

Electronic Supplementary Information

Crack-tips Enriched Platinum-Copper Superlattice Nanoflakes as Highly Efficient Anode Electrocatalyst for Direct Methanol Fuel Cells

Lijun Zheng,^a Dachi Yang,^{*a} Rong Chang,^a Chengwen Wang,^a Gaixia Zhang^b and Shuhui Sun^{*b}

Contents

1. Experimental Section

1.1 Sample preparation

1.2 Characterization.

1.3 Electrochemical measurements.

1.4 The calculation of ECSA

2. Fig. S1-S13

Fig. S1. The EDS analysis (line-scanning) of Pt-Cu NWs before modification.

Fig. S2. The SEM images of Pt-Cu NFs.

Fig. S3. The “blade” thickness of Pt-Cu NFs.

Fig. S4. The SEM images of Pt-Cu NWs and Pt-Cu NFs.

Fig. S5. The SEM images of Pt-Cu NFs transformed from various diameter NWs

Fig. S6. The SEM images of Pt-Cu NFs modified with various chemical etching solution

Fig. S7. The elemental mapping of representative Pt-Cu NFs.

Fig. S8. The HRTEM image of Pt-Cu NFs

Fig. S9. An X-ray diffraction pattern of Pt-Cu NWs.

Fig. S10. The CV curves in 1 M CH₃OH + 0.5 M H₂SO₄ at 50 mV s⁻¹ (black for commercial Pt/C, red for Pt-Cu NFs) from 1st to 100th.

Fig. S11. The plots of the i_f / i_b vs CV cycles.

Fig. S12. The electrochemical evaluation of Pt-Cu NFs with various Pt/Cu atomic ratios

Fig. S13. The CO stripping measurements of Pt-Cu NFs catalysts with various Pt/Cu atomic ratios

3. References

1. Experimental Section

1.1 Sample preparation.

The AAO templates were fabricated similar to the previously reported routines.^{1, 2} The electrolyte for Pt-Cu NWs electrodeposition contains 0.5 mM $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (chloroplatinic acid), 0.1 mM $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (copper (II) sulfate pentahydrate) and 0.1 mM H_3BO_3 (boric acid). The electrolyte was buffered to $\text{pH} \approx 2 - 3$ with diluted HCl (hydrochloric acid) solution.³ A thick Au layer was sputtered onto one surface side of the AAO templates fully blocking the pores to serve as working electrode. With a graphite plate as the counter electrode, the Pt-Cu NWs were electrodeposited inside the nanochannels of AAO template under a constant voltage of 1.5 ~ 3.0 V at ambient temperature. The as-synthesized Pt-Cu NWs were released by completely dissolving the AAO template in 5% (w/w) H_3PO_4 (phosphorous acid) solution, and then rinsed in deionized water thoroughly. An etching solution of 20% HNO_3 (nitric acid) was used to partially etch the Cu off the as-synthesized Pt-Cu NFs, and finally the samples were thoroughly rinsed in deionized water and dried in air.

1.2 Characterization.

The samples were characterized by field-emission scanning electron microscope (FESEM, ZEISSMERLIN Compact, operated at 2KV) with energy dispersive X-ray spectroscopy (EDX, OXFORD), transmission electron microscope (TEM) and high resolution TEM (HR-TEM, FEI Tecnai G2 F20, operated at 200KV). The Pt loadings were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Thermo IRIS Advantage).

1.3 Electrochemical measurements.

The electrochemical performances of the Pt-Cu superlattice NFs were measured by using an electrochemical workstation (AMETEK VersaSTAT 4, Princeton) with rotation control (ATA-1B, Jiangfen Instruments) with a three-electrodes system, which is consisted of a glassy carbon (GC) rotating disk electrode (RDE) serving as the working electrode substrate, a Pt-wire electrode as the counter electrode and a Hg / Hg₂SO₄ (saturated K₂SO₄) electrode as the reference electrode, respectively. All potentials used in this work have been converted to potentials relative to the reversed hydrogen electrode (RHE) potential, unless otherwise specified.

The working electrode was coated with the catalyst layer through a typical procedure which is similar to those reported in previous publications.⁴ In our cases, 2 mg of the crack-tips enriched Pt-Cu superlattice NFs catalyst was firstly mixed with 1.6 ml deionized water, 0.4 mL isopropyl alcohol and 50 μ L 5 wt% nafion solution, and then the aqueous solution was under ultrasonic treatment for 30 minutes. The concentration of Pt in the Pt-Cu NFs aqueous solution was determined through ICP analysis. Catalysts suspension was pipetted onto the GC RDE (5 mm in diameter, 0.196 cm²) to get a Pt loading of 20 μ g_{Pt} cm⁻², which were finally dried under N₂ atmosphere at ambient temperature. The 20 wt% Pt/C commercial catalyst (HiSPEC 4000, JM (Johnson Matthey), UK) was prepared with the same procedure.

Before the cyclic voltammetry (CV) measurements, pure Ar was firstly purged into the 0.5 M H₂SO₄ solution for about 30 minutes to guarantee Ar saturation, and the Ar was kept flowing during the measurements. The working electrode was firstly cycled for 50 times with the scanning rate of 50 mV s⁻¹ between 0 and 1.2 V at room temperature to obtain a clean catalyst surface. Then, the CV measurements were carried out by cycling the potential from 0 to 1.2 V, with the scanning rate of 50 mV s⁻¹.

