



## Journal of Materials Chemistry A

### Supporting Information

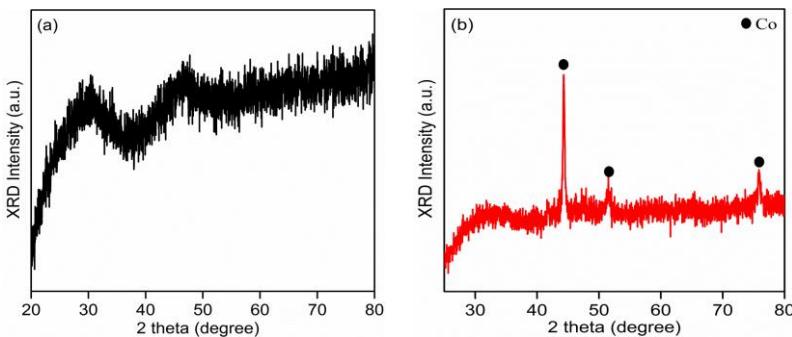
## Cobalt Nickel Boride as an Active Electrocatalyst for Water Splitting

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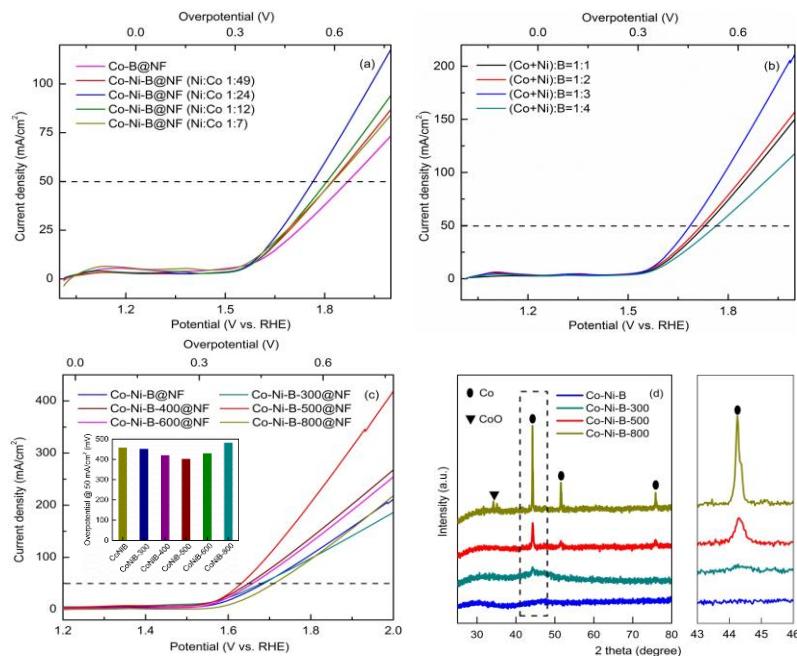
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**Figure S1.** XRD patterns of the as-prepared and 500 °C-annealed Co–Ni–B powder.



**Figure S2.** OER polarization curves (without iR compensation) of the as-prepared Co–Ni–B@NF catalyst (a) with different Ni/Co molar ratios, (b) with different (Co+Ni)/B ratios, (c) annealed at different temperatures. (d) XRD patterns of the as-prepared and annealed Co–Ni–B powders.

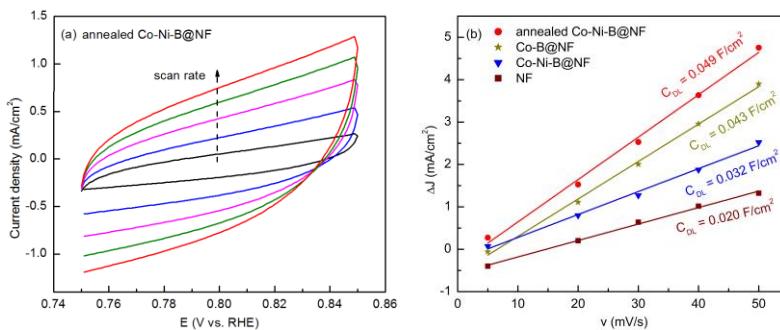
Figure S2 (a) shows the OER activity dependence on the nominal Ni:Co molar ratio. It was observed that the OER activity of the Co–Ni–B@NF catalyst first increases with increasing the Ni/Co molar ratio and reaches its maximum at a Ni/Co molar ratio of 1/24. Further increasing the Ni content results in activity degradation. For the Co–Ni–B@NF catalyst with an optimal Ni/Co molar ratio of 1/24, an overpotential of 535 mV is required to achieve a current density of 50 mA/cm<sup>2</sup>. According to the XPS

