Supporting Information

Transition-metal single atoms embedded into defective BC_3 as efficient electrocatalysts for oxygen evolution and reduction reactions

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Fig. S1. Optimized structures of models: (a) (3x3) p-BC_3 monolayer, (b) (3x3) V_B monolayer, (c) (3x3) V_C monolayer, (d) (3x3) V_{BC} monolayer and (e) (3x3) V_{CC} monolayer. The red line indicates the unit cell. The calculated density of states (DOS) of (f) (3x3) p-BC_3 monolayer, (g) (3x3) V_B monolayer, and (h) (3x3) V_C monolayer, respectively. The Fermi level is set at zero represented by the black dash line.

Fig. S2. Gibbs free energy of adsorbates corresponding to the d band center for (a) TM@V_B and (b) TM@V_C.

Fig. S3. Schematic diagrams of Rh/H and Pd/H substitution reactions for catalysts: (a) Rh@V_B and (b) Pd@V_C.

Fig. S4. The minimum energy pathway of adsorbed Rh atom diffused from the vacancy adsorption site to a neighboring hollow site on Rh@V_B catalyst.

Table S1 The detailed parameters for the optimized TM@V_B structures. $d_{TM\text{-}C}$ is the bond distance between TM atom and its nearest C neighbor. Q refers to charges transfer from TM

atoms to the V_B substrate obtained by Bader charge analysis.

Table S2 The detailed parameters for the optimized TM@V_C structures. $d_{TM\text{-}C/B}$ is the bond distance between TM atom and its nearest C/B neighbor. Q refers to charges transfer from TM atoms to the V_C substrate obtained by Bader charge analysis.

Table S3 Computed adsorption free energies of HO*, O* and HOO* (ΔG_{HO*}, ΔG_{O*}, and ΔG_{HOO*}), overpotentials for OER (η^{OER}) and ORR (η^{ORR}) on TM@V_B systems, as well as the d band center values that related to Fermi level of TM@V_B. The unit for ΔG is eV, while for η is V.

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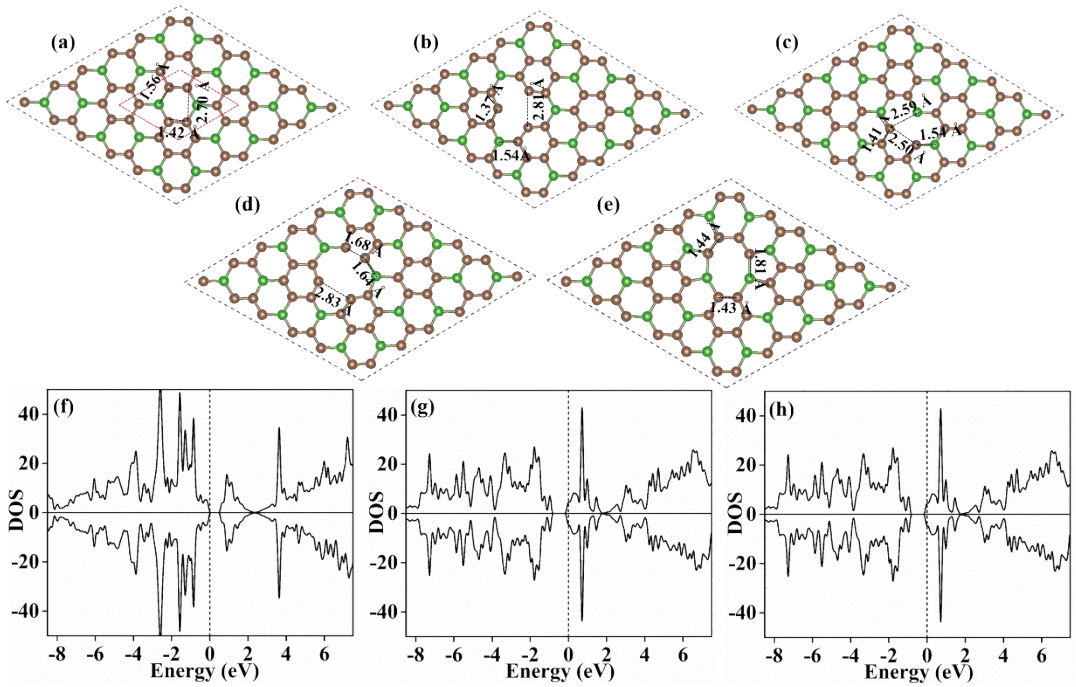
Table S5 $\Delta G_{(TM^{n+})}$ and $\Delta G_{diss}(0)$ values in this work. Positive value of $\Delta G_{diss}(0)$ indicates the TM@V_B catalyst is stable against dissolution at pH = 0 condition. pH_{min} is the minimum pH value corresponding to the $\Delta G_{diss}(0)$. In this work, the maximum and minimum pH values are set as 16.0 and -2.0, respectively, which are realistic in this region.