For the CO stripping voltammetry, CO (99.99% v/v in purity) was purged into 0.5 M H₂SO₄ solution at the position close to the working electrode for about 30 minutes, while keeping the working electrode potential at 0 V to guarantee the Pt surface was fully covered

by CO monolayer. Then the dissolved CO in the H₂SO₄ solution was purged out by purging Ar into the solution for about 30 minutes. Immediately, two consecutive cycles of CVs were carried out in the solution between the potential of 0.1 ~ 1.2 V at 50 mV s⁻¹. For MOR evaluation, the CVs were recorded between the potential of 0 ~ 1.2 V at 50 mV s⁻¹ in the solution containing 1 M CH₃OH and 0.5 M H₂SO₄ saturated with Ar. **Finally, the durability of the catalysts was evaluated by CA curves, the potentials applied on the electrode of the Pt-Cu NFs and the commercial Pt/C are both 0.88V.**

1.4 The calculation of ECSA

The ECSA of Pt was calculated from the CV plots based on the relation $ECSA = Q_H / (Q_{ref} m)$. In the formula above, the Q_H represents the charge for H adsorption/desorption (mC cm⁻²) which were calculated by integrating the hydrogen-adsorption/desorption region charge in the CV plots between the potential range 0.05 and 0.4 V, where Q_{ref} represents the charge of the monolayer adsorption of hydrogen on the Pt surface.⁵ It is generally accepted as 210 μC cm⁻² for the polycrystalline Pt electrodes, corresponding to a surface density of 1.3×10^{15} Pt atoms /cm², and m represents the mass (mg cm⁻²) of Pt on the total GC working electrode.

2. Fig. S1-S13

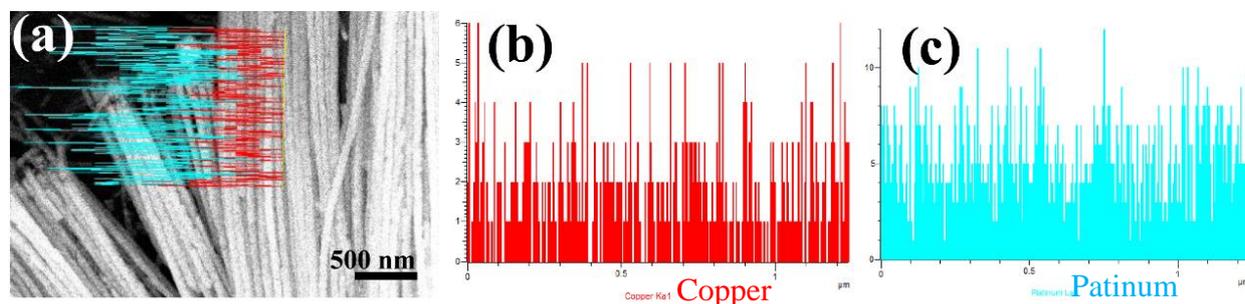


Fig. S1 The line-scanning EDS of a representative Pt-Cu NWs. (a) The SEM image of Pt-Cu NWs. (b) and (c) the EDS spectrum corresponding to Cu and Pt, respectively.

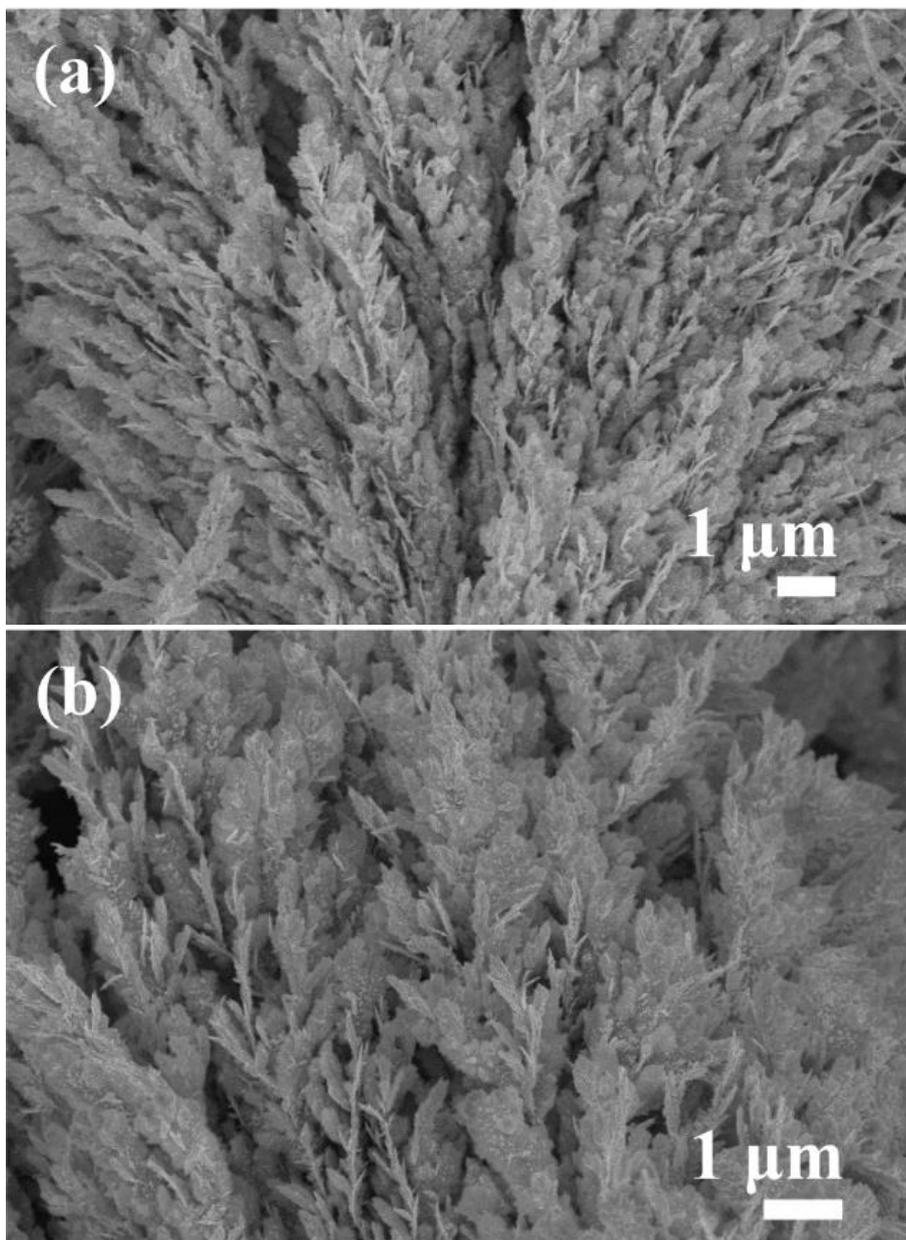


Fig. S2 The SEM images of Pt-Cu NFs. (a) Massive production. (b) A selected Magnification.

