Supporting Information

Effect of External Electric Field, Aqueous Solution and Specific Adsorption on Segregation of Pt_{ML}/M_{ML}/Pt(111) (M=Cu, Pd, Au): A DFT Study

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Figures and Tables

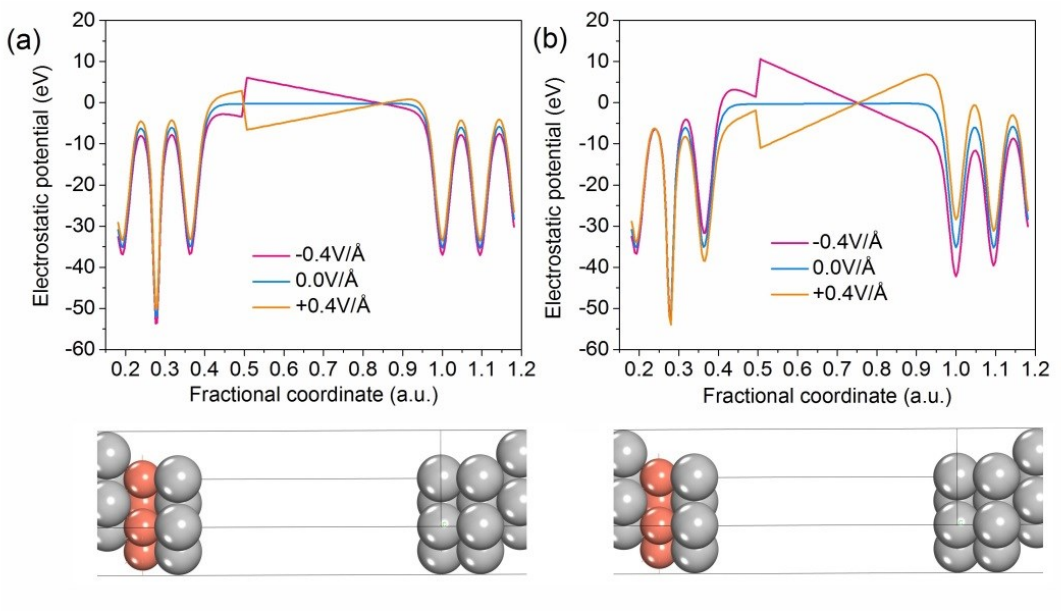

Figure S 1 The electrostatic potential of $Pt_{ML}/Cu_{ML}/Pt(111)$ alloy under (a) vacuum and (b) aqueous solution condition. Gray: Pt; Brown: Cu

