Supporting information

Medium entropy alloy wavy nanowires as highly effective and selective alcohol oxidation reaction catalysts for energy-saving hydrogen production and alcohol upgrade

Xiaoyang Fu[a, d], Chengzhang Wan[a], Huaixun Huyan[c], Sibo Wang[a], Ao Zhang[b], Jingxuan Zhou[b], Hongtu Zhang[a], Xun Zhao[e], Jun Chen[e], Xiaoqing Pan[c], Yu Huang[b, *] and Xiangfeng Duan[a, *]

[a]Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, CA 90095, USA. Email: xduan@chem.ucla.edu

[b]Department of Materials Science and Engineering, University of California, Los Angeles, Los Angeles, CA 90095, USA. Email: yhuang@seas.ucla.edu

[c]Department of Materials Science and Engineering, University of California, Irvine, Irvine, CA 92697, USA

[d]School of Materials Science and Engineering, Peking University, Beijing, 100871, China

[e]Department of Bioengineering, University of California, Los Angeles, Los Angeles, CA 90095, USA.

Experimental Section

Chemicals

Potassium tetrachloroplatinate (IV) (K_2PtCl_4, 98%), silver nitrate ($AgNO_3$, analytical grade), sodium hexachlororhodate (III) (Na_3RhCl_6, analytical grade), copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), gold (III) chloride trihydrate ($AuCl_3 \cdot 3H_2O$), polyvinylpyrrolidone (PVP, MW. ~55000) were purchased from Sigma Aldrich. Commercial Pt on graphitized carbon (Pt/GC, 20%) was purchased from the Alfa Aesar and the chemicals were used as received without any further purification. Carbon paper (Freudenberg H23) and anion exchange membrane (AEM) (FAS-50) were purchased from fuelcellstore. The electrolyser setup was purchased from Gaoss Union with graphite bipolar plates with serpent channels and active area of 1.0 cm^2 as shown in Fig. S15.

Synthesis

160 mg PVP were dissolved into 4.0 mL of EG after ultrasonication and then the aqueous solution of 0.018 mmol K_2PtCl_4, 0.018 mmol $AgNO_3$, 0.018 mmol Na_3RhCl_6, 0.018 mmol $CuSO_4 \cdot 5H_2O$, 0.0020 mmol $AuCl_3 \cdot 3H_2O$ were added in turn. The vial was then heated at 210 ^oC for 8h. The products were collected via centrifugation after the addition of acetone and then washed with water for 2 times and ethanol for 2 times and finally dispersed in ethanol.

Structural characterizations

XRD was tested on a Panalytical X'Pert Pro X-ray Powder Diffractometer with Cu-Kα radiation with a scan rate of 0.01^o/s. XPS was tested on Kratos AXIS Ultra DLD spectrometer and charge corrected at 284.8 eV for C spectrum. TEM images were taken on FEI T12 transmission electron microscope operated at 120 kV. STEM image and EDX mapping were tested on Joel Jem-300CF (Grand Arm) operated at 300 kV. The noble metal (*e.g.* Pt, Rh, Au) loading and elemental ratio of the nanowires on the electrode was determined from ICP-AES.

Electrochemical measurements

The electrochemical studies were carried out via three-electrode test system with glassy carbon electrode (GCE) with a geometry area of 0.196 cm^2, Pt coil as counter electrode and Hg/HgO (1.0 M KOH) as the reference electrode for electrochemical test in alkaline media; and graphite rod as counter electrode and Ag/AgCl as the reference electrode in acidic media. The electrocatalysts were homogeneously dispersed in ethanol and 10.0 μL of the ink was drop-cast onto the surface of the electrode surface and dried at room temperature. The noble metal (e. g. Pt, Rh, Au) loading of the nanowires on the electrode is determined from ICP-AES, and the noble metal loading is ranging in 1.00-1.50 μg (5.10-7.65 μg/cm^2).

