Supplementary Information for:

Designing water splitting catalysts using rules of thumb: advantages, dangers and alternatives

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Table S1. Free energies of adsorption of *O, *OH and *OOH (ΔG_O, ΔG_{OH}, ΔG_{OOH}, in eV), a metric for the breaking of the *OOH vs *OH scaling relation ($\gamma_{OOH/OH}$, in V), OER/ORR electrochemical-step symmetry index ($ESSI_{OER}$ / $ESSI_{ORR}$ in V), OER overpotentials (η_{OER} in V) and the additive inverse of the ORR overpotentials ($-\eta_{ORR}$ in V) for all the materials included in this work. Values taken from references.[1,2,3,4,5,6,7,8,9,10]

Material	ΔG_O	ΔG_{OH}	ΔG_{OOH}	$\gamma_{OOH/OH}$	$ESSI_{OER}$	η_{OER}	$ESSI_{ORR}$	$-\eta_{ORR}$
Doped and undoped TiO_2								
TiO_2	4.60	2.07	5.08	0.27	1.07	1.30	-1.07	-1.39
V-TiO_2 (5cM)	2.35	1.38	4.50	0.33	0.53	0.91	-0.53	-0.80
V-TiO_2 (5cM)	3.17	1.18	4.67	0.51	0.51	0.75	-0.51	-0.98
V-TiO_2 (6cM)	2.76	0.38	3.97	0.56	1.14	1.15	-0.38	-0.84
V-TiO_2 (6cM)	3.40	1.02	4.56	0.54	1.14	1.15	-0.38	-0.87
V-TiO_2 (6cM)	3.46	1.12	4.63	0.52	1.11	1.11	-0.37	-0.94
Nb-TiO_2 (5cM)	1.38	-0.08	3.39	0.51	0.44	0.76	-1.31	-1.31
Nb-TiO_2 (5cM)	2.14	0.23	3.74	0.52	0.52	0.67	-0.52	-0.99
Nb-TiO_2 (6cM)	2.33	0.10	3.61	0.52	0.37	1.00	-1.12	-1.12
Nb-TiO_2 (6cM)	2.38	0.05	3.59	0.54	0.60	1.13	-0.60	-1.17
Nb-TiO_2 (6cM)	2.69	0.29	3.80	0.54	1.17	1.19	-0.39	-0.93
Ta-TiO_2 (5cM)	1.50	-0.51	3.04	0.55	0.58	0.78	-1.74	-1.74
Ta-TiO_2 (5cM)	1.86	-0.02	3.52	0.54	0.42	0.65	-1.25	-1.25
Ta-TiO_2 (6cM)	2.33	0.07	3.60	0.53	0.38	1.02	-1.15	-1.15
Ta-TiO_2 (6cM)	2.17	-0.35	3.37	0.63	0.80	1.31	-0.80	-1.58
Ta-TiO_2 (6cM)	2.55	0.13	3.64	0.53	0.62	1.20	-0.62	-1.10
Cr-TiO_2 (5cM)	2.43	1.85	4.87	0.28	0.92	1.20	-0.92	-1.18
Cr-TiO_2 (5cM)	3.44	1.61	5.14	0.53	0.48	0.59	-1.45	-1.45
Cr-TiO_2 (6cM)	2.91	1.23	4.76	0.53	0.36	0.61	-1.07	-1.07

