First-principles design of a superior electrocatalyst to Pt for hydrogen production in alkaline media

Haeshik Lee[1], Jinwoo Park[2], Jae-Min Myoung[3], and Byungchan Han[1*]

[1] Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul 03722, Republic of Korea

[2] Department of Physics, University of Seoul, Seoul 02504, Republic of Korea

[3] Department of Materials Science and Engineering, Yonsei University, Seoul 03722, Republic of Korea

* Corresponding author: bchan@yonsei.ac.kr

Table S1. Calculated adsorption energies for H and OH on Pt(111), Pt/W(110) surfaces, Pt_{55}, W@Pt nanoparticles with difference force cutoff values (0.04, 0.02 and 0.01 eV/Å). Adsorption energies are calculated with Eq (1).

		0.04 eV/Å	0.02 eV/Å	0.01 eV/Å
$\Delta E_{ads}(H*)$	Pt(111)	-0.53 eV	-0.53 eV	-0.53 eV
	Pt/W(110)	-0.28 eV	-0.28 eV	-0.28 eV
	Pt_{55}	-0.67 eV	-0.65 eV	-0.65 eV
	W@Pt	-0.38 eV	-0.40 eV	-0.40 eV
$\Delta E_{ads}(OH*)$	Pt(111)	0.86 eV	0.85 eV	0.85 eV
	Pt/W(110)	0.56 eV	0.56 eV	0.55 eV
	Pt_{55}	0.26 eV	0.26 eV	0.26 eV
	W@Pt	0.36 eV	0.35 eV	0.34 eV

