# **Supporting information**

Step by step strategy to design active and stable quaternary intermetallic compounds for hydrogen evolution reaction

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## **EXPERIMENTAL SECTION**

#### **Chemical Reagents**

The chemical reagents for material synthesis and electrochemical measurement were acquired from Aladdin Chemical Company and Ming-Ling Chemical Company that include tantalum power (99.99 %), cobalt sheet (99.8 %), nickel power (99.5 %), copper power (99.9 %), ruthenium power (99.95 %), polyvinyl butyral (99.9 %) and KOH (ACS grade). Sulfuric acid (98 %) and ethanol absolute (99.7 %) were obtained from Sinopharm Chemical Reagent Co., Ltd. and Yonghua Chemical Co., Ltd., respectively.

### Synthesis

Arc-melting technique and solid-state synthesis were applied to prepare multinary intermetallic compounds,  $TaCo_2$ ,  $TaCu_{0.25}Co_{1.75}$ ,  $TaCu_{0.125}Ru_{0.125}Co_{1.75}$  and to fabricate these samples into electrodes. The following procedures describe the details of synthetic steps for pristine materials and the process to disperse these materials on carbon cloth as working electrode.

**Preparation of pristine TaCo<sub>2</sub>, TaCu<sub>0.25</sub>Co<sub>1.75</sub>, TaCu<sub>0.125</sub>Ru<sub>0.125</sub>Co<sub>1.75</sub>: total mass of ca. 800 mg of metal powder was weighed according to the stoichiometric ratio of the nominal chemical composition for TaCo<sub>2</sub>, TaCu<sub>0.25</sub>Co<sub>1.75</sub>, TaCu<sub>0.125</sub>Ru<sub>0.125</sub>Co<sub>1.75</sub>. These metals powders were mixed homogenous with mortar and pestle. The mixture was then pressed into pellet with a diameter of 8 mm at a pressure of 20 MPa. The pellet was placed on the copper substrate in an arc-melting furnace. To avoid oxidation of the material, the furnace chamber was repeatedly vacuumed and refilled with argon gas (99.999 %) three times. An electric arc (21.5 V, 50 A) was applied to melt the pellet into a silvery shiny ball. This silver shinny ball was turned overed and remelted it to ensure the homogeneity. After repeated three times of this melting process, the metallic ball was transferred to an argon-filled glovebox and grounded into fine powder before further characterization and electrochemical measurement.** 

**Preparation of working electrode:** the particle size of as-synthesized TaCo<sub>2</sub>, TaCu<sub>0.25</sub>Co<sub>1.75</sub>, TaCu<sub>0.125</sub>Ru<sub>0.125</sub>Co<sub>1.75</sub> samples were reduced by using ball-milling process with 600 r.p.m for 3 hours (denoted TaCo<sub>2</sub>/ball, TaCu<sub>0.25</sub>Co<sub>1.75</sub>/ball, TaCu<sub>0.125</sub>Ru<sub>0.125</sub>Co<sub>1.75</sub>/ball hereafter). Around 0.785 g of polyvinyl butyral (PVB) was dissolved in 10 mL of ethanol absolute to form a transparent binder solution. Consequently, ca. 50 mg of the ball-milled fine powder and 0.2 mL of binder solution were mixed to form a suspension paste. Carbon cloth (CC) as current collector was covered with the paste on the surface (10 mm × 5 mm) by using pipette. After vacuum drying for 12 hours,

TaCo<sub>2</sub>/ball/CC, TaCu<sub>0.25</sub>Co<sub>1.75</sub>/ball/CC and TaCu<sub>0.125</sub>Ru<sub>0.125</sub>Co<sub>1.75</sub>/ball/CC films were obtained. In order to improve the bonding strength between particles, the as-prepared film was enclosed in a quartz tube (vacuum pumping below 0.1 torr) with flame sealing and heated at high temperature. The sealed ampoule was placed in a muffle furnace and heating from room temperature to 500 °C in 8 hours, kept at 500 °C for 0.5 hours, then heating to 800 °C in 5 hours, kept at 800 °C for 4 hours, then cooling down to 500 °C in 5 hours. Finally, it was cooled down to room temperature in the muffle furnace naturally by turning off the power of the furnace. The quartz tube was cutting open carefully to retrieve the electrode films and rinsed with absolute ethanol and deionized water three times. These films were vacuum-died for 12 hours and used as working electrode for later electrochemical testing.

