Supplementary information for

Selective electrochemical reduction of CO_2 to adjustable alcohol products by an organically doped alloy catalyst

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1. Materials and Instruments

All reagents except for PYD were used as received.

The synthesis and characterization of PYD were described in reference 25.

Potentiostatic electrolysis and linear sweep voltammograms were performed using a CHI 660C electrochemical Station (CH Instruments, Inc. Austin, USA).

Liquid phase products were analyzed by ^{1}H-NMR spectra recorded on an Ascend 400 (400 MHz, Bruker, Germany) spectrometer in $CO(CD_3)_2$ with Me_4Si as an internal standard.

The dopant amount in filtrate were determined by a high performance liquid chromatography (HPLC) instrument (DIONEX Ultimate 3000 pump) equipped with a UV (RS Variable Wavelength) detector.

Microstructure and EDX mapping were analyzed using Hitachi S-4800 field emission Scanning Electron Microscope (FE-SEM) equipped with an energy dispersive X-ray fluorescence spectrometer (EDX, Oxford; UK) and TECNAI G2F30 Transmission Electron Microscope (TEM).

X-ray diffraction (XRD) patterns were recorded by a Ultima IV X-ray powder diffractometer using Cu Kα radiation (k= 1.5406 Å).

UV-vis spectra were recorded on Agilent 8453 UV-visible spectroscopy system.

ICP data was detected by IRIS II XSP, Thermo Electron Corporation.

2. General methods

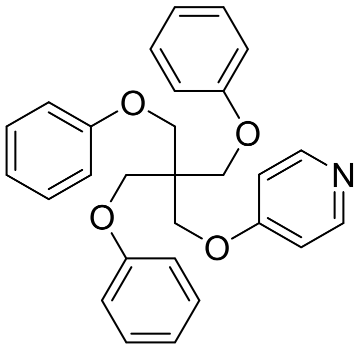
Synthesis of [PYD]@Cu-Pt: For entrapment of PYD to produce [PYD]@Cu-Pt, a 50 mL water solution of 0.9 g of sodium dodecyl sulphate, 24 mg PYD, 0.52 g $CuCl_2 \cdot 2H_2O$ and 0.653 g K_2PtCl_4 was stirred at 550 rpm for a few minutes, until all reagents were fully dissolved. Then 0.5 g of zinc powder was added to the solution, and the combined slurry was stirred for another 6 hours. The precipitate, [PYD]@Cu–Pt, was filtered and washed with 10 mL HCl 1 M to remove zinc residues and metal salts, followed by another wash with 20 mL distilled water for three times and then dried under vacuum for 6 hours. Fine and dark powder was achieved after filtration and drying (Figure S2).

Synthesis of Cu-Pt alloy: Cu-Pt alloy was prepared in the same way except for the absence of PYD in reducing solution. Fine and dark powder was achieved after filtration and drying (Figure S3).

Synthesis of pure Cu NPs: pure Cu NPs (Figure S4) was prepared in the same way except for the absence of K_2PtCl_4 and PYD in reducing solution.

Synthesis of [PYD]@Pt: K_2PtCl_4 (5.6 mmol) in 125 ml of distilled water was poured into a stirred solution of sodium dodecyl sulfate (3.1 mmol) and PYD (0.03 mmol) in 50 ml of water. After stirring, NaH_2PO_2 was slowly added, and the combined black slurry was stirred for 2 h. The precipitate was filtered, washed with water and dried over night. Dark powder was achieved, then pressed into coin (D= 1cm，Figure S5) and used as cathode.

Synthesis of pure Pt NPs: pure Pt NPs (Figure S6) was prepared in the same way as [PYD]@Pt except for the absence of PYD in reducing solution.



4-(3-phenoxy-2,2-bis(phenoxymethyl)propoxy)pyridine

Figure S1. Molecular structure of PYD.

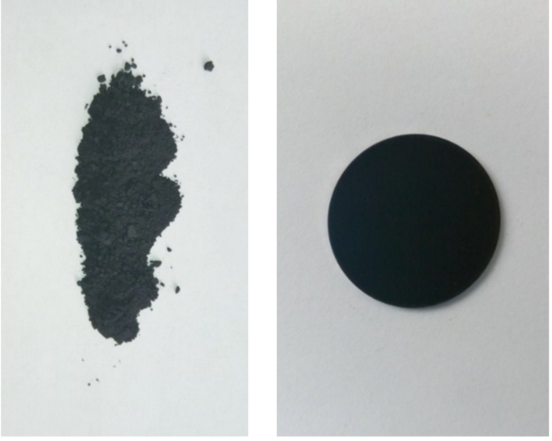


Figure S2. [PYD]@Cu-Pt composite before (left) and after (right) press.

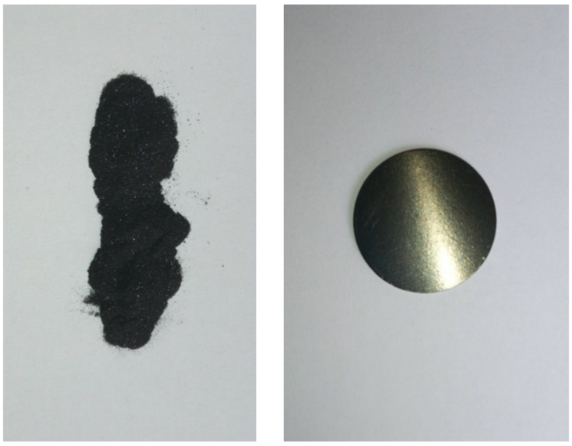


Figure S3. Cu-Pt alloy before (left) and after (right) press.

