Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

Ultrathin Nickel Boride Nanosheets Anchored on Functionalized Carbon Nanotubes as Bifunctional Electrocatalysts for Overall Water Splitting

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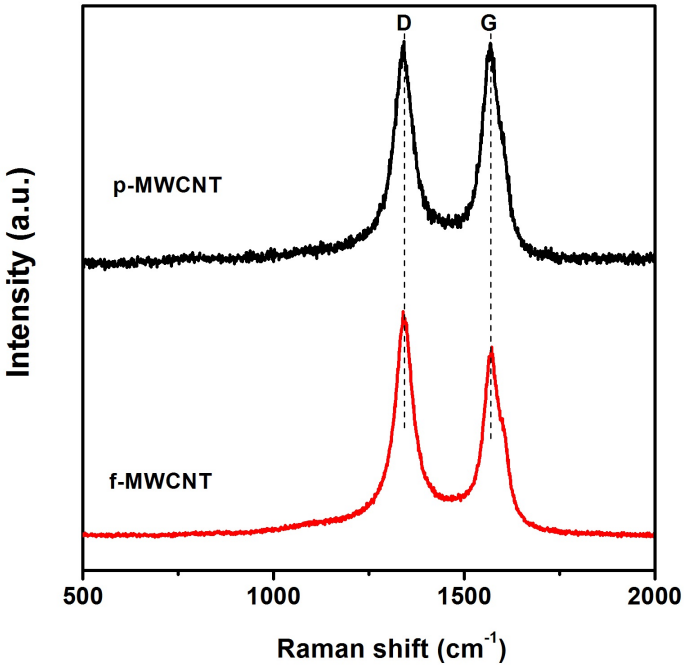

Fig. S1 Raman spectra of commercial multi-walled carbon nanotubes (MWCNTs) at pristine and chemically functionalized forms: p-MWCNTs and f-MWCNTs. (Note that pristine MWCNTs were not subjected to chemical cleaning and tested in their as-received form.)

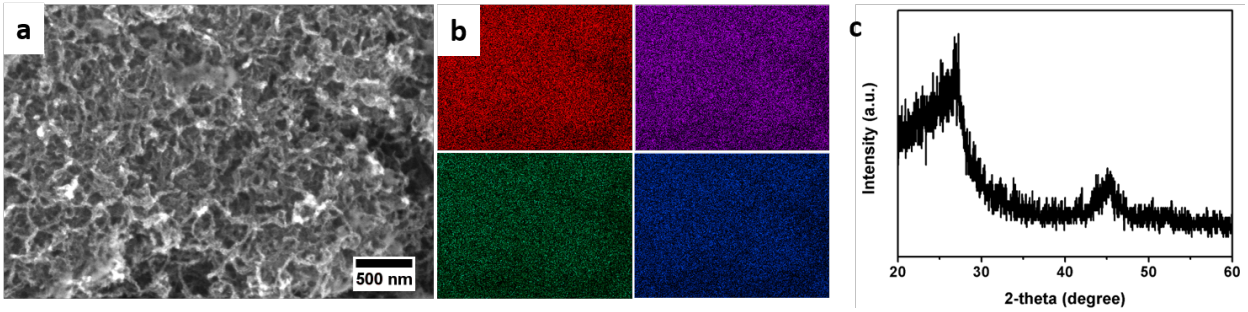

Fig. S2 Characterization of the morphology and structure properties of NixB/f-MWCNT hybrids before 300 ºC calcination. (a) SEM; (b) the corresponding EDX elemental mappings of the whole region of (a); (c) XRD.

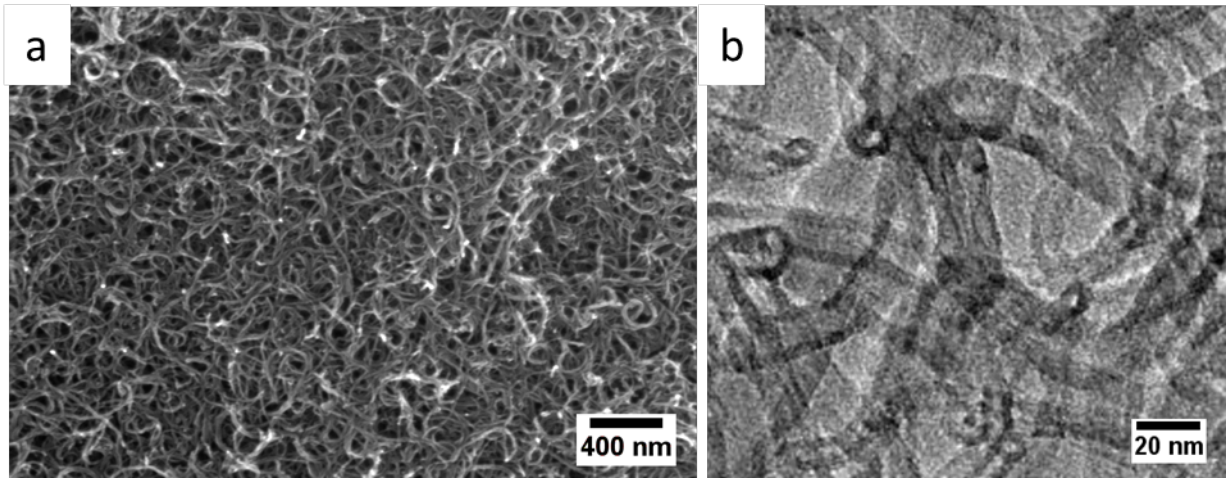

Fig. S3 (a) SEM and (b) TEM images of f-MWCNTs.