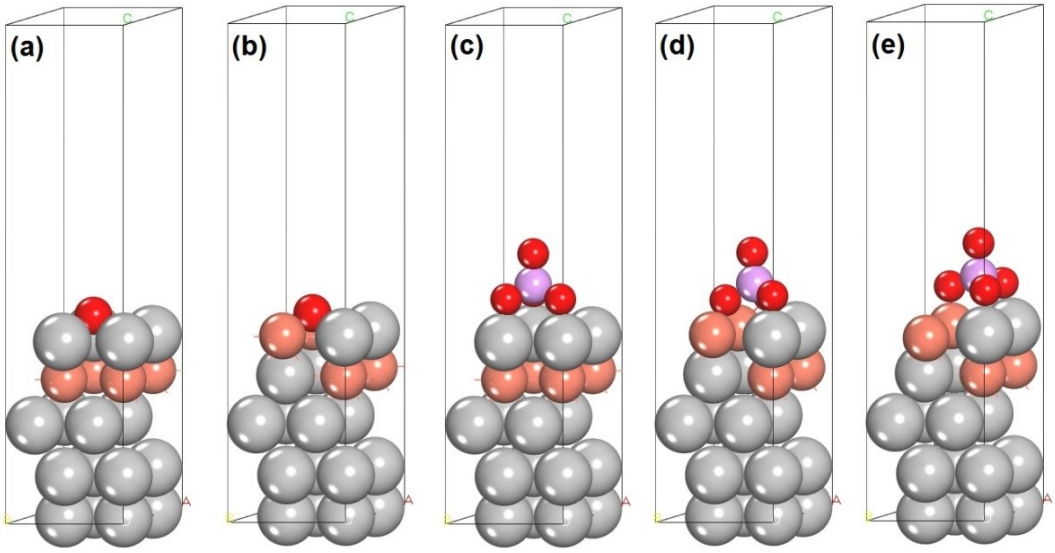

Figure S 2 Optimized structures of PtCu alloys under adsorption: (a) $Pt_{ML}/Cu_{ML}/Pt(111)$ with O atom adsorption, (b) $Pt_2Cu_2/Pt_2Cu_2/Pt(111)$ with O atom adsorption, (c) $Pt_{ML}/Cu_{ML}/Pt(111)$ with PO_4^{3-} adsorption;(d) $Pt_2Cu_2/Pt_2Cu_2/Pt(111)$ with PO_4^{3-} adsorption; (e) $Pt_2Cu_2/Pt_2Cu_2/Pt(111)$ with PO_4^{3-} adsorption under aqueous solution and -0.4V/Å. Gray: Pt; Brown: Cu

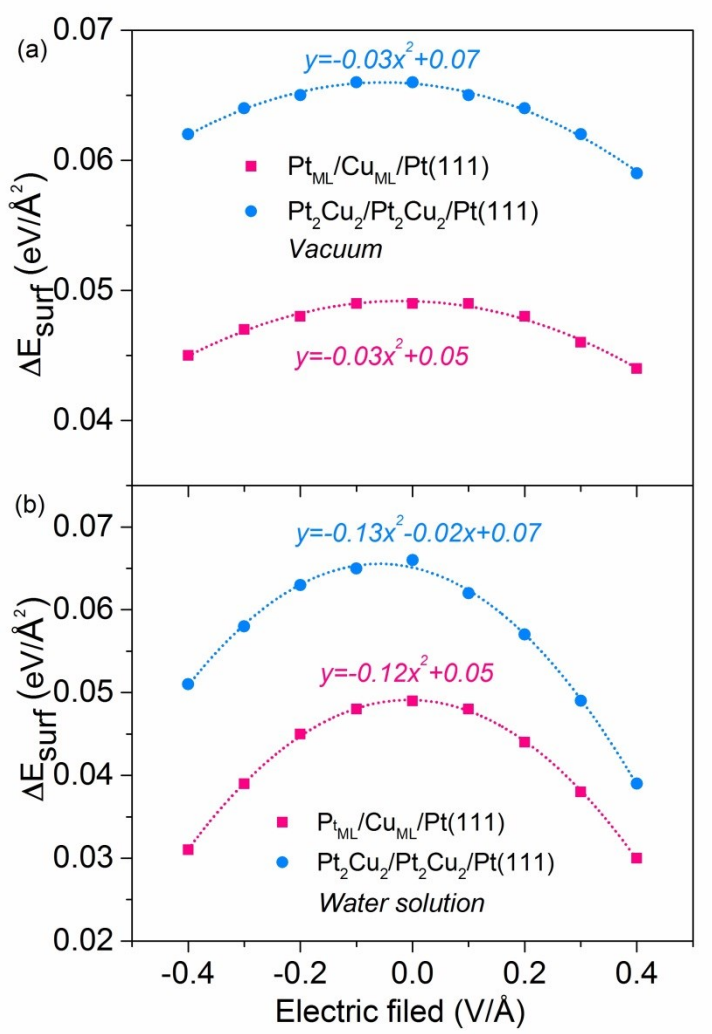

Figure S 3 The calculated surface energy of PtCu alloy, as a function of electric field, under vacuum and aqueous solution: (a) surface energy of $Pt_{ML}/Cu_{ML}/Pt(111)$ and $Pt_2Cu_2/Pt_2Cu_2/Pt(111)$ alloy under vacuum condition; (b) surface energy of $Pt_{ML}/Cu_{ML}/Pt(111)$ and $Pt_2Cu_2/Pt_2Cu_2/Pt(111)$ alloy with aqueous solution