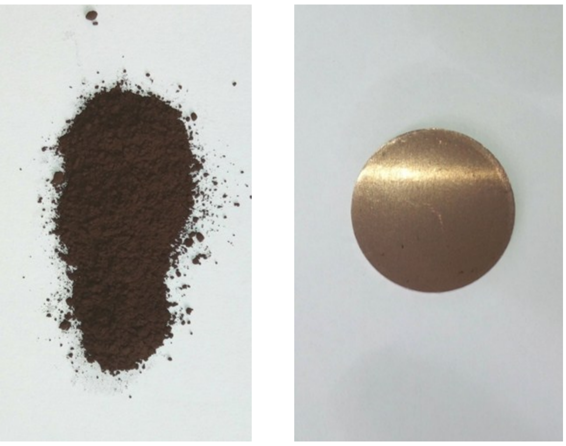


Figure S4. Pure Cu NPs before (left) and after (right) press.

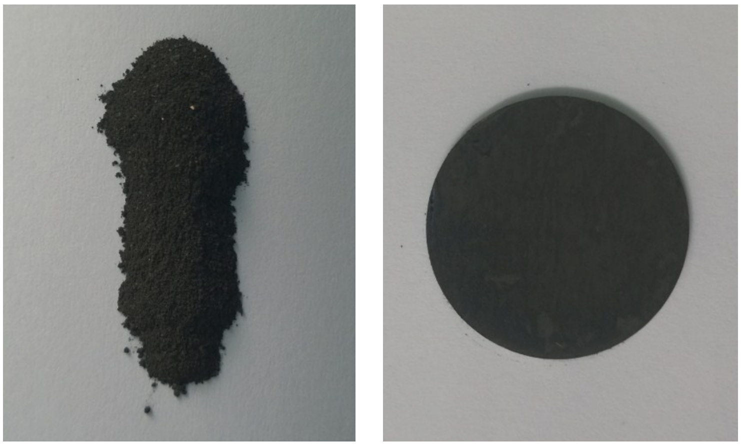


Figure S5. [PYD]@Pt before (left) and after (right) press.

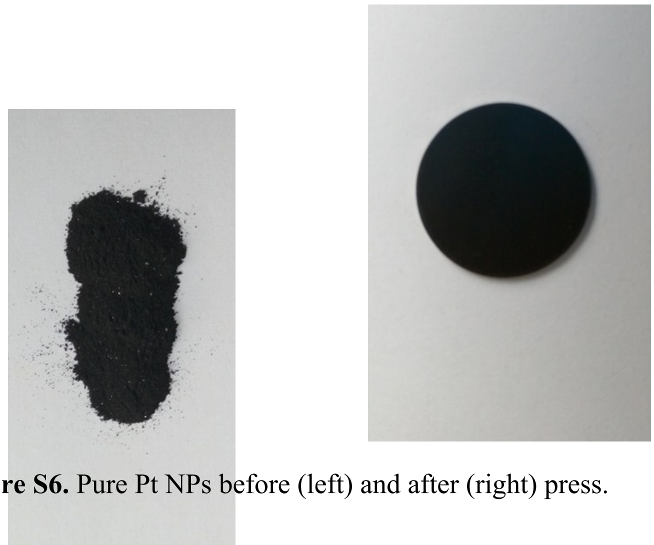


Figure S6. Pure Pt NPs before (left) and after (right) press.

Potentiostatic CO_2 reduction procedure: Powder of [PYD]@Cu-Pt (or other powder) was compacted into coin （D= 1cm，Figure 1）and used as cathode to test the catalytic activity for CO_2 electroreduction. It was performed with a conventional three-electrode electrochemical H-type cell, in which a piece of Nafion®117 membrane was used as a separator. A saturated calomel electrode (SCE) saturated with KCl was the reference electrode, and a Pt foil (99.999% purity, 10 mm × 10 mm) was the counter electrode. An aqueous electrolyte of 10 mL 0.5 M KCl was used as electrolyte, which was bubbled with 1.0 atm CO_2 (99.995%) to be saturated with CO_2. The pH was preserved at 5.4. The potential was from -0.5 V to -1.3 V, and charge used was 50 C.

Linear sweep voltammograms were recorded in an undivided cell. A saturated calomel electrode (SCE) saturated with KCl was the reference electrode, and a Pt foil (99.999% purity, 10 mm × 10 mm) was the counter electrode. An aqueous electrolyte of 10 mL 0.5 M KCl was used as electrolyte, which was bubbled with 1.0 atm N_2 or CO_2 (99.995%). The pH was preserved at 5.4. Scan rate was 0.1 V s^{-1}.