Table S6 $\Delta G_{(TM^{n+})}$ and $\Delta G_{diss}(0)$ values in this work. Positive value of $\Delta G_{diss}(0)$ indicates the TM@V_C catalyst is stable against dissolution at pH = 0 condition. pH_{min} is the minimum pH value corresponding to the $\Delta G_{diss}(0)$. In this work, the maximum and minimum pH values are set as 16.0 and -2.0, respectively, which are realistic in this region.



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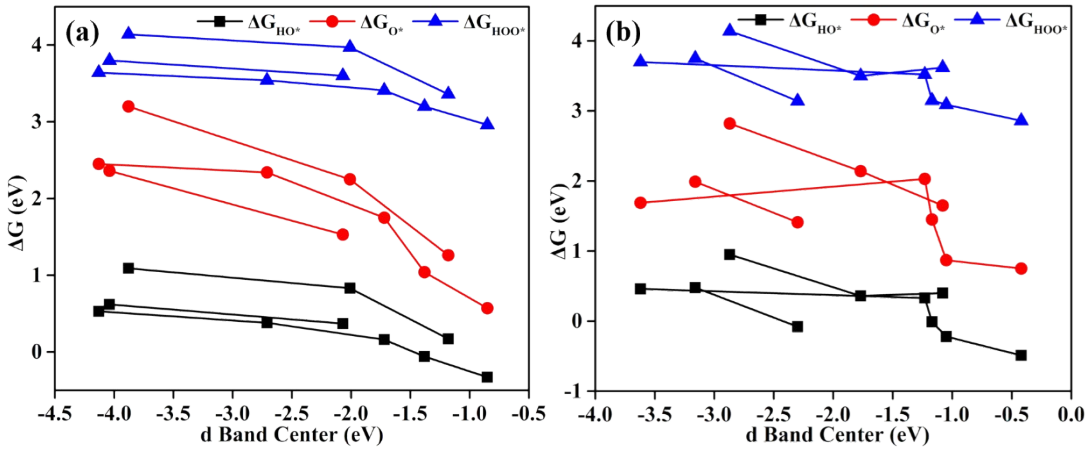

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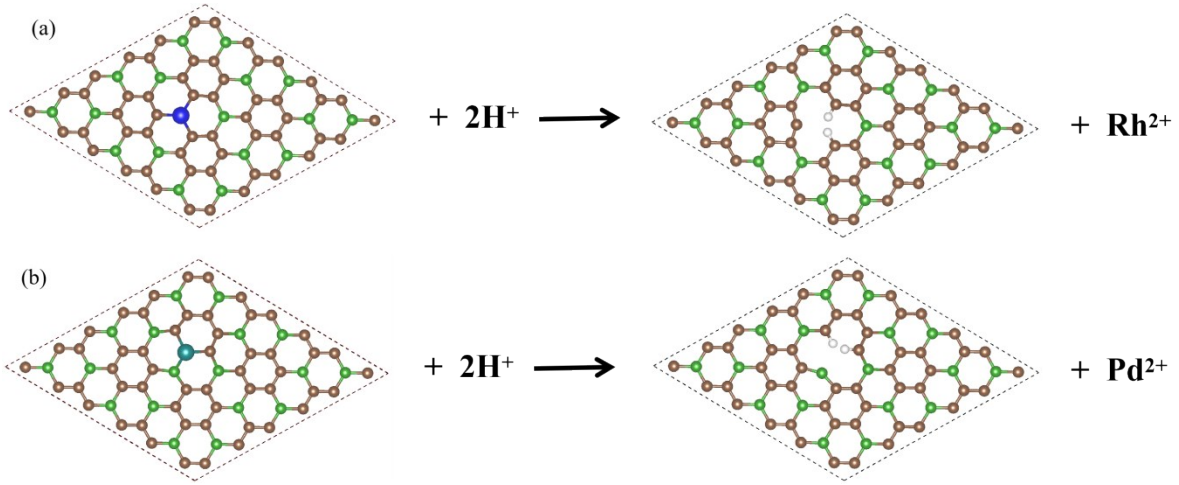

