

Supporting Information

Elemental doping inhibits surface-state-mediated charge carrier trapping for promoting photocatalytic selective oxidation

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Preparation of Samples

For the synthesis of V-Bi₂O₂CO₃, 1 mmol of Bi(NO₃)₃·5H₂O dissolved in 10 ml of distilled water and 6 mmol of Na₂CO₃ dissolved in 15 mL of distilled water were denoted as solutions A and B, respectively. Then solution B was added to solution A slowly and keep stirring for 5 min. After that, 5 mg of sodium orthovanadate (V) dodecahydrate was poured into the above mixture. After stirring for 30 min, the mixed solution was transferred into a 35 mL Teflon-lined stainless autoclave, sealed in the autoclave and heated at 180 °C for 24 h. After being cooled to room temperature, the obtained solid product was collected by centrifugation, washed several times with deionized water and ethanol repeatedly and finally dried at 60 °C under vacuum for 12 h. Bi₂O₂CO₃ was synthesized in the same way as above without adding sodium orthovanadate (V) dodecahydrate.

Electron Spin Resonance Trapping Measurements

1 mL of distilled water and 20 μL of DMPO solution were used to prepare the trapping agent solution, and 10 mg of catalyst and 1 mL of water were used to prepare the catalyst solution. Subsequently, 0.5 mL of aqueous solution, 50 μL of catalyst solution and 50 μL of trapping agent solution were mixed. Further, illuminate the mixed solution for 30 s and then characterized by using a JEOL JES-FA200 electron spin resonance spectrometer (298 K, 9.062 GHz).

Photocatalytic Molecular Oxygen Activation Tests

Methyl orange (MO) was selected as the probe molecule to evaluate the photocatalytic molecular oxygen activation. 6.6 mg of methyl orange was added to 500 mL of acetonitrile solution to prepare MO solution. In a typical test, 10 mg of catalyst was added into 50 mL of MO solution. After having been stirred in the dark for 10min, the mixture was illuminated by using a xenon lamp (Au-Light CEL-HXF300) as the light source. The concentration of methyl orange was measured by UV-VIS

spectroscopy at different time. Atmosphere-dependent tests were performed under O₂, air, and Ar bubbles.

Calculation method

The present first principle DFT calculations are performed by Vienna Ab initio Simulation Package(VASP)¹ with the projector augmented wave (PAW) method² The exchange-functional is treated using the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)³ functional. The energy cutoff for the plane wave basis expansion was set to 450 eV and the force on each atom less than 0.02 eV/Å was set for convergence criterion of geometry relaxation. A 2×2×1 supercell of Bi₂O₂CO₃ was adopted for further calculations. The Brillouin zone integration was performed using 2×2×1 and 3×3×1 k-point sampling for structure optimization and electron self-consistent calculation, respectively. The self-consistent calculations apply a convergence energy threshold of 10⁻⁵ eV.

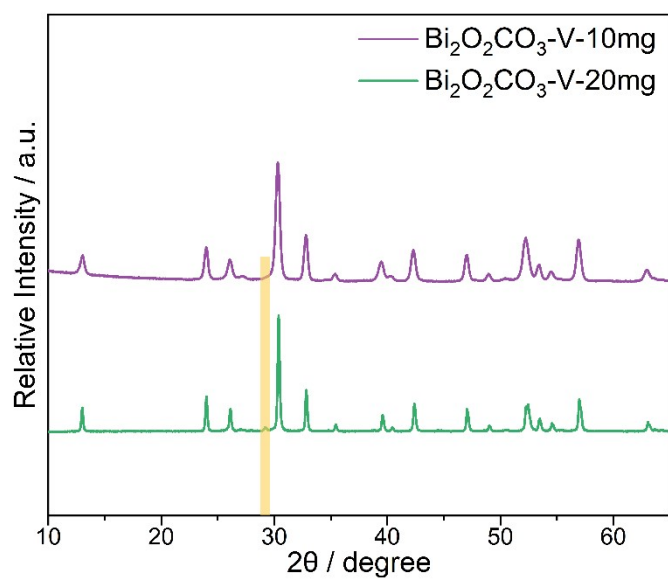


Figure S1. XRD patterns of different doping amounts of V element.