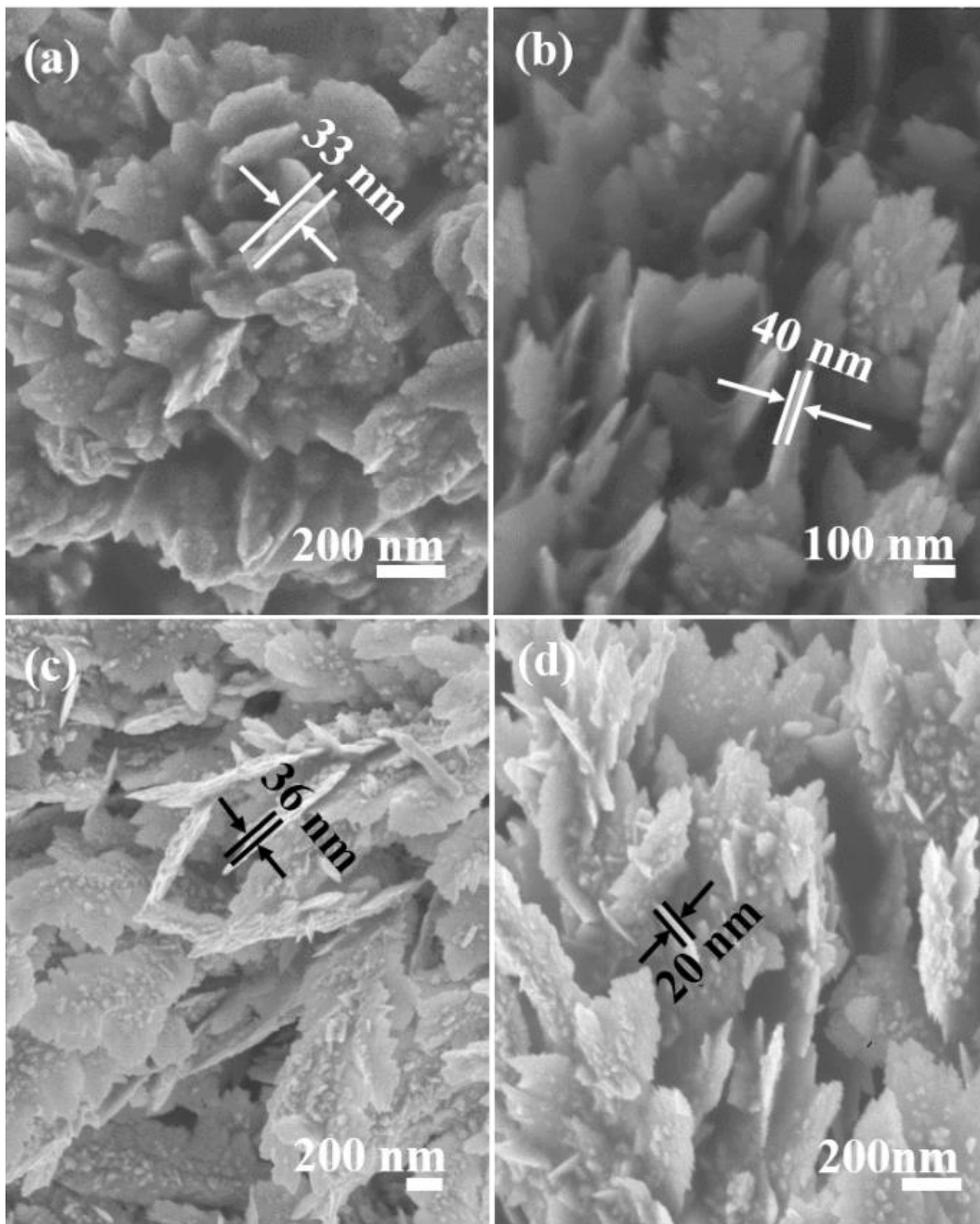


Fig. S3 The thickness of Pt-Cu NFs.