#### Characterization

The crystal structure, phase purity and chemical composition of the asprepared materials and working electrode were characterized by using Bruker D8 ADVANCE, X-ray powder diffractometer (XRD, Cu k<sub>a1</sub>: 1.54056 Å), with 2 $\theta$ ranging from 20° to 60° (scan rate: 5 °/min). Zeiss Supra55, a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray detector (EDX, accelerating voltage: 30 keV) was used to observe the morphology, particle size and chemical composition of the materials. Thermo Scientific ESCALAB 250 Xi, X-ray photoelectron spectroscopy (XPS) was used to analyze the valence states of corresponding elements in the as-prepared materials.

#### **Electrochemical measurement**

The electrochemical measurements were carried out in 1.0 M KOH (ca. 40 ml) and 0.5 M H<sub>2</sub>SO<sub>4</sub> (ca. 40 ml) with using commercial electrochemical workstation from Jiangsu Donghua Analytical Instrument Co., Ltd (model: DH7006). In order to understand the influence of ball-milling process and sintering treatment, there are total three kinds of test subjects prepared for electrochemical measurements. The first two are TaCo<sub>2</sub>, TaCu<sub>0.25</sub>Co<sub>1.75</sub>, and TaCu<sub>0.125</sub>Ru<sub>0.125</sub>Co<sub>1.75</sub> samples before and after ball-milling process. Without any additives (e.g., binder), these samples were pressed into pellets (8 mm diameter) and test their electrochemical behaviors of HER directly. In this way, one can investigate the impact of particle size to their HER performance. The third kind of samples are the electrode films, TaCo<sub>2</sub>/ball/CC, TaCu<sub>0.25</sub>Co<sub>1.75</sub>/ball/CC, and TaCu<sub>0.125</sub>Ru<sub>0.125</sub>Co<sub>1.75</sub>/ball/CC (i.e., powder after ball-milling and use carbon cloth as support). These electrode films were used as working electrode. Saturated calomel electrode and graphite rod were used as the reference electrode and counter electrode, respectively. The potentials were converted to the reversible hydrogen electrode (RHE) potential, and

compensated for a 90% of ohmic potential drop (R<sub>u</sub>).

E<sub>RHE</sub> = E<sub>ref</sub>+0.05916×pH-0.9\*i\*R<sub>u</sub>

To reveal the intrinsic HER activity of these multinary intermetallic compounds, their roughness factor (RF) and electrochemical active surface area (ECSA) calculated from cyclic voltammetry at different scanning rates (10 - 50 mV/s) to eliminate the influence of electrode surface area (i.e., extrinsic property). The potential range was set from -0.2 to -0.15 V and from -1.05 to - 1.0 V (V vs. SCE) for 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1.0 M KOH, respectively.