analysis, the authentic Ni/Co molar ratio is around 1/21, which is in good agreement with the nominal molar ratio estimated from the precursors concentration.

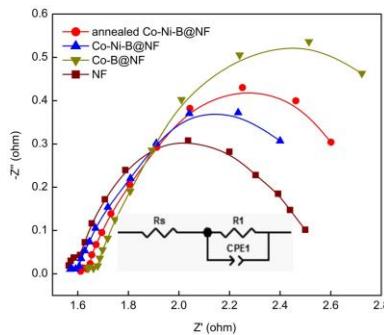
Figure S2 (b) shows the OER activity dependence of the Co–Ni–B@NF catalyst on the (Co+Ni)/B molar ratio. According to the polarization curves, an optimal (Co+Ni)/B molar ratio is determined as 1/3. Thus the Co–Ni–B@NF catalyst with a Ni/Co molar ratio of 1/24 and a (Co+Ni)/B molar ratio of 1/3 was selected for further studies.

Figure S2 (c) shows the OER activity dependence of the Co–Ni–B@NF catalyst on the calcination temperature. It was observed that the OER activity of the Co–Ni–B@NF catalyst first increases with elevating the calcination temperature, and reaches its maximum at 500°C. Further increasing the calcination temperature results in activity degradation.

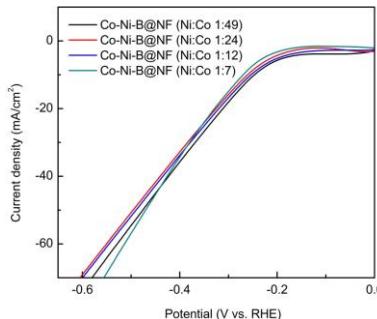
Figure S2 (d) presents the XRD patterns of the as-prepared and the annealed Co–Ni–B catalyst powder. It was found that the as-prepared Co–Ni–B possesses an amorphous structure, which persists at a calcination temperature up to 300°C. Further increasing the calcination temperature to 500°C resulted in the partial crystallization of the amorphous phase. The calcined catalyst at 500°C shows weak peaks at  $2\theta = 44.22^\circ$ ,  $51.52^\circ$  and  $75.85^\circ$ , which can be assigned to the *fcc* Co (JCPDS card 15-0806). Further increasing the calcination temperature up to 800°C results in significant increase of peak intensity, indicating increase of the grain size of metallic Co. The metallic Ni cannot be clearly identified in the XRD pattern. Presumably, Ni atoms dissolve into the lattice of metallic Co, resulting in the formation of Co–Ni alloy at elevated temperatures. In addition, XRD analysis of the calcined catalyst sample at 800 °C detected a weak peak centered at  $2\theta = 34.11^\circ$ , which is temporarily assigned to crystalline CoO (JCPDS card 42-1300).



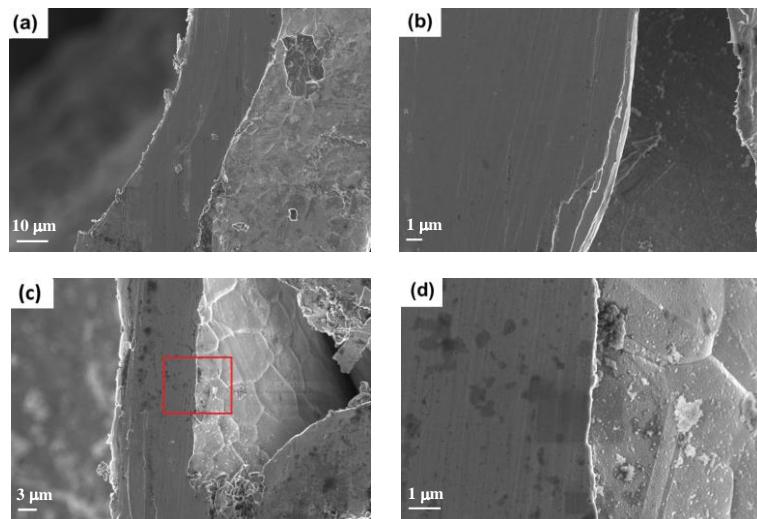
**Figure S3.** (a) CV curves of the 500 °C-calcined Co–Ni–B@NF catalyst at varied scan rates. (b) The differences in current density ( $\Delta J = j_a - j_c$ ) at OCP as a function of scan rate.