The structure changes of samples with different V doping concentrations show that when 20 mg sodium orthovanadate (V) dodecahydrate was added, a new peak appeared, indicating the generation of impurities.

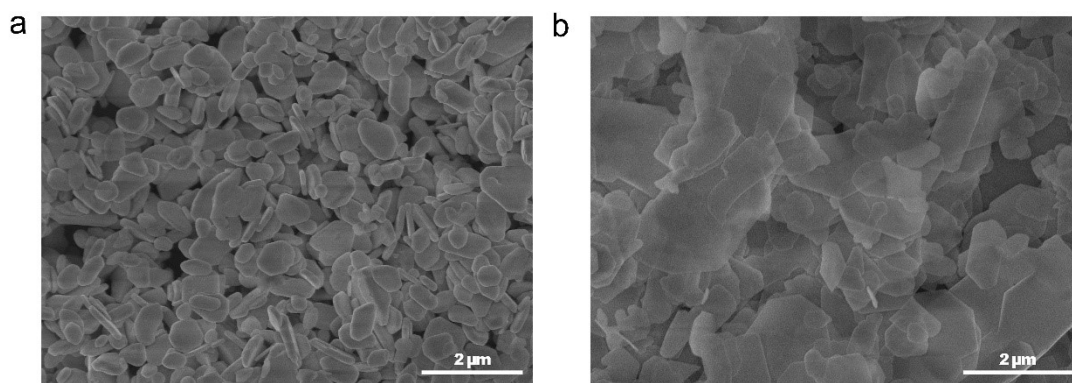


Figure S2. SEM images of (a) $\text{Bi}_2\text{O}_2\text{CO}_3$ and (b) $\text{V-Bi}_2\text{O}_2\text{CO}_3$.

