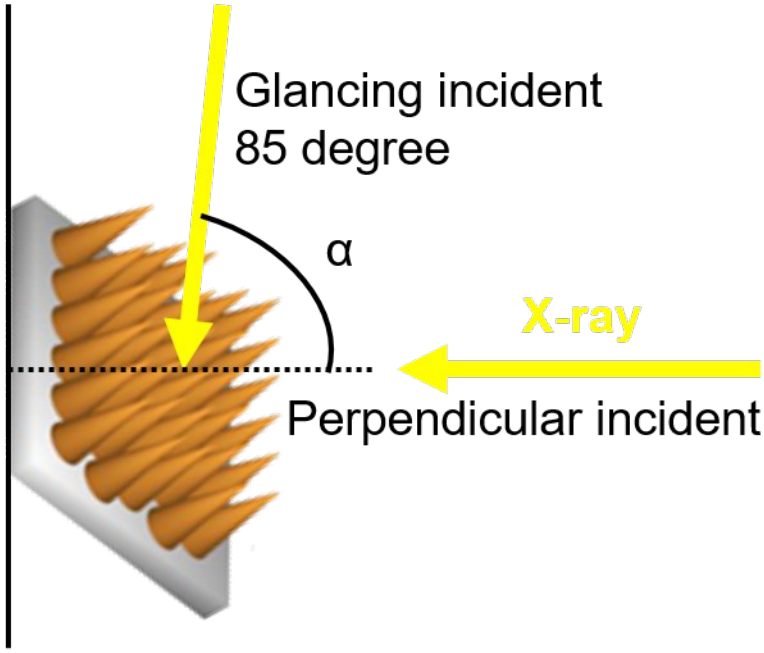


Supplementary Figure 2| $BiVO_4$ unit cell. Wave-function electron density distributions for the bands (at G-point) which contribute to highlighted DOS features. High symmetry points labeling is made assuming monoclinic C2/c space group (unique axis c).

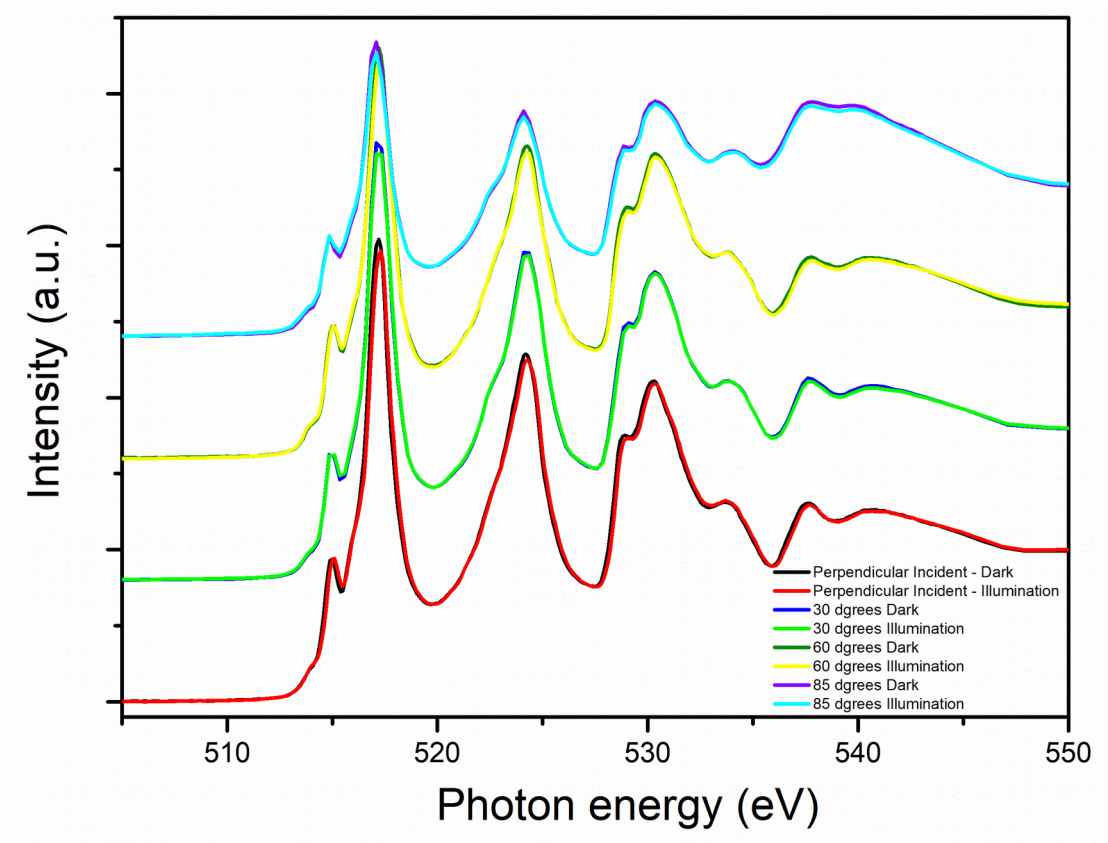
The band-structure simulation for $BiVO_4$ is mapped against computed total DOS profile. DOS features span the range 8.7 - 9.4 eV (assuming Fermi energy Ef is zero). The wave-functions for these bands at G-point was plotted. There are about 3 bands at G-point which contribute to the highlighted features 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 $BiVO_4$.

