Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Computational screening of transition-metal doped boron nanotubes as efficient electrocatalysts for water splitting

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Table S1. The adsorption energies (E_{ad}) of OOH on Rh-doped BNTs with different actual truncation radius (R).

R/Å	E_{ad}/eV
4.6	-1.752
4.8	-1.759
5.0	-1.761
5.2	-1.756
5.4	-1.758

Table S2. The adsorption energies (E_{ad}) of OOH on Rh-doped BNTs with different energy convergence.

energy convergence tolerance/Ha	E_{ad}/eV
2.0×10^{-5}	-1.753
1.0×10^{-5}	-1.756
5.0×10^{-6}	-1.753
1.0×10^{-6}	-1.753

Table S3. The calculated free energy corrections: total energy (E), zero-point energy (ZPE), entropy (S), and heat capacity (C_p). T is temperature and equals 298.15. All results are in unit of eV.

		OOH	O	OH	H
Cr	*ZPE*	5.293506702	5.004571286	5.265493453	5.183014816
	TS	1.617317608	1.265156822	1.430881066	1.185656247
	E	-61224.70686	-59158.63813	-59174.94896	-57121.88001
	$\int C_p dT$	0.862339739	0.768933333	0.818108293	0.734545552
Mn	*ZPE*	5.316619801	4.985360962	5.26098358	5.140908214
	TS	1.41133238	1.30178475	1.312541699	1.202619128
	E	-64073.45415	-62007.61707	-62024.11431	-59971.44081
	$\int C_p dT$	0.823398721	0.779861102	0.791569426	0.738838604
Co	*ZPE*	5.337304507	4.974173008	5.243854736	5.082583415
	TS	1.45575651	1.319600947	1.334365894	1.260592877
	E	-70359.7429	-68292.94172	-68310.3351	-66257.73077
	$\int C_p dT$	0.837492074	0.788707391	0.80119627	0.760217136
Ni	*ZPE*	5.451872624	5.076989438	5.345456969	5.086529554
	TS	1.408669001	1.279327034	1.284602076	1.214591405
	E	-73789.82846	-71722.59598	-71740.52904	-69687.98182
	$\int C_p dT$	0.826607669	0.771491818	0.774614038	0.750633656
Mo	*ZPE*	5.308987708	5.05929686	5.323427975	5.052575414
	TS	1.417628815	1.296703644	1.46306141	1.270367219
	E	-143306.0084	-141239.85	-141255.8074	-139202.371
	$\int C_p dT$	0.835800871	0.780121287	0.811473576	0.770277622
Ru	*ZPE*	5.428239156	5.037137773	5.319785385	5.015325599
	TS	1.445658942	1.367257334	1.349350634	1.283141096
	E	-156852.9609	-154786.6387	-154803.654	-152750.7681
	$\int C_p dT$	0.832505195	0.786322362	0.79963516	0.767025309
Rh	*ZPE*	5.403608311	5.062072166	5.319048194	5.039436073
	TS	1.430531982	1.296768289	1.352207948	1.278111706
	E	-164072.2031	-162005.4275	-162022.9822	-159970.5737
	$\int C_p dT$	0.836668155	0.762472072	0.802193645	0.772575922
Pd	*ZPE*	5.328805131	4.95335821	5.201748134	5.008951067
	TS	1.620136136	1.40085987	1.452382035	1.377096322
	E	-171819.6199	-169752.2532	-169770.3234	-167717.9861
	$\int C_p dT$	0.86901782	0.790398593	0.8029742	0.764900465
W	*ZPE*	5.28015054	5.007303229	5.337477963	5.082540051
	TS	1.487923925	1.407725182	1.473986436	1.260308438
	E	-465835.9737	-463769.8431	-463785.3431	-461731.9791
	$\int C_p dT$	0.840310744	0.790355229	0.816677276	0.766331483

