Understanding the effect of interfacial interaction on metal/metal oxides electrocatalysts for hydrogen evolution and hydrogen oxidation reactions on the basis of first-principle calculations

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Supporting information



Figure S1. Optimized geometries (side-view and top-view) of (a) $Pt/O-TiO_2(OH)_n$ and (b) $Pt/Ti-TiO_2(OH)_n$, (c) Pt(111), (d) Pt(111)-s surface and (e) Pt/Pt(100) respectively.

As the exposed TiO₂ surface are easily hydroxylated in real HOR electrochemical condition and

prone to adsorbing and dissociating water molecular¹, the hydroxylation of the exposed TiO₂(110) surface was approximated by adding hydroxyl groups on all exposed Ti atoms and attaching H on exposed bridging oxygen² and exhibited in Figure S1(a) and(b). To compare with pure Pt surface, the bare Pt(111) surface and Pt(111) surfaces with 5.5% tensile strain in y direction (denote as Pt(111)-s) surfaces were modeled using five atomic layers ($2 \times 4\sqrt{3}$) supercell (Fig.S1(c) and (d)). And the idealized complex Pt/Pt(100) with Pt nanorod supported on (2×4) Pt(100)surface (Fig.1(e)) was constructed by the same way and the tensile strain of 5.5% in y direction of this system was introduced artificially.



Figure S2 (a), (b) Two-dimension charge density difference plots (ranging from 0.01 to $-0.01e\text{Å}^{-3}$) of Pt/O-TiO₂ and Pt/Ti-TiO₂ interface. (c), (b) Bader charge and (d), (e) d-band center of Pt for Pt/O-TiO₂ and Pt/Ti-TiO₂.



Figure S3. (a)Possible adsorption sites for H and OH adsorption. And corresponding color map of (b),(c) ΔE_{*H} and (d),(e) ΔE_{*OH} on stable sites of Pt/O-TiO₂ and Pt/Ti-TiO₂. For H adsorption on Pt^I, the most stable sites are fcc(f) sites on Pt/O-TiO₂ and hcp(h) sites on Pt/Ti-TiO₂, and on Pt^{II}, the most stable sites are top(t) sites on Pt/O-TiO₂ or bridge (b) sites on Pt/Ti-TiO₂). For H adsorption on Pt^{III} atoms, the most stable sites are bridge (b) sites.



Figure S4. (a) Correlation between ΔE_{*H} and $\mathcal{E}_{d.}$ (b) ΔG_{*H} change with the θ_{H} on Pt nanorod.



Figure S5. (a)-(b) Three-dimension charge density difference of Pt/O-TiO₂(OH)_n and Pt/Ti-TiO₂(OH)_n (iso-surface levels are 0.0035eÅ⁻³, cyan and yellow represent electron depletion and accumulation respectively). (e) ΔE_{*H} on different Pt sites of Pt/O-TiO₂(OH)_n and Pt/Ti-TiO₂(OH)_n. (f) Free energy diagrams for H migration on Pt nanorod of Pt/O-TiO₂(OH)_n and Pt/Ti-TiO₂(OH)_n with $\theta_{H}=0$ and $\theta_{H}=0.5$. (g) Energy barrier for H migration on Pt/O-TiO₂(OH)_n pt/Ti-TiO₂(OH)_n with different H coverage. (h) Free energy diagrams for H ad-desorption and migration on Pt nanorods of Pt/O-TiO₂H_n and Pt/Ti-TiO₂H_n (Pt/O-TiO₂H_n and Pt/Ti-TiO₂H_n represent the exposed bridge O was hydrogenated) compared with that on Pt nanorods of Pt/O-TiO₂ and Pt/Ti-TiO₂ respectively.



Figure S6. (a) H and OH competitive adsorption site on Pt nanorod at different θ_{H} . (θ_{H} =0 represent clean surface).

(b)*H and *OH adsorption potential range on Pt^{III} of Pt/O-TiO₂ and Pt/Ti-TiO₂ at different θ_{H} .