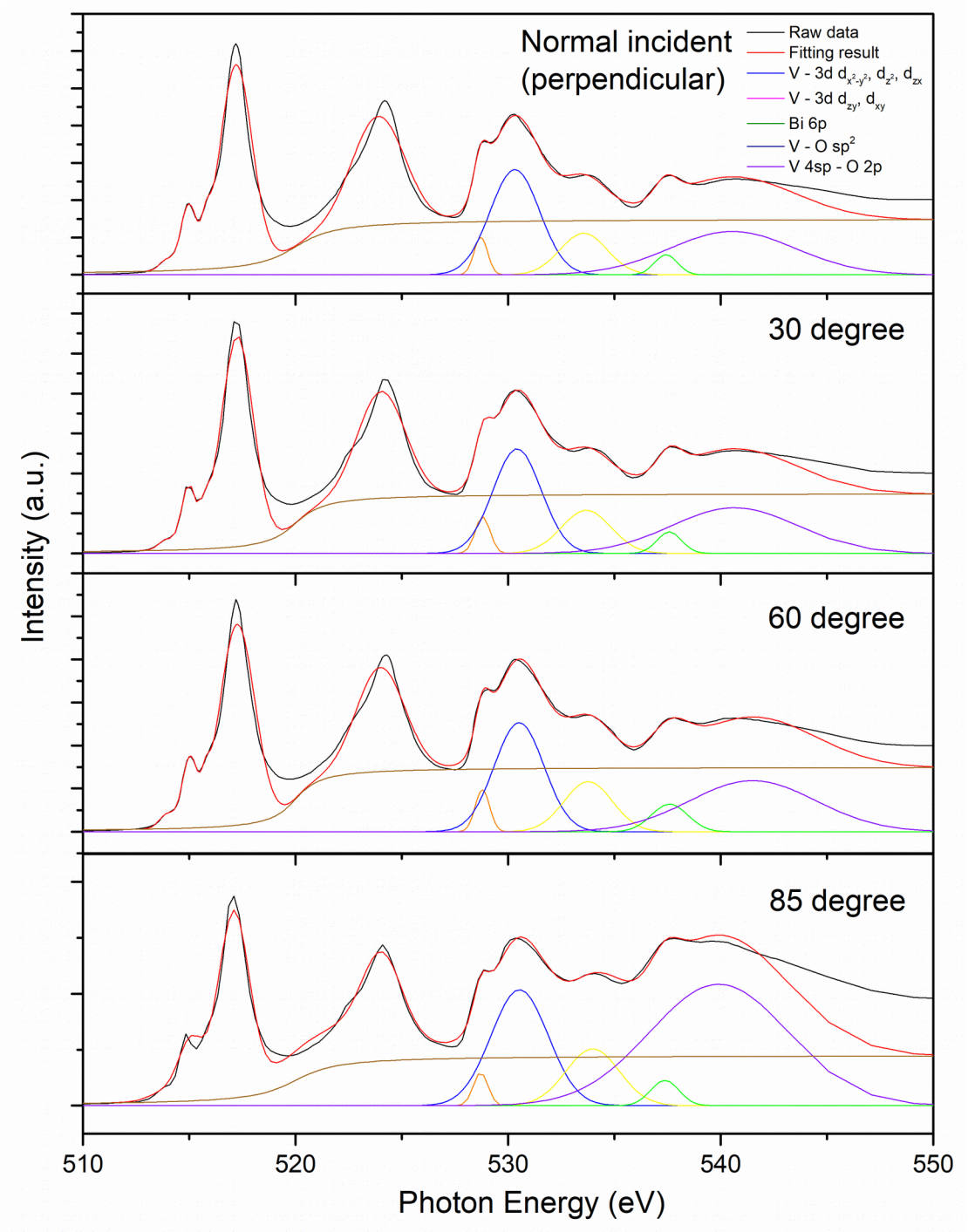


Supplementary Figure 4 | Schematic geometry diagram of normal incident (perpendicular) and glancing incident.

