Variable-valence element doping mediated photogenerated electron trapping for selective oxidation reactions

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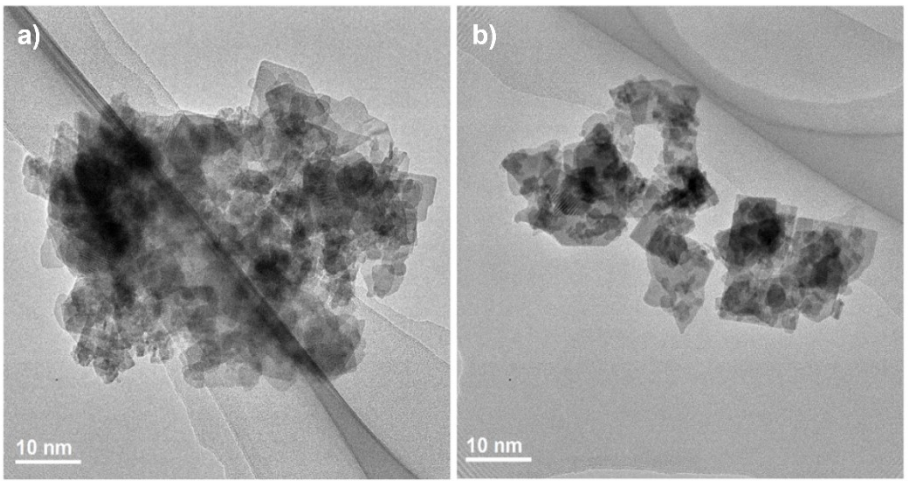

Fig. S1 TEM images of (a) Bi_2WO_6 and (b) Cu-Bi_2WO_6.

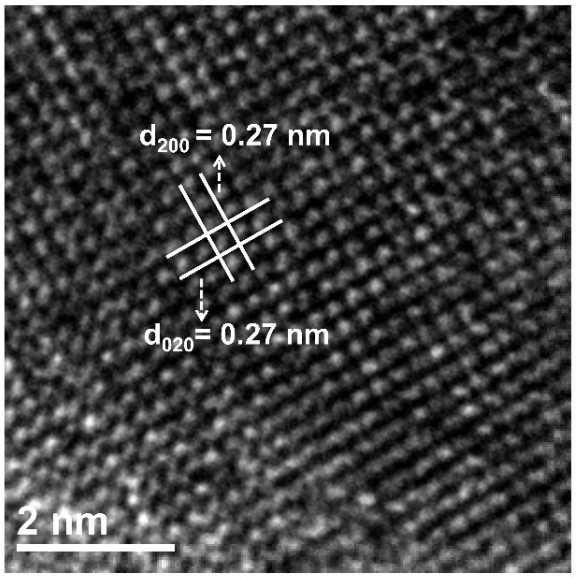

Fig. S2 HRTEM image of Bi_2WO_6.

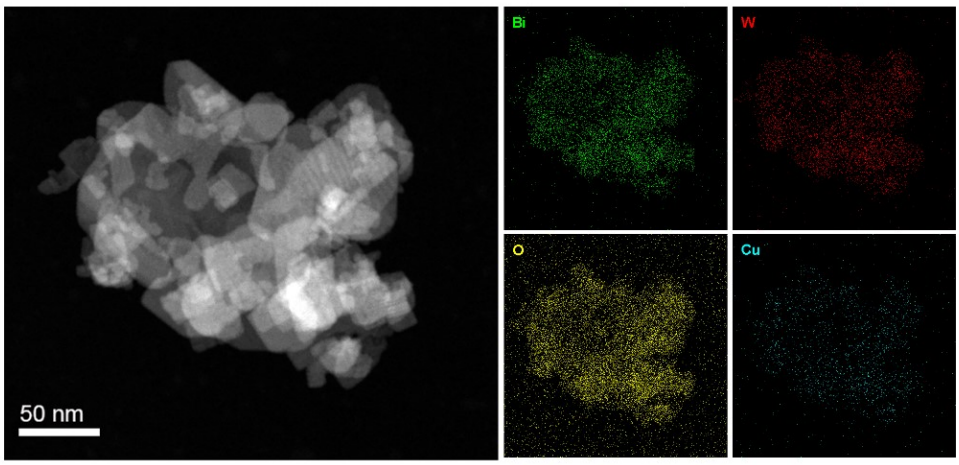

Fig. S3 HAADF-STEM images and the corresponding EDS mapping images of Cu-Bi_2WO_6.

