

Supplementary Information

**Surface Microenvironment Engineering of Black Vanadia
Nanostructures for Visible Light Photodegradation of Methylene
Blue**

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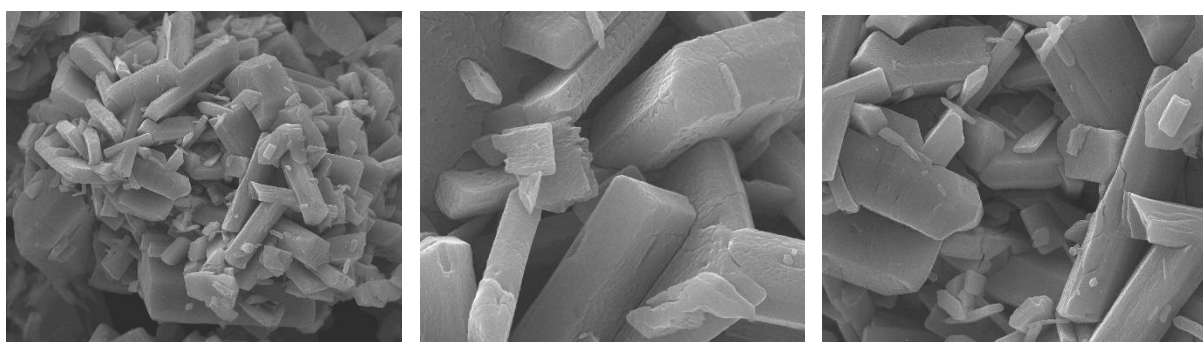


Figure S1. SEM images of pV₂O₅

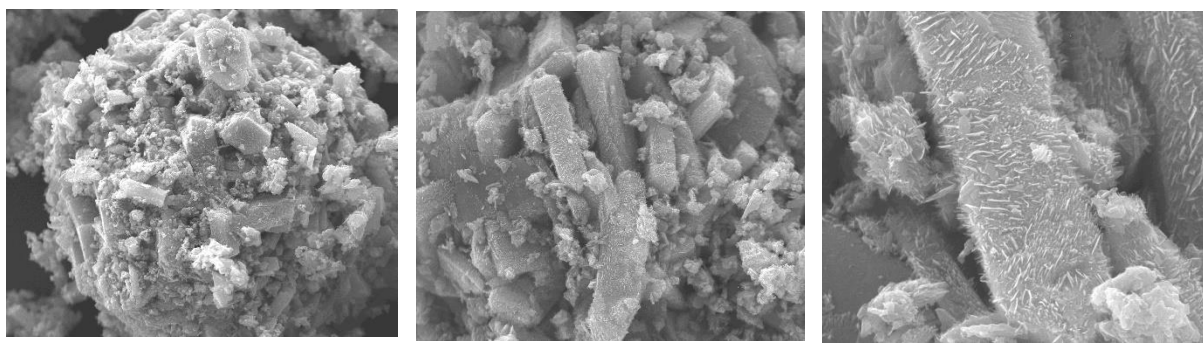


Figure S2. SEM images of bV₂O₅

Table S1. Neutral-pH Zeta Potential of pristine and black V₂O₅

Sample	Sample Frequency (Hz)	Liquid viscosity (cP)	Index of refraction	Dielectric constant	Sample temperature (C°)	Neutral pH Zeta Potential (mV)
pV ₂ O ₅	277.77	0.933	1.333	78.5	23	-20.77
bV ₂ O ₅	277.77	0.933	1.333	78.5	23	-61.15

Table S2. Lattice parameters a, b and c of pristine and black V₂O₅

Sample	a	b	c	α	γ	β
pV ₂ O ₅	11.5156	3.56524	4.37370	90°	90°	90°
bV ₂ O ₅	11.4962	3.56437	4.3758	90°	90°	90°