Cr-TiO_2 (6cM)	4.14	1.72	5.23	0.52	0.84	1.20	-0.84	-1.54
Cr-TiO_2 (6cM)	3.84	1.56	5.04	0.51	0.69	1.05	-0.69	-1.35
Mo-TiO_2 (5cM)	0.49	0.42	3.72	0.42	2.00	1.99	-0.67	-1.17
Mo-TiO_2 (5cM)	1.46	0.61	4.16	0.54	1.46	1.45	-0.49	-0.61
Mo-TiO_2 (6cM)	0.86	0.28	3.83	0.54	1.74	1.73	-0.58	-0.94
Mo-TiO_2 (6cM)	2.18	0.62	4.17	0.54	0.54	0.74	-0.54	-0.60
Mo-TiO_2 (6cM)	2.35	0.58	4.10	0.53	0.53	0.53	-0.53	-0.64
W-TiO_2 (5cM)	-0.33	-0.23	3.16	0.47	1.39	2.26	-1.40	-1.46
W-TiO_2 (5cM)	0.42	0.34	3.90	0.55	2.25	2.25	-0.75	-1.16
W-TiO_2 (6cM)	0.26	0.05	3.50	0.49	1.10	2.01	-1.10	-1.17
W-TiO_2 (6cM)	1.16	0.05	3.60	0.55	0.65	1.20	-0.65	-1.17
W-TiO_2 (6cM)	1.46	0.21	3.71	0.52	0.52	1.00	-0.52	-1.01
Mn-TiO_2 (5cM)	3.38	1.92	4.82	0.22	0.38	0.69	-1.13	-1.13
Mn-TiO_2 (5cM)	4.22	2.06	5.07	0.27	0.88	0.92	-0.88	-1.38
Mn-TiO_2 (6cM)	4.20	1.94	5.09	0.34	0.87	1.03	-0.87	-1.40
Mn-TiO_2 (6cM)	4.50	2.01	5.07	0.29	1.02	1.25	-1.02	-1.38
Mn-TiO_2 (6cM)	4.48	2.01	5.10	0.31	1.01	1.24	-1.01	-1.41
Fe-TiO_2 (5cM)	3.73	2.10	4.95	0.19	0.63	0.88	-0.63	-1.26
Fe-TiO_2 (5cM)	4.31	2.16	5.10	0.24	0.93	0.93	-0.93	-1.41
Fe-TiO_2 (6cM)	3.81	1.55	5.06	0.48	0.67	1.03	-1.37	-1.37
Fe-TiO_2 (6cM)	3.98	1.55	5.06	0.52	0.76	1.20	-0.76	-1.37
Fe-TiO_2 (5cM)	3.88	1.50	4.94	0.49	0.71	1.16	-0.71	-1.25
Ru-TiO_2 (5cM)	2.15	1.05	4.19	0.34	0.81	0.80	-0.27	-0.50
Ru-TiO_2 (5cM)	3.55	1.73	5.12	0.46	0.48	0.58	-1.43	-1.43
Ru-TiO_2 (6cM)	2.98	0.49	4.53	0.79	0.79	1.26	-0.79	-0.84
Ru-TiO_2 (6cM)	3.83	1.42	4.96	0.54	0.69	1.19	-0.69	-1.27
Ru-TiO_2 (6cM)	3.90	1.47	4.95	0.51	0.72	1.20	-0.72	-1.26
Ir-TiO_2 (5cM)	1.81	0.61	3.68	0.30	0.32	0.63	-0.33	-0.61
Ir-TiO_2 (5cM)	3.45	1.75	4.68	0.23	0.45	0.53	-0.50	-0.99
Ir-TiO_2 (6cM)	2.72	1.13	4.64	0.52	0.52	0.67	-0.52	-0.95
Ir-TiO_2 (6cM)	3.78	1.44	4.94	0.52	0.65	1.11	-0.66	-1.25
Ir-TiO_2 (6cM)	3.64	1.35	4.86	0.52	0.59	1.06	-0.59	-1.17
Ni-TiO_2 (5cM)	4.55	2.03	4.80	0.15	1.04	1.29	-1.04	-1.10
Ni-TiO_2 (5cM)	4.59	2.08	5.12	0.14	1.06	1.28	-1.06	-1.43
Ni-TiO_2 (6cM)	4.27	2.03	5.31	0.41	0.90	1.01	-0.90	-1.62
Ni-TiO_2 (6cM)	4.57	2.08	5.08	0.27	1.05	1.25	-1.05	-1.39
Ni-TiO_2 (6cM)	4.47	2.04	5.06	0.28	1.00	1.19	-1.00	-1.37
Porphyrins								
Cr-H	0.85	0.26	3.53	0.40	0.81	1.45	-0.81	-0.97
Cr-F	1.00	0.38	3.63	0.39	0.73	1.40	-0.73	-0.85
Cr-OH	0.76	0.22	3.49	0.40	0.85	1.50	-0.85	-1.01
Cr-CH_3	0.61	0.18	3.33	0.35	0.92	1.49	-0.92	-1.05
Cr-BH_2	0.94	0.36	3.58	0.38	0.76	1.41	-0.76	-0.87
Cr-NH_2	0.60	0.10	3.33	0.38	0.92	1.49	-0.93	-1.13
Mn-H	0.93	0.27	3.53	0.39	0.76	1.36	-0.76	-0.96
Mn-F	1.13	0.46	3.70	0.39	1.34	1.34	-0.45	-0.77

