Supporting Information

Enhancement of Hydrogen Evolution Reaction Performance of Graphitic Carbon Nitride with Incorporated Nickel Boride

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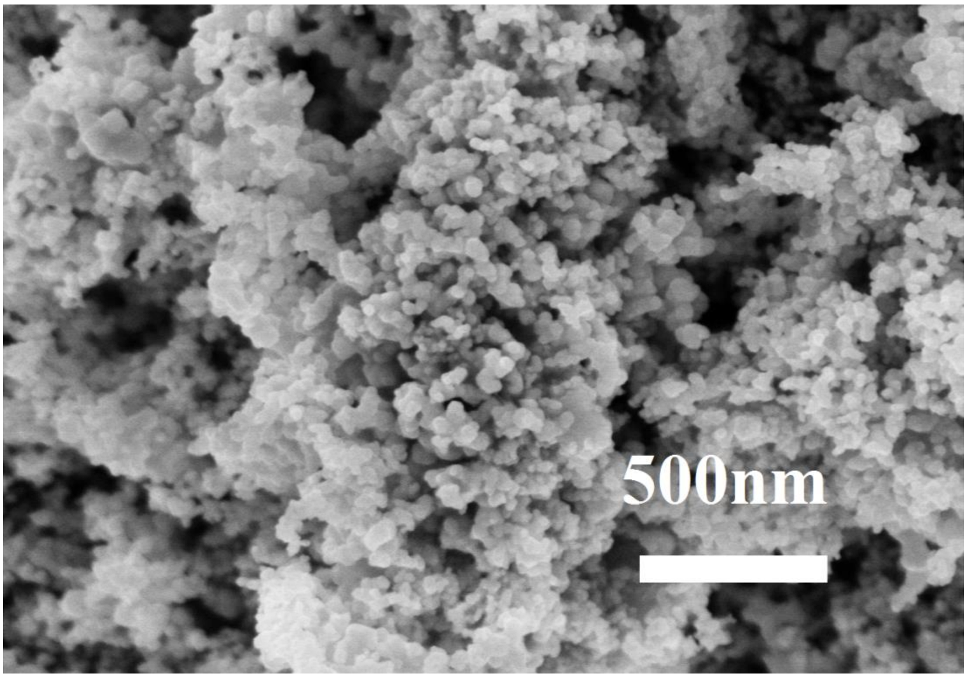

Figure S1. SEM imagine of Ni_2B.

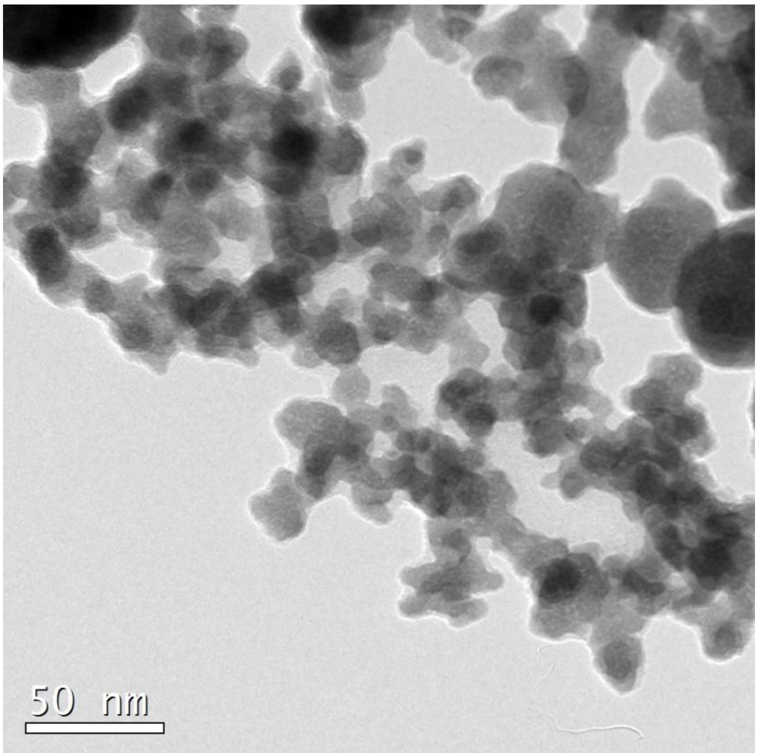

Figure S2. TEM imagine of Ni_2B.

The SEM and TEM spectra exhibit the granular morphology of Ni_2B precursor.