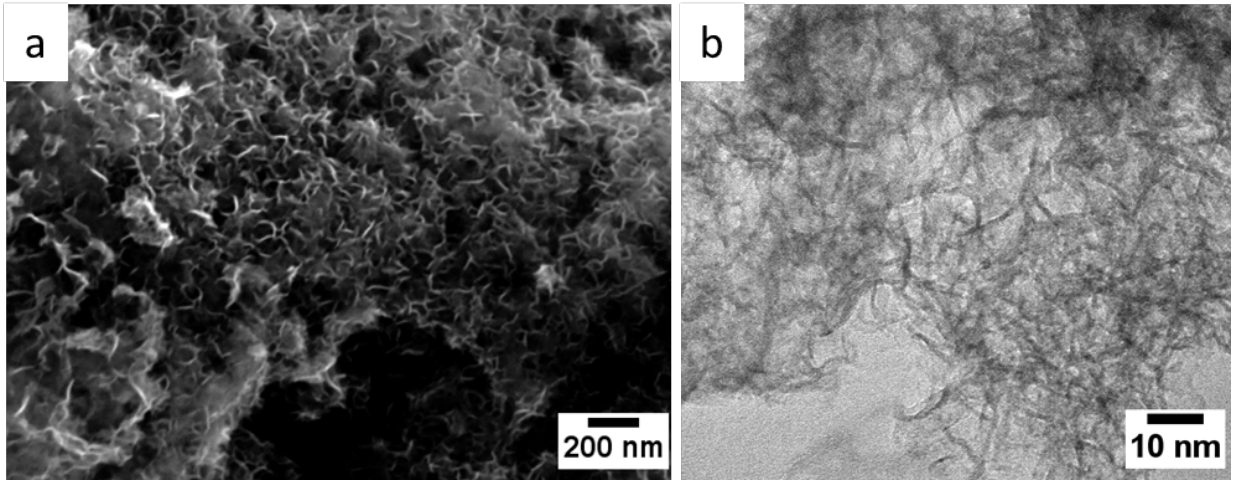

Fig. S4 (a) SEM and (b) TEM images of Ni_xB nanosheets.

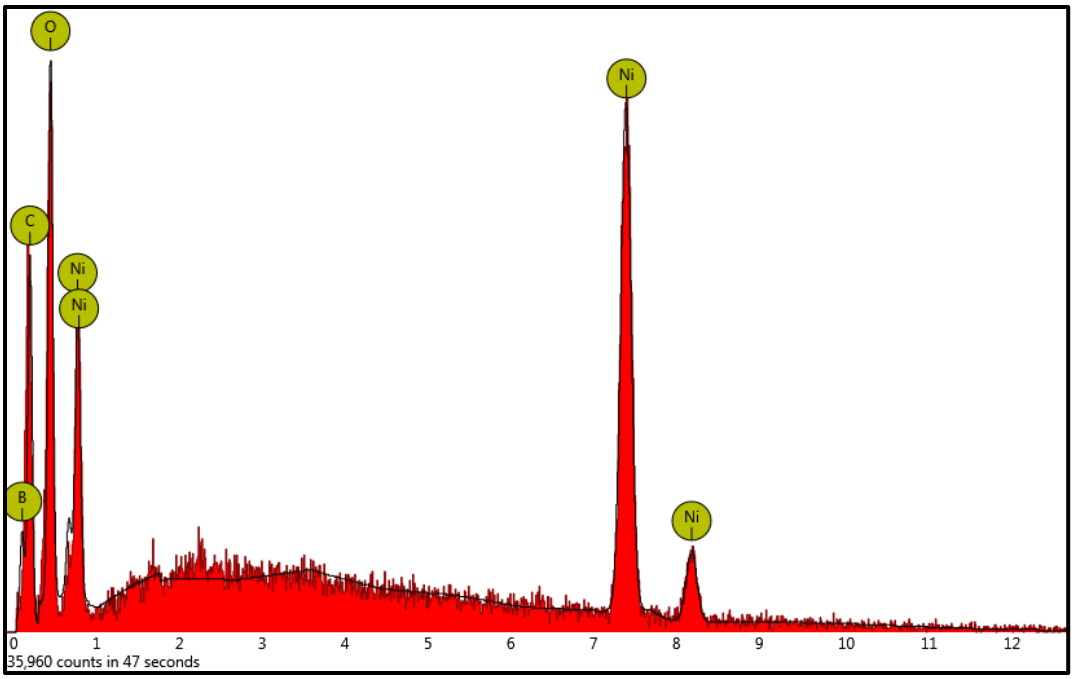

Fig. S5 EDS spectrum of Ni_xB/f-MWCNT.

Table S1 Elemental compositions (at. %) of f-MWCNT, Ni_xB, and Ni_xB/f-MWCNT determined by EDX[a], XPS[b], and ICP[c].

Materials	**C**	**O**	**B**	**Ni**
f-MWCNT[b]	77.7	22.3	–	–
Ni_xB[b]	–	–	26.31	73.69
Ni_xB/f-MWCNT[a]	61.87	15.31	5.82	17.01
Ni_xB/f-MWCNT[b]	47.10	20.02	8.13	24.75
Ni_xB/f-MWCNT[c]	–	–	25.8	74.2

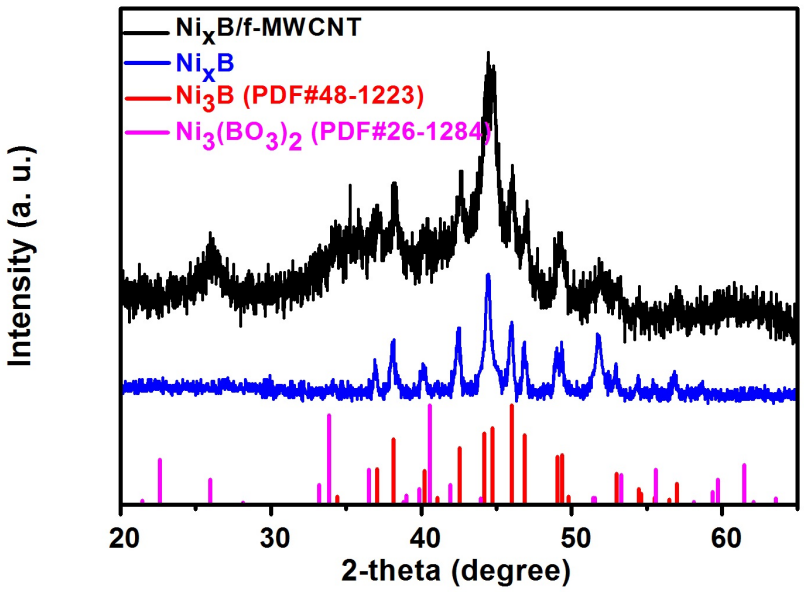

Fig. S6 XRD patterns of Ni_xB/f-MWCNT and Ni_xB. The reference XRD peaks of Ni_3B (red vertical lines, JCPDS No. 48-1223) and $Ni_3(BO_3)_2$ (pink vertical lines, JCPDS No. 26-1284).