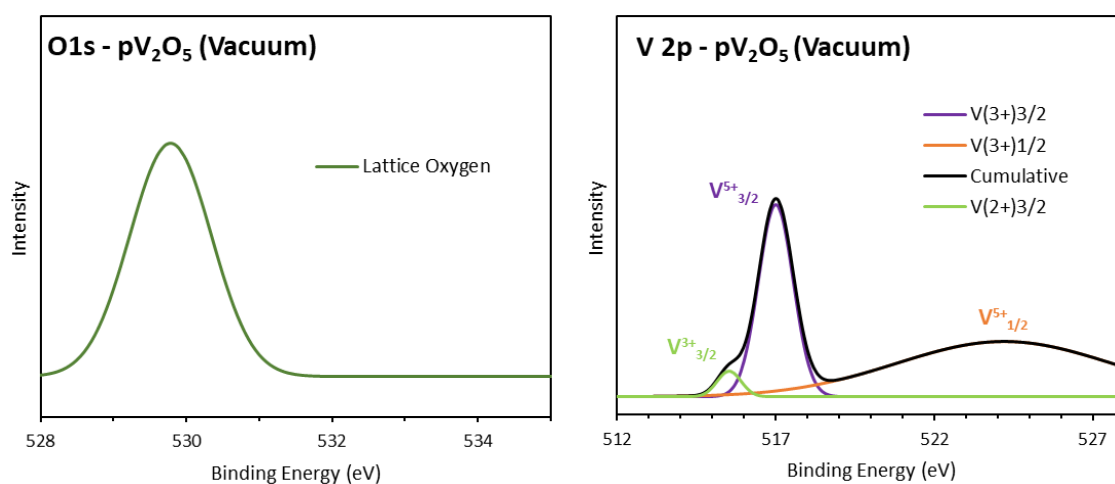


Figure S3. XPS analysis of pV₂O₅ (Vacuum) showing V³⁺ states but no O_v

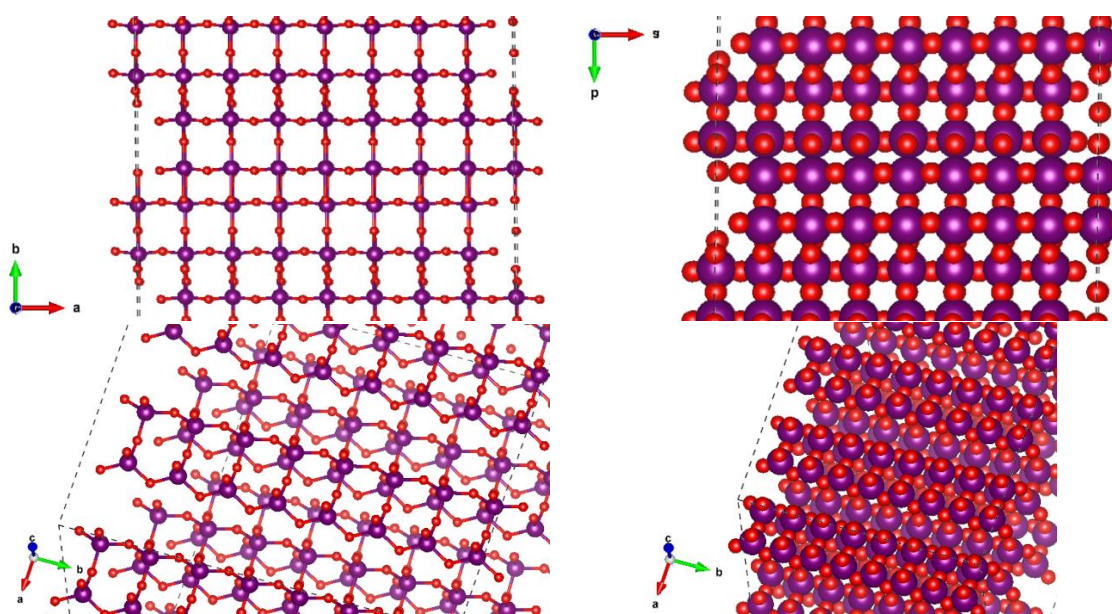


Figure S4. Schematic representation of (110) surface (top row) and (001) surface (bottom row) for pristine Vanadia

