Electronic Supplementary Information

An architecture of CdS/H$_2$Ti$_5$O$_{11}$ ultrathin nanobelt for photocatalytic hydrogenation of 4-nitroaniline with highly efficient performance

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Details for preparation of working electrode are as follows:

Firstly, after the FTO was cleaned by sonication in acetone, ethanol and deionized water for 30 min each, a square with 0.5 cm × 0.5 cm was inclosed by adhesive tape on the conductive side of the FTO; Secondly, 10 μL of the well dispersed sample (5 mg of photocatalyst powder was well dispersed in 0.5 mL of DMF via ultrasonication) was extracted by a pipette with a volume range of 2-20 μL and then dropped onto the area mentioned above; thirdly, after air drying naturally, the uncoated parts of the electrode were isolated with an epoxy resin. Subsequently, the electrodes were put into an oven at 100 °C for 2 h. After that, the photocatalytic film with an area of 0.25 cm² was prepared successfully.

High Performance Liquid Chromatogram (HPLC) analysis conditions: Agilent 1260; Ultimate AQ-C18 column (4.6 × 250 mm); H₂O:CH₃CN=75%:25%, v/v, 1mL/min); detection wavenumber (λ =228 nm).
Fig. S1, the FFT patterns of the CdTi-5

**Note:** As evidenced by the analysis of the HRTEM and the corresponding FFT patterns of the CdTi-5, both of the clear crystal lattice and the selected area electron diffraction spots corresponding to CdS and the nanobelt are observed, respectively, indicating that the structure of the nanobelt was sustained. Additionally, it’s clear that the FTIR spectrum of the CdTi-5 (Fig. S2) has no absorption peak at 1360-1480 cm\(^{-1}\), which corresponds to the absorption of $\delta_{as}(\text{CH}_3)$ and $\delta_s(\text{CH}_3)$, indicating that the TBA\(^+\) was decomposed during the hydrothermal process. Furthermore, the reaction solution after hydrothermal process is faintly acid (pH=6), which may transform the titanate nanobelt into protonated H\(_2\)Ti\(_5\)O\(_{11}\). Hence, we believe that the composition of the final photocatalyst is CdS/H\(_2\)Ti\(_5\)O\(_{11}\) nanocomposition.
Fig. S2, FTIR spectrum of the CdS, CdTi-5 and TBAOH, respectively.

Note: It’s clear that the FTIR spectrum of the CdTi-5 has no absorption peak at 1360-1480 cm\(^{-1}\), which corresponds to the absorption of \(\delta_{as}(\text{CH}_3)\) and \(\delta_{s}(\text{CH}_3)\), indicating that the TBA\(^+\) was decomposed during the hydrothermal process. The adsorption at 1650 cm\(^{-1}\) and 2372 cm\(^{-1}\) of the samples are attributed to the dissolved H\(_2\)O and CO\(_2\), respectively. The adsorption at 802 cm\(^{-1}\) of the FTIR of the CdTi-5 arises from the Ti-O.

Fig. S3 the UV-vis spectral changes of the 4-NA aqueous solution; A) CdTi-5 without light; B) no catalyst with light.

Note: the increment of the adsorption range from 200-230 nm arises from the addition of the ammonium formate.
Fig. S4 the analysis of the product by use high performance liquid chromatogram (HPLC); A) qualitative analysis of the retention time of the 4-NA (black) and PPD (red), respectively; B) the analysis of the product during the photocatalytic reduction of 4-NA. The inset in B is the Uv-vis spectral changes of the 4-NA aqueous solution over CdTi-5 under the irradiation of light.

Fig. S4 clearly demonstrates that the content of the 4-NA decreased and that of the PPD increased along with the reaction. Based on the calculation via peak area, the conversion and the selectivity from 4-NA to PPD are 96 and 86%, respectively. This result is slightly different from that via the analysis of Uv-vis, which may result from the different LOD (limit of detection) of the analytical method. Hence, based on the result above, it is certain that the variation of the concentration of the 4-NA arises from photocatalytic reaction rather than adsorption.
Table 1. peak area of the product in different reaction time

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<tr>
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<th>4-NA</th>
<th>PPD</th>
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<tbody>
<tr>
<td>$S_{20 \text{ ppm}}$</td>
<td>521</td>
<td>295</td>
</tr>
<tr>
<td>$S_0$</td>
<td>482</td>
<td>0</td>
</tr>
<tr>
<td>$S_3$</td>
<td>20</td>
<td>189</td>
</tr>
</tbody>
</table>

Note: $S_{20 \text{ ppm}}$ of 4-NA and PPD represents the peak area of the origin 20 ppm of 4-NA and PPD, respectively.

$S_0$ and $S_3$ represent the peak area of the product after photocatalytic reaction for 0 and 3 mins, respectively.

Conversion (%) of 4-NA = \( \frac{S_3 \cdot S_0}{S_0} \)

Selectivity (%) of PPD = \( \frac{S_3}{S_{\text{theoretical value}}} \)

\[
S_{\text{theoretical value}} = \frac{M_{\text{PPD}}}{M_{4-\text{NA}}} \times S_{20\text{ppm (PPD)}} \times \text{Conversion (4-NA)}
\]
Fig. S5A) Pseudo-first-order kinetic plots for the reduction of 4-NA over the typical samples. The inset in A is the corresponding time course of the reduction of 4-NA; B) comparison of rate constant over the typical samples.

Note: The pseudo-first-order rate constants are calculated from the slope of the kinetic curve.
Fig. S6, the XPS spectra of the Ti 2p, O 1s, Cd 3d and S 2p for the CdTi-5 before and after the photocatalytic reaction, respectively.

Fig. S7, the XRD patterns of the CdTi-5 before and after the photocatalytic reaction.
Fig. S8 Typical Mott-Schottky plots of A) (TBA)$_2$Ti$_5$O$_{11}$; B) Layered H$_2$Ti$_5$O$_{11}$. The inset is the corresponding UV-vis DRs absorption spectrum.

Note: Based on the analysis of the Mott-Schottky plots and the Uv-vis spectra, the energy band position and the bandgap of the layered H$_2$Ti$_5$O$_{11}$ and the (TBA)$_2$Ti$_5$O$_{11}$ nanoblet are displayed below (Table 2). It's clear that the energy band position and the bandgap of the ultrathin nanobelt are different from that of the layered H$_2$Ti$_5$O$_{11}$, which is similar with the case of the exfoliation of the H$_2$Ti$_4$O$_9$ reported by Allen[1].


Table 2. the energy band position and the bandgap of the ultrathin nanobelt and layered compound

<table>
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<tr>
<th></th>
<th>CB</th>
<th>VB</th>
<th>$E_g$</th>
</tr>
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<tbody>
<tr>
<td>Layered-H$_2$Ti$<em>5$O$</em>{11}$</td>
<td>-1.02</td>
<td>2.22</td>
<td>3.24</td>
</tr>
<tr>
<td>(TBA)$_2$Ti$<em>5$O$</em>{11}$</td>
<td>-0.76</td>
<td>2.43</td>
<td>3.19</td>
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