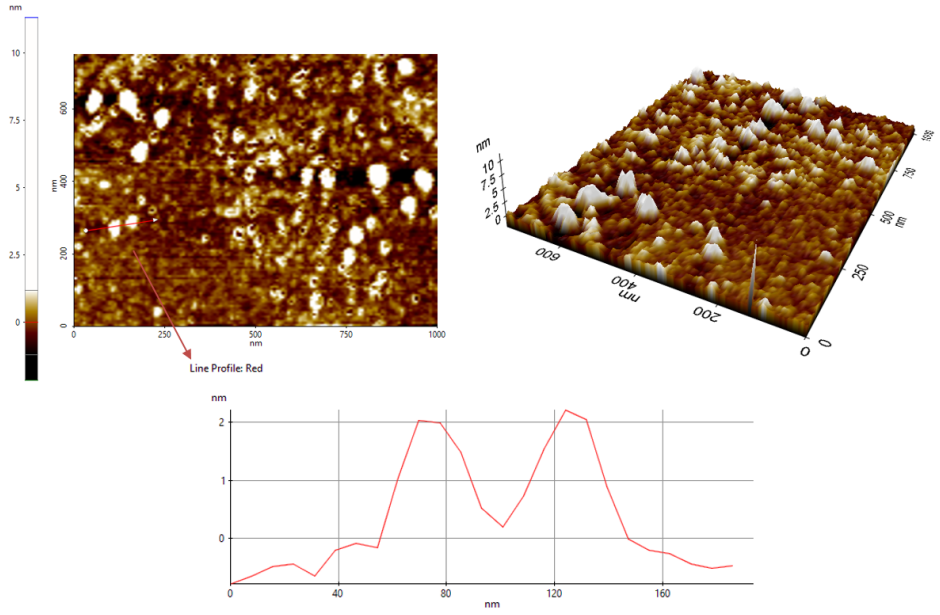

Figure S7 AFM images of Ni_xB/f-MWCNT in 2D and 3D projection, recorded in the tapping mode, and the corresponding height profile.

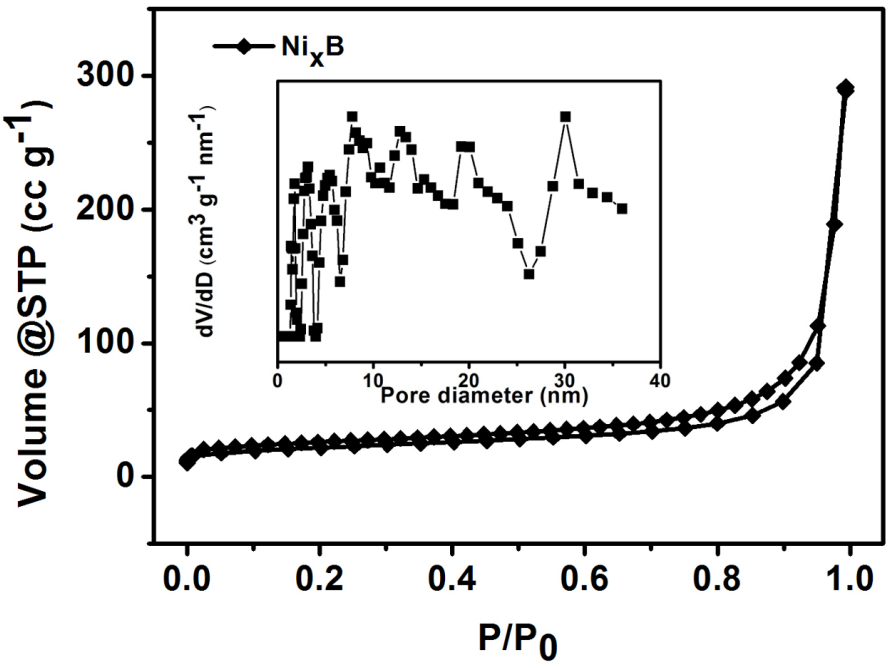

Fig. S8 Nitrogen adsorption-desorption isotherms of Ni_xB. The inset shows the pore size distribution of Ni_xB.

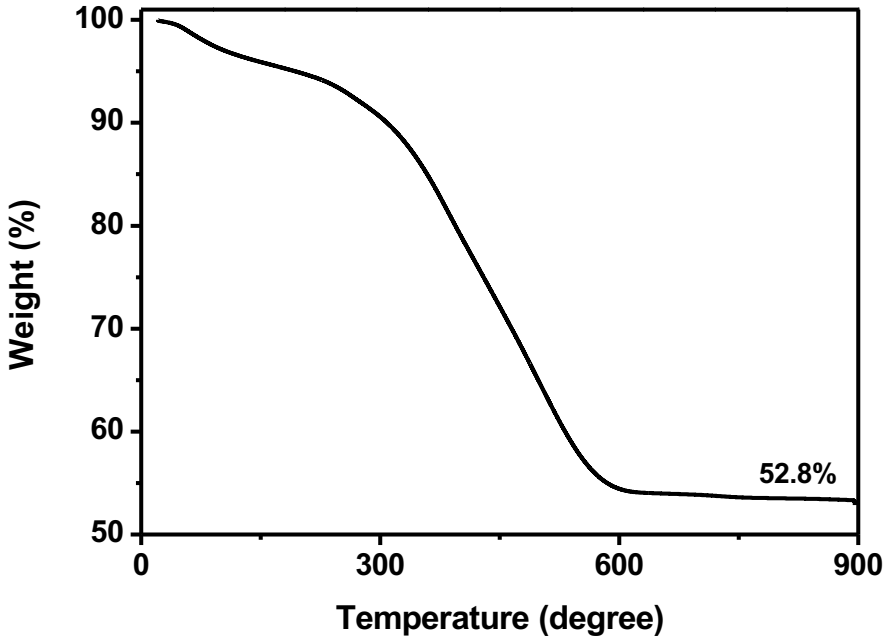

Fig. S9 TGA profile of Ni_xB/f-MWCNT.

