Electronic Supplementary Information

Galvanic replacement mediated 3D porous PtCu nano-frames

for enhanced ethylene glycol oxidation

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Experimental section

Materials

Potassium chloroplatinate, cetylpyridinium chloride monohydrate (CPC), sodium borohydride, ascorbic acid (AA) and Nafion were purchased from Sigma–Aldrich. Cu NWs were from Xianfeng Nano Technology Co., Ltd. The deionized water (DIW, 18.2 M Ω) was used for the synthesis.

Synthesis of PtNPs

To synthesize PtNPs, the K_2PtCl_6 (24 mM) dispersed in suitable amount of water. The diluted sodium borohydride solution slowly dropped into the K_2PtCl_6 with the violent shock. Then the product was wash/centrifugated three times to obtain the PtNPs.

Synthesis of 3D P-PtCu_{5.3} NFs

In a typical synthesis, 10 mg Cu NWs were dispersed in the 0.02 g mL⁻¹ CPC solution followed by 30 min ultrasonication. The mixture solution was kept in a 50 mL glass bottle at 65 °C for 10 min. Then 100 μ L K₂PtCl₆ (24 mM) was slowly dropped into the bottle under magnetic stirring. Two minutes later, 400 μ L of 100 mM AA was injected and reacted for 30 minutes. The products were wash/centrifugated three times with ethanol and the 3D P-PtCu_{5,3} NFs can be obtained.

Synthesis of 3D P-PtCu_{5.2} NFs

In the synthesis of 3D P-PtCu_{5.2} NFs, the reaction process is similar to the above while the amount of K_2 PtCl₆ is 120 μ L (24 mM). The products were wash/centrifugated three times with ethanol and the P-PtCu_{5.2} NFs can be obtained.

Structural characterizations

TEM images were obtained on JEOL-2100F. HAADF-STEM and EDX elemental mapping images were characterization by JEM-ARM 200F. XRD data were acquireed from X-ray diffractometer (Rigaku SmartLab) using Cu K α (γ =1.54178 A) radiation. ESCALAB 250Xi XPS

system with Mg as the excitation source was used to obtain the XPS results. ICP-MS data was received from Optima 7300 DV.

Electrochemical measurements

EGEO tests were carried out on a CHI 660E electrochemical workstation (CH Instruments, Inc., Shanghai) with a standard three-electrode system at room temperature. Glassy Carbon Electrode (GCE) (5 mm in diameter) was polished with 1.0 and 0.3 μ m alumina sequentially. The moderate Pt or PtCu catalysts were added to the mixture of Nafion and isopropanol solution (volume ratio=1/9) and to form an ink by sonicating for 30 min. The concentration of Pt content of the cataysts was measured by ICP-MS. The loading amount of Pt on the GCE for PtNPs, 3D P-PtCu_{5.3} and 3D P-PtCu_{5.2} were 46.8 μ g/cm², 42 μ g/cm², 54.8 μ g/cm², respectively. The aqueous solution (0.5 M H₂SO₄) was used as the electrolyte. The Ag/AgCl electrode and graphite rod were used as the reference electrode and counter electrode, respectively. All the measured potentials vs Ag/AgCl were converted to reversible hydrogen electrode (RHE). The CV measurement was tested at a scan rate of 50 mV s⁻¹. EGEO test was studied in a N₂-saturated 0.5 M H₂SO₄ and 1 M EG mixed solution at room temperature with a sweep rate of 50 mV s⁻¹. The stability was tested by chronoamperometry at 1.0 V vs RHE.



Fig. S1. (A-D) The TEM images of the Cu NWs.



Fig. S2. (A-D) The TEM images of the 3D P-PtCu NFs.



Fig. S3. The TEM-EDX curves of the 3D P-PtCu $_{5.3}$ NFs.



Fig. S4. (A-C) The EDX-mapping images of the 3D P-PtCu NFs.



Fig. S5. The HAADF image of the 3D P-PtCu NFs. The green square is the selected area for the Fig. 1G.



Fig. S6 (A-H) TEM images of the PtCu nanorods obtained in the absence of CPC.



Fig. S7 (A-D) The HAADF image and the corresponding EDX-mapping images of the PtCu

nanorods obtained in the absence of CPC.



Fig. S8. (A-D) The TEM images of the PtCu NFs with long reaction time.



Fig. S9. The TEM image of the PtNPs (A) and the corresponding size distribution (B).



Fig. S10. (A) Ethylene glycol electro-oxidation activity for the three Pt-based catalysts based on ECSA; (B) The calculated specific activity of the three catalysts.

The specific activity of the 3D P-PtCu NFs and PtNPs were calculated based on ECSA which show the consistent results with the mass activity in the Fig. 4. Those results reveal the 3D P-PtCu_{5.3} NFs have good potential as ethylene glycol electro-oxidation catalysis.



Fig. S11. (A) The CV curves of the 3D P-PtCu_{5.3} NFs and PtNPs after stability test; (B) The ethylene glycol electro-oxidation activity based on ECSA and normalized loading amount of Pt.

Table S1. The chemical composition of Pt and Cu in 3D P-PtCu NFs obtained from the results of EDX, XPS and ICP-MS.

Sample	Element	Atomic	Atomic	Atomic
		percentage	percentage	percentage
		(EDX)	(XPS)	(ICP-MS)
P-PtCu _{5.3} NFs	Pt	6.370	3.99	4.2345237
	Cu	93.629	18.86	22.26430907
P-PtCu _{5.2} NFs	Pt	/	/	4.25639401
	Cu	/	/	22.0158125

Table S2. The ICP-MS data of the electrolyte before and after ethylene glycol electro-catalysis test.

Elements Solution	Pt	Cu		
0.5 M H ₂ SO ₄			ma/I	ICD MS
(before test)	0.0132	0.0150	ing/L	ICF-INIS
0.5 M H ₂ SO ₄				
(after test)	0.0056	1.6404		