Supporting Information

Catalytic oxidation of formaldehyde over a Au@Co$_3$O$_4$ nanocomposite catalyst enhanced by visible light: Moisture indispensability and reaction mechanism

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Text S1. Catalyst synthesis

In order to ensure the objectivity of the control experiment, we prepared TiO$_2$, Au@TiO$_2$, Au@Co$_3$O$_4$-0.5, Au@Co$_3$O$_4$-2 by the same method as Co$_3$O$_4$ and Au@Co$_3$O$_4$.

TiO$_2$: 0.142 mL of Titanium isopropoxide solution ($C_{12}H_{28}O_4Ti$, 0.954 g cm$^{-3}$) was added into 150 mL water (70 °C), and stirred continuously at 15 rpm for 1 min. After that, 9 mL of ammonia solution (NH$_3$·H$_2$O, 0.16-0.19 M) was added and stirred continuously at 15 rpm for 22 min (70 °C). After cooling down to room temperature (30 °C), the precipitate was collected by centrifugation (12000 rpm, 5 min), and washed with distilled water (100 mL) and methanol (40 mL). Finally, the obtained black powder (noted as TiO$_2$) was dried at 70 °C for 12 h. And proved to be amorphous TiO$_2$ by XRD (Fig. S11).

Au@TiO$_2$: 1260 μL of chloroauric acid solution (HAuCl$_4$, 0.029 M) was mixed with 150 mL water (70 °C), and stirred at 15 rpm for 1 min. Then, 0.142 mL of Titanium isopropoxide solution ($C_{12}H_{28}O_4Ti$, 0.954 g cm$^{-3}$) was added into the obtained solution, and stirred continuously at 15 rpm for 1 min. After that, 9 mL of ammonia solution (NH$_3$·H$_2$O, 0.16-0.19 M) was added and stirred continuously at 15 rpm for 22 min (70 °C). After cooling down to room temperature (30 °C), the precipitate was collected by centrifugation (12000 rpm, 5 min), and washed with distilled water (100 mL) and methanol (40 mL). Finally, the obtained black powder (noted as Au@TiO$_2$) was dried at 70 °C for 12 h. It mainly contains Au and amorphous TiO$_2$ was ensured by XRD (Fig. S11).

Au@Co$_3$O$_4$-0.5, 500 μL of chloroauric acid solution (HAuCl$_4$, 0.029 M) was mixed with 150 mL water (70 °C), and stirred at 15 rpm for 1 min. Then, 4.8 mL of cobalt nitrate solution (Co(NO$_3$)$_2$, 0.1 M) was added into the obtained solution, and stirred continuously at 15 rpm for 1 min. After that, 9 mL of ammonia solution (NH$_3$·H$_2$O, 0.16-0.19 M) was added and stirred continuously at 15 rpm for 22 min (70 °C). After cooling down to room temperature (30 °C), the precipitate was collected by centrifugation (12000 rpm, 5 min), and washed with distilled water (100 mL) and methanol (40 mL). Finally, the obtained black powder (noted as Au@Co$_3$O$_4$-0.5) was dried at 70 °C for 12 h. It mainly contains Au and Co$_3$O$_4$ was ensured by XRD (Fig. S11).
Au@Co₃O₄-2, 2000 μL of chloroauric acid solution (HAuCl₄, 0.029 M) was mixed with 150 mL water (70 °C), and stirred at 15 rpm for 1 min. Then, 4.8 mL of cobalt nitrate solution (Co(NO₃)₂, 0.1 M) was added into the obtained solution, and stirred continuously at 15 rpm for 1 min. After that, 9 mL of ammonia solution (NH₃·H₂O, 0.16-0.19 M) was added and stirred continuously at 15 rpm for 22 min (70 °C). After cooling down to room temperature (30 °C), the precipitate was collected by centrifugation (12000 rpm, 5 min), and washed with distilled water (100 mL) and methanol (40 mL). Finally, the obtained black powder (noted as Au@Co₃O₄-2) was dried at 70 °C for 12 h. It mainly contains Au and Co₃O₄ was ensured by XRD (Fig. S11).