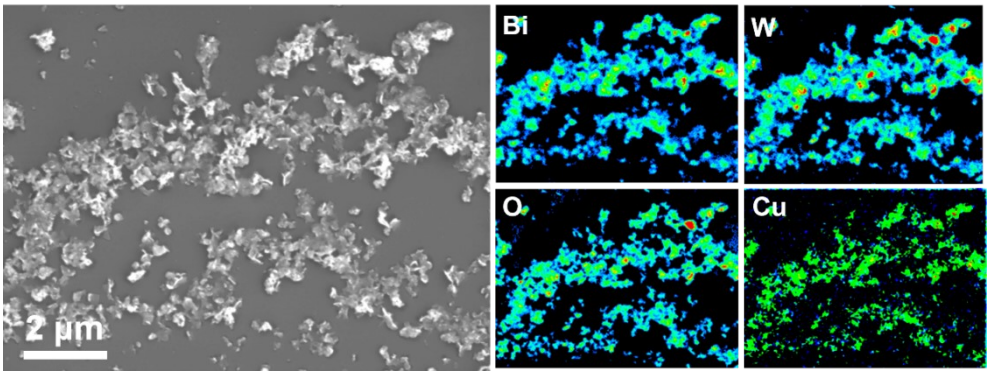

Fig. S4 EPMA analysis of the relevant elements of Cu-Bi_2WO_6.

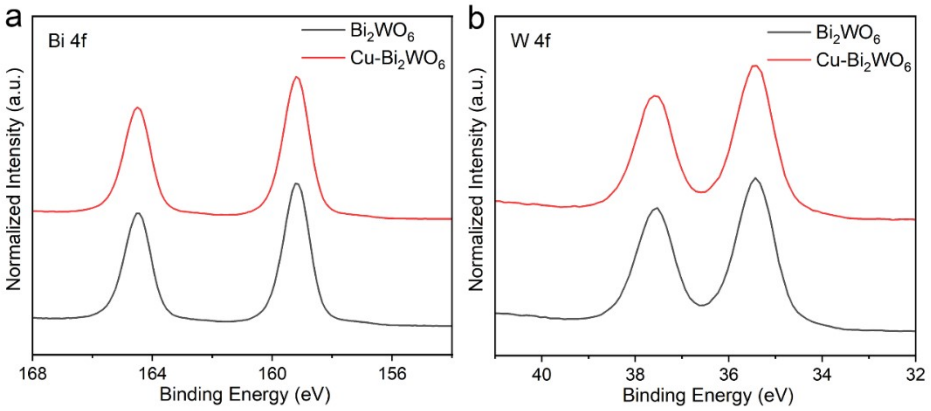

Fig. S5 XPS spectra of Bi_2WO_6 and Cu-Bi_2WO_6. (a) Bi 4f, (b) W 4f.

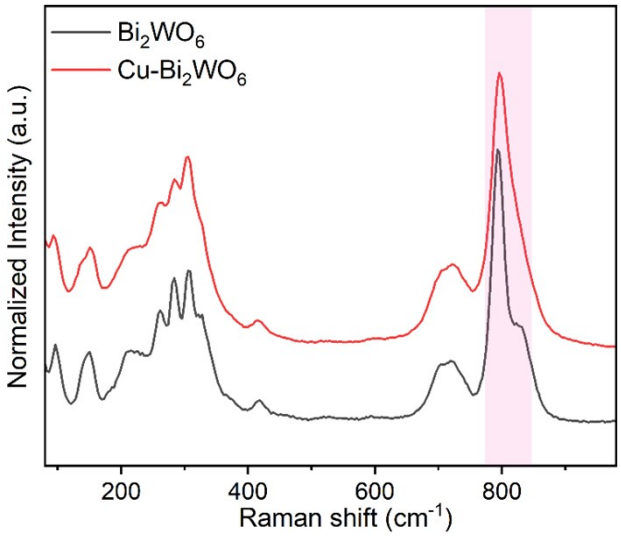

Fig. S6 Raman spectra of Bi_2WO_6 and Cu-Bi_2WO_6.

