Supporting information

Design of transition-metal-doped TiO_2 as a multipurpose support for fuel cell applications: using a computational high-throughput material screening approach

Meng-Che Tsai,[†] John Rick,[†] Wei-Nien Su,[‡] and Bing-Joe Hwang[*,†,§]

[†]Nano Electrochemistry Laboratory, Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan

[‡]Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 106, Taiwan

[§]National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan

[*]Corresponding author: Bing-Joe Hwang (bjh@mail.ntust.edu.tw)

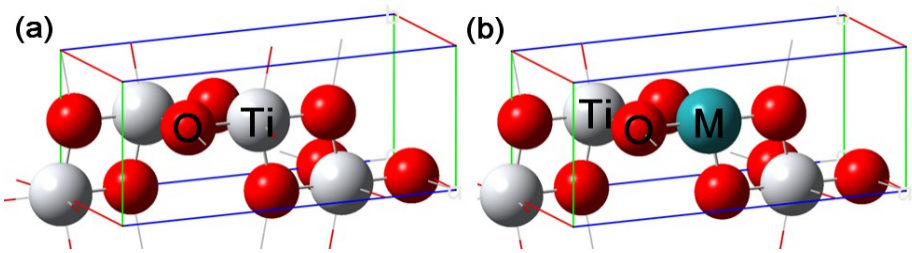


Figure S1 Bulk models of (a) anatase-TiO_2 and (b) anatase-$TiMO_2$ with 25 atomic percent of dopant M. The atomic ratio in the unit-cell is 3(Ti):1(M):8(O). White, red and Teal balls represent Ti, O and transition metal dopant (M), respectively. These bulk models are used to calculate electronic structure by HSE method.

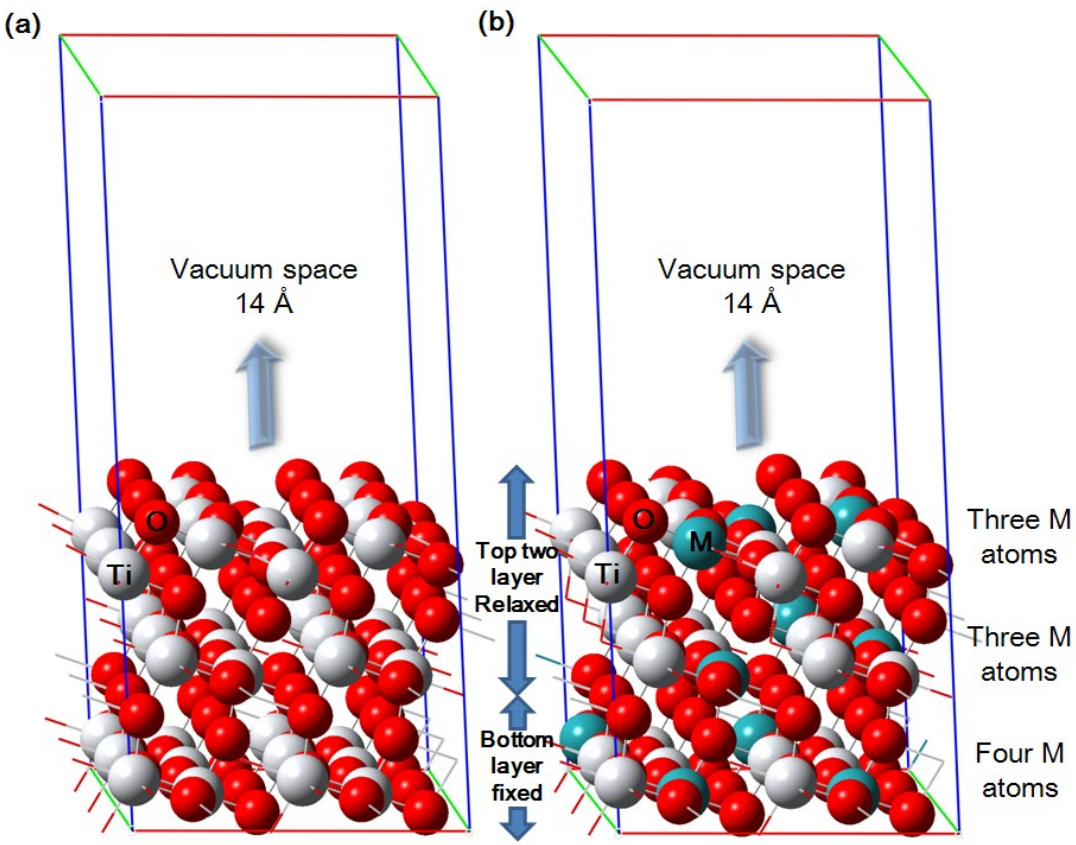


Figure S2 Slab models of (a) anatase-TiO_2 (101), and (b) anatase-$TiMO_2$ (101) with around 30 atomic percent of dopant M. White, red and Teal balls represent Ti, O and transition metal dopant (M), respectively. Numbers of M on each layer is specified for the different $TiMO_2$ models.

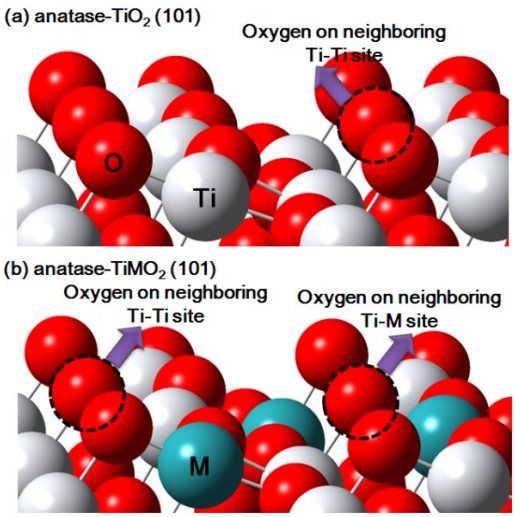


Figure S3 Oxygen vacancy formations, created on (a) neighboring Ti-Ti site of anatase-TiO_2 (101), and (b) neighboring Ti-Ti and Ti-M sites of anatase-$TiMO_2$ (101). White, red and teal balls represent Ti, O and transition metal dopant (M), respectively.