#### **Theoretical Calculation**

In order to understand the intrinsic HER activity of these multinary intermetallic compounds, the adsorption energies of H<sup>\*</sup> ( $\Delta G_{Had}$ ) on the surface of TaCo<sub>2</sub> (binary), TaCu<sub>0.25</sub>Co<sub>1.75</sub> (ternary) and TaCu<sub>0.125</sub>Ru<sub>0.125</sub>Co<sub>1.75</sub> (quaternary) were calculated using the atomic simulation environment (ASE) software package equipped with a GPAW calculator. The revised Perdew-Burke-Ernzerhof (RPBE) functional was used to calculate exchange-correlation energy in the system. The model was set to a (001) slab with six atomic layers, and a vacuum spacing of 15 Å was placed between each slab. Various models for the inclusion of Cu and Ru atoms were calculated and the one with the lowest total energy (i.e., the most stable) was selected as model for TaCu<sub>0.25</sub>Co<sub>1.75</sub> and TaCu<sub>0.125</sub>Ru<sub>0.125</sub>Co<sub>1.75</sub> to calculate corresponding  $\Delta G_{Had}$ . During structural optimization, the bottom three layers were fixed, and the top three layers and adsorbed hydrogen atoms were relaxed. The condition for determining the final structure was that the maximum force was less than 0.05 eV Å<sup>-1</sup>. Zero-point energy and entropy contribution of adsorbed hydrogen were calculated in order to convert electron energy into free energy ( $\Delta G = \Delta E + \Delta Z P E$ - TΔS).[1, 2]

To reveal the influence of bonding scheme to HER activity for these multinary intermetallic compounds especially when one incorporates Cu and Ru element. The crystal orbital Hamiltonian populations (COHP) method was applied to evaluate the bonding strength and bonding character of interatomic interactions in these transition metals with using Stuttgart TB-LMTO 4.7 program. [3, 4]



**Figure S1.** Experimental powder X-ray diffraction (XRD) patterns of  $TaCo_2$ ,  $TaCu_{0.25}Co_{1.75}$  and  $TaCu_{0.125}Ru_{0.125}Co_{1.75}$  with internal Si standard (asterisk sign) for calibration.



**Figure S2.** SEM image (top) and EDS spectrum (bottom) of  $TaCo_2$ ,  $TaCu_{0.25}Co_{1.75}$  and  $TaCu_{0.125}Ru_{0.125}Co_{1.75}$ . The atomic ratio between Ta, Cu, Ru and Co for each sample derived from EDX analysis is tabulated in Table S1.



Figure S3. SEM image of  $TaCo_2$ ,  $TaCu_{0.25}Co_{1.75}$  and  $TaCu_{0.125}Ru_{0.125}Co_{1.75}$  after ball-milling process.



**Figure S4.** Cyclic voltammograms (CV) and linear regression slope derived from CV of (a)  $TaCo_2$  (b)  $TaCu_{0.25}Co_{1.75}$  (c)  $TaCu_{0.125}Ru_{0.125}Co_{1.75}$  (d)  $TaCo_2$ /ball (e)  $TaCu_{0.25}Co_{1.75}$ /ball (f)  $TaCu_{0.125}Ru_{0.125}Co_{1.75}$ /ball (g)  $TaCo_2$ /ball/CC (h)  $TaCu_{0.25}Co_{1.75}$ /ball/CC (i)  $TaCu_{0.125}Ru_{0.125}Co_{1.75}$ /ball/CC in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Capacitive current density as a function of scan rate (10 – 50 mV/s).



**Figure S5.** Cyclic voltammograms (CV) and linear regression slope derived from CV of (a)  $TaCo_2$  (b)  $TaCu_{0.25}Co_{1.75}$  (c)  $TaCu_{0.125}Ru_{0.125}Co_{1.75}$  (d)  $TaCo_2$ /ball (e)  $TaCu_{0.25}Co_{1.75}$ /ball (f)  $TaCu_{0.125}Ru_{0.125}Co_{1.75}$ /ball (g)  $TaCo_2$ /ball/CC (h)  $TaCu_{0.25}Co_{1.75}$ /ball/CC (i)  $TaCu_{0.125}Ru_{0.125}Co_{1.75}$ /ball/CC in 1.0 M KOH. Capacitive current density as a function of scan rate (10 – 50 mV/s).