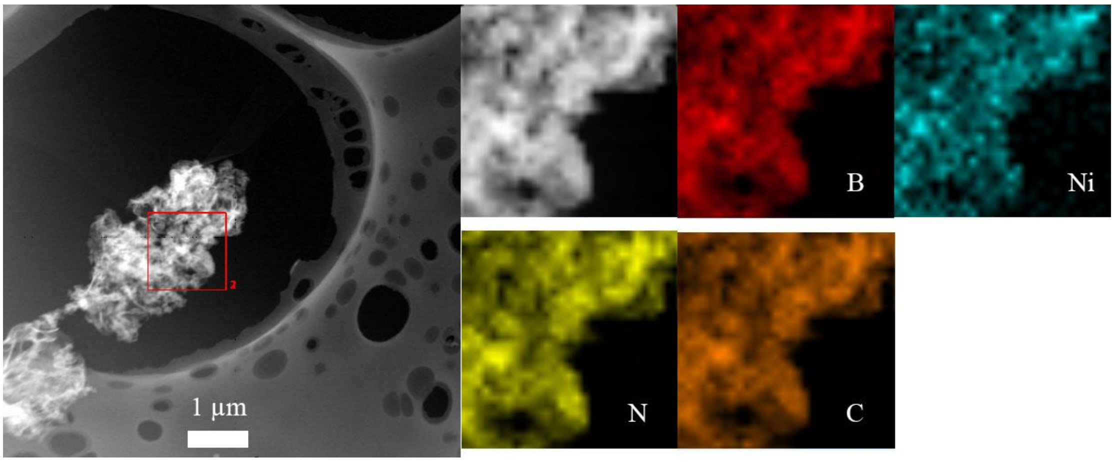

Figure S3. The TEM image and the corresponding elemental mapping for B, Ni, N, C, respectivily.

The elemental mappings revealed the coexistent and homogenerous distribution of Ni and B elements on g-C_3N_4 sheets.