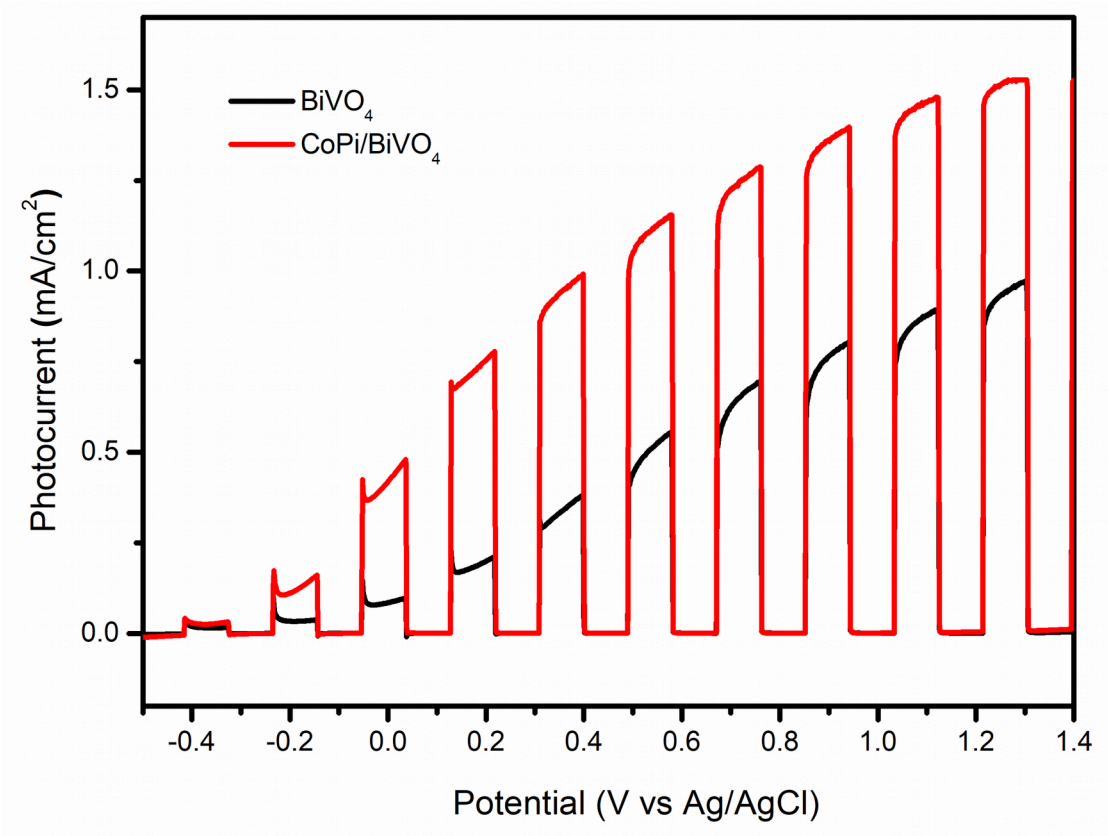


Supplementary Figure 5 | **In-situ Illumination** O K-edge XAS of nano-pyramidal

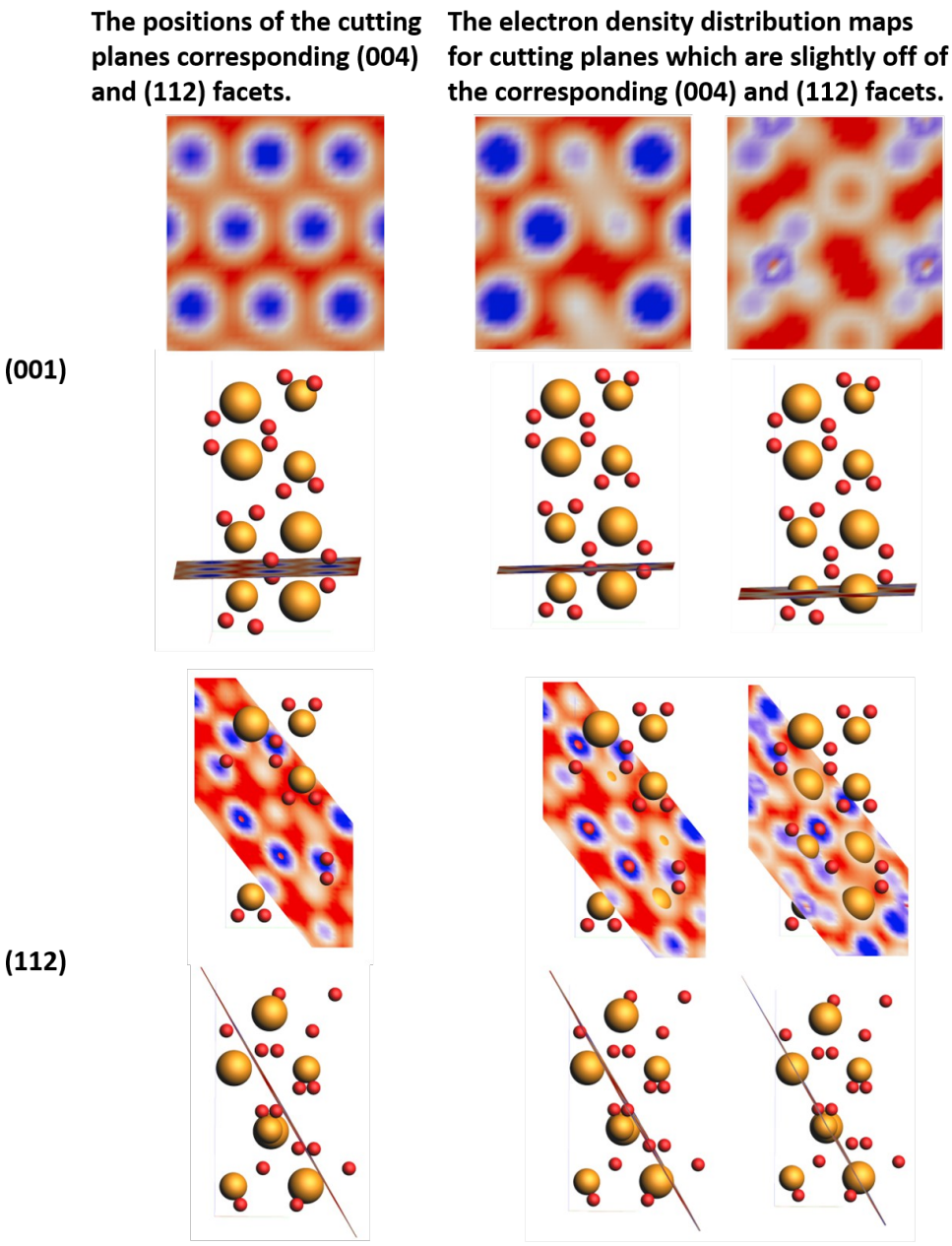
$BiVO_4$.



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 mBiVO$_4$ crystal (001 and 112 crystal planes in the unit cell of BiVO$_4$). Total electron density distribution for several crystal planes in the unit cell of BiVO$_4$. 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 $BiVO_4$

incidence angle	h of tip	H of bottom	r of tip	R of bottom	volume of tip	volume of bottom	R' of inner bottom	volume of inner diameter	TEY contributed volume of bottom	Ratio of tip/bottom	log
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

1.Shen, S. *et al.* Surface engineered doping of hematite nanorod arrays for improved photoelectrochemical water splitting. *Sci. Rep.* **4**, 6627 (2014).

2.Kao, L. C., Liou, S. Y. H., Dong, C. L., Yeh, P. H. & Chen, C. L. Tandem structure of QD cosensitized TiO_2 nanorod arrays for solar light driven hydrogen generation. *ACS Sustain. Chem. Eng.* **4**, 210-218 (2015).