Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information

Engineering heterometallic bonding in bimetallic electrocatalysts: towards optimized hydrogen oxidation and evolution reactions

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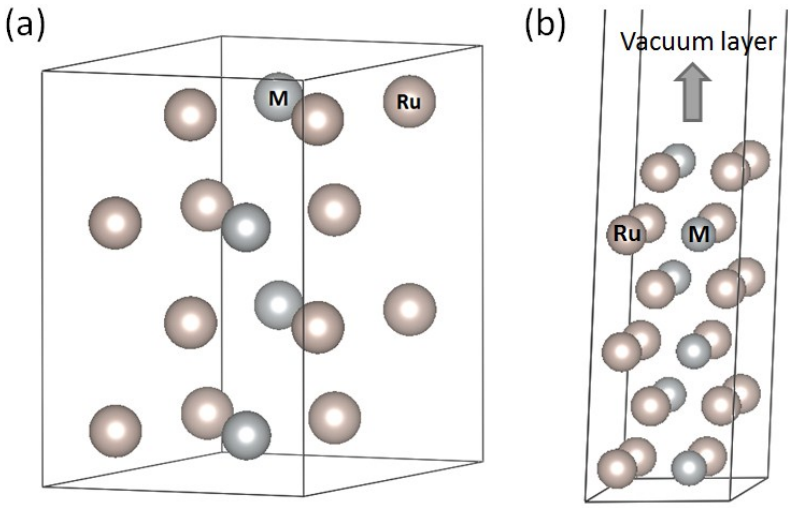

Figure S1. (a) Extended HCP-Ru_3-M_1 bulk model and (b) Ru_3-M_1 (0001) surface model, where Ru and M atoms are indicated.