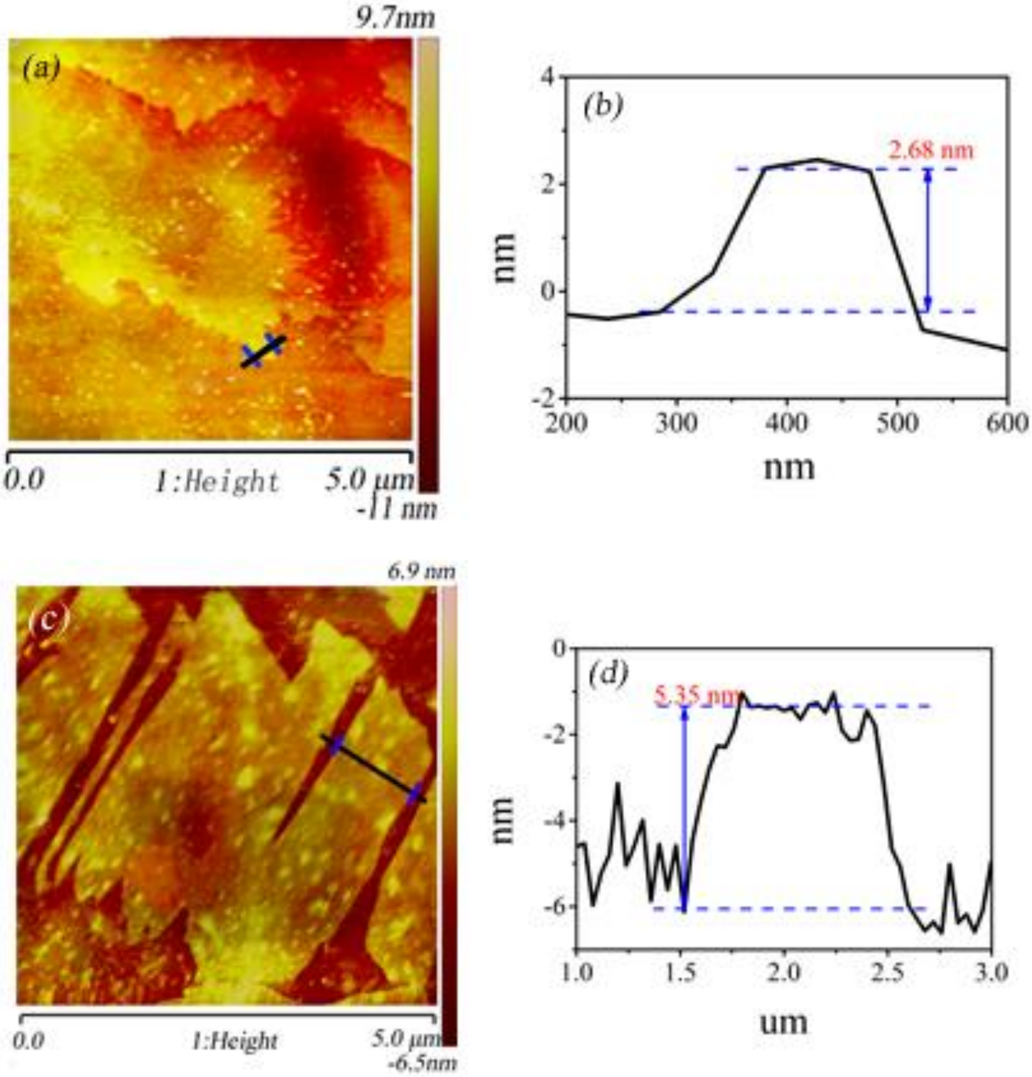

Figure S4. AFM imagines of (a)NC-5 and (b)CN-0.

Stacked layers can be observed from AFM imagines, the height can corresond to the thickness of the g-C_3N_4 layers. The Ni_2B modified g-C_3N_4 layers displayed thinner layers at thickness of 2.68 nm meanwhile thickness of pure g-C_3N_4 was 5.35 nm.

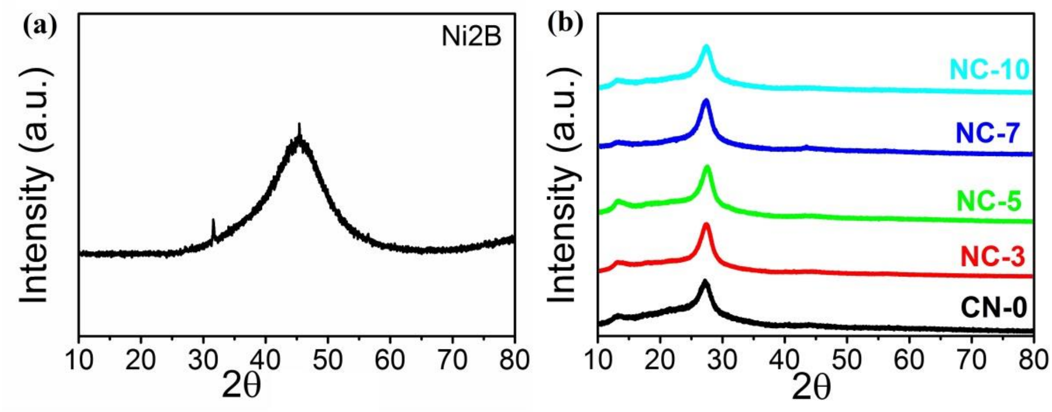

Figure S5.XRD patterns of Ni_2B (a) and Ni_2B modified g-C_3N_4.

XRD pattern of Ni_2B a board peak at 2θ=45º indicating the amorphous character of Ni_2B powders. From the XRD patterns of Ni_2B modified g-C_3N_4, all samples represent the typical diffraction peak at 27.4º and a weaker peak around 13º, which means the incorporation of Ni_2B doesn't change the graphitic in-plane structure.

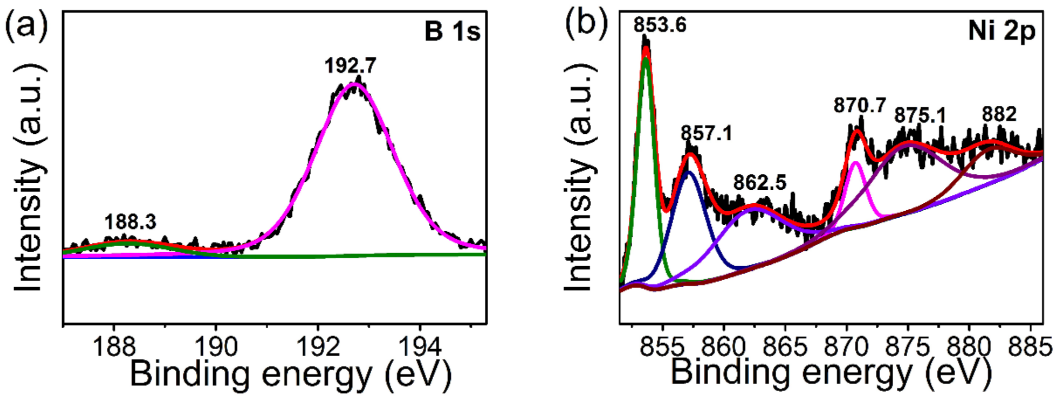

Figure S6.XPS High-resolution spectrum of Ni_2B sample on (a)B 1s and (b)Ni 2p.