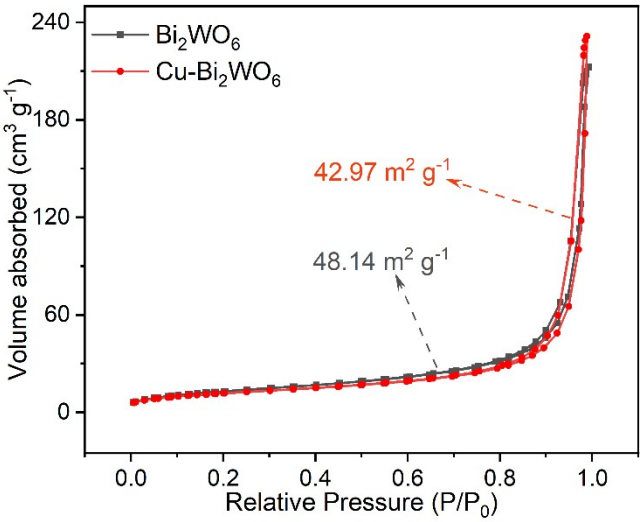

Fig. S7 N_2 adsorption/desorption isotherms of Bi_2WO_6 and Cu-Bi_2WO_6.

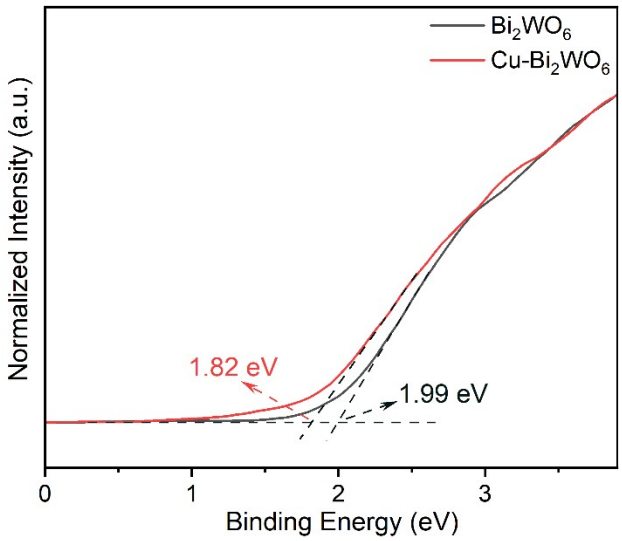

Fig. S8 XPS valence band spectra of Bi_2WO_6 and Cu-Bi_2WO_6.

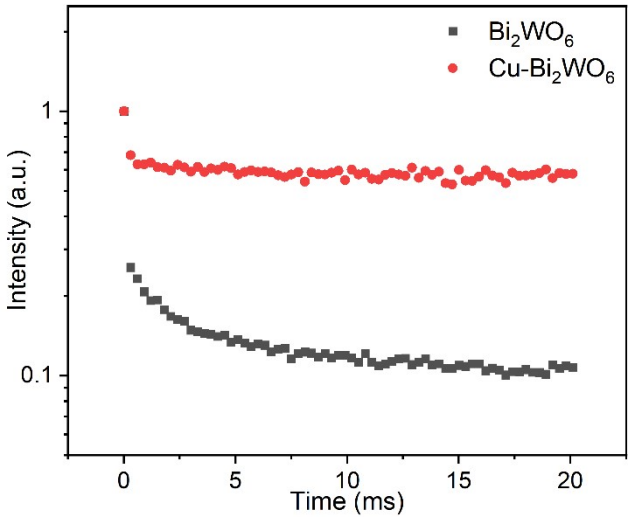

Fig. S9 Low-temperature (10 K) time-resolved phosphorescence (PH) spectra of Bi_2WO_6 and Cu-Bi_2WO_6.