CV tests were performed at first in Ar-saturated 0.1 M $HClO_4$ electrolyte with a scan rate of 50 mV/s ranging from 0.05 V_{RHE} to 1.00 V_{RHE} for electrocatalysts activation and ECSA measurement by integrating hydrogen desorption charge using the constant of 210 μC/cm^2. The electrocatalytic EOR and EGOR were tested via CVs in inert gas saturated 1.0 M KOH + 1.0 M EtOH and 1.0 M KOH + 1.0 M EG electrolyte, respectively, at a scan rate of 50 mV/s. The CA was tested at 0.67 V vs. RHE for 1h. The commercial Pt/GC (20%) was used as control sample and the catalyst ink was 1.00 mg/mL commercial Pt/GC (20%) with ethanol: Nafion (5 wt%) = 99:1 as the ink solvent. And 10.0 μL of the Pt/C catalyst ink was drop-cast onto the GCE and dried to ensure a platinum loading of 2.00 μg (10.2 μg/cm^2) on the working electrode.

Alcohol assisted water electrolysis

The anion exchange membrane was sandwiched between two 1 cm^2 carbon paper electrodes with PTFE gaskets. The anode electrocatalyst is the Au-doped PtAgRhCu wavy NWs with a noble metal (Pt, Rh, Au) loading of 1 mg. The cathode electrocatalyst is commercial Pt/GC with Pt loading of 1 mg. For the controlled study, commercial Pt/GC was employed for both anode and cathode with 1 mg Pt loading. The anolyte is 1.0 M KOH + 1.0 M EtOH or 1.0 M KOH + 1.0 M EG, respectively, and catholyte is 1.0 M KOH at a flow rate ~80 mL/min. Polarization curves were obtained via LSV from 0 V to 1.2 V at 2 mV/s and CP was carried out at 100

mA/cm^2. For the product analysis, ^{1}H NMR tests were carried on Bruker AVS400 instrument. The aliquots were mixed with concentrated hydrochloric acid, and 3-(Trimethylsilyl)propionic-2,2,3,3-d4 acid sodium salt (internal standard) D_2O solution with a volumetric ratio of 8.00:2.00:1.11."

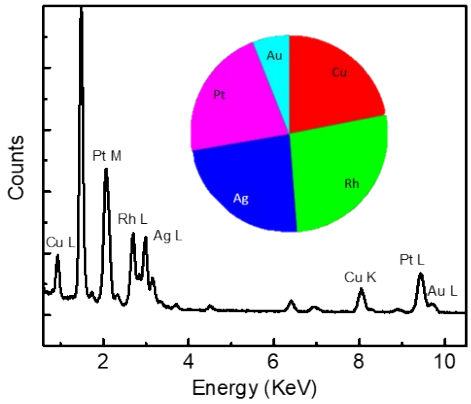

Figure S1. EDX spectrum of Au-doped PtAgRhCu wavy nanowires.