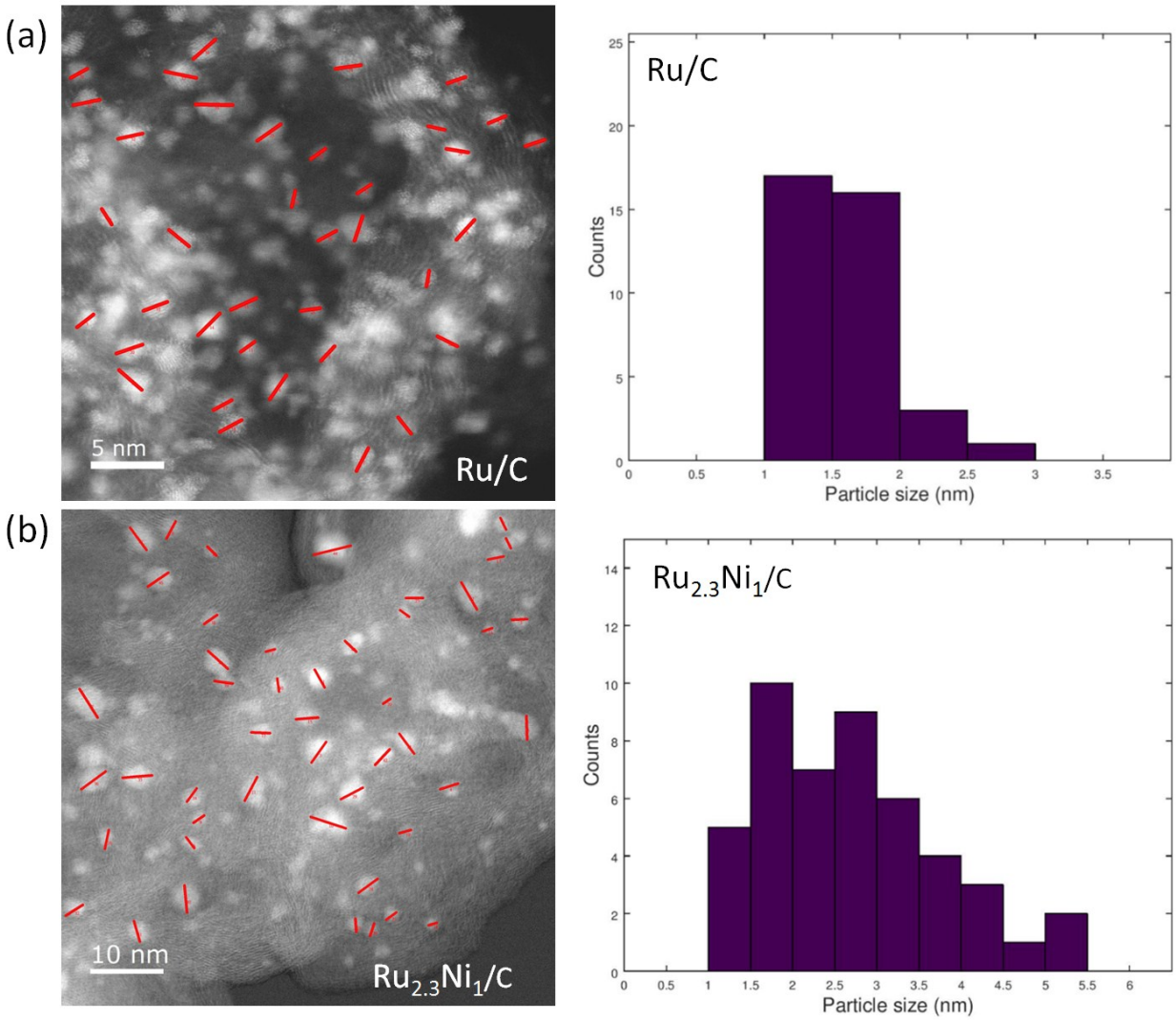

Figure S2. STEM images of: (a) Ru/C and (b) $Ru_{2.3}Ni_1/C$ and the corresponding particle size distribution.