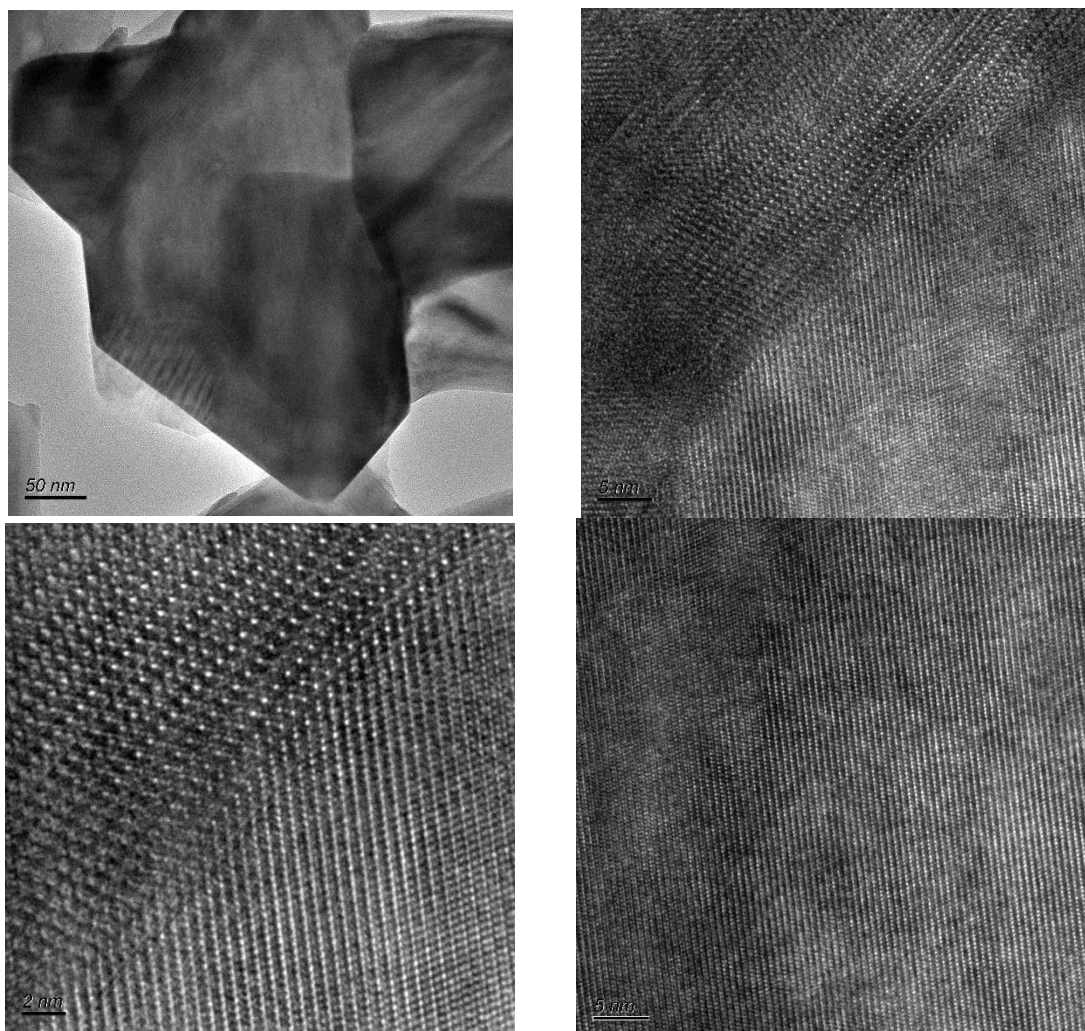


Figure S5. HRTEM images of pV_2O_5

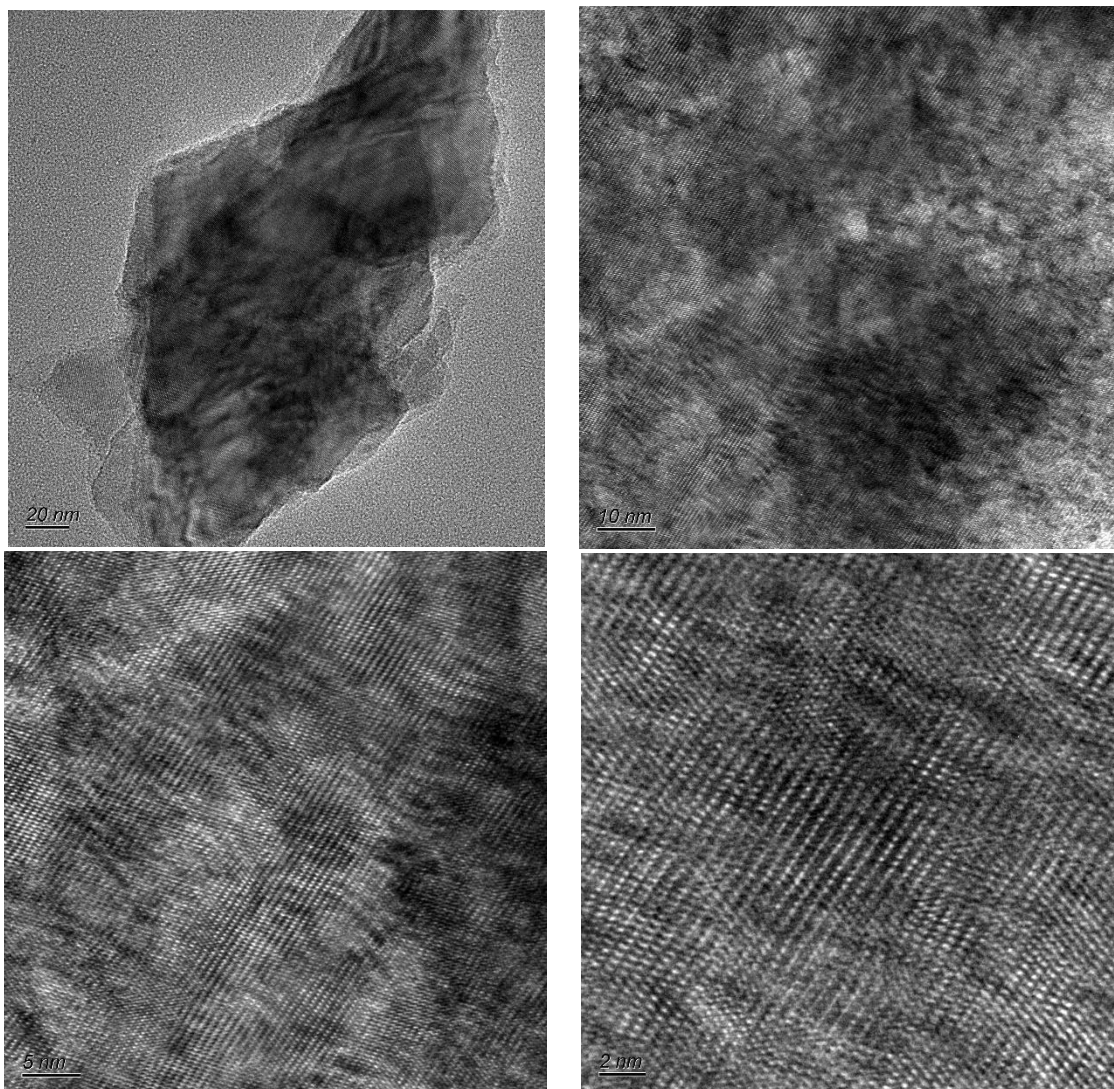


Figure S6. HRTEM images of bV_2O_5

Table S2. Band gap edges, energies and lattice parameters a, b and c of pristine V2O5 under different approaches and *U* values

Theoretical Approach	$U = U_d = U_p$ (eV)	a	b	c	Band gap (eV)	VBM (eV)	CBM (eV)
GGA/PBE	--	11.599	3.564	4.594	1.754	-0.7685	0.9856
PBE + U	1.5	11.554	3.590	4.611	1.980	-0.8419	1.1389
	2	11.552	3.595	4.607	2.076	-0.8530	1.2239
	2.5	11.554	3.607	4.618	2.130	-0.8133	1.3169
	3	11.527	3.613	4.614	2.293	-0.9044	1.3886
	4	11.534	3.634	4.637	2.458	-0.8549	1.6034

Note: All band structures obtained resulted in VBM and CBM at varying *k*-point mesh. This means that for all systems studied (including oxygen vacant systems), the band gaps are indirect in character. This is in good agreement with experiment findings.