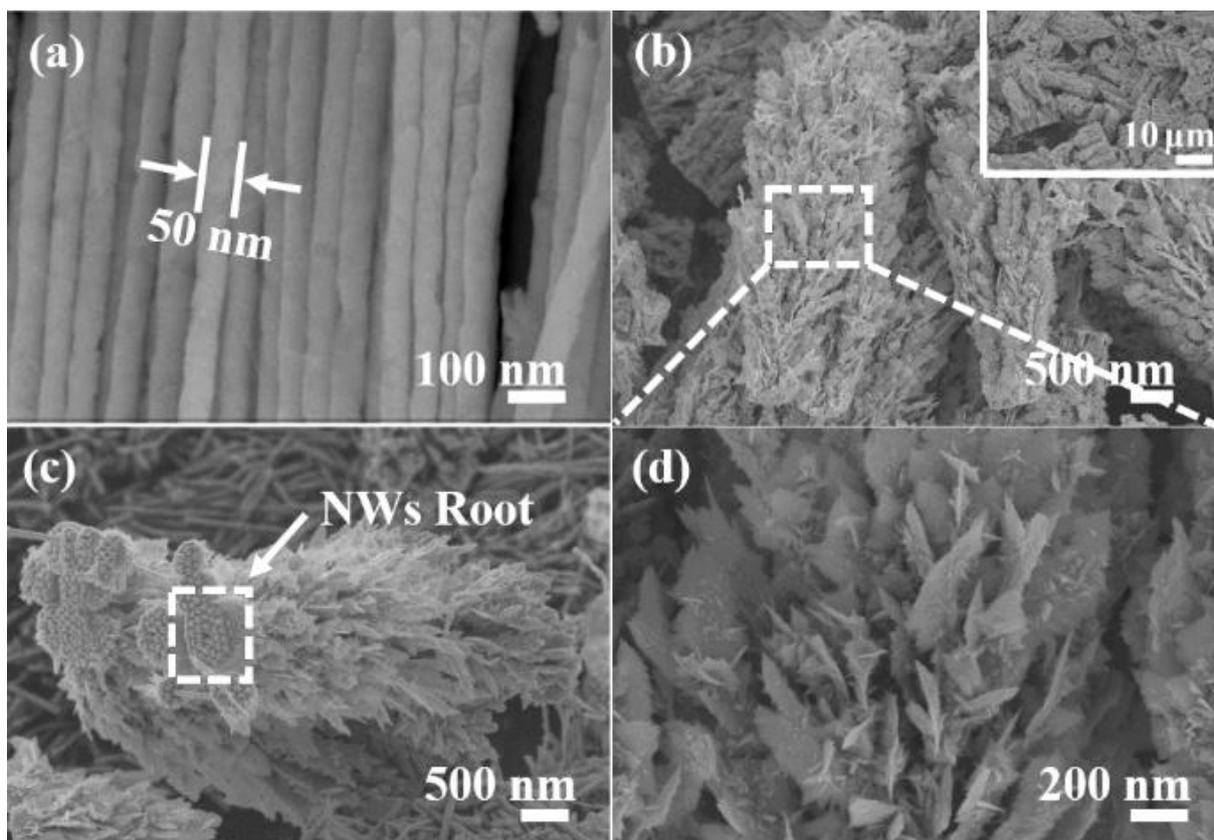


Fig. S4 The SEM images of Pt-Cu NWs and Pt-Cu NFs. (a) The side-view of Pt-Cu NWs before modification. (b) and (c) The Pt-Cu NFs. (d), The magnified side-view SEM image of the blades from dashed rectangle in (b).

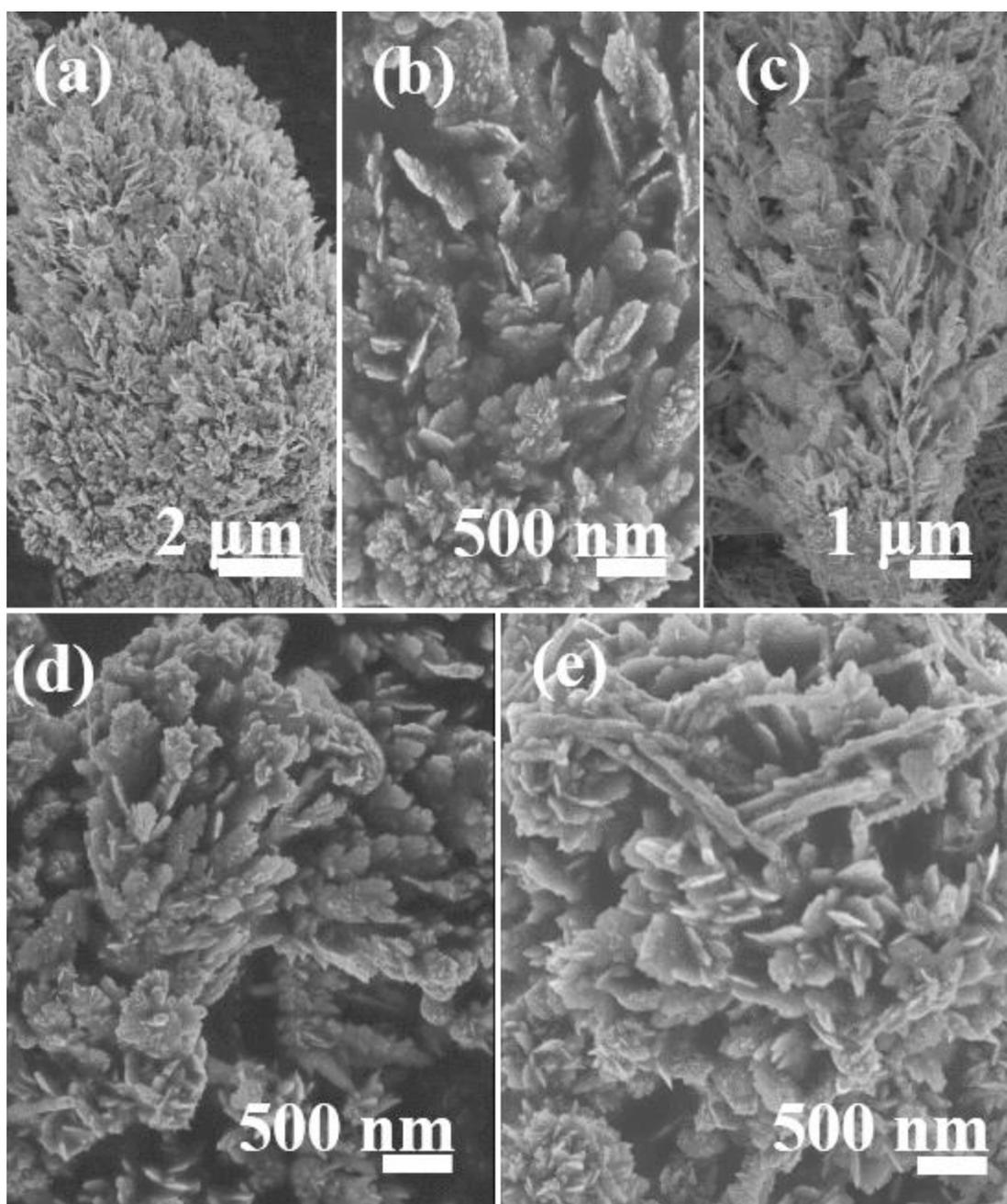


Fig. S5 The Pt-Cu NFs obtained from NWs with the diameters (a) 40 nm, (b) 55 nm, (c) 60 nm, (d) 80 nm and (e) 90 nm, respectively.

y.