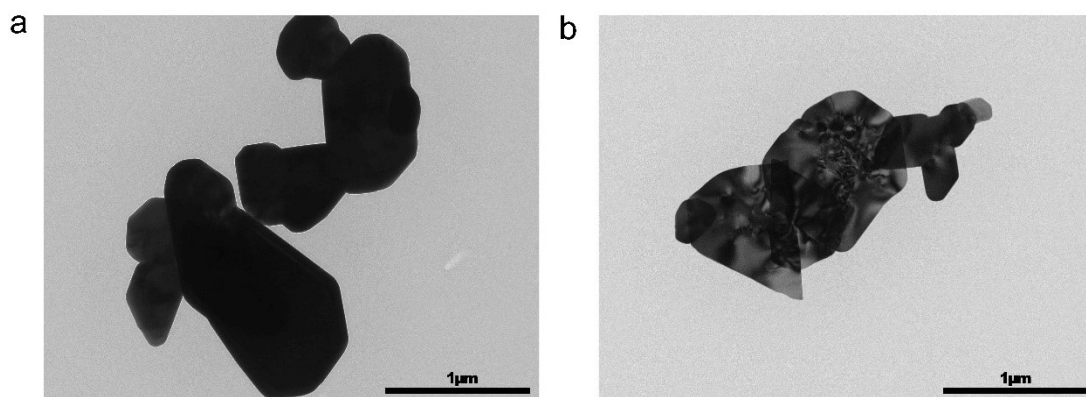


Figure S3. TEM images of (a) Bi₂O₂CO₃ and (b) V-Bi₂O₂CO₃

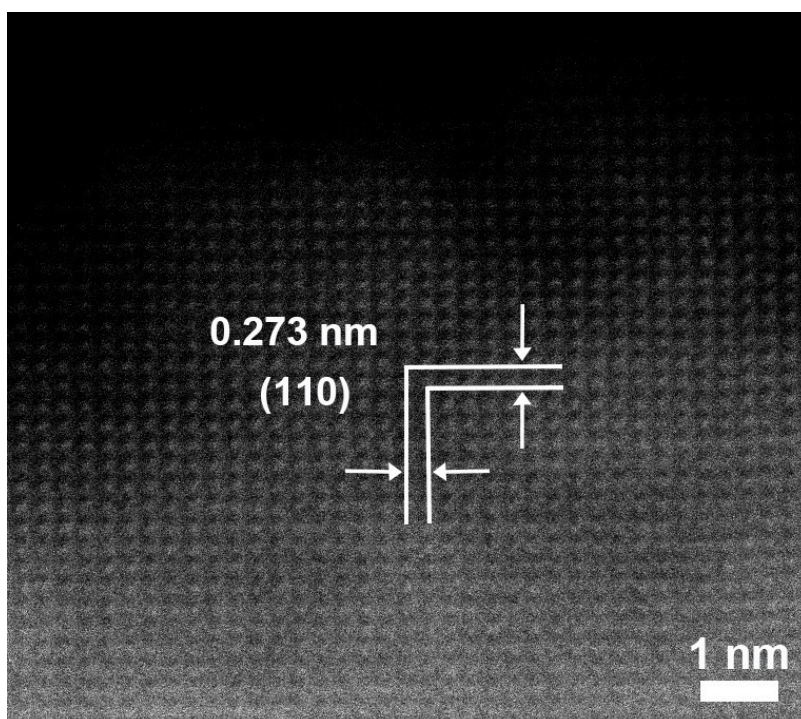


Figure S4. Atomic-resolution HAADF-STEM image of Bi₂O₂CO₃.

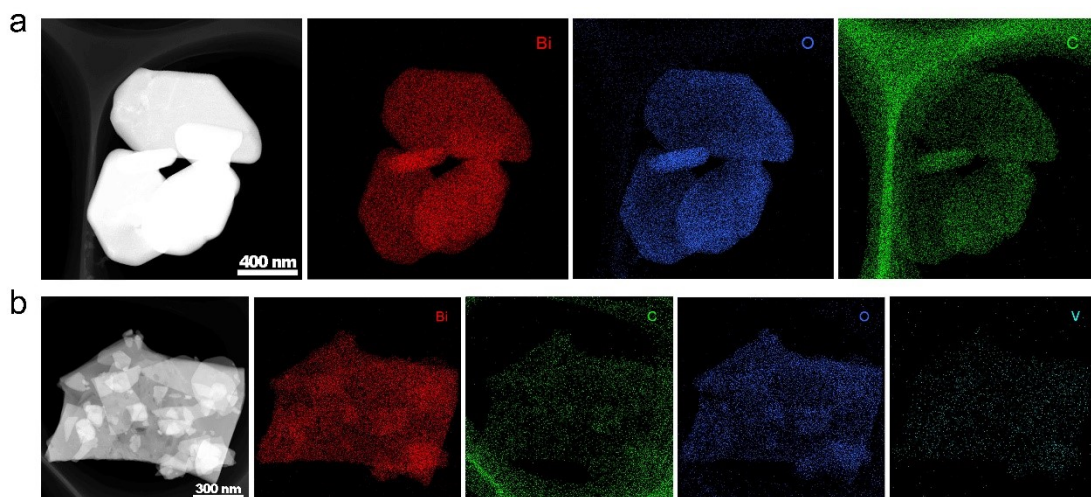


Figure S5. HAADF-STEM images and the corresponding EDS mapping images of (a) $\text{Bi}_2\text{O}_2\text{CO}_3$ and (b) $\text{V-Bi}_2\text{O}_2\text{CO}_3$.