3. TEM and EDAX spectra of [PYD]@Cu-Pt composite

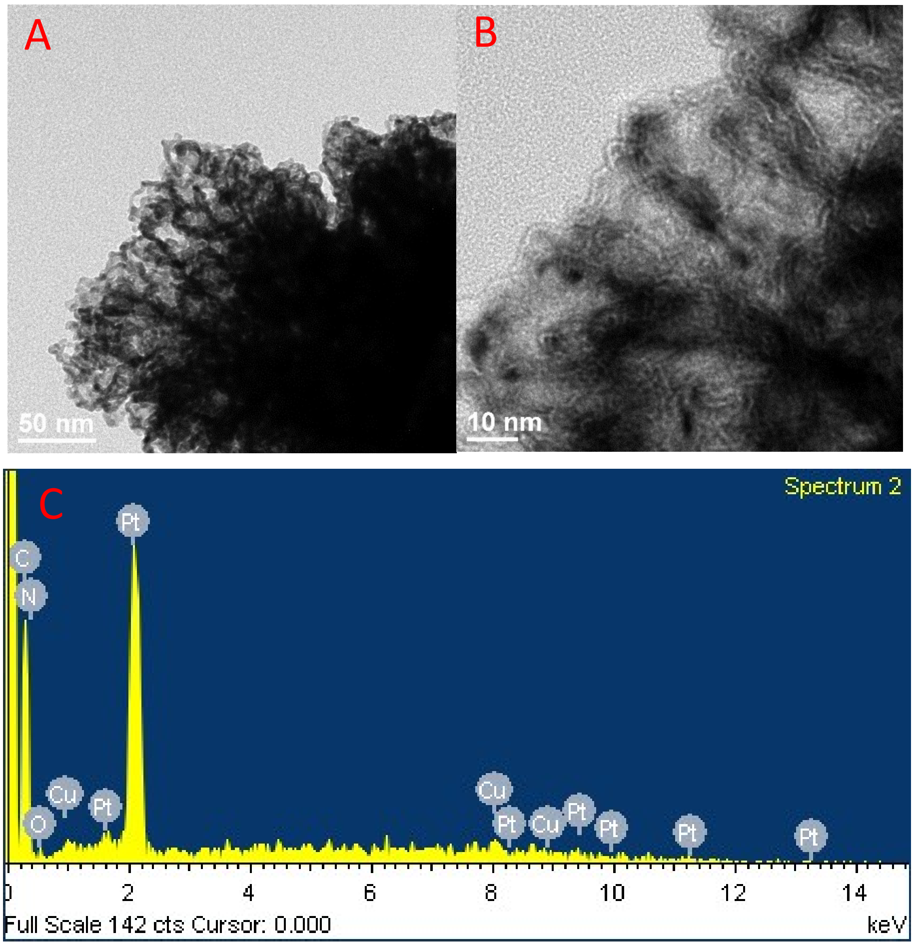


Figure S7. The TEM patterns of [PYD]@Cu-Pt composite with different scale bar, A (50 nm), B (10 nm); C: EDX spectrum of [PYD]@Cu-Pt composite, which showed signals corresponding to copper, platinum, nitrogen, carbon and oxygen.

4. Differences between physical adsorption and entrapment

FT-IR further explored the difference between entrapment and adsorption. After physical adsorption in PYD solution, FT-IR spectra of Cu-Pt alloy (d) was almost identical to pure PYD (c). In [PYD]@Cu-Pt composite, PYD could not be detected by FT-IR spectra (a), but the presence of dopant could be confirmed by other characterization methods, like XRD or EDX. If (d) was washed with MeCN, there was also no trace of PYD in FT-IR spectra (b), indicating that this adsorption is highly unstable. In summary, entrapment was fundamentally different from adsorption and much more stable.