Table S 1 Segregation energies (eV) for various Pt-M-Pt(111) alloys under vacuum conditions

	$\Delta E_{seg}(1)$	$\Delta E_{seg}(2)$	$\Delta E_{seg}(3)$	$\Delta E_{seg}(4)$
PtCu	0.51	0.89	1.33	1.81
PtPd	0.08	0.18	0.22	0.26
PtAu	-0.14	-0.36	-0.78	-1.24

Table S 2 The interlayer distance (d_I, the distance between the first layer and the second layer; d_{II}, the distance between the second layer and the third layer) of PtM alloys under electric field with or without aqueous solution

(a) Pt_{ML}/Cu_{ML}/Pt(111) and Pt_2Cu_2/ Pt_2Cu_2/Pt(111) with or without aqueous solution

Electric field(V/Å)	Vacuum				Aqueous solution			
	Pt_{ML}		Pt_2Cu_2		Pt_{ML}		Pt_2Cu_2	
	d_I	d_{II}	d_I	d_{II}	d_I	d_{II}	d_I	d_{II}
-0.4	2.08	2.08	2.09	2.22	2.09	2.09	2.10	2.23
-0.3	2.08	2.08	2.09	2.22	2.09	2.08	2.10	2.22
-0.2	2.08	2.08	2.08	2.22	2.08	2.08	2.09	2.22
-0.1	2.08	2.08	2.08	2.22	2.08	2.08	2.08	2.22
0.0	2.08	2.08	2.08	2.22	2.08	2.08	2.08	2.22
0.1	2.08	2.08	2.08	2.22	2.08	2.08	2.08	2.22
0.2	2.08	2.08	2.08	2.22	2.08	2.08	2.08	2.22
0.3	2.08	2.08	2.08	2.22	2.08	2.08	2.08	2.22
0.4	2.08	2.08	2.08	2.22	2.07	2.09	2.08	2.22

(b) O atom adsorbed Pt_2Cu_2/ Pt_2Cu_2/Pt(111) and Pt_{ML}/Cu_{ML}/Pt(111) with and without aqueous solution

Electric field(V/Å)	Vacuum				Aqueous solution			
	Pt_{ML}		Pt_2Cu_2		Pt_{ML}		Pt_2Cu_2	
	d_I	d_{II}	d_I	d_{II}	d_I	d_{II}	d_I	d_{II}
-0.4	2.10	2.08	2.09	2.23	2.11	2.09	2.09	2.24
-0.3	2.10	2.08	2.09	2.23	2.10	2.08	2.09	2.24
-0.2	2.10	2.08	2.09	2.23	2.10	2.08	2.09	2.23
-0.1	2.10	2.08	2.09	2.23	2.10	2.08	2.09	2.23
0.0	2.10	2.08	2.09	2.23	2.10	2.08	2.09	2.23
0.1	2.10	2.08	2.09	2.23	2.10	2.08	2.09	2.23
0.2	2.10	2.08	2.09	2.23	2.10	2.08	2.09	2.23
0.3	2.10	2.08	2.09	2.23	2.10	2.08	2.09	2.23
0.4	2.10	2.08	2.09	2.23	2.10	2.08	2.09	2.23

(c) PO_4^{3-}* adsorbed Pt_2Cu_2/ Pt_2Cu_2/Pt(111) and Pt_{ML}/Cu_{ML}/Pt(111) with and without aqueous solution

Electric field(V/Å)	Vacuum				Aqueous solution			
	Pt_{ML}		Pt_2Cu_2		Pt_{ML}		Pt_2Cu_2	
	d_I	d_{II}	d_I	d_{II}	d_I	d_{II}	d_I	d_{II}