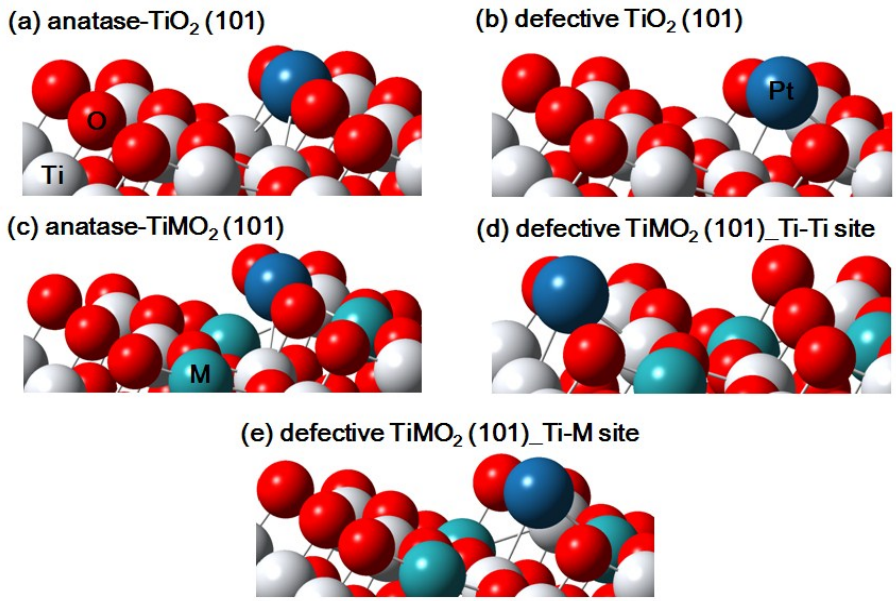


Figure S4 The adsorption configurations for a single Pt adatom on: (a) defect-free site of anatase-TiO_2, (b) neighboring Ti-Ti site (vacancy) of defective TiO_2, (c) defect-free site of anatase-$TiMO_2$, (d) neighboring Ti-Ti site of defective $TiMO_2$ and (e) neighboring Ti-M site of defective $TiMO_2$. White, red, teal and blue balls represent Ti, O, transition metal dopant (M) and Pt, respectively.

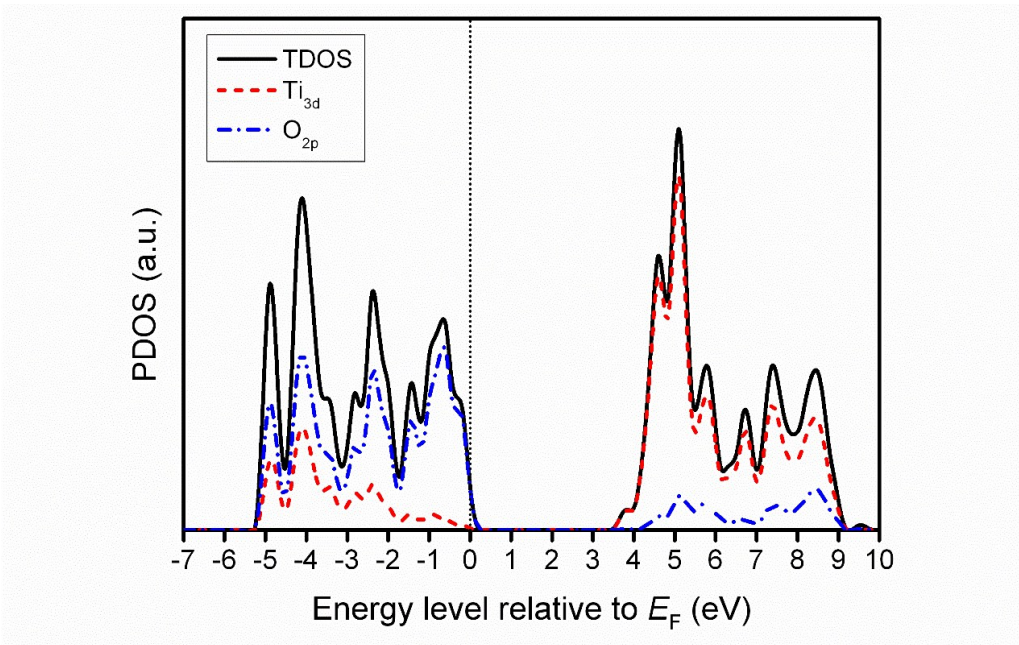
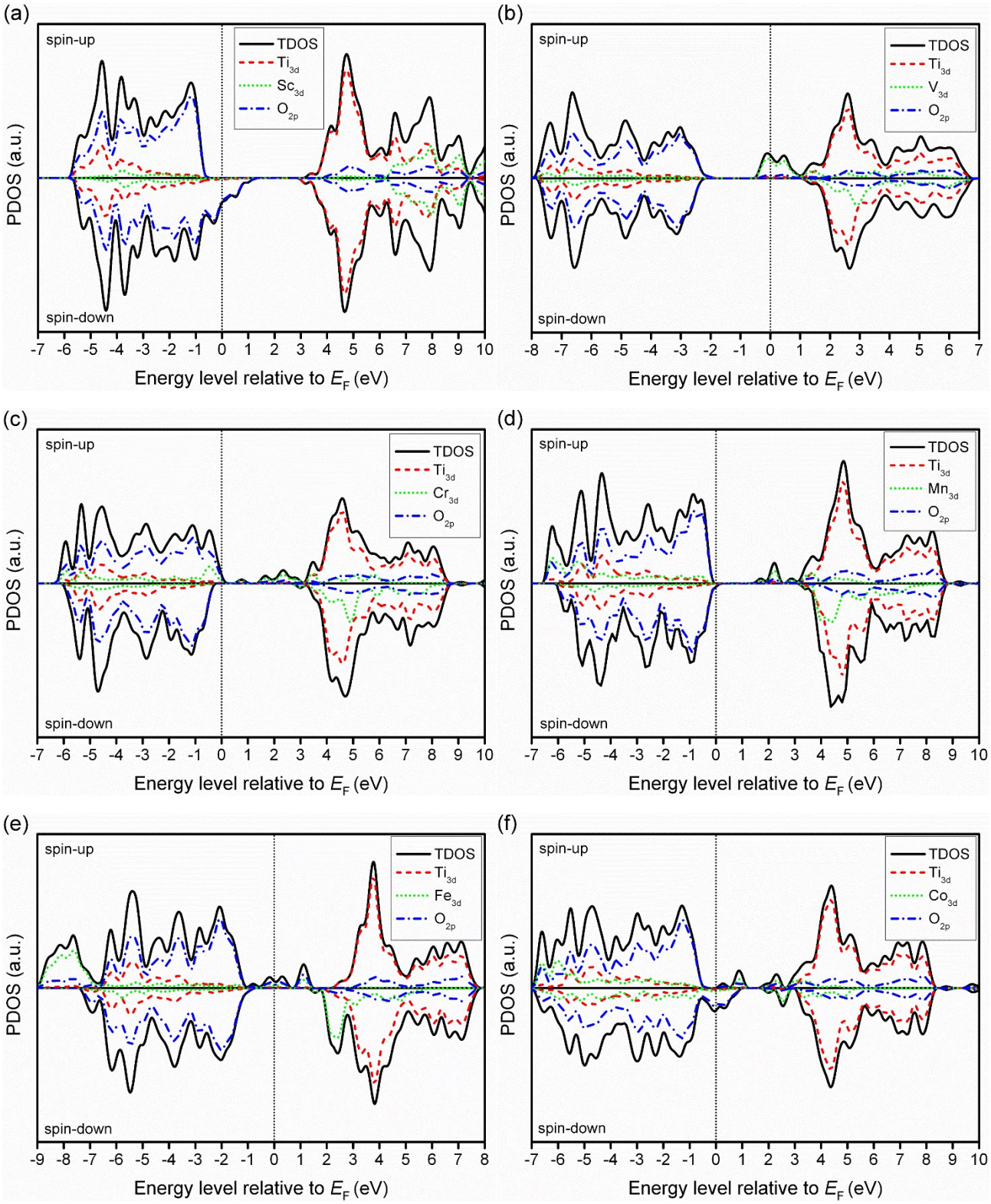