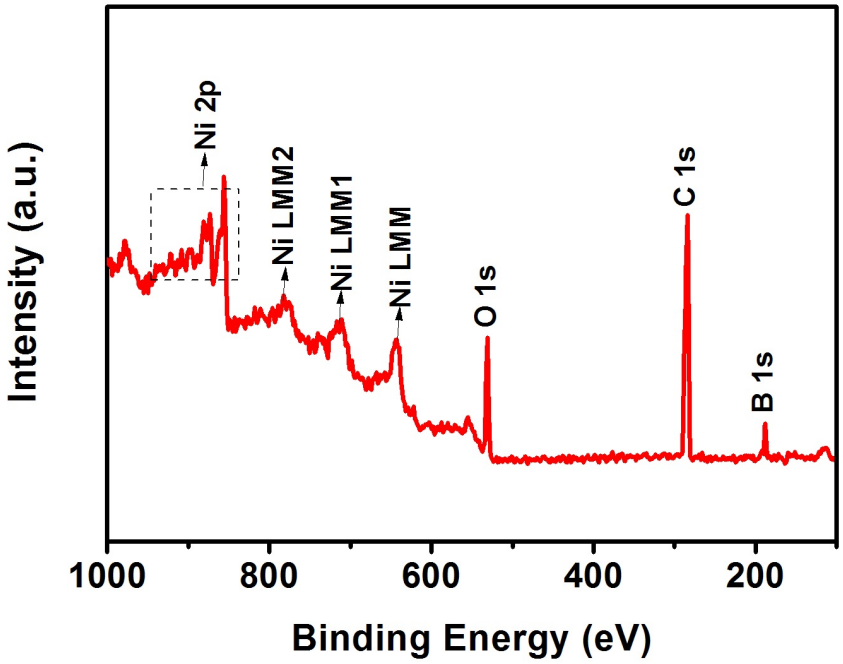

Fig. S10 XPS survey scan of Ni_xB/f-MWCNT.

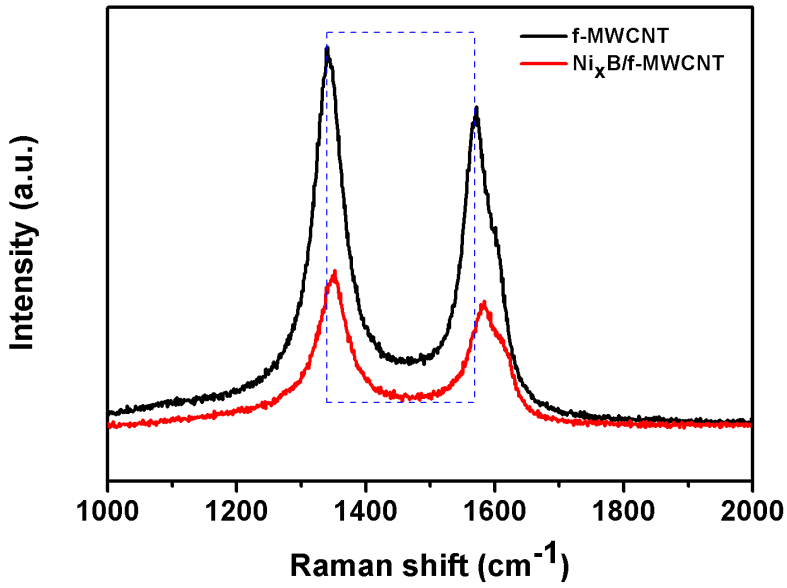

Fig. S11 Raman spectra of Ni_xB/f-MWCNT and f-MWCNT.

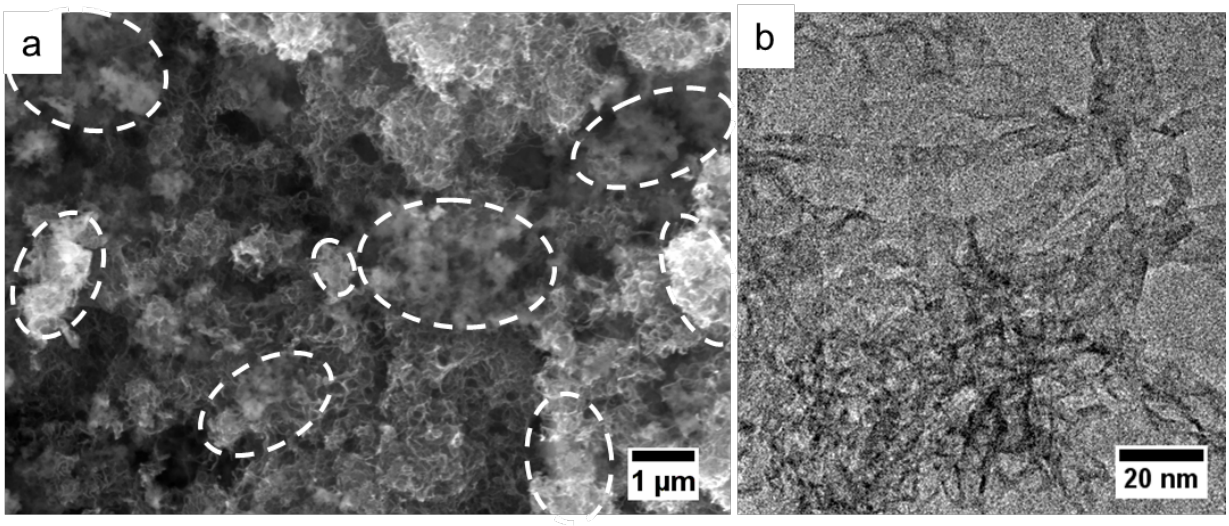

Fig. S12 (a) SEM and (b) TEM images of the physical mixture Ni_xB and f-MWCNT (Ni_xB+f-MWCNT). The areas circled by dashed lines show aggregated Ni_xB particles.

Table S2 Comparison of OER activity of recently reported nickel-based or metal-boride based electrocatalysts. (Note that the support material used in all examples given below.)