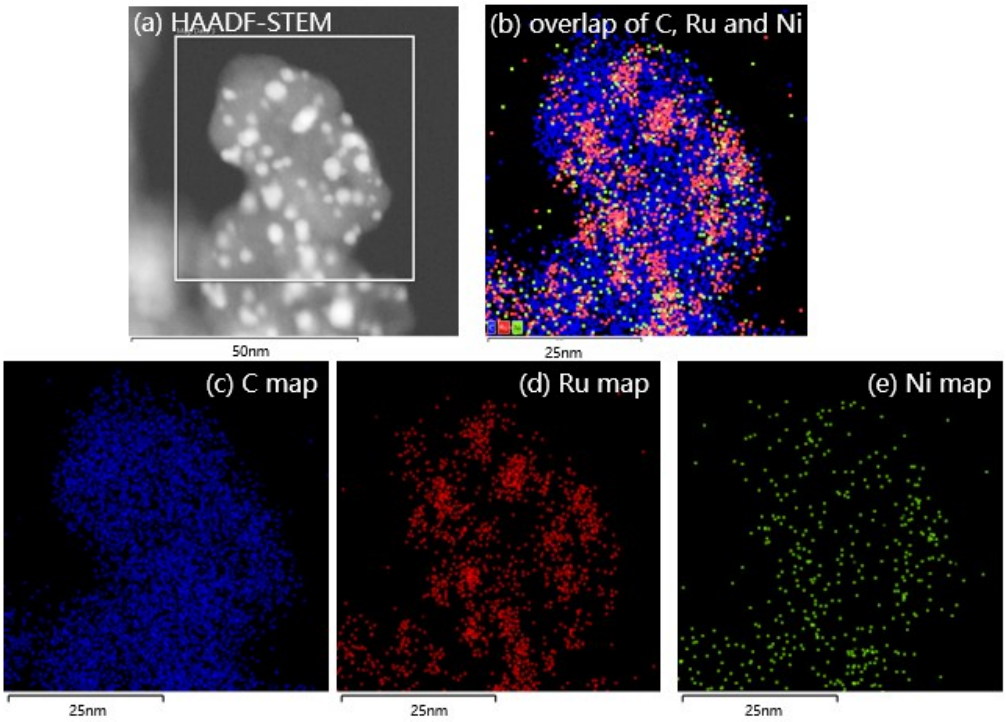

Figure S3. STEM-EDS elemental maps of the $Ru_{2.3}Ni_1$/C catalyst. (a) HAADF-STEM image, (b) overlap of C, Ru and Ni elemental map signals, (c) C elemental map signals, (d) Ru elemental map signals, and (e) Ni elemental map signals.

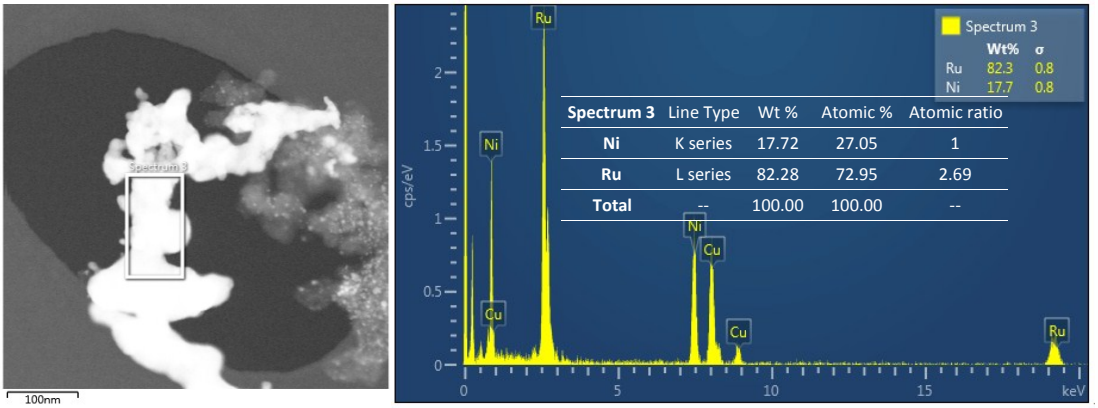

Figure S4 (a) STEM image and (b) EDS analysis of synthesized RuNi NPs.

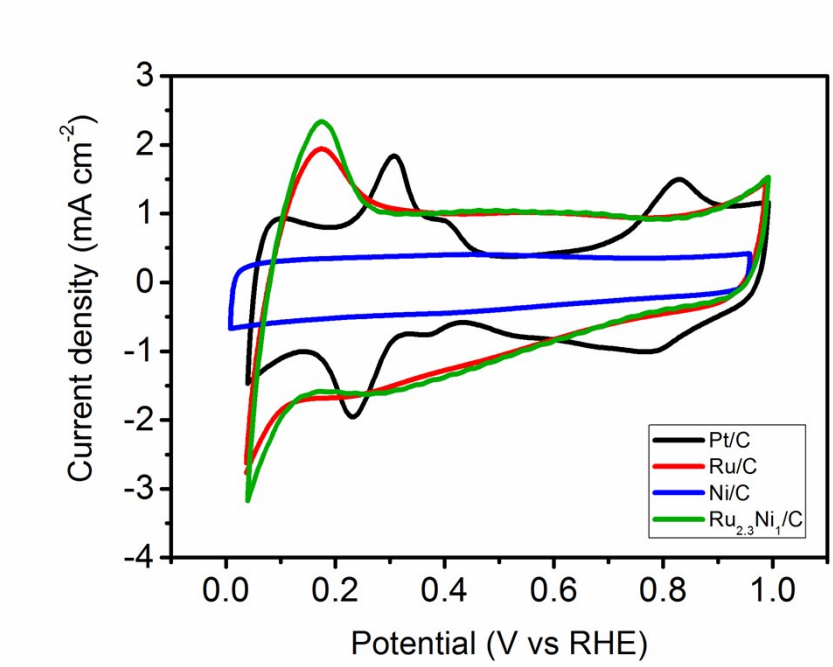

Figure S5 Cyclic voltammetric curve of Pt/C, Ru/C, Ni/C and $Ru_{2.3}Ni_1/C$ in Ar-saturated 0.1 M KOH at 50 mV s^{-1}.