Mn-OH	0.74	0.23	3.51	0.41	0.86	1.54	-0.86	-1.01
Mn-CH_3	0.74	0.18	3.39	0.37	0.86	1.41	-0.86	-1.05
Mn-BH_2	1.41	0.75	3.94	0.37	1.30	1.30	-0.43	-0.56
Mn-NH_2	0.46	-0.05	3.18	0.38	1.00	1.49	-1.00	-1.28
Fe-H	1.19	0.63	3.77	0.34	1.36	1.36	-0.45	-0.67
Fe-F	1.37	0.68	3.85	0.36	1.26	1.26	-0.42	-0.55
Fe-OH	1.07	0.48	3.62	0.34	0.69	1.31	-0.69	-0.75
Fe-CH_3	1.10	0.57	3.73	0.35	1.39	1.39	-0.46	-0.70
Fe-BH_2	1.51	0.88	4.09	0.38	1.35	1.35	-0.45	-0.59
Fe-NH_2	0.89	0.34	3.45	0.32	0.78	1.32	-0.78	-0.89
Co-H	2.30	1.21	4.09	0.21	0.56	0.56	-0.19	-0.40
Co-F	1.97	1.04	4.09	0.29	0.89	0.89	-0.30	-0.40
Co-OH	1.65	0.88	3.95	0.31	1.07	1.07	-0.36	-0.46
Co-CH_3	2.14	1.00	4.07	0.30	0.69	0.69	-0.23	-0.38
Co-BH_2	2.47	1.24	4.29	0.29	0.20	0.58	-0.60	-0.60
Co-NH_2	1.26	0.77	3.86	0.31	1.37	1.37	-0.46	-0.74
Ni-H	3.66	1.82	4.85	0.28	0.60	0.61	-0.60	-1.16
Ni-F	3.43	1.85	4.93	0.31	0.41	0.62	-1.25	-1.25
Ni-OH	3.21	1.58	4.78	0.37	0.37	0.40	-1.10	-1.10
Ni-CH_3	3.82	1.84	4.60	0.15	0.68	0.75	-0.68	-0.91
Ni-BH_2	3.85	1.93	4.78	0.20	0.70	0.70	-0.70	-1.10
Ni-NH_2	3.10	1.32	4.46	0.34	0.26	0.55	-0.77	-0.77
Cu-H	4.12	2.07	5.07	0.27	0.83	0.84	-0.83	-1.38
Cu-F	4.15	2.04	5.01	0.25	0.85	0.88	-0.85	-1.33
Cu-OH	3.69	1.62	4.94	0.43	0.42	0.84	-1.25	-1.25
Cu-CH_3	3.76	1.83	4.89	0.30	0.65	0.69	-0.65	-1.20
Cu-BH_2	4.61	1.78	4.99	0.37	1.07	1.61	-1.08	-1.30
Cu-NH_2	2.69	0.92	4.48	0.55	0.55	0.56	-0.55	-0.80
				$SrMO_3$				
$SrScO_3$	5.23	2.38	5.21	0.18	1.38	1.61	-1.39	-1.52
$SrTiO_3$	3.91	1.61	4.90	0.42	0.72	1.07	-0.73	-1.22
$SrVO_3$	-0.07	0.13	3.35	0.38	1.26	2.19	-1.27	-1.43
$SrCrO_3$	0.92	0.75	3.99	0.39	1.84	1.84	-0.61	-1.06
$SrMnO_3$	2.29	1.21	4.41	0.37	0.88	0.88	-0.29	-0.72
$SrFeO_3$	2.98	1.67	4.70	0.28	0.33	0.47	-1.00	-1.00
$SrCoO_3$	3.00	1.54	4.44	0.22	0.25	0.31	-0.76	-0.76
$SrNiO_3$	3.84	2.17	4.92	0.15	0.69	0.94	-0.69	-1.24
$SrCuO_3$	4.75	2.32	5.31	0.26	1.14	1.19	-1.15	-1.62
$SrZnO_3$	5.16	2.56	5.40	0.19	1.35	1.37	-1.35	-1.72
$SrGeO_3$	4.44	1.74	5.22	0.51	0.99	1.47	-0.99	-1.53
$SrRuO_3$	2.26	1.11	4.09	0.26	0.59	0.59	-0.20	-0.40
				$LaMO_3$				
$LaScO_3$	4.80	1.82	4.88	0.30	1.17	1.75	-1.17	-1.19
$LaTiO_3$	-1.82	-1.16	2.23	0.46	2.14	2.82	-2.14	-2.39
$LaVO_3$	-0.74	-0.22	2.95	0.36	1.60	2.48	-1.60	-1.75
$LaCrO_3$	0.69	0.56	3.69	0.33	1.76	1.76	-0.59	-1.10