Catalyst	Loading (mg cm^{-2})	Tafel slope (mV dec^{-1})	η_{10} (mV)	TOF (s^{-1})	Ref.
Ni_xB/f-MWCNT	**0.2**	**46.3**	**286**	**0.058**	***This work***
Ni_xB nanosheets	**0.2**	**107.1**	**375**	**0.0432**	***This work***
IrO_2 (reference)	**0.2**	**71.2**	**338**	**–**	***This work***
Pc-Ni-B@NB	0.3	52	302	0.026 0.052	*Angew. Chem. Int. Ed*. **2017**, *56*, 6572
Ni_xB-300	0.21	N/A	380	0.048	*Adv. Energy Mater*. **2017**, *7*, 1700381
Co_2B-500	0.21	45	380	–	*Adv. Energy Mater*. **2016**, *6*, 1502313
CoB NS/G	0.285	53	290	–	*Angew. Chem. Int. Ed*. **2016**, *55*, 2488
FeB_2	0.2	52.4	296	–	*Adv. Energy Mater*. **2017**, *7*, 1700513
Ni3B–rGO	0.2	88.4	290	–	*Electrochem. Commun*. **2018**, 86, 121
Ni-Fe-B/rGO	0.2	58	265	–	J. Solid State Chem. **2018**, 265,13.
Co-Mo-B	2.1	150	320	–	*Electrochimica Acta.* **2017**, 232, 64
Co-Ni-B@NF	–	131	313	–	*J. Mater. Chem. A, 2017, 5, 12379.*
NiO	0.14	65	365	–	*Energy Environ. Sci.* **2015**, *8*, 2347
Ni_2P	0.14	47	290	–	*Energy Environ. Sci.* **2015**, *8*, 2347
Ni-P	0.2	64	300	–	*Energy Environ. Sci.* **2016**, *9*, 1246
$NiPS_3$	0.2	80	350	–	*ACS Catal.* **2017**, *7*, 229
NiPS3-G-1:1	0.2	42.6	294	0.0564	*ACS Nano* **2018**, *12*, 5297
$Ni_{0.6}Co_{1.4}(OH)_2$	0.35	80	300	–	*Adv. Funct. Mater.* **2018**, *28*, 1706008
$Ni(OH)_2$	0.2	42	331	0.0361	*J. Am. Chem. Soc.* **2014**, *136*, 7077
Ni_3Se_2	0.217	79.5	310	0.044	*Energy Environ. Sci.* ***2016***, *9*. 1771
NGO/Ni_7S_6	0.21	45.4	380	–	*Adv. Funct. Mater.* **2017**, *27*, 1700451

† N/A: not available.

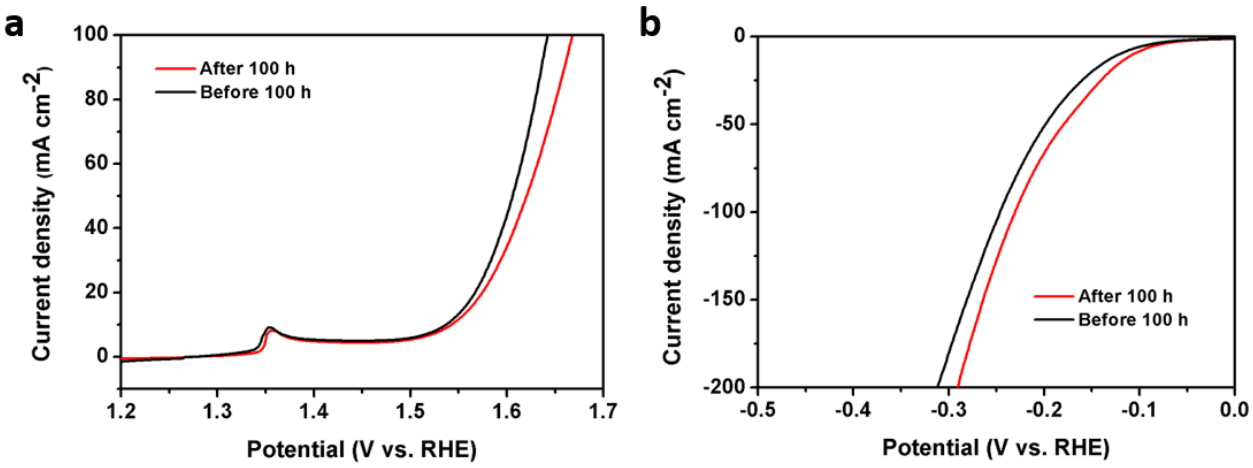

Fig. S13 Linear sweep voltammograms (LSVs) of Ni_xB/f-MWCNT in 1.0 M KOH before and after Chronopotentiometry operation for 100 h under the current density of 20 mA cm^{-2}. a) OER, and b) HER.

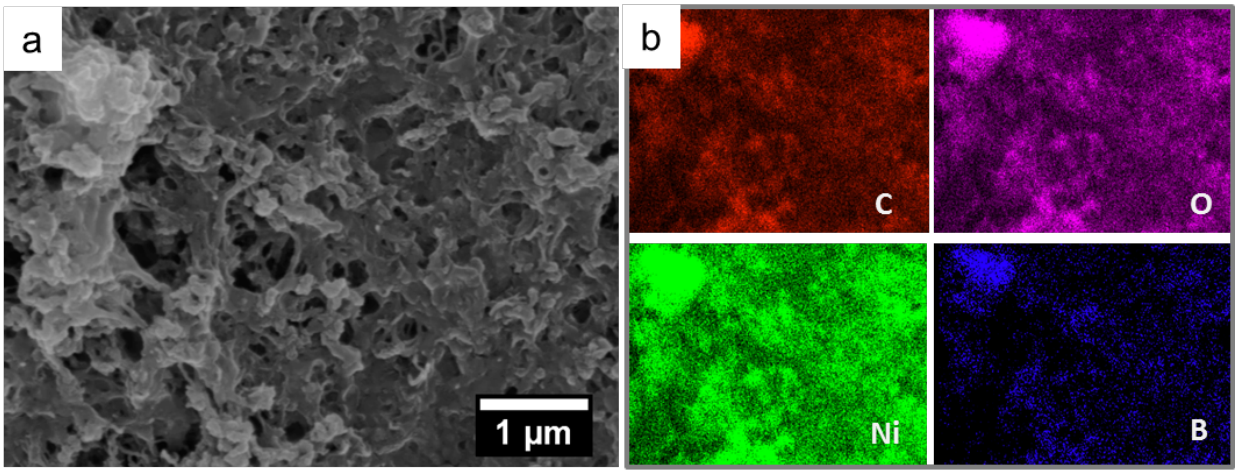

Fig. S14 Characterization of Ni_xB/f-MWCNT after the 100-hour OER test in 1 M KOH electrolyte under the current density of 20 mA cm^{-2}. (a) SEM image and (b) the corresponding EDX elemental mappings of C, O, Ni, and B.

