Supplementary information

Synergistic Effect of 2D Ti$_2$C and g-C$_3$N$_4$ for efficient photocatalytic hydrogen production

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Fig. S1 XRD patterns of Ti$_2$C and Ti$_2$AlC.

Fig. S2 SEM images of (a) Ti$_2$AlC and (b) Ti$_2$C. EDX elemental mapping for (c) Ti$_2$AlC and (d) Ti$_2$C.
Fig. S3 (a) TG curves of g-C₃N₄ and TiCN and (b) the enlarged views of (a) in a range of 700-800 °C.

Fig. S4 XPS spectra of N 1s and O 1s for g-C₃N₄, TiCN-0.4 and TiCN-1.0.

Fig. S5 N₂ adsorption-desorption isotherms of g-C₃N₄, TiCN-0.1, TiCN-0.2, TiCN-0.4,
TiCN-0.8 and TiCN-1.0.

Fig. S6 Photocatalytic hydrogen production rates of g-C$_3$N$_4$, TiCN-0.4, TiCN-0.4-mixed (Ti$_2$C and g-C$_3$N$_4$ physical mixing), Ti$_2$AlC/g-C$_3$N$_4$-0.4 and no catalyst.

Fig. S7 Recycling studies of hydrogen production over g-C$_3$N$_4$ (a) and Ti$_2$C (b). The reaction system was purged with N$_2$ before every cycling.
Fig. S8 XRD patterns of TiCN-0.4 and after cycling 10 times.

Fig. S9 SEM images of TiCN-0.4: as prepared (a, b) and after cycling 10 times (c, d).
Fig. S10 EDS elemental mapping for TiCN-0.4: a) as prepared and b) after cycling 10 times; XPS spectra of O 1s for TiCN-0.4: as prepared and after cycling 10 times. Notes: the high percentage of Cu in the EDS mapping of TiCN-0.4 is attributed to the Cu substrate.
**Fig. S11 UV-vis adsorption spectra of TiCN-0.4: as prepared and after cycling 10 times.**
<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Amount of photocatalyst (mg)</th>
<th>Co-catalyst</th>
<th>Loading method</th>
<th>Optimum loading</th>
<th>Light source</th>
<th>Hydrogen production rate (μmol/h/g)</th>
<th>Reference</th>
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<tr>
<td>TiCN-0.4</td>
<td>50</td>
<td>Ti₂C</td>
<td>Calcination</td>
<td>0.4 wt%</td>
<td>solar simulator AM 1.5</td>
<td>950</td>
<td>This work</td>
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<td>Pt/g-C₃N₄</td>
<td>50</td>
<td>Pt</td>
<td>Adsorption-deposition</td>
<td>1 wt%</td>
<td>350 W Xe lamp</td>
<td>588</td>
<td>1</td>
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<tr>
<td>MoSₓ/g-C₃N₄</td>
<td>50</td>
<td>MoSₓ</td>
<td>Adsorption-in situ transformation</td>
<td>3 wt%</td>
<td>four low-power LEDs</td>
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<td>2</td>
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<td>CoP/g-C₃N₄</td>
<td>100</td>
<td>CoP</td>
<td>Grinding</td>
<td>0.25 wt%</td>
<td>300 W Xe lamp</td>
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<td>Ni/g-C₃N₄</td>
<td>10</td>
<td>Ni</td>
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<tr>
<td>Cu/g-C₃N₄</td>
<td>50</td>
<td>Cu</td>
<td>Milling</td>
<td>3 wt%</td>
<td>Xe lamp</td>
<td>20.5</td>
<td>5</td>
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<tr>
<td>Ag₂S/g-C₃N₄</td>
<td>50</td>
<td>Ag₂S</td>
<td>Photodeposition</td>
<td>5 wt%</td>
<td>Four low power UV-LEDs</td>
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<td>NiS/g-C₃N₄</td>
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<td>NiS</td>
<td>Hydrothermal</td>
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<td>Ni₂P/g-C₃N₄</td>
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<td>Ni₂P</td>
<td>Hydrothermal</td>
<td>0.4 wt%</td>
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<td>WS₂/g-C₃N₄</td>
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<td>WS₂</td>
<td>Impregnation-sulfidation</td>
<td>0.3 wt%</td>
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<td>Graphene/g-C₃N₄</td>
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<td>Carbon nanotubes/g-C₃N₄</td>
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<td>Carbon nanotubes</td>
<td>Heat treatment</td>
<td>0.5 wt%</td>
<td>300 W Xe lamp</td>
<td>42</td>
<td>11</td>
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Computational method

The density functional theory (DFT) calculations were performed by using the Vienna ab initio simulation package (VASP).\textsuperscript{12,13} To describe the valence and core states, plane wave basis set and projector augmented wave (PAW) potentials were employed with a kinetic energy cutoff of 500 eV.\textsuperscript{14} The Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) exchange and correlation functional was used.\textsuperscript{15} For structure relaxation, both lattice constants and atom coordinates were optimized until the forces converged to less than 0.02 eV/Å. The Monkhorsk-Pack k-point sampling of g-C\textsubscript{3}N\textsubscript{4} and Ti\textsubscript{2}C were 5 × 5 and 15 × 15, respectively. For density of states (DOS) calculations, Gaussian smearing was 0.05 eV and Monkhorsk-Pack k-point sampling of g-C\textsubscript{3}N\textsubscript{4} and Ti\textsubscript{2}C were 7 × 7 and 21 × 21. The vacuum layer was 20 Å in vertical direction.
Fig. S12 The structural models of Ti$_2$AlC, Ti$_2$C and g-C$_3$N$_4$. 
Fig. S13 The calculated band structure of (a) g-C$_3$N$_4$ and (c) TiCN; and the total density of states of (b) g-C$_3$N$_4$ and (d) TiCN.

References: