Electronic Supporting information for manuscript

Chromium-Titanium nitride as efficient co-catalyst for photocatalytic hydrogen production

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Table S1. XPS data for evaluation of the valence states of Ti, Cr, and N and the content of metal-N on the surface of TMN nanocomposites co-catalysts.

Table S2. Comparison of hydrogen production ratio for Cr$_{0.5}$Ti$_{0.5}$N-CdS with the ever-reported metal nitrides and carbides-based photocatalysts.
III. Supplementary References

I. Experimental Procedures

1. Computational Methodology and Model Detail.

The optimized stable structure and electronic characteristic calculations are conducted based on Density Functional Theory (DFT) implemented in quantum Espresso Package\(^1\) in a plane wave basis, with the ultrasoft pseudo-potentials for electron-core interactions. The atomic valence electrons configurations are 2s\(^2\) 2p\(^3\) for N, 3d\(^2\) 3p\(^6\) 4s\(^1\) 3d\(^5\) and 3s\(^2\) 3p\(^6\) 4s\(^2\) 3d\(^2\) for Cr and Ti, respectively. Variable cell optimization was performed using Broyden, Fletcher, Goldfarb, and Shannon (BFGS) algorithm\(^2\). We used our experimental results for the starting point and then the structures were fully relaxed until the residual forces on each atom is less than 10-3 eV. In wave vector K space, plane wave cut-off energy is considered 55 Ry in all calculations and we used a 6×6×6 k-point mesh, generated by the Montkhorste Pack method\(^3\).
II. Supplementary illustrations and explanations

![XRD patterns](image)

**Fig. S1.** XRD patterns of TiN, Cr$_{0.5}$Ti$_{0.5}$N and CrN.

**Note:** The refined lattice parameters of TiN, Cr$_{0.5}$Ti$_{0.5}$N and CrN are $4.2349(6)$ Å, $4.2079(7)$ Å and $4.1515(3)$ Å, respectively, which also indicates the large difference among the three specimens.

![EIS Nyquist plots](image)

**Fig. S2.** EIS Nyquist plots of the sample (a) CrN-Cr$_2$O$_3$; (b) TiN-TiO$_2$.

![DRS](image)

**Fig. S3.** DRS of (a)CrN, Cr$_2$O$_3$, (b)TiN, TiO$_2$ and (c)Cr$_{0.5}$Ti$_{0.5}$N.
Fig. S4. SEM images of pure (a) TiN, (b) CrN, and (c) Cr$_{0.5}$Ti$_{0.5}$N (the inset image is statistic histogram of diameters); TEM images of pure (d) TiN, (e) CrN, and (f) Cr$_{0.5}$Ti$_{0.5}$N.

Note: The nitride product TMNs sample displays the morphology of small nanoparticle and their average particle size are respectively 32.7 nm (TiN), 51 nm (CrN), and 47.8 nm (Cr$_{0.5}$Ti$_{0.5}$N) in the inset image of Fig. S4.

Fig. S5. (a) The HRTEM image of TiN; (b-c) HAADF-STEM image and the element mapping images of Ti, N.
**Fig. S6.** (a) The HRTEM image of CrN; (b-c) HAADF-STEM image and the element mapping images of Cr, N.

**Fig. S7.** (a) XPS survey spectra of TiN, Cr$_{0.5}$Ti$_{0.5}$N, and CrN.

**Fig. S8** TEM images of (a,c) CdS NWs and (b,d) CdS-N NWs.

**Note:** CdS-N NWs are the samples of NH$_3$ treated CdS nanowires.
Fig. S9. Zeta potential of functionalized TMNs and blank CdS NWs.

Note: As shown in Fig. S9, after functionalized with SDS, the Zeta potential of TMNs is changed from positive to negative. Whereas, the Zeta potential analysis on CdS NWs reveals a positively charged surface of CdS. Thus, it is reasonable that the negatively charged SDS-functionalized TMNs and positively charged CdS NWs can spontaneously establish a solid basis of electrostatic attraction for the self-assembly construction of TMNs-CdS composites.

Fig. S10. XRD patterns of CdS and CdS-N NWs.

Note: CdS-N NWs are the samples of NH$_3$ treated CdS nanowires.

Fig. S11. SEM images of (a) CdS NWs; (b) CrN-5-CdS; (c) TiN-10-CdS and (d) Cr$_{0.5}$Ti$_{0.5}$N-12-CdS.
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Fig. S13. UV–vis DRS of (a) CrN-x-CdS; (b) TiN-x-CdS and (c) Cr$_{0.5}$Ti$_{0.5}$N-x-CdS.
Fig. S14. Photocatalytic H$_2$ evolution rates for (a) CrN-x-CdS; (b) TiN-x-CdS and (c) Cr$_{0.5}$Ti$_{0.5}$N-x-CdS.

