SUPPORTING INFORMATION

Ultrapure Graphene Is a Poor Electrocatalyst: Definitive Proof of the Key Role of Metallic Impurities in Graphene-Based Electrocatalysis

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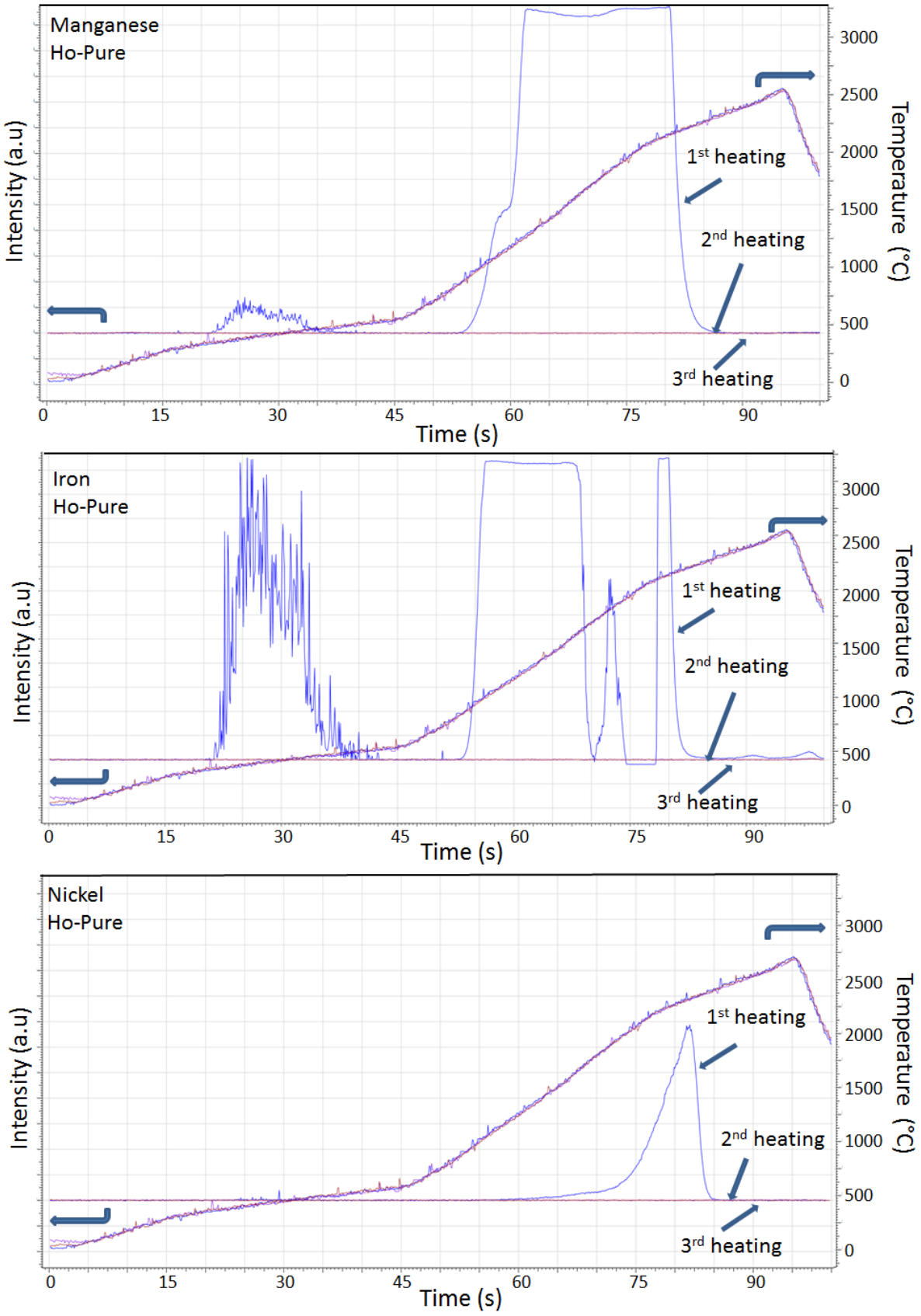

Figure S1. Intensity signal of the emission lines.

