Supplementary information for

Dynamic Evolution of Hydroxylated Layer in Ruthenium Phosphide Electrocatalysts for Alkaline Hydrogen Evolution Reaction

Jae-Chan Kim,[a] Chan Woo Lee *[b] and Dong-Wan Kim *[a]

[a] School of Civil, Environmental and Architectural Engineering, Korea University, Seoul 02841, Republic of Korea.

[b] Department of Chemistry, Kookmin University, 77, Jeongneung-ro, Seongbuk-gu, Seoul 02707, Republic of Korea.

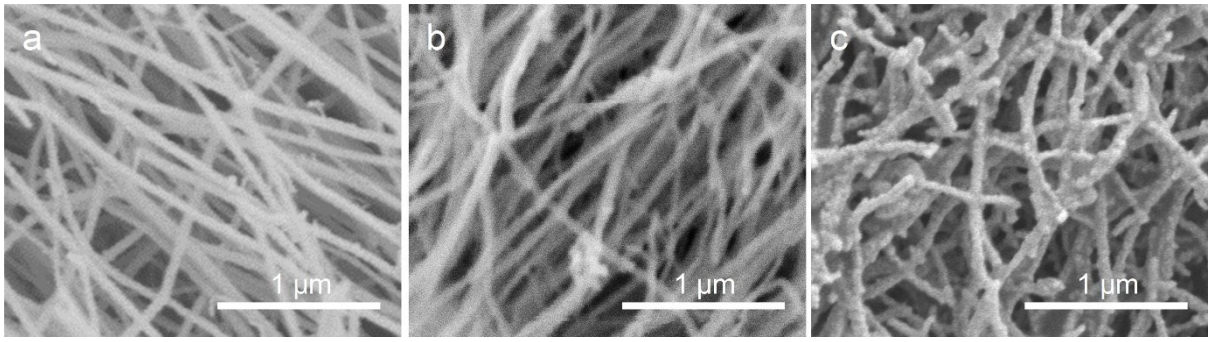


Figure S1. Low-magnification SEM images of (a) RuO_2, (b) Ru_xP-2, and (c)Ru_xP-3 NFs.

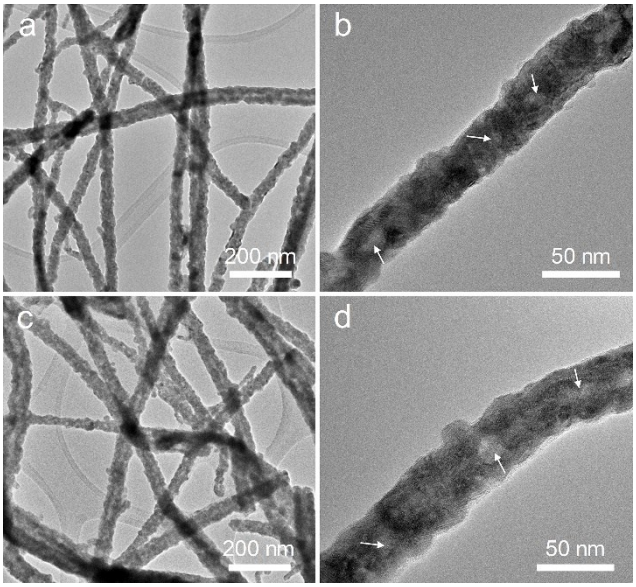


Figure S2. TEM images of (a, b) Ru_xP-2 NFs and (c, d) Ru_xP-3NFs obtained at different magnifications. Both of Ru_xP-2 and Ru_xP-3 NFs included void space as white arrow in Figure S2b and d.

