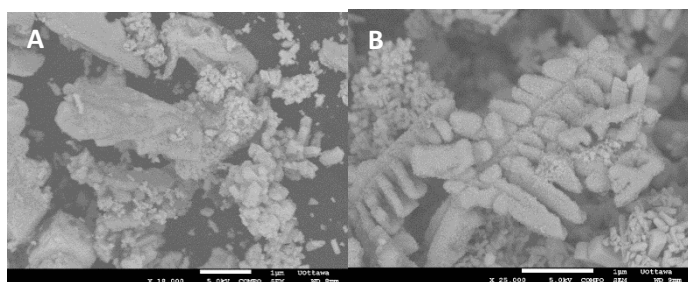


Supplementary Information

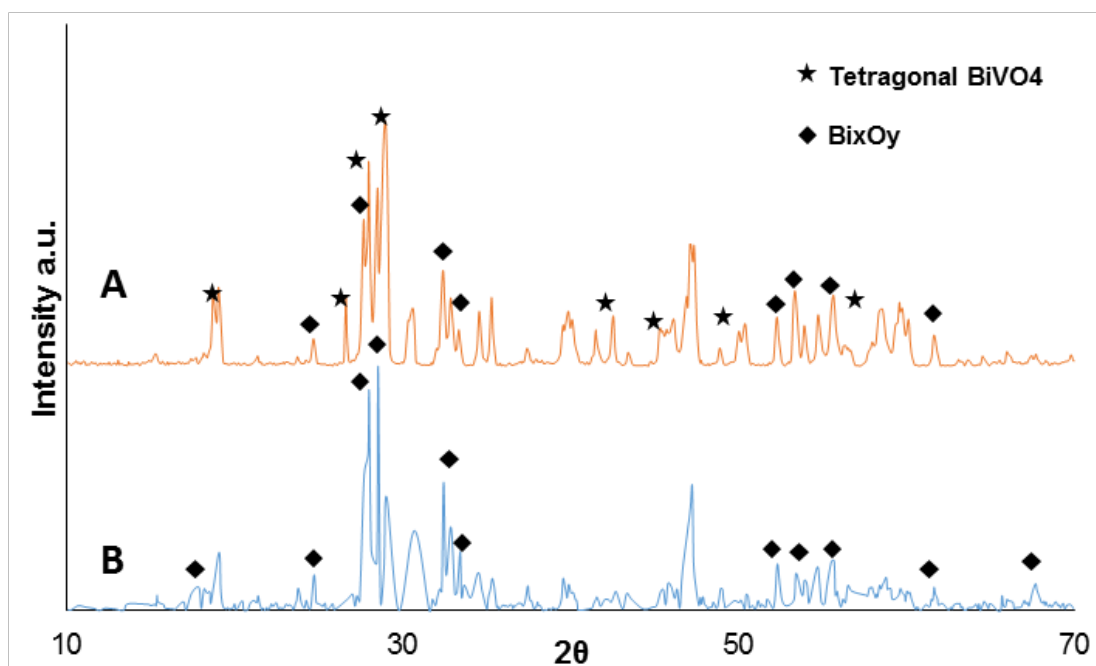
Vanadium-spiked BiVO₄ photoreduction of CO₂

To test the effect of vanadium in the stabilization and activation of BiVO₄, soluble vanadium species were added to the photochemical reaction solution. First, pristine *hyp*-BiVO₄ was added to a solution of vanadium oxides obtained from the filtrate of a previous *hyp*-BiVO₄ reaction. Second, pristine *hyp*-BiVO₄ was added to a solution of 15 mM NH₄VO₃ with 1M NaOH. Both solutions were degassed and filled with CO₂ followed by illumination, although neither was capable of CO₂ reduction.



SI Figure 1. Comparison of post-reaction SEM images for *hyp*-BiVO₄ reactions spiked with a) ammonium vanadate and b) vanadium filtrate from previous reaction.

After filtration and drying the post-reaction catalysts, the ammonium vanadate doped catalyst exhibited a color change to tan, in contrast to the yellow of pristine *hyp*-BiVO₄, and the catalysts reacted in the presence of the vanadium filtrate. Both the structure and morphology of BiVO₄ was modified in two different ways, as shown in Figures 1 and 2.



SI Figure 2. Comparison of post-reaction powder XRD patterns for *hyp*-BiVO₄ reactions spiked with a) ammonium vanadate and b) vanadium filtrate from previous reaction.

To confirm the EDS measurements, XRF data were obtained on the BiVO₄ polyhedra before and after catalytic testing

Sample	Bi mass %	V mass %	O mass % (balance)	Change in V (mass %)
BiVO ₄ before testing	50.26	14.47	35.27	-
BiVO ₄ after testing	57.35	14.20	28.45	0.27

SI Figure 3. Comparison of XRF data of as-synthesized and post-reaction polyhedral BiVO₄