-0.4	2.08	2.07	2.09	2.22	2.08	2.08	2.11	2.23
-0.3	2.08	2.07	2.07	2.23	2.08	2.07	2.09	2.23
-0.2	2.08	2.07	2.06	2.23	2.08	2.07	2.07	2.23
-0.1	2.08	2.07	2.06	2.23	2.08	2.07	2.06	2.23
0.0	2.08	2.07	2.06	2.23	2.08	2.07	2.06	2.23
0.1	2.08	2.07	2.06	2.23	2.08	2.07	2.06	2.23
0.2	2.08	2.07	2.06	2.23	2.08	2.07	2.06	2.23
0.3	2.08	2.07	2.06	2.23	2.08	2.07	2.06	2.23
0.4	2.08	2.07	2.07	2.23	2.08	2.07	2.06	2.23

(d) $Pt_{ML}/Pd_{ML}/Pt(111)$ and $Pt_2Pd_2/ Pt_2Pd_2/Pt(111)$ with or without aqueous solution

Electric field(V/Å)	Vacuum				Aqueous solution			
	Pt_{ML}		Pt_2Pd_2		Pt_{ML}		Pt_2Pd_2	
	d_I	d_{II}	d_I	d_{II}	d_I	d_{II}	d_I	d_{II}
-0.4	2.30	2.28	2.29	2.29	2.31	2.29	2.30	2.29
-0.3	2.30	2.28	2.29	2.28	2.31	2.28	2.30	2.29
-0.2	2.30	2.28	2.29	2.28	2.30	2.28	2.29	2.29
-0.1	2.30	2.28	2.29	2.28	2.30	2.28	2.29	2.28
0.0	2.30	2.28	2.29	2.28	2.30	2.28	2.28	2.28
0.1	2.30	2.28	2.29	2.28	2.30	2.28	2.28	2.29
0.2	2.30	2.28	2.29	2.28	2.30	2.28	2.28	2.29
0.3	2.30	2.28	2.28	2.28	2.30	2.28	2.27	2.29
0.4	2.30	2.28	2.28	2.29	2.30	2.28	2.27	2.29

(e) $Pt_{ML}/Au_{ML}/Pt(111)$ and $Pt_2Au_2/ Pt_2Au_2/Pt(111)$ with or without aqueous solution

Electric field(V/Å)	Vacuum				Aqueous solution			
	Pt_{ML}		Pt_2Au_2		Pt_{ML}		Pt_2Au_2	
	d_I	d_{II}	d_I	d_{II}	d_I	d_{II}	d_I	d_{II}
-0.4	2.45	2.44	2.49	2.37	2.46	2.44	2.51	2.38
-0.3	2.45	2.44	2.49	2.37	2.45	2.44	2.50	2.38
-0.2	2.45	2.44	2.49	2.37	2.45	2.44	2.49	2.37
-0.1	2.45	2.44	2.49	2.37	2.45	2.44	2.49	2.37
0.0	2.45	2.44	2.49	2.37	2.45	2.44	2.49	2.37
0.1	2.45	2.44	2.49	2.37	2.45	2.44	2.49	2.37
0.2	2.45	2.44	2.49	2.37	2.43	2.44	2.49	2.37
0.3	2.45	2.44	2.49	2.37	2.43	2.43	2.49	2.38
0.4	2.45	2.44	2.49	2.37	2.43	2.44	2.53	2.38

(f) $Cu_{ML}/Pt(111)$, $Pd_{ML}/Pt(111)$ and $Au_{ML}/Pt(111)$ without aqueous solution

Electric field(V/Å)	Vacuum					
	$Cu_{ML}/Pt(111)$		$Pd_{ML}/Pt(111)$		$Au_{ML}/Pt(111)$	
	d_I	d_{II}	d_I	d_{II}	d_I	d_{II}
-0.4	2.06	2.35	2.30	2.32	2.49	2.34

