Interface Engineering in BNNS@Ti$_3$C$_2$ Intercalation Structure for Enhanced Electrocatalytic Hydrogen Evolution


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S1 Morphology of Ti$_3$C$_2$

Fig. S1. SEM image of Ti$_3$C$_2$

Fig. S1 shows that Ti$_3$C$_2$ presents layer structure after HF etching treatment.

S2 AFM image and height profile of BNNS
**Fig. S2.** AFM image and the corresponding height profile (right) of flat BNNS. It can be seen that BNNS possesses the thickness of about 4 nm through effective exfoliation process of NaOH.

**S3 SEM image of BNNS**

**Fig. S3.** SEM image of BNNS

In **Fig. S3**, after NaOH treatment, bulk h-BN is exfoliated to few separated layers successfully.

**S4 SEM image of Ti$_3$C$_2$ after the ball-milling treatment**

**Fig. S4.** SEM image of Ti$_3$C$_2$ after the ball-milling treatment.

As shown in **Fig. S4**, the construction of Ti$_3$C$_2$ is destroyed and becomes broken pieces via ball-milling process.

**S5 SEM images of BNNS@Ti$_3$C$_2$ with different compound ratios**
**Fig. S5.** SEM images of BNNS@Ti$_3$C$_2$ with different compound ratios of Ti$_3$C$_2$. (a) BT0, (b) BT0.01, (c) BT0.03, (d) BT0.05, (e) BT0.1, (f) BT0.15.

From **Fig. S5**, Ti$_3$C$_2$ breaks to pieces and gradually get into the layers of BNNS.

**S6 TEM-HRTEM images of BNNS.**

**Fig. S6.** TEM-HRTEM images of (a-c) BNNS under different magnification.

It can be seen that the exfoliated BNNS aggregate irregularly and crumpled sheets overlap with each other. HRTEM image of BNNS reveals the inter-planar d-spacing of ≈0.33 nm corresponding to the (002) plane of h-BN (JCPDS No. 45-0893). Due to the vulnerable stability to electron beam irradiation at 200 kV, the monolayer BNNS can’t be presented clearly.

**S7 XRD patterns of bulk h-BN and Ti$_3$C$_2$.**
Fig. S7. XRD patterns of bulk h-BN and Ti$_3$C$_2$.

S8 XRD pattern contrast of BNNS@Ti$_3$C$_2$ with different compound ratios of Ti$_3$C$_2$.

Fig. S8. XRD pattern contrast of BNNS@Ti$_3$C$_2$ with different compound ratios of Ti$_3$C$_2$. (a) Before calcination, (b) After calcination.

It can be seen evidently in Fig. S8 that XRD patterns only have both peaks of h-BN and Ti$_3$C$_2$ before calcination and the (102) peak of h-BN fades away as the compound ratio increases, which means that the ball-milling process is a physical mixing experience. After calcination, the (110) peak of Ti$_3$C$_2$ disappears and a new peak belonged to (BN)$_{0.33}$C$_{0.67}$ appears, whose intensity increasing with the increase of compound ratio.

S9 Raman spectrum of Ti$_3$C$_2$. 
**Fig. S9.** Raman spectrum of Ti$_3$C$_2$.

**Fig. S9** shows that Ti$_3$C$_2$ displays three peaks at 260, 420, and 605 cm$^{-1}$ of Ti-C vibration. In addition, there are weak peaks at 1320 and 1590 cm$^{-1}$. These peaks are associated with the A$_{1g}$ and E$_{2g}$ vibrational modes of graphite, which indicates the presence of some unreacted carbon.

**S10 Full XPS spectrum of the BT0.05 sample**

**Fig. S10.** XPS survey spectrum of the BT0.05 sample.

**S11 The LSV curve of bulk h-BN**
**Fig. S11.** The LSV curve of bulk h-BN.

**Fig. S11** shows that the bulk h-BN electrode has large onset potential (-126 mV) and high overpotential (-157 mV at the current density of 10 mA·cm$^{-2}$).