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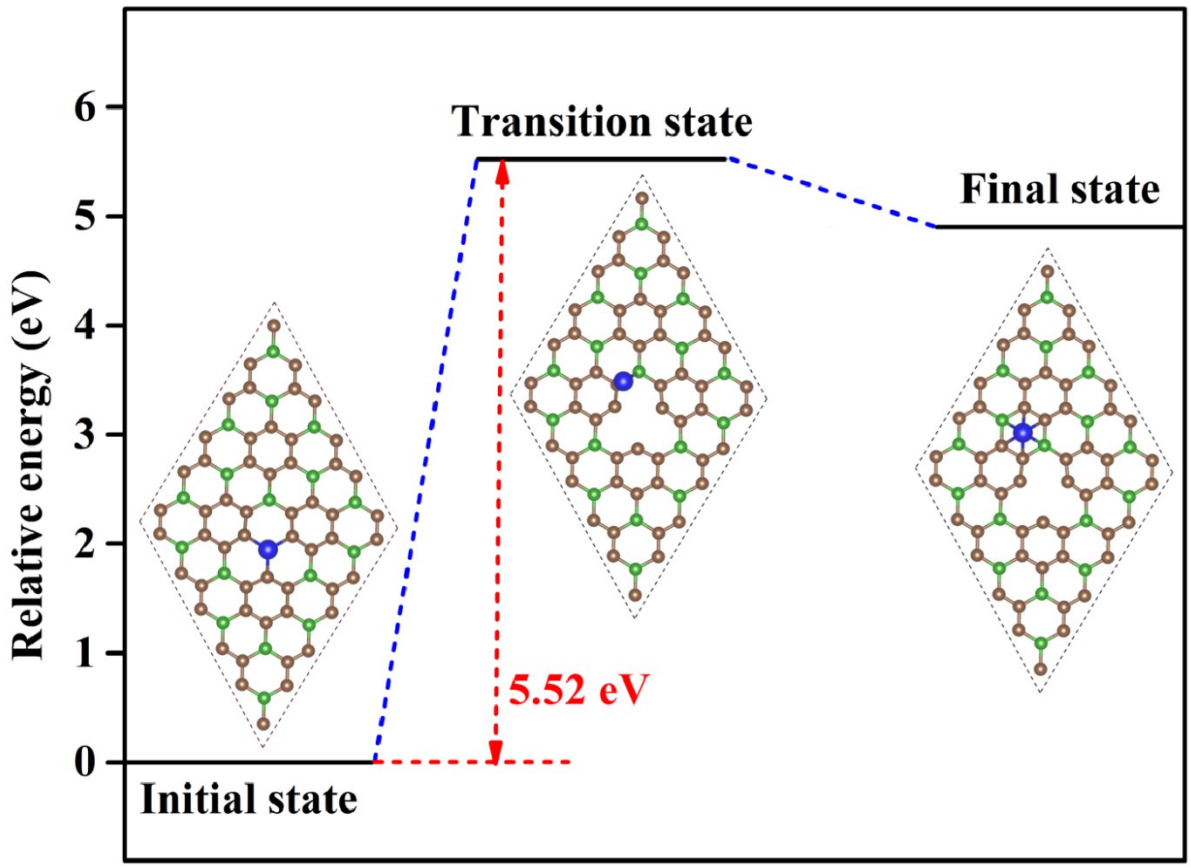

Fig. S4. The minimum energy pathway of adsorbed Rh atom diffused from the vacancy adsorption site to a neighboring hollow site on Rh@V_B catalyst.

Table S1 The detailed parameters for the optimized TM@V_B structures. d_{TM-C} is the bond distance between TM atom and its nearest C neighbor. Q refers to charges transfer from TM atoms to the V_B substrate obtained by Bader charge analysis.

System	d_{TM-C} (Å)	Q (*e*)
Mn@V_B	1.88	1.00
Fe@V_B	1.82	0.79
Co@V_B	1.80	0.66
Ni@V_B	1.84	0.56
Cu@V_B	1.91	0.61
Ru@V_B	1.90	0.64

$Rh@V_B$	1.91	0.42
$Pd@V_B$	1.97	0.40
$Ir@V_B$	1.92	0.46
$Pt@V_B$	1.95	0.34

Table S2 The detailed parameters for the optimized $TM@V_C$ structures. $d_{TM\text{-}C/B}$ is the bond distance between TM atom and its nearest C/B neighbor. Q refers to charges transfer from TM atoms to the V_C substrate obtained by Bader charge analysis.

