

Electronic Supplementary Information

Restructuring gold nanocatalyst by an electrochemical treatment to recover its excellent H₂-evolving catalytic activity

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Supplementary

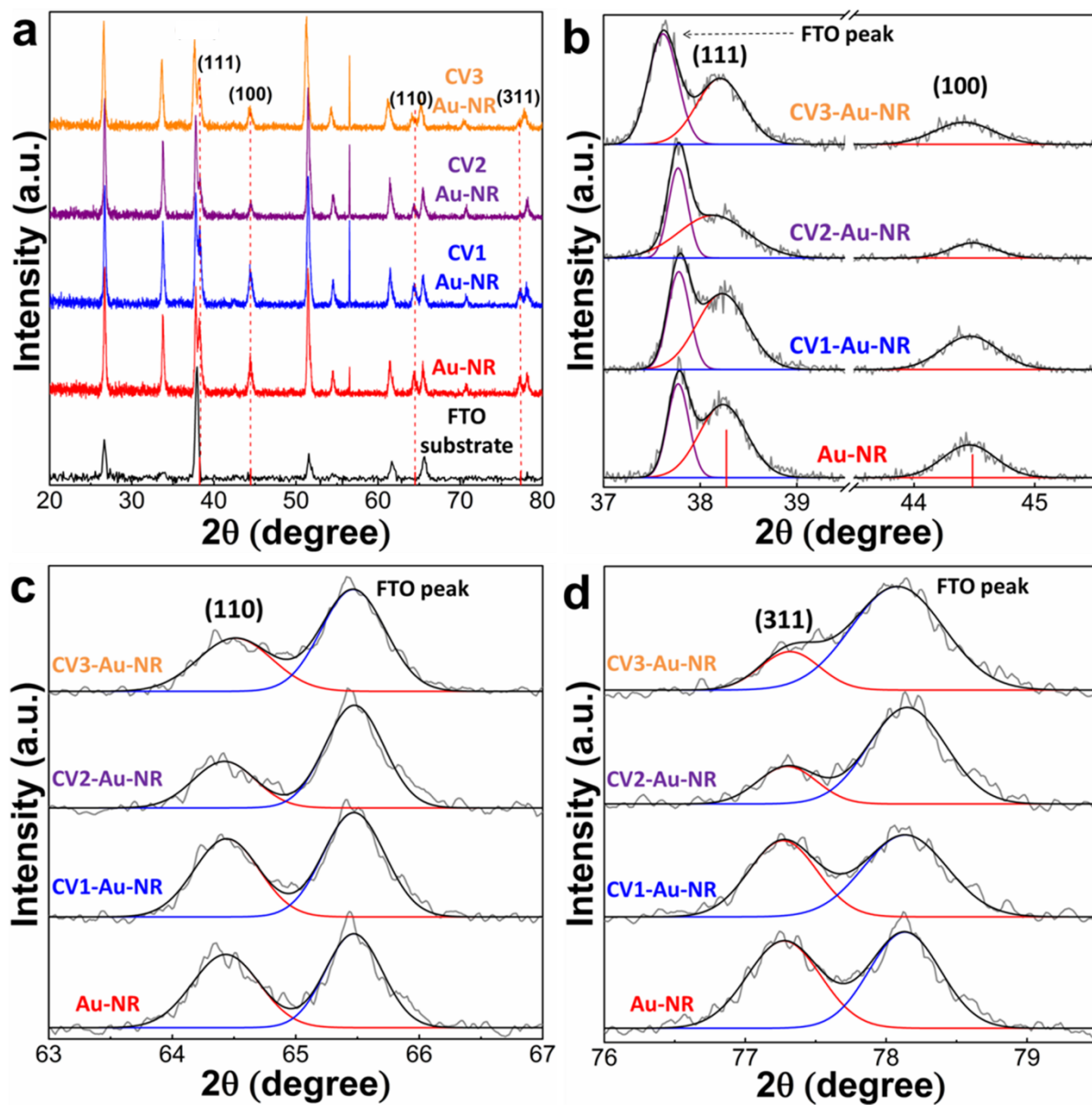


Fig.S1. XRD patterns of Au-NR (a) and fitting curves with different crystal planes of Au-NR catalysts (b, c, d).