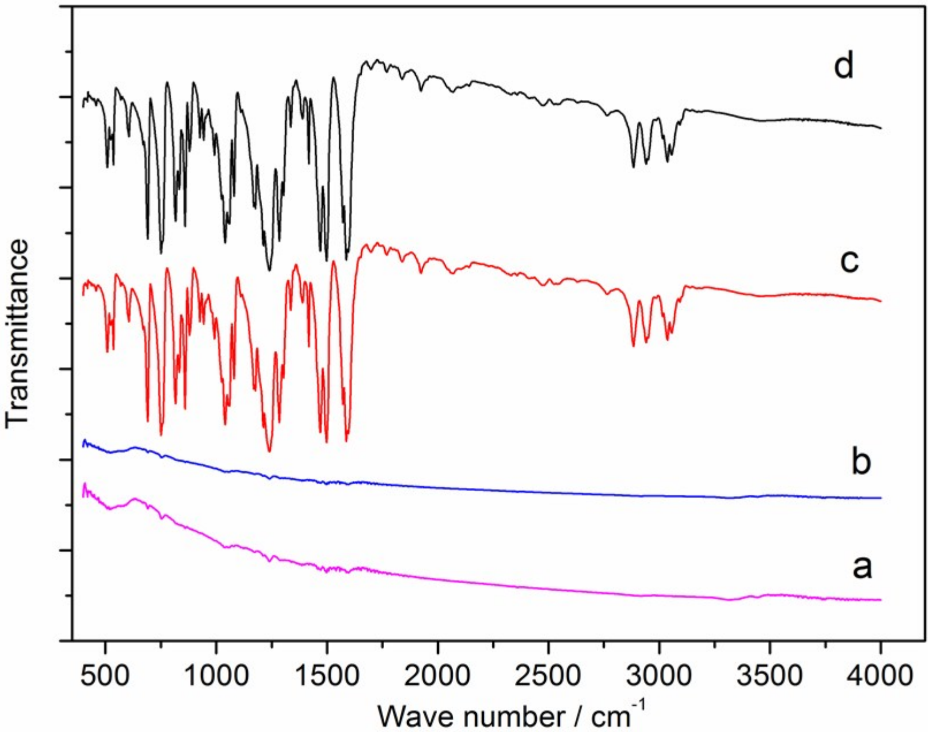
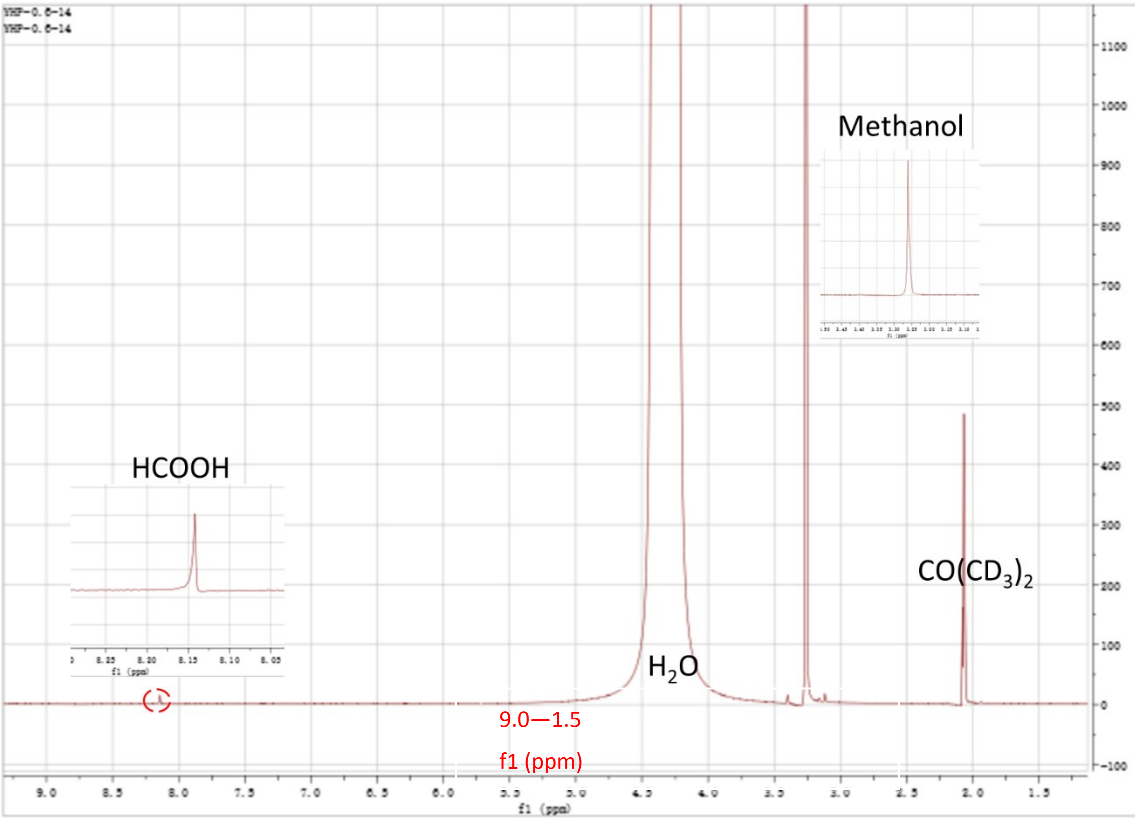
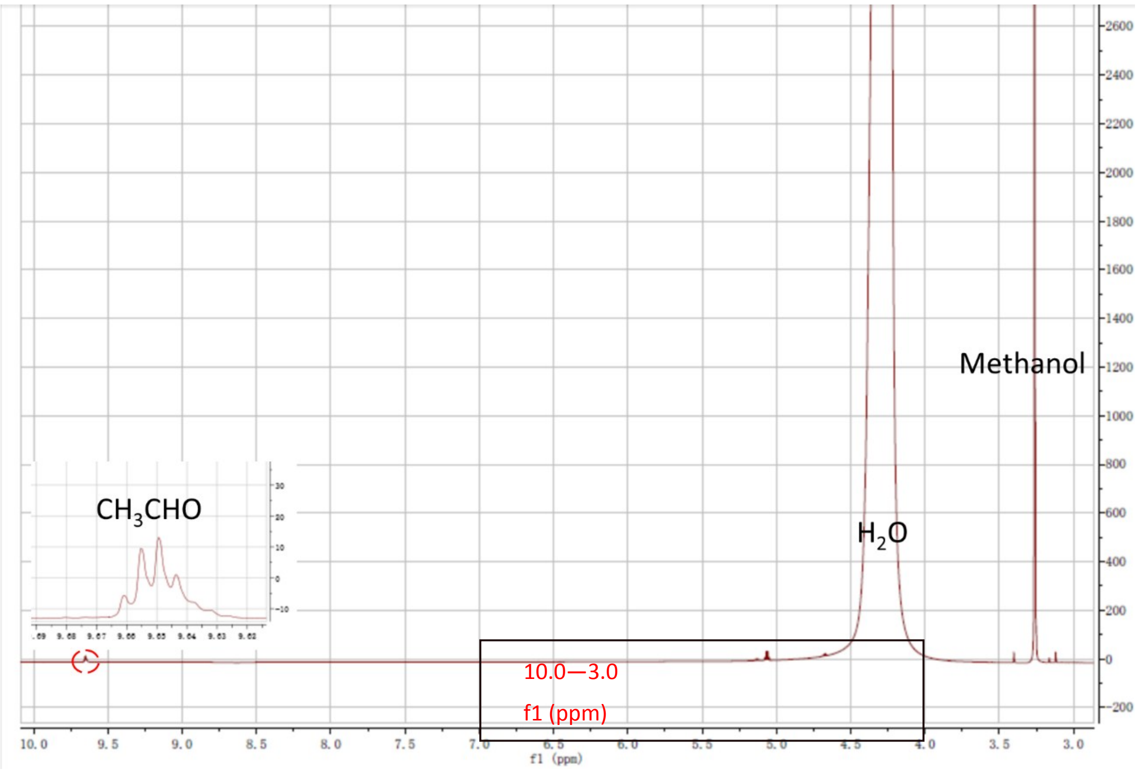


Figure S8. FT-IR spectra of [PYD]@Cu-Pt (a), pure PYD (c), Cu-Pt alloy after physical adsorption (d), (d) after washed with MeCN (b).