-0.3	2.06	2.35	2.30	2.32	2.49	2.34
-0.2	2.06	2.35	2.30	2.32	2.49	2.34
-0.1	2.06	2.35	2.30	2.32	2.49	2.34
0.0	2.06	2.35	2.30	2.32	2.49	2.34
0.1	2.06	2.35	2.30	2.32	2.49	2.34
0.2	2.06	2.35	2.30	2.32	2.49	2.34
0.3	2.06	2.35	2.30	2.32	2.49	2.34
0.4	2.06	2.35	2.30	2.32	2.49	2.34

(g) Cu_{ML}/Pt(111), Pd_{ML}/Pt(111) and Au_{ML}/Pt(111) with aqueous solution

Electric field(V/Å)	Aqueous solution					
	Cu_{ML}/Pt(111)		Pd_{ML}/Pt(111)		Au_{ML}/Pt(111)	
	d_I	d_{II}	d_I	d_{II}	d_I	d_{II}
-0.4	2.08	2.36	2.30	2.33	2.49	2.34
-0.3	2.06	2.35	2.30	2.32	2.49	2.34
-0.2	2.06	2.35	2.30	2.32	2.49	2.34
-0.1	2.06	2.35	2.30	2.32	2.49	2.34
0.0	2.06	2.35	2.30	2.32	2.49	2.34
0.1	2.06	2.35	2.30	2.32	2.47	2.33
0.2	2.06	2.35	2.30	2.32	2.47	2.33
0.3	2.06	2.36	2.29	2.32	2.47	2.33
0.4	2.07	2.36	2.29	2.33	2.47	2.34

Table S 3 The segregation energy (eV) of PM alloy under electric field with or without aqueous solution effect

(a) Pt_2Cu_2/ Pt_2Cu_2/Pt(111), Pt_2Pd_2/ Pt_2Pd_2/Pt(111) and Pt_2Au_2/ Pt_2Au_2/Pt(111) alloy with and without aqueous solution

Electric field(V/Å)	Vacuum			Aqueous solution		
	Pt_2Cu_2	Pt_2Pd_2	Pt_2Au_2	Pt_2Cu_2	Pt_2Pd_2	Pt_2Au_2
-0.4	0.96	0.22	-0.31	1.10	0.28	-0.17
-0.3	0.95	0.21	-0.33	1.06	0.26	-0.22
-0.2	0.93	0.20	-0.34	1.01	0.24	-0.27
-0.1	0.91	0.19	-0.35	0.94	0.22	-0.32
0	0.89	0.18	-0.36	0.89	0.18	-0.36
0.1	0.87	0.17	-0.37	0.78	0.13	-0.41
0.2	0.85	0.16	-0.38	0.69	0.08	-0.44
0.3	0.83	0.15	-0.40	0.59	0.03	-0.49
0.4	0.81	0.14	-0.41	0.49	-0.02	-0.53

(b) Cu_{ML}/Pt(111), Pd_{ML}/Pt(111) and Au_{ML}/Pt(111) alloy with and without aqueous solution

Electric field(V/Å)	Vacuum			Aqueous solution		
	Cu_{ML}	Pd_{ML}	Au_{ML}	Cu_{ML}	Pd_{ML}	Au_{ML}

-0.4	1.93	0.34	-1.17	2.20	0.48	-0.95
-0.3	1.91	0.32	-1.19	2.12	0.45	-1.03
-0.2	1.87	0.30	-1.20	2.01	0.40	-1.10
-0.1	1.84	0.28	-1.22	1.88	0.33	-1.17
0	1.81	0.26	-1.24	1.81	0.26	-1.24
0.1	1.77	0.24	-1.26	1.55	0.15	-1.31
0.2	1.73	0.22	-1.27	1.36	0.05	-1.37
0.3	1.69	0.20	-1.29	1.16	-0.07	-1.43
0.4	1.65	0.18	-1.30	0.95	-0.18	-1.48

Table S 4 The segregation energy (eV) of Pt_2Cu_2/ Pt_2Cu_2/Pt(111) alloy under electric field with or without aqueous solution effect

