Electronic Supplementary Information

Realizing Regulated Carrier Separation and Exciton Generation of Bi$_{24}$O$_{31}$Cl$_{10}$ via Carbon Doping Strategy

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20. Table S1. The content of Bi, O, Cl and C in BOC-350.
Fig. S1. TEM image (a) and EDS mapping (b-f) of the precursor.
Fig. S2. Simultaneously DSC-TGA curves of the precursor.
Fig. S3. The morphologies of the as-prepared samples. (a) BOC-250, (b) BOC-300, (c) BOC-350 (d) BOC-400, (e) BOC-500 and (f) BOC-600.
The XRD patterns of precursor, BOC-250 and BOC-300 are shown in Fig. S4. The BOC-300 can be indexed to pure hexagonal structures of BiOCl (JCPDS File No. 73-2060), while three unknown peaks appeared in the precursor and BOC-250, which may be ascribed to the residual organics. The peaks of BiOCl and three unknown peaks are obviously found in the XRD pattern of the precursor and the unknown peaks gradually reduce with the increase of temperature. When the temperature reached to 300 °C and 350 °C, the precursor completely transformed to pure BiOCl and Bi$_{24}$O$_{31}$Cl$_{10}$, respectively. This result is consistent with the above DSC-TGA analysis of precursor.
Fig. S5. XRD (a) and the magnified XRD patterns (b) of C-doped Bi$_2$O$_3$Cl$_{10}$ via calcining the precursor at 350-600 °C.
Fig. S6. The Raman spectra of BOC-350, BOC-400, BOC-500 and BOC-600.
Fig. S7. The DRS spectra (a) and the plots of $(ahv)^{1/2}$ vs. photon energy ($hv$) (b) of BOC-350, BOC-400, BOC-500 and BOC-600. The insert is the photograph of samples.
Fig. S8. Cl 2p XPS spectra of BOC-350 and BOC-600.
Fig. S9. The DOS plots of C-doped Bi$_{24}$O$_{31}$Cl$_{10}$ (a) and undoped Bi$_{24}$O$_{31}$Cl$_{10}$ (b).
Fig. S10. Photocatalytic Cr(VI) reduction over BOC-350 and BOC-600 under 475 nm (a) and 500 nm (b) monochromatic light irradiation.

Compared to the very limited activity of Cr(VI) reduction on BOC-600, BOC-350 exhibits a desirable activity under 475 and 500 nm monochromatic light irradiation. It confirms the enhanced optical ability of BOC-350 and suggests the band structure is changed by carbon doping strategy.
Fig. S11. Time-dependent absorption spectra of (a) NBT and (b) TA oxidation using BOC-350.
Fig. S12. Photocatalytic Cr(VI) reduction over as-synthesized under visible light irradiation. (a) Dynamic curves, (b) pseudo-first-order kinetic plots and rate constant $k$, (c) absorption spectra variations and (d) cycling experiments of Cr(VI) reduction over of BOC-350.

The photocatalytic activities for Cr(VI) reduction of the samples under visible light are displayed in Fig. S12. Fig. S12a shows the time-dependent reduction curves of Cr(VI) within 30 min. It is clearly observed that BOC-350 reveals the best performance among all of the photocatalysts, with a nearly 100% reduction efficiency. The pseudo-first-order kinetic plots and rate constant $k$ of Cr (VI) reduction with different photocatalysts are shown in Fig. S12b. The rate constant $k$ of BOC-350 reaches 0.135 min$^{-1}$, which is higher than the other materials. Additionally, the absorbance variation of Cr(VI) solutions during the photocatalytic process over BOC-350 is described in Fig. S12c. It is noteworthy that the Cr(VI) are completely reduced to Cr(III) after 30 min. Furthermore, BOC-350 exhibits a good cycling performance for Cr(VI) reduction, which demonstrates BOC-350 is a stable photocatalyst (Fig. S12d).
Fig. S13. CO generation rate using CO\textsubscript{2} and Ar as reaction gas.
**Fig. S14.** Degradation universality of BOC-350. Dynamic curves of photodegradation (a) oxytetracycline hydrochloride (OTC), (b) phenol A (BPA) and (c) rhodamine B (RhB) on BOC-350 and BOC-600 under visible light irradiation. (d) Trapping experiment of active species for RhB degradation of BOC-350.
Fig. S15. Nitrogen adsorption–desorption isotherms of BOC-350 and BOC-600.
Fig. S16. Simultaneous DSC-TGA curves of as-synthesised precursor using tetracycline hydrochloride as halide source.
Fig. S17. XRD pattern of as-prepared sample with the strategy by using tetracycline hydrochloride as halide source (a) and magnified peaks from 22 ° to 27 ° (b). The insert picture is the sample by treating the precursor at 350 °C.
Fig. S18. SEM images (a,b) and EDS spectrum (c) of as-prepared Bi$_{24}$O$_{31}$Cl$_{10}$ obtained at 350 °C by using tetracycline hydrochloride as organic halide source.
Fig. S19. Photocatalytic activity for Cr(VI) reduction under (a) visible light and (b) 500 nm monochromatic light irradiation over as-prepared samples.

The carbon doping strategy is regulated by using tetracycline hydrochloride as halide and carbon source to detect the universality. The DSC-TGA curve of the precursor (Fig. S16), the XRD pattern (Fig. S17), the SEM images (Fig. S18) and the photocatalytic activities towards Cr(VI) reduction (Fig. S19) are consistent with the results of carbon doping strategy involving oxytetracycline hydrochloride.
Table S1. The content of Bi, O, Cl and C in BOC-350.

<table>
<thead>
<tr>
<th>Element</th>
<th>Bi 4f</th>
<th>Cl 2p</th>
<th>O 1s</th>
<th>C 1s</th>
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<tr>
<td>PP At%</td>
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<td>4.1</td>
<td>12.83</td>
<td>3.52</td>
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