Supporting Information

Constructing amorphous/amorphous heterointerfaces in nickel borate/boride composites for efficient electrocatalytic methanol oxidation

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Supporting information: DFT calculation method and Figures S1-S10.

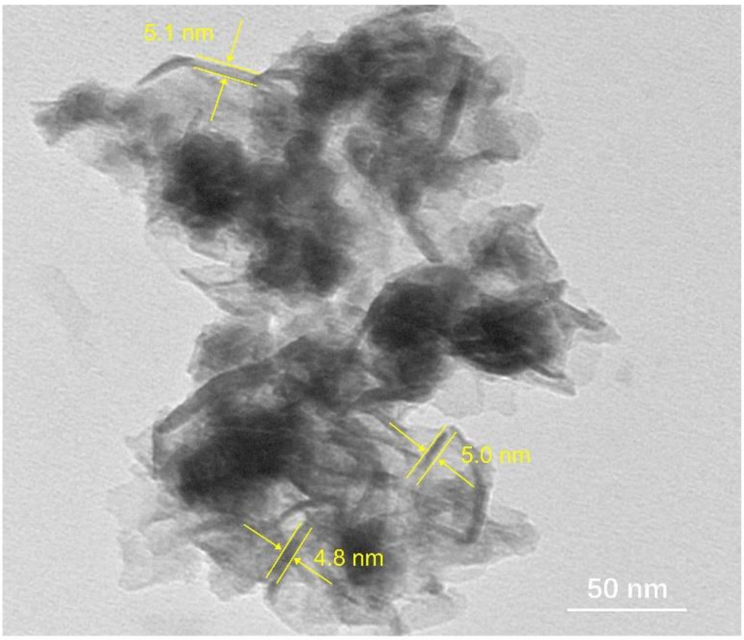

Figure S1. TEM image of the a-Ni-B_i/Ni_xB hybrid sample, from which the thickness of nanosheets can be identified to be about 5.0 nm.

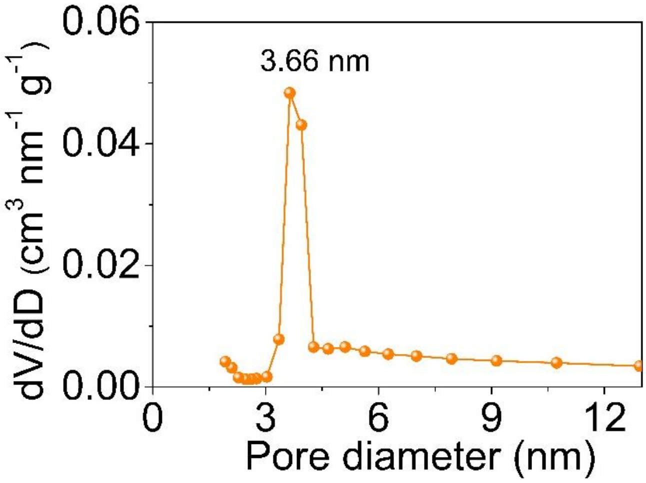

Figure S2. The pore size distribution curve of a-Ni-B_i/Ni_xB hybrid sample.

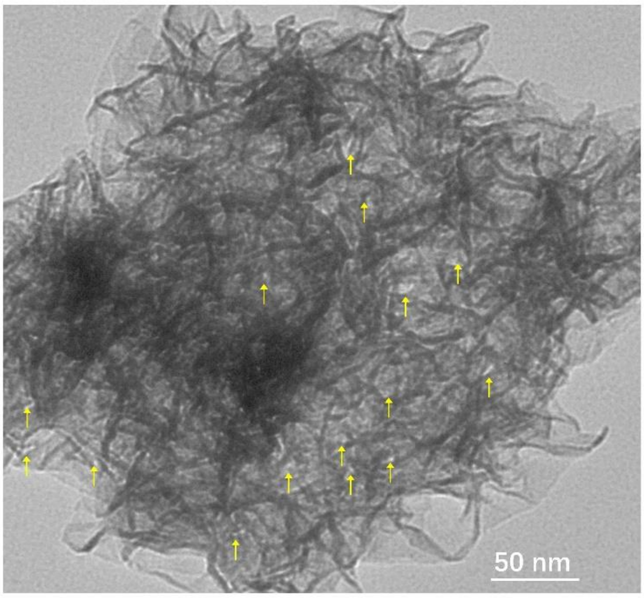

Figure S3. TEM image of the ultrathin a-Ni-B_i nanosheets, where abundant nanopores can be clearly observed.

