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Supplemental Information

The Orientation Dependence of the Photochemical Reactivity of $BiVO_4$

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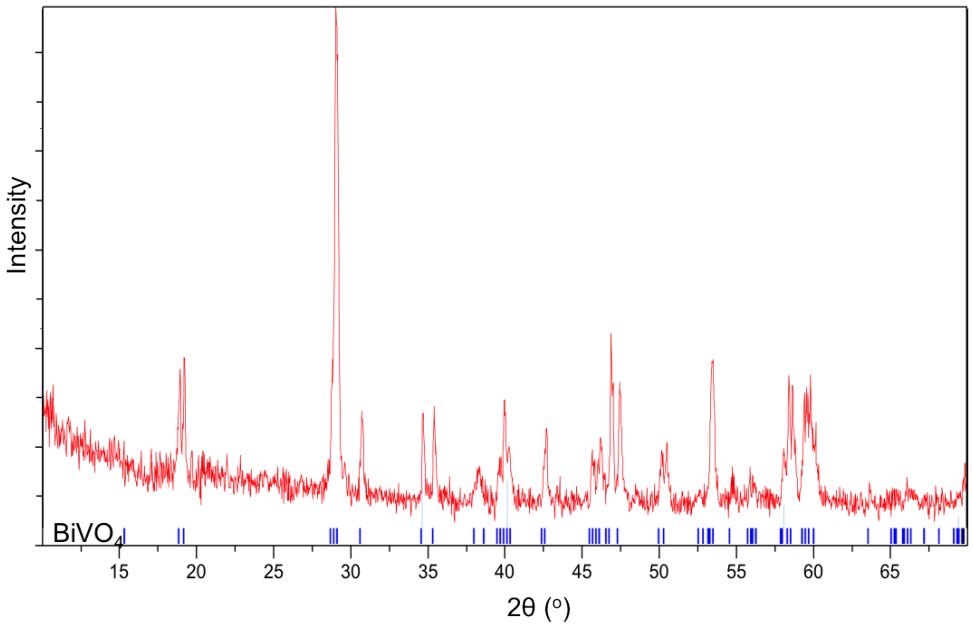
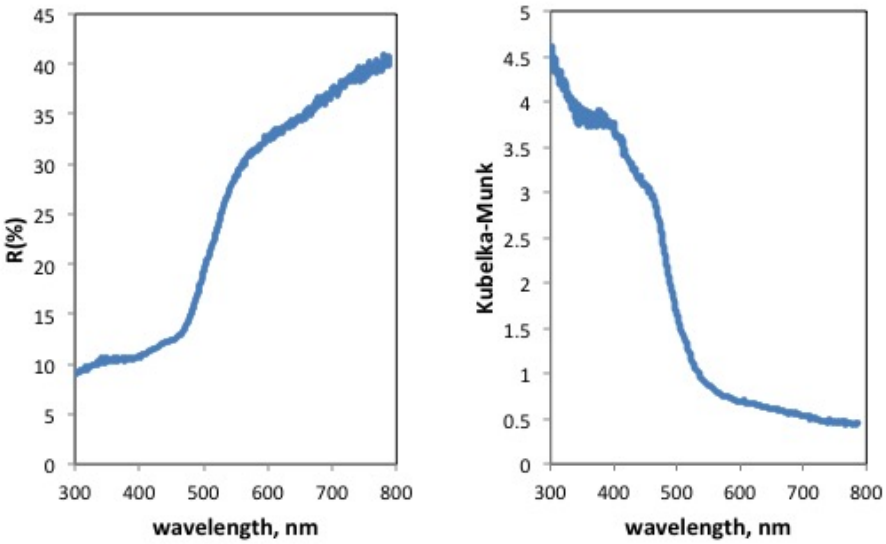
X-ray diffraction patterns were obtained from $BiVO_4$ synthesized via a solid-state reaction (Fig. S1). The measurement used a Panalytical X'Pert Pro MPD diffractometer with a CuK_α source operated at 45 kV and 40 mA. The step size of the scan was 0.0263 °, the time per step was 48 s, and a 1° fixed divergence slit was used.



Supplementary Figure S1. X-ray diffraction patterns of bulk $BiVO_4$. The XRD pattern was obtained from a bulk $BiVO_4$ sample synthesized via a solid-state reaction method. The blue lines below the diffraction patterns show the positions of peaks expected for monoclinic fergusonite $BiVO_4$. All observed peaks are consistent with the standard patterns.

