Template free mild hydrothermal synthesis of core-shell Cu$_2$O(Cu)@CuO visible light photocatalysts for N-acetyl-para-aminophenol degradation

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Fig. S1. Low magnification FE-SEM images of (a) Cu$_2$O@CuO-A, (b) Cu$_2$O@CuO-B, (c) Cu$_2$O@CuO-C, and (d) Cu$_2$O@CuO-D.
**Fig. S2.** N$_2$ adsorption-desorption isotherms of Cu$_2$O@CuO photocatalysts.

**Fig. S3.** Low magnification TEM images of (a) Cu$_2$O@CuO-A, (b) Cu$_2$O@CuO-B, (c) Cu$_2$O@CuO-C, and (d) Cu$_2$O@CuO-D, and (e-f) EDX elemental maps of Cu$_2$O@CuO-B.
Fig. S4. (a-c) Dark field (S)TEM and (b) bright field TEM images of Cu$_2$O@CuO-B, and (d) variation in EDX elemental compositions determined across a single rattle-like core-shell nanoparticle.
**Fig. S5.** Tauc plot for (a) Cu$_2$O@CuO-A, (b) Cu$_2$O@CuO-B, (c) Cu$_2$O@CuO-C, and (d) Cu$_2$O@CuO-D.

**Fig. S6.** Valence band XP spectra of Cu$_2$O@CuO photocatalysts.
Table S1. Photocatalytic APAP degradation comparison.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rate constant / min⁻¹</th>
<th>Catalyst mass and APAP concentration</th>
<th>Flux of light source</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>0.0105</td>
<td>0.4 g.L⁻¹ catalyst, 4 μM APAP</td>
<td>15 W UV-C lamp (254 nm), 12.6 mW/cm²</td>
<td>1</td>
</tr>
<tr>
<td>Cu/TiO₂</td>
<td>0.0243</td>
<td>4.0 g.L⁻¹ catalyst APAP 25 mL</td>
<td>Rayonet RPR-100 photoreactor equipped with 16 visible light lamps</td>
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</tr>
<tr>
<td>Pt/TiO₂</td>
<td>0.030</td>
<td>5 mg.L⁻¹ catalyst, 40 μM APAP</td>
<td>UV-C low-pressure Hg lamp (254 nm) 107.4 W/cm²</td>
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<tr>
<td>ZnO nanorod</td>
<td>0.0125</td>
<td>100 mg catalyst, 50 mg.L⁻¹ APAP</td>
<td>300 W Xe lamp (UV) with external applied bias</td>
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</tr>
<tr>
<td>ZnFe-LDH/rGO</td>
<td>0.0074</td>
<td>25 mg catalyst, 5 mg.L⁻¹ APAP</td>
<td>500 W Xe lamp (300 nm cut-off filter)</td>
<td>5</td>
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<tr>
<td>Hollow TiO₂</td>
<td>0.0448</td>
<td>50 mg.L⁻¹ APAP</td>
<td>500W Hg-lamp (UV)</td>
<td>6</td>
</tr>
<tr>
<td>Cu₂O@CuO-B</td>
<td>0.0679</td>
<td>20 mg catalyst, 0.06 mM APAP</td>
<td>500 W Xe lamp with 400 nm cut-off filter, 1.82 mW/cm²</td>
<td>Present work</td>
</tr>
</tbody>
</table>

Fig. S7. HPLC of reaction mixture (a) before and (b) after photocatalytic APAP degradation presence of Cu₂O@CuO-B.
**Fig. S8.** HPLC of reactively-formed DNPH-HCHO resulting from DMSO oxidation to formaldehyde in the presence of Cu$_2$O@CuO-B under visible light. Conditions: 20 mg Cu$_2$O@CuO-B; 50 mL of 250 µM DMSO; 1 mL samples derivatized using 20 µL H$_3$PO$_4$-NaH$_2$PO$_4$ buffer and 200 µL of 240 µmol/L DNPH. JASCO LC-netII/ADC HPLC with UV-2075 (355 nm) detector and a Shodex C18M4E analytical column (4.6 mm I.D × 250 mm) held at 32.2 °C and 17.4 MPa; mobile phase of 60:40 (v/v) methanol:water; flow rate of 0.8 mL/min.

**Fig. S9.** Recycling of APAP photocatalytic degradation over Cu$_2$O@CuO under visible light.
Apparent quantum efficiency (AQE) determination
The apparent quantum efficiency under visible light irradiation was measured at 420 nm with a band-pass filter
according to the following equations:

$$\text{Apparent quantum efficiency (\%)} = \frac{\text{Mols of reacted electrons per unit time}}{\text{Mols of incident photons per unit time}} \times 100 \quad (S1)$$

Mols incident photons per unit time ($N_{\text{Einstein}}$) = Number incident photons per unit time / $N_{\lambda}$

Number of incident photons $N_p$ per unit time can be calculated by:

$$N_p = \frac{\text{Intensity (E)}}{\text{Photon energy (E_p)}} \quad \text{and} \quad \text{photon energy (E_p)} = \frac{hc}{\lambda} \quad (S2)$$

$$E = \text{Irradiance} \times \text{reactor area illuminated}$$

$$E_p = \frac{(6.625 \times 10^{-34} \text{ J.s}) (3 \times 10^{17} \text{ nm.s}^{-1})}{\lambda (\text{nm})} = \frac{19.88 \times 10^{-17}}{\lambda (\text{nm})} = 4.73 \times 10^{-19} \text{ J} \quad (S3)$$

$$N_p = \frac{E}{E_p} = \frac{0.00819}{4.73 \times 10^{-19}} = 1.73 \times 10^{16} \text{ s}^{-1} \quad (S4)$$

$$N_{\text{Einstein}} = \frac{N_p}{N_{\lambda}} = 2.87 \times 10^{-6} \text{ mols.s}^{-1} \quad (S5)$$

For APAP photodegradation:

$$\text{Quantum efficiency (\%)} = \frac{\text{APAP removal rate (mols} - 1\text{)}}{N_{\text{Eins}}} \times 100 \quad (S6)$$
Scheme S1. Band positions of Cu$_2$O@CuO.

References