Supplementary Information

## Accelerating Water Dissociation Kinetics by Isolating Cobalt Atoms into Ruthenium Lattice

Mao et al

## **Supplementary Figures and Tables**



**Supplementary Figure 1.** TEM images of Co-substituted Ru nanosheets with different magnifications. **a** Scar bar: 200 nm. **b** Scar bar: 60 nm.



**Supplementary Figure 2.** TEM image of the assembly of Co-substituted Ru nanosheets, scar bar: 200 nm.



**Supplementary Figure 3.** XRD pattern of Co-substituted Ru nanosheets. The standard pattern of Ru (JCPDS card No. 06-0663) are shown beneath the plot.



**Supplementary Figure 4.** XRD pattern of RuCo alloy. The standard pattern of Ru (JCPDS card No. 06-0663) are shown beneath the plot.



**Supplementary Figure 5.** EDX pattern of Co-substituted Ru nanosheets. The Ru: Co atomic ratio was 94 : 6.



Supplementary Figure 6. Photograph of the three-electrode system for the electrochemical test.



**Supplementary Figure 7.** LSV curves of Pt in 1.0 M KOH solution ( $H_2$ -saturated), used for calibration of the SCE with respect to RHE. Scan rate: 5 mV s<sup>-1</sup>.



**Supplementary Figure 8.** LSV curves of Co-substituted Ru catalyst at different loading weight in 1.0 M KOH. Scan rate: 5 mV s<sup>-1</sup>.



Supplementary Figure 9. a EDX analysis. Ru : Co atomic ratio was 32:68 (close to 1:2). b TEM image of  $RuCo_2$  catalyst. Scar bar:100 nm.



**Supplementary Figure 10. a** LSV curves of RuCo<sub>2</sub> catalyst in 1 M KOH solution. **b** Tafel plots of the polarization curves in a.



**Supplementary Figure 11.** Copper UPD in the presence of 5 mM CuSO<sub>4</sub> on **a** Co-substituted Ru, and **b** Pt/C catalyst.



**Supplementary Figure 12.** TOF values of **a** Co-substituted Ru (red line), Pt/C (black line), **b** RuCo alloy and **c** Ru/C catalyst.



**Supplementary Figure 13.** Chronopotentiometric curves of Co-substituted Ru catalyst recorded at a constant current density of 10 mA cm<sup>-2</sup> in 1.0 M KOH.



**Supplementary Figure 14.** TEM images of the Co-substituted Ru /C catalyst **a** before and **b** after electrochemical test. Scar bar: 100 nm.



**Supplementary Figure 15.** EDS analysis of Co-substituted Ru catalyst after electrochemical test. The Ru : Co atomic ratio was 94 : 6.

## **Supplementary Table 1.**

Comparison of HER performance between Co-substituted Ru NSs and other reported Pt-free catalysts in alkaline medium.

Catalysts	Electrode	Loading	Electrolyte	Overpotenti	Tafel	Ref.
		amount		al at 10	plots	
		(mg cm <sup>-2</sup> )		mAcm <sup>-2</sup>	(mVde	
				(mV)	c <sup>-1</sup> )	
Co-substituted	GC	0.153	1 M KOH	13	29	This
Ru						work
CoOx@CN	GC	0.42	1 М КОН	232	115	1
Co/Co <sub>3</sub> O <sub>4</sub>	NF	0.85	1 M KOH	90	44	2
Ru/C <sub>3</sub> N <sub>4</sub> /C	GC	0.204	0.1 M KOH	79	/	3
MoP@RGO	GC	0.28	1 М КОН	93 (η <sub>20</sub> )	58	4
Zn <sub>0.3</sub> Co <sub>2.7</sub> S <sub>4</sub>	GC	0.285	1 М КОН	85	/	5
Co <sub>2</sub> P@NPG	GC	0.5	1 М КОН	165	96	6
Mo <sub>1</sub> N <sub>1</sub> C <sub>2</sub>	GC	0.408	0.1 M KOH	132	90	7
FePO <sub>4</sub> /NF	NF	0.285	1 M KOH	123	104.49	8
FeSe <sub>2</sub>	NF/FTO	3/1	1 M KOH	178/235	/	9
CoP NWs	CC	N/A	1 M KOH	146 (ŋ <sub>100</sub> )	42.8	10
40s/CC						
Mo <sub>2</sub> N-	GC	0.337	1 M KOH	154	68	11
Mo <sub>2</sub> C/HGr-3						
$MoB/g-C_3N_4$	GC	0.25	1 M KOH	133	46	12
RuP <sub>2</sub> @NPC	GC	1.0	1 M KOH	52	69	13
RuCo@NC	GC	0.275	1 M KOH	28	31	14
Ru@C <sub>2</sub> N	GC	0.285	1 M KOH	17	38	15
CoP/rGO-400	GC	0.28	1 M KOH	150	38	16
MoCx nano	GC	0.8	1 M KOH	151	59	17
octahedrons						
IrCo@NC-500	GC	0.285	1 M KOH	45	80	18
RuCoP	CNF	0.3	1 M KOH	23 mV	37	19

Note: GC stands for glassy carbon. NF stands for nickel foam; FTO stands for fluorine-doped tin oxide. CC stands for carbon cloth. CNF stands for carbon nanofiber. "/": the data was not given.