5. Characterization of products





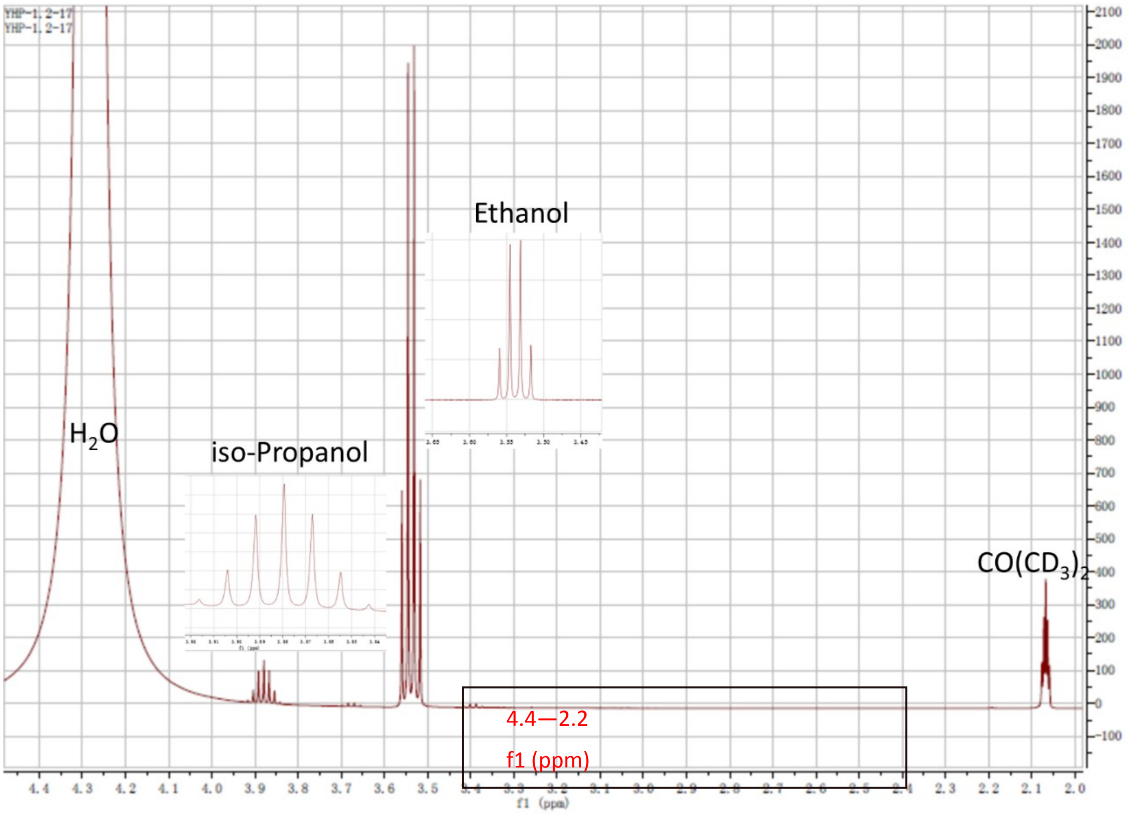


Figure S9. ^{1}H NMR spectrum of products obtained at [PYD]@Cu-Pt with -0.6 V (up), -0.7 V (middle) and -1.2 V vs SCE (down) cathode potential.

6. Stability and reusability test of [PYD]@Cu-Pt cathode

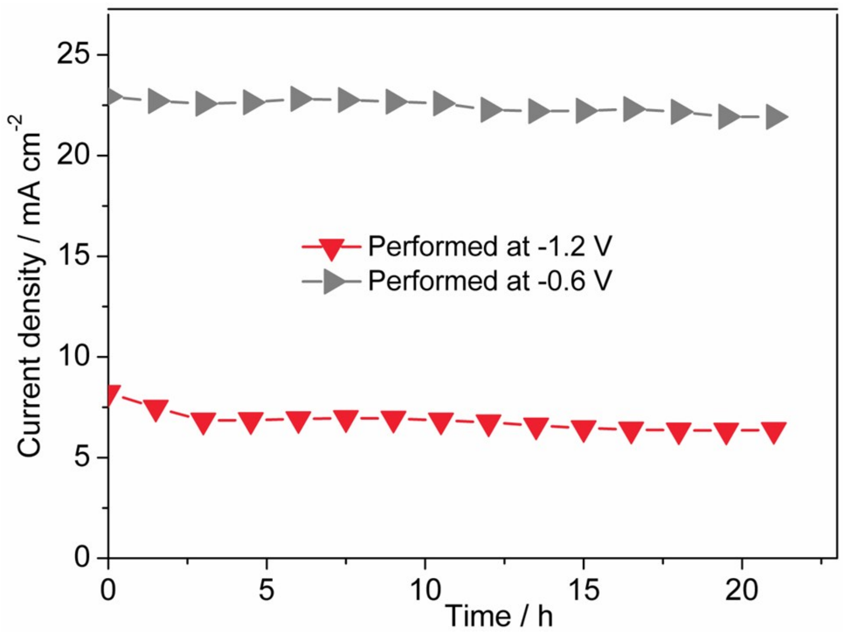


Figure S10. Long-term running of [PYD]@Cu-Pt performed at -0.6 V and -1.2 V vs SCE.

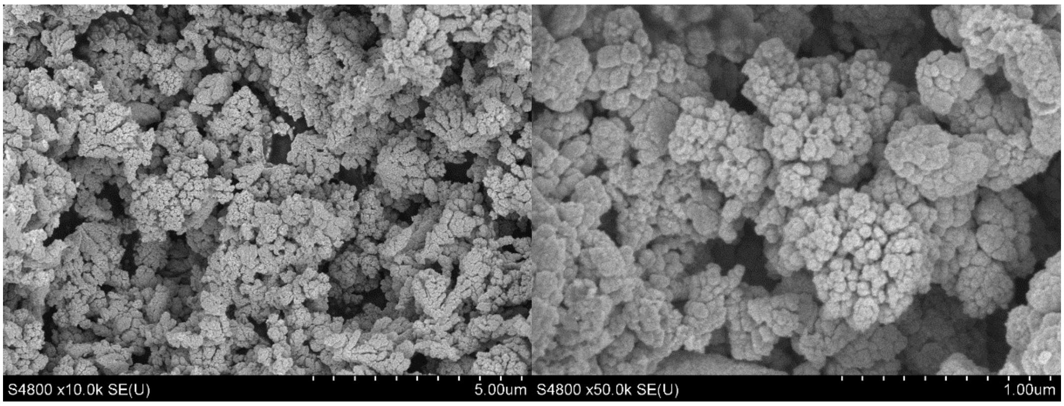


Figure S11. FE-SEM patterns of [PYD]@Cu-Pt after long-time running and reuse with different magnification, left (25k), right (50k). [PYD]@Cu-Pt remained its porous structure after reuse.

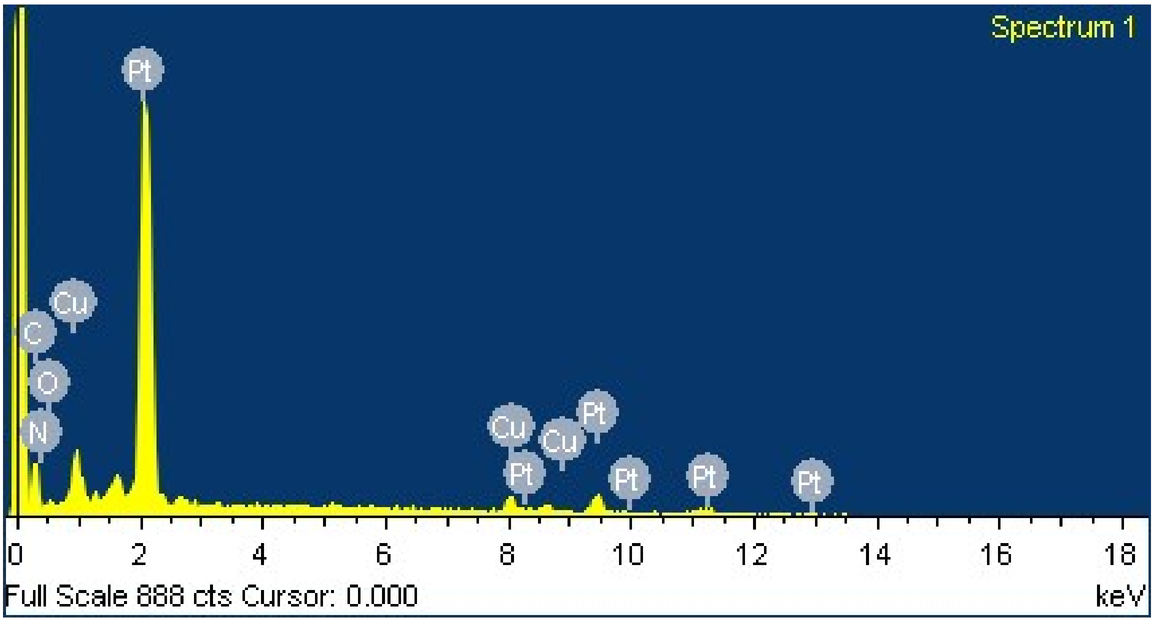


Figure S12. EDX patterns of [PYD]@Cu-Pt after reuse show signals corresponding to copper, platinum, nitrogen, carbon and oxygen.

7. Characterization of Cu NPs, Pt NPs, Cu-Pt alloy and [PYD]@Pt.

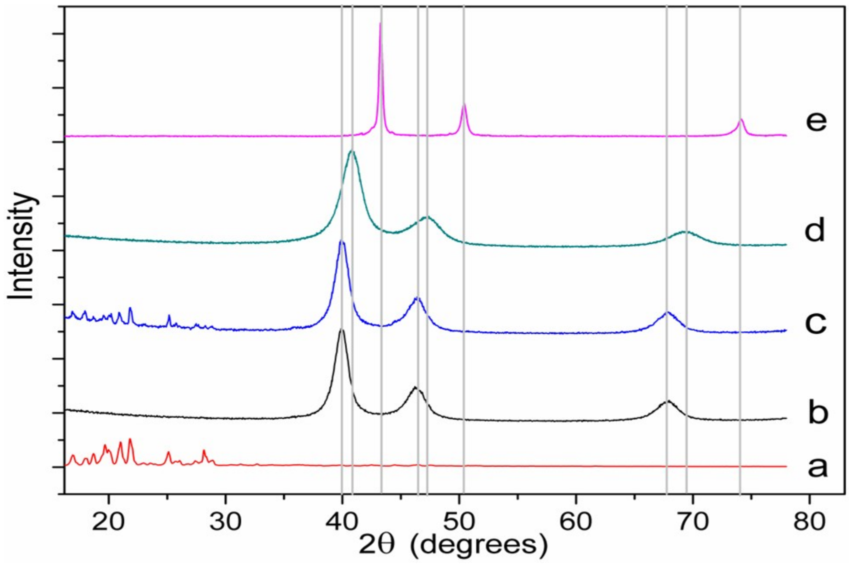


Figure S13. XRD patterns of pure PYD (a), Pt NPs (b), [PYD]@Pt (c), Cu-Pt alloy (d), and Cu NPs (e).

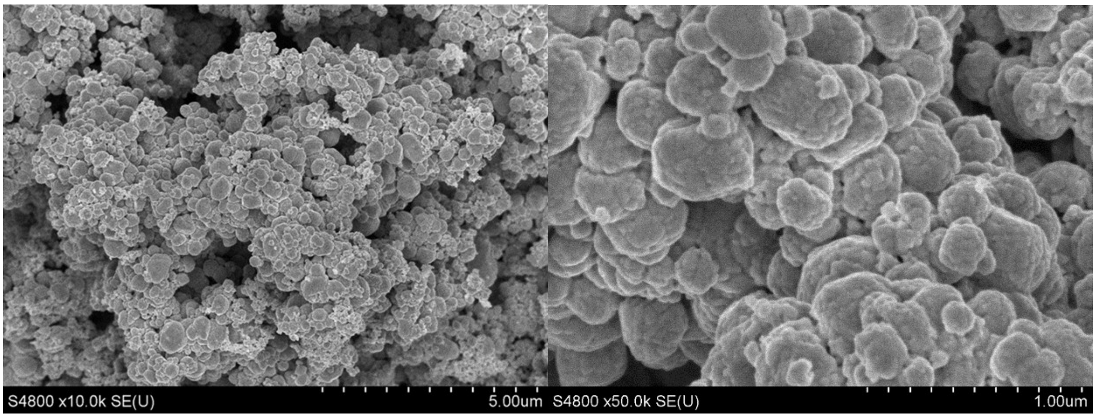


Figure S14. FE-SEM patterns of Cu NPs with different magnification, left (10k), right (50k).

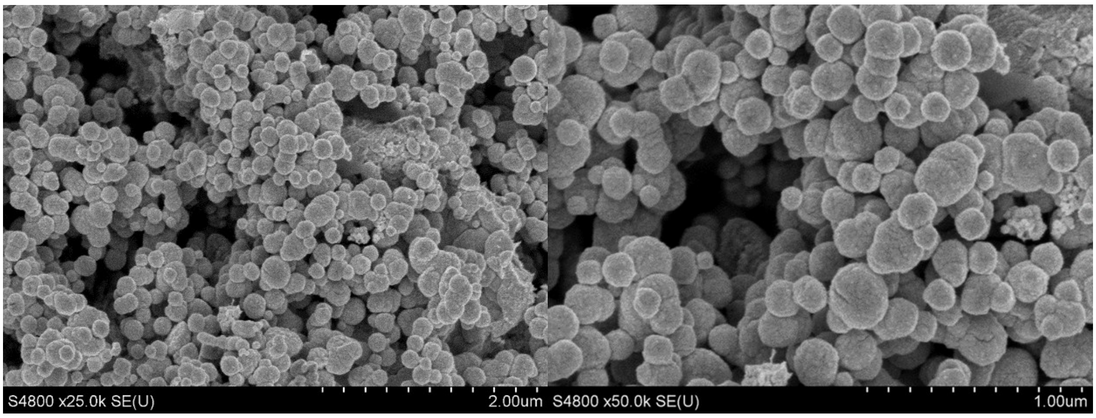


Figure S15. FE-SEM patterns of Pt NPs with different magnification, left (25k), right (50k).

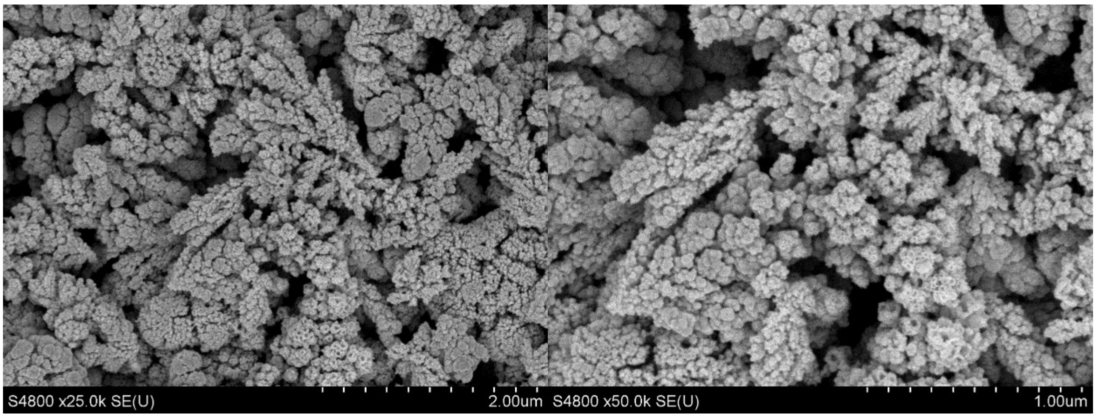


Figure S16. FE-SEM patterns of Cu-Pt alloy with different magnification, left (25k), right (50k).

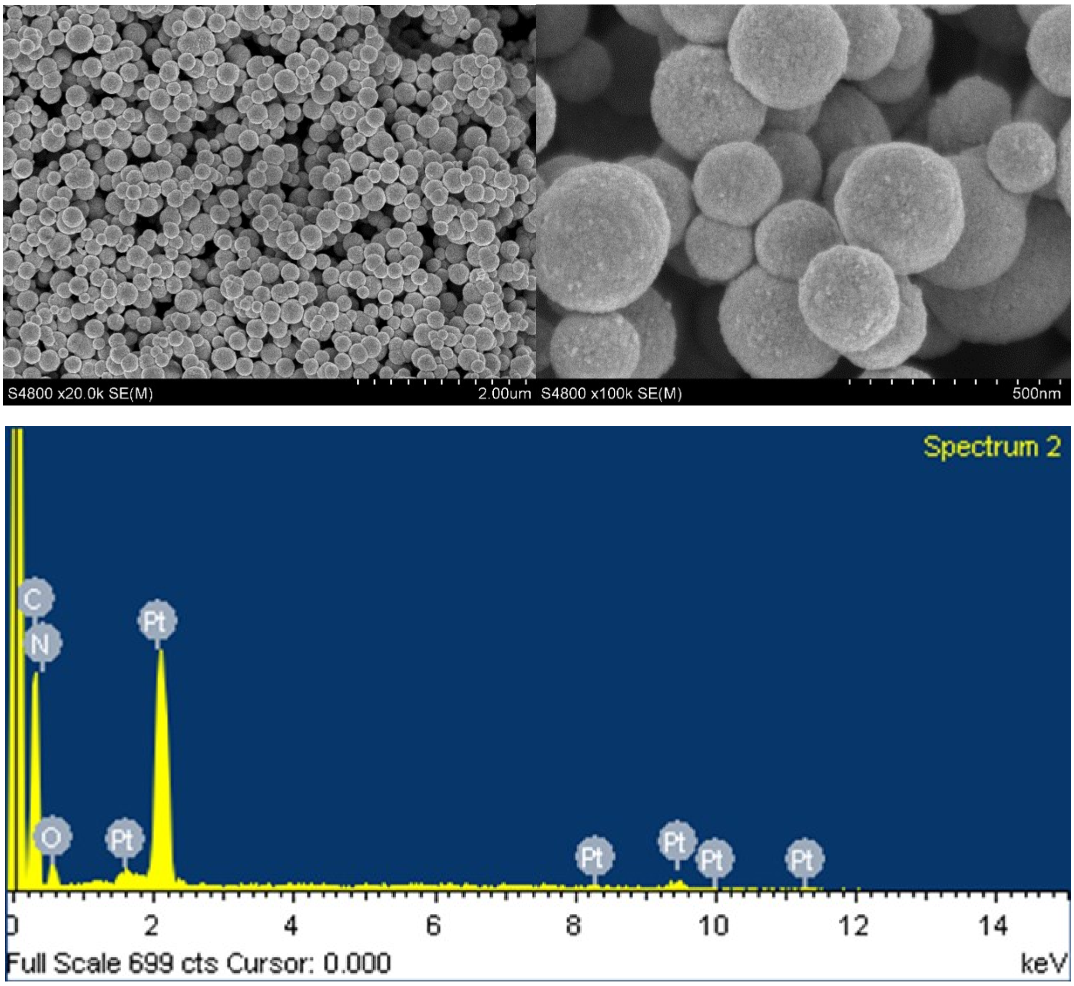


Figure S17. FE-SEM patterns of [PYD]@Pt (up) with different magnification, left (20k), right (100k); EDX patterns of [PYD]@Pt (down) show signals corresponding to platinum, nitrogen, carbon and oxygen.

8. LSV scans recorded at different cathodes

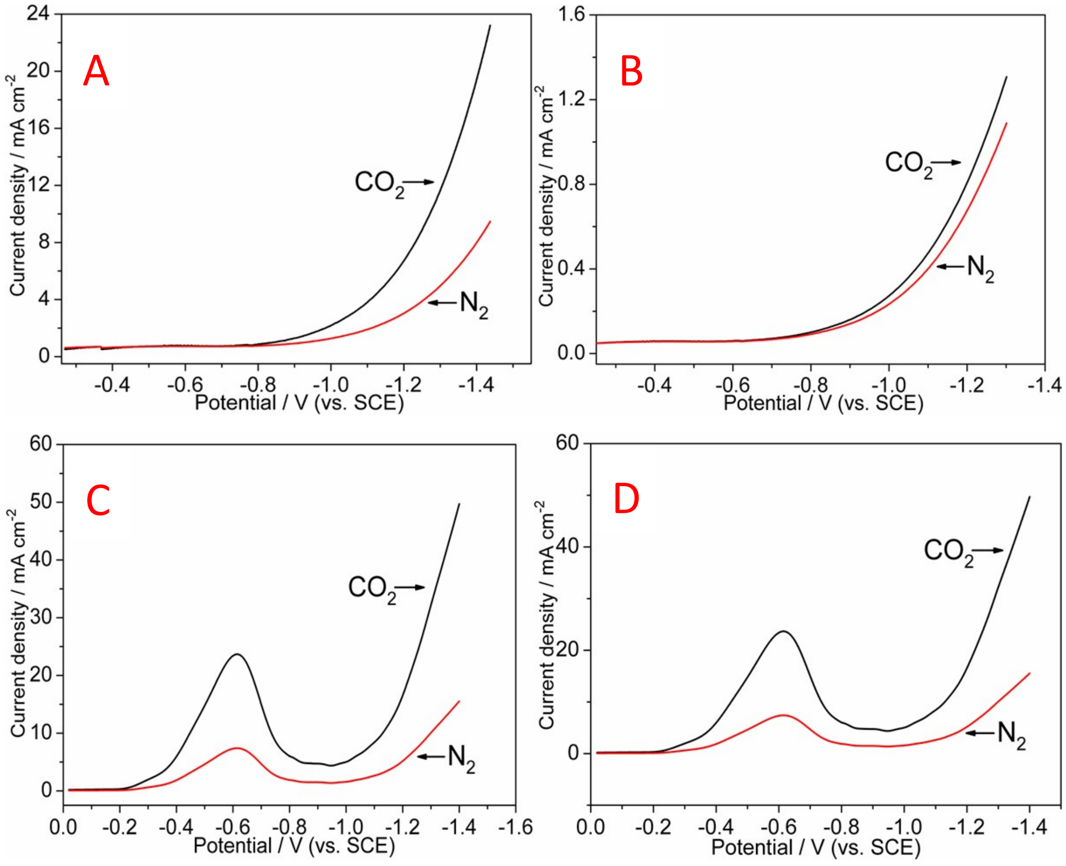


Figure S18. Linear sweep voltammograms recorded at a sweep rate of 0.1 V s^{-1} in 10 mL 0.5 M KCl solution at Cu-Pd alloy (A), Cu NPs (B), [PYD]@Pt pure (C) and [PYD]@Cu-Pt electrode (D). Black: saturated of CO_2, red: saturated of N_2. pH: 5.4. Temperature: 25 °C.

9. Confirmation of active sites for corresponding alcohols

Table S1. Electrochemical reduction of CO_2 on different cathodes.[a]

Entry	Cathode	Potential / V vs. SCE	MeOH FE[b]/ %	EtOH (PrOH)[b] FE[b]/ %
1	[PYD]@Cu-Pt	-0.6	37	-
		-1.2	-	24 (1)
2	[PYD]@Pt	-0.6	24	-
		-1.2	-	-
3	Cu-Pt alloy	-0.6	-	-
		-1.2	-	21 (2)
4	Cu NPs	-0.6	-	-
		-1.2	-	1
5	Pt NPs	-0.6	-	-
		-1.2	-	-

[a] Anode: Pt foil, 10 mL CO_2-saturated 0.5 M KCl solution, charge: 100 C, room temperature. [b] Determined by ^1H NMR.