Fig. S15. Time-resolved hydrogen evolution amount of (a) CrN-x-CdS; (b) TiN-x-CdS; (c) Cr$_{0.5}$Ti$_{0.5}$N-x-CdS and Pt-1-CdS.

Fig. S16. (a) The photocatalytic H$_2$ evolution rate of CdS and CdS-N NWs, (b) Photocatalytic H$_2$ evolution rate of Pt-x-CdS NWs.

Fig. S17. Photocatalytic HER rate over EY-sensitized CrN, TiN, and Cr$_{0.5}$Ti$_{0.5}$N

Note: Typically, 10 mg of the prepared catalyst and 20 mg of Eosin Y were dispersed in 80
mL of a 10% (v/v) triethanolamine-water (TEOA-H$_2$O) solution by ultrasonication for 15 min.

Fig. S18. (a) Cycling tests of Cr$_{0.5}$Ti$_{0.5}$N-12-CdS composite over a period of 24 h, and (b) long-term online tests of Cr$_{0.5}$Ti$_{0.5}$N-12-CdS composite over a period of 96 h.

Fig. S19. (a) XRD patterns, (b-c) SEM of Cr$_{0.5}$Ti$_{0.5}$N-12-CdS nanocomposite before and after the photocatalytic reaction.

Fig. S20 Transient I–t curves of CrN-(3-8)-CdS, Cr$_{0.5}$Ti$_{0.5}$N-(10-15)-CdS, and TiN-(8-10)-CdS without bias potential.
**Fig. S21.** EIS Nyquist plots of CrN, TiN, and $\text{Cr}_{0.5}\text{Ti}_{0.5}\text{N}$. 

**Fig. S22.** Cyclic voltamogram curves of (a) CrN, (b) $\text{Cr}_{0.5}\text{Ti}_{0.5}\text{N}$, and (c) TiN in the double layer capacitive region at the scan rates of from 10 mV to 90 mV.

**Scheme 1** Proposed mechanism for the photocatalytic $\text{H}_2$ generation of the CdS NWs (a) and 1D TMN-CdS nanocomposites (b) under visible light irradiation with lactic acid as the sacrificial agent.
Table S1. XPS data for evaluation of the valence states of Ti, Cr, and N and the content of metal-N on the surface of TMN nanocomposites co-catalysts.