Os	*ZPE*	5.244678655	4.973696003	5.164585047	5.054309981
	TS	1.548043892	1.31678242	1.423498593	1.394602222
	E	-426011.7737	-423945.735	-423961.8052	-421909.1313
	$\int C_p dT$	0.86485486	0.793477449	0.834109669	0.792306616
Ir	*ZPE*	5.259335742	4.921008545	5.190950458	5.013894581
	TS	1.539743458	1.386780162	1.292618072	1.304344697
	E	-454751.2832	-452685.1408	-452702.3489	-450649.7351
	$\int C_p dT$	0.869841739	0.805489322	0.784457703	0.782159402
Pt	*ZPE*	5.278155789	5.002489807	5.333878738	5.045810605
	TS	1.473314127	1.483553914	1.364167297	1.295863257
	E	-440697.3276	-438630.8744	-438648.1334	-436595.6972
	$\int C_p dT$	0.851325242	0.814335611	0.799765252	0.775481321

Table S4. The calculated free energy corrections: total energy (*E*), zero-point energy (*ZPE*), entropy (*S*), and heat capacity (C_p) for gas phase H_2 and H_2O. *T* is temperature and equals 298.15. All results are in unit of eV.

	H_2	H_2O
ZPE	0.319116873	0.566249236
TS	0.024513432	0.040222197
E	-31.88072753	-2084.655378
$\int C_p dT$	0.005160335	0.051950267

Table S5. Adsorption energies (E_{ad}) of free metal atoms on pristine BNTs. All results are in unit of eV.

	Cr	Mn	Co	Ni	Mo	Ru
E_{ad}	–2.67	–2.80	–4.13	–4.03	–4.23	–5.40
	Rh	Pd	W	Os	Ir	Pt
E_{ad}	–4.42	–2.84	–6.56	–6.01	–5.58	–4.36

Table S6. Adsorption energies (E_{ad}) of metal atoms on pristine BNTs respect to bulk metal. All results are in unit of eV.

	Cr	Mn	Co	Ni	Mo	Ru
E_{ad}	2.21	0.96	0.69	0.57	2.50	1.71
	Rh	Pd	W	Os	Ir	Pt
E_{ad}	1.06	0.88	3.52	2.78	1.90	1.75

Table S7. Adsorption energies of the reaction intermediates on different TM-doped BNTs. All results are in unit of eV.

	Cr	Mn	Co	Ni	Mo	Ru
OOH	–3.69	–3.01	–2.03	–1.83	–3.87	–2.33
O	–6.86	–6.41	–4.47	–3.83	–6.94	–5.24
OH	–4.53	–4.26	–3.22	–3.12	–4.26	–3.62
H	–2.51	–2.94	–1.28	–0.93	–2.89	–1.70
	Rh	Pd	W	Os	Ir	Pt
OOH	–1.76	–1.43	–4.93	–3.43	–2.12	–2.55
O	–4.21	–3.30	–8.03	–6.62	–5.21	–5.33
OH	–3.13	–2.73	–4.90	–4.06	–3.78	–3.95
H	–1.05	–0.59	–2.57	–2.14	–1.27	–1.42

