SUPPLMENTARY INFORMATION

Photocatalytic reduction of chlorite in water using bismuth vanadate ($BiVO_4$): Effect of irradiance conditions and presence of oxalate on the reactivity and by-product selectivity

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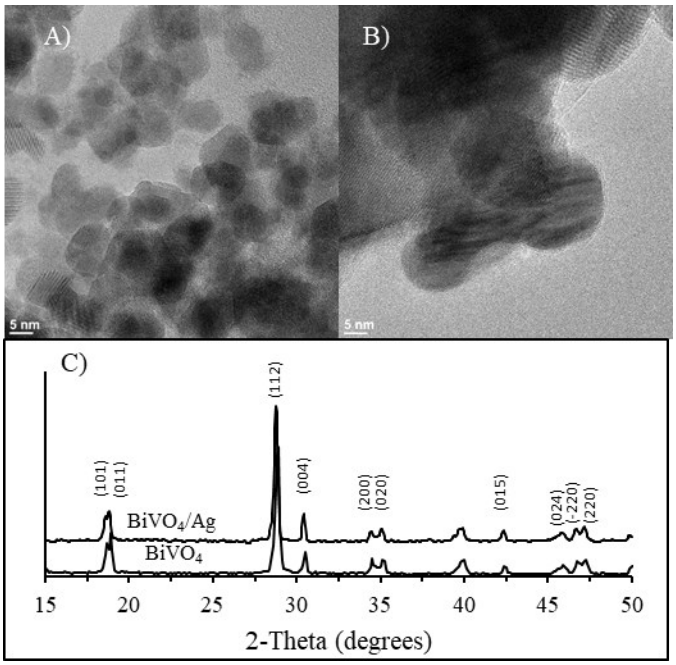

Figure S1. TEM images of A) $BiVO_4$ and B) $BiVO_4$/Ag as well as C) pXRD spectra of photocatalysts with assigned facets.

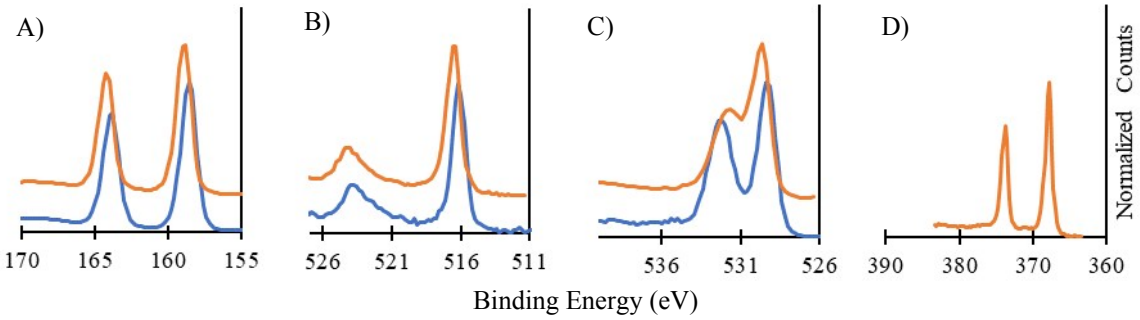

Figure S2. XPS spectra of $BiVO_4$ (blue) and Ag-$BiVO_4$ (orange). A) Bismuth, B) Vanadium, C) Oxygen, and D) Silver

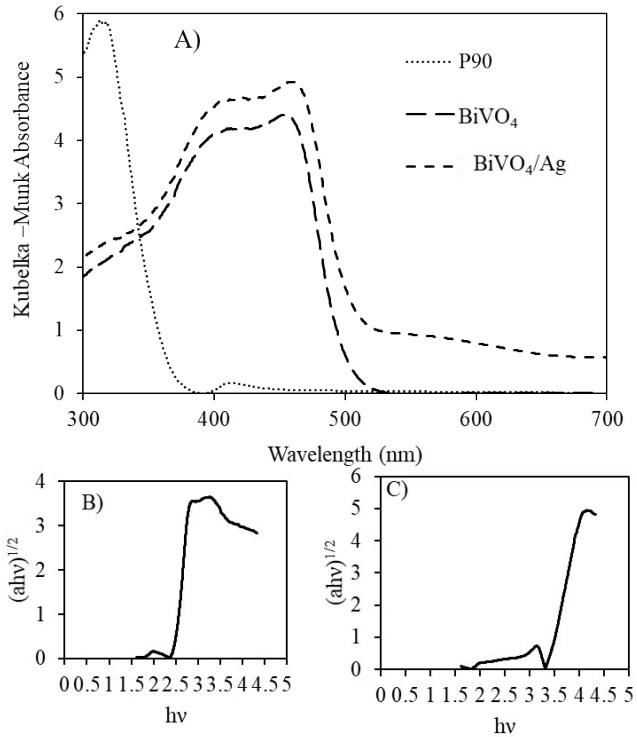

Figure S3. A) Kubelka-Munk Absorbance spectra of the tested photocatalysts, B) Tauc plot showing the energy of the indirect, allowed transition of P90, and C) Tauc plot showing energy of the indirect, allowed transition of $BiVO_4$.