Table S1. Composition of thermally and chemically reduced graphene and purified graphene obtained by ETV ICP-OES. Contents of individual elements are in mg per kg of sample.

	HU-Pure	HO-Pure	HU-TRG	HO-TRG	HU-CRG	HO-CRG
Ag	< 0.01	< 0.01	0.25	1.89	0.543	0.301
Al	< 0.01	< 0.01	74.5	164.4	141.5	46.5
As	< 0.01	< 0.01	0.764	8.98	0.567	0.286
Ba	< 0.01	< 0.01	4.48	26.4	21.5	2.47
Ca	< 0.01	< 0.01	755.8	659.2	1325	389.9
Cd	< 0.01	< 0.01	0.239	0.594	0.366	0.319
Ce	< 0.01	< 0.01	1.29	1.35	1.09	1.02
Co	< 0.01	< 0.01	5.97	1.35	58.4	2.96
Cr	< 0.01	< 0.01	9.95	12.1	5.06	3.66
Cu	< 0.01	< 0.01	5.42	52.2	38.3	1.97
Fe	< 0.01	< 0.01	76.2	203.6	234.7	41.3
K	< 0.01	< 0.01	824.6	519.0	113.4	161.3
La	< 0.01	< 0.01	0.821	< 0.01	0.69	0.569
Mg	< 0.01	< 0.01	42.5	30.5	108.8	15.7
Mn	< 0.01	< 0.01	3652	49.5	4029	4.23
Mo	< 0.01	< 0.01	10.8	11.4	2.54	0.844
Na	< 0.01	< 0.01	76.3	70.4	69.4	70.4
Ni	< 0.01	< 0.01	6.48	10.0	393.4	2.21
Sc	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.174
Se	< 0.01	< 0.01	< 0.01	3.08	3.53	0.339
Sr	< 0.01	< 0.01	5.84	2.47	2.88	0.256
Ti	< 0.01	< 0.01	2.07	21.0	46.2	6.15
V	< 0.01	< 0.01	1.60	0.875	0.341	< 0.01
Zn	< 0.01	< 0.01	0.98	63.1	51.3	3.22

Table S2. Composition of thermally and chemically reduced graphene obtained by neutron activation analysis. Contents of individual elements are in mg per kg of sample with the corresponding combined uncertainties (coverage factor k=1).