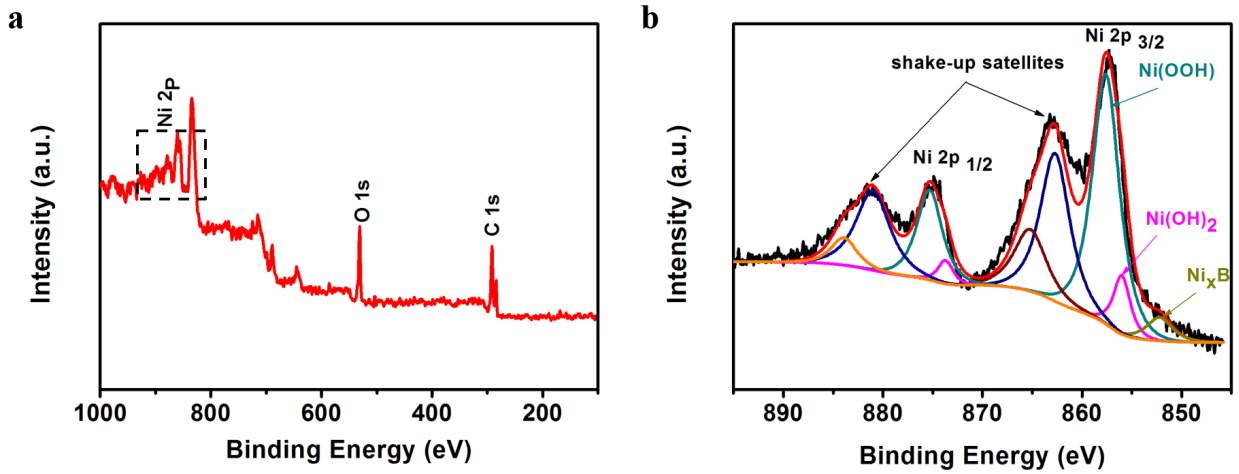

Fig. S15 (a) XPS survey spectrum of Ni_xB/f-MWCNT after the 100-hour OER test in 1 M KOH electrolyte under the current density of 20 mA cm^{-2}, and (b) the corresponding core-level XPS spectra near the region of Ni2p.

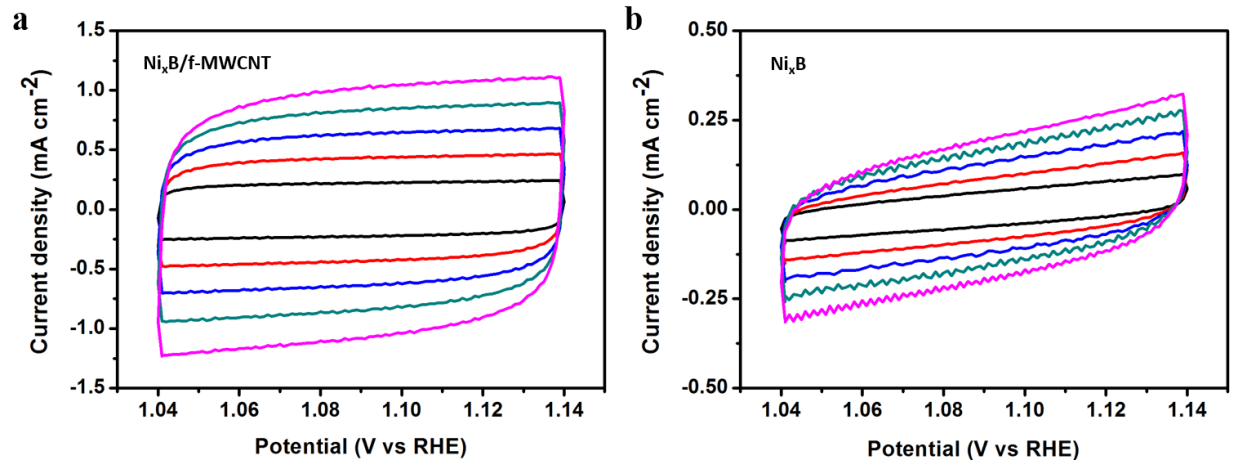

Fig. S16 Cyclic voltammogram (CV) curves of (a) Ni_xB/f-MWCNT and (b) Ni_xB recorded in a non-Faradic region in 1 M KOH at different scan rates of 20, 40, 60, 80, and 100 mV s^{-1}.

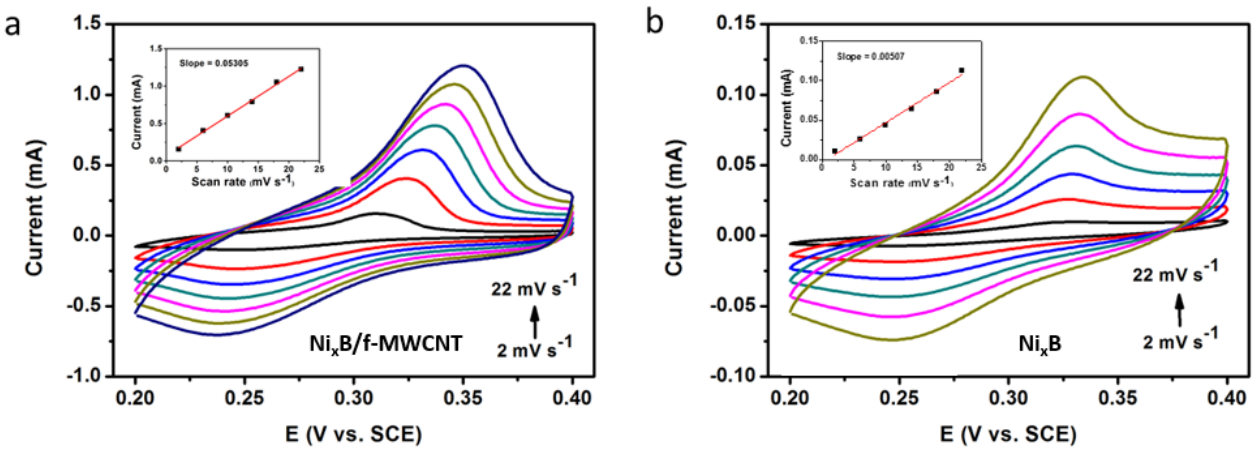

Fig. S17 CV curves of (a) Ni_xB/f-MWCNT and (b) Ni_xB at the different scan rates from 2 to 22 mV s^{-1} in 1 M KOH electrolyte. The inset figures show the corresponding plots of the oxidation peak current *vs.* the scan rate extracted from (a) and (b), respectively.