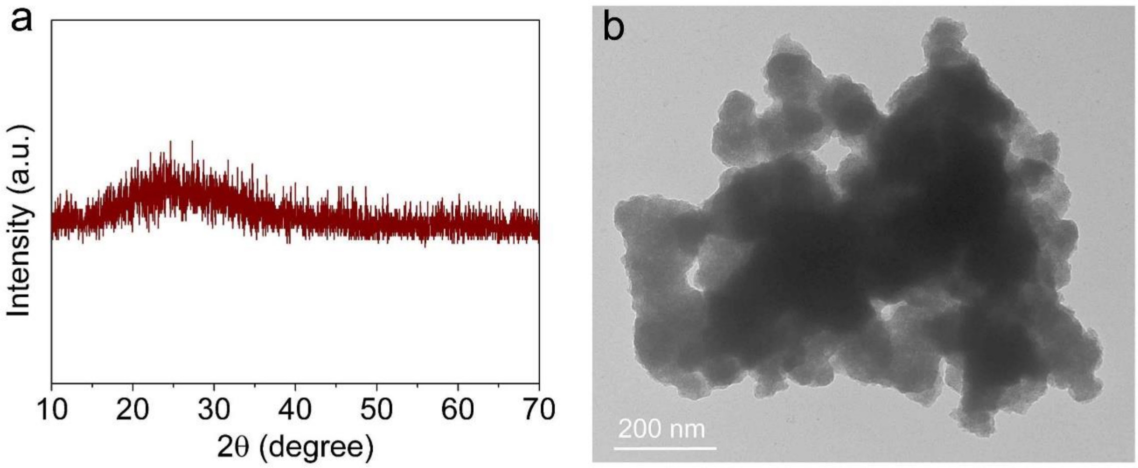

Figure S4. (a) XRD pattern and (b) TEM image of the as-prepared a-Ni_xB sample.