	HU-Pure	HO-Pure	HU-TRG	HO-TRG	HU-CRG	HO-CRG
F	NA[a]	344±21	NA[a]	NA[a]	< 10	1004±30
Na	20.9±0.3	6.6±0.8	88.1±0.9	137.4±1.5	82.1±0.8	98.1±1.1
Mg	< 160	< 60	< 410	< 390	< 430	51±9
Al	< 30	8.9±0.2	52±4	170±4	164±4	51.3±0.6
Cl	120±4	78.9±1.4	134±10	2234±26	177±11	63.2±1.1
K	< 5	3.8±0.5	1074±14	576±14	114±2	176±2
Ca	< 50	< 10	< 175	543±44	3086±760	301±9
Sc	0.009±3E-4	7E-4±3E-5	0.007±2E-4	0.027±0.001	0.024±8E-4	0.006±2E-4
Ti	< 12	< 4.1	< 88	< 36	< 17	4.8±0.8
V	< 0.06	< 0.017	< 0.58	0.87±0.10	< 0.46	0.050±0.007
Cr	1.9±0.2	0.41±0.02	14.7±0.4	95.1±2.1	5.1±0.1	1.64±0.04
Mn	0.270±0.046	0.056±0.020	4011±41	50.0±0.6	4414±45	4.54±0.05
Fe	< 35	7.34±0.15	97.0±9.3	929±34	244±9	45.2±2.4
Co	0.057±0.014	< 0.009	0.399±0.016	1.99±0.05	48.7±0.1	1.28±0.01
Ni	< 8	< 1.6	6.5±1.9	< 17	474±11	< 1
Cu	2.12±0.07	0.37±0.02	7.86±0.15	47.8±0.6	39.8±0.4	1.92±0.04
Zn	2.38±0.03	1.04±0.07	2.86±0.2	99.8±2.4	49.7±1.0	3.6±0.1
As	0.026±0.004	0.039±0.002	0.74±0.02	0.75±0.02	0.26±0.01	0.24±0.04
Se	0.09±0.02	< 0.09	<0.3	4.4±0.4	2.3±0.1	0.31±0.02
Br	1.25±0.03	0.31±0.007	7.81±0.09	21.2±0.2	18.5±0.2	0.76±0.01
Rb	< 1.6	< 0.3	< 1.2	< 3.3	< 1.1	< 0.2
Sr	< 17	< 3.5	< 12	< 34	< 7	< 2
Mo	1.70±0.15	0.31±0.01	2.28±0.20	12.7±1.1	7.05±0.12	0.76±0.01
Ag	0.46±0.06	0.06±0.01	< 0.12	1.61±0.14	0.17±0.03	0.26±0.01
Cd	< 0.8	< 0.5	< 1.3	< 5.4	< 1.1	< 0.8
In	0.376±0.008	0.030±0.002	< 0.085	1.22±0.02	< 0.085	0.072±0.001
Sb	0.044±0.003	0.019±0.004	0.045±0.013	7.172±1.930	0.047±0.008	0.011±0.003
I	1.21±0.16	0.25±0.06	< 3	< 1.3	90.5±1.7	1.98±0.04
Cs	< 0.038	< 0.008	0.064±0.011	< 0.084	< 0.024	< 0.006
Ba	< 24	< 4.6	< 16	< 48	23.7±3.6	< 2.8
La	0.16±0.01	1.68±0.02	0.66±0.01	0.90±0.02	0.65±0.01	0.54±0.01
Ce	< 0.30	2.42±0.06	1.00±0.10	1.61±0.32	1.23±0.05	0.82±0.02
Nd	< 1.6	< 0.8	< 4.2	< 8	< 6.5	< 0.5
Sm	0.005±0.001	< 0.001	0.022±0.001	0.018±0.003	0.095±0.001	0.004±0.001
Eu	0.031±0.005	0.007±0.001	0.020±0.002	0.037±0.007	0.006±0.002	0.004±0.0006
Gd	< 0.94	< 0.19	< 0.65	< 1.9	< 0.25	< 0.11
Tb	< 23	< 4	< 15	< 43	600±12	< 3
Ho	0.022±0.002	< 0.05	0.18±0.01	1.00±0.02	0.33±0.01	0.019±0.001
Tm	< 48	< 10	< 34	137±18	82±3	< 6
Yb	< 0.03	< 0.02	< 0.05	< 0.03	0.11±0.02	< 0.019
Lu	< 7	< 6	< 11	<60	41±5	< 4
Hf	< 40	< 9	< 28	311±32	320±10	52±3
Ta	< 35	< 7	< 25	< 70	90±6	13±2
W	0.16±0.01	0.041±0.005	0.18±0.02	0.24±0.05	6.41±0.07	0.78±0.01
Th	< 42	< 8	88±12	< 82	< 12	7±2
U	< 0.09	< 0.03	0.85±0.04	< 0.26	1.51±0.04	< 0.02

a –not analyzed

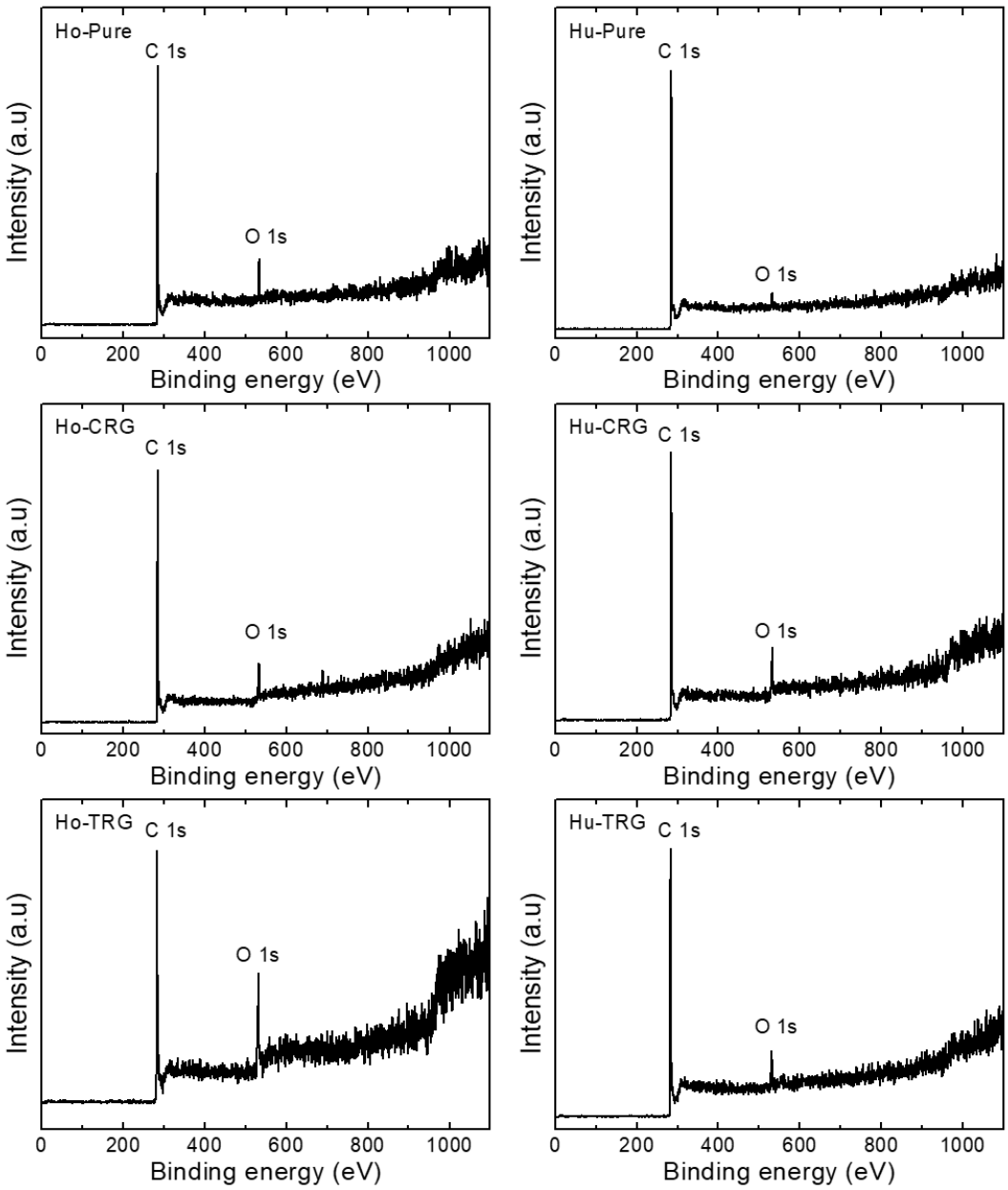

Figure S2. The XPS survey spectra of chemically, thermally reduced samples and purified samples. The C/O ratio in atomic percent was 16.7 and 7.7 for Hu-TRG and Ho-TRG, 14.9 and 13.1 for Hu-CRG and Ho-CRG, 50.5 and 16.7 for Hu-Pure and Ho-Pure.

Table S3. The composition of samples obtained by elemental combustion analysis.

Sample	C (wt.%)	H (Wt.%)	N (wt.%)	O (wt.%)
Ho-CRG	88.21	0.93	0.50	10.37
Hu-CRG	82.53	0.73	2.52	14.23
Ho-TRG	97.09	0.36	0.00	2.55
Hu-TRG	95.70	0.23	0.06	4.02
Ho-Pure	99.69	0.00	0.00	0.31
Hu-Pure	99.65	0.00	0.00	0.35

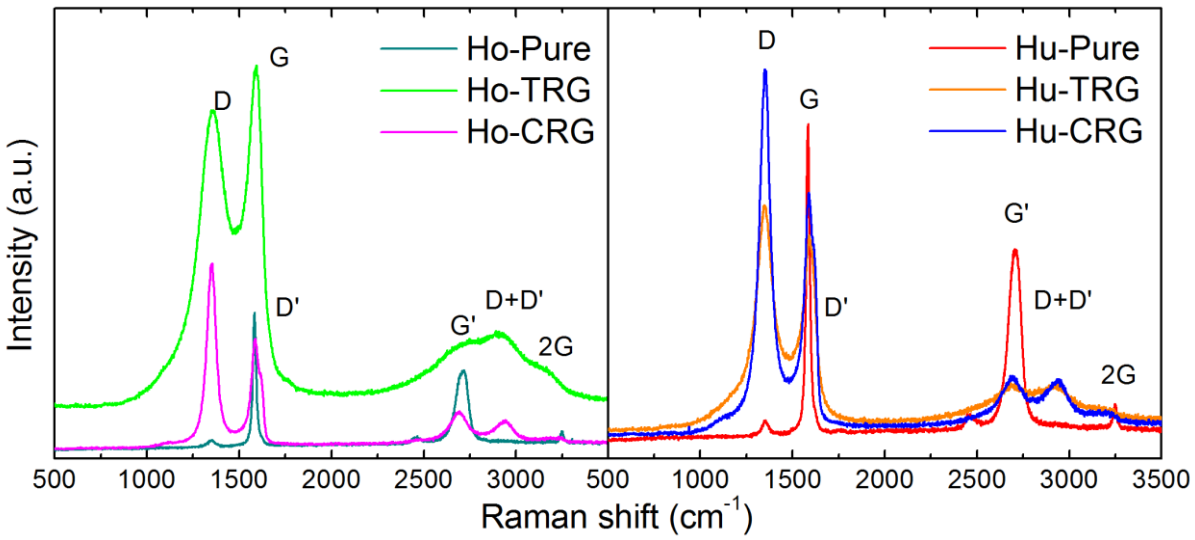

Figure S3. Raman spectra of the reduced and purified graphene prepared from graphene oxide made by Hofmann and Hummers method. Raman spectra were obtained with 532 nm laser.

Table S4. D- and G-band intensity ratio obtained from Raman spectra.

Sample	I_D/I_G
Hu-Pure	0.04
Ho-Pure	0.05
Hu-TRG	1.19
Ho-TRG	0.88
Hu-CRG	1.53
Ho-CRG	1.73

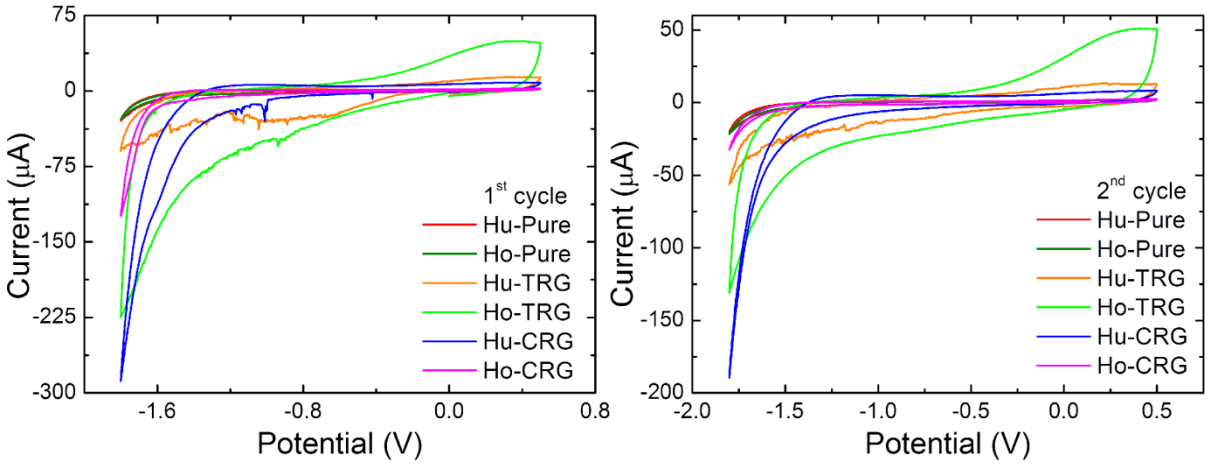

Figure S4. Inherent electrochemistry measured in 50 mM PBS.

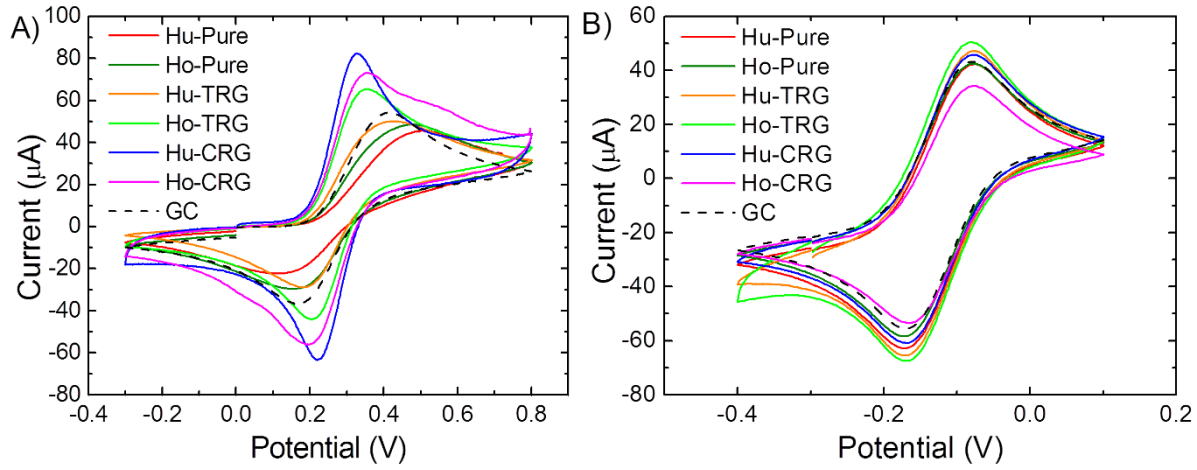

Figure S5. Heterogeneous electron transfer (HET) measured with 5 mM HET probe in 100 mM KCl supporting electrolyte. Two HET probes were used: A) inner-sphere $[Fe(CN_6)]^{4-/3-}$ and B) outer-sphere $[Ru(NH_3)_6]^{2+/3+}$.