The reflectance of a solid, sintered, $BiVO_4$ ceramics was measured by UV-VIS multichannel spectroradiometer (OL770, Optronics Laboratories, Inc.) with the illumination of a Xenon source. A white reflectance standard of PTFE was used for the measurement and the reflectance and

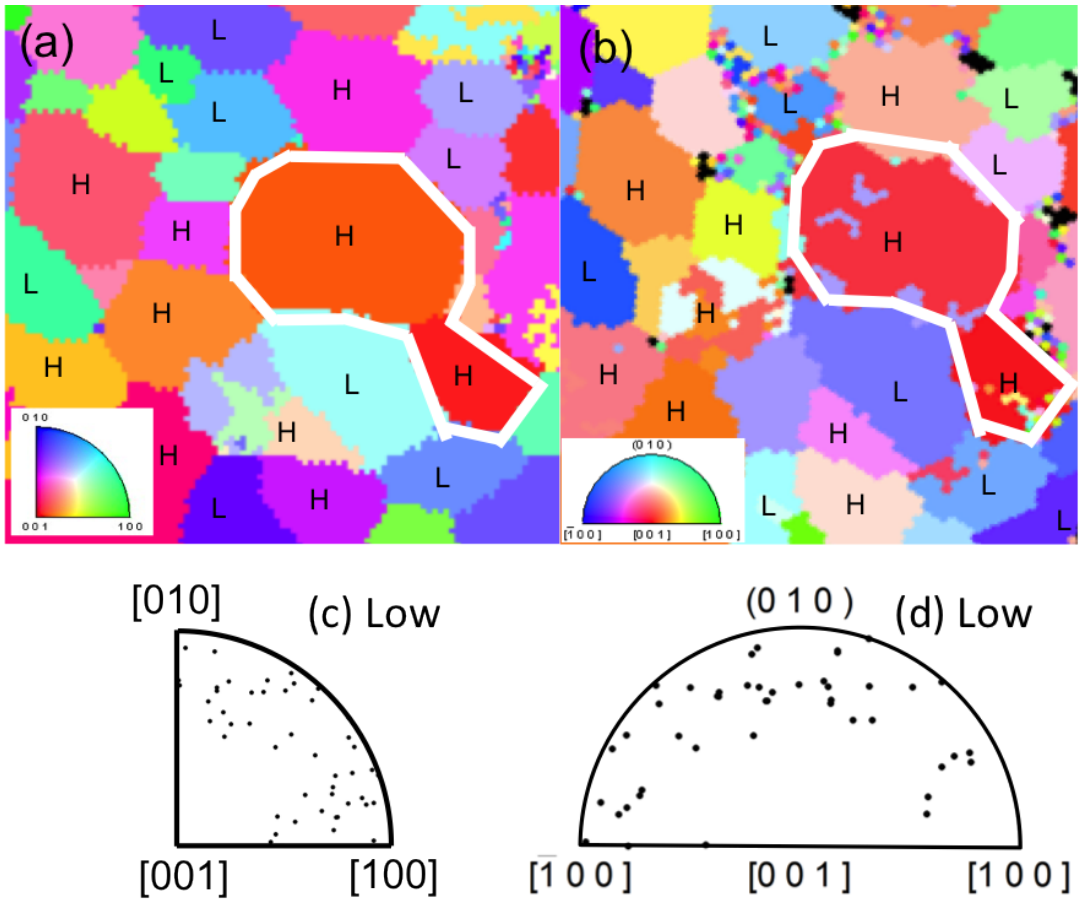
calculated absorbance is shown in Fig. S2. The onset of strong absorption at 500 nm is characteristic of $BiVO_4$.



(a) (b)

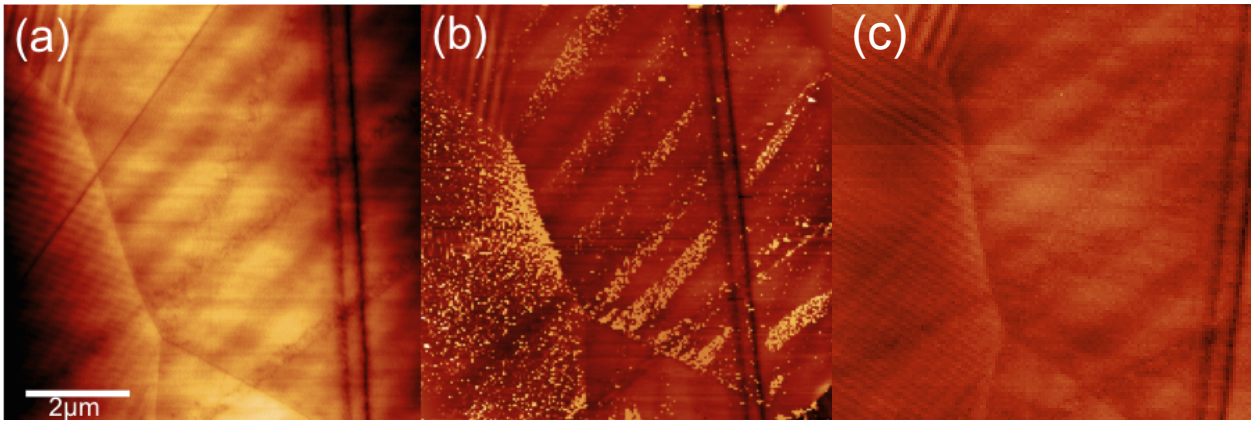
Supplementary Figure S2. (a) UV-vis reflectance spectrum of solid $BiVO_4$. (b) Kubelka-Munk transformed spectrum of bulk $BiVO_4$.