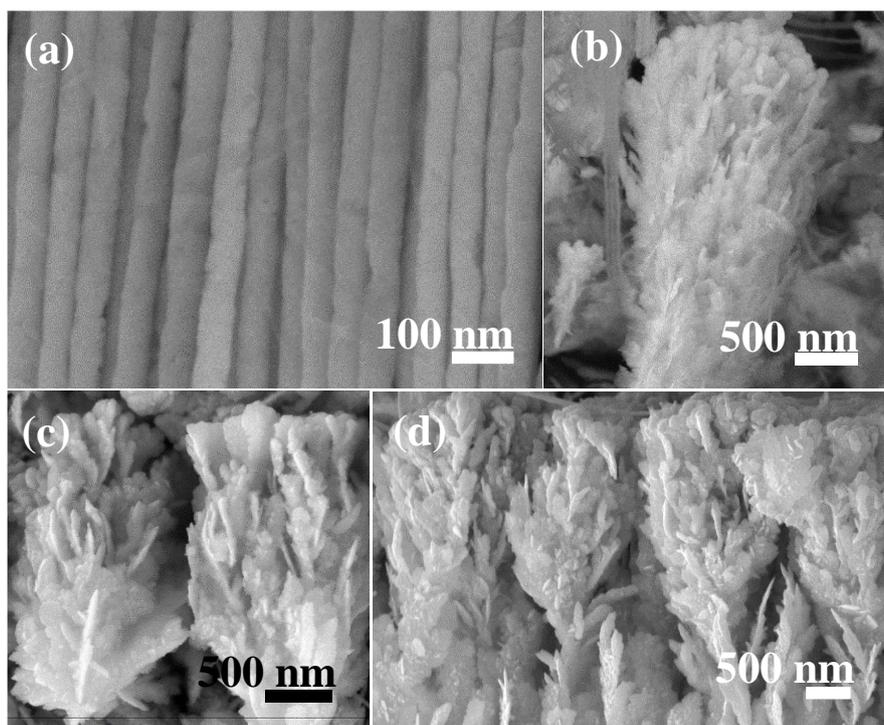


Fig. S6 The SEM images of Pt-Cu NFs modified in various etching solution of (b) 0.3M CuCl_2 , (c) 20% HNO_3 and (d) 0.3M NaOH , respectively.

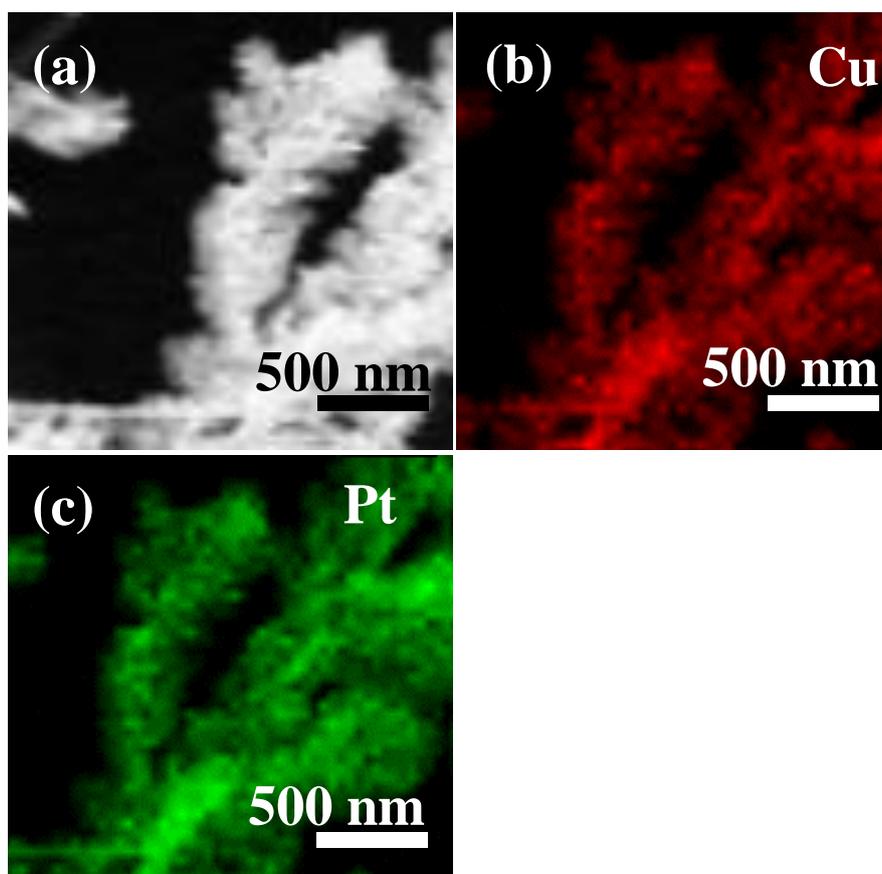


Fig. S7 The elemental mapping of representative Pt-Cu NFs. (a) TEM image. (b) and (c) the elemental mapping image of Cu and Pt.