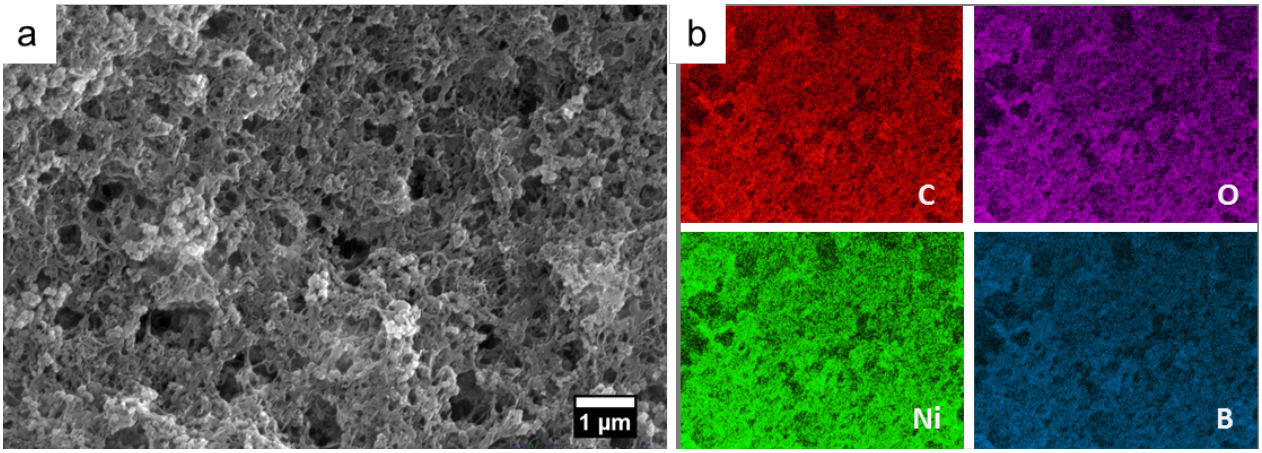

Fig. S18 Characterization of Ni_xB/f-MWCNT after the 100-hour HER test in 1 M KOH electrolyte under the current density of 20 mA cm^{-2}. (a) SEM image and (b) the corresponding EDX elemental mappings of C, O, Ni, and B.

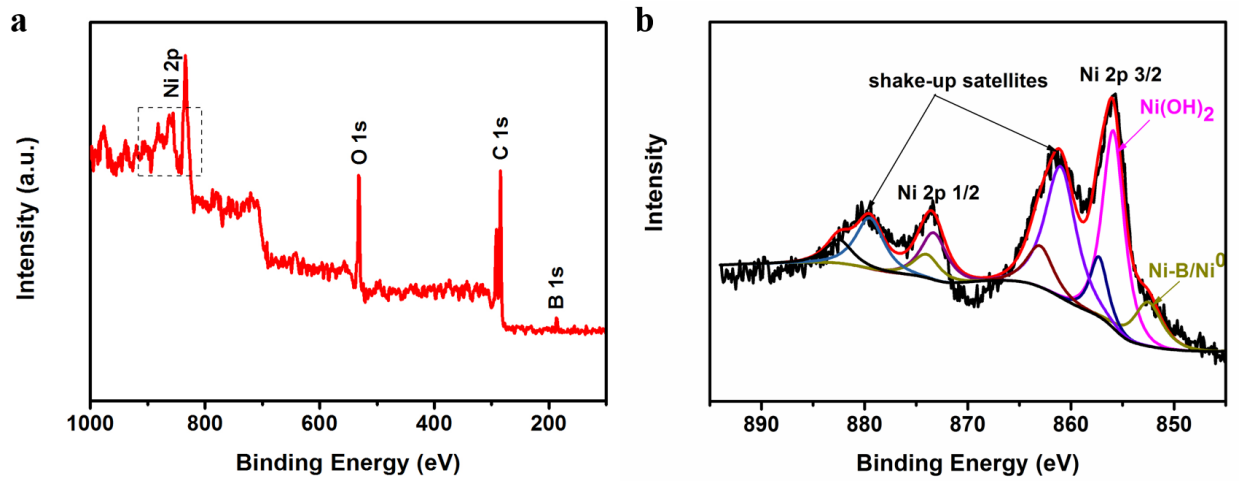

Fig. S19 (a) XPS survey spectrum of Ni_xB/f-MWCNT after the 100-hour HER test in H_2-saturated 1 M KOH electrolyte under the current density of 20 mA cm^{-2}, and (b) the corresponding core-level XPS spectra near the region of Ni2p.

Table S3. The HER performance of recently reported nickel- or TMB-based electrocatalysts.