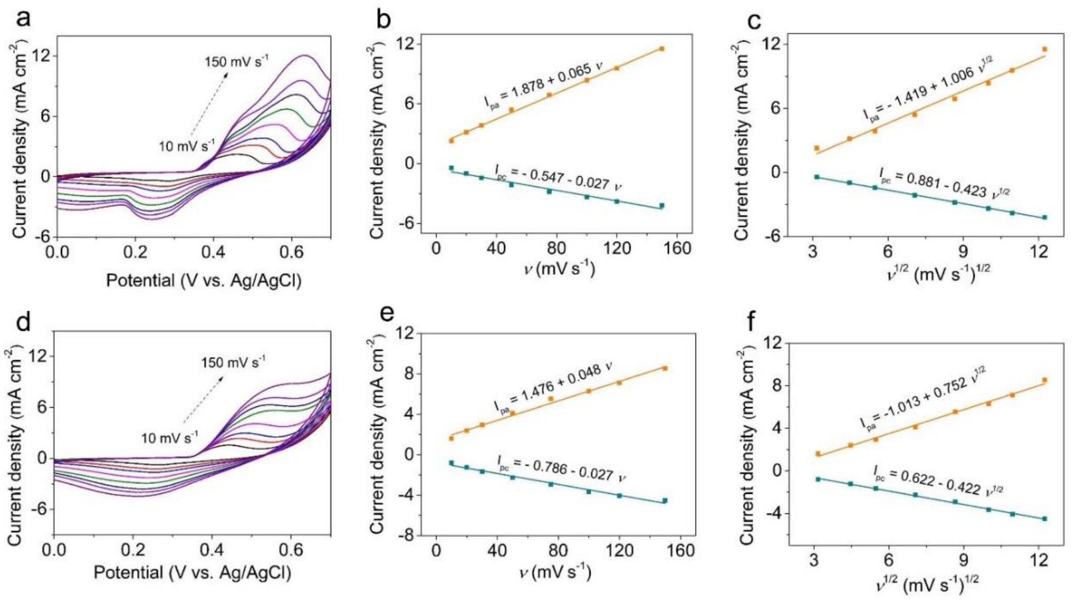

Figure S5. CV curves of (a) a-Ni-B_i and (d) a-Ni_xB samples recorded in 1 M KOH solution at different scan rates of 10, 20, 30, 50, 75, 100, 120 and 150 mV s^{-1}. The linear relationship between anodic and cathodic peak current densities and scan rates: (b) a-Ni-B_i sample and (e) a-Ni_xB sample. Linear relationship between anodic and cathodic peak current densities and square root of the scan rate: (c) a-Ni-B_i sample and (f) a-Ni_xB sample.

The surface coverage of Ni(II)/Ni(III) redox species (Γ^*) in a-Ni-B_i/Ni_xB hybrid, a-Ni_xB and a-Ni-B_i samples are determined according to the following equation:

$$I_p = (n^2F^2/4RT)\nu A\Gamma^*$$

where I_p, n, F, R, T, A and ν are respectively the peak current, the number of transferred electron (supposed to be 1 in this case), the Faraday constant, the gas constant, the temperature (298 K), the geometric area of glassy carbon electrode and the sweep rate of potential. Based on the average of the anodic and the cathodic data in Figure S3b and S3e, the calculated Γ^* values for the a-Ni-B_i/Ni_xB hybrid, a-Ni_xB and a-Ni-B_i samples are 3.77×10^{-7}, 3.96×10^{-8} and 4.86×10^{-8} mol cm^{-2}, respectively. Moreover, the linear dependences between the anodic and cathodic peak current densities and the square root of sweep rate for a-Ni-B_i/Ni_xB hybrid, a-Ni_xB and a-Ni-B_i electrodes are presented in Figure S3c and S3f. In terms of these results, the proton diffusion coefficient (D) can be calculated by the Randles-Sevcik equation:

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C \nu^{1/2}$$

where I_p, n, A, D, C, and ν represent respectively the peak current, the number of transferred electron, the geometric area of glassy carbon electrode, the proton concentration (estimated to be 0.043 mol cm^{-3} in this case)[6], and the sweep rate of potential. According to the average of the anodic and the cathodic results the linear dependences, the D values of for the a-Ni-B_i/Ni_xB hybrid, a-Ni_xB and a-Ni-B_i samples are found to be 2.35×10^{-7}, 2.58×10^{-9} and 3.82×10^{-9} cm^2 s^{-1}, respectively.

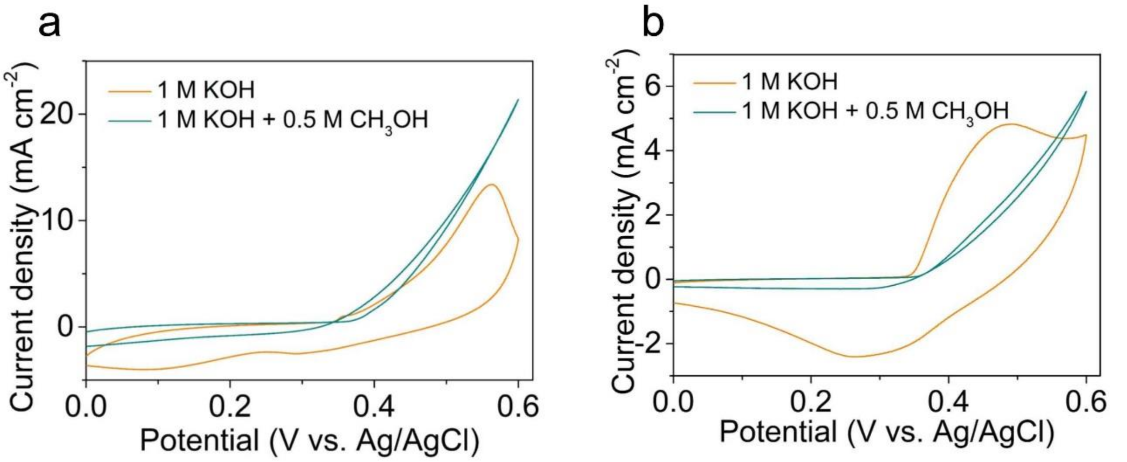

Figure S6. CV curves of (a) a-Ni-B_i and (b) a-Ni_xB samples obtained at a scan rate of 50 mV s^{-1} in 1 M KOH solution with and without 0.5 M methanol.