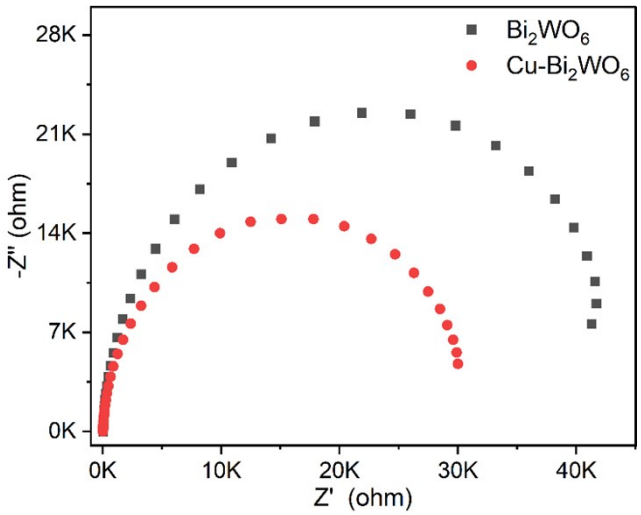

Fig. S10 Electrochemical impedance spectroscopy of Bi_2WO_6 and Cu-Bi_2WO_6.

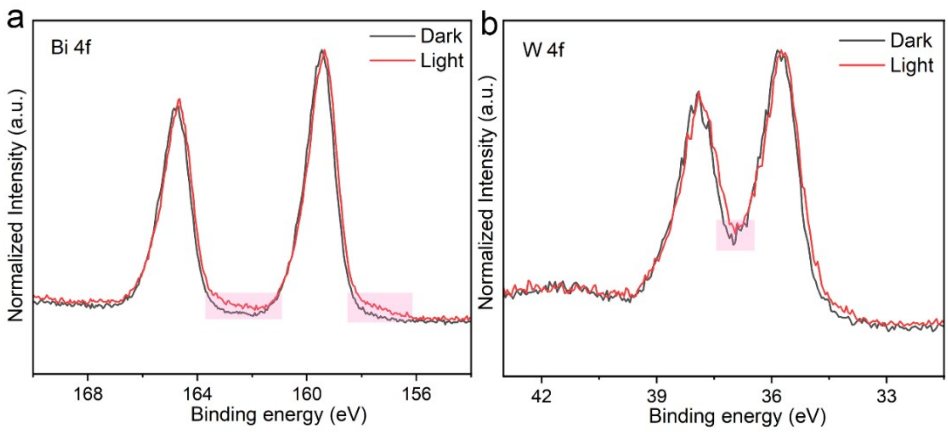

Fig. S11 *In-situ* high resolution XPS spectra of Bi 4f and W 4f of Cu-Bi_2WO_6.

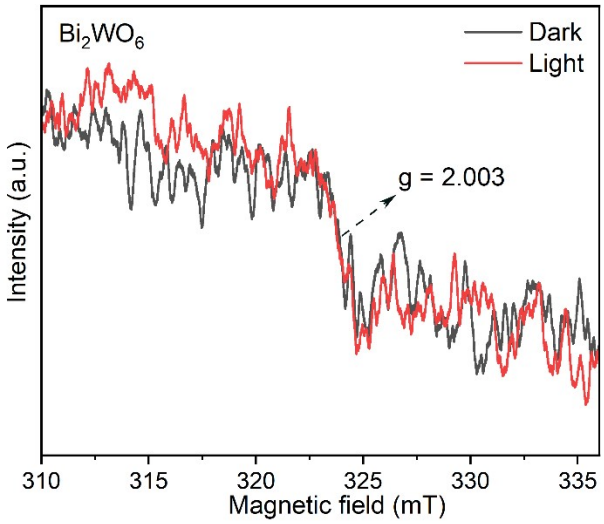

Fig. S12 *In-situ* ESR spectra of Bi_2WO_6 under dark and illumination conditions.