Figure S5 Calculated total and partial density of states of bulk anatase-TiO_2. Black solid line represents total density of states, red dash and blue dash dot lines represent contributions of Ti_{3d} and O_{2p} electrons, respectively.


(a)
spin-up
spin-down
TDOS
Ti3d
Sc3d
O2p
PDOS (a.u.)
Energy level relative to EF (eV)
(b)
spin-up
spin-down
TDOS
Ti3d
V3d
O2p
PDOS (a.u.)
Energy level relative to EF (eV)
(c)
spin-up
spin-down
TDOS
Ti3d
Cr3d
O2p
PDOS (a.u.)
Energy level relative to EF (eV)
(d)
spin-up
spin-down
TDOS
Ti3d
Mn3d
O2p
PDOS (a.u.)
Energy level relative to EF (eV)
(e)
spin-up
spin-down
TDOS
Ti3d
Fe3d
O2p
PDOS (a.u.)
Energy level relative to EF (eV)
(f)
spin-up
spin-down
TDOS
Ti3d
Co3d
O2p
PDOS (a.u.)
Energy level relative to EF (eV)

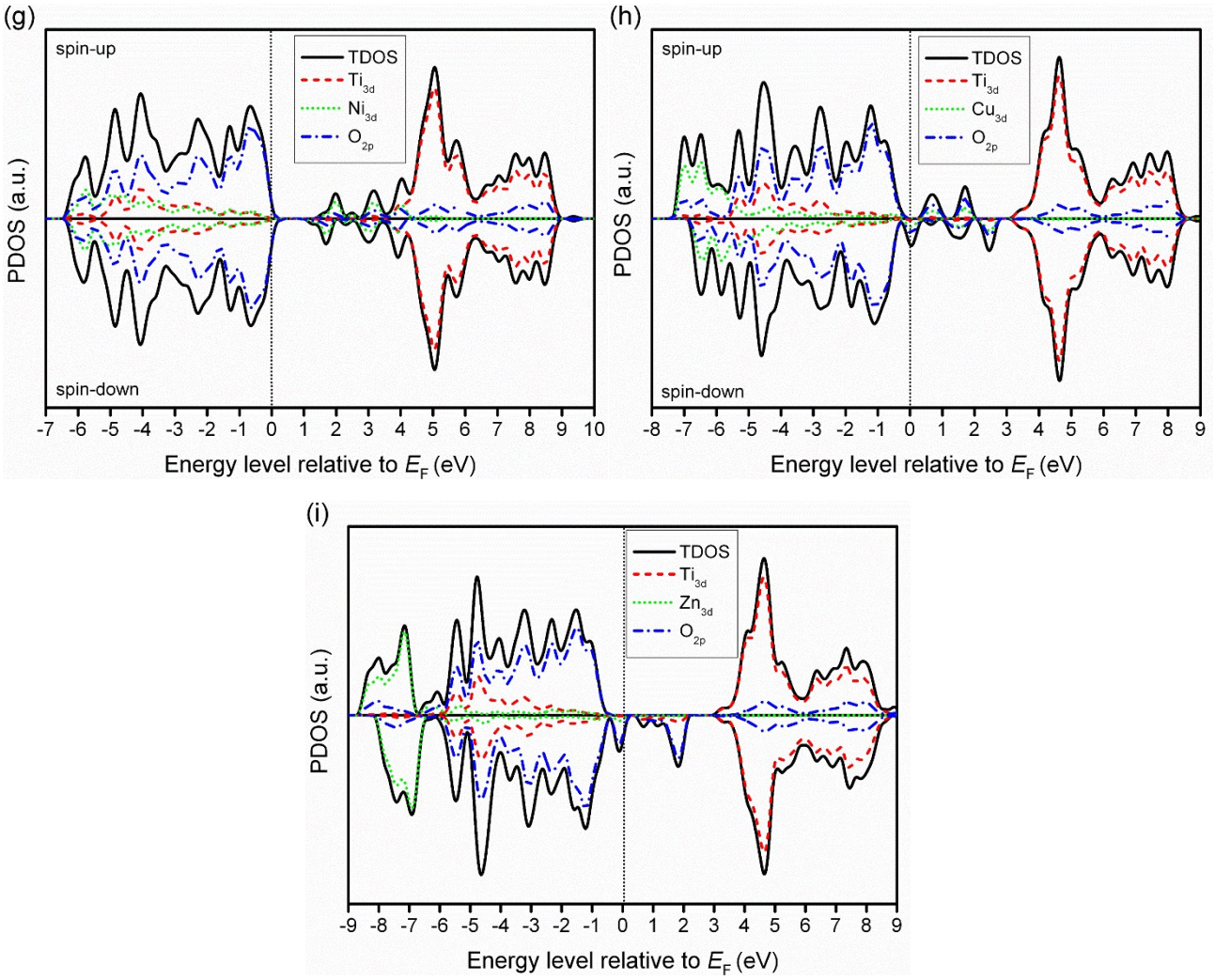
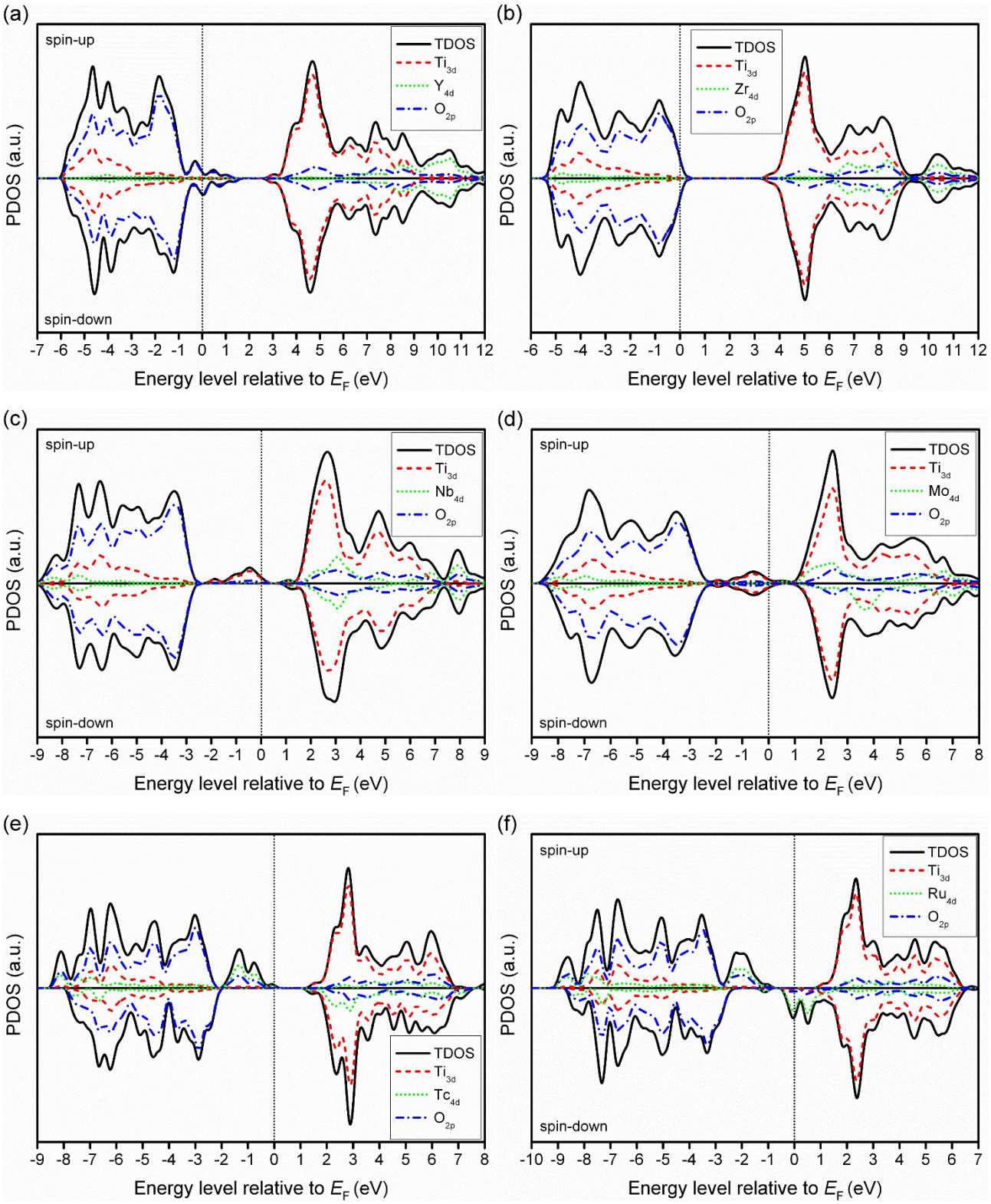


Figure S6 Calculated total and partial density of states of bulk anatase-$TiM_{3d}O_2$: (a) $TiScO_2$, (b) $TiVO_2$, (c) $TiCrO_2$, (d) $TiMnO_2$, (e) $TiFeO_2$, (f) $TiCoO_2$, (g) $TiNiO_2$, (h) $TiCuO_2$, and (i) $TiZnO_2$. Black solid line represents total density of states, red dash, green dot and blue dash dot lines represent the contributions of Ti_{3d}, M_{3d} and O_{2p} electrons, respectively.