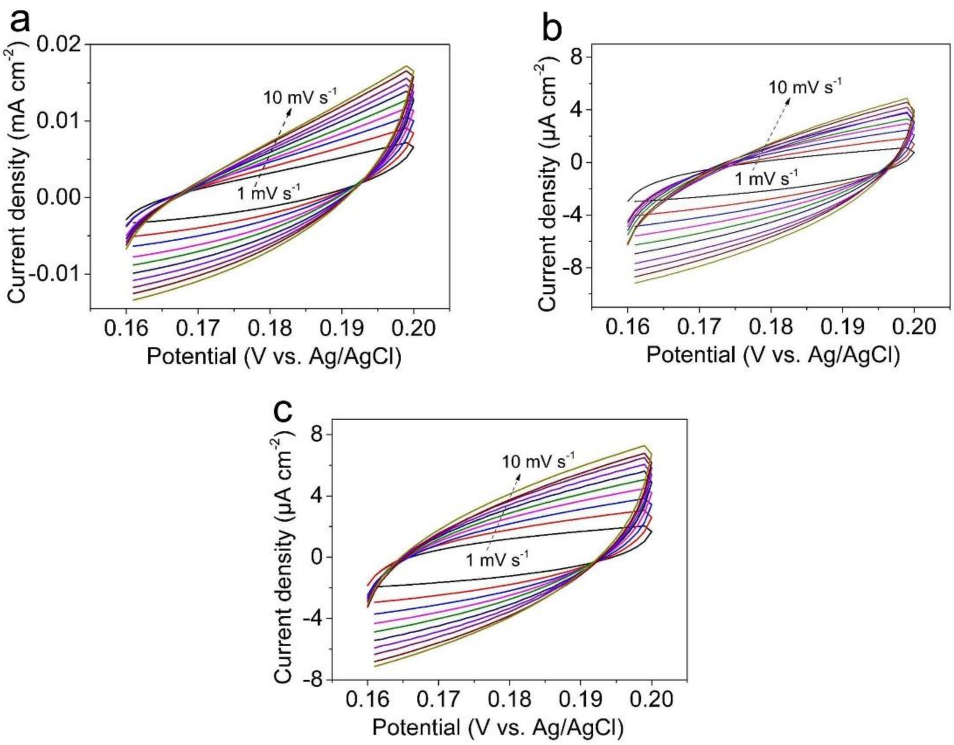

Figure S7. Cyclic voltammetry curves of a-Ni-B_i/Ni_xB hybrid, a-Ni_xB and a-Ni-B_i samples measured in 1 M KOH solution at different scan rates from 1 to 10 mV s^{-1}.

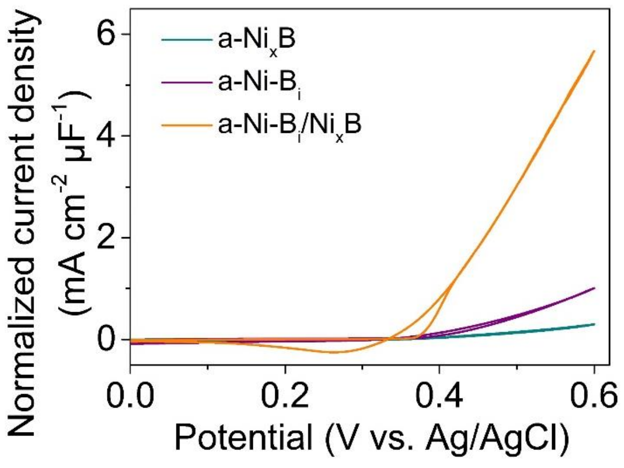

Figure S8. Cyclic voltammetry curves normalized by the C_{dl} values of a-Ni-B_i/Ni_xB hybrid, a-Ni_xB and a-Ni-B_i samples.