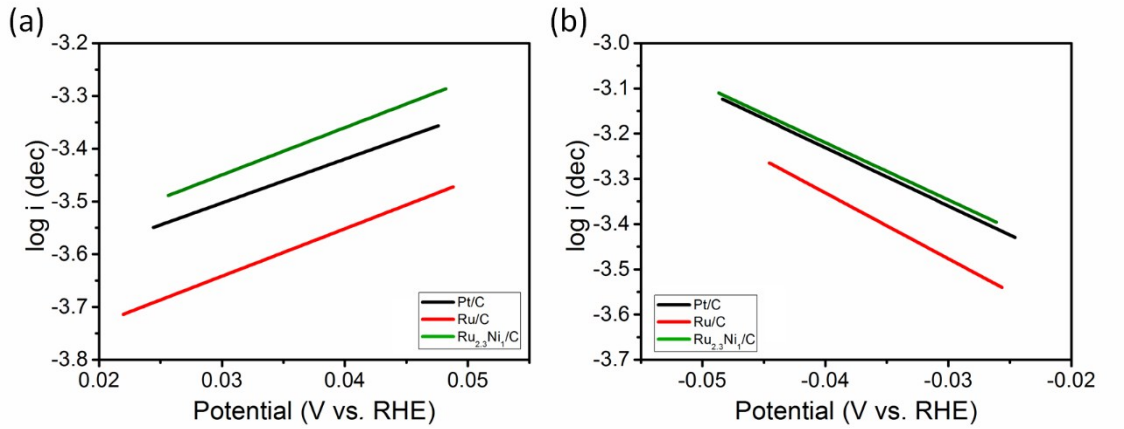

Figure S6. Tafel plots of Pt/C, Ru/C and $Ru_{2.3}Ni_1/C$ in alkaline (a) HOR and (b) HER.