$LaMnO_3$	1.39	0.65	3.85	0.37	1.23	1.24	-0.41	-0.58
$LaFeO_3$	2.74	1.25	4.55	0.42	0.29	0.57	-0.86	-0.86
$LaCoO_3$	2.22	1.49	4.50	0.27	0.66	1.05	-0.66	-0.81
$LaNiO_3$	3.09	1.54	4.61	0.30	0.31	0.32	-0.93	-0.92
$LaCuO_3$	4.92	2.42	5.39	0.26	1.23	1.27	-1.23	-1.70
$LaZnO_3$	5.18	2.48	5.27	0.17	1.36	1.47	-1.36	-1.58
$LaGaO_3$	4.88	1.95	5.02	0.30	1.21	1.70	-1.21	-1.33
$LaRuO_3$	1.87	0.74	3.74	0.27	0.64	0.64	-0.21	-0.49
MO								
CaO	5.38	2.32	5.04	0.13	1.46	1.82	-1.46	-1.57
ScO	-0.90	-1.52	1.98	0.52	1.69	1.70	-1.68	-2.75
TiO	-1.61	-1.05	2.32	0.46	2.03	2.71	-2.04	-2.28
VO	-0.94	-0.71	2.56	0.41	1.70	2.27	-1.70	-1.94
CrO	0.22	-0.13	2.90	0.29	1.12	1.44	-1.12	-1.36
MnO	1.42	0.42	3.66	0.39	0.52	1.01	-0.52	-0.81
FeO	1.76	0.38	3.75	0.45	0.45	0.76	-0.45	-0.85
CoO	1.98	0.78	3.92	0.34	0.71	0.71	-0.24	-0.45
NiO	2.49	1.03	4.12	0.31	0.31	0.40	-0.31	-0.43
CuO	3.93	2.00	4.75	0.14	0.74	0.77	-0.74	-1.06
FGMs								
Cr	0.89	0.35	3.60	0.40	0.78	1.49	-0.78	-0.88
Mn	1.89	0.88	4.08	0.37	0.95	0.96	-0.32	-0.39
Fe	2.11	1.03	4.11	0.30	0.76	0.76	-0.25	-0.42
Co	2.93	1.22	4.11	0.21	0.48	0.48	-0.16	-0.42
Ni	4.16	2.14	4.91	0.15	0.85	0.92	-0.85	-1.22
Cu	4.52	2.31	5.11	0.17	1.03	1.08	-1.03	-1.42
Ru	1.72	0.58	3.63	0.30	0.37	0.68	-0.37	-0.65
Rh	2.84	1.23	4.19	0.25	0.17	0.37	-0.51	-0.50
Pd	4.65	2.50	5.08	0.05	1.09	1.28	-1.10	-1.39
Ag	4.77	2.52	5.12	0.07	1.16	1.30	-1.16	-1.43
Ir	2.41	1.24	4.26	0.28	0.32	0.61	-0.32	-0.57
Pt	4.61	2.42	5.11	0.11	1.08	1.19	-1.08	-1.42
Au	4.84	2.62	5.11	0.01	1.19	1.40	-1.19	-1.42
$BaNiO_x$								
$BaNiO_3$	3.88	1.87	4.99	0.33	0.71	0.78	-0.71	-1.30
$BaNiO_3$-d1	3.54	1.93	5.00	0.31	0.44	0.70	-1.31	-1.31
$BaNiO_3$-d2	3.94	1.78	5.15	0.46	0.74	0.93	-0.74	-1.46
$BaNiO_2$	3.46	1.85	4.78	0.24	0.36	0.62	-1.09	-1.09
$Sr_xNa_yRuO_3$								
$Sr_{7/8}Na_{1/8}RuO_3$	3.16	1.56	4.43	0.21	0.25	0.37	-0.74	-0.74
$Sr_{6/8}Na_{2/8}RuO_3$	3.31	1.59	4.76	0.36	0.36	0.49	-1.07	-1.07
$Sr_7Ru_8O_{24}$	3.38	1.58	5.02	0.49	0.44	0.58	-1.33	-1.33
$Sr_6Na_1Ru_8O_{24}$	3.44	1.62	4.79	0.36	0.37	0.58	-1.10	-1.10
$Sr_5Na_2Ru_8O_{24}$	2.66	0.94	4.34	0.47	0.47	0.49	-0.47	-0.65
LSNMR								
Mn @ LSNMR	3.12	0.96	4.08	0.33	0.93	0.93	-0.31	-0.39