Electric field(V/Å)	Vacuum		Aqueous solution	
	O atom	PO_4^{3-}	O atom	PO_4^{3-}
-0.4	0.15	-0.27	0.11	-0.57
-0.3	0.15	-0.33	0.13	-0.21
-0.2	0.15	-0.43	0.14	-0.35
-0.1	0.15	-0.53	0.14	-0.47
0	0.15	-0.62	0.13	-0.58
0.1	0.14	-0.71	0.11	-0.65
0.2	0.14	-0.78	0.09	-0.70
0.3	0.14	-0.84	0.07	-0.74
0.4	0.13	-0.91	0.03	-0.77

Table S 5 The shell-layer d band center (eV) of PM alloy under electric field with or without aqueous solution effect

(a) $Pt_{ML}/Cu_{ML}/Pt(111)$, Pt_2Cu_2/ Pt_2Cu_2/Pt(111) and $Cu_{ML}/Pt(111)$ alloy with and without aqueous solution

Electric field(V/Å)	Vacuum			Aqueous solution		
	Pt_{ML}	Pt_2Cu_2	Cu_{ML}	Pt_{ML}	Pt_2Cu_2	Cu_{ML}
-0.4	-2.45	-2.13	-2.09	-2.50	-2.16	-2.12
-0.3	-2.45	-2.13	-2.08	-2.48	-2.15	-2.11
-0.2	-2.44	-2.13	-2.08	-2.47	-2.14	-2.09
-0.1	-2.44	-2.12	-2.07	-2.45	-2.13	-2.07
0.0	-2.43	-2.12	-2.07	-2.43	-2.11	-2.05
0.1	-2.42	-2.11	-2.06	-2.41	-2.09	-2.02
0.2	-2.42	-2.11	-2.06	-2.39	-2.07	-1.99
0.3	-2.41	-2.11	-2.05	-2.37	-2.05	-1.96
0.4	-2.41	-2.10	-2.05	-2.36	-2.03	-1.93

(b) $Pt_{ML}/Pd_{ML}/Pt(111)$, Pt_2Pd_2/ Pt_2Pd_2/Pt(111) and$Pd_{ML}/Pt(111)$ alloy with and without aqueous solution

Electric field(V/Å)	Vacuum			Aqueous solution		
	Pt_{ML}	Pt_2Pd_2	Pd_{ML}	Pt_{ML}	Pt_2Pd_2	Pd_{ML}
-0.4	-2.41	-2.23	-2.03	-2.44	-2.25	-2.05
-0.3	-2.41	-2.23	-2.03	-2.43	-2.25	-2.05
-0.2	-2.41	-2.23	-2.03	-2.43	-2.24	-2.04
-0.1	-2.40	-2.23	-2.03	-2.41	-2.24	-2.03
0.0	-2.40	-2.23	-2.02	-2.40	-2.22	-2.02
0.1	-2.40	-2.22	-2.02	-2.39	-2.22	-2.01
0.2	-2.40	-2.22	-2.02	-2.38	-2.21	-2.00
0.3	-2.39	-2.22	-2.02	-2.37	-2.20	-1.99
0.4	-2.39	-2.22	-2.01	-2.37	-2.19	-1.98

(c) $Pt_{ML}/Au_{ML}/Pt(111)$, $Pt_2Au_2/\ Pt_2Au_2/Pt(111)$ and $Au_{ML}/Pt(111)$ alloy with and without aqueous solution