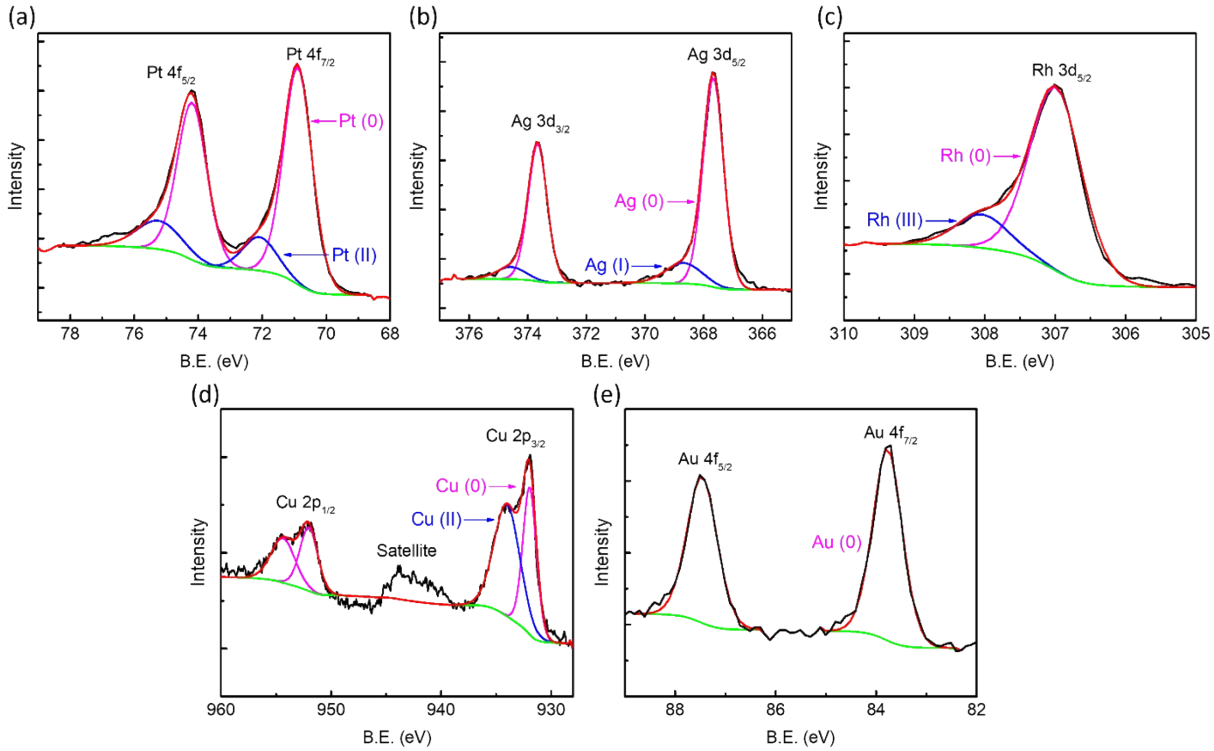

Figure S2 XPS study of Au-doped PtAgRhCu wavy nanowires regarding (a) Pt, (b) Ag, (c) Rh, (d) Cu and (e) Au elements.

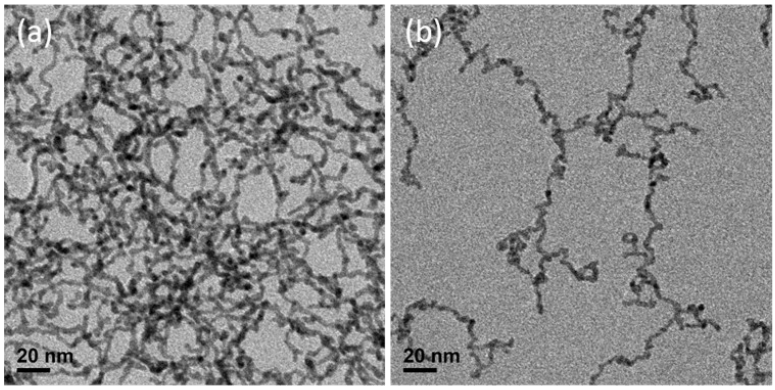

Figure S3. TEM pictures of (a) PtAgRh and (b) PtAgRhCu wavy nanowires.