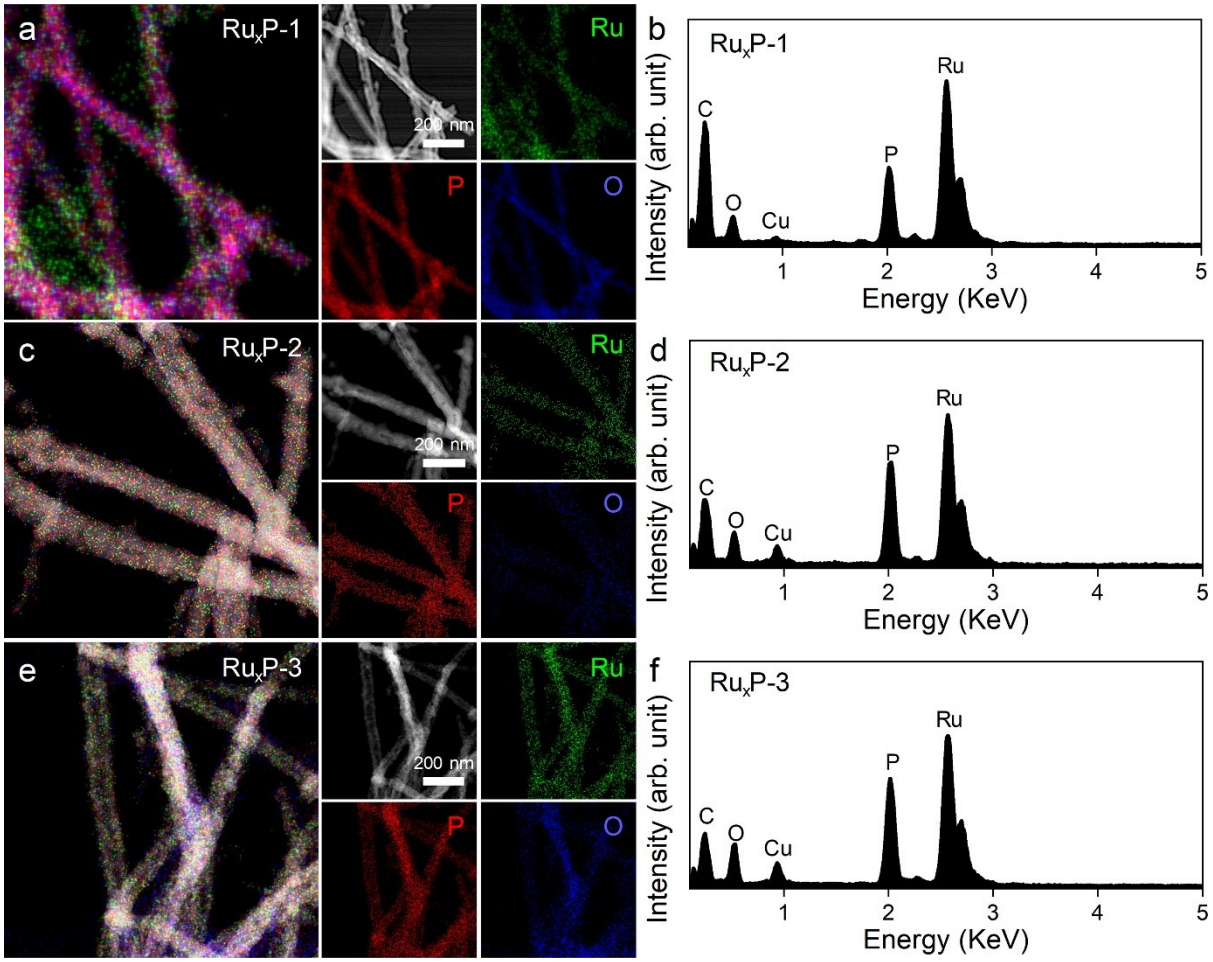


Figure S3. STEM-EDS mapping result and EDS spectrum measured using a bundle of (a,b) Ru_xP-1, (c,d) Ru_xP-2, and (e,f) Ru_xP-3 NFs for analyzing the bulk composition.