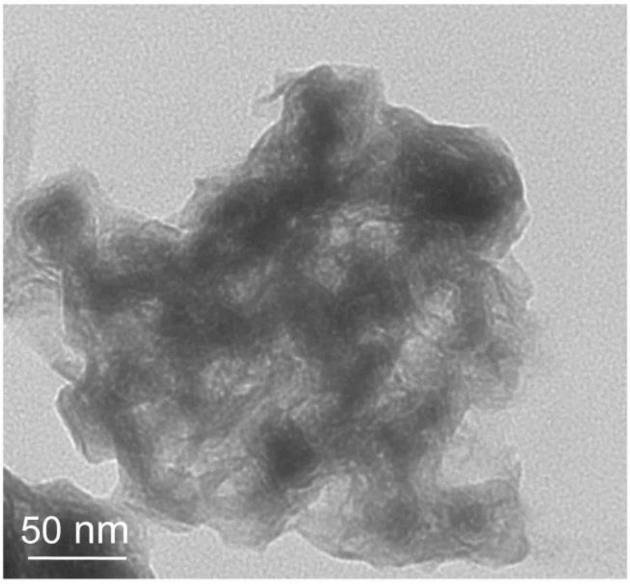

Figure S9. TEM image of a-Ni-B_i/Ni_xB hybrid sample after the chronoamperometry test in 1 M KOH solution containing 0.5 M methanol.