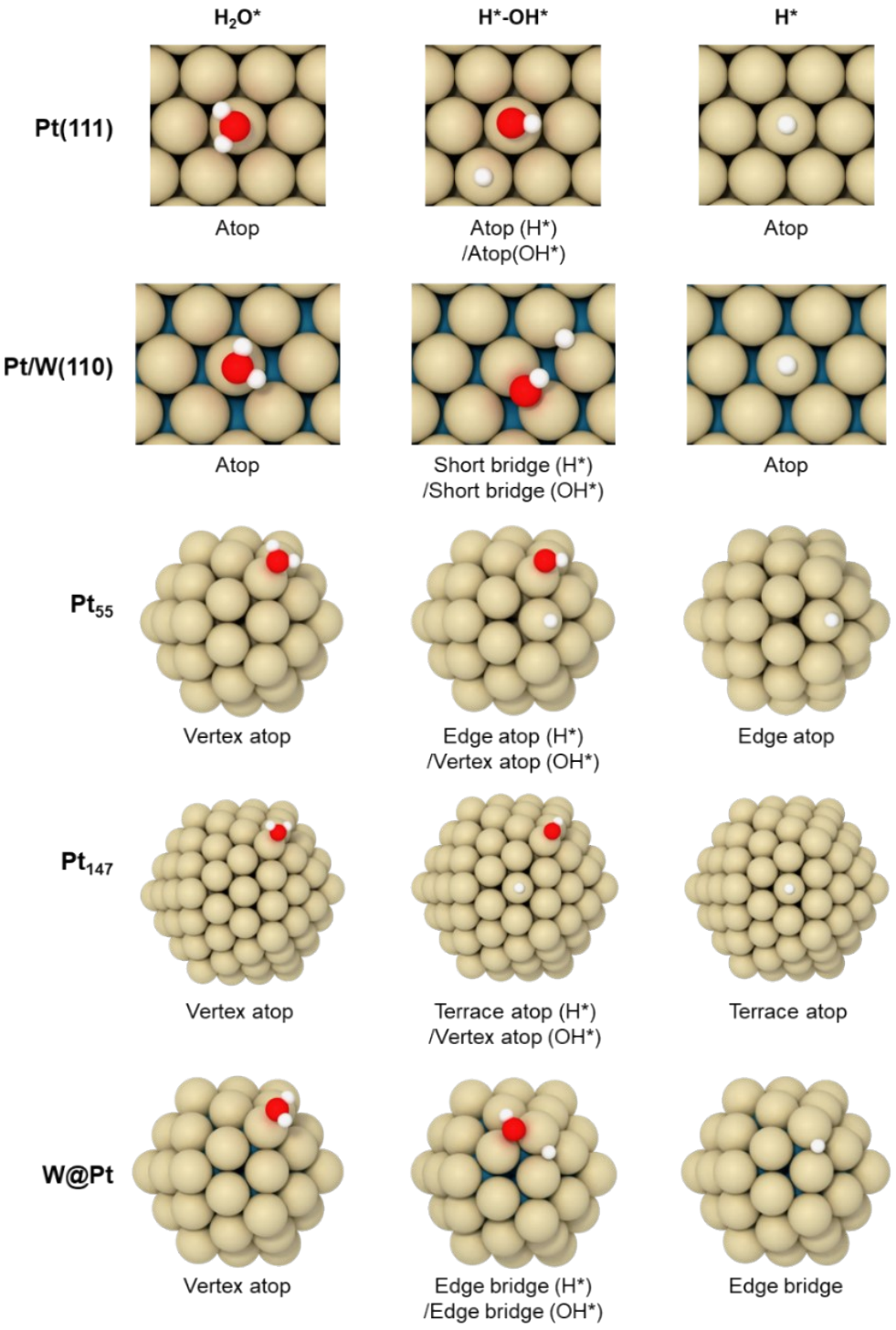
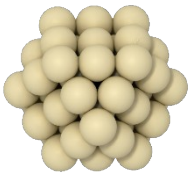
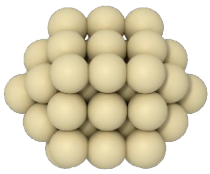
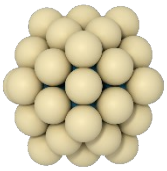
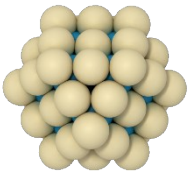
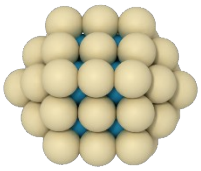
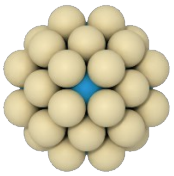


Figure S1. Adsorption sites of each intermediate (H_2O*, H*-OH*, and H*) in the alkaline HER pathway on five model systems (Pt(111), Pt/W(110) surfaces, Pt_{55}, Pt_{147}, W@Pt nanoparticles).

Table S2. Calculated formation energies (E_f) and excess energies (E_{exc}) of different configurations (icosahedron, cuboctahedron, decahedron, and BCC-based structure) for the Pt_{55} and W@Pt nanoparticles. E_f and E_{exc} calculated with Eq (s1) and Eq (s2).

	Icosahedron	Cuboctahedron	Decahedron	BCC-based
Pt_{55}				-
E_f	1.46 eV/atom	1.49 eV/atom	1.48 eV/atom	-
W@Pt				
E_f	1.07 eV/atom	1.20 eV/atom	1.11 eV/atom	1.24 eV/atom
E_{exc}	-0.59 eV/atom	-	-	-0.40 eV/atom

$$E_f = \frac{E_{structure\ with\ n\ atoms\ A\ and\ m\ atoms\ B} - nE_{A\ bulk} - mE_{B\ bulk}}{n+m} \quad \text{(s1)}$$

$$E_{exc} = \frac{E_{structure\ with\ n\ atoms\ A\ and\ m\ atoms\ B} - \frac{n}{n+m}E_{A\ sphere} - \frac{m}{n+m}E_{B\ sphere}}{n+m} \quad \text{(s2)}$$

Table S3. Calculated adsorption energies of alkaline HER intermediates on Pt_{55}, Pt_{147} nanoparticles and Pt(111) surface.