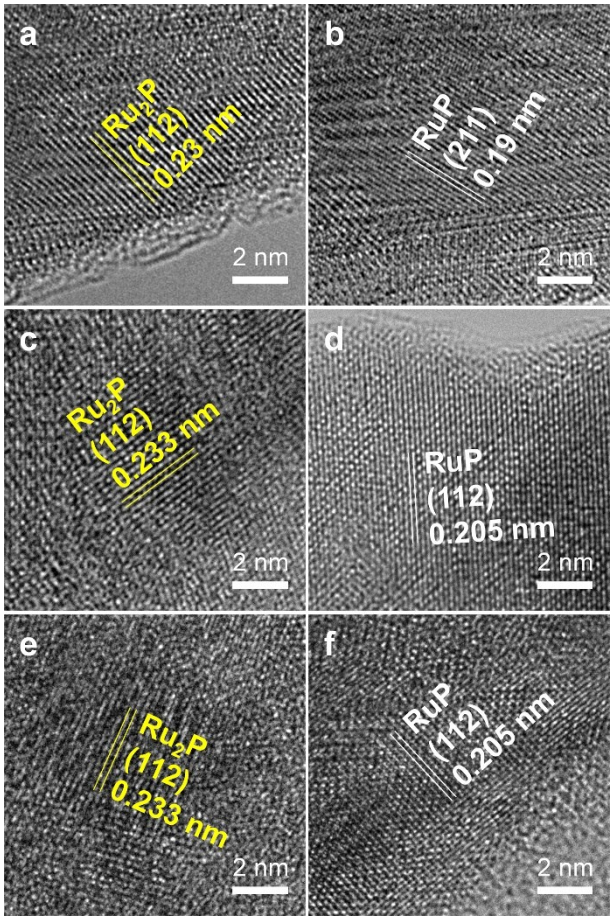


Figure S4. HRTEM images of (a,b) Ru_xP-1, (c,d) Ru_xP-2, and (e,f) Ru_xP-3.

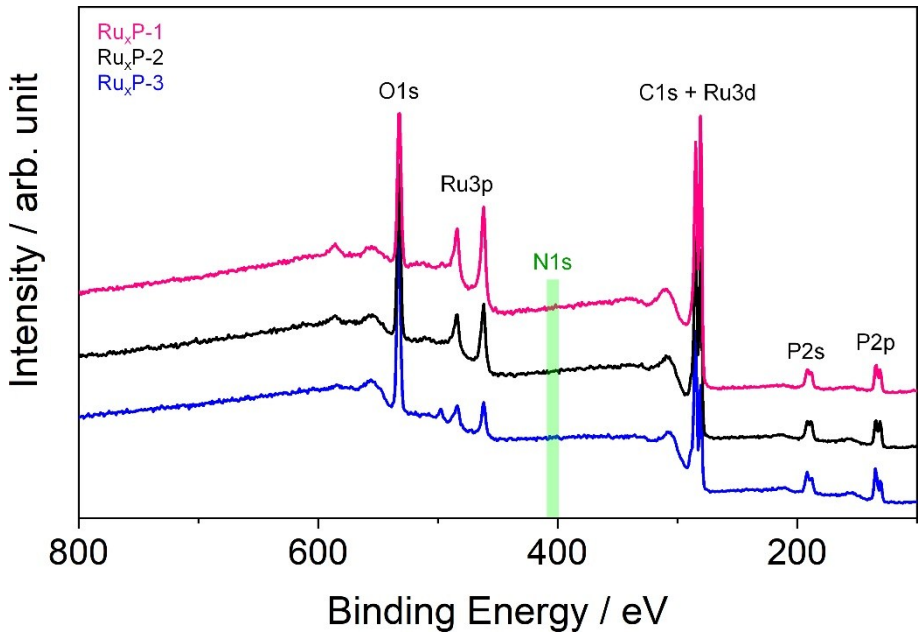


Figure S5. XPS survey spectra of Ru_xP-1, Ru_xP-2, and Ru_xP-3 NFs.

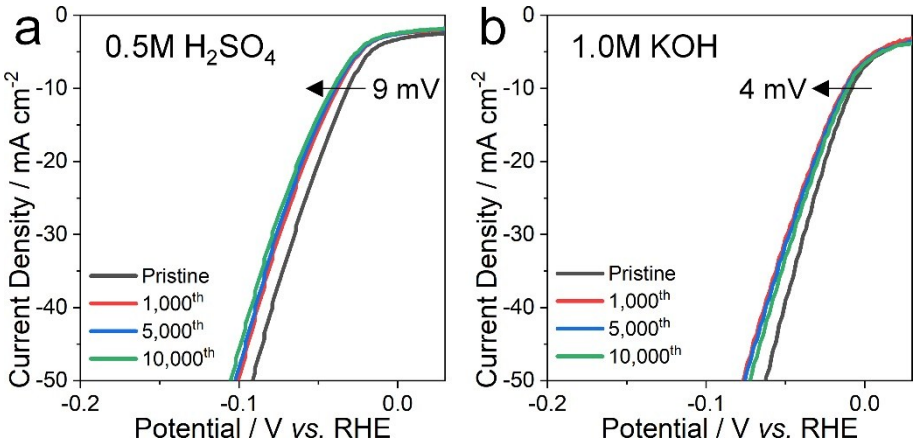


Figure S6. The linear sweep voltammetry curves of Ru_xP-1 in (a) 0.5 M H_2SO_4 and (b) 1.0 M KOH electrolytes. Polarization curves of Ru_xP-1 were measured after the 1,000th, 5,000th, and 10,000th cyclic voltammetry between 0.05 V and -0.14 V.