(a)
spin-up
spin-down
TDOS
Ti3d
Y4d
O2p
PDOS (a.u.)
Energy level relative to EF (eV)
(b)
TDOS
Ti3d
Zr4d
O2p
PDOS (a.u.)
Energy level relative to EF (eV)
(c)
spin-up
spin-down
TDOS
Ti3d
Nb4d
O2p
PDOS (a.u.)
Energy level relative to EF (eV)
(d)
spin-up
spin-down
TDOS
Ti3d
Mo4d
O2p
PDOS (a.u.)
Energy level relative to EF (eV)
(e)
TDOS
Ti3d
Tc4d
O2p
PDOS (a.u.)
Energy level relative to EF (eV)
(f)
spin-up
spin-down
TDOS
Ti3d
Ru4d
O2p
PDOS (a.u.)
Energy level relative to EF (eV)

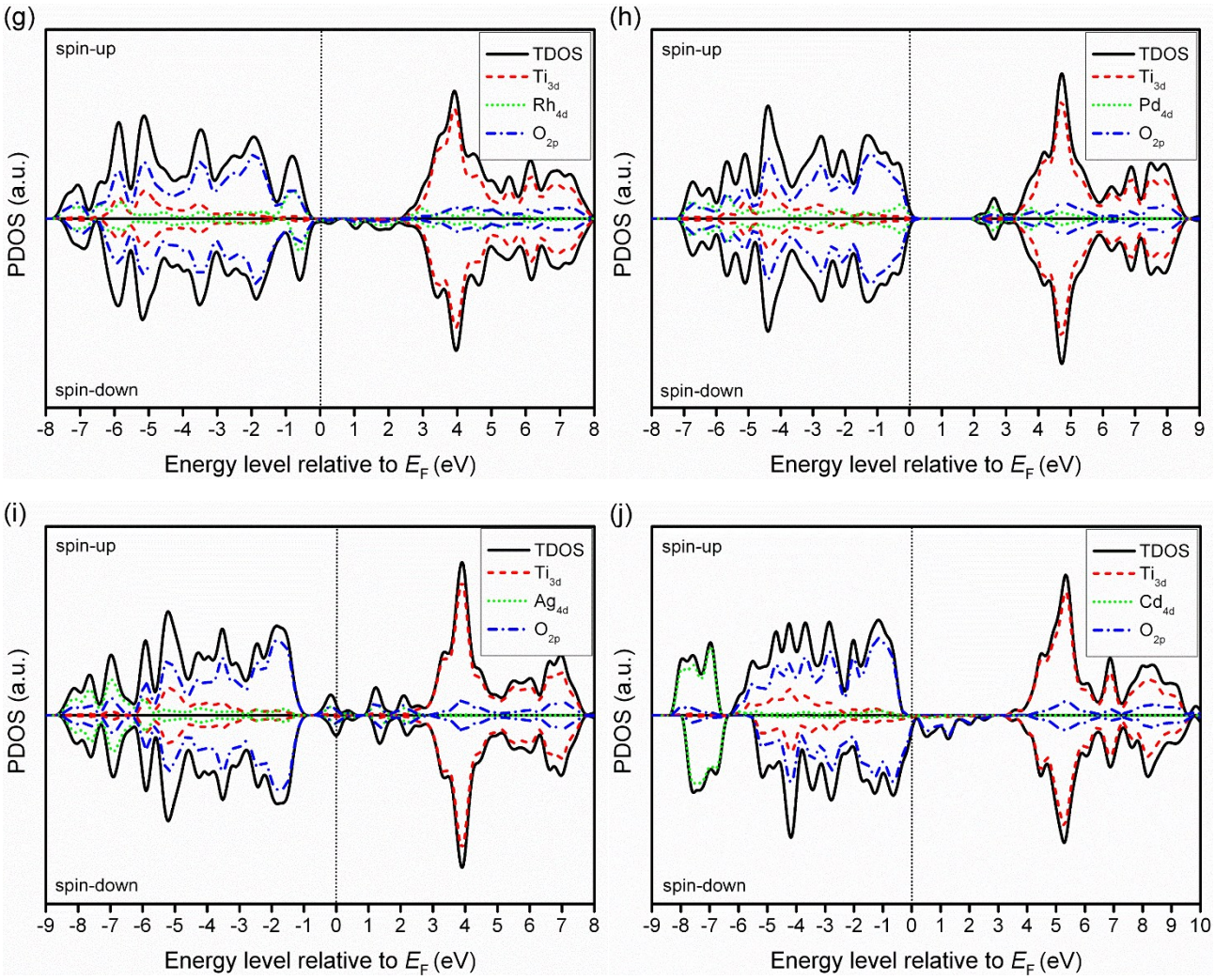
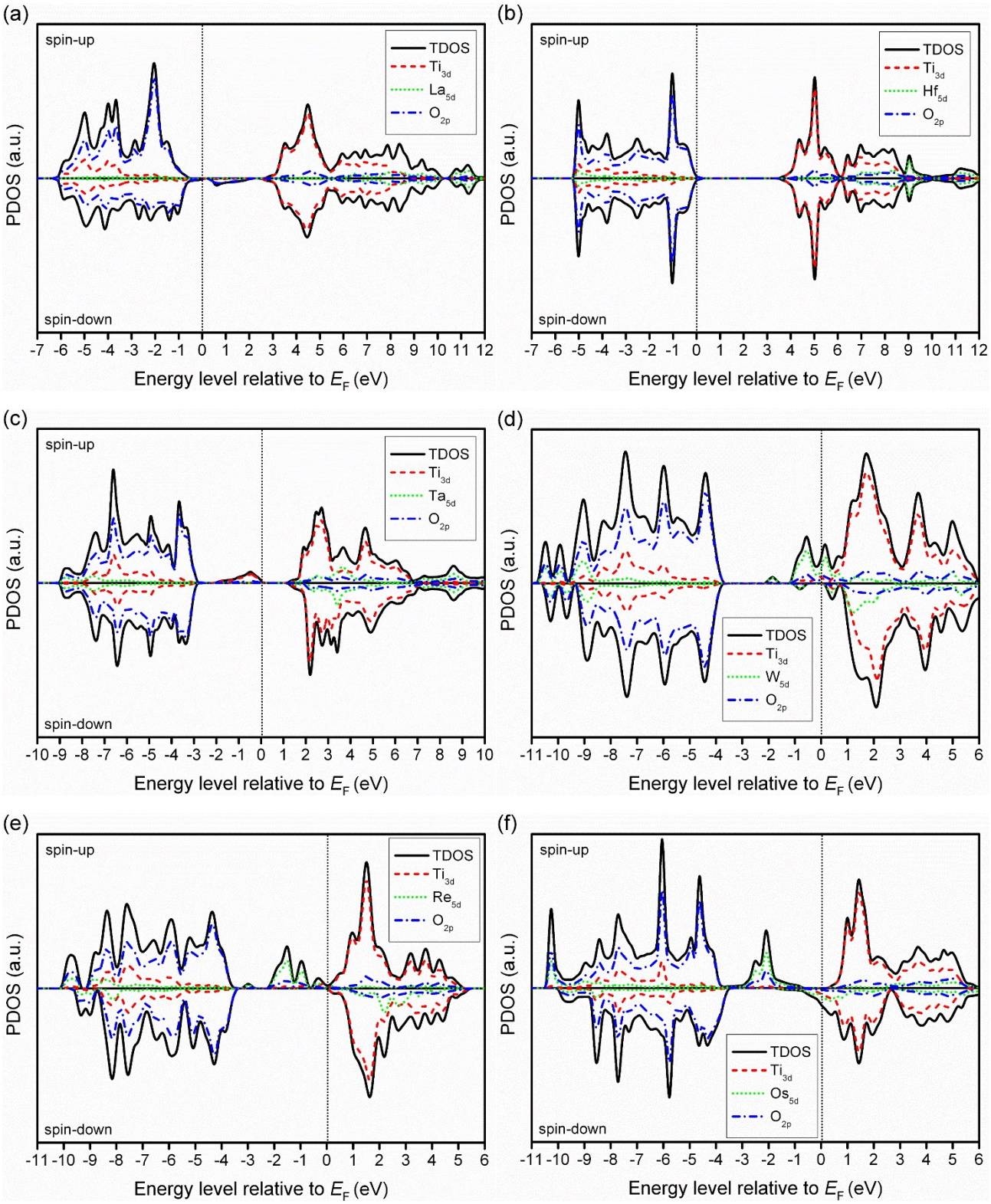