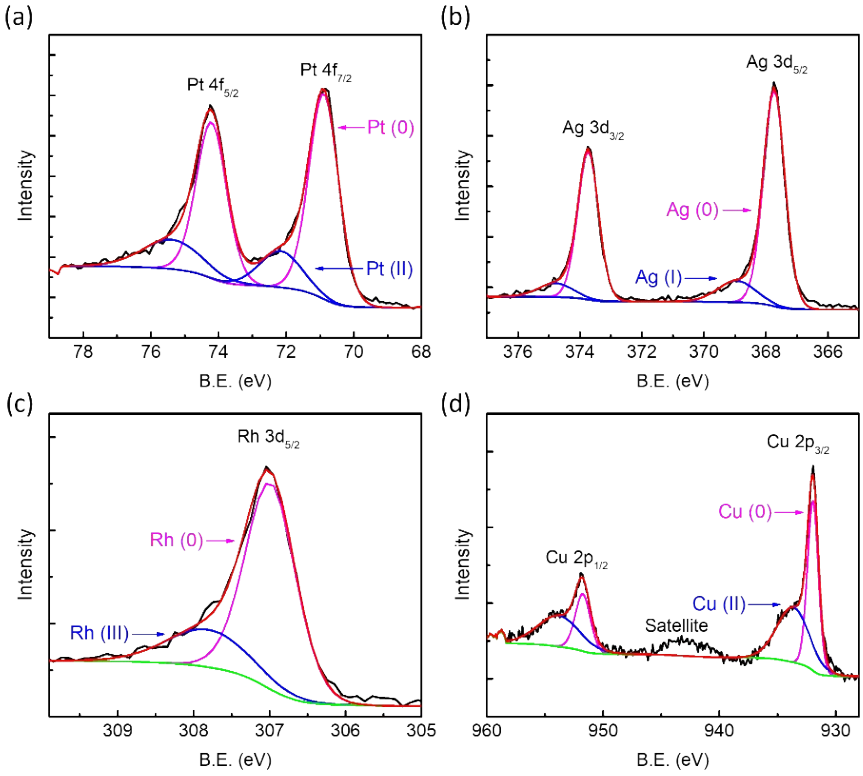

Figure S4. XPS study of PtAgRhCu wavy nanowires regarding (a) Pt, (b) Ag, (c) Rh and (d) Cu.

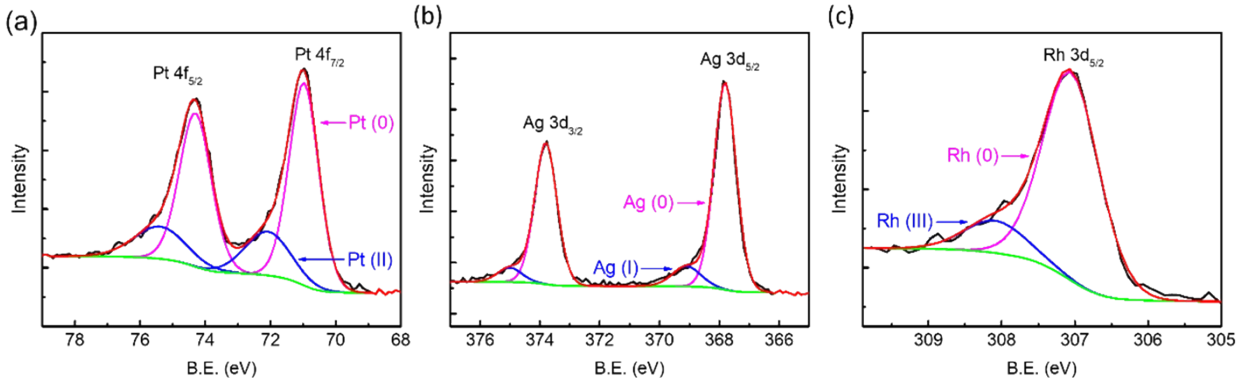

Figure S5. XPS study of PtAgRh wavy nanowires regarding (a) Pt, (b) Ag and (c) Rh.

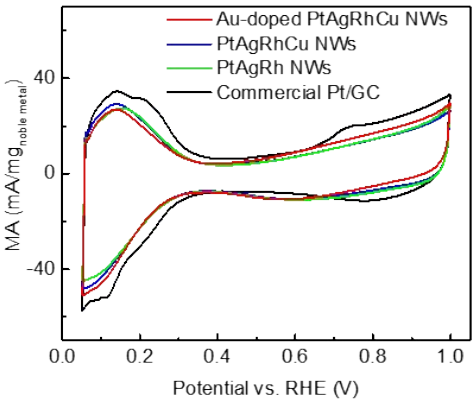

Figure S6 Mass-normalized CV curves of the electrocatalysts in 0.1 M $HClO_4$ electrolyte at scan rate of 50 mV/s.