<table>
<thead>
<tr>
<th>Cocatalyst</th>
<th>Ti 2p3/2 (eV) and Area (%)</th>
<th>BE shift</th>
<th>Cr 2p3/2 (eV) and Area (%)</th>
<th>BE shift</th>
<th>N1s (eV)</th>
<th>Metal-N (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN</td>
<td>Ti-N 455.6 (11.94%)</td>
<td></td>
<td>Cr-N 575.66 (57.46%)</td>
<td>+0.24 eV</td>
<td>Cr/Ti-N 396.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ti-O 458.5 (40.13%)</td>
<td></td>
<td>Cr-N 575.66 (57.46%)</td>
<td>+0.24 eV</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ti-O-N 456.95 (47.93%)</td>
<td></td>
<td>Cr-N 575.42 (72.66%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr0.5Ti0.5N</td>
<td>Ti-N 455.88 (31.38%)</td>
<td>+0.28 eV</td>
<td>Cr-O-N 577.1 (42.54%)</td>
<td>-0.25 eV</td>
<td>N-H 399.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ti-O 458.5 (44.82%)</td>
<td>0</td>
<td>Cr-O-N 577.1 (42.54%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ti-O-N 456.72 (23.8%)</td>
<td>-0.23 eV</td>
<td>Cr-O-N 577.1 (42.54%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CrN</td>
<td>Cr-N 575.68 (27.34)</td>
<td></td>
<td>Cr-N 575.42 (72.66%)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: As shown in Table 2, the high-resolution Ti 2p spectra for Cr0.5Ti0.5N and TiN samples. For the high-resolution Ti 2p spectrum of the TiN, the peaks located at 455.6 eV (2p3/2) and 461.32 eV (2p1/2) are in accordance with a metallic state of Ti while peaks of 456.72 eV (2p3/2) and 462.07 eV (2p1/2) are assigned to the Ti-O-N bonds in TiN sample. The peaks of 485.5 eV (2p3/2) revealed the existence of Ti-O, suggesting an oxidized surface which is easily obtained in TMNs materials. Similarly, Cr0.5Ti0.5N also shows three couples of peaks corresponding metallic state of Ti (455.88 eV for Ti 2p3/2 and 461.04 eV for 2p1/2), Ti-O-N bonds (456.95 eV for Ti 2p3/2 and 462.07 eV for 2p1/2) and Ti-O bonds (485.5 eV for Ti 2p3/2), respectively. Notably, over 0.2 eV of Ti 2p spectra for Cr0.5Ti0.5N as compared to that of TiN are observed. This result reveals the reduced electron density of the Ti (TiN Ti) atoms in Ti-N and increased electron density of the Ti atoms in Ti-O-N over Cr0.5Ti0.5N after grafting. As mirrored in Fig. 2c, the peaks at 575.42 eV (CrN-Cr 2p3/2) and 575.66 eV (Cr0.5Ti0.5N-Cr 2p3/2) reveal the existence of Cr-N bonds, while the other two peaks at 577.1 eV (CrN-Cr 2p3/2) and 576.85 eV (Cr0.5Ti0.5N-Cr 2p3/2) are related to Cr-O-N. Clearly, the Cr 2p3/2 and Cr 2p1/2 peaks of Cr-N in the Cr0.5Ti0.5N cocatalyst are shifted about 0.2 eV toward higher binding energy, which indicates the reduction in electron density. Meanwhile, the peaks of Cr-O-N are shifted toward the opposite direction, which reveals that the electron density of the Cr (Cr-O-N) atoms increasing after grafting. These XPS peak shifts could be attributed to the changes of TiN and CrN chemical states in ternary nitride Cr0.5Ti0.5N.
### Table S2. Comparison of hydrogen production ratio for Cr$_{0.5}$Ti$_{0.5}$N-CdS with the ever-reported metal nitrides and carbides-based photocatalysts.

<table>
<thead>
<tr>
<th>Cocatalyst</th>
<th>Photocatalyst</th>
<th>Light source</th>
<th>Reaction solution</th>
<th>PHER rate</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$<em>{0.5}$Ti$</em>{0.5}$N</td>
<td>CdS</td>
<td>300 W Xe, 420 ≥nm</td>
<td>10 v% lactic acid</td>
<td>120</td>
<td>This work</td>
</tr>
<tr>
<td>Ni$_3$N</td>
<td>CdS</td>
<td>300 W Xe, 420 ≥nm</td>
<td>0.25 M Na$_2$S/0.35 M Na$_2$SO$_3$</td>
<td>10</td>
<td>[1]</td>
</tr>
<tr>
<td>Co$_3$N</td>
<td>CdS</td>
<td>300 W Xe, 420 ≥nm</td>
<td>0.75 M Na$_2$S/1.05 M Na$_2$SO$_3$</td>
<td>6.5</td>
<td>[2]</td>
</tr>
<tr>
<td>InN</td>
<td>TiO$_2$</td>
<td>300 W Xe, 420 ≥nm</td>
<td>rhodamine B (Rhb, 2.5 × 10$^{-5}$ mol L$^{-1}$)</td>
<td>45</td>
<td>[3]</td>
</tr>
<tr>
<td>TiN</td>
<td>TiO$_2$</td>
<td>300 W Xe, UV-Vis, 420 ≥nm</td>
<td>10 v% methanol (CH$_3$OH)</td>
<td>UV-Vis 19; Vis 1.3</td>
<td>[4]</td>
</tr>
<tr>
<td>MoC (QDs)/Carbon Film</td>
<td>ZnIn$_2$S$_4$</td>
<td>300 W Xe, 400 ≥nm</td>
<td>10 v% lactic acid</td>
<td>4.8</td>
<td>[5]</td>
</tr>
<tr>
<td>Mo$_2$C@C</td>
<td>CdS</td>
<td>300 W Xe, 420 ≥nm</td>
<td>10 v% lactic acid</td>
<td>25.7</td>
<td>[6]</td>
</tr>
<tr>
<td>Ni$_3$C</td>
<td>CdS</td>
<td>350 W Xe, 420 ≥nm</td>
<td>0.25 mol L$^{-1}$ of Na$_2$S–Na$_2$SO$_3$</td>
<td>7.7</td>
<td>[7]</td>
</tr>
</tbody>
</table>

**Note:** PHER rate denotes the hydrogen evolution rate of times higher than pristine photocatalyst.
III. Supplementary References:


