Supporting Information

Hierarchical Branched Platinum-Copper Tripods as Highly Active and Stable Catalysts

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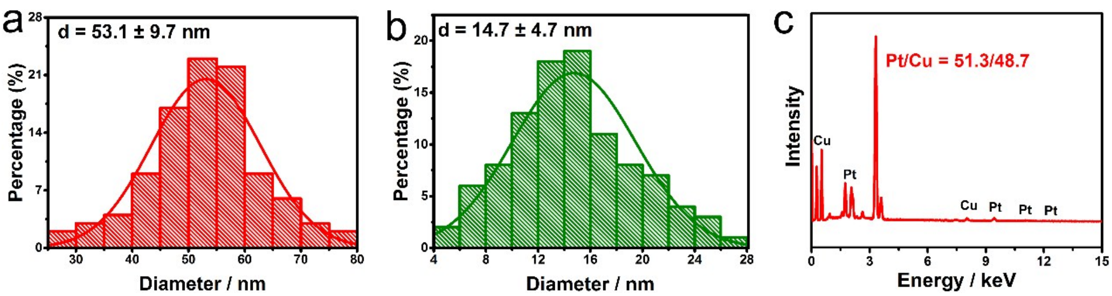

Figure S1 Length distributions of (a) three main branches, (b) secondary branches in $Pt_{52}Cu_{48}$ HTNCs. (c) SEM-EDS analyses of $Pt_{52}Cu_{48}$ HTNCs.

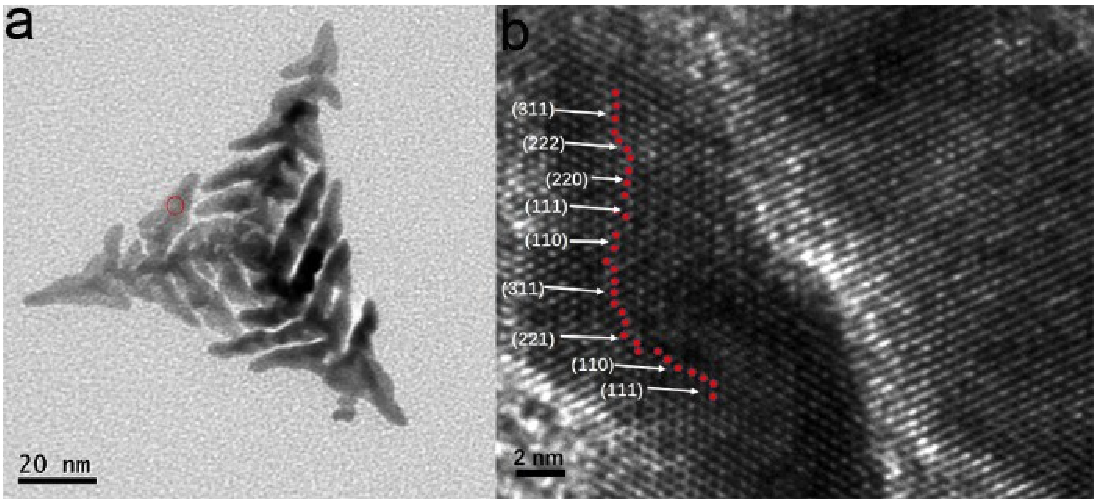

Figure S2 Representative (a) TEM and (b) corresponding HRTEM images of individual Pt-Cu HTNCs.

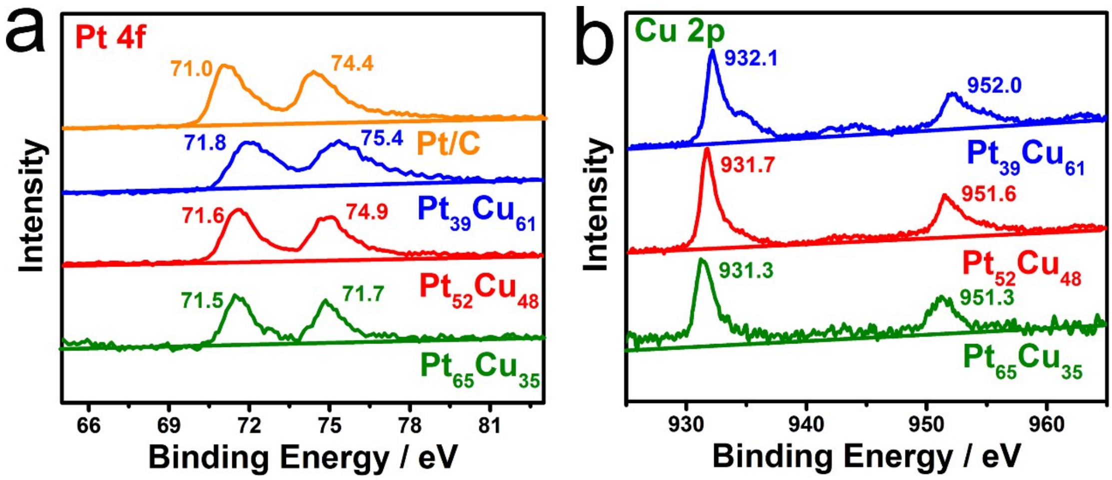

Figure S3 XPS spectra of (a) Pt 4f and (b) Cu 2p in different catalysts.

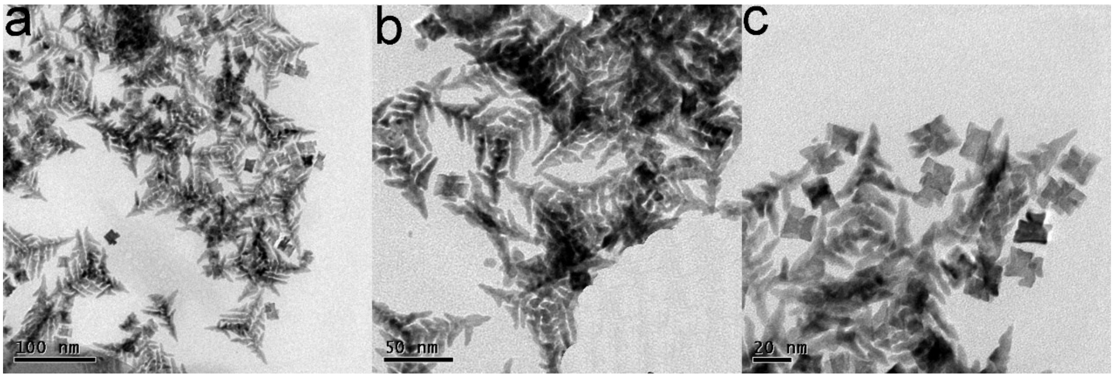

Figure S4 TEM images of Pt-Cu NCs prepared in the absence of PVP, while keeping other conditions the same.

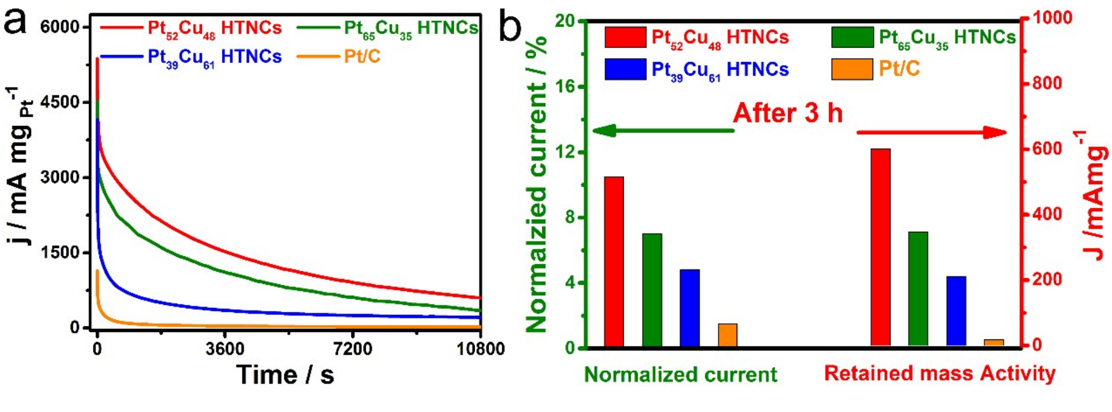

Figure S5 (a) Chronoamperometry (CA) curves of different electrocatalysts conducted at the potential of -0.25 V in 1.0 M KOH + 1.0 M EG solution. (b) The recorded normalized current and retained mass activity of different electrocatalysts after CA measurements for 3 h.

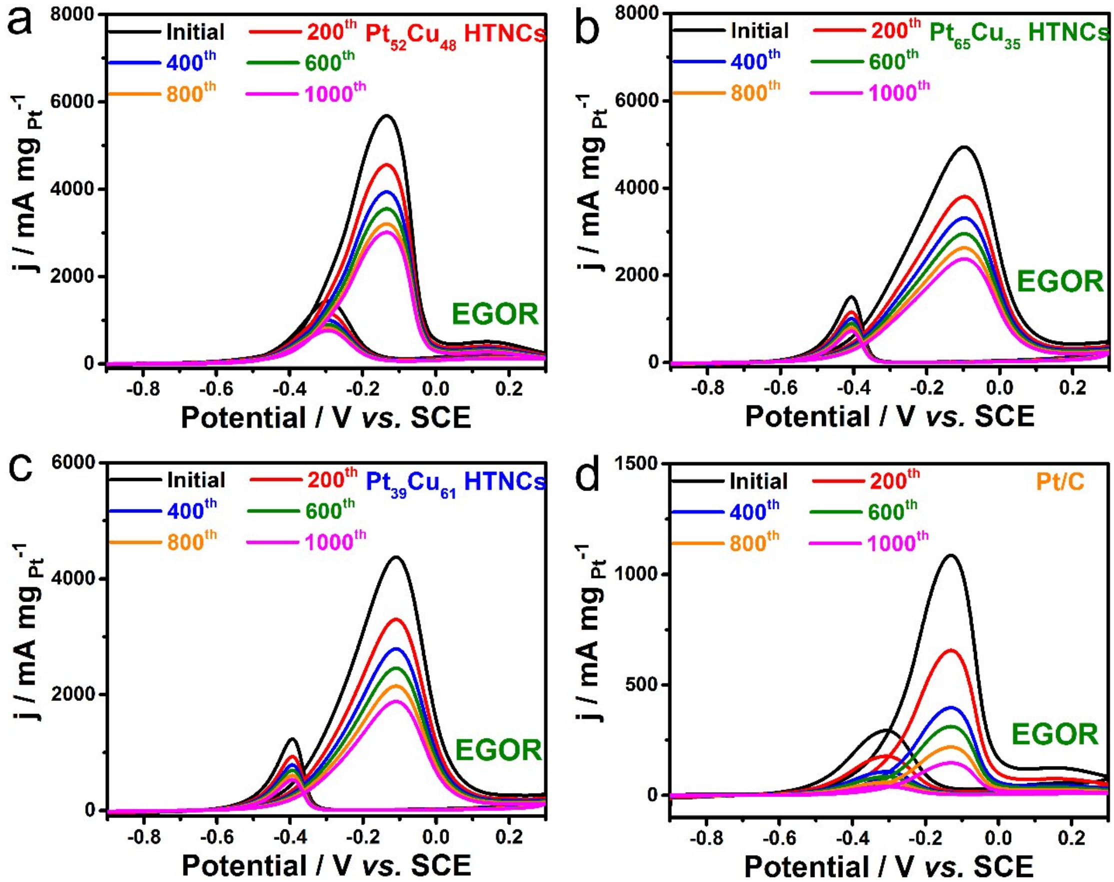

Figure S6 Cyclic voltammograms (1st, 200th, 400th, 600th, 800th and 1000th cycle) of (a) the $Pt_{52}Cu_{48}$ HTNCs, (b) the $Pt_{65}Cu_{35}$ HTNCs, (c) the $Pt_{39}Cu_{61}$ HTNCs and (d) commercial Pt/C for EGOR, respectively. Potential was continuously scanned for 1000 sweeping cycles at 50 mV s^{-1} in 1.0 M KOH + 1.0 M EG for EGOR durability test.

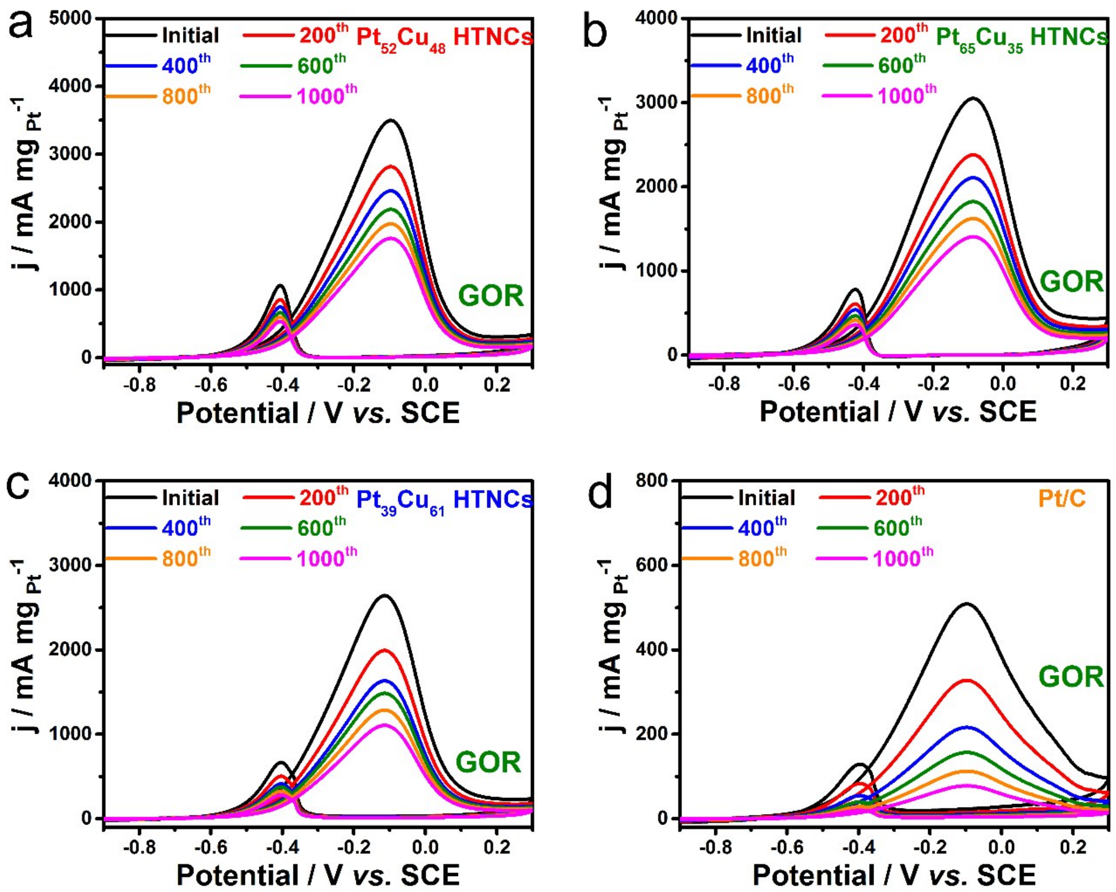

Figure S7 Cyclic voltammograms (1st, 200th, 400th, 600th, 800th and 1000th cycle) of (a) the $Pt_{52}Cu_{48}$ HTNCs, (b) the $Pt_{65}Cu_{35}$ HTNCs, (c) the $Pt_{39}Cu_{61}$ HTNCs and (d) commercial Pt/C for GOR, respectively. Potential was continuously scanned for 1000 sweeping cycles at 50 mV s^{-1} in 1.0 M KOH + 1.0 M glycerol for GOR durability test.

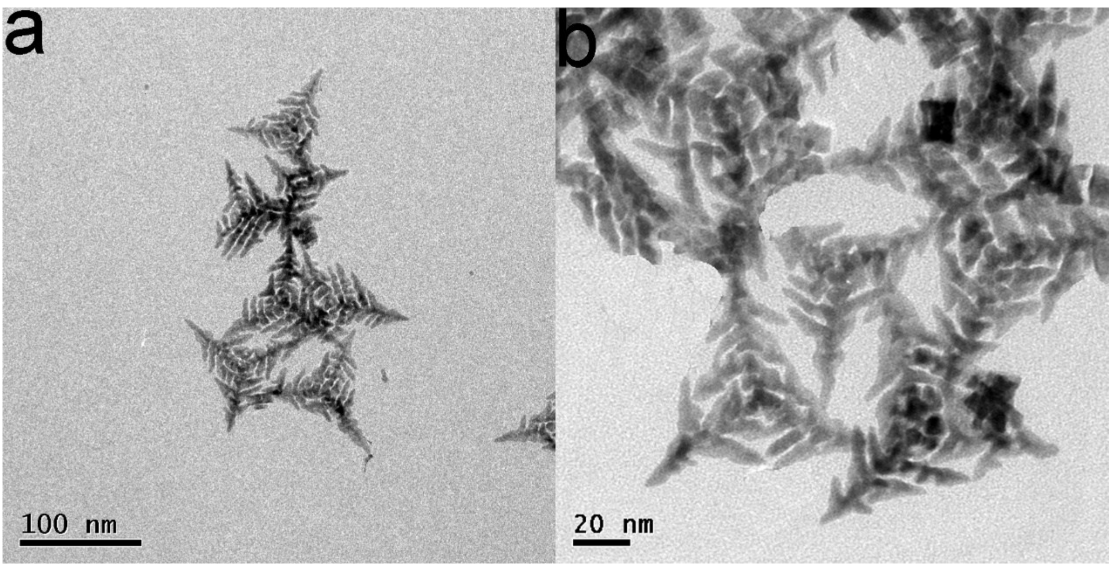

Figure S8 Representative TEM images of $Pt_{52}Cu_{48}$ HTNCs after stability tests.

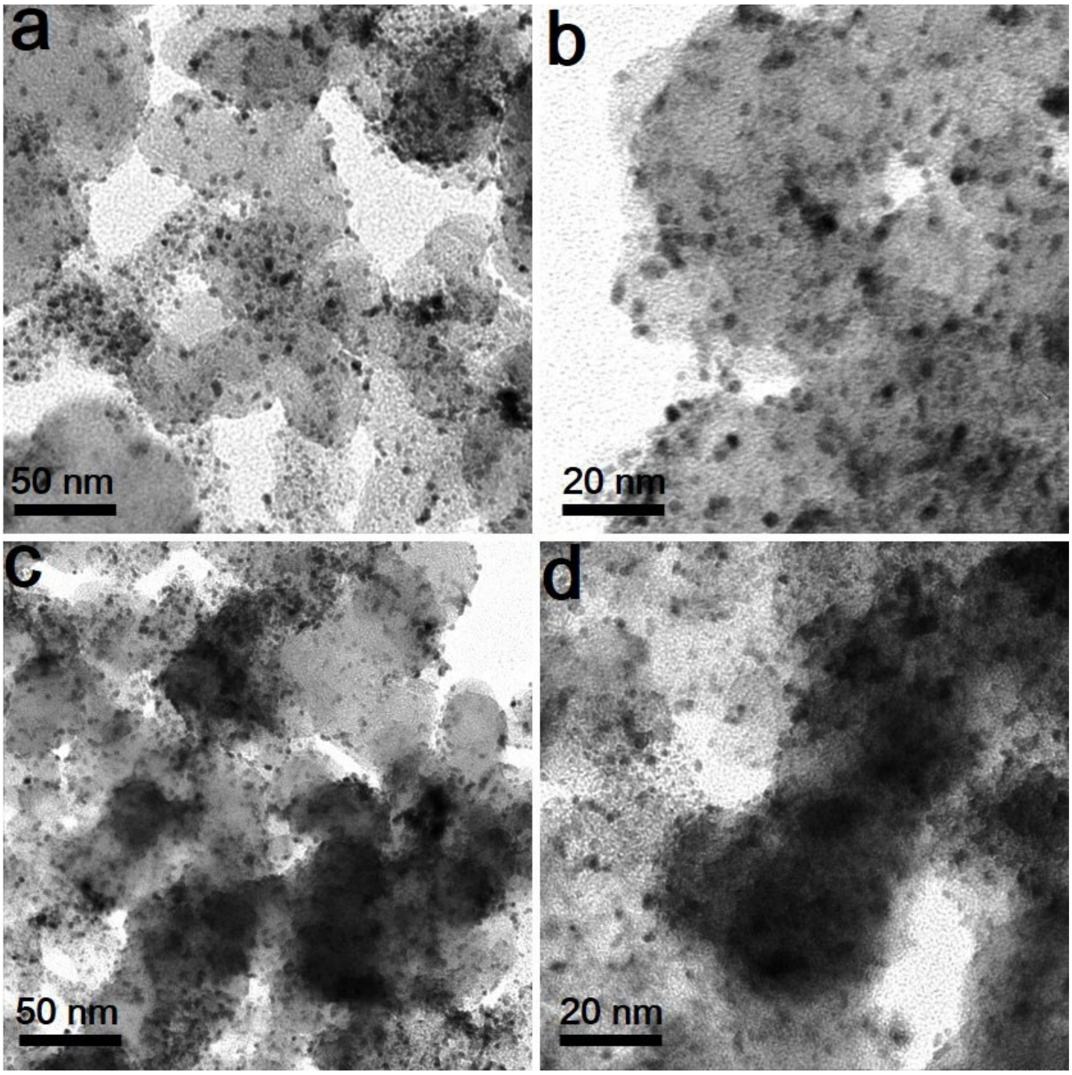

Figure S9 Representative TEM images of Pt/C catalysts after stability tests.

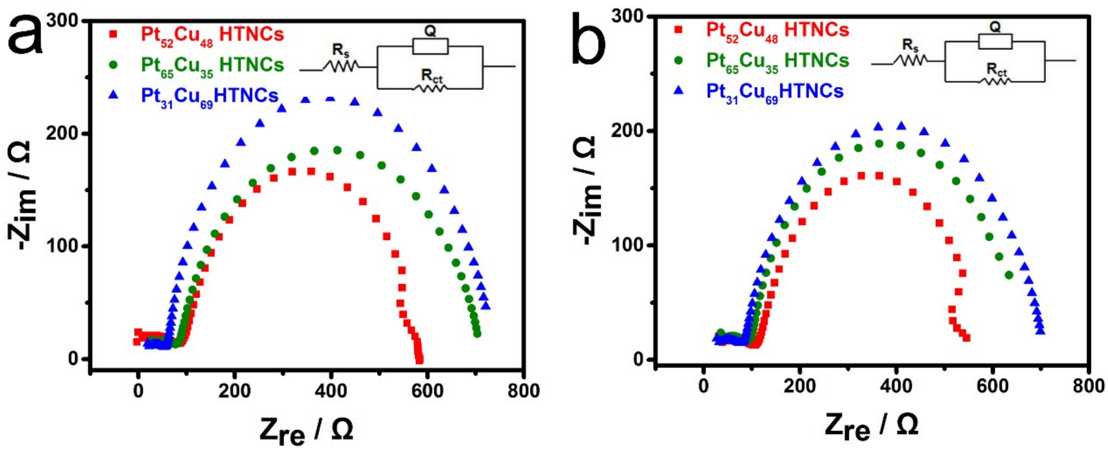

Figure S10 Nyquist plots of the $Pt_{52}Cu_{48}$ HTNCs, $Pt_{65}Cu_{35}$ HTNCs, $Pt_{39}Cu_{61}$ HTNCs and (d) commercial Pt/C in (a)1.0 M KOH + 1.0 M EG and (b)1.0 M KOH + 1.0 M glycerol solutions at the potential of -0.20 and -0.15V, respectively.

Table S1 EGOR performances of $Pt_{52}Cu_{48}$ HTNCs and various electrocatalysts from published works

Catalysts	Peaks currents from CV curves		Electrolyte	References
	J_m (A/mg)	J_s (mA/cm^2)		
$Pt_{52}Cu_{48}$ HTNCs	5.7	11.2	1.0 M KOH + 1.0 M EG	This work
AuPt@Pt Nanocrystals/rGO	0.6		0.1 M H_2SO_4 + 0.5 M EG	Electrochim. Acta **2016**, *219*, 321-329.
$Pt_{4.5}Pb$ NWs	0.73	0.30	0.1M $HClO_4$ + 0.5 M EG	Small **2016**, *12*, 4464- 4470
$Pt_{5.7}Pb$ NWs	0.63	0.22		
Pt-Sn Nanocrystals/CNT	0.22		0.5 M H_2SO_4 + 1 M EG	Int. J. Hydrogen Energy **2011**, *36*, 5, 3313-3321
Pt/Ru/XC72 Catalyst	0.24		0.5 M H_2SO_4 + 0.4M EG	J. Power Sources **2011**, *196*, 1078-1083.
Pt-Ru Nanocrystals/CNT	0.175		0.5 M H_2SO_4 + 1 M EG	Int. J. Hydrogen Energy **2012**, *37*, 9941-9947.
PtPd@Pt Nanocrystals/rGO	0.23		0.5 M H_2SO_4 + 0.5 M EG	Electrochim. Acta **2016**, *18*, 576-583.
$PtNi_{0.67}Pb_{0.26}$ NWs/C	0.42	0.65	0.1 M $HClO_4$ + 0.2 M EG	J. Mater. Chem. A **2017**, *5*, 18977-18983

Pd_1Cu_1 nanosphere	3.58		1.0 M KOH + 1.0 M EG	Electrochim. Acta **2018**, *261*, 521-529.
PdCuBi nanoparticles	0.171		1 M KOH + 0.5 M EG	J. Power Sources. **2014**, *249*, 9-12
PtCu nanocrystals	4.259		1.0 M KOH + 1.0 M EG	Int. J. Hydrogen Energy **2018**, *43*, 1489-1496
PtRu alloy	3.052		1.0 M KOH + 1.0 M EG	Int. J. Hydrogen Energy **2017**, *42*, 20720-20728
PdAg nanoparticle	0.169		0.1 M KOH + 1.0 M EG	Int. J. Hydrogen Energy **2015**, *40*, 2225-2230
PtPd@Pt nanocrystals	1.167		0.5 M KOH + 0.5 M EG	Electrochim. Acta **2016**, *187*, 576-583.

Table S2 GOR performances of $Pt_{52}Cu_{48}$ HTNCs and various electroatalysts from published works

Catalysts	Peaks currents from CV curves		Electrolyte	References
	J_m (A/mg)	J_s (mA/cm^2)		
$Pt_{52}Cu_{48}$ HTNCs	3.2	6.2	1.0 M KOH + 1.0 M Glycerol	This work
$PtNi_{0.67}Pb_{0.26}$ NWs/C	0.36	0.61	0.1 M $HClO_4$ + 0.2 M Glycerol	J. Mater. Chem. A **2017**, **5**, 18977-18983
Pt Nanoparticles		~ 0.23	0.1 M H_2SO_4 + 0.255 M Glycerol	Electrochim. Acta **2013**, 98, 25-31.
Pt NOs		~ 0.35	0.1 M H_2SO_4 + 0.1 M Glycerol	Electrocatal. **2011**, 2, 96- 105.
Pt/MWCNT		0.16	0.1 M $HClO_4$ + 1.0 M Glycerol	Electrochim. Acta **2012**, 66, 180-187.

PtNi/C	0.204	0.27	0.5 M KOH + 2.0 M Glycerol	Appl. Catal. A **2012**, 429-430, 39-47
Pd-CNx/G	1.1		0.5 M KOH + 0.5 M Glycerol	ACS Catal. **2015**, 5, 3174-3180
Pd_5Ru-PEDOT/C		4.3	1 M KOH + 0.5 M Glycerol	Electrochim. Acta **2015**, *180*, 339-352
$Pd_{50}Ni_{50}$/C	0.190		0.1 M KOH + 0.1 M Glycerol	Electrocatal. **2013**, 4, 167-178
Pd_3Sn/phen-C	0.175		0.1 M KOH + 0.5 M Glycerol	Int. J. Hydrogen Energy **2016**, *41*, 1272-14280
Pd-NiOx-P/C	0.364		0.1 M KOH + 0.5 M Glycerol	Chem. Eng. J. **2017**, 38, 419-427
PtAg nanotubes	0.208	6.0	0.5 M KOH + 0.5 M Glycerol	Electrochem. Commun. **2014**,46,36-39

Table S3 The parameters of R_{ct} from equivalent circuits for different catalysts in different solutions

Catalysts	1.0 M KOH + 1.0 M EG (Ω cm^2)	1.0 M KOH + 1.0 M glycerol (Ω cm^2)
$Pt_{52}Cu_{48}$ HTNCs	239	242
$Pt_{65}Cu_{35}$ HTNCs	271	302
$Pt_{31}Cu_{69}$ HTNCs	347	325