Catalyst	Support	Loading (mg cm^{-2})	Tafel slope (mV dec^{-1})	η_{10} (mV)	Ref.
Ni_xB/f-MWCNT	**Glassy carbon**	**0.2**	**70.4**	**116**	***This work***
Ni_xB nanosheets	**S/A**	**0.2**	**152.1**	**277**	***This work***
Ni_xB+f-MWCNT	**S/A**	**0.2**	**103.9**	**209**	***This work***
Pt/C (reference)	**S/A**	**0.2**	**57.2**	**62**	***This work***
Co_2B-500/NG	S/A	0.21	92.4	127	*Adv. Energy Mater.* **2016**, *6*, 1502313
FeB_2	S/A	0.2	87.5	61	*Adv. Energy Mater.* **2017**, *7*, 1700513
NiO/Ni-CNT	S/A	0.28	82	<100	*Nat. Commun.* **2014**, *5*, 4695
NiO nanorods	S/A	0.2	100	~110	*Nano Energy.* **2018**, *43*, 103
$1TMoS_2/Ni^{2+\delta}O_\delta(OH)_{2-\delta}$	S/A	0.4	105	185	*Adv. Sci.* **2018**, *5*, 1700644
MoC_x	S/A	0.8	59	151	*Nat. Commun.* **2015**, *6*, 6512
Mo_xC-Ni@NCV	S/A	1.1	93	126	*J. Am. Chem. Soc.* **2015**, *137*, 15753
Ni_2P	S/A	1.8	–	220	*Energy Environ. Sci.* **2015**, *8*, 2347
Ni_2P	S/A	1	–	~180	*J. Am. Chem. Soc.* **2013**, *135*, 9267
CoP	Carbon cloth	0.92	129	209	*J. Am. Chem. Soc.* **2014**, *136*, 7587
$NiCo_2S_4$	Nickel foam	–	58.9	210	*Adv. Funct. Mater.* **2016**, *26*, 4661
N-doped Ni_3S_2	S/A	0.6	113	155	*Adv. Energy Mater.* **2018**, *8*, 1703538
NF-NiS_2	S/A	–	63	122	*Nano Energy*. **2017**, *41*, 148
Ni/NiS	S/A	–	123.3	230	*Adv. Funct. Mater*. **2016**, *26*, 3314
o-$CoSe_2$|P	o-$CoSe_2$|P	1.02	69	104	*Nat. Commun*. **2018**, *9*, 2533
NiSe/NF	Nickel foam	–	120	96	*Angew. Chem. Int. Ed*. **2015**, *54*, 9351

† S/A: same as above.

Table S4. Comparison of the bifunctional water splitting activity of the Ni_xB/f-MWCNT catalyst with other recently reported bifunctional electrocatalysts in 1 M alkaline electrolytes.

Anode	Cathode	Loading (mg cm^{-2})	η_{10} (mV)	Ref.
Ni_xB/f-MWCNT	**Ni_xB/f-MWCNT**	**1.0**	**1.60**	***This work***
IrO_2 (reference)	**Pt/C (reference)**	**1.0**	**1.62**	***This work***
Ni/NiP	Ni/NiP	10.58	1.61	*Adv. Funct. Mater.* ***2016***, *26*, 3314
Ni_2P	Ni_2P	5	1.63	*Energy Environ. Sci.* ***2015***, *8*, 2347
$NiCo_2P_2$/G NSs	$NiCo_2P_2$/G NSs	0.31	161	*Nano Energy*. **2018**, *48*, 284
$Ni_{11}(HPO_3)_8(OH)_6$	$Ni_{11}(HPO_3)_8(OH)_6$	3	1.65	*Energy Environ. Sci.*, **2018**, *11*, 1287
NiSe/NF	NiSe/NF	2.8	1.63	*Angew. Chem. Int. Ed.* **2015**, *54*, 9351
$NiCo_2O_4$	$Ni_{0.33}Co_{0.67}S_2$	0.3	1.72	*Adv. Energy Mater*. **2015**, *5*, 1402031
$Co_{0.85}$Se/NiFe-LDH	$Co_{0.85}$Se/NiFe-LDH	4	1.66	*Energy Environ. Sci.* **2016**, *9*, 478
BSCF/NF	BSCF/NF	0.387	1.72	*Sci. Adv.* **2017**, *3*, e1603206
Ni_5P_4 films/Ni	Ni_5P_4 films/Ni	3.5	~1.68	*Angew. Chem. Int. Ed.* **2015**, *127*, 12538
SNCF-NR	SNCF-NR	3	1.68	*Adv. Energy Mater*. **2017**, *7*, 1602122
Fe-doped CoP	Fe-doped CoP	1.03	1.60	*Adv. Mater.* **2017**, *29*, 1602441
$NiCo_2S_4$/NF	$NiCo_2S_4$/NF	6.5	1.61	*Adv. Mater. Interf.* **2018**, *5*, 1701396
CP/CTs/Co-S	CP/CTs/Co-S	0.32	1.743	*ACS Nano.* **2016**, *10*, 2342
$NiFeO_x$/CFP	$NiFeO_x$/CFP	1.6	~1.61	*Nat. Commun.* ***2015***, *6*, 8261
NiFe LDH/NF	NiFe LDH/NF	–	1.70	*Science* **2014**, *345*, 1593
Ni_3FeN/r-GO	Ni_3FeN/r-GO	0.5	1.60	*ACS Nano* **2018**, *12*, 245

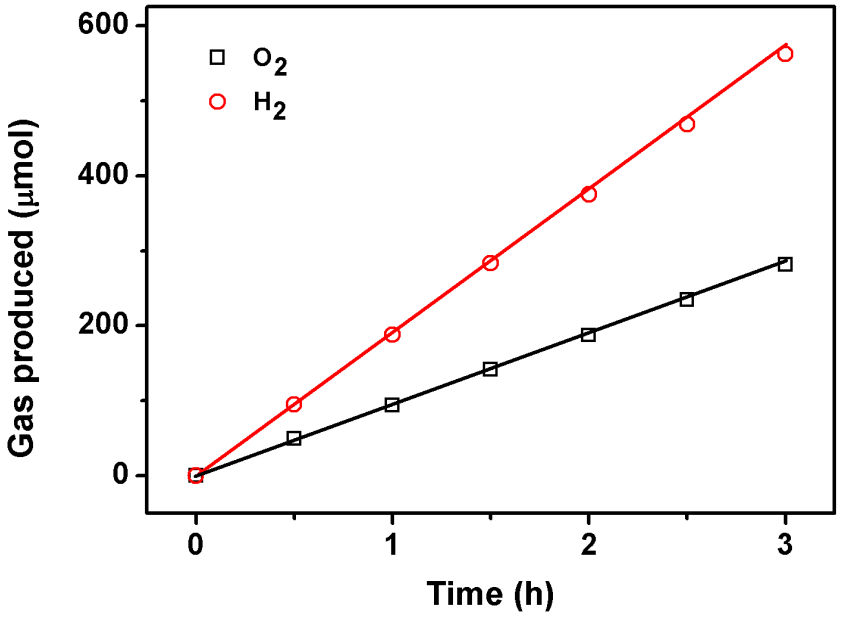

Fig. S20. The amount of gas theoretically calculated and experimentally measured vs. time for OER and HER vs. time for Ni_xB/f-MWCNT.