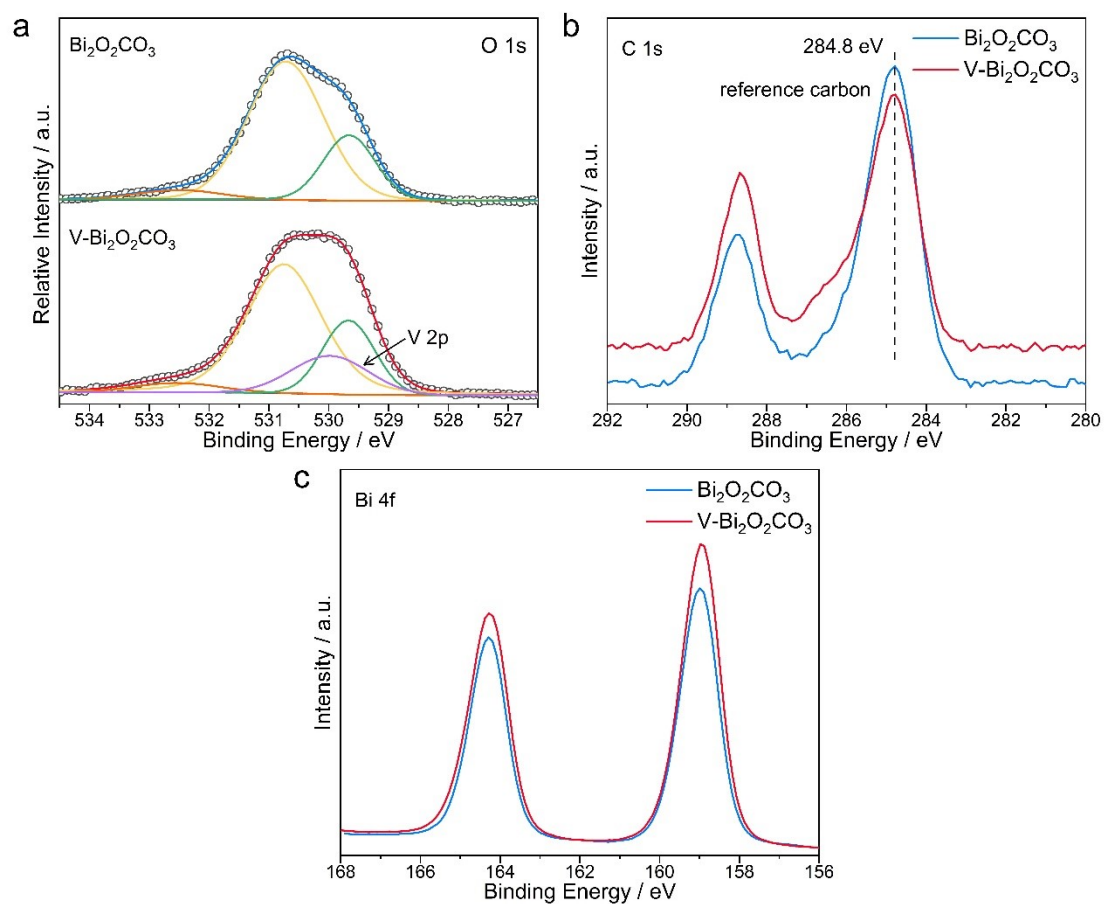


Figure S6. XPS analyses of $\text{Bi}_2\text{O}_2\text{CO}_3$ and $\text{V-Bi}_2\text{O}_2\text{CO}_3$, respectively. (a) O 1s, (b) C 1s, and (c) Bi 4f spectra.

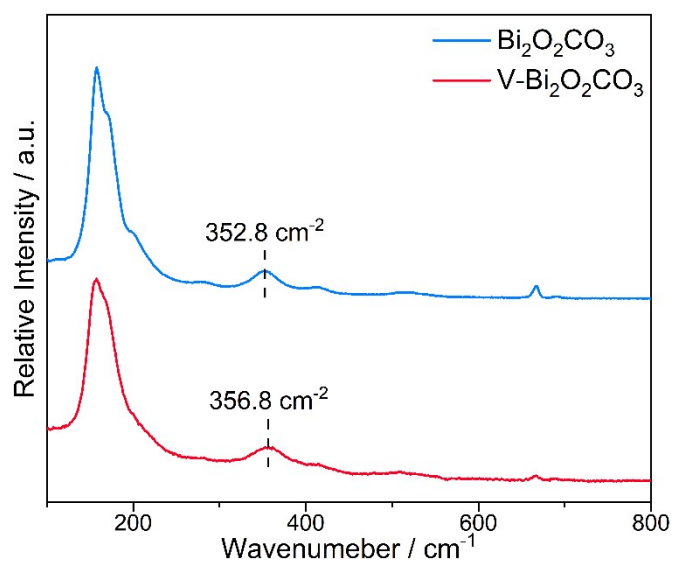


Figure S7. Raman spectra of $\text{Bi}_2\text{O}_2\text{CO}_3$ and $\text{V-Bi}_2\text{O}_2\text{CO}_3$.