Text S2. Determination of formaldehyde and intermediate byproducts by GC-MS

The tail gas was extracted by solid-phase microextraction and detected by a gas chromatography-mass spectrometry system (GCMS) (Agilent 7890B-5977B) with O-(2,3,4,5,6-Pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) as derivate reagent, with a DB-5ms capillary column (30 m × 0.25 mm × 0.25 μm). GC temperature program of column was 60 °C for 1 min, rose to 260 °C at 7 °C min⁻¹ holding for 1 min. Mass spectra was performed in full scan mode with an m/z range of 30-280, while the temperature of the transfer line was 300 °C, recorded in electron ionization mode at an ion source temperature of 230 °C.

Text S3. Determination of intermediate byproducts by HPLC

Total 10 mg of the catalyst after the catalytic reaction was immersed in 2 ml of deionized water, and filtering it after ultrasonic treatment for 5 min. Then the filtrate was detected by High-performance liquid chromatography (HPLC) (Agilent 1260) with an Athena C18-WP chromatographic column (10 nm, 4.6 × 150 mm, 5 μm). The amount of sample injected each time is 20 μL, 0.02% phosphoric acid solution is used as the mobile phase, the detection wavelength is 210 nm, and the flow rate is 1 mL min⁻¹. Use formic acid solution and sodium bicarbonate solution for qualitative analysis.

All reagents used above were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China) and employed as received without further purification.
Table S1. Overview of the photocatalytic activities in formaldehyde oxidation of various catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight/g</th>
<th>Concentration/ppm</th>
<th>GHSV/mL g⁻¹ h⁻¹</th>
<th>Catalytic conditions</th>
<th>Removal efficiency</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au@Co₃O₄</td>
<td>0.01</td>
<td>75</td>
<td>300000</td>
<td>200 mW/cm² Xenon lamp 360 – 850 nm, Dynamic flow, 25 °C, RH 76%</td>
<td>91.5%: 15 min (dark) 98.7%: 15 min (light)</td>
<td>This work</td>
</tr>
<tr>
<td>g-C₃N₄</td>
<td>0.1</td>
<td>180</td>
<td></td>
<td>8w fluorescent lamp Chamber</td>
<td>26%: (dark) 57%: 7h (light)</td>
<td>¹</td>
</tr>
<tr>
<td>g-C₃N₄/CeO₂</td>
<td>0.1</td>
<td>180</td>
<td></td>
<td>8w fluorescent lamp Chamber</td>
<td>21%: (dark) 70%: 7h (light)</td>
<td>¹</td>
</tr>
<tr>
<td>CeO₂</td>
<td>0.1</td>
<td>180</td>
<td></td>
<td>8w fluorescent lamp Chamber</td>
<td>22%: (dark) 63%: 7h (light)</td>
<td>¹</td>
</tr>
<tr>
<td>g-C₃N₄/CeO₂</td>
<td>0.1</td>
<td>140</td>
<td></td>
<td>8w fluorescent lamp Chamber</td>
<td>70.0%: 9h (dark) 77.1%: 9h (light)</td>
<td>²</td>
</tr>
<tr>
<td>CeO₂/CN-1:1</td>
<td>0.3</td>
<td>65 ± 5</td>
<td></td>
<td>100 mW/cm² Xe lamp ≥420 nm, Dynamic flow, RH 60%</td>
<td>52%: 120 min (dark) 100%: 90 min (light)</td>
<td>³</td>
</tr>
<tr>
<td>Sn-CaSn(OH)₆</td>
<td>0.4</td>
<td>47.8</td>
<td></td>
<td>Uv lamp (365 nm) Dynamic flow,</td>
<td>79.3%: 12min (light)</td>
<td>⁴</td>
</tr>
<tr>
<td>BiSbO₄</td>
<td>0.4</td>
<td>150000</td>
<td></td>
<td>Mercury lamp, 300W Dynamic flow,</td>
<td>92.0%: 20min (light)</td>
<td>⁵</td>
</tr>
<tr>
<td>CuO/TiO₂</td>
<td>0.1</td>
<td>180</td>
<td></td>
<td>500W Xe lamp Chamber, RH 40%</td>
<td>90.3%: 150min (light)</td>
<td>⁶</td>
</tr>
<tr>
<td>Eu/CeO₂</td>
<td>0.1</td>
<td>500</td>
<td></td>
<td>100W halogen lamp Chamber, 25 °C</td>
<td>80.0%: 120 min (light)</td>
<td>⁷</td>
</tr>
<tr>
<td>CeO₂</td>
<td>0.1</td>
<td>500</td>
<td></td>
<td>100W halogen lamp Chamber, 25 °C</td>
<td>18.8%: 120min (light)</td>
<td>⁷</td>
</tr>
</tbody>
</table>
**Scheme S1.** Schematic of the experimental system. (1) Check value; (2) Pressure gage; (3) Evaporation tank with water; (4) RH gage; (5) Xenon lamp and its power supply; (6) Sample bin; (7) Sample port for gas detection tube.