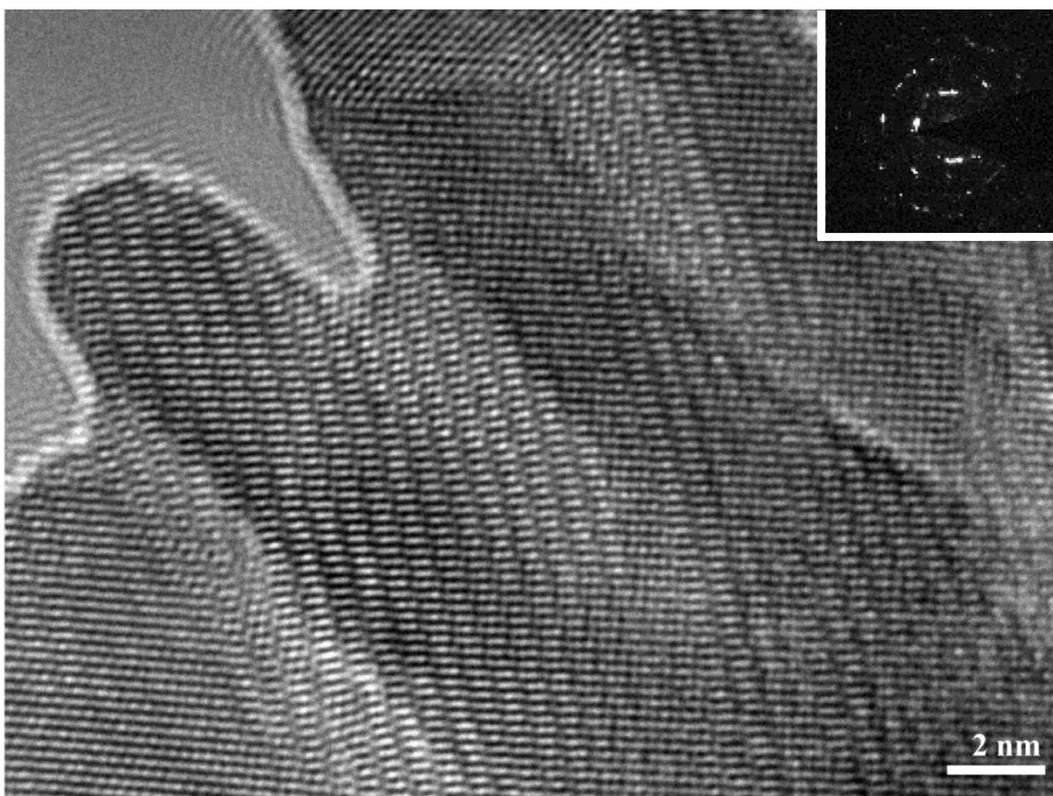


Fig. S8 A HRTEM image of Pt-Cu superlattice NFs, which is taken from Fig. 3b in the text

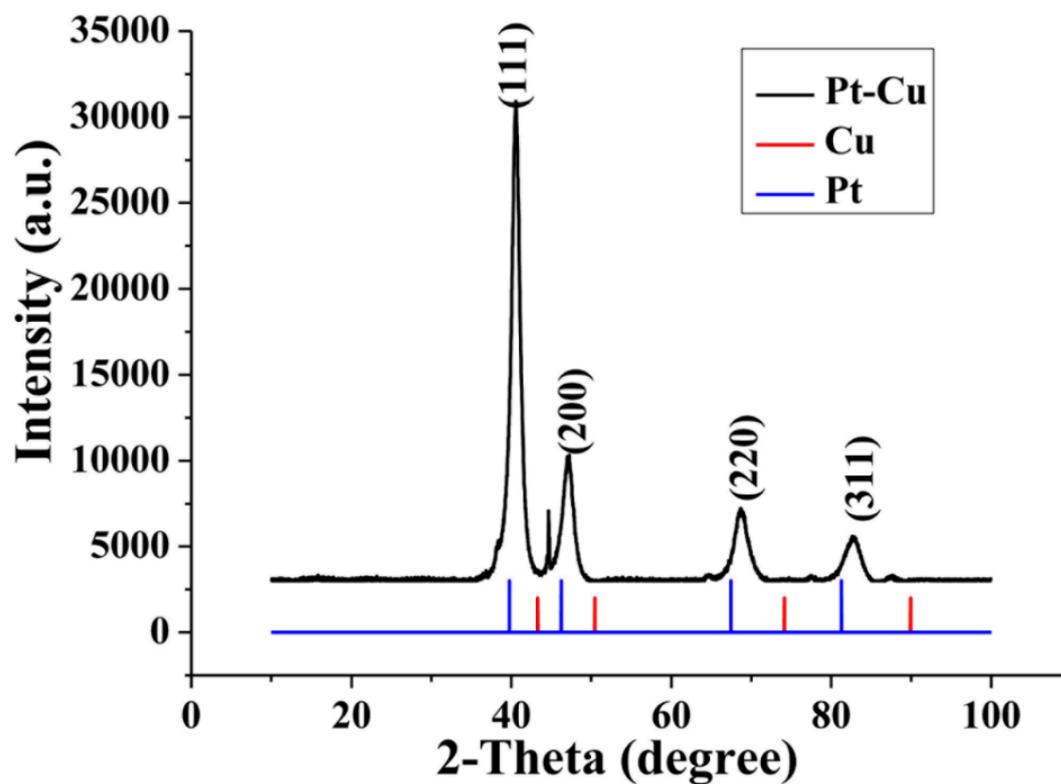


Fig. S9 An X-ray diffraction pattern of Pt-Cu NWs.