System	$d_{TM\text{-}C}$ (Å)	$d_{TM\text{-}B}$ (Å)	Q (*e*)
$Mn@V_C$	1.85	2.03	0.76
$Fe@V_C$	1.82	1.89	0.52
$Co@V_C$	1.78	1.86	0.32
$Ni@V_C$	1.81	1.89	0.27
$Cu@V_C$	1.89	2.00	0.39
$Ru@V_C$	1.88	1.95	0.21
$Rh@V_C$	1.90	1.97	0.06
$Pd@V_C$	1.97	2.00	0.07
$Ir@V_B$	1.90	1.97	0.04
$Pt@V_C$	1.95	1.99	0.11

Table S3 Computed adsorption free energies of HO*, O* and HOO* (ΔG_{HO*}, ΔG_{O*}, and ΔG_{HOO*}), overpotentials for OER (η^{OER}) and ORR (η^{ORR}) on $TM@V_B$ systems, as well as the d band center values that related to Fermi level of $TM@V_B$. The unit for ΔG is eV, while for η is V.

System	ΔG_{HO*}	ΔG_{O*}	ΔG_{HOO*}	η^{OER}	η^{ORR}
$Mn@V_B$	-0.33	0.57	2.96	1.16	1.56
$Fe@V_B$	-0.06	1.04	3.20	0.93	1.29
$Co@V_B$	0.16	1.75	3.41	0.43	1.07
$Ni@V_B$	0.38	2.34	3.54	0.73	0.85

Cu@V_B	0.53	2.45	3.64	0.69	0.70
Ru@V_B	0.17	1.26	3.36	0.87	1.06
Rh@V_B	0.83	2.25	3.97	0.49	0.40
Pd@V_B	1.09	3.20	4.14	0.88	0.45
Ir@V_B	0.37	1.53	3.60	0.84	0.86
Pt@V_B	0.62	2.36	3.80	0.51	0.61

Table S4 Computed adsorption free energies of HO*, O* and HOO* (ΔG_{HO*}, ΔG_{O*}, and ΔG_{HOO*}), overpotentials for OER (η^{OER}) and ORR (η^{ORR}) on TM@V_C systems, as well as the d band center values that related to Fermi level of TM@V_C. The unit for ΔG is eV, while for η is V.

System	ΔG_{HO*}	ΔG_{O*}	ΔG_{HOO*}	η^{OER}	η^{ORR}
Mn@V_C	-0.49	0.75	2.86	0.88	1.72
Fe@V_C	-0.22	0.87	3.09	0.99	1.45
Co@V_C	-0.01	1.45	3.15	0.54	1.24
Ni@V_C	0.33	2.03	3.52	0.47	0.90
Cu@V_C	0.46	1.69	3.70	0.78	0.77
Ru@V_C	0.40	1.65	3.62	0.74	0.83
Rh@V_C	0.36	2.14	3.50	0.55	0.87
Pd@V_C	0.95	2.82	4.14	0.64	0.45
Ir@V_C	-0.08	1.41	3.14	0.55	1.31
Pt@V_C	0.48	1.99	3.75	0.53	0.75

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TM	$\Delta G_{(TM^{n+})}$	n	$\Delta G_{diss}(0)$	pH_{min}

Mn	-1.18	2	-3.68	>16.0
Fe	-0.45	2	-2.42	>16.0
Co	-0.28	2	-1.43	12.15
Ni	-0.26	2	-1.67	14.16
Cu	0.34	2	-2.19	>16.0
Ru	0.46	2	-1.23	10.42
Rh	0.60	2	0.43	<-2.0
Pd	0.95	2	0.61	-5.13
Ir	1.16	3	0.51	<-2.0
Pt	1.18	2	1.19	<-2.0

Table S6 $\Delta G_{(TM^{n+})}$ and $\Delta G_{diss}(0)$ values in this work. Positive value of $\Delta G_{diss}(0)$ indicates the TM@V_C catalyst is stable against dissolution at pH = 0 condition. pH_{min} is the minimum pH value corresponding to the $\Delta G_{diss}(0)$. In this work, the maximum and minimum pH values are set as 16.0 and -2.0, respectively, which are realistic in this region.

TM	$\Delta G_{(TM^{n+})}$	n	$\Delta G_{diss}(0)$	pH_{min}
Mn	-1.18	2	-3.90	>16.0
Fe	-0.45	2	-2.42	>16.0
Co	-0.28	2	-1.68	14.23
Ni	-0.26	2	-1.50	12.72
Cu	0.34	2	-1.36	11.54
Ru	0.46	2	-0.86	7.32
Rh	0.60	2	0.16	-1.38
Pd	0.95	2	0.88	<-2.0
Ir	1.16	3	1.35	<-2.0
Pt	1.18	2	1.57	<-2.0