**Figure S6.** Normalized linear sweep voltammogram (LSV) based on the RF and Tafel slope of (a)  $TaCo_2$ ,  $TaCu_{0.25}Co_{1.75}$  and  $TaCu_{0.125}Ru_{0.125}Co_{1.75}$  (b)  $TaCo_2$ /ball,  $TaCu_{0.25}Co_{1.75}$ /ball and  $TaCu_{0.125}Ru_{0.125}Co_{1.75}$ /ball (c)  $TaCo_2$ /ball/CC,  $TaCu_{0.25}Co_{1.75}$ /ball/CC and  $TaCu_{0.125}Ru_{0.125}Co_{1.75}$ /ball/CC in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



**Figure S7.** Normalized linear sweep voltammogram (LSV) based on the RF and Tafel slope of (a)  $TaCo_2$ ,  $TaCu_{0.25}Co_{1.75}$  and  $TaCu_{0.125}Ru_{0.125}Co_{1.75}$  (b)  $TaCo_2$ /ball,  $TaCu_{0.25}Co_{1.75}$ /ball and  $TaCu_{0.125}Ru_{0.125}Co_{1.75}$ /ball (c)  $TaCo_2$ /ball/CC,  $TaCu_{0.25}Co_{1.75}$ /ball/CC and  $TaCu_{0.125}Ru_{0.125}Co_{1.75}$ /ball/CC in 1.0 M KOH.



**Figure S8.** Linear sweep voltammogram (LSV) for the hydrogen evolution reaction (HER) of  $TaCo_2/ball/CC$ ,  $TaCu_{0.25}Co_{1.75}/ball/CC$  and  $TaCu_{0.125}Ru_{0.125}Co_{1.75}/ball/CC$  in (a) acid (0.5 M H<sub>2</sub>SO<sub>4</sub>) and (b) alkaline electrolyte (1.0 M KOH).



**Figure S9.** Comparison of the overpotentials at 10 mA/cm<sup>2</sup> with recently reported catalysts in (a) acid (0.5 M H<sub>2</sub>SO<sub>4</sub>) and (b) alkaline electrolyte (1.0 M KOH). The corresponding values of overpotential ( $\eta_{10}$ ), Tafel slope and relevant references for these reported samples were tabulated in Table S5 and S6, respectively.



Figure S10. Examining the OH poison effect on the surface of  $TaCu_{0.125}Ru_{0.125}Co_{1.75}$ .

Table S1. Element analysis of TaCo2, TaCu0.25Co1.75 and			
TaCu <sub>0.125</sub> Ru <sub>0.125</sub> Co <sub>1.75.</sub>			
Sample Element Atomic ratio (%			
TaCa	Та	33.03	
	Со	67.97	
TaCu <sub>0.25</sub> Co <sub>1.75</sub>	Та	33.27	
	Cu	10.03	
	Со	56.70	
TaCu <sub>0.125</sub> Ru <sub>0.125</sub> Co <sub>1.75</sub>	Та	31.60	
	Cu	2.53	
	Ru	2.90	
	Со	62.97	

Table S2. Refined lattice constants (Å) and Co-Co bond distances of TaCo <sub>2</sub> ,					
TaCu <sub>0.25</sub> Co <sub>1.75</sub> and TaCu <sub>0.125</sub> Ru <sub>0.125</sub> Co <sub>1.75</sub> .					
Sample a=b=c d <sub>Co-Co</sub>					
TaCo <sub>2</sub> 6.7878(0.005) 2.400					
TaCu <sub>0.25</sub> Co <sub>1.75</sub>	TaCu <sub>0.25</sub> Co <sub>1.75</sub> 6.8023(0.006)      2.405				
TaCu <sub>0.125</sub> Ru <sub>0.125</sub> Co <sub>1.75</sub>	6.8249(0.006)	2.413			