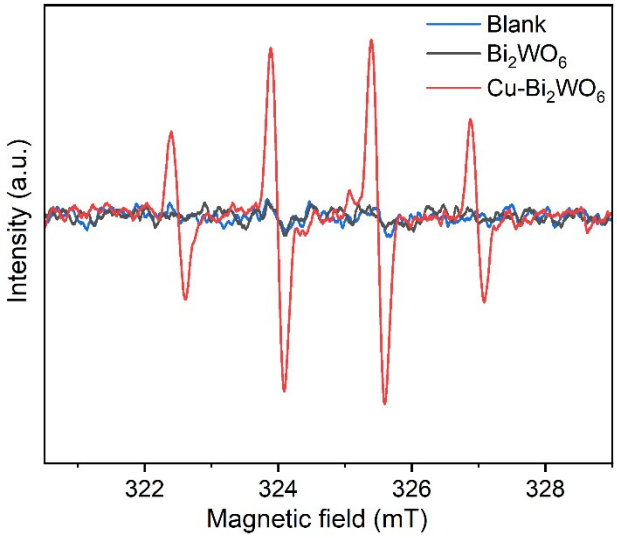

Fig. S13 ESR spectra of different samples in the presence of DMPO in water.

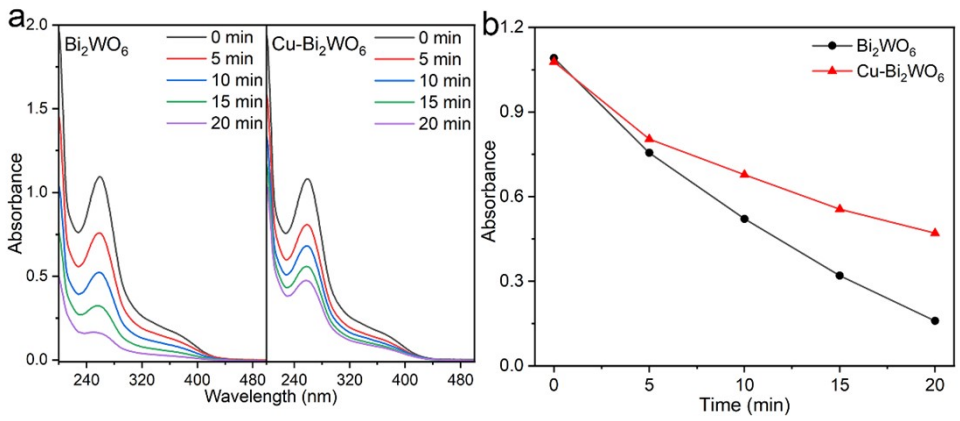

Fig. S14 (a) Time-dependent absorption spectra of NBT reduction for Bi_2WO_6 and Cu-Bi_2WO_6. (b) Evolutions of the absorbance peak monitored at 260 nm.

The $\bullet O_2^-$ can be detected by nitro blue tetrazorium (NBT), which could be reduced by $\bullet O_2^-$, resulting in decrease of absorbance spectra.[1] The time-dependent absorption curve shows that Cu-Bi_2WO_6 has a weaker ability to generate $\bullet O_2^-$ due to the trapping of photogenerated electrons at the Cu sites.