## **Supplementary References**

- Jin, H. et.al. In situ Cobalt-Cobalt Oxide/N-Doped Carbon Hybrids As Superior Bifunctional Electrocatalysts for Hydrogen and Oxygen Evolution. J. Am. Chem. Soc. 137, 2688-2694 (2015).
- Yan, X., Tian, L., He, M. & Chen, X. Three-Dimensional Crystalline/Amorphous Co/Co3O4 Core/Shell Nanosheets as Efficient Electrocatalysts for the Hydrogen Evolution Reaction. *Nano Lett.* 15, 6015-6021 (2015).
- 3. Zheng, Y. et.al. High Electrocatalytic Hydrogen Evolution Activity of an Anomalous Ruthenium Catalyst. *J. Am. Chem. Soc.* **138**, 16174-16181 (2016).
- 4. Zhang, G. et.al. Highly Active and Stable Catalysts of Phytic Acid-Derivative Transition Metal Phosphides for Full Water Splitting. *J. Am. Chem. Soc.* **138**, 14686-14693 (2016).
- Huang, Z. et.al. Hollow Cobalt-Based Bimetallic Sulfide Polyhedra for Efficient All-pHValue Electrochemical and Photocatalytic Hydrogen Evolution. J. Am. Chem. Soc. 138, 1359-1365 (2016).
- 6. Zhuang, M. et.al. Polymer-Embedded Fabrication of Co<sub>2</sub>P Nanoparticles Encapsulated in N,P-Doped Graphene for Hydrogen Generation. *Nano Lett.* **16**, 4691-4698 (2016).
- 7. Chen, W. et al. Rational Design of Single Molybdenum Atoms Anchored on N-Doped Carbon for Effective Hydrogen Evolution Reaction. *Angew. Chem. Int. Ed.* **129**, 16302-16306 (2017).
- Yang, L. et al. Vertical Growth of 2D Amorphous FePO<sub>4</sub> Nanosheet on Ni Foam: Outer and Inner Structural Design for Superior Water Splitting. *Adv. Mater.* 29, 1704574-1704582 (2017).
- 9. Panda, C. et al. From a Molecular 2Fe-2Se Precursor to a Highly Efficient Iron Diselenide Electrocatalyst for Overall Water Splitting. *Angew. Chem. Int. Ed.* **56**, 10506-10510 (2017).
- Xu, K. et al. Controllable Surface Reorganization Engineering on Cobalt Phosphide Nanowire Arrays for Efficient Alkaline Hydrogen Evolution Reaction *Adv. Mater.* **30**, 1703322-1703327 (2017).
- 11. Yan, H. Holey Reduced Graphene Oxide Coupled with an Mo<sub>2</sub>N-Mo<sub>2</sub>C Heterojunction for Efficient Hydrogen Evolution *Adv. Mater.* **30**, 1704156-1704163 (2018).
- Zhuang, Z. et al. MoB/g-C<sub>3</sub>N<sub>4</sub> Interface Materials as a Schottky Catalyst to Boost Hydrogen Evolution. *Angew. Chem. Int. Ed.* 57, 496-500 (2018).
- Pu, Z. et al. RuP<sub>2</sub>-Based Catalysts with Platinum-like Activity and Higher Durability for the Hydrogen Evolution Reaction at All pH Values *Angew. Chem. Int. Ed.* 56, 11559-11564 (2017).
- Su, J. et al. Ruthenium-cobalt nanoalloys encapsulated in nitrogen-doped graphene as active electrocatalysts for producing hydrogen in alkaline media. *Nat. Commun.* 8, 14969-14978 (2017).
- 15. Mahmood, J. et al. An efficient and pH-universal ruthenium-based catalyst for the hydrogen evolution reaction. *Nat. Nanotechnol.* **12**, 441-446 (2017).
- Jiao, L., Zhou, Y. & Jiang, H. Metal-organic framework-based CoP/reduced graphene oxide: high-performance bifunctional electrocatalyst for overall water splitting. *Chem. Sci.*, 7, 1690-1695 (2016).
- 17. Wu, H. et al. Porous molybdenum carbide nano-octahedrons synthesized via confined carburization in metal-organic frameworks for efficient hydrogen production. *Nat. Commun.*

**6,** 6512-6519 (2015).

- Jiang, P. et al. Tuning the Activity of Carbon for Electrocatalytic Hydrogen Evolution via an Iridium-Cobalt Alloy Core Encapsulated in Nitrogen-Doped Carbon Cages. *Adv. Mater.* 30, 1705324-1705334 (2018).
- 19. Xu, J. et al. Boosting the hydrogen evolution performance of ruthenium clusters through synergistic coupling with cobalt phosphide. *Energy Environ. Sci.* **11**, 1819-1827 (2018).