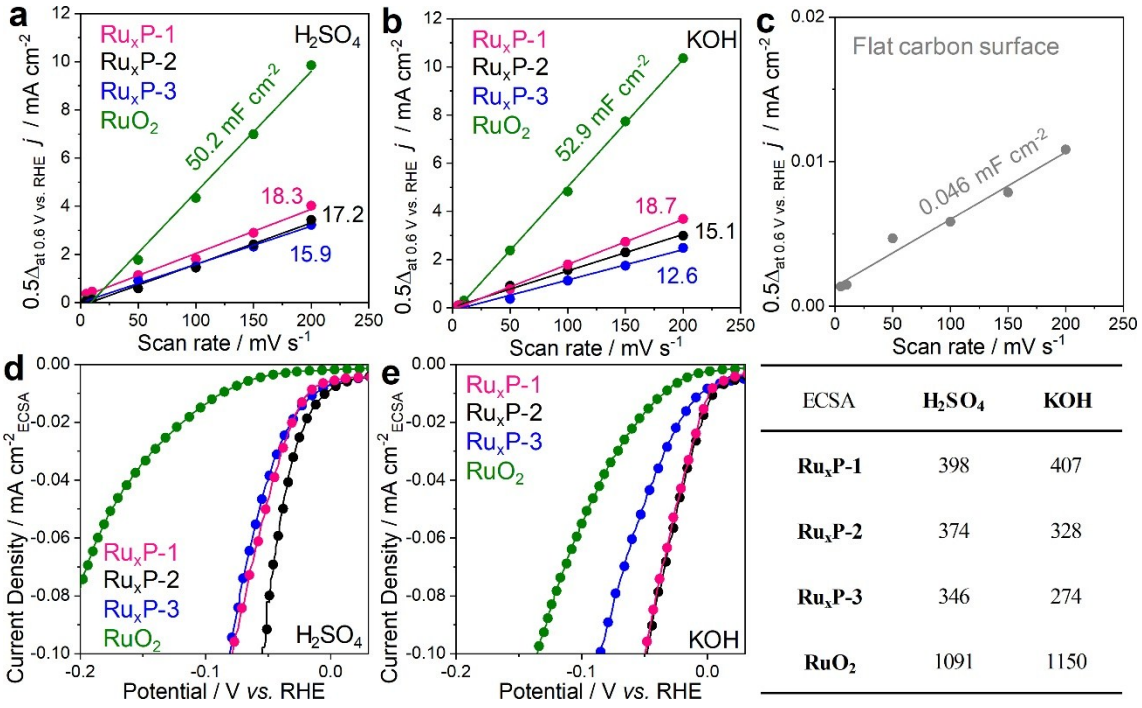
Table S1. The bulk composition of Ru_xP-1, Ru_xP-2, and Ru_xP-3 NFs were measured by the EDS spectrum.

EDS	**Ru_xP-1** [at.%]	**Ru_xP-2** [at.%]	**Ru_xP-3** [at.%]
Ru	47.2	45.2	34.2
P	24.0	34.5	35.2
O	28.8	20.3	30.6
Ru/P	1.97	1.31	0.97

Table S2. Comparison of HER performance in acid and alkaline media for Ru_xP NFs with previously reported ruthenium phosphide-based electrocatalysts.