**Fig. S1.** Schematic of the synthetic route of Au@Co₃O₄ nanocomposite.
**Fig. S2.** The spectral range of the xenon lamp: all optical (a), <420 nm (b), 420-800 nm (c), >800 nm (d).

**Fig. S3.** SEM image of Au@Co$_3$O$_4$ nanocomposite (a), Co(OH)$_2$ and prepared Co$_3$O$_4$. 
Fig. S4. EDS spectrum map of Au@Co$_3$O$_4$ nanocomposite.

Fig. S5. XRD patterns of Co(OH)$_2$. 
Fig. S6. XRD patterns of prepared Co$_3$O$_4$ and Au@Co$_3$O$_4$ nanocomposite.

Fig. S7. Nitrogen adsorption-desorption isotherms (a) and the corresponding pore size distributions (b) of prepared Co$_3$O$_4$ and Au@Co$_3$O$_4$ nanocomposite.

Fig. S8. Pyr-DRIFT (a) and NH$_3$-DRIFT (b) of prepared Co$_3$O$_4$ and Au@Co$_3$O$_4$ nanocomposite.
Fig. S9. XPS of Au@Co₃O₄-OTT: survey (a), Co 2p (b), Au 4f (c) and O1 s (d).

Fig. S10. ESR of Au@Co₃O₄ nanocomposition.
Fig. S11. XRD patterns of TiO$_2$, Au@TiO$_2$, Au@Co$_3$O$_4$-0.5 and Au@Co$_3$O$_4$-2.
Fig. S12. Control experiment: formaldehyde elimination efficiency (a, b), CO\(_2\) concentration (c, d) and formaldehyde mineralization (e, f) of TiO\(_2\), Au@TiO\(_2\), Au@Co\(_3\)O\(_4\)-0.5, Au@Co\(_3\)O\(_4\)-2 in the dark and visible-light irradiation (RH: 45%) in a flow of formaldehyde (75 ppm) at GHSV of 300000 mL h\(^{-1}\) g\(^{-1}\) (30 °C, 300 W Xenon lamp).
**Fig. S13.** Formaldehyde elimination efficiency both in the dark and visible-light irradiation at RH 45% in a flow of formaldehyde (75 ppm) at GHSV of 300000 mL h⁻¹ g⁻¹ (30 °C, 300 W Xenon lamp).

**Fig. S14.** XRD pattern (a) and SEM image (b) of Au@Co₃O₄ nanocomposite after catalytic reaction.
Fig. S15. Formaldehyde elimination efficiency both in the dark and visible-light irradiation at the low concentration of formaldehyde (1 ppm) in the simulate actual indoor conditions (RH 45%).

Fig. S16. PTR-QMS mass spectra with formaldehyde elimination in the dark and visible-light irradiation over Au@Co$_3$O$_4$ nanocomposite. (The tail gas collected via gas bag and diluted with nitrogen, followed by pumped into PTR-QMS)
Fig. S17. HPLC chromatogram of the intermediate byproducts of formaldehyde under different conditions (a), CH$_2$O (b), and NaHCO$_3$ (c).

Fig. S18. Dynamic changes of in situ DRIFTS of Au@Co$_3$O$_4$ nanocomposite in different conditions, dehydration with N$_2$ purging at 120 °C (a), adsorption and activated H$_2$O at 30 °C (b), adsorption or elimination of formaldehyde after adsorption and activated H$_2$O at 30 °C (c) and N$_2$ + H$_2$O purging after elimination of formaldehyde at RH 45%, 30 °C.
**Fig. S19.** $O_2$-TPD profiles of Au@Co$_3$O$_4$ nanocomposite (Au@Co$_3$O$_4$ adsorbed oxygen under light).

**Fig. S20.** PL spectra of prepared Co$_3$O$_4$ and Au@Co$_3$O$_4$ nanocomposition.
References