Electric field(V/Å)	Vacuum			Aqueous solution		
	Pt_{ML}	Pt_2Au_2	Au_{ML}	Pt_{ML}	Pt_2Au_2	Au_{ML}
-0.4	-2.24	-2.84	-3.48	-2.28	-2.88	-3.57
-0.3	-2.23	-2.83	-3.47	-2.27	-2.87	-3.54
-0.2	-2.23	-2.83	-3.47	-2.26	-2.86	-3.51
-0.1	-2.23	-2.82	-3.46	-2.24	-2.83	-3.47
0.0	-2.22	-2.81	-3.45	-2.22	-2.81	-3.44
0.1	-2.22	-2.81	-3.44	-2.21	-2.79	-3.43
0.2	-2.21	-2.80	-3.43	-2.20	-2.77	-3.40
0.3	-2.21	-2.79	-3.43	-2.19	-2.74	-3.36
0.4	-2.21	-2.79	-3.42	-2.18	-2.71	-3.33

Table S 6 The surface energy (eV/Å^2) of PM alloy under electric field with or without aqueous solution effect

(a) $Pt_{ML}/Cu_{ML}/Pt(111)$, $Pt_{ML}/Pd_{ML}/Pt(111)$ and $Pt_{ML}/Au_{ML}/Pt(111)$ alloy with and without aqueous solution

Electric field(V/Å)	Vacuum			Aqueous solution		
	Pt_{ML}-Cu	Pt_{ML}-Pd	Pt_{ML}-Au	Pt_{ML}-Cu	Pt_{ML}-Pd	Pt_{ML}-Au
-0.4	0.05	0.08	0.09	0.03	0.06	0.07
-0.3	0.05	0.08	0.09	0.04	0.07	0.08
-0.2	0.05	0.08	0.09	0.05	0.08	0.09
-0.1	0.05	0.08	0.10	0.05	0.08	0.09
0	0.05	0.08	0.10	0.05	0.08	0.10
0.1	0.05	0.08	0.10	0.05	0.08	0.09
0.2	0.05	0.08	0.09	0.04	0.08	0.09
0.3	0.05	0.08	0.09	0.04	0.07	0.08
0.4	0.04	0.08	0.09	0.03	0.06	0.08

(b) $Pt_2Cu_2/\ Pt_2Cu_2/Pt(111)$, $Pt_2Pd_2/\ Pt_2Pd_2/Pt(111)$ and $Pt_2Au_2/\ Pt_2Au_2/Pt(111)$ alloy with and without

aqueous solution

Electric field(V/Å)	Vacuum			Aqueous solution		
	Pt_2Cu_2	Pt_2Pd_2	Pt_2Au_2	Pt_2Cu_2	Pt_2Pd_2	Pt_2Au_2
-0.4	0.06	0.08	0.08	0.05	0.07	0.07
-0.3	0.06	0.08	0.09	0.06	0.08	0.08
-0.2	0.07	0.08	0.09	0.06	0.08	0.08
-0.1	0.07	0.09	0.09	0.07	0.09	0.09
0	0.07	0.09	0.09	0.07	0.09	0.09
0.1	0.07	0.09	0.09	0.06	0.08	0.09
0.2	0.06	0.08	0.09	0.06	0.08	0.08
0.3	0.06	0.08	0.09	0.05	0.07	0.08
0.4	0.06	0.08	0.08	0.04	0.06	0.07

(c) Cu_{ML}/Pt(111), Pd_{ML}/Pt(111) and Au_{ML}/Pt(111) alloy with and without aqueous solution

Electric field(V/Å)	Vacuum			Aqueous solution		
	Cu_{ML}	Pd_{ML}	Au_{ML}	Cu_{ML}	Pd_{ML}	Au_{ML}
-0.4	0.08	0.08	0.07	0.07	0.07	0.06
-0.3	0.08	0.09	0.07	0.08	0.08	0.06
-0.2	0.08	0.09	0.07	0.08	0.08	0.07
-0.1	0.08	0.09	0.07	0.08	0.09	0.07
0	0.08	0.09	0.07	0.08	0.09	0.07
0.1	0.08	0.09	0.07	0.08	0.08	0.07
0.2	0.08	0.09	0.07	0.07	0.08	0.07
0.3	0.08	0.08	0.07	0.06	0.07	0.06
0.4	0.07	0.08	0.07	0.05	0.06	0.05