As on non-interface Pt site of Pt/O-TiO₂ and Pt/Ti-TiO₂, the OH adsorption potential is much positive than HER potential ($0V_{RHE}$), thus no stable co-adsorbed OH and H exist in HER potential range ($< 0V_{RHE}$). While in HOR process, the Pt-based catalyst is covered with *H, and with increasing potential, some *H desorbed from surface and provide available sites for adsorption of OH which are likely competitive with H. In Figure S6, when θ_H large than 0.4 (here is 0.5), the stable OH adsorption potential on Pt^{III} site of Pt/TiO₂ is much higher than H desorption potential due to the weak H and OH adsorption, thus the OH would not co-adsorb or compete with H. However, when the adjacent H desorbed from Pt^{III} site and the θ_H of Pt/TiO₂ corresponding to 0.4, the OH adsorption potential range overlap with H adsorption potential range, thus the OH can co-adsorb or compete with H. Therefore, the phenomenon of H and OH competitive or co-adsorption is inevitable in HOR with increasing potential.



Figure S7. Schematic diagram of possible HOR pathway when OH competitive adsorption with H.

As show in the Figure 7(c) and(d), when OH compete or co-adsorb with H, the H adsorption on Pt^I and Pt^{II} of both surfaces become stronger and H adsorption on Pt^{III} is weaker than that on clean surface. And the H adsorption on non-interface Pt^{III} site is weaker than Pt^{II} and Pt^I sites which enable that both Pt^I and Pt^{III} as *H desorption/oxidation active sites. However, due to the much strong H adsorption on Pt^{III} site, the *H migration from Pt^{II} to Pt^I or Pt^{III} is more difficult than *H desorption/oxidation (on Pt^{II}, Pt^I and Pt^{III} sites). In this way H₂ is likely to dissociate on Pt^I and Pt^{III} directly then be oxidized to H₂O. When increasing U to $0.32V_{RHE}$ which corresponding to OH competitive adsorption potential (θ_{H} is 0.4 in Figure 6), both non-interfacial and interfacial Pt sites can dissociate H₂

spontaneously and then oxidize *H exothermally. With these in mind, we proposed the revised HOR mechanism on $Pt/TiO_2(OH)_n$ shown in Figure S7. H₂ is dissociated on non-interface Pt site or interface Pt site to produce *H anchored on the adjacent site and then *H combined with OH⁻ to form H₂O. In this circumstance, Pt nanorods of both surfaces provide more HOR active sites than clean surface.

Systems	Bonds	E _a (eV)	E _f (eV)
Pt/O-TiO ₂	4 Pt-O 2 Pt-Ti	-8.03	0.63
Pt/Ti-TiO ₂	10 Pt-Ti	-12.35	0.38
Pt/Pt(100)	24 Pt-Pt	-15.82	0.22

Table S1. The interface bonds between Pt nanorod and support, the adsorption energy $({}^{E}a)$ of Pt nanorod on support and the interface formation energy $({}^{E}f)$.

Table S2. The H adsorption energy on interface Pt of each systems.

systems	H adsorption site	$\Delta E_{*H}(eV)$
Pt/O-TiO ₂	$f(Pt^{I})$	-0.23
	t (Pt ^{II})	-0.44
Pt/Ti-TiO ₂	h (Pt ^I)	-0.50
	b (Pt ^{II})	-0.53
Pt(111)	f	-0.50
Pt(111)-s	f	-0.51
Pt/Pt(100)	$f(Pt^{I})$	-0.44
	t (Pt ^{II})	-0.47

Table S3. OH formation potential (U $_{\rm OH}\!/V)$ of various systems.

Pt(111)	Pt/O-	-TiO ₂	Pt/Ti	-TiO ₂	
	Pt ^Ⅲ -	Ti-site	Pt ^Ⅲ -	Ti-site	TiO ₂ (110)
	site		site		
1.13	0.29	0.04	0.22	-0.22	0.06

Table S4. Reaction energy of H₂ dissociation (H₂+* \rightarrow 2*H) on Pt^{II} and Pt^{II} site of Pt/O-TiO₂(OH)_n and Pt/Ti-TiO₂(OH)_n with different coverage.

	θ _H =0.5		θ_{H+OI}	θ _{H+OH} =0.5	
	Pt ^{III} -site	Pt ^I -site	Pt ^m -site	Pt ^I -site	
Pt/O-TiO ₂ (OH) _n	-	-0.67	-	-0.90	
Pt/Ti-TiO ₂ (OH) _n	-	-0.63	-	-0.61	

* '-' means no stable H_2 on Pt^{III} site and H_2 dissociated into two *H when DFT optimization which denoting favorable H_2 dissociation.

References

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