		0.5 M H_2SO_4		1 M KOH			
Catalysts	**Morphology**	**η_{10}**[a] [mV]	**Tefel slope** [mV dec^{-1}]	**η_{10}** [mV]	**Tefel slope** [mV dec^{-1}]	**Areal loading mass** [mg cm^{-2}]	**Reference**
Ru_xP-1	Nanofibers	35	47	9	38	2	This study
Ru_xP-2	Nanofibers	27	45	13	43		
Ru_xP-3	Nanofibers	42	69	41	79		
Ru-Ru_2P	Nanoparticles	66	41	64	36.7	0.38	10
Ru	Nanoparticles	78	56	72	40.1		
Ru_2P	Nanoparticles	55	34.1	54	29.3		
Ru_2P/RGO	Nanoparticles	22	29	13	40	1	12
Ru_2P	Nanoparticles	117	30	32	62		
RuP_2@NPC	Nanoparticles	38	38	52	69	1	9
RuP_2 NPs	Nanoparticles	129	109	90	73		
RuP-475	Nanoparticles	47	39	47	45	0.345	27
RuP_2-550	Nanoparticles	122	83	76	74		
L-RuP/C	Nanoparticles (32 nm)	19	37	18	34	2	7
S-RuP/C	Nanoparticles (3 nm)	-	-	17	35		
RuP/CC	Nanoparticles	13	22	-	-	3.3~4.2	11
RuP_2/CC	Nanoparticles	33	56	-	-		
RuP_x/NPC	Nanoparticles	55	59	74	70	0.12	8
Ru_2P/Graphene	Nanoparticles	18	32	-	-	1	28
RuP/Graphene	Nanoparticles	24	41	-	-		
RuP_2/Graphene	Nanoparticles	49	71	-	-		
Ru_2P-BM-C	Nanoparticles	-	-	36	59	0.34	29
Ru_2P	Nanocrystals	≈ 120	101	57	43	0.06	30
RuP	Nanocrystals	≈ 100	76	74	49		
Ru-Ru_2P@NPC	Nanoparticles	42	39.75	46	39.75	0.357	31
Ru_2P/PC-2	Nanoparticles	-	51	43.4	35.1	0.285	16
Pt/C	Nanoparticles	30	50	30	40	2	32

[a] Overpotential for hydrogen evolution reaction at the current density of 10 mA cm^{-2}



ECSA	H_2SO_4	KOH
Ru_xP-1	398	407
Ru_xP-2	374	328
Ru_xP-3	346	274
RuO_2	1091	1150

Figure S7. Electrochemical double-layer capacitance measurements (C_{dl}) of Ru_xP-1, Ru_xP-2, Ru_xP-3, and RuO_2 NFs to compare electrochemically active surface area (ECSA) in (a) 0.5 M H_2SO_4 and (b) 1.0 M KOH electrolyte. (c) The specific capacitance for flat carbon surface (C_s) was measured in a potential range of 0.5 ~ 0.7 V vs. RHE. ECSA-normalized polarization curves of Ru_xP-1, Ru_xP-2, Ru_xP-3, and RuO_2 NFs, which were measured in (d) 0.5 M H_2SO_4 and (e) 1.0 M KOH electrolyte. The ECSA was calculated using the specific capacitance of flat carbon surface and the values were presented in Table.

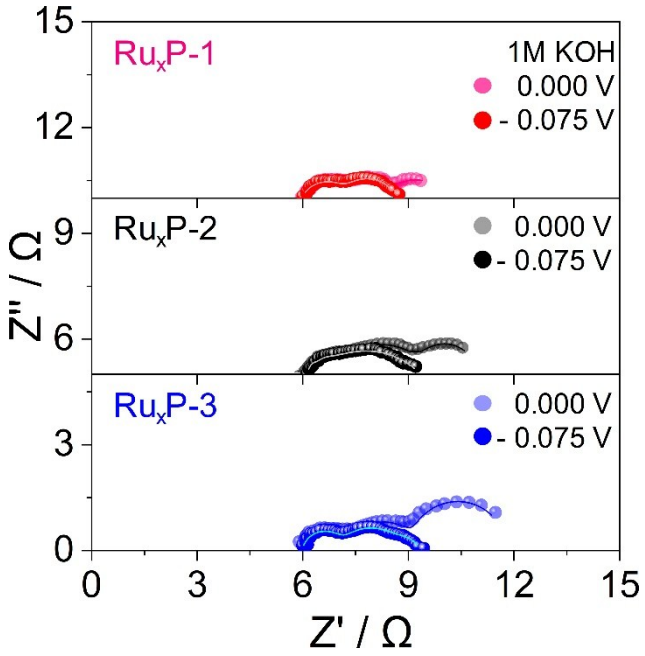


Figure S8. Electrochemical impedance spectroscopy conducted for analyzing resistance for Ru_xP-1, Ru_xP-2, and Ru_xP-3 NFs electrocatalysts at 0.000 V and −0.075 V in 1.0M KOH electrolyte.