**Table S1.** Comparison of HER performance of BNNS@Ti$_3$C$_2$ electrocatalyst and other non-noble metal-based electrocatalysts.

<table>
<thead>
<tr>
<th>Electro catalyst</th>
<th>Onset overpotential (mV)</th>
<th>Overpotential at 10 mA·cm$^{-2}$</th>
<th>Tafel slope (mV·dec$^{-1}$)</th>
<th>(Ref.)</th>
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<tbody>
<tr>
<td>Ti$_2$CT$_x$</td>
<td>-75</td>
<td>-170</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>Mo$_2$CT$_x$</td>
<td>-131</td>
<td>-283</td>
<td>N/A</td>
<td>2</td>
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<tr>
<td>MoP</td>
<td>-50</td>
<td>-130</td>
<td>48</td>
<td>3</td>
</tr>
<tr>
<td>N-MoSe$_2$/VG</td>
<td>-45</td>
<td>-98</td>
<td>49</td>
<td>4</td>
</tr>
<tr>
<td>MoN</td>
<td>-100</td>
<td>-232</td>
<td>90</td>
<td>5</td>
</tr>
<tr>
<td>MoSe$_2$/NiSe$_2$</td>
<td>-20</td>
<td>-69</td>
<td>42</td>
<td>6</td>
</tr>
<tr>
<td>Ni$_2$P</td>
<td>-43</td>
<td>-110</td>
<td>N/A</td>
<td>7</td>
</tr>
<tr>
<td>Ni$_3$(VO$_4$)$_2$</td>
<td>N/A</td>
<td>-90</td>
<td>50</td>
<td>8</td>
</tr>
<tr>
<td>BNNS@Ti$_3$C$_2$</td>
<td>-23</td>
<td>-52</td>
<td>39</td>
<td>This work</td>
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</table>
S12 Tafel plots of BNNS@Ti$_3$C$_2$ with different compound ratios under different calcination temperatures

![Tafel plots of BNNS@Ti$_3$C$_2$ with different compound ratios under different calcination temperatures](image)

**Fig. S12.** Tafel plots of the BT0.01, BT0.03, BT0.05, BT0.1 and BT0.15 with different calcination temperatures. (a) 700 °C, (b) 750 °C, (c) 850 °C, (d) 950 °C.

As shown in **Fig. S12**, the smallest Tafel slope can be obtained through tuning the compound ratios.

S13 SEM images of BT0.05 after 20 h stability test

![SEM images of BT0.05 after 20 h stability test](image)

**Fig. S13.** SEM images of BT0.05 after 20 h stability test.

We can see in **Fig. S13** that the morphology of BT0.05 can keep well after 20 h stability test.
Fig. S14. XRD pattern of BT0.05 after 20 h stability test. Fig. S14 shows that the crystal structure of BT0.05 can be preserved well after 20 h stability test.

Fig. S15. High-resolution XPS spectra of the BT0.05 after 20 h stability test: (a) B 1s
states, (b) N 1s states, (c) Ti 2p states, (d) C 1s states.

**Table S2: Fitting results for equivalent circuits of different samples**

<table>
<thead>
<tr>
<th>Samples</th>
<th>$R_s$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
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<tbody>
<tr>
<td>BNNS</td>
<td>4.27</td>
<td>1134</td>
</tr>
<tr>
<td>BT0.05</td>
<td>2.76</td>
<td>463</td>
</tr>
</tbody>
</table>

S16 The schematic structural model of BNNS.

![Schematic structural model of BNNS](image)

**Fig. S16.** The structural model for BNNS.

S17 Density of states of BNNS.
Fig. S17. Density of states of BNNS.

Fig. S18. Density of states of BT0.05.

Fig. S19. UV–vis absorption spectra of BNNS and BT0.05.
Fig. S19. UV–vis absorption spectra of BNNS and BT0.05.

S20 N₂ adsorption–desorption isotherms of h-BN, BNNS and BT0.05.
References