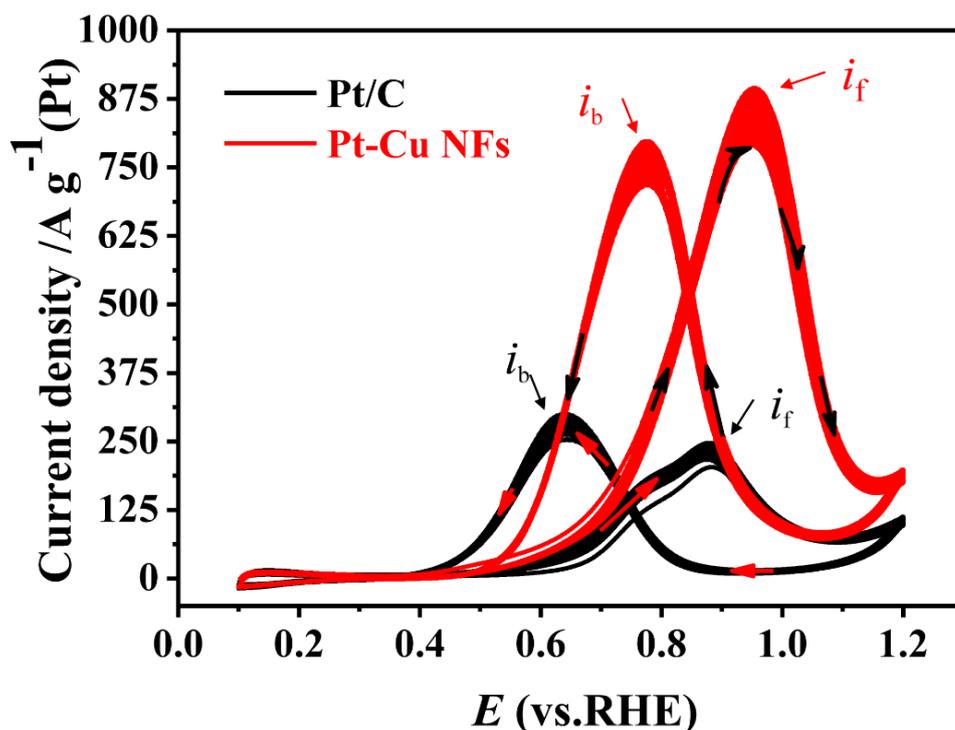


Fig. S10 The CV curves in 1 M CH₃OH + 0.5 M H₂SO₄ at 50 mV s⁻¹ (black for commercial Pt/C, red for Pt-Cu NFs) from 1st to 100th.

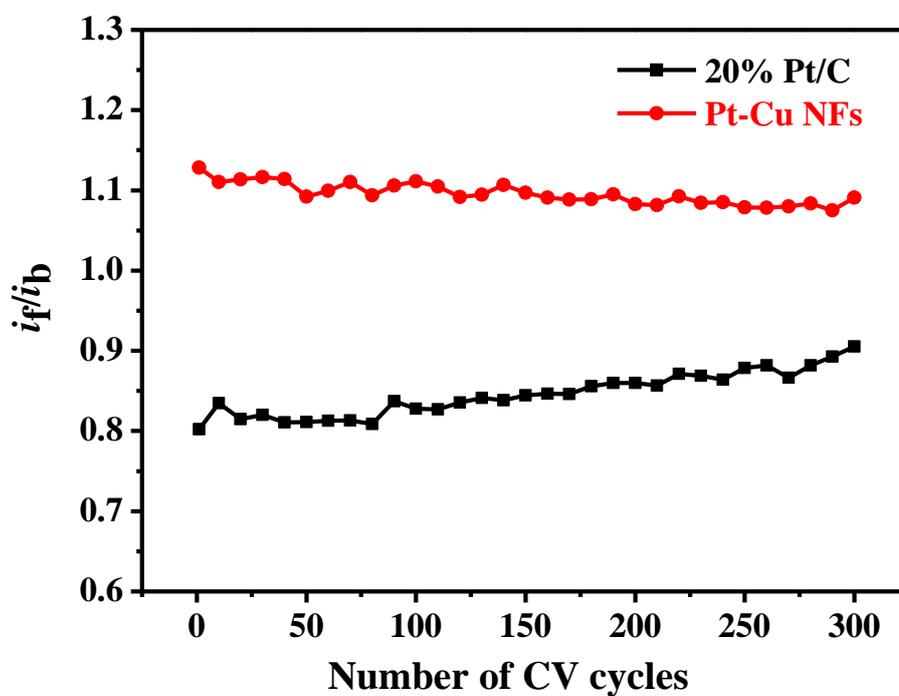


Fig. S11 The plots of the i_f / i_b vs CV cycles.