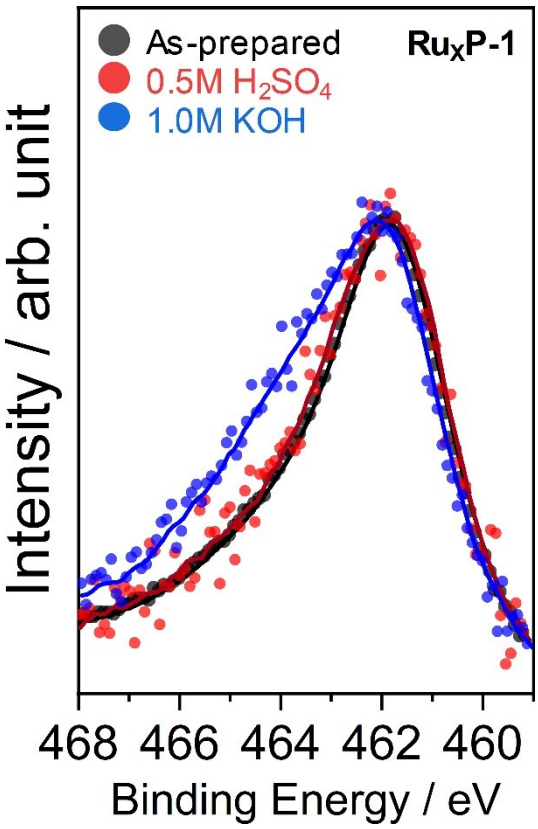


Figure S9. The normalized Ru 3p core level spectra of as-prepared Ru_xP-1 NFs (black circle) and Ru_xP-1 NFs after 1000 cycles of LSV in 0.5M H_2SO_4 (red circle) and 1M KOH (blue circle).

Table S3. XPS analysis conducted using Ru_xP-1, Ru_xP-2, and Ru_xP-3 NFs electrocatalysts for analyzing XPS composition change before and after HER test.

	Ru_xP-1 [at.%]		**Ru_xP-2 [at.%]**		**Ru_xP-3 [at.%]**	
	As-prepared	After HER	As-prepared	After HER	As-prepared	After HER
Ru	30.8	13.1	24.1	25.1	15.7	19.1
P	17.8	1.8	20	4.7	21.1	4.9
Ru/P	1.73	7.28	1.2	5.34	0.74	3.9

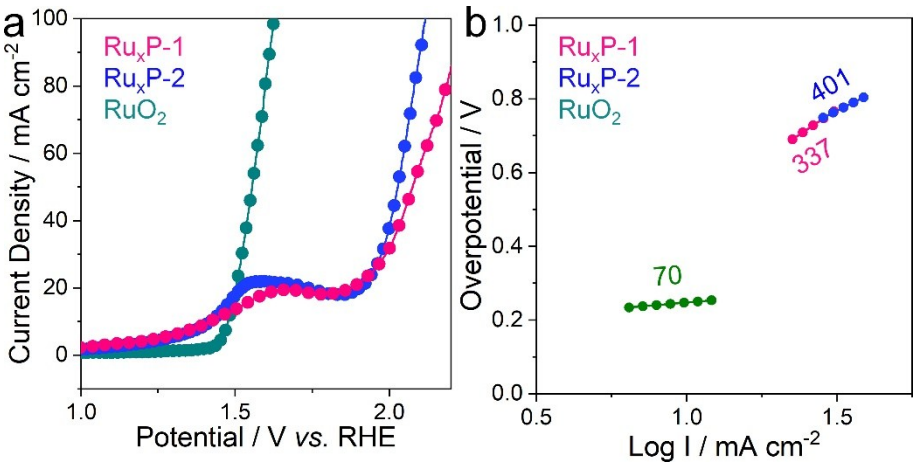


Figure S10. (a) The OER polarization curves and (b) Tafel slopes of Ru_xP-1, Ru_xP-2, and RuO_2 NFs NFs as electrocatalysts. Polarization curves for OER measured in 1.0 M KOH electrolyte.