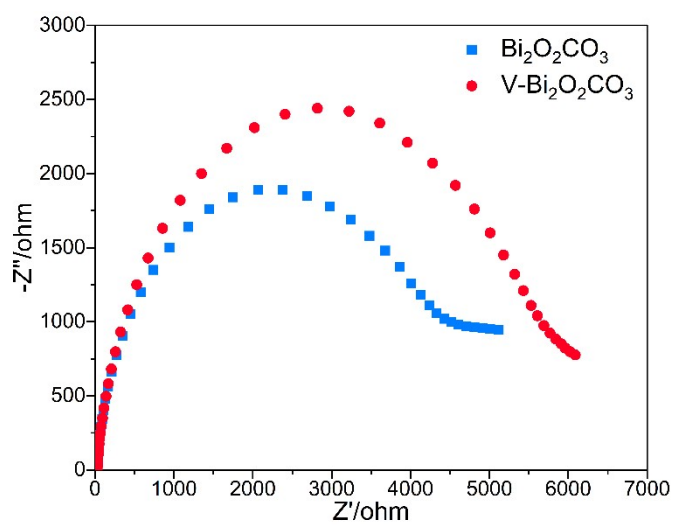


Figure S8. EIS measurements (vs Ag/AgCl, pH 6.6). The increased electrochemical impedance of $\text{V-Bi}_2\text{O}_2\text{CO}_3$ excludes the potential effect of electrical conductivity on judging the original of initial photocurrent spike.

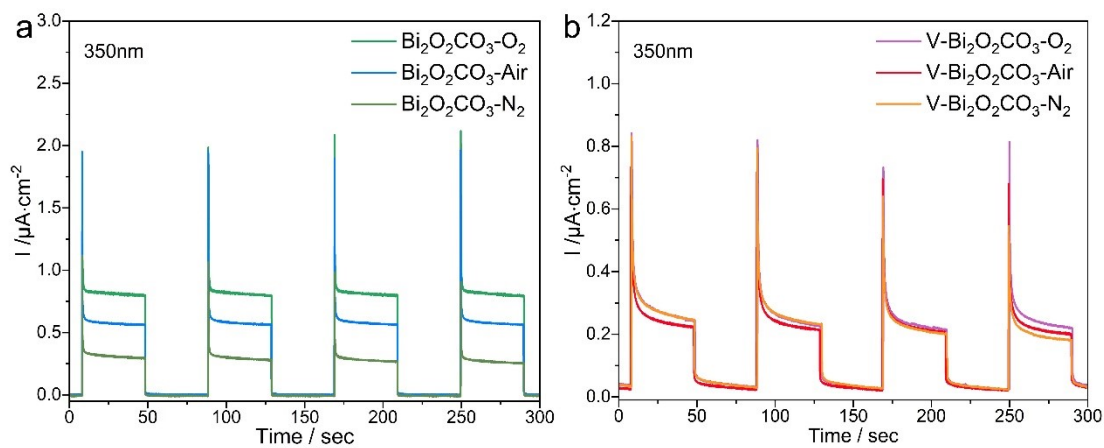


Figure S9. Transient photocurrent responses of (c) $\text{Bi}_2\text{O}_2\text{CO}_3$ and (d) $\text{V-Bi}_2\text{O}_2\text{CO}_3$ under different atmospheres with a 350-nm illumination.