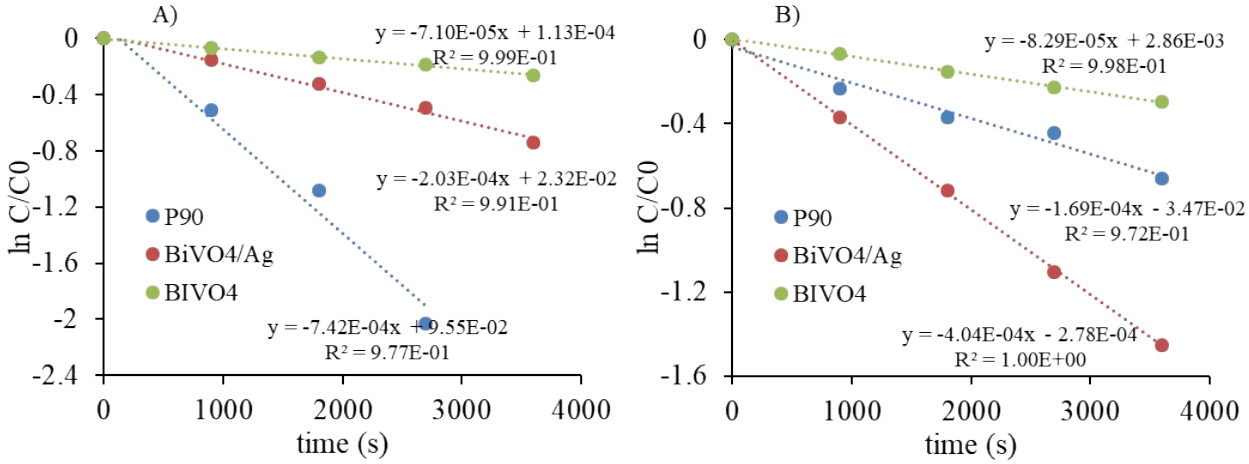

Figure S4. Pseudo-first order reaction plots A) in the absence of oxalate and B) in the presence of oxalate.

Calculation for By-product Selectivity

$$\%S_X = \frac{X_{final} - X_{initial}}{ClO_{2_{initial}}^{-} - ClO_{2_{final}}^{-}} \times 100$$

Where, $\%S_X$ is the selectivity of *X* compound (e.g., Cl^-, ClO_3^-) and *initial* and *final* represent the initial and final concentrations, respectively, as mg-Cl.

Sample Calculation of Photon Fluence

Estimate bandgap from Tauc Plot of photocatalyst absorbance spectra (Figure S1):

For $BiVO_4$, bandgap (E_g) = 2.54 eV

Calculate maximum wavelength of absorption for the photocatalyst:

$$\lambda = \frac{1240.8}{E_g} = \frac{1240.8}{2.54} = 488.5\ nm$$

Calculate the energy of a photon absorbed by the photocatalyst:

$$E_p = \frac{hc}{\lambda} = \frac{3 \times 10^8 m\, s^{-1} \times 6.626\ \times 10^{-34} m^2\, kg\, s^{-1}}{4.885 \times 10^{-7}\, m\, s^{-1}} = 4.06\ \times 10^{-19} J$$

c = speed of light = 3×10^8 m/s
h = Planck's constant = 6.626×10^{-34} m^2 kg / s
E_p = Energy of absorbed photon (J)

Determine energy flux available to the catalyst by integrating the energy of the excitation source across the range of absorbable wavelengths:

$$F_e = \int_{250}^{488} y d\lambda = \Sigma\left(\frac{y_1 + y_2}{2}\right) \times (\lambda_1 - \lambda_2) = 3390\ \mu W\ cm^{-2}$$

where $y = f(\lambda)$ is the energy flux at the specified wavelength (μW cm^{-2} nm^{-1})

F_e = energy flux (μW cm^{-2})

Convert to W/cm^2:

$$F_e = 3390\ \mu W/cm^2 = 0.00339\ W cm^{-2}$$

Now, determine photon flux by converting the energy into photons:

$$F_p = \frac{F_e}{E_p} = \frac{0.00339\ kg\, m^2\, s^{-3} cm^{-2}}{4.06\ \times\ 10^{-19}\ kg\, m^2\, s^{-2}} = 8.33\ \times 10^{15} photons\, s^{-1}\, cm^{-2}$$

Then, photon fluence can be determined by multiplying the photon flux by the time of exposure of the sample. Photon fluence will be dependent upon light source emission spectra, maximum absorbable wavelength of the catalyst, and exposure time.

Table S1. Example time and photon fluence data for $BiVO_4$ with the AM1.5 filter.

Time (min)	Time (s)	Photon Fluence (photons/cm^2)
0	0	0
15	900	7.50 x10^{18}
30	1800	1.50 x10^{19}
45	2700	2.25 x10^{19}
60	3600	3.00 x10^{19}

Table S2. Dose to achieve 2-log removal (J/cm^2). Calculations are based on the range of photons capable of excitation. Energy calculations assume a 100% photon-to-reaction conversion efficiency and are based on μW/cm^2 irradiance measurements (i.e., Figure 1). Dashes indicate data was not available. NR = no removal.

	Dose for 2-Log Removal (J/cm^2)			
	Unfiltered	**280nm cut-on**	**AM 1.5**	**400 nm cut-on**
Photolysis (<360 nm)	5.14	5.72	NR	NR
BiVO4 (<485 nm)	241	216	185	189
$BiVO_4$/Ag (<485 nm)	-	-	45.5	-
P90 (<288 nm)	-	-	5.11	-