Ni @ LSNMR	3.71	1.47	4.41	0.24	0.63	1.01	-0.63	-0.72
Ru @ LSNMR	2.27	0.54	3.89	0.45	0.45	0.50	-0.45	-0.69
				MO_2				
IrO_2	1.65	0.29	3.45	0.35	0.31	0.57	-0.94	-0.94
RuO_2	2.72	1.35	4.35	0.27	0.22	0.40	-0.66	-0.66
MnO_2	3.20	1.84	5.04	0.37	0.45	0.61	-1.35	-1.35
PtO_2	2.35	1.21	4.22	0.28	0.64	0.64	-0.21	-0.53

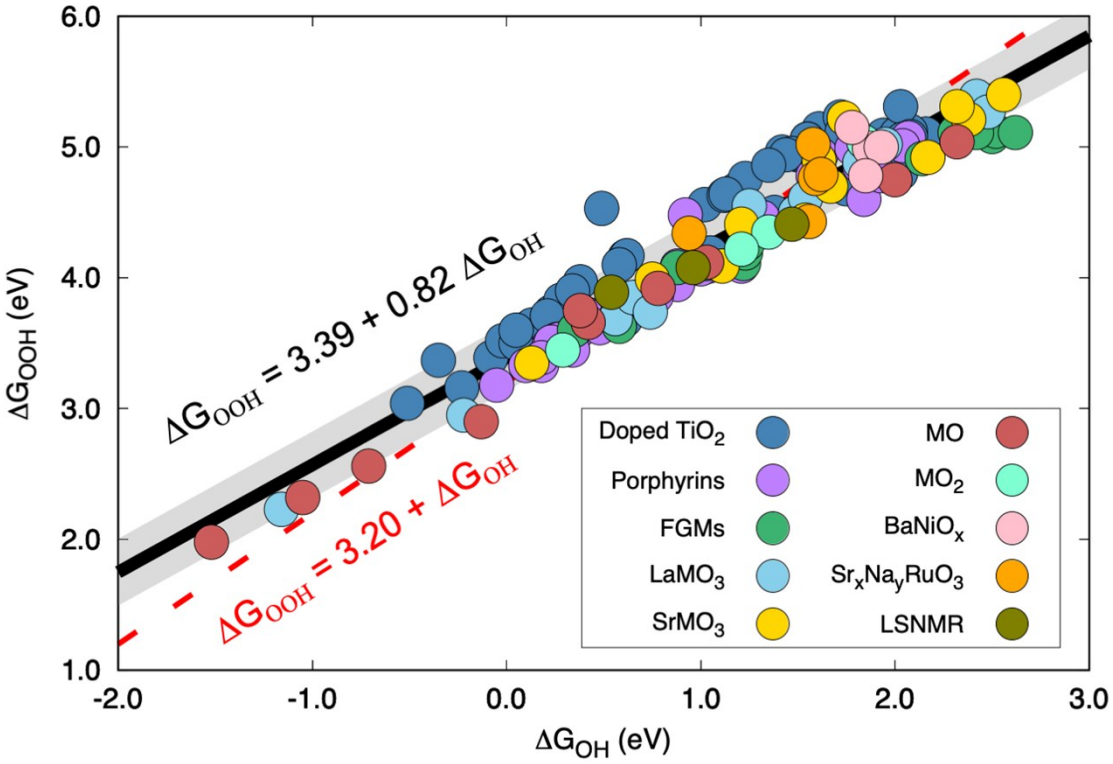

Figure S1. Adsorption energies of *OOH as a function of those of *OH. The least-squares linear fit (black line) is provided together with a red, dashed line in which the slope is 1 and the offset is 3.20 eV. The grey zone, which contains 76% of the data, spans over ± 1.5 MAE around the black line, with MAE = 0.17 eV. MAE: mean absolute error. Values taken from references 1-10.