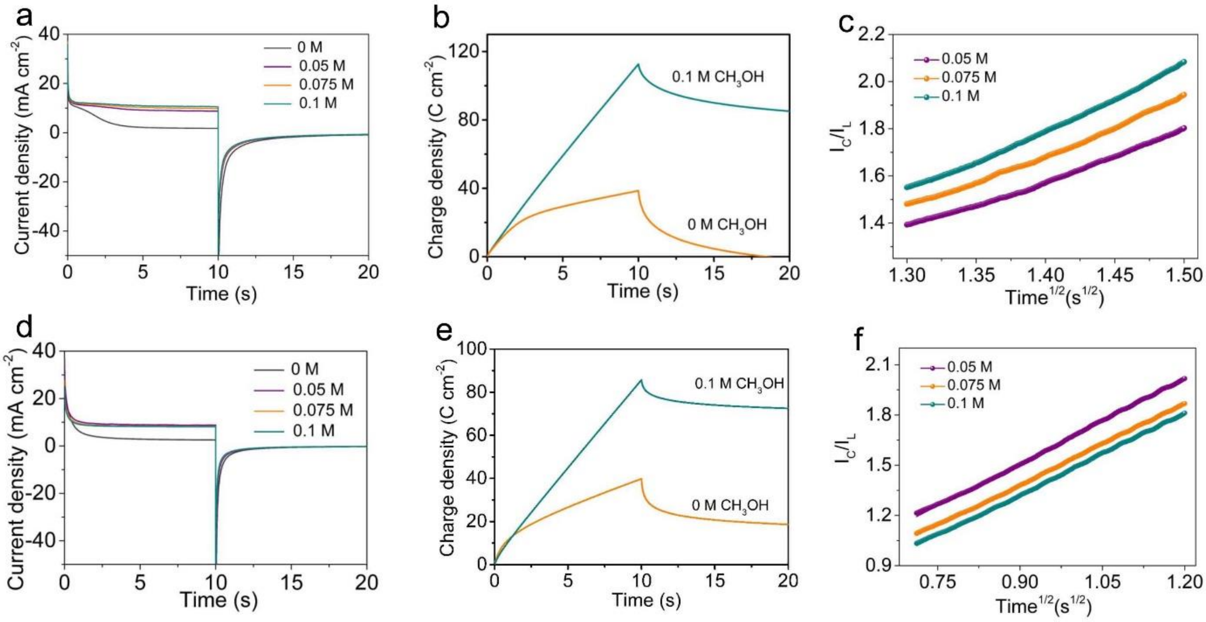

Figure S10. (a) Double-potential-step chronoamperograms of a-Ni-B_i sample obtained in 1 M KOH solution with different concentrations of methanol. (b) Dependence of charge density (C cm^{-2}) on time and (c) the linear plots of I_C/I_L ratio against $(time)^{1/2}$ derived from the corresponding chronoamperograms in (a). (d) Double-potential-step chronoamperograms of a-Ni_xB sample obtained in 1 M KOH solution with different concentrations of methanol. (e) Dependence of charge density (C cm^{-2}) on time and (f) the linear plots of I_C/I_L ratio against $(time)^{1/2}$ derived from the corresponding chronoamperograms in (d).

Table S1. Comparison of the electrocataltyic MOR performance between the a-Ni-B_i/Ni_xB hybrid sample and recently reported efficient non-noble catalysts.

Catalyst	Electrolyte	Scan rate (mV s^{-1})	Current density (mA cm^{-2}) at 1.62 V vs. RHE	Onset potential (V vs. RHE)
a-Ni-B_i/Ni_xB this work	1.0 M KOH + 0.5 M CH_3OH	50	213	1.40
NiO/CNT[1]	1.0 M KOH + 0.5 M CH_3OH	50	~ 140	1.37
$Ni_{0.75}Cu_{0.25}$[2]	1.0 M NaOH + 0.5 M CH_3OH	50	~ 75	1.37
CuO NS/CF[3]	1.0 M KOH + 1.0 M CH_3OH	50	180	1.38
Ni_3C[4]	1.0 M KOH + 1.0 M CH_3OH	50	127	~ 1.40

NiO/CuO MOF[5]	1.0 M KOH + 3.0 M CH_3OH	50	190	1.40
$Ni_{97}Bi_3$[6]	1.0 M KOH + 1.0 M CH_3OH	50	~ 200	1.33
rGO-FeO/NiO[7]	1.0 M NaOH + 3.0 M CH_3OH	50	170	1.40
$NiCo_2O_4$/rGO[8]	1.0 M KOH + 0.5 M CH_3OH	50	78	1.36
$NiCo_2O_4$[9]	1.0 M KOH + 0.5 M CH_3OH	50	148	1.43

References

[1] X. L. Tong, Y. Qin, X. Y. Guo, O. Moutanabbir, X. Y. Ao, E. Pippel, L. B. Zhang, M. Knez, *Small* **2012**, *8*, 3390.

[2] X. Cui, P. Xiao, J. Wang, M. Zhou, W. L. Guo, Y. Yang, Y. J. He, Z. W. Wang, Y. K. Yang, Y. H. Zhang, Z. Q. Lin, *Angew. Chem. Int. Ed.* **2017**, *56*, 4488.

[3] X. F. Wei, Y. Li, L. S. Chen, J. L. Shi, *Angew. Chem. Int. Ed.*, **2021**, *60*, 3148.

[4] J. S. Li, R. L. Wei, X. Wang, Y. Zuo, X. Han, J. Arbiol, J. Llorca, Y. Y. Yang, A. Cabot, C. H. Cui, *Angew. Chem. Int. Ed.* **2020**, *59*, 20826.

[5] T. Noor, S. Pervaiz, N. Iqbal, *Nanomaterials* **2020**, *10*, 1601.

[6] A. A. Dubale, Y. Y. Zheng, H. L. Wang, R. Hübner, Y. Li, J. Yang, J. W. Zhang, N. K. Sethi, L. He, Z. K. Zheng, W. Liu, *Angew. Chem. Int. Ed.* **2020**, *59*, 13891.

[7] T. Noor, M. Mohtashim, N. Iqbal, S. R. Naqvi, N. Zaman, L. Rasheed, M. Yousuf, *J. Electroanal. Chem.* **2021**, *890*, 115249.

[8] N. Narayanan, N. Bernaurdshaw, *ChemCatChem* **2020**, *12*, 771.

[9] Y. Yu, B. Yang, Y. Wang, *ACS Appl. Energy Mater.* **2020**, *3*, 9076.