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

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**Fig. S1** TEM images of (a) Bi$_2$WO$_6$ and (b) Cu-Bi$_2$WO$_6$.

**Fig. S2** HRTEM image of Bi$_2$WO$_6$.
**Fig. S3** HAADF-STEM images and the corresponding EDS mapping images of Cu-Bi$_2$WO$_6$.

**Fig. S4** EPMA analysis of the relevant elements of Cu-Bi$_2$WO$_6$. 
Fig. S5 XPS spectra of Bi₂WO₆ and Cu-Bi₂WO₆. (a) Bi 4f, (b) W 4f.

Fig. S6 Raman spectra of Bi₂WO₆ and Cu-Bi₂WO₆.
Fig. S7 $\text{N}_2$ adsorption/desorption isotherms of $\text{Bi}_2\text{WO}_6$ and $\text{Cu-Bi}_2\text{WO}_6$.

Fig. S8 XPS valence band spectra of $\text{Bi}_2\text{WO}_6$ and $\text{Cu-Bi}_2\text{WO}_6$. 
Fig. S9 Low-temperature (10 K) time-resolved phosphorescence (PH) spectra of Bi$_2$WO$_6$ and Cu-Bi$_2$WO$_6$.

Fig. S10 Electrochemical impedance spectroscopy of Bi$_2$WO$_6$ and Cu-Bi$_2$WO$_6$.
**Fig. S11** *In-situ* high resolution XPS spectra of Bi 4f and W 4f of Cu-Bi$_2$WO$_6$.

**Fig. S12** *In-situ* ESR spectra of Bi$_2$WO$_6$ 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$_2$WO$_6$ and Cu-Bi$_2$WO$_6$. (b) Evolutions of the absorbance peak monitored at 260 nm.

The •O$_2^-$ can be detected by nitro blue tetrazorium (NBT), which could be reduced by •O$_2^-$, resulting in decrease of absorbance spectra. The time-dependent absorption curve shows that Cu-Bi$_2$WO$_6$ has a weaker ability to generate •O$_2^-$ due to the trapping of photogenerated electrons at the Cu sites.
Fig. S15 Mott–Schottky plots of Bi$_2$WO$_6$ and Cu-Bi$_2$WO$_6$.

Fig. S16 Schematic diagram of hole-mediated oxidative coupling of amines to imines.$^2$
Fig. S17 *In-situ* ESR spectra of DMPO–C$_6$H$_5$CH$_2$NH$_2$•+ for Cu-Bi$_2$WO$_6$.

*In-situ* ESR spectroscopy measurements utilizing 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin-trapping agent provide direct evidence of C$_6$H$_5$CH$_2$NH$_2$•+ generation. Under irradiation, a specific signal attributed to a DMPO–C$_6$H$_5$CH$_2$NH$_2$•+ spin adduct was clearly observed for Cu-Bi$_2$WO$_6$, and the signal intensity increased gradually with irradiation time.

References