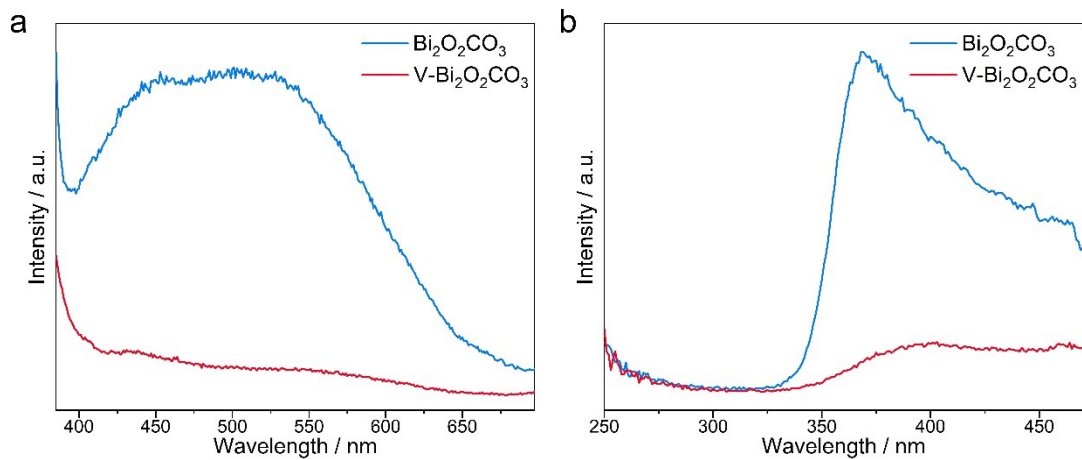


Figure S10. Steady-state photoluminescence (a) emission and (b) excitation spectra of $\text{Bi}_2\text{O}_2\text{CO}_3$ and $\text{V-Bi}_2\text{O}_2\text{CO}_3$.

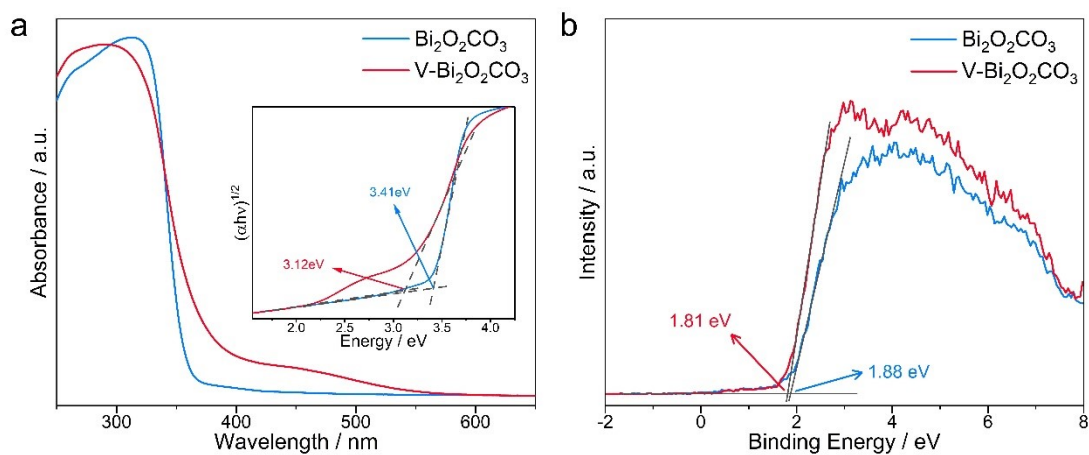


Figure S11. (a) UV-vis absorption spectra (inset: the corresponding Tauc plots.); (b) XPS valence band spectra.