Figure S7 Calculated total and partial density of states of bulk anatase-$TiM_{4d}O_2$: (a) $TiYO_2$, (b) $TiZrO_2$, (c) $TiNbO_2$, (d) $TiMoO_2$, (e) $TiTcO_2$, (f) $TiRuO_2$, (g) $TiRhO_2$, (h) $TiPdO_2$, (i) $TiAgO_2$, and (j) $TiCdO_2$. Black solid line represents total density of states, red dash, green dot and blue dash dot lines represent contributions of Ti_{3d}, M_{4d} and O_{2p} electrons, respectively.


(a)
spin-up
spin-down
TDOS
Ti3d
La5d
O2p
PDOS (a.u.)
Energy level relative to EF (eV)
(b)
spin-up
spin-down
TDOS
Ti3d
Hf5d
O2p
PDOS (a.u.)
Energy level relative to EF (eV)
(c)
spin-up
spin-down
TDOS
Ti3d
Ta5d
O2p
PDOS (a.u.)
Energy level relative to EF (eV)
(d)
TDOS
Ti3d
W5d
O2p
PDOS (a.u.)
Energy level relative to EF (eV)
(e)
spin-up
spin-down
TDOS
Ti3d
Re5d
O2p
PDOS (a.u.)
Energy level relative to EF (eV)
(f)
spin-up
spin-down
TDOS
Ti3d
Os5d
O2p
PDOS (a.u.)
Energy level relative to EF (eV)