**Figure S4.** EIS Nyquist plots and fitting curves at 1.62 V (vs. RHE) for various electrocatalysts.



**Figure S5.** HER polarization curves (without iR compensation) of the as-prepared Co–Ni–B@NF catalyst with different Ni/Co molar ratios.



**Figure S6.** Cross-section FE-SEM images of as-prepared Co–Ni–B@NF at different magnifications. (d) High-magnification view of the region indicated by the red rectangle in (c).

**Table S1.** Summary of OER activities, ECSA and  $R_c$  for various catalysts in this work

Catalyst	$\eta$ (mV) at 10 mA/cm <sup>2</sup>	$\eta$ (mV) at 50 mA/cm <sup>2</sup>	Tafel slope (mV/dec)	ECSA (cm <sup>2</sup> )	$R_c$ (Ω)
Annealed Co–Ni–B@NF	313	402	120	1225	1.24
Co–Ni–B@NF	339	457	131	800	1.14
Co–B@NF	341	534	154	1075	1.50
NF	391	602	181	500	0.96

**Table S2.** Comparison of OER activity for various catalysts

Catalyst	$\eta$ (mV) at 10 mA/cm <sup>2</sup>	Tafel slope (mV/dec)	References
Annealed Co–Ni–B@NF	313	120	This work
Co–Ni–B@NF	339	131	This work
Co–B@NF	341	154	This work
NF	391	181	This work
Ni <sub>3</sub> S <sub>2</sub> Nanosheet Arrays@NF	339	131	[1]
Ni–P Foam	312	180	[2]
Co–P Films@Cu Foil	345	47	[3]
Co@N-rich Carbon	370	76	[4]
Ni@C	330	145	[5]
TiN@Ni <sub>3</sub> N	350	94	[6]
CoP@N-doped Graphene	338	54	[7]
IrO <sub>2</sub>	338	47	[8]
IrO <sub>2</sub>	427	49	[9]
RuO <sub>2</sub>	305	60	[10]
RuO <sub>2</sub>	390	63	[11]

**Table S3.** Comparison of HER activity for various catalysts

Catalyst	$\eta$ (mV) at 10 mA/cm <sup>2</sup>	$\eta$ (mV) at 20 mA/cm <sup>2</sup>	References
Annealed Co–Ni–B@NF	205	279	This work
NF	298	373	This work
CoP@CC	209	\	[12]
Co <sub>2</sub> P@Ti	150	\	[13]
CoO <sub>x</sub> @CN	232	\	[14]
CoN <sub>x</sub> @C	170	\	[15]
Co-N-CNTs	370	450	[16]
Ni(OH) <sub>2</sub> @Ni	338	54	[17]
NiB <sub>0.54</sub> @Cu Foil	135	\	[18]
NiB <sub>0.54</sub> @Ni Foil	306	\	[18]
NiB <sub>0.54</sub> @Pt Foil	165	\	[18]
Ni <sub>3</sub> S <sub>2</sub> NAs@NF	220	\	[1]
NiFe LDH@NF	200	250	[19]
FePNAs@CC	218	\	[20]
MoC <sub>x</sub> @C	151	175	[21]
Mo <sub>2</sub> C@NC	60	\	[22]
Porous Mo <sub>2</sub> C NRs@GC	150	\	[23]
WP NAs@CC	150	\	[24]
W <sub>2</sub> N NAs@CC	285	\	[25]

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