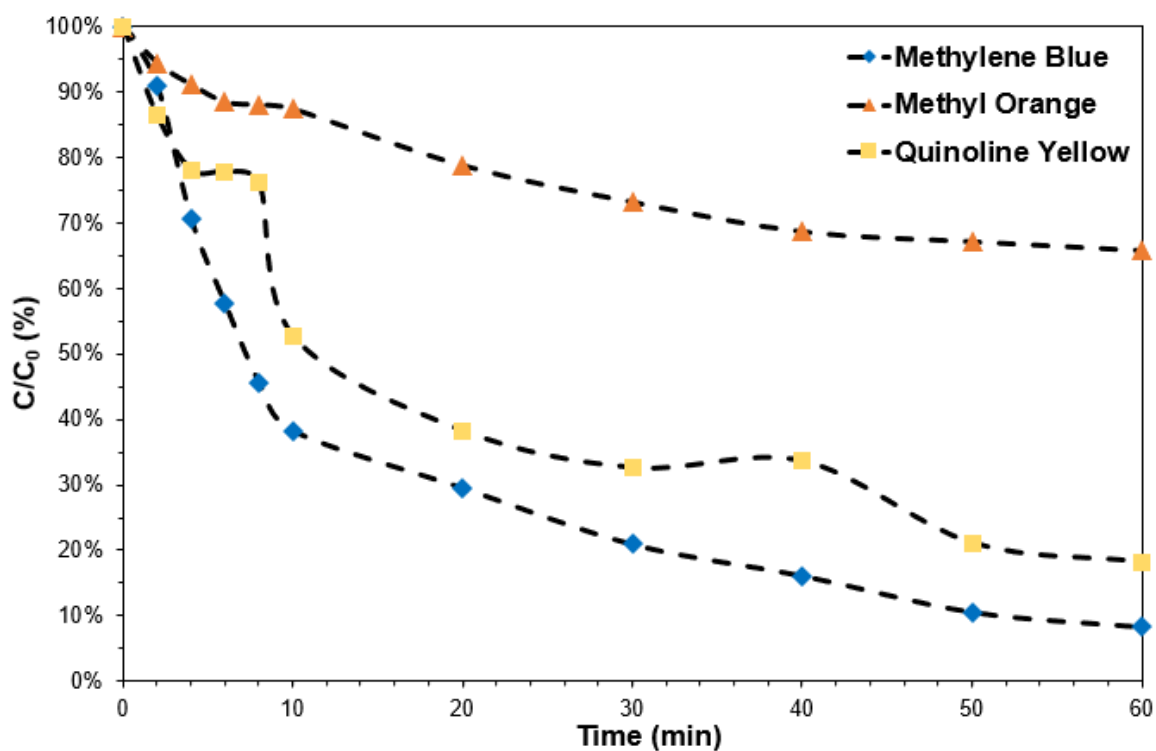


Figure S7. Liquid UV-Vis spectroscopy on cationic Methylene Blue (MB), neutral Quinoline Yellow (QY), and anionic Methyl Orange (MO) visible-light photodegradation using bV_2O_5 with respect to time. The initial concentration C_0 was regulated based on adsorption capacity of dye on bV_2O_5 such that concentration at start of photodegradation experiments (i.e., 0 (min)) is ~ 20 mg/L.

Table S3. Concentrations adsorbed (mg/L = ppm) of MB, QY, and MO on bV₂O₅ after 3-hours of dark adsorption conditions

	Cationic	Neutral	Anionic
	MB	QY	MO
Concentration Adsorbed	75.6	4.9	3.2

Table S4. Percentage degradation of organic contaminants with respect to time on bV₂O₅ and first-order reaction constant k obtained through $-\ln(C/C_0) = kt$.

	Cationic	Neutral	Anionic
Time (min)	MB	QY	MO
2	9.1	13.7	5.6
4	29.4	21.9	8.9
6	42.3	22.2	11.5
8	54.4	23.9	12.0
10	61.7	47.3	12.6
20	70.5	61.8	21.2
30	79.0	67.4	26.8
40	83.8	66.4	31.3
50	89.4	78.9	32.8
60	91.7	81.8	34.2
Rate Constant (k) (min⁻¹)	0.0394	0.0274	0.0083

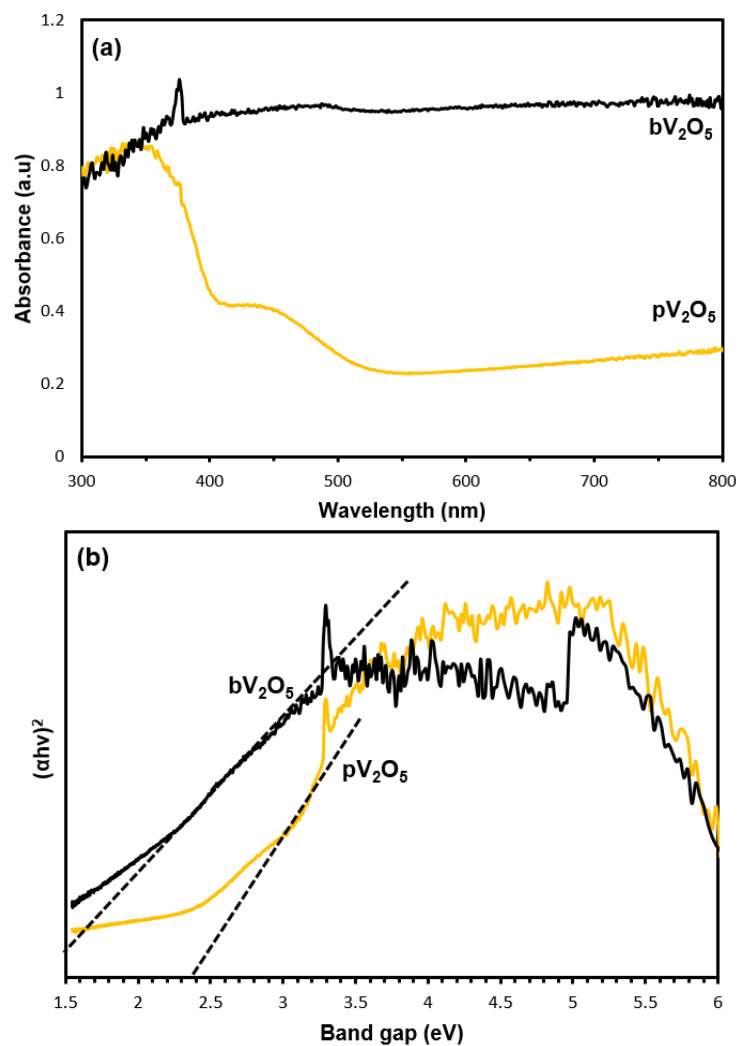
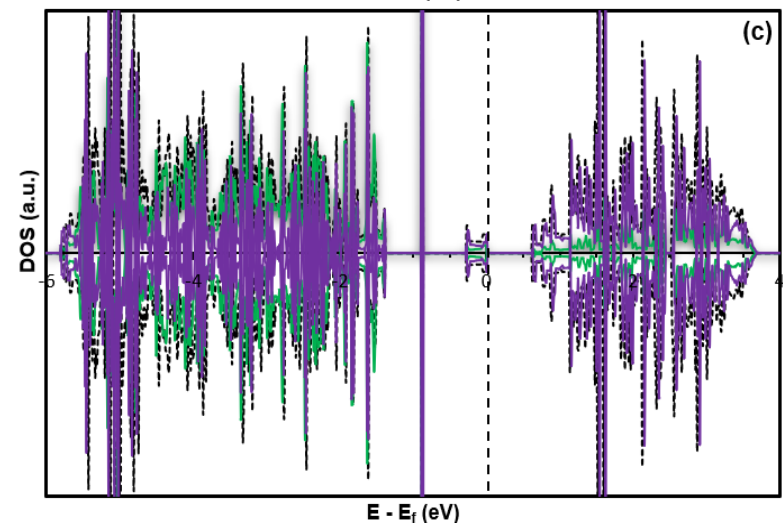
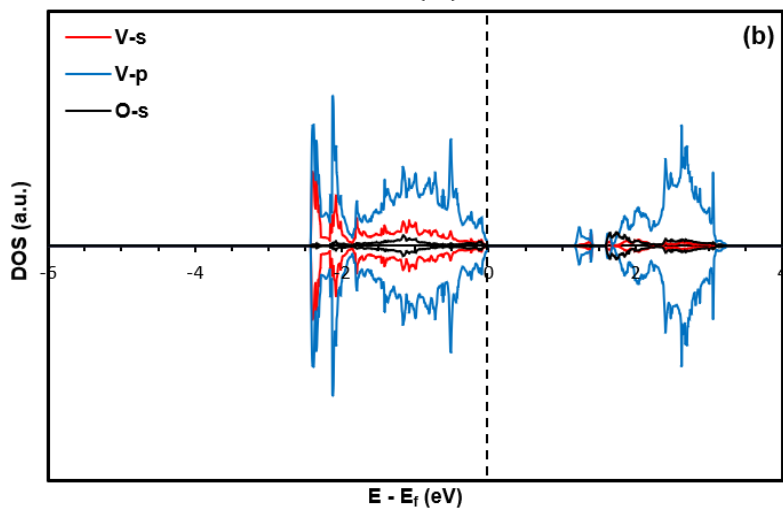
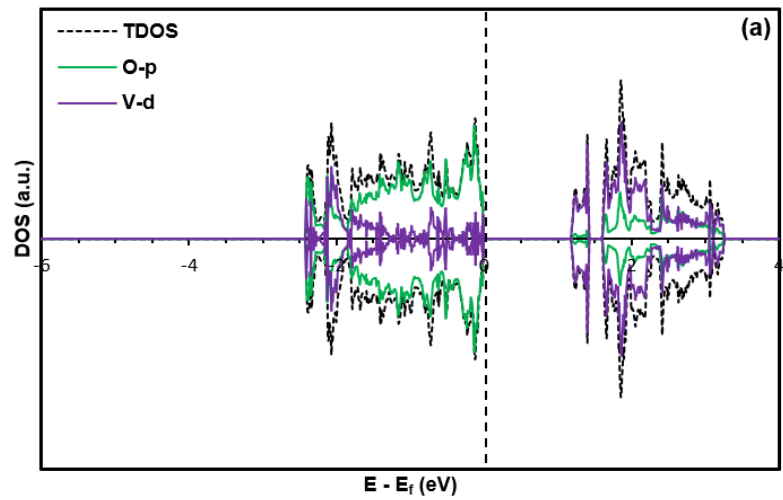