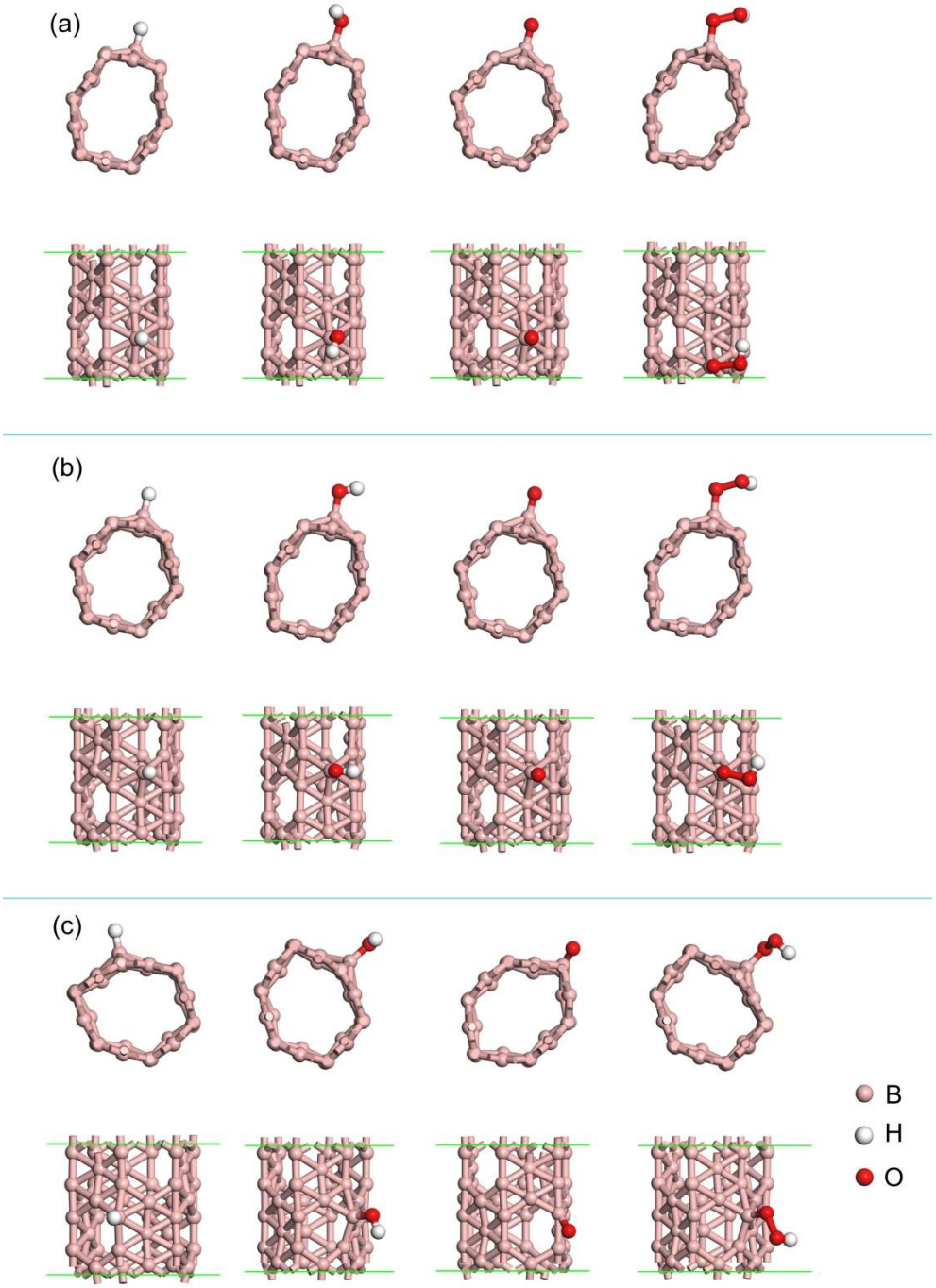

Fig. S1 Atomic structures of reaction intermediates (H, OH, O, OOH, and O_2) on pristine BNTs with three different adsorption sites.