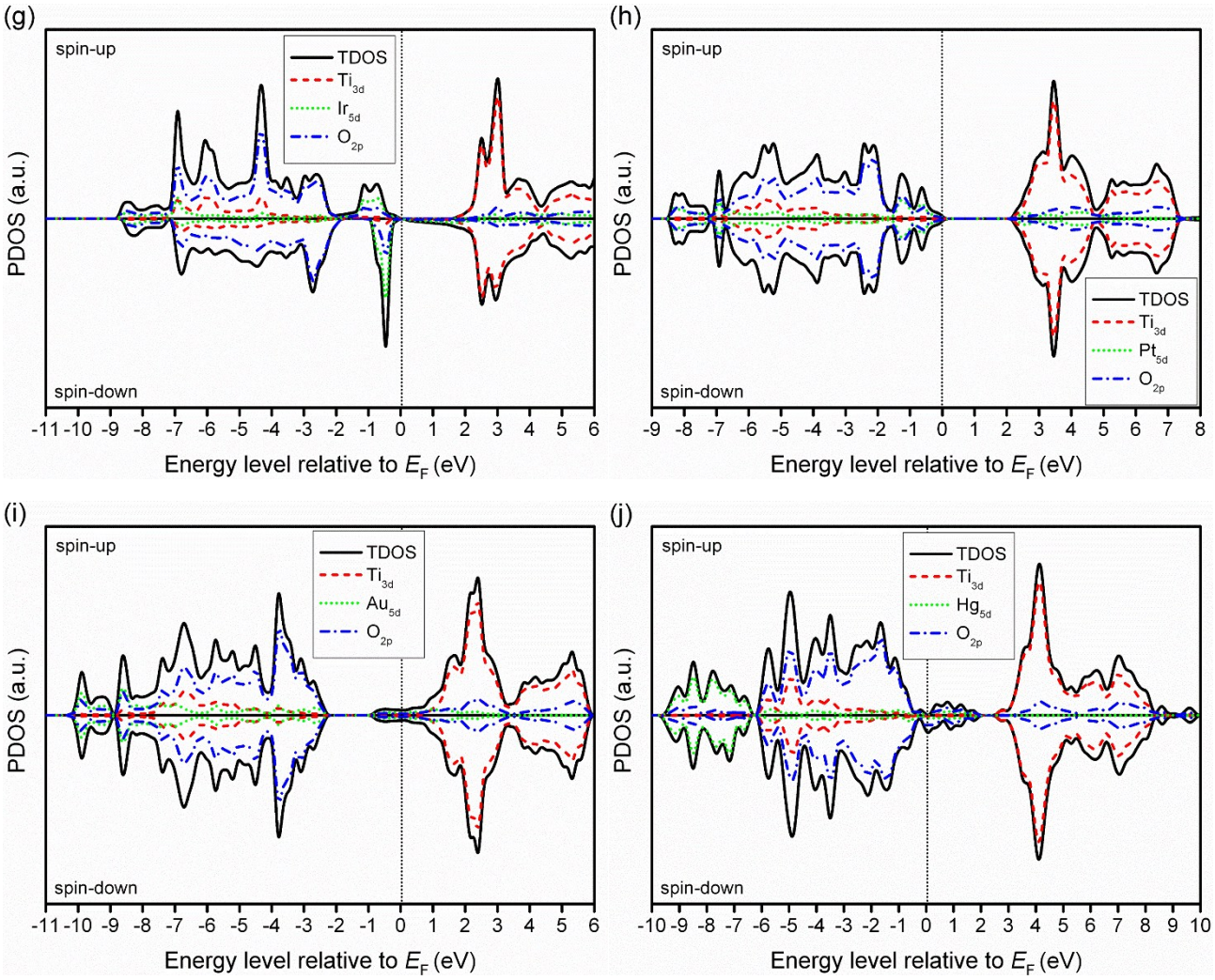


Figure S8 Calculated total and partial density of states of bulk anatase-$TiM_{5d}O_2$: (a) $TiLaO_2$, (b) $TiHfO_2$, (c) $TiTaO_2$, (d) $TiWO_2$, (e) $TiReO_2$, (f) $TiOsO_2$, (g) $TiIrO_2$, (h) $TiPtO_2$, (i) $TiAuO_2$, and (j) $TiHgO_2$. Black solid line represents total density of states, red dash, green dot and blue dash dot lines represent contributions of Ti_{3d}, M_{5d} and O_{2p} electrons, respectively.

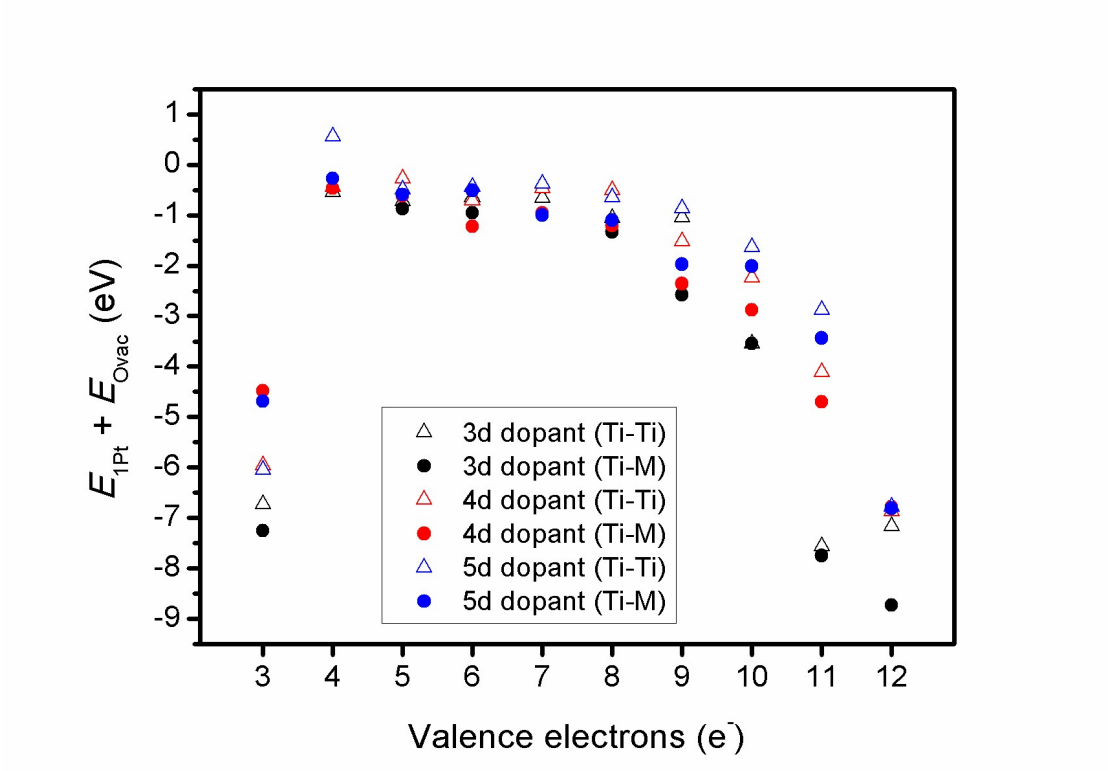


Figure S9. Energy difference of E_{1Pt} and E_{Ovac}, indicates that whether the adsorption of Pt atom is thermodynamically favorable on defect site, i.e. negative value means Pt favors defect site. Y axis: $\Delta E^{*}_{1Pt} = E_{1Pt} + E_{Ovac}$.

Table S1 Bader charge analysis for Ti ions of anatase-$TiMO_2$ obtained by HSE method.