Figure S8. (a) DRS UV-Vis-NIR absorption spectra and (b) $(\alpha h\nu)^{3/2}$ vs E_g (eV) plots of as-prepared pV_2O_5 and bV_2O_5



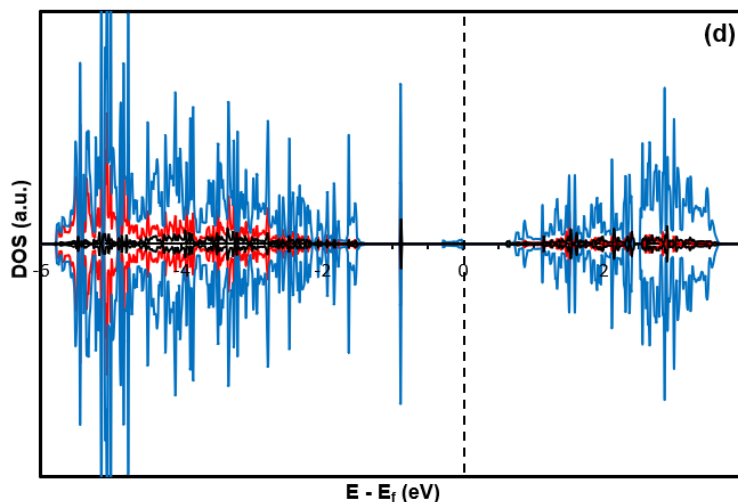


Figure S9. (a, b) Total and Projected Density of States (T/PDOS) of pristine V₂O₅ and (c, d) polar (001) black V₂O₅ with oxygen vacancy at the 1-C oxygen site

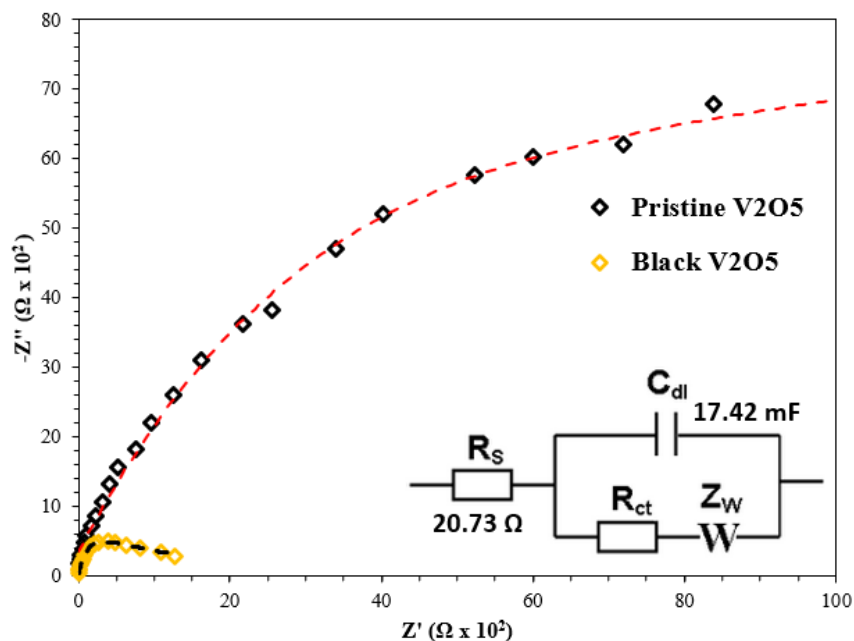


Figure S10. EIS Nyquist plots of the as-prepared Vanadia photocatalysts measured in a DI water. Nyquist plots were obtained in the frequency range of 1 MHz to 1 Hz by passing an input sinusoidal wave of amplitude 5 mV at the open circuit potential (OCP). The realized Nyquist plots were fitted with an appropriate circuit to obtain the charge transfer resistance (R_{ct}) for each catalyst. R_s represents the uncompensated solution resistance which was found to be 20.73 Ohms (Nyquist plot normalized).

