Supporting Information

Elegant Z-scheme-Dictated g-C₃N₄ Enwrapped WO₃

Superstructures: A Multifarious Platform for Versatile Photoredox Catalysis

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Fig. S1. TGA results of (a) g-C$_3$N$_4$ and (b) W-AA-CN, W-EA-CN, W-NTA-CN, WO$_3$. 
Fig. S2. Molecular structures of acetic acid (AA), ethanedioic acid (EA) and nitrilotriacetic acid (NTA) used for the synthesis of different WO₃ superstructures.
Fig. S3. FESEM images of WO$_3$ prepared without using organic acids.
Fig. S4. ESR spectra of oxygen vacancy for W-AA, W-EA and W-NTA.
Fig. S5. (a) Possible growth mechanism of WO$_3$ superstructures induced by organic acids. TEM images of (b) W-AA-CN, (c) W-EA-CN and (d) W-NTA-CN heterostructures.
**Note:** Fig. S6 shows the FTIR spectra of W-EA, g-C$_3$N$_4$, and W-EA-CN. The FTIR spectra of W-EA and W-EA-CN illustrate the characteristic absorption bands at 450–760 cm$^{-1}$, which are attributed to the W-O stretching and W-O-W bridging stretching modes$^{1,2}$. FTIR spectrum of g-C$_3$N$_4$ is featured by the presence of several peaks located between 1200 and 1650 cm$^{-1}$, which can be assigned to the stretching vibration mode of aromatic C-N heterocycles containing either trigonal N(-C)$_3$ or bridging C-NH-C units, indicating the formation of C-N-C bonds$^{3,4}$. Additionally, a broad band at around 3430 cm$^{-1}$ was clearly seen in the FTIR spectrum of g-C$_3$N$_4$, indicative of the stretching vibration mode of N-H groups$^{5,6}$. Noteworthily, all characteristic peaks of g-C$_3$N$_4$ can be clearly observed in the FTIR spectrum of W-EA-CN, verifying successful attachment of g-C$_3$N$_4$ on the WO$_3$ framework.

**Fig. S6.** FTIR spectra of W-EA, g-C$_3$N$_4$, and W-EA-CN.
Fig. S7. Survey XPS spectra of (a) W-AA, (b) W-EA and (c) W-NTA.
**Tab. S1.** $E_g$, $E_{CB}$ and $E_{VB}$ of WO$_3$ and g-C$_3$N$_4$ in blank sample and heterostructures.

<table>
<thead>
<tr>
<th></th>
<th>$E_g$/eV</th>
<th>$E_{VB}$/eV</th>
<th>$E_{CB}$/eV</th>
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<tbody>
<tr>
<td>W-AA</td>
<td>2.75</td>
<td>+3.37</td>
<td>+0.62</td>
</tr>
<tr>
<td>W-EA</td>
<td>2.56</td>
<td>+3.27</td>
<td>+0.71</td>
</tr>
<tr>
<td>W-NTA</td>
<td>2.67</td>
<td>+3.33</td>
<td>+0.66</td>
</tr>
<tr>
<td>g-C$_3$N$_4$</td>
<td>2.68</td>
<td>+1.57</td>
<td>−1.11</td>
</tr>
<tr>
<td>W-AA-CN</td>
<td>2.70</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>W-EA-CN</td>
<td>2.61</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>W-NTA-CN</td>
<td>2.66</td>
<td>–</td>
<td>–</td>
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</table>
Fig. S8. Survey and high-resolution XPS spectra of W-EA-CN heterostructure before and after five successive cyclic photocatalytic reactions.
Fig. S9. Specific surface areas of (a) W-AA, (b) W-EA, (c) W-NTA, (d) W-AA-CN, (e) W-EA-CN and (f) W-NTA-CN heterostructures.

Tab. S2. Specific surface area, pore volume and pore size of different samples.

<table>
<thead>
<tr>
<th></th>
<th>BET surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (nm)</th>
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<tbody>
<tr>
<td>W-AA</td>
<td>97.5</td>
<td>0.385</td>
<td>6.2</td>
</tr>
<tr>
<td>W-AA-CN</td>
<td>44.2</td>
<td>0.291</td>
<td>10.3</td>
</tr>
<tr>
<td>W-EA</td>
<td>128.9</td>
<td>0.200</td>
<td>5.3</td>
</tr>
<tr>
<td>W-EA-CN</td>
<td>65.6</td>
<td>0.175</td>
<td>8.4</td>
</tr>
<tr>
<td>W-NTA</td>
<td>167.6</td>
<td>0.488</td>
<td>10.4</td>
</tr>
<tr>
<td>W-NTA-CN</td>
<td>112.7</td>
<td>0.154</td>
<td>11.2</td>
</tr>
</tbody>
</table>
Fig. S10. UV-vis spectra of phenol (270 nm) degraded by (a) W-EA, (b) g-C$_3$N$_4$ and W-EA-CN.

Fig. S11. UV-vis spectra of salicylic acid (300 nm) degraded by (a) W-EA, (b) g-C$_3$N$_4$ and W-EA-CN.

Fig. S12. UV-vis spectra of Cr(VI) (364 nm) degraded by (a) W-EA, (b) g-C$_3$N$_4$ and W-EA-CN.
Fig. S13. UV-vis spectra of 4-nitroaniline (380 nm) degraded by (a) W-EA, (b) g-C$_3$N$_4$ and W-EA-CN.

Fig. S14. UV-vis spectra of 2-nitroaniline (412 nm) degraded by (a) W-EA, (b) g-C$_3$N$_4$ and W-EA-CN.

Fig. S15. UV-vis spectra of 3-nitroaniline (279 nm) degraded by (a) W-EA, (b) g-C$_3$N$_4$ and W-EA-CN.
Fig. S16. UV-vis spectra of nitrobenzene (268 nm) degraded by (a) W-EA, (b) g-C$_3$N$_4$ and W-EA-CN.

Fig. S17. UV-vis spectra of 2-nitrophenol (352 nm) degraded by (a) W-EA, (b) g-C$_3$N$_4$ and W-EA-CN.

Fig. S18. UV-vis spectra of 3-nitrophenol (272 nm) degraded by (a) W-EA, (b) g-C$_3$N$_4$ and W-EA-CN.

Fig. S19. UV-vis spectra of 4-nitrophenol (317 nm) degraded by (a) W-EA, (b) g-C$_3$N$_4$ and W-EA-CN.
Appendix: bandgap energy calculation

The bandgap energy of the photocatalysts is calculated based on the following equations\textsuperscript{7,8}:

\[ \alpha h\nu = A(h\nu - E_g)^{n/2} \]  \hspace{1cm} (1)

where \( h \), \( \nu \), \( A \), and \( E_g \) are absorption coefficient, Planck constant, light frequency, proportionality and bandgap energy, respectively.

The band edge positions of CB and VB for semiconductors can be determined by the following equations:

\[ E_{VB} = X - E_e + 0.5E_g \]  \hspace{1cm} (2)

\[ E_{CB} = E_{VB} - E_g \]  \hspace{1cm} (3)
where $X$ is the absolute electronegativity of the semiconductor, $X$ are 4.73 and 6.49 eV for $\text{g-C}_3\text{N}_4$ and $\text{WO}_3$ and $E_e$ is the energy of free electrons on the hydrogen scale (ca. 4.5 eV).

References