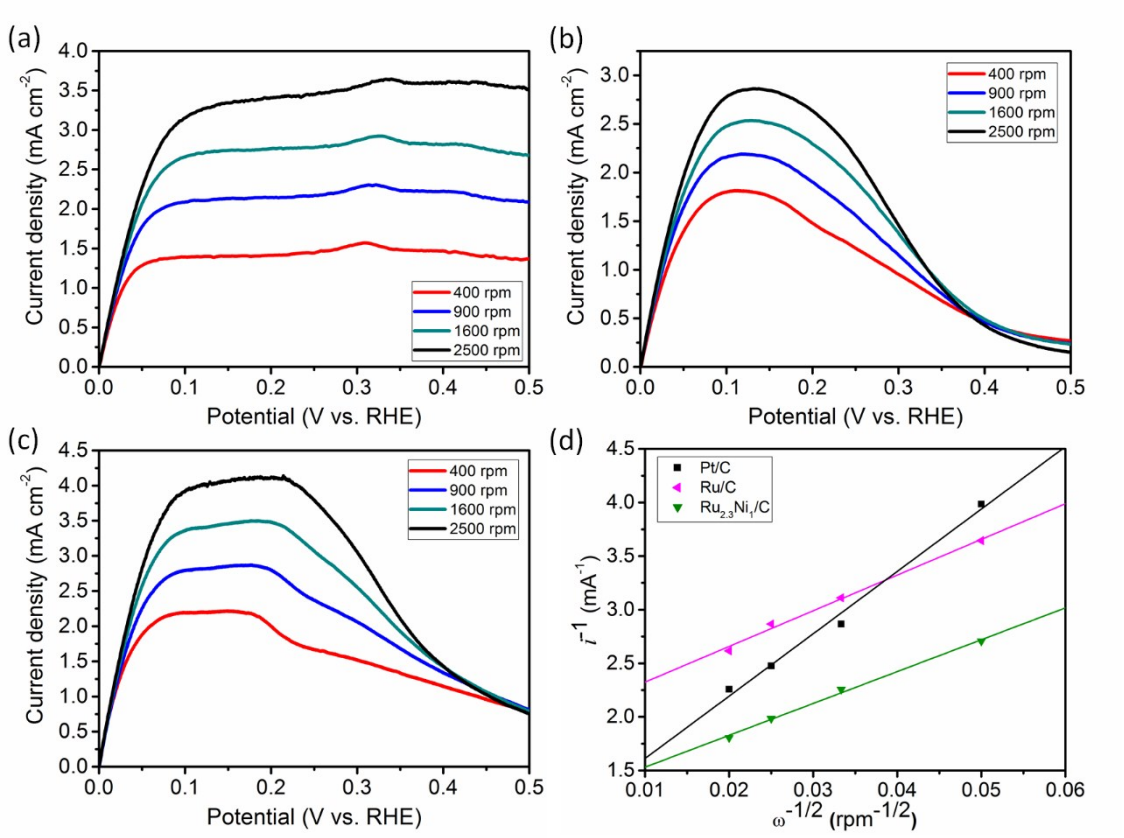

Figure S7. Rotating-disk voltammograms of: (a) Pt/C, (b) Ru/C and (c) $Ru_{2.3}Ni_1/C$ in H_2-saturated 0.1 M KOH at 10 mV s^{-1}. (d) Koutechy-Levich plots of the different catalysts.

Table S1. Tafel slope and exchange current density of Pt/C, Ru/C and $Ru_{2.3}Ni_1/C$ in alkaline HOR and HER.

Catalysts	Tafel slope (mV/dec)		Exchange current density (mA/ cm^2_{Metal})
	HOR	HER	
Pt/C	120	78	0.046
Ru/C	111	76	0.019
$Ru_{2.3}Ni_1/C$	112	79	0.031