Supplementary Note – Synthesis of all materials discussed in main text

Synthesis of Pristine V_2O_5

2.5 g of ammonium metavanadate, purchased from Sigma-Aldrich and used as such, was measured out into an alumina crucible and placed inside a muffle furnace. The sample was then calcined at 550 °C in an air atmosphere for one hour. The precursor was initially heated from 25 °C to 550 °C at a heating rate of 40 °C/min, after which it was allowed to calcinate at 550 °C for 1 hour. After the reaction time was completed, the produced pristine V_2O_5 was allowed to cool, with no further purifications or washing required.

Synthesis of reduced ‘black’ V_2O_5 (1:1.05)

1 g of the pristine V_2O_5 obtained from the procedure mentioned above was mixed well with 0.22 g of $NaBH_4$ (maintaining a mole ratio of the V_2O_5 to $NaBH_4$ at 1:1.05) using a pestle and mortar, and then transferred to a crucible and placed in a tubular furnace. The mixture was then reduced in a tubular furnace at 400 °C in an argon atmosphere, with a 1 hour heating time (6.25 °C/min) and 1 hour reaction holding time at 400 °C. The resulting sample was allowed to cool before being washed with deionized water and centrifuged three times to remove any unreacted $NaBH_4$. The washed sample was then vacuum-dried at a pressure of -0.1 mbarg and 75 °C for 7 hours.

Synthesis of reduced ‘black’ V_2O_5 (1:1.25)

The same procedure for synthesizing the black V_2O_5 was replicated, with the only difference being the amount of $NaBH_4$ added for the reduction process. 0.26 g of $NaBH_4$ were added to 1 g of the pristine V_2O_5 , maintaining a 1:1.25 molar ratio of the V_2O_5 catalyst to the $NaBH_4$ reducing agent. All other steps were repeated without any modifications.

Synthesis of reduced ‘black’ V_2O_5 (vacuum)

1 g of the pristine V_2O_5 prepared was mixed well with 0.22 g of $NaBH_4$ and reduced in a muffle furnace at 255 °C under vacuum conditions instead of an argon atmosphere. The heating rate, reaction time and catalyst to $NaBH_4$ mole ratio were kept identical to that mentioned in the ‘Synthesis of ‘black’ V_2O_5 ’ section above.

Synthesis of black TiO_2

Commercial P25 (p- TiO_2), purchased from Sigma-Aldrich, was used as the precursor for synthesizing black TiO_2 . 1 g of the p- TiO_2 catalyst was measured and mixed thoroughly with 0.5 g of $NaBH_4$ (maintaining a catalyst to $NaBH_4$ mole ratio of 1:1.05) and reduced in the muffle furnace at 400 °C, with a one hour heating time (6.25 °C/min) and 1 hour reaction holding time at 400 °C. The reduced sample was allowed to cool and then washed with deionized water and centrifuged three times to remove any unreacted $NaBH_4$. The washed sample was then vacuum-dried in a muffle furnace at a pressure of -0.1 mbarg and 75 °C for 7 hours.

Synthesis of ZnO

$ZnCl_2$ and NaOH were purchased from Sigma-Aldrich and used as the precursors for ZnO synthesis. 0.65 g of $ZnCl_2$ was dissolved in 200 mL of water. 1.85 g of NaOH was added to the

solution under constant stirring, with $\text{Zn}(\text{OH})_2$ precipitating in solution. The solution was then covered and placed in an oven at 75°C for 12 hours, after which it was washed with deionized water and centrifuged three times to remove the excess NaOH . The washed sample was then vacuum-dried in a muffle furnace at a pressure of -0.1 mbarg and 75°C for 7 hours. The resulting solid was then calcinated in the muffle furnace at 450°C , with a 1 hour heating time ($7^\circ\text{C}/\text{min}$) and 1 hour reaction holding time. The produced ZnO was allowed to cool and crushed well.