$TiM_{3d}O_2$	δ_{Ti} / e^-	$TiM_{4d}O_2$	δ_{Ti} / e^-	$TiM_{5d}O_2$	δ_{Ti} / e^-
$TiScO_2$	1.1284	$TiYO_2$	1.1231	$TiLaO_2$	1.1171
TiO_2	1.1491	$TiZrO_2$	1.1265	$TiHfO_2$	1.1159
$TiVO_2$	1.1391	$TiNbO_2$	1.2616	$TiTaO_2$	1.2909
$TiCrO_2$	1.1396	$TiMoO_2$	1.1359	$TiWO_2$	1.3229
$TiMnO_2$	1.1377	$TiTcO_2$	1.1315	$TiReO_2$	1.1430
$TiFeO_2$	1.1309	$TiRuO_2$	1.1579	$TiOsO_2$	1.1666
$TiCoO_2$	1.1426	$TiRhO_2$	1.1526	$TiIrO_2$	1.1384
$TiNiO_2$	1.1469	$TiPdO_2$	1.1345	$TiPtO_2$	1.1342
$TiCuO_2$	1.1396	$TiAgO_2$	1.1283	$TiAuO_2$	1.1368
$TiZnO_2$	1.1283	$TiCdO_2$	1.1146	$TiHgO_2$	1.1369

Table S2 Pt/TM-doped TiO_2 applied in fuel cell reactions

Catalyst system	Electrical conductivity (S/cm)	Support composition	Electron transfer	application	Year, ref
$Pt/TiNbO_2$	0.1	NA	Support to Pt	ORR	2007[1]
$Pt/TiNbO_2$	6.1×10^{-4}	$Ti_{0.9}Nb_{0.1}$	NA	ORR	2009[2]
$Pt/TiNbO_2$	1.11 (900°C)	$Ti_{0.75}Nb_{0.25}O_2$	NA	ORR	2010[3]
$Pt/TiMoO_2$	2.8×10^{-4}	$Ti_{0.7}Mo_{0.3}O_2$	Support to Pt	ORR	2011[4]
$Pt/TiMoO_2$	2.8×10^{-4}	$Ti_{0.7}Mo_{0.3}O_2$	Support to Pt	ORR	2016[5]
$Pt/TiTaO_2$	0.2	$Ti_{0.7}Ta_{0.3}$	NA	ORR	2013[6]
$Pt/TiTaO_2$	0.2	$Ti_{0.7}Ta_{0.3}$	Support to Pt	ORR	2014[7]
$Pt/TiCrO_2$	Good but no value indicated	$Ti_{0.95}Cr_{0.05}$	Support to Pt	ORR	2014[8]
$Pt/TiTaNbO_2$	8.73×10^{-4}	$Ta_{0.08}Nb_{0.2}$	Electronic transfer is important	ORR	2014[9]
$Pt/TiRuO_2$	NA	$Ti_{0.7}Ru_{0.3}O_2$	Support to Pt	MOR	2011[10]
$Pt/TiRuO_2$	Good but no value indicated	$Ti_{0.9}Ru_{0.1}O_2$	NA	MOR, CO stripping	2015[11]
$Pt/TiWO_2$	0.02-0.9	$Ti_{0.7}W_{0.3}O_2$	NA	ORR	2010[12]
$Pt/TiWO_2$	0.02-0.9	$Ti_{0.7}W_{0.3}O_2$	NA	HOR, CO stripping	2010[13]
$Pt/TiWO_2$	Adding carbon to ensure sufficient conductivity	$Ti_{0.7}W_{0.3}O_2$	Support slightly modifies Pt electronic structure	HOR, CO stripping	2015[14]

1. K.-W. Park and K.-S. Seol, *Electrochem. Commun.*, 2007, **9**, 2256-2260.
2. H. Chhina, S. Campbell and O. Kesler, *J. Electrochem. Soc.*, 2009, **156**, B1232-B1237.
3. S.-Y. Huang, P. Ganesan and B. N. Popov, *Applied Catalysis B: Environmental*, 2010, **96**, 224-231.
4. V. T. T. Ho, C.-J. Pan, J. Rick, W.-N. Su and B.-J. Hwang, *J. Am. Chem. Soc.*, 2011, **133**, 11716-11724.
5. M.-C. Tsai, T.-T. Nguyen, N. G. Akalework, C.-J. Pan, J. Rick, Y.-F. Liao, W.-N. Su and B.-J. Hwang, *ACS Catalysis*, 2016, **6**, 6551-6559.
6. A. Kumar and V. Ramani, *J. Electrochem. Soc.*, 2013, **160**, F1207-F1215.
7. A. Kumar and V. Ramani, *ACS Catalysis*, 2014, **4**, 1516-1525.
8. J.-H. Kim, S. Chang and Y.-T. Kim, *Applied Catalysis B: Environmental*, 2014, **158–159**, 112-118.

9. Y.-J. Wang, D. P. Wilkinson, V. Neburchilov, C. Song, A. Guest and J. Zhang, *Journal of Materials Chemistry A*, 2014, **2**, 12681-12685.
10. V. T. Thanh Ho, K. C. Pillai, H.-L. Chou, C.-J. Pan, J. Rick, W.-N. Su, B.-J. Hwang, J.-F. Lee, H.-S. Sheu and W.-T. Chuang, *Energy & Environmental Science*, 2011, **4**, 4194-4200.
11. M. D. Obradović, U. Č. Lačnjevac, B. M. Babić, P. Ercius, V. R. Radmilović, N. V. Krstajić and S. L. Gojković, *Applied Catalysis B: Environmental*, 2015, **170–171**, 144-152.
12. C. V. Subban, Q. Zhou, A. Hu, T. E. Moylan, F. T. Wagner and F. J. DiSalvo, *J. Am. Chem. Soc.*, 2010, **132**, 17531-17536.
13. D. Wang, C. V. Subban, H. Wang, E. Rus, F. J. DiSalvo and H. D. Abruña, *J. Am. Chem. Soc.*, 2010, **132**, 10218-10220.
14. D. Gubán, I. Borbáth, Z. Pászti, I. Sajó, E. Drotár, M. Hegedűs and A. Tompos, *Applied Catalysis B: Environmental*, 2015, **174–175**, 455-470.