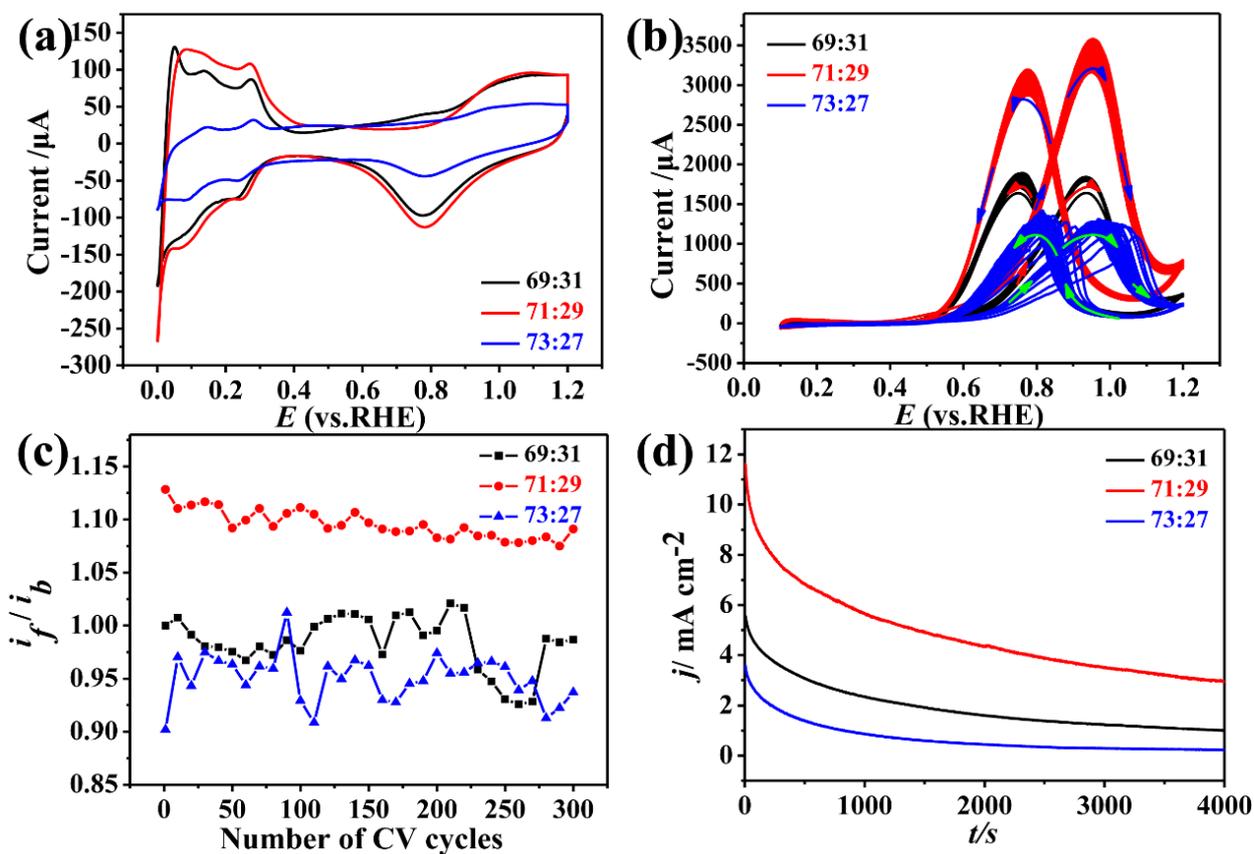


Fig. S12 The CV curves of Pt-Cu NFs with various Pt/Cu atomic ratios which are 69:31 (black), 71:29 (red) and 73:27 (blue), respectively. CV plots were obtained (a) for all the cycles in 0.5 M H₂SO₄ solution and (b) from 1st to the 100th cycle in 1 M CH₃OH + 0.5 M H₂SO₄ at 50 mV s⁻¹. (c), The plots of the i_f/i_b vs CV cycles. (d), The CA curves of the Pt-Cu NFs with Pt/Cu atomic ratios which are 69:31 (black), 71:29 (red) and 73:27 (blue) measured in 1 M CH₃OH + 0.5 M H₂SO₄.

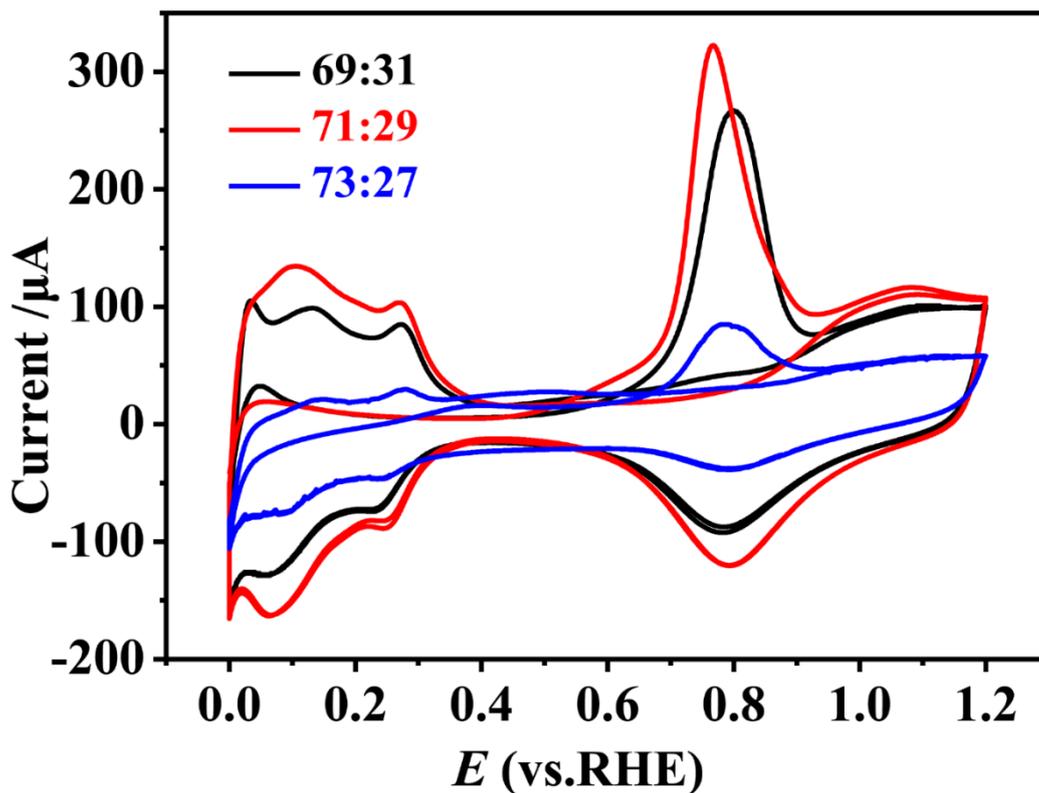


Fig. S13 The CO stripping measurements of Pt-Cu NFs catalysts with various Pt/Cu atomic ratios which are 69:31 (black), 71:29 (red) and 73:27 (blue), respectively, in 0.5 M H₂SO₄ at 50 mVs⁻¹ at room temperature.

3. References

- 1 H. Masuda and K. Fukuda, *Science*, 1995, **268**, 1466-1468.
- 2 D. Yang, L. Valentín, J. Carpena, W. Otaño, O. Resto and L. F. Fonseca, *Small*, 2013, **9**, 188-192.
- 3 D. Yang, J. Carpena-Núñez, L. F. Fonseca, A. Biaggi-Labiosa and G. W. Hunter, *Sci. Rep.-UK*, 2014, **4**, 3773.
- 4 S. Sun, G. Zhang, D. Geng, Y. Chen, R. Li, M. Cai and X. Sun, *Angew. Chem.*, 2011, **123**, 442-446.
- 5 T. J. Schmidt, H. A. Gasteiger, G. D. Stäb, P. M. Urban, D. M. Kolb and R. J. Behm, *J. Electrochem. Soc.*, 1998, **145**, 2354-2358.