	Pt_{55}	Pt_{147}	Pt(111)
H_2O*	-0.88 eV	-0.92 eV	-0.46 eV
OH*	0.26 eV	0.26 eV	0.85 eV
H*	-0.67 eV	-0.77 eV	-0.53 eV
H*OH*	-0.40 eV	-0.50 eV	0.31 eV

Table S4. Calculated formation energies (E_f) of different Pt/W configurations (FCC based Pt/W(111), BCC based Pt/W(110), and BCC based Pt/W(001)). All systems consist of 45 atoms (9 Pt atoms and 36 W atoms) and Pt monolayer covers each of the W surfaces. E_f calculated with Eq (s1).

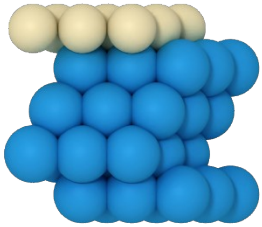
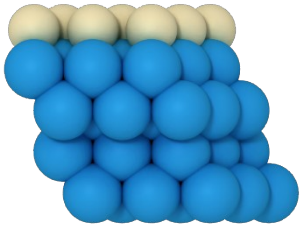
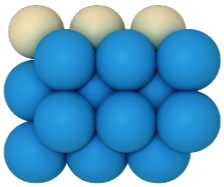
	Pt/W(111) FCC	Pt/W(110) BCC	Pt/W(001) BCC
			
E_f	0.76 eV/atom	0.51 eV/atom	1.00 eV/atom

Table S5. Calculated adsorption energies of alkaline HER intermediates on Pt/W(110) surfaces; relaxed upon adsorption (original) and fixed upon adsorption.

	Original	Fixed upon adsorption
H_2O*	-0.48 eV	-0.47 eV
OH*	0.56 eV	0.64 eV
H*	-0.28 eV	-0.28 eV
H*OH*	0.03 eV	0.31 eV

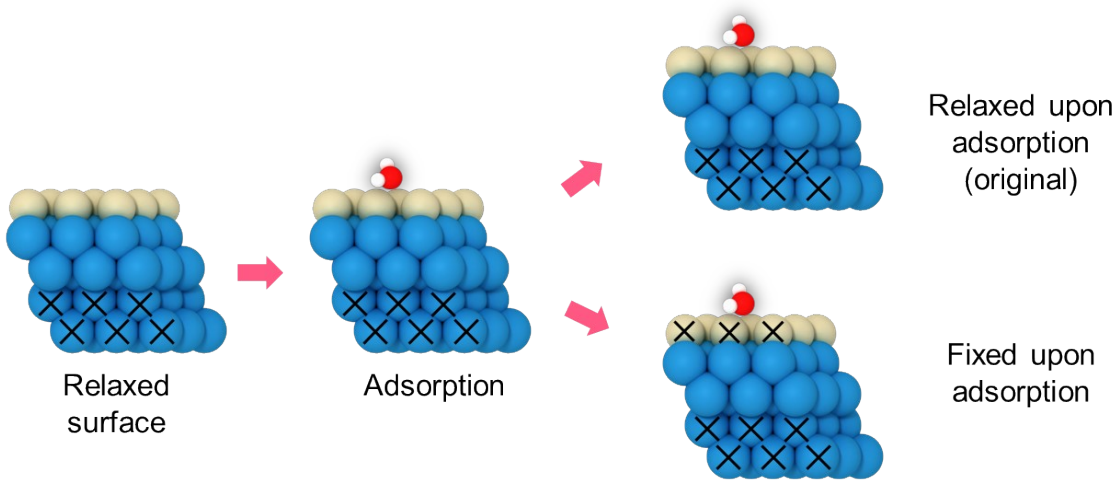


Figure S2. Calculated model systems to decouple the effect of adsorbate-induced eigenstress.