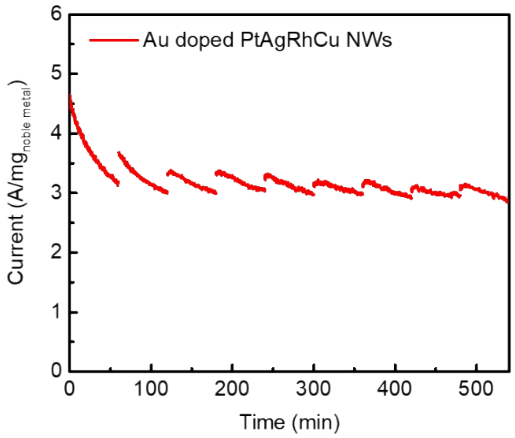

Figure S7 Cumulative CA tests at 0.67 V vs. RHE in the 1.0 M KOH + 1.0 M EG electrolyte

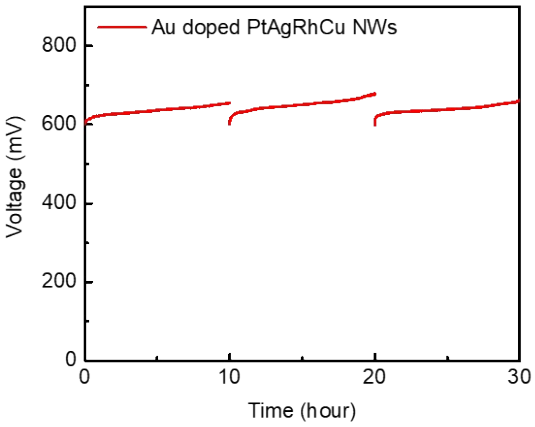

Figure S8 Cumulative CP tests at 100 mA/cm^2 in the 1.0 M KOH + 1.0 M EG electrolyte with electrolyte refresh after each 10-hour CP test.

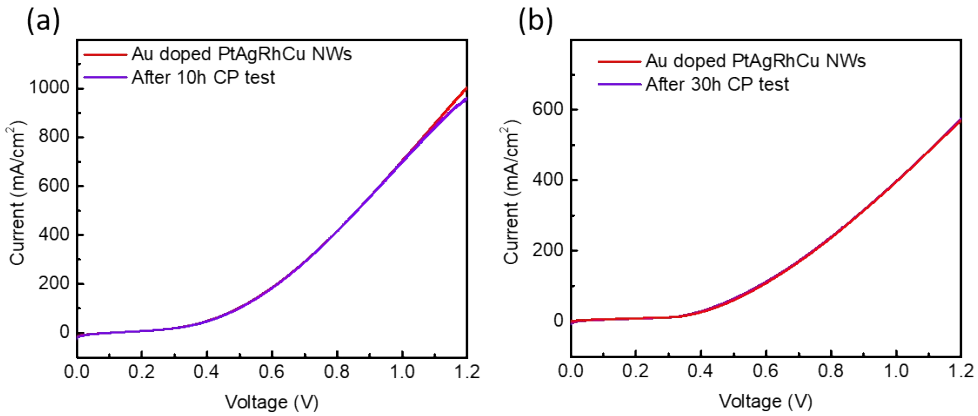

Figure S9 Performance comparison of (a) EtOH assisted water electrolysers and (b) EG assisted water electrolysers before and after CP tests (with electrolyte refresh after the CP test).

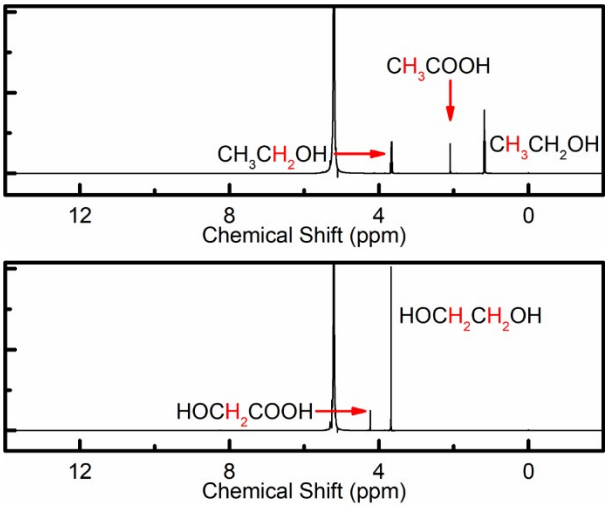

Figure S10 ^{1}H NMR analysis of products after EOR and EGOR, respectively.

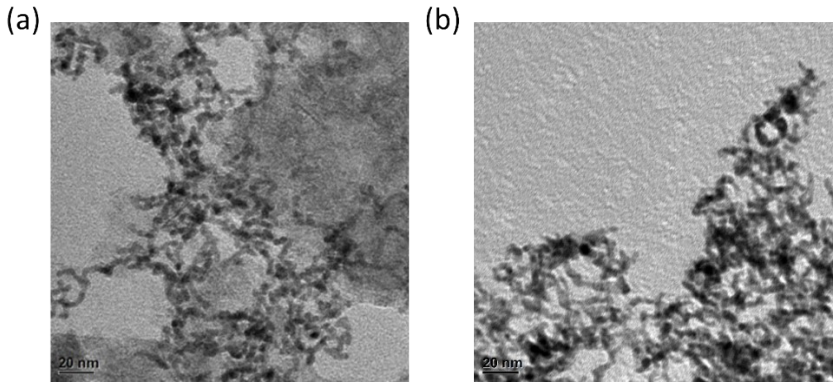

Figure S11. TEM pictures of electrocatalysts after CP tests. (a) EOR (b) EGOR.

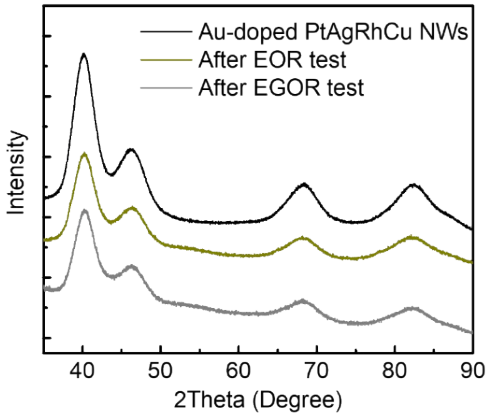

Figure S12. XRD of the electrocatalysts before and after the CP tests (EOR and EGOR).

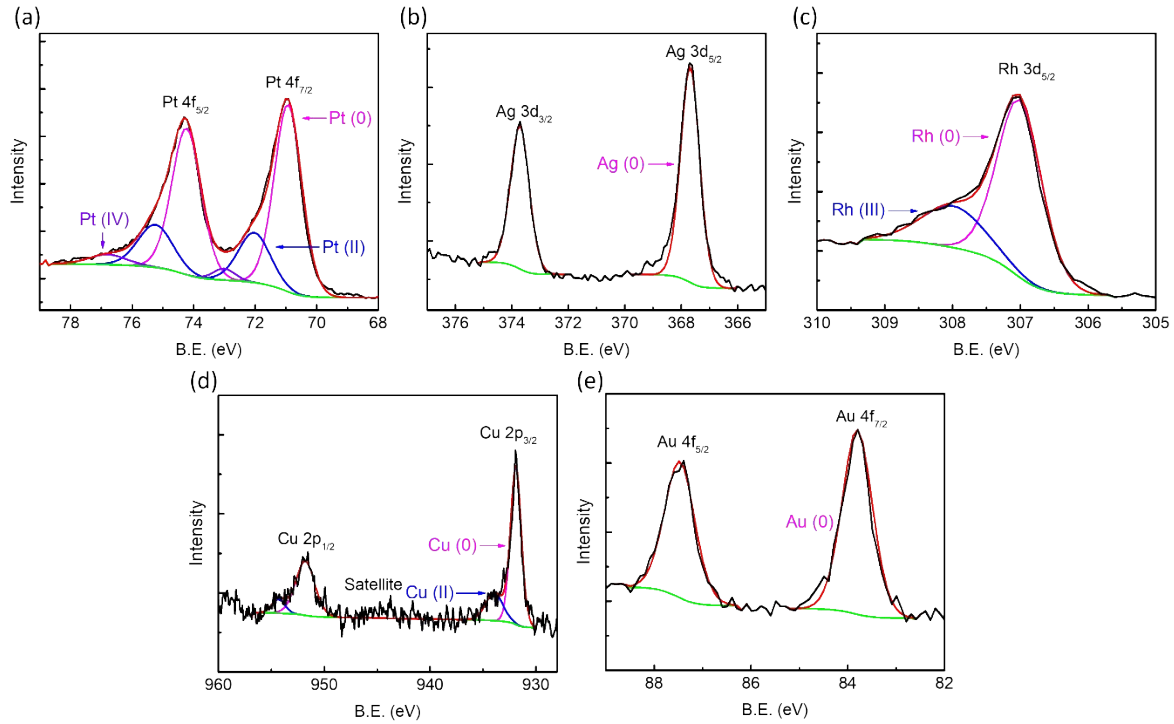

Figure S13 XPS study of the electrocatalysts after CP test (EOR) regarding (a) Pt, (b) Ag, (c) Rh, (d) Cu and (e) Au elements.

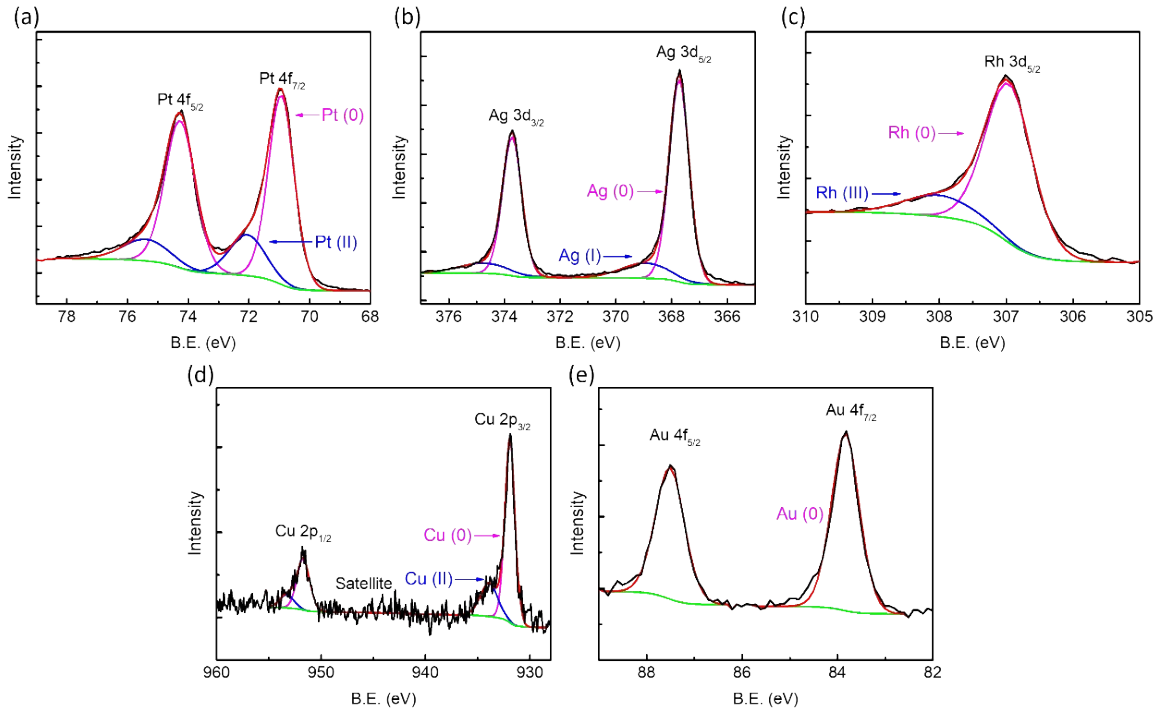

Figure S14. XPS study of the electrocatalysts after EGOR CP test regarding (a) Pt, (b) Ag, (c) Rh, (d) Cu and (e) Au elements.

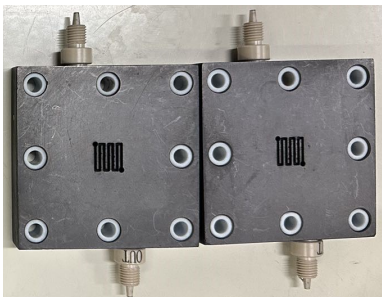

Figure S15. Picture of bipolar plates.