Table S3. Overpotential ( $\eta_{10}$ , mV), roughness factor (RF) and Tafel slope					
(mV•decade <sup>-1</sup> ) of TaCo <sub>2</sub> , TaCu <sub>0.25</sub> Co <sub>1.75</sub> and TaCu <sub>0.125</sub> Ru <sub>0.125</sub> Co <sub>1.75</sub> for					
hydrogen evolution reaction (HER) in 0.5 M H <sub>2</sub> SO <sub>4</sub> .					
Sample	Sample η <sub>10</sub> (mV) RF Tafel(mV/dec)				
TaCo <sub>2</sub> 223 153 104					
TaCu <sub>0.25</sub> Co <sub>1.75</sub> 254 106.75 107					
TaCu <sub>0.125</sub> Ru <sub>0.125</sub> Co <sub>1.75</sub>	103	168.5	95		
TaCo <sub>2</sub> /ball 138 481.5 86					

TaCu <sub>0.25</sub> Co <sub>1.75</sub> /ball	159	345.75	91
TaCu <sub>0.125</sub> Ru <sub>0.125</sub> Co <sub>1.75</sub> /ball	72	672.5	52
TaCo <sub>2</sub> /ball/CC	170	793.75	69
TaCu <sub>0.25</sub> Co <sub>1.75</sub> /ball/CC	106	2419	74
TaCu <sub>0.125</sub> Ru <sub>0.125</sub> Co <sub>1.75</sub> /ball/CC	35	2248.75	34

**Table S4.** Overpotential ( $\eta_{10}$ , mV), roughness factor (RF) and Tafel slope (mV•decade<sup>-1</sup>) of TaCo<sub>2</sub>, TaCu<sub>0.25</sub>Co<sub>1.75</sub> and TaCu<sub>0.125</sub>Ru<sub>0.125</sub>Co<sub>1.75</sub> for hydrogen evolution reaction (HER) in 1.0 M KOH.

Sample	η <sub>10</sub> (mV)	RF	Tafel (mV/dec)
TaCo <sub>2</sub>	159	317.25	97
TaCu <sub>0.25</sub> Co <sub>1.75</sub>	230	159.5	100
TaCu <sub>0.125</sub> Ru <sub>0.125</sub> Co <sub>1.75</sub>	77	139.5	47
TaCo <sub>2</sub> /ball	105	667.75	78
TaCu <sub>0.25</sub> Co <sub>1.75</sub> /ball	140	849.75	114
TaCu <sub>0.125</sub> Ru <sub>0.125</sub> Co <sub>1.75</sub> /ball	52	969.5	44
TaCo <sub>2</sub> /ball/CC	146	780.5	81
TaCu <sub>0.25</sub> Co <sub>1.75</sub> /ball/CC	123	1860.75	87
TaCu <sub>0.125</sub> Ru <sub>0.125</sub> Co <sub>1.75</sub> /ball/CC	46	1158.5	32

<b>Table S5.</b> Comparison of the overpotentials ( $\eta_{10}$ ) and Tafel slope at 10 mA			
cm <sup>-2</sup> with other reported electrocatalysts in 0.5 M H <sub>2</sub> SO <sub>4</sub> .			
Sample	η <sub>10</sub> (mV)	Tafel (mV/dec)	Reference
TaCo <sub>2</sub>	223	104	This work
TaCu <sub>0.25</sub> Co <sub>1.75</sub>	254	107	This work
TaCu <sub>0.125</sub> Ru <sub>0.125</sub> Co <sub>1.75</sub>	103	95	This work
TaCo <sub>2</sub> /ball	138	86	This work
TaCu <sub>0.25</sub> Co <sub>1.75</sub> /ball	159	91	This work
TaCu <sub>0.125</sub> Ru <sub>0.125</sub> Co <sub>1.75</sub> /ball	72	52	This work
TaCo <sub>2</sub> /ball/CC	170	69	This work
TaCu <sub>0.25</sub> Co <sub>1.75</sub> /ball/CC	106	74	This work
TaCu <sub>0.125</sub> Ru <sub>0.125</sub> Co <sub>1.75</sub> /ball/CC	35	34	This work
Co-N-Ni <sub>9</sub> S <sub>8</sub> /Nb <sub>2</sub> O <sub>5</sub>	171	89	[5]
Cu <sub>sub</sub> @MoS <sub>2</sub>	160	86	[6]
Co-MoS <sub>2</sub>	155	80	[7]
C+MoS <sub>2</sub> @Si	120	41	[8]
Pt <sub>1%</sub> –CoMoS <sub>2</sub> /C	118	68	[9]
Ni-GF/VC	111	86	[10]
NiCo <sub>2</sub> P <sub>x</sub>	104	59.6	[11]
C <sub>ia</sub> -MoS <sub>2</sub>	87	45	[12]