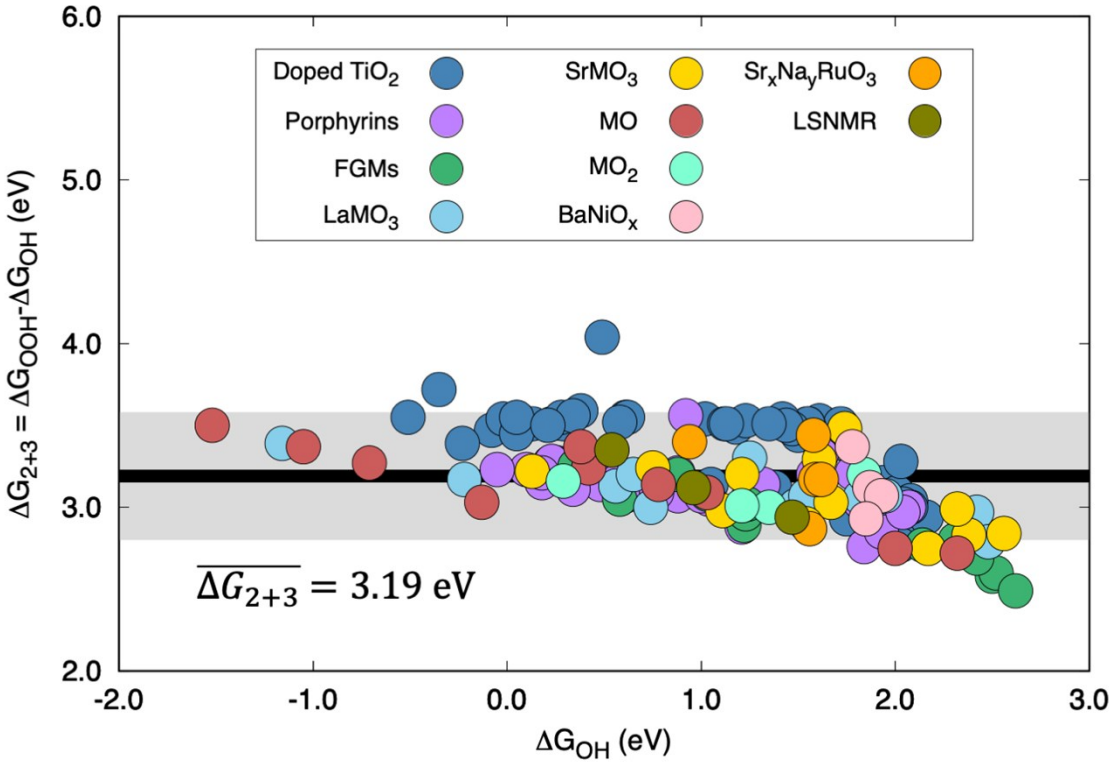

Figure S2. Sum of the reaction energies of steps 2 and 3 (ΔG_{2+3}) as a function of those of *OH. The black line is the average of all values, namely 3.19 eV. The grey zone, which contains 91% of the data, spans over ± 1.5 STDEV around the black line, with STDEV = 0.26 eV. STDEV: standard deviation. A grey zone spanning over ± 1.25 STDEV around the black line would contain 78% of the data. STDEV: standard deviation. Values taken from references 1-10.

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