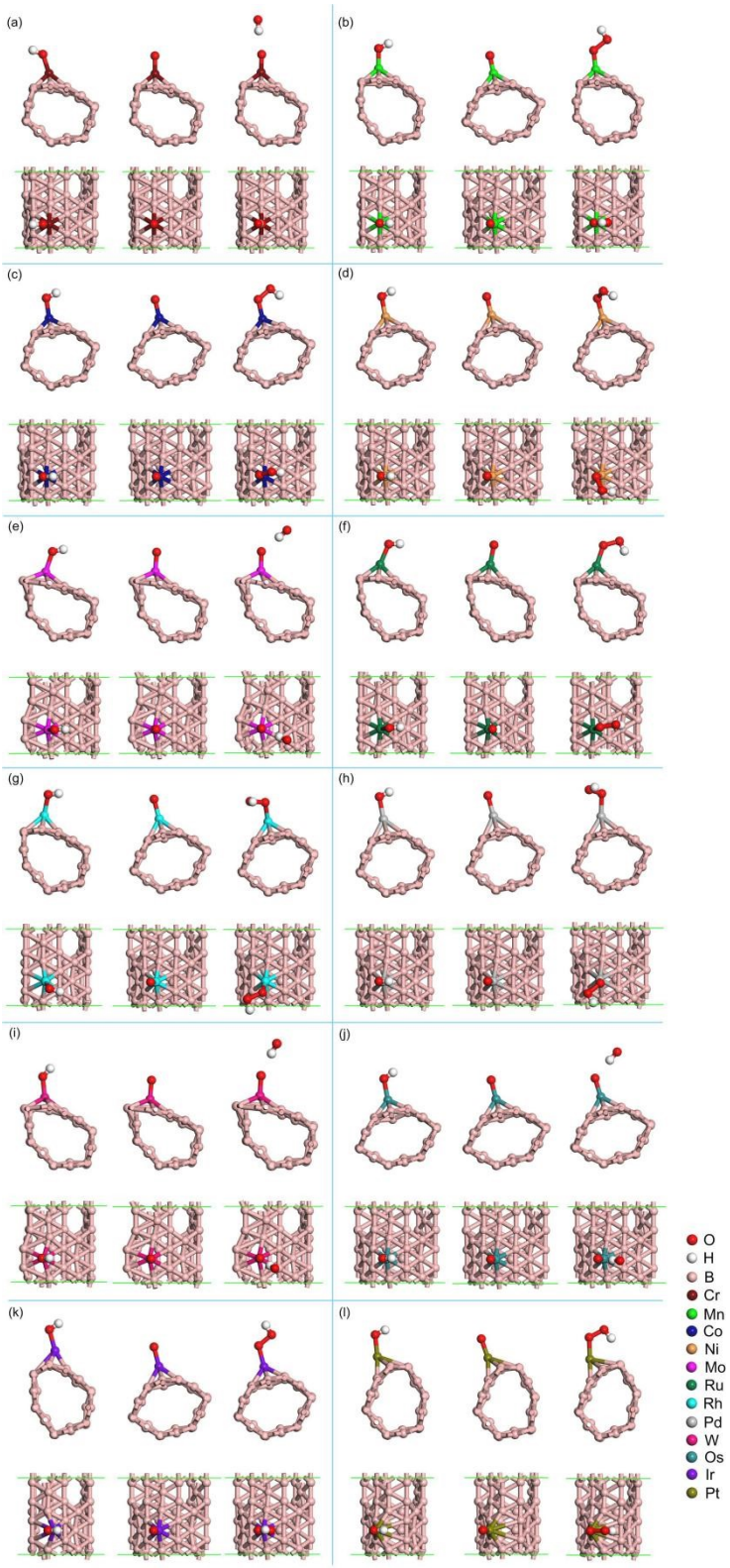

Fig. S2 Atomic structures of reaction intermediates (OH, O, OOH, and O_2) for OER on TM-doped BNTs. (a) Cr, (b) Mn, (c) Co, (d) Ni, (e) Mo, (f) Ru, (g) Rh, (h) Pd, (i) W, (j) Os, (k) Ir, (l) Pt.

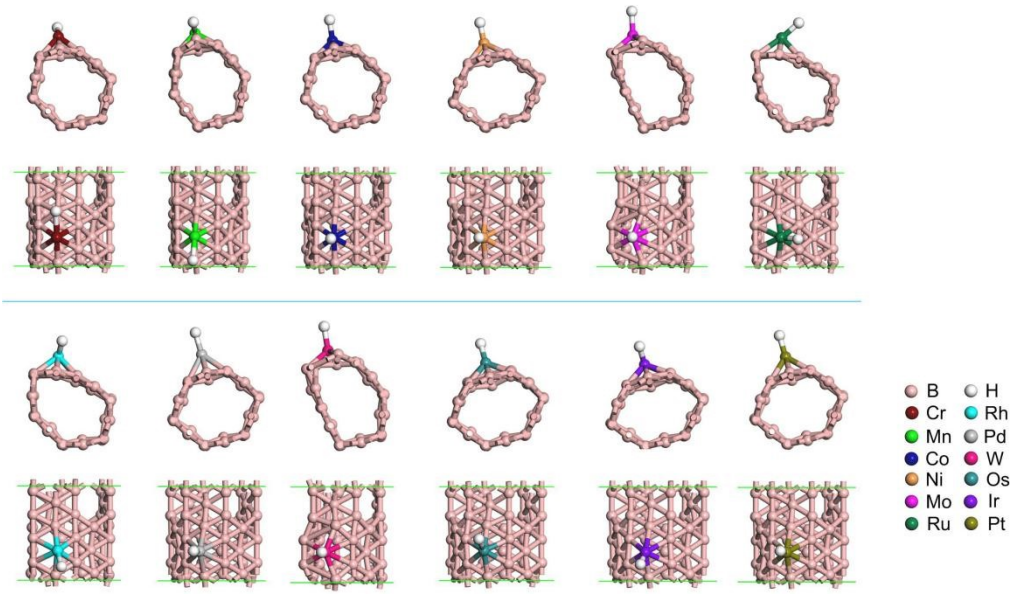

Fig. S3 Atomic structures of H adsorbed on TM-doped BNTs.