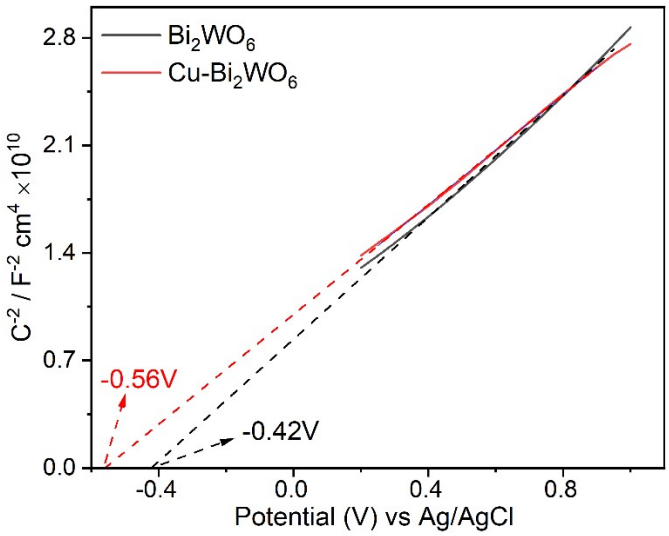

Fig. S15 Mott–Schottky plots of Bi_2WO_6 and Cu-Bi_2WO_6.

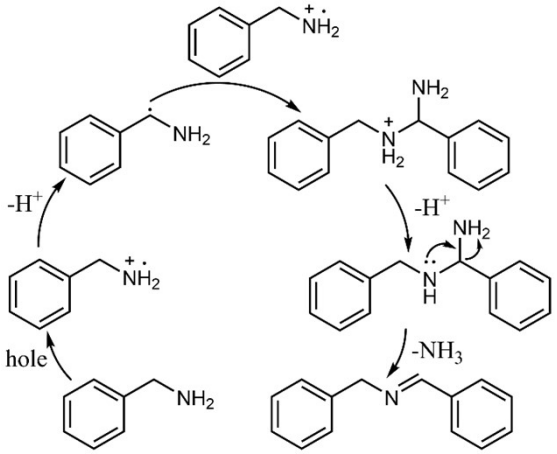

Fig. S16 Schematic diagram of hole-mediated oxidative coupling of amines to imines.[2]

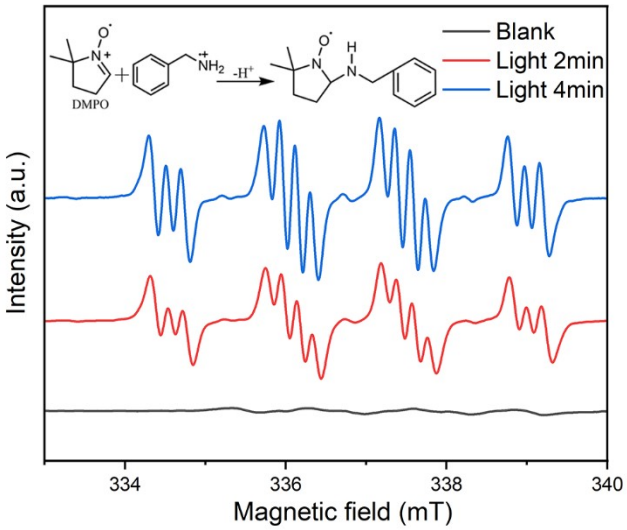

Fig. S17 *In-situ* ESR spectra of DMPO−$C_6H_5CH_2NH_2^{\bullet+}$ for Cu-Bi_2WO_6.

In-situ ESR spectroscopy measurements utilizing 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin-trapping agent provide direct evidence of $C_6H_5CH_2NH_2^{\bullet+}$ generation. Under irradiation, a specific signal attributed to a DMPO−$C_6H_5CH_2NH_2^{\bullet+}$ spin adduct was clearly observed for Cu-Bi_2WO_6, and the signal intensity increased gradually with irradiation time.

References

1 Y. Nosaka and A. Y. Nosaka, *Chem. Rev.*, 2017, **117**, 11302–11336.
2 H. Liu, C. Xu, D. Li, and H. Jiang, *Angew. Chem., Int. Ed.*, 2018, **57**, 5379–5383.
3 W. Liu, Y. Wang, H. Huang, J. Wang, G. He, J. Feng, T. Yu, Z. Li, and Z. Zou, *J. Am. Chem. Soc.*, 2022, **144**, 23396−23404.