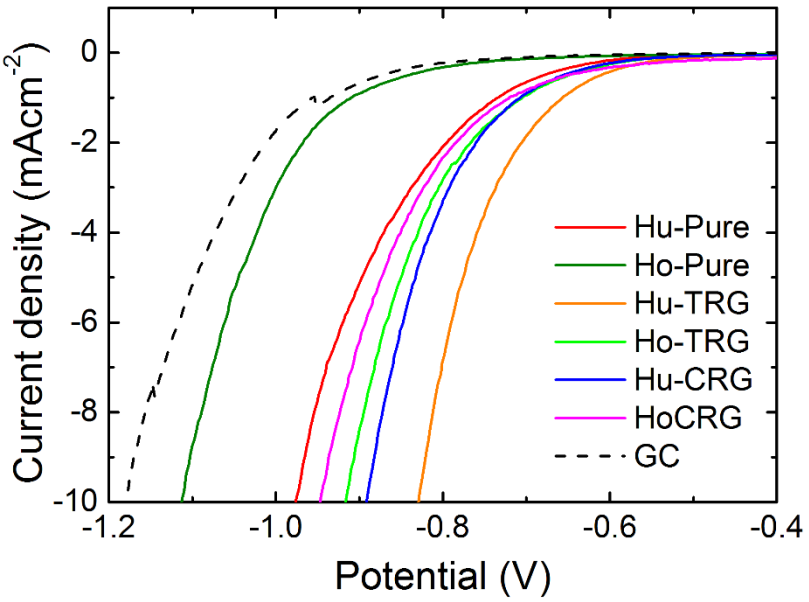

Figure S6. Linear sweep voltammetry of hydrogen evolution reaction conduced in 0.5 M H_2SO_4.

Table S5. The INAA results for NIST SRM 1515 and the declared values with the corresponding expanded uncertainties (coverage factor k=2).

Element, unit	**NIST SRM 1515 [a] (100.64)**	**NIST value [b]**
F, mg kg^{-1}	NA	-
Na, mg kg^{-1}	37.4±0.09[c]	24.4±1.2
Mg, mg kg^{-1}	2600±92	2710±80
Al, mg kg^{-1}	284±6	286±9
Cl, mg kg^{-1}	570±4	579±23
K, mg kg^{-1}	15930±320	16100±200
Ca, mg kg^{-1}	15260±300	14700±314
Sc, µg kg^{-1}	33±0.6	(30)
Ti, mg kg^{-1}	9.8±1.8	-
V, mg kg^{-1}	0.28±0.04	0.26±0.3
Cr, mg kg^{-1}	0.34±0.06	(0.30)
Mn, mg kg^{-1}	52.5±1.1	54±3
Fe, mg kg^{-1}	84.5±0.6	83±5
Co, mg kg^{-1}	0.089±0.004	(0.09)
Ni, mg kg^{-1}	< 1.5	0.91±0.12
Cu, mg kg^{-1}	6.1±0.6	5.64±0.24
Zn, mg kg^{-1}	12.3±0.6	12.5±0.3
As, mg kg^{-1}	0.043±0.008	0.038±0.007
Se, mg kg^{-1}	< 0.05	0.050±0.009
Br, mg kg^{-1}	1.65±0.02	(1.8)
Rb, mg kg^{-1}	10.3±0.6	10.2±1.5
Sr, mg kg^{-1}	25.4±1.4	25±2
Mo, mg kg^{-1}	< 0.5	0.094±0.013
Ag, mg kg^{-1}	< 0.25	-
Cd, mg kg^{-1}	< 1.0	0.013±0.002
In, mg kg^{-1}	< 0.004	-
Sb, µg kg^{-1}	14±2	(13)

I, mg kg^{-1}	0.35±0.06	(0.3)
Cs, µg kg^{-1}	8±2	-
Ba, mg kg^{-1}	46.5±3.8	49±2
La, mg kg^{-1}	20.6±0.2	(20)
Ce, mg kg^{-1}	2.83±0.12	(3)
Nd, mg kg^{-1}	16.1±1.0	(17)
Sm, mg kg^{-1}	2.7±0.2	(3)
Eu, mg kg^{-1}	0.22±0.01	(0.2)
Gd, mg kg^{-1}	2.46±0.12	(3)
Tb, µg kg^{-1}	410±20	(400)
Ho, mg kg^{-1}	0.35±0.01	-
Tm, µg kg^{-1}	51±4	-
Yb, mg kg^{-1}	0.30±0.02	(0.3)
Lu, µg kg^{-1}	19±6	-
Hf, µg kg^{-1}	11±3	-
Ta, µg kg^{-1}	< 4	-
W, mg kg^{-1}	< 0.035	(0.007)
Th, µg kg^{-1}	28.9±2.4	(30)
U, mg kg^{-1}	0.039±0.013	0.038±0.006

[a] – measured value ± expanded uncertainty (coverage factor k=2).

[b] – certified values are furnished with uncertainties, noncertified values are given in parenthesis.

[c] – the sodium certified value has increased due to glass corrosion on the long-time storage of the material in a (original) glass bottle.