The two peaks for B 1s were obeserved with binding energy (BE) of 188.3eV and 192.7eV. they are response to elemental and oxidized boron, respectively. The binding energy of elemental boron in compounds positive shift 1.2eV compare to pure boron element(with binding energy of 187.1eV). This shift indicates an electron immigrated from alloying B to vacant d-orbital of metallic Ni which makes boron electron deficient while Ni metals are enriched with the electron in all the catalyst powders. That make the Ni_2B a good active site for HER. The Ni 2p spectrum can deconvoluted into two manifolds, two main peaks located at 853.6eV and 870.7eV corresponded to metallic Ni and satellite peaks around 857.1eV and 875.1eV which attributed to Ni $2p_{3/2}$ and Ni $2p_{1/2}$, the peak at 862.5eV related to oxidized Ni compounds[1-2].

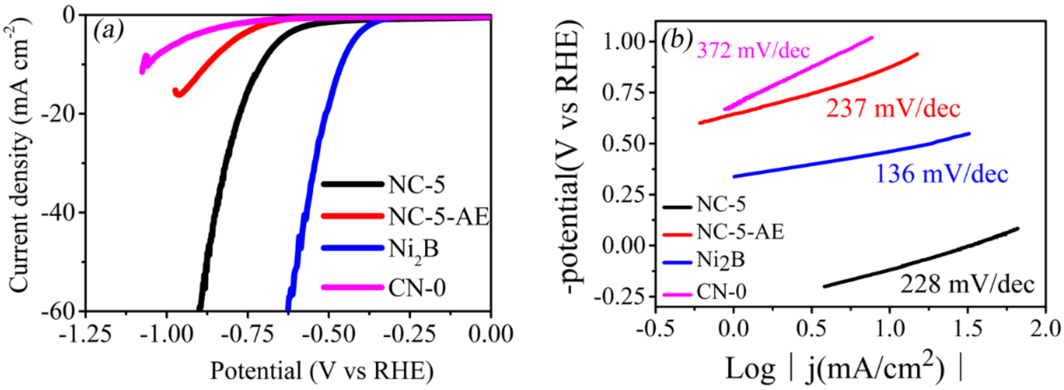

Figure S7.HER performance of Ni2B, NC-5-AE, NC-5 and CN-0 samples
(a) Polarization curves, and (b) corresponding Tafel plots

The NC-5 was sonicated in 10% hydrochloric acid for 30 min to remove the nickel ions doped in the sample, and then washed three times with deionized water and alcohol, and then vacuum dried in an oven at 60 °C for 3 hours. The sample obtained is named NC-5-AE. The onset overpotential of Ni_2B working electrode is 335 mV and the overpotential to drive cathodic current densities of 10 mA cm^{-2} reaches 459 mV, meanwhile the onset overpotential of NC-5-AE working electrode is 640 mV and overpotential at cathodic current densities of 10 mA cm^{-2} is 875 mV. The Tafel slope (Shown in Fig. S7(b)) of NC-5-AE (~237 mV dec^{-1}, and 136 mV dec^{-1} for the Ni_2B particle working electrode) is much lower than pure g-C_3N_4 samples (372 mV dec^{-1}), it proved the Ni_2B particles incorporated on g-C_3N_4 layers can really enhance the electrocatalyst performance.

Table S1. The list of electrocatalytic parameters of the Pt/C, pure g-C_3N_4, and the Ni_2B modified g-C_3N_4.

cathode	Onset overpotential (mV)	Overpotential at current density of 10mA/cm^2 (mV)	Overpotential at current density of 20mA/cm^2 (mV)	Slope of Tafel plot(mV/dec)
Pt/C	4	56		36
CN-0	686	1056		372
NC-3	248	900		348
NC-5	300	707	773	221
NC-7	359	915		350
NC-10	503	923	1031	339

Table S2. Comparison of electrocatalytic performance for g-C_3N_4-based catalysts

Catalyst	Current density	overpotential	Tafel slope	reference
Ni_2B/g-C_3N_4	10 mA cm^{-2}	707 mV	221 mV/dec	this work
Ni/g-C_3N_4	10 mA cm^{-2}	760 mV		Ref.[3]
Zn/g-C_3N_4	10 mA cm^{-2}	800 mV		Ref.[3]
Fe/g-C_3N_4	10 mA cm^{-2}	770 mV		Ref.[3]
Co/g-C_3N_4	10 mA cm^{-2}	730 mV		Ref.[3]
Cu/g-C_3N_4	10 mA cm^{-2}	390 mV	112 mV/dec	Ref.[3]
Ni/C_3N_4	10 mA cm^{-2}	222 mV	128 mV/dec	Ref.[4]
TC@WO_3@g-C_3N_4	10 mA cm^{-2}	535 mV	246 mV/dec	Ref.[5]
g-C_3N_4@Ni-NiO	10 mA cm^{-2}	725 mV	286 mV/dec	Ref.[5]

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