NPNi-MoS <sub>2</sub> /RGO	85	71.3	[13]
Ni-ReSe <sub>2</sub>	82	54	[14]
RuTe <sub>2</sub> /Gr	72	32	[15]
NFP/C-3	72	54	[16]
CoP/CC	67	/	[17]
Mo@NMCNFs	66	48.9	[18]
MoO <sub>2</sub> -Ni@NC	58	35.1	[19]
Ru <sub>2</sub> P	55	34	[20]
Ni <sub>0.89</sub> Co <sub>0.11</sub> Se <sub>2</sub> MNSN/NF	52	39	[21]
Co-SAC/RuO <sub>2</sub>	45	58	[22]

<b>Table S6.</b> Comparison of the overpotentials ( $\eta_{10}$ ) and tafel slope at 10 mA cm <sup>-2</sup> with other reported electrocatalysts in 1.0 M KOH.				
Tafel				
Sample	η <sub>10</sub> (mV)	(mV/dec)		
TaCo <sub>2</sub>	159	97	This work	
TaCu <sub>0.25</sub> Co <sub>1.75</sub>	230	100	This work	
TaCu <sub>0.125</sub> Ru <sub>0.125</sub> Co <sub>1.75</sub>	77	47	This work	
TaCo <sub>2</sub> /ball	105	78	This work	
TaCu <sub>0.25</sub> Co <sub>1.75</sub> /ball	140	114	This work	
TaCu <sub>0.125</sub> Ru <sub>0.125</sub> Co <sub>1.75</sub> /ball	52	44	This work	
TaCo <sub>2</sub> /ball/CC	146	81	This work	
TaCu <sub>0.25</sub> Co <sub>1.75</sub> /ball/CC	123	87	This work	
TaCu <sub>0.125</sub> Ru <sub>0.125</sub> Co <sub>1.75</sub> /ball/CC	46	32	This work	
CoP/CC	209	/	[17]	
Ni/NC-0.35	133	109	[23]	
Ni-GF/VC	128	80	[10]	
α-MoC-5h	126	67	[24]	
Fe(OH) <sub>x</sub> @Cu-MOF	112	76	[25]	
Ni-ReSe <sub>2</sub>	109	81	[14]	
Cu-N-Ni <sub>9</sub> S <sub>8</sub> /Nb <sub>2</sub> O <sub>5</sub>	109	51	[5]	
Ni-SA/NC	102	120	[26]	
NFP/C-3	95	72	[16]	
Ni <sub>0.89</sub> Co <sub>0.11</sub> Se <sub>2</sub> MNSN/NF	85	52	[21]	
Ni-N <sub>2+2</sub> -S	83	100.5	[27]	
Co-MoS <sub>2</sub>	67	67	[7]	
Co <sub>0.6</sub> (VMnNiZn) <sub>0.4</sub> PS <sub>3</sub>	65.9	65.5	[28]	
NiCo2P <sub>x</sub>	58	34.3	[11]	
c-Ni@a-Ni(OH) <sub>2</sub>	57	44.8	[29]	
Co/NiCoP-350 NPs	54	84	[30]	
Ru <sub>2</sub> P	54	29	[20]	
W-ACs	53	38	[31]	

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