

Supporting Information:

Highly Stable Ordered Intermetallic PtCo Alloy Catalyst Supported on Graphitized Carbon Containing Co@CN for Oxygen Reduction Reaction

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