Figure S3 compares results obtained by indexing $BiVO_4$ as if were tetragonal and by indexing in the true monoclinic system. One can see a reasonable correspondence between the orientation maps (a) and (b). However, there is more noise in the map when indexed in the monoclinic system. This results from the near equivalence of the lengths of the *a* and *b* axes; because of this, multiple orientations with 90° rotations about [001] frequently provide comparable fits to the observed Kikuchi diffraction patterns. The orientations of the grains that have a low reactivity for silver reduction are plotted in the tetragonal and monoclinic systems in (c) and (d), respectively. In both cases, the data show that the grains that reduce the least silver are inclined from the [001] direction. Because use of the lower symmetry cell introduces noise in the orientation map without changing the conclusions about the reactivity, we chose to use the tetragonal system.



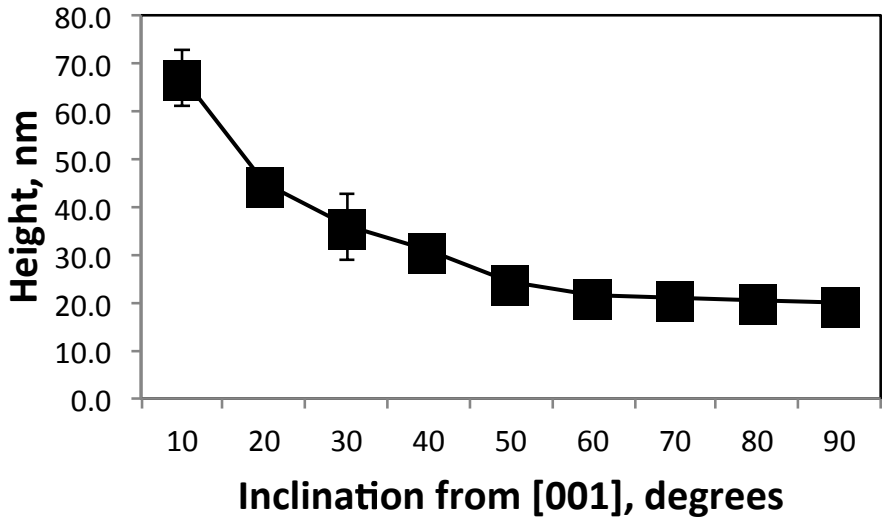
Supplementary Figure S3. (a) Orientation map of the $BiVO_4$ sample colored by orientation when diffraction patterns are indexed with a tetragonal cell and point symmetry 4/m. (b) Orientation map of the same area in (a), but using the monoclinic cell and point symmetry 2/m. The color key of each reference frame is shown in the inset. The reactivity for each grain in the map has assigned as H or L (H = high reactivity and L = low reactivity). The field of view is 60 x 60 μm. (c) and (d) Orientations of low reactivity of grains on the $BiVO_4$ surface for the photochemical reduction of Ag indexed in the tetragonal and monoclinic structure, respectively. Each point corresponds to an observed grain and the points are plotted in stereographic projection.

Supplementary Fig. S4 illustrates the efficacy of the procedure to clean reduced Ag from the $BiVO_4$ surface. The images are of approximately the same area and have a grain boundary tri-junction (lower center) and two parallel polishing scratches (vertical on the right side) that can be used as fiducial marks. The images indicate that most of the silver is certainly removed.



Supplementary Figure S4. AFM topographic images of the same area (a) Before reaction; vertical height = 13 nm. (b) After reaction; vertical height = 24 nm (c) After cleaning; vertical height = 11nm. The field of view is 8 x 8 μm.

Supplementary Fig. S5 shows the average heights of reduced silver observed on different grains as a function of inclination from [001]. The standard deviations reflect the standard deviation from grain-to-grain, rather than from different silver particles. On any given $BiVO_4$ grain, the variations in Ag heights are about 10 nm.



Supplementary Figure S5. The average height of highly reactive grains in relation to the corresponding inclined angles from [001]. The included error bar shows the standard deviation of the average heights from a range of different grains.