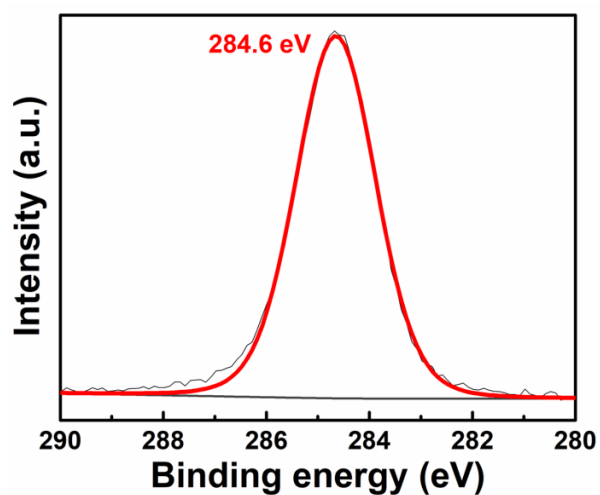


Fig.S2. XPS analysis (C1s core level) conducted on a CTAB-stabilized Au-NR sample

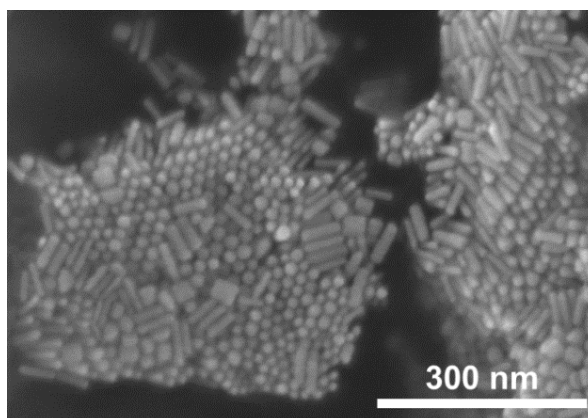


Fig.S3. SEM image of a CTAB-stabilized Au-NR catalyst electrode (loaded on FTO substrate)

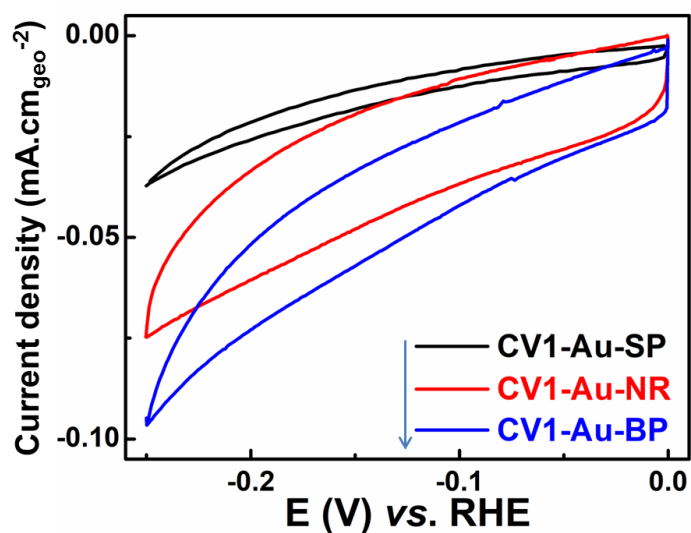


Fig.S4. The 1st cyclic voltammogram recorded for CTAB-stabilized Au-NR, Au-SP and Au-BP catalysts. 0.5 M H₂SO₄ electrolyte solution. Potential scan rate of 50 mV s⁻¹.

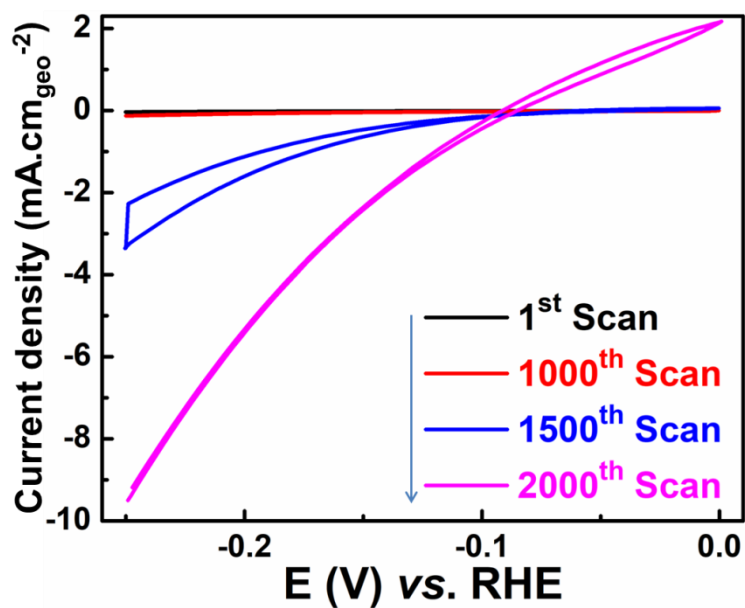


Fig.S5. Selected cyclic voltammograms recorded on the CTAB-stabilized Au-SP catalyst electrode immersed in a 0.5 M H₂SO₄ electrolyte solution, potential scan rate of 50 mV s⁻¹.

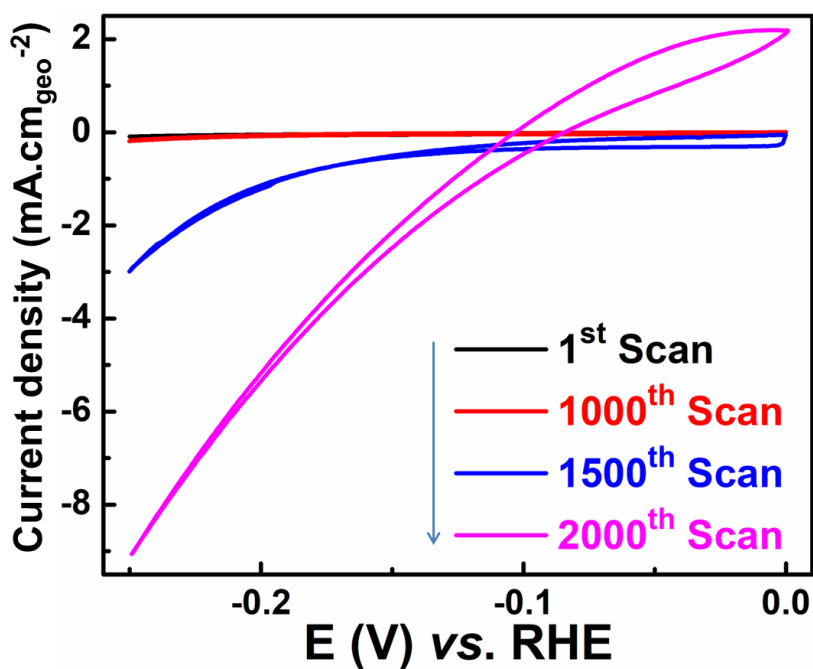


Fig.S6. Selected cyclic voltammograms recorded on the CTAB-stabilized Au-BP catalyst electrode immersed in a 0.5 M H₂SO₄ electrolyte solution, potential scan rate of 50 mV s⁻¹.

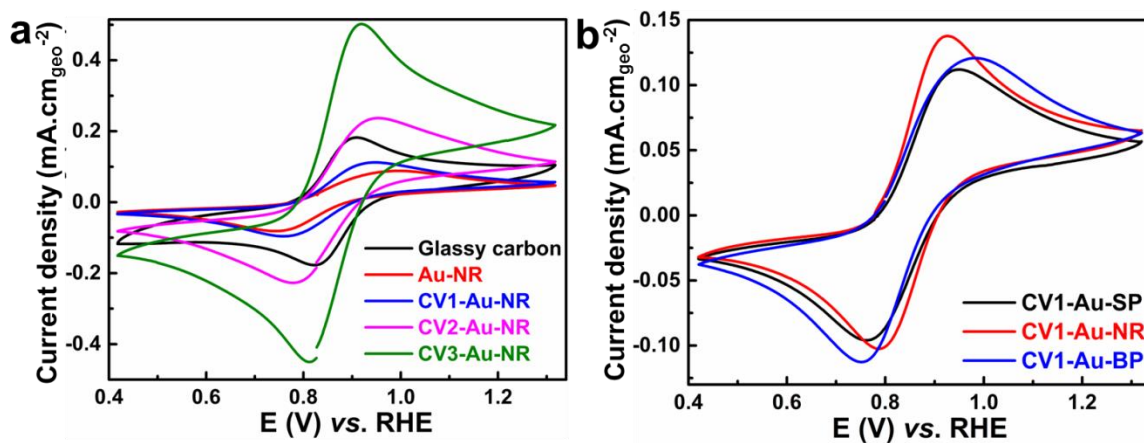


Fig.S7. Cyclic voltammograms of 1 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ solution in pH 7 phosphate buffer (0.1 M) recorded on a glassy carbon or Au nanoparticles-coated FTO electrodes. Potential scan rate of 20 mV s^{-1} .

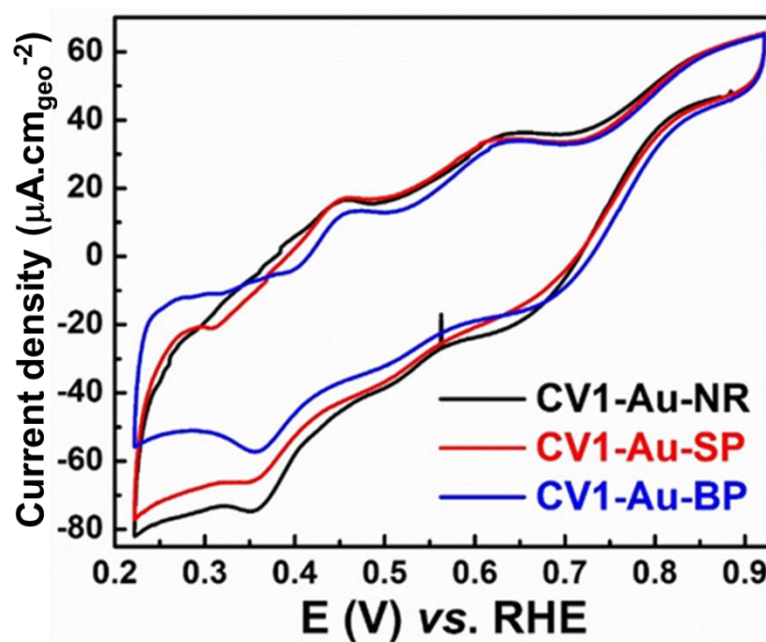


Fig.S8. Cyclic voltammograms recorded on CV1-Au-NR, CV1-Au-SP and CV1-Au-BP using 1 mM $Pb(NO_3)_2$ solution in 0.1 M NaOH electrolyte. Potential scan rate of 20 mV s^{-1} .

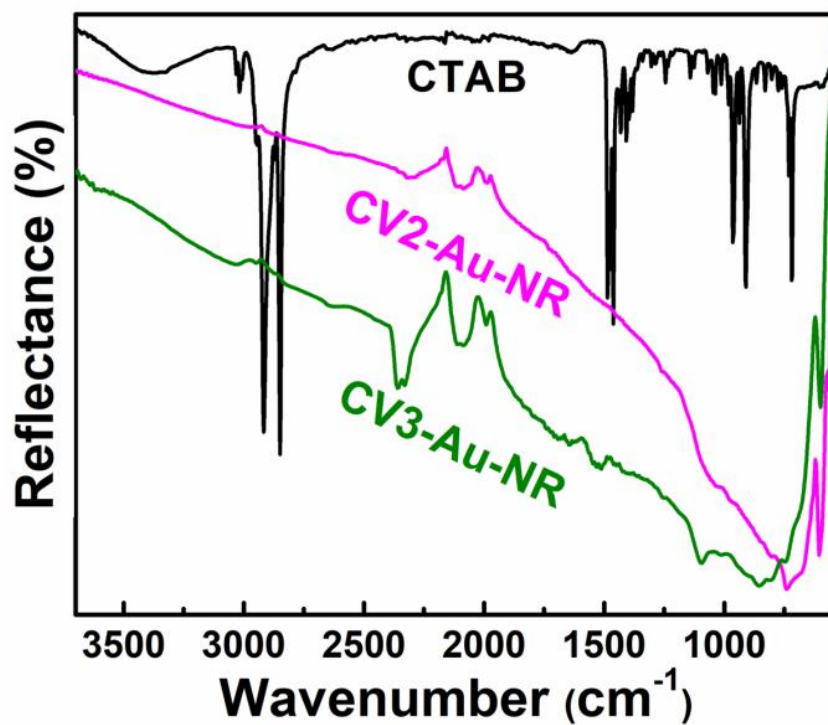


Fig.S9. FT-IR spectra of CV2-Au-NR, CV3-Au-NR samples and CTAB powder

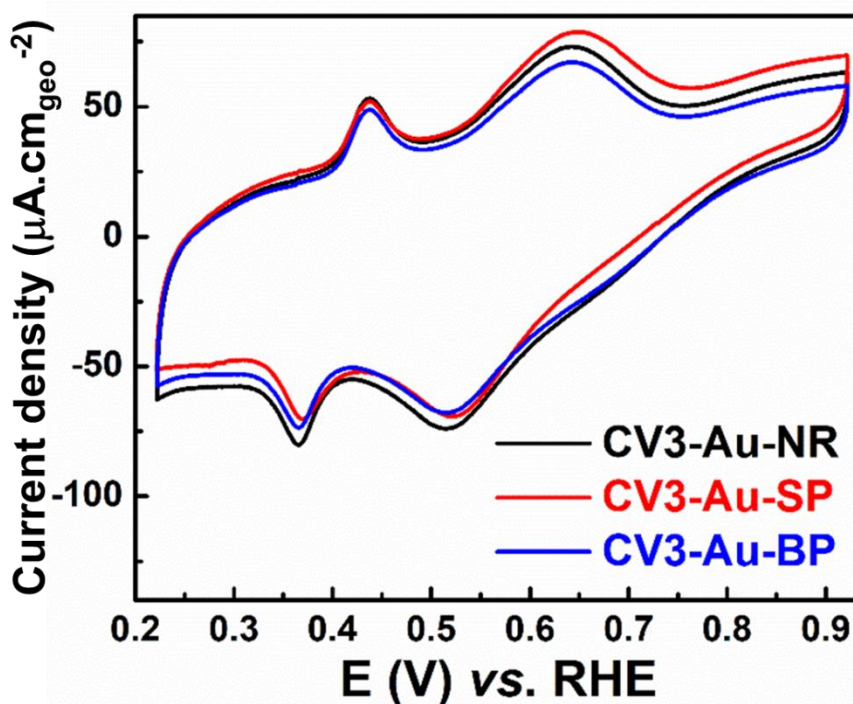


Fig.S10. Cyclic voltammograms recorded on CV3-Au-NR, CV3-Au-SP and CV3-Au-BP using 1mM $\text{Pb}(\text{NO}_3)_2$ solution in 0.1 M NaOH electrolyte. Potential scan rate of 20 mV s^{-1} .

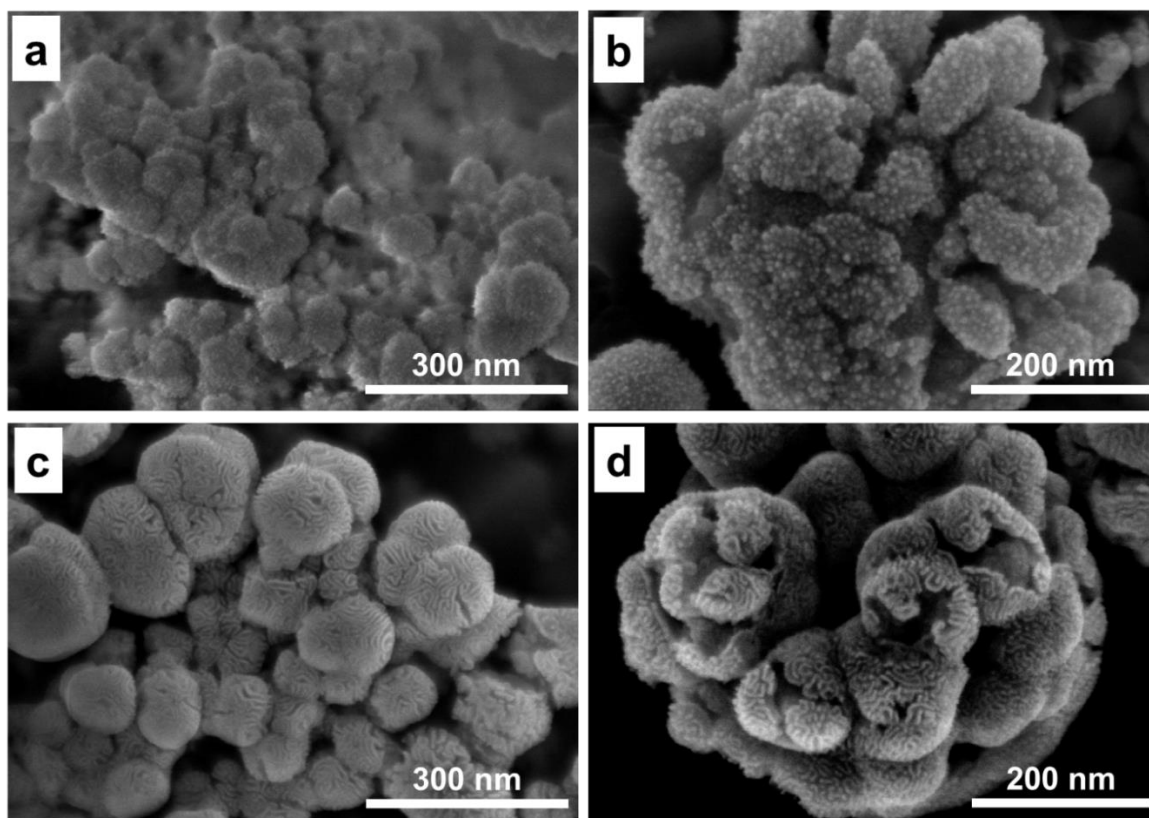


Fig.S11. SEM images of CV3-Au-BP (a, b) and CV3-Au-SP (c, d) samples

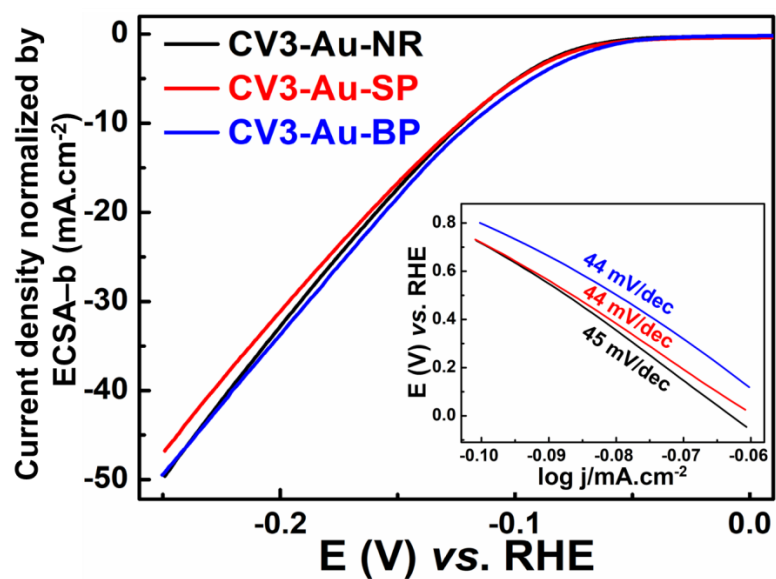


Fig.S12. I-V curves recorded on CV3-Au-NR, CV3-Au-SP and CV3-BP catalyst electrodes immersed in a 0.5M H₂SO₄ electrolyte solution. Potential scan rate of 5 mV s⁻¹. Current density is normalized by the relative electrochemical surface area of these electrodes.

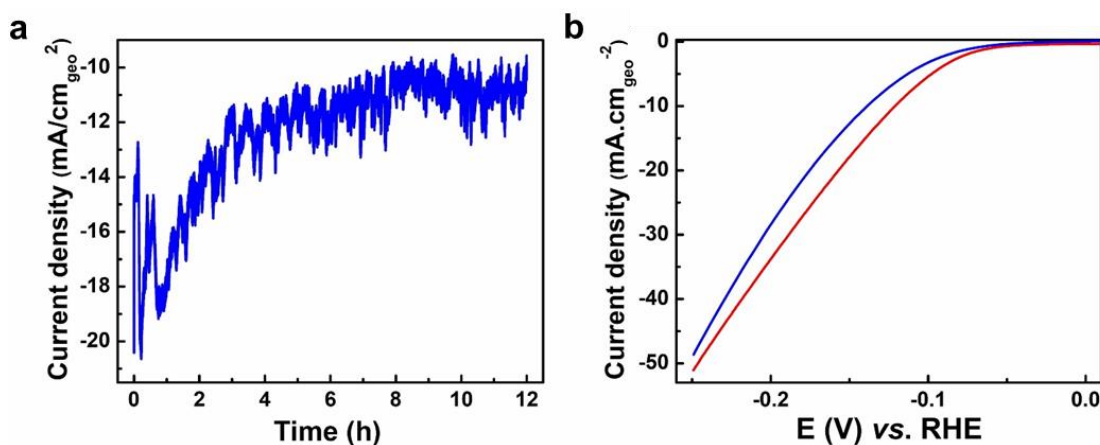


Fig.S13. I-t curve recorded on a CV3-Au-NR electrode at -0.15 V vs. RHE (a) and I-V curves recorded on the same CV3-Au-NR electrode before (*red trace*) and after (*blue trace*) being conditioned at -0.15 V vs. RHE for 12 hours (b). Electrolyte is a 0.5 M H₂SO₄ solution.

Table S1. Crystalline size of various Au-NR facets and the proportion of peak intensities

Sample	Au(111)		Au(100)		Au(110)		Au(311)	
	Size (nm)	Int.	Size (nm)	Int.	Size (nm)	Int.	Size (nm)	Int.
Au-NR	14.505	4.216	16.721	1.909	14.702	1.224	16.661	1.0
CV1-Au-NR	13.644	4.449	15.712	1.953	15.194	1.271	17.869	1.0
CV2-Au-NR	9.937	5.885	19.773	2.076	15.881	1.854	20.709	1.0
CV3-Au-NR	14.637	8.011	15.017	2.682	13.296	2.005	20.611	1.0

Note: **Int.** represents relative peak intensity of Au facets

Table S2. H₂ evolution catalytic activity of some selected catalysts assayed in a 0.5 M H₂SO₄ solution

Entry	Catalyst	Apparent catalytic activity					Reference	
		Onset overpotential (η_{onset} , mV)	Overpotential to sustain 10 mA/cm _{geo} ² (η_{10} , mV)	Current density at 200 mV overpotential (mA/cm _{geo} ²)	Tafel slope (mV/decade)	Catalyst loading amount ($\mu\text{g}/\text{cm}_{\text{geo}}^2$)		TOF at 200 mV overpotential (/s)
1	CV1-Au-NR	110	230	6	57	250	0.10	<i>This work</i>
2	CV1-Au-SP	110	-	3.5	59	250	0.06	<i>This work</i>
3	CV1-Au-BP	110	245	4.0	58	250	0.07	<i>This work</i>
4	CV2-Au-NR	50	169	14	52	250	0.23	<i>This work</i>
5	CV2-Au-BP	50	170	14	51	250	0.23	<i>This work</i>
6	CV2-Au-SP	50	180	13	51	250	0.21	<i>This work</i>
7	CV3-Au-NR	50	120	34	45	250	0.56	<i>This work</i>
8	CV3-Au-BP	50	120	34	44	250	0.56	<i>This work</i>
9	CV3-Au-SP	50	125	33	44	250	0.54	<i>This work</i>
10	Au-SP	50	180	11	60	350	0.13	[1]
11	Pt-Graphitic Tubes-FeCo/Cu	~0	18	-	24	281.4	-	[2]
12	Ru@C ₂ N	10	22	-	30	285	-	[3]
13	Dual atoms MoW/ N-doped Gr	~0	24	-	30	823	-	[4]
14	Laser-generated Ag NPs	~0	32	302	31	200	-	[5]
15	N-CoP ₂	~0	38	>100	46	-	-	[6]
16	Cu _{0.075} Co _{0.925} P/Carbon paper	~0	47	>100	47	5000	-	[7]
17	Single atom Pt/N-doped Gr	~0	50	-	29	76.5	-	[8]
18	P-Fe ₂ N/rGO	22	64.8	70	49	337	-	[9]
19	MoSSe/CNTs	25	102	-	38	1760	-	[10]
20	P-doped MoN	50	105	>350	43	200	-	[11]
21	η -MoC	30	122	60	53	300	-	[12]
22	CoP ₂	50	125	60	73	-	-	[6]
23	MoS _x -2 μm thick fim	125	129-140	100	48	-	-	[13]
24	MoS _x -100 nm thick film	150	175-189	70	35	-	-	[13]
25	a-WO _x /WC	100	200	10	69	320	-	[14]
26	S-vacancy MoS ₂ single layer	75	340	2.5	-	-	-	[15]

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