## **Electronic Supplementary Information**

### Decoupled Hydrogen Evolution from Water/Seawater Splitting by

### Integrating Ethylene Glycol Oxidation on PtRh<sub>0.02</sub>@Rh Nanowires

#### with Rh Atoms Modifying

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# Figure



Fig. S1. The synthesis process of PtRh<sub>0.02</sub>@Rh NWs.



Fig. S2. The SEM images of (a)  $PtRh_{0.1}@Rh NWs$ , (b)  $PtRh_{0.34}@Rh NWs$ .



Fig. S3. The SEM image of Pt NWs.



Fig. S4. The TEM image of single ultrafine PtRh<sub>0.02</sub>@Rh NWs.



Fig. S5. The line scan of single PtRh<sub>0.02</sub>@Rh NWs.



Fig. S6. The PXRD pattern of PtRh<sub>0.1</sub>@Rh NWs, PtRh<sub>0.034</sub>@Rh NWs, and Pt NWs.



Fig. S7. The EDX result of PtRh<sub>0.02</sub>@Rh NWs.



Fig. S8. The LSV curves of the reduction potential of (a) Pt<sup>II</sup> precursor to Pt<sup>0</sup> and (b) Rh<sup>III</sup>

precursor to Rh<sup>0</sup>.



Fig. S9. The elemental mappings of Pt nanoparticles at the first formation stage of PtRh<sub>0.02</sub>@Rh

NWs.



Fig. S10. The elemental mappings of PtRh NWs after maintaining 1 h at 180 °C.



Fig. S11. The Tafel plots of PtRh<sub>0.02</sub>@Rh NWs, PtRh<sub>0.034</sub>@Rh NWs, PtRh<sub>0.1</sub>@Rh NWs, Pt NWs,

and JM-Pt black in alkaline seawater, respectively.



Fig. S12. Comparison of overpotential at the current densities of 10 mA cm<sup>-2</sup> and Tafel slopes for the state-of-the-art HER catalysts in alkaline media.



**Fig. S13**. Polarization curves of PtRh<sub>0.02</sub>@Rh NWs, PtRh<sub>0.034</sub> @Rh NWs, PtRh<sub>0.1</sub> @Rh NWs, Pt NWs, and JM-Pt black in alkaline fresh water and alkaline seawater, respectively.



Fig. S14. The CV curves of Pt NWs,  $PtRh_{0.02}$ @Rh NWs,  $PtRh_{0.034}$ @Rh NWs,  $PtRh_{0.1}$ @Rh NWs, and JM-Pt black in N<sub>2</sub>-saturated 0.1 M KOH solution.



**Fig. S15**. The Nyquist plots of Pt NWs, PtRh<sub>0.02</sub>@Rh NWs, PtRh<sub>0.034</sub>@Rh NWs, PtRh<sub>0.1</sub>@Rh NWs, and JM-Pt black at 50 mV vs. RHE.



Fig. S16. The CV curves of  $PtRh_{0.02}$  @Rh NWs in N<sub>2</sub>-saturated 0.1 M KOH solution with a scan rate of 50 mV·s<sup>-1</sup>.



**Fig. S17**. (a) The CV curves of Pt black in N<sub>2</sub>-saturated 0.1 M KOH solution with a scan rate of 50 mV·s<sup>-1</sup>. (b) Polarization curves of Pt black before and after 3000 CV cycles.



Fig. S18. Full XPS spectrum of PtRh<sub>0.02</sub>@Rh NWs after long-time durability in the water.



Fig. S19. TEM image of PtRh<sub>0.02</sub>@Rh NWs after long-time durability in the water.



Fig. S20. The long-term stability tests of  $PtRh_{0.02}$  @Rh NW, Pt NW, and JM-Pt black at 10 mA cm<sup>-2</sup> without iR compensation.



**Fig. S21**. Full XPS spectrum of  $PtRh_{0.02}$  @Rh NWs after long-time durability in the alkaline seawater.



Fig. S22. TEM image of  $PtRh_{0.02}$  (@Rh NWs after long-time durability in the alkaline seawater.



**Fig. S23**. The ECSA-normalized CV curves of PtRh<sub>0.02</sub>@Rh NWs, PtRh<sub>0.034</sub> @Rh NWs, PtRh<sub>0.1</sub> @Rh NWs, Pt NWs, and Pt black in 0.1 M KOH and 0.5 M Ethylene glycol solution.



**Fig. S24**. CO stripping curves of PtRh<sub>0.02</sub>@Rh NWs, PtRh<sub>0.034</sub>@Rh NWs, PtRh<sub>0.1</sub>@Rh NWs, Pt NWs, and JM-Pt black.



**Fig. S25**. The product was analyzed by 1H NMR using CH<sub>2</sub>Br<sub>2</sub> (1 mmol) as the internal standard.1H NMR (500 MHz, DMSO-d6) spectra of compound glycollate.



**Fig. S26**. The product was analyzed by 1H NMR using  $CH_2Br_2$  (1 mmol) as the internal standard.1H NMR (500 MHz, DMSO-d6) spectra of compound glycollate. (a) PtRh<sub>0.02</sub>@Rh NWs, (b) Pt NWs, (c) Pt black, and (d) without catalyst.

Component	Atomic conc. [%]	Error [%]	Mass conc. [%]	Error [%]
Rh 3d	8.84	0.30	17.84	0.36
Pt 4f	16.65	0.47	63.70	0.52

Table S1. The surface atomic ratio of Pt:Rh.