Simultaneous Induction of High Level Thermo- and Visible Light-Catalytic Activities to Titanium(IV) Oxide by Surface Modification with Cobalt(III) Oxide Clusters

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Experimental

Conversion of 2-naphthol to CO₂: In both the thermocatalytic and photocatalytic reactions, TiO₂ or Co₂O₃/TiO₂ (0.25 g) was added to an aqueous solution of 1 mmol dm⁻³ 2-naphthol (10 mL). The suspension was placed in a glass test tube (30 mL). In the dark reaction, the temperature was maintained at 323 K. In the photocatalytic reaction, the test tube was irradiated with a Xe lamp (Wacom XRD-501SW) through a high pass filter (L-42, Toshiba) to cut off UV-light (I₄20-480 nm = 4.0 mW cm⁻²) at 298 K. The CO₂ dissolved in the solution was liberated into the gas phase by adding 0.1 mL sulfuric acid, and then the amount of CO₂ was quantified by gas chromatography (GC-2014, Shimadzu) with methanizer (MTN-1, Shimadzu) [measurement conditions: column = Porapak-Q 80-100 (GL science); N₂ flow rate = 50 mL min⁻¹].

Fig. S1 TEM images of Co₂O₃/TiO₂ with τ = 0, 0.15, and 0.23.

Fig. S2 Time courses for the CO₂ generation in the thermocatalytic reaction in the dark at 323 K in the presence of Co₂O₃(τ = 0.17)/TiO₂ with (red solid circle) and without (red open circle) 2-naphthol, and in the presence of TiO₂ with 2-naphthol (black solid circle).
**Fig. S3** Arrhenius plot for the Co$_2$O$_3$($\Gamma = 0.17$)/TiO$_2$-thermocatalyzed degradation of 2-naphthol (left), and numerical values are shown in the right table.

<table>
<thead>
<tr>
<th>$T / \text{K}$</th>
<th>$k_d / \text{h}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>0.055 ± 0.001</td>
</tr>
<tr>
<td>298</td>
<td>0.100 ± 0.001</td>
</tr>
<tr>
<td>323</td>
<td>0.87 ± 0.02</td>
</tr>
<tr>
<td>353</td>
<td>4.80 ± 0.23</td>
</tr>
</tbody>
</table>

**Fig. S4** (A) Time courses for the CO$_2$ generation in the thermocatalytic degradation of formic acid in the dark at 323 K in the presence of TiO$_2$ (black solid circle) and Co$_2$O$_3$($\Gamma = 0.17$)/TiO$_2$ (red solid circle), and in the presence of TiO$_2$ (black open circle) and Co$_2$O$_3$($\Gamma = 0.17$)/TiO$_2$ (red open circle) without formic acid. (B) Plots of conversion to CO$_2$ at 1 h vs. $\Gamma$. 

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Fig. S5 Time courses for the CO₂ generation in the 2-naphthol degradation under visible-light irradiation at 298 K in the presence of TiO₂ (black solid circle) and Co₂O₃ (Γ = 0.17)/TiO₂ (red solid circle). Plot (red open circle) is the data for Co₂O₃ (Γ = 0.17)/TiO₂ without 2-naphthol.

Fig. S6 (A) Time courses for the CO₂ generation in the degradation of formic acid under visible-light irradiation at 298 K in the presence of TiO₂ (black solid circle) and Co₂O₃ (Γ = 0.17)/TiO₂ (red solid circle), and in the presence of TiO₂ (black open circle) and Co₂O₃ (Γ = 0.17)/TiO₂ (red open circle) without formic acid. (B) Plots of conversion to CO₂ at 1 h vs. Γ.
Fig. S7 Valence-band XPS spectra for Co$_2$O$_3$/TiO$_2$ with varying $\Gamma$. 
**Fig. S8** Current (I/mA)-potential (E/V vs. Ag/AgCl) curves of the mp-TiO$_2$/FTO electrodes with and without the Co$_2$O$_3$-surface modification in a 0.1 mol dm$^{-3}$ NaClO$_4$ aqueous solution in the dark.