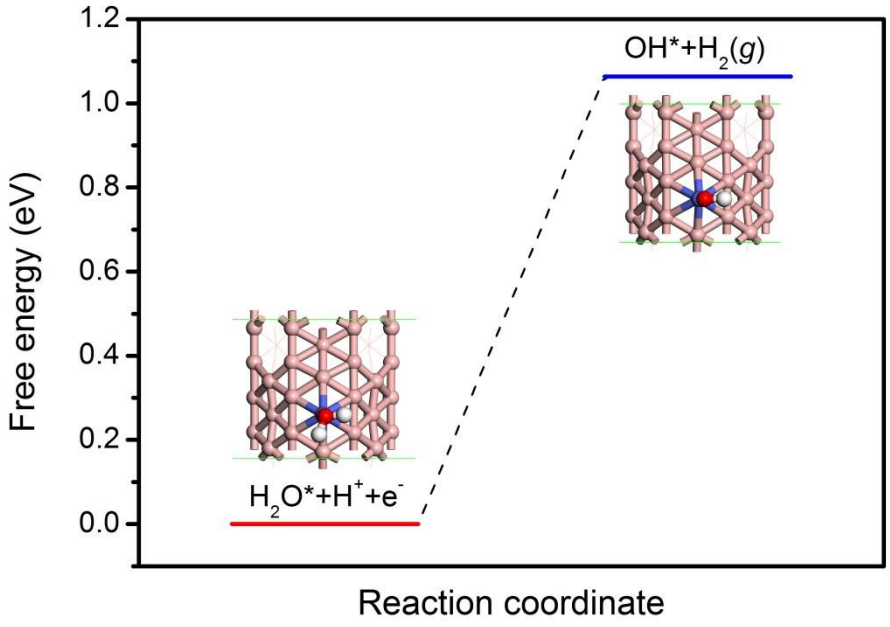

Fig. S4 Free energy profile for HER on Co-doped BNTs via H_2O.

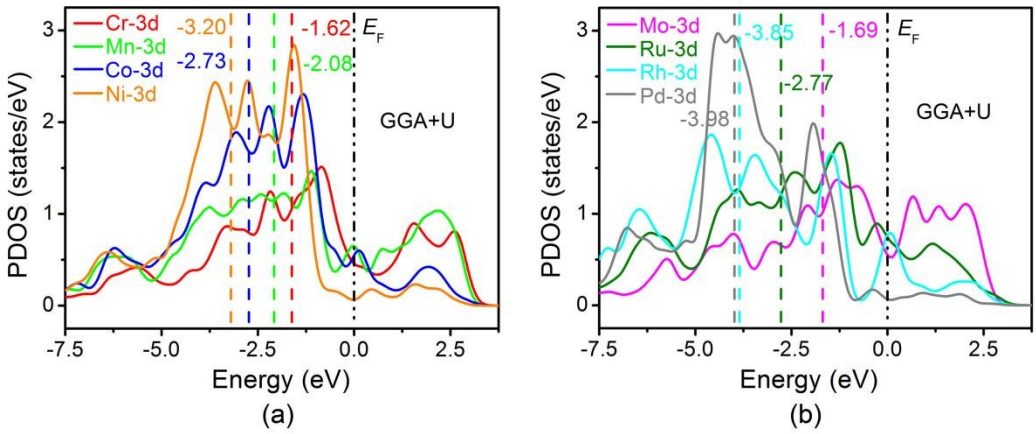

Fig. S5 The partial density of states (PDOS) of the transition metal doped BNTs with GGA+U approach. The U values for Cr, Mn, Co, Ni, Mo, Ru, Rh, and Pd were set as 2.5, 2.5, 2.5, 2.5, 2.0, 2.0, 2.0, 2.0 eV, respectively.