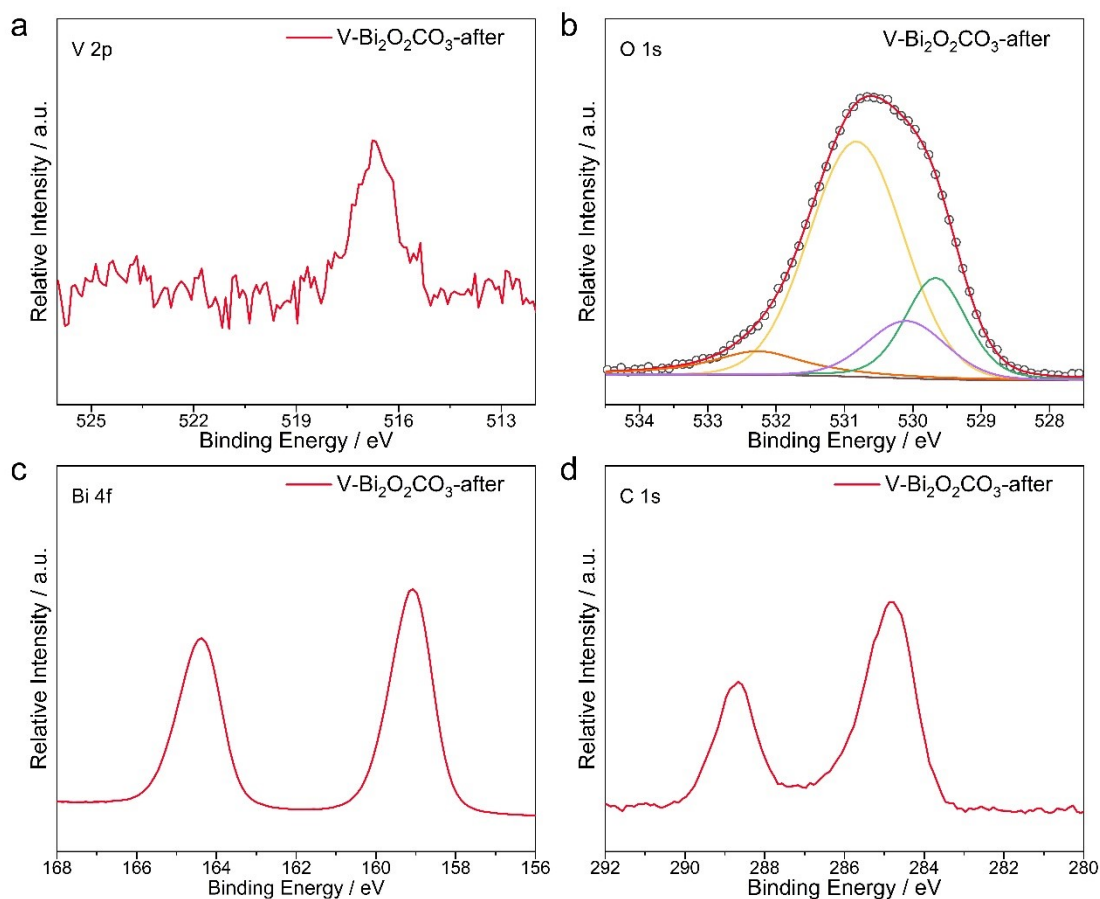


Figure S12. XPS analyses of V-Bi₂O₂CO₃ after reaction (a) V 2p, (b) O 1s, (c) Bi 4f and (d) C 1s.

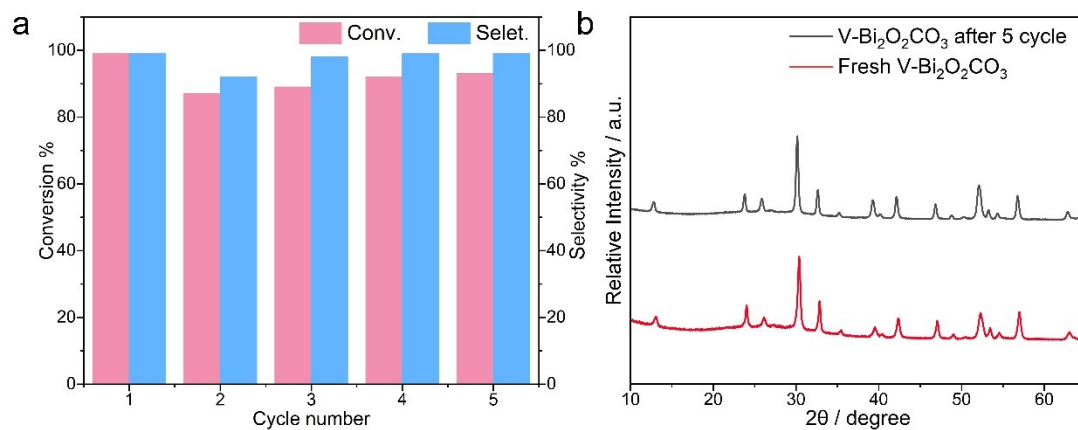


Figure S13. (a) Cycling tests of oxidative coupling of benzylamine for V-Bi₂O₂CO₃; (b) XRD patterns for V-Bi₂O₂CO₃ before and after cycling tests.

References

1. G. Kresse and J. Furthmuller, *Comput. Mater. Sci.*, 1996, **6**, 15-50.
2. P. E. Blochl, *Phys. Rev. B*, 1994, **50**, 17953-17979.
3. J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B*, 1992, **46**, 6671-6687.