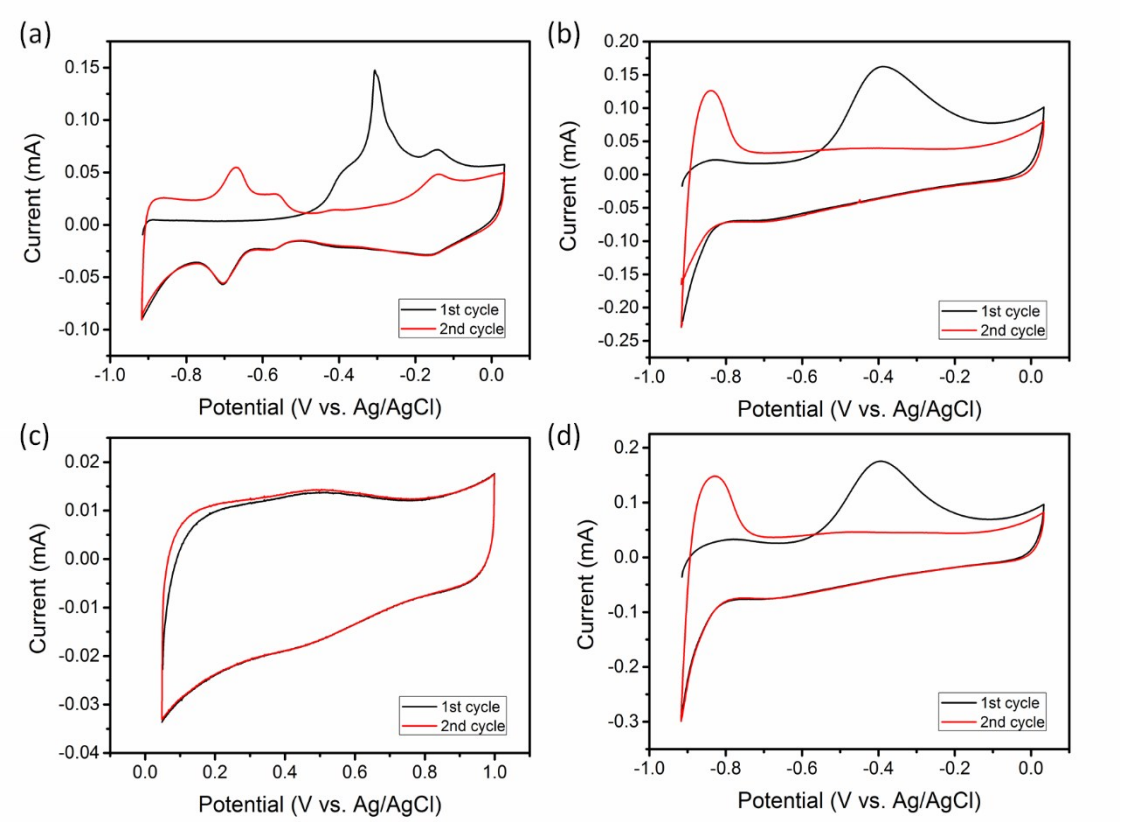

Figure S8. CO stripping voltammograms of: (a) Pt/C, (b) Ru/C, (c) Ni/C and (d) $Ru_{2.3}Ni_1/C$ in CO-saturated 0.1 M KOH at 10 mV s^{-1}.

Table S2. Electrochemical surface area (ECSA) and the specific activities (j_k) of Pt/C, Ru/C and $Ru_{2.3}Ni_1/C$.

Catalysts	ECSA[a] (m^2/g_{Metal})	j_k@0.05 V_{RHE} (mA/cm^2_{Metal})	j@-0.05 V_{RHE} (mA/cm^2_{Metal})
Pt/C	53	0.233	-0.182
Ru/C	118	0.054	-0.053
$Ru_{2.3}Ni_1/C$	103	0.100	-0.098

[a] Normalized by weight of all metals

Table S3. Catalyst loading, specific activity and mass activity for alkaline HOR and HER on the Ru-based catalysts.

Catalysts	Catal. Loading (mg_{metal} cm^{-2})	i_s (mA cm^{-2}_{metal})	i_m (mA mg^{-1})	Ref.
HOR				
Ru/C	0.01	0.047	60	1
Pt/C	0.04	0.233	56	This work
Ru/C		0.054	45	
$Ru_{2.3}Ni_1/C$		0.100	82[a]	
HER				
Pt/C	0.041	-0.095	-74	2
Ru/C	0.041	-0.099	-24	2
$Ru/C_3N_4/C$	0.048	-0.172	-78	2
Pt/C	0.04	-0.182	-96	This work
Ru/C		-0.053	-62	
$Ru_{2.3}Ni_1/C$		-0.098	-125[a]	

All the catalysts were performed in 0.1 M KOH.

[a]The mass activity is calculated based on precious metal (Ru).

Table S4. Specific activity of the RuNi nanocatalysts with the different Ru/Ni ratios in HOR and HER.

Catalysts	i_s@0.05 V_{RHE} (mA cm^{-2}_{metal})
HOR	
Pt/C	0.233
Ru/C	0.054
$Ru_{2.3}Ni_1/C$	0.100
$Ru_1Ni_{1.2}/C$	0.125
$Ru_1Ni_{2.4}/C$	0.099
HER	
Pt/C	-0.182
Ru/C	-0.053
$Ru_{2.3}Ni_1/C$	-0.098
$Ru_1Ni_{1.2}/C$	-0.126
$Ru_1Ni_{2.4}/C$	-0.098

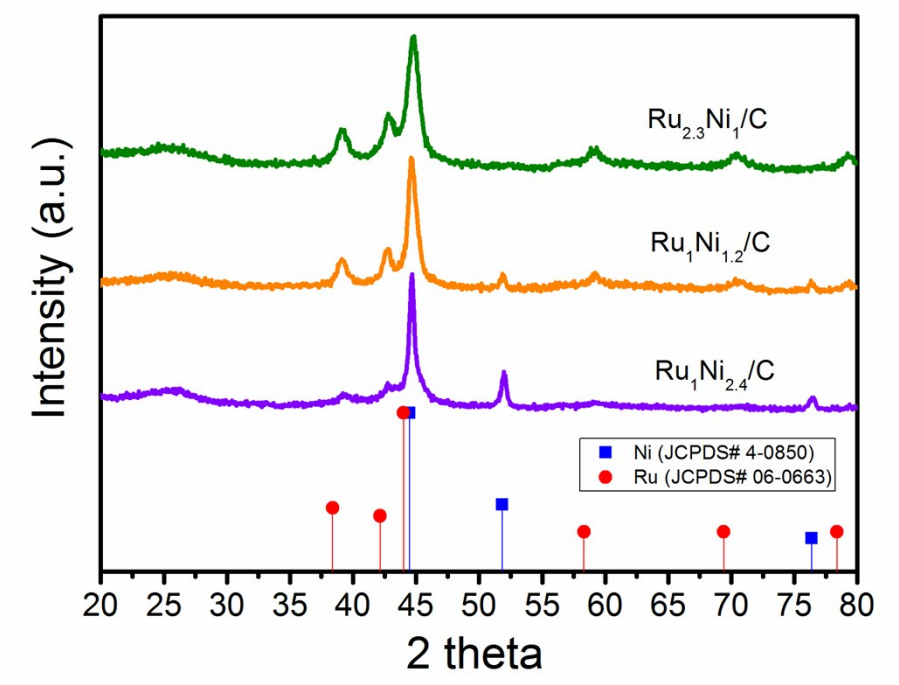

Figure S9. XRD patterns of $Ru_{2.3}Ni_1/C$, $Ru_1Ni_{1.2}/C$ and $Ru_1Ni_{2.4}/C$ nanocatalysts.

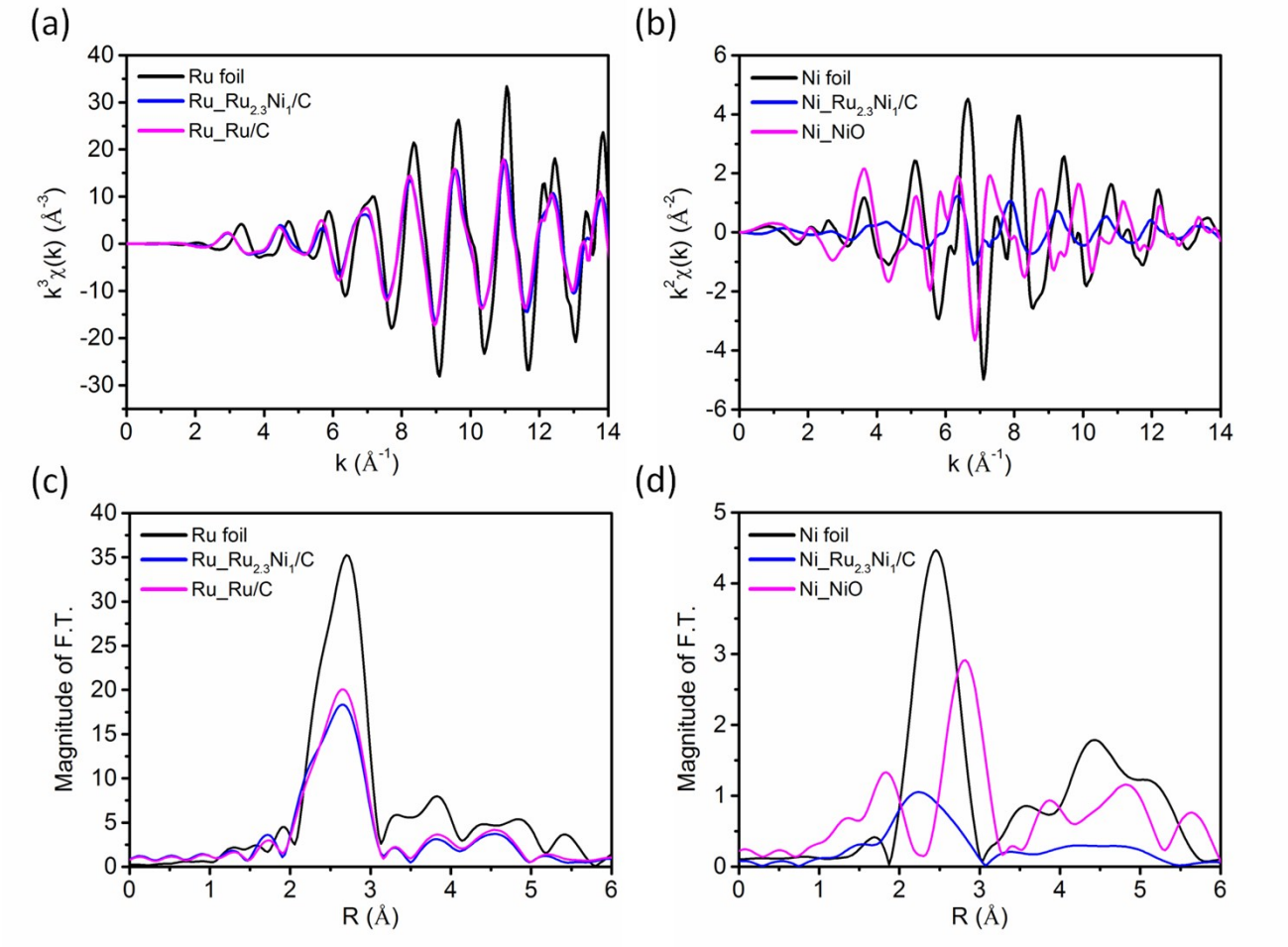

Figure S10. *k*-space and r-space of (a, c) Ru K-edge and (b, d) Ni K-edge for the $Ru_{2.3}Ni_1/C$ catalyst.

Table S5. EXAFS fitting results of $Ru_{2.3}Ni_1/C$.

Sample	Shell	N	R (Å)	ΔE_0 (eV)	σ^2(Å^2)	R-factor ($\times10^{-3}$)
Ru foil	Ru-Ru	12.0±1.20	2.68±0.01	5.59	0.004	0.9
Ni foil	Ni-Ni	12.0±0.60	2.47±0.01	6.12	0.006	0.1
$Ru_{2.3}Ni_1/C$	Ru-Ru	7.02±1.22	2.67±0.01	-4.96	0.004	1.8
	Ru-Ni	2.51±1.08	2.61±0.09		0.022	
	Ni-Ni	2.06±0.89	2.49±0.05		0.004	
	Ni-Ru	5.77±1.08	2.61±0.09		0.032	
	Ni-O	2.17±1.09	2.04±0.21		0.008	

References

(1) Ohyama, J.; Sato, T.; Yamamoto, Y.; Arai, S.; Satsuma, A., Size Specifically High Activity of Ru Nanoparticles for Hydrogen Oxidation Reaction in Alkaline Electrolyte *J. Am. Chem. Soc.* **2013,** *135* (21), 8016-8021.

(2) Zheng, Y.; Jiao, Y.; Zhu, Y.; Li, L. H.; Han, Y.; Chen, Y.; Jaroniec, M.; Qiao, S.-Z., High Electrocatalytic Hydrogen Evolution Activity of an Anomalous Ruthenium Catalyst *J. Am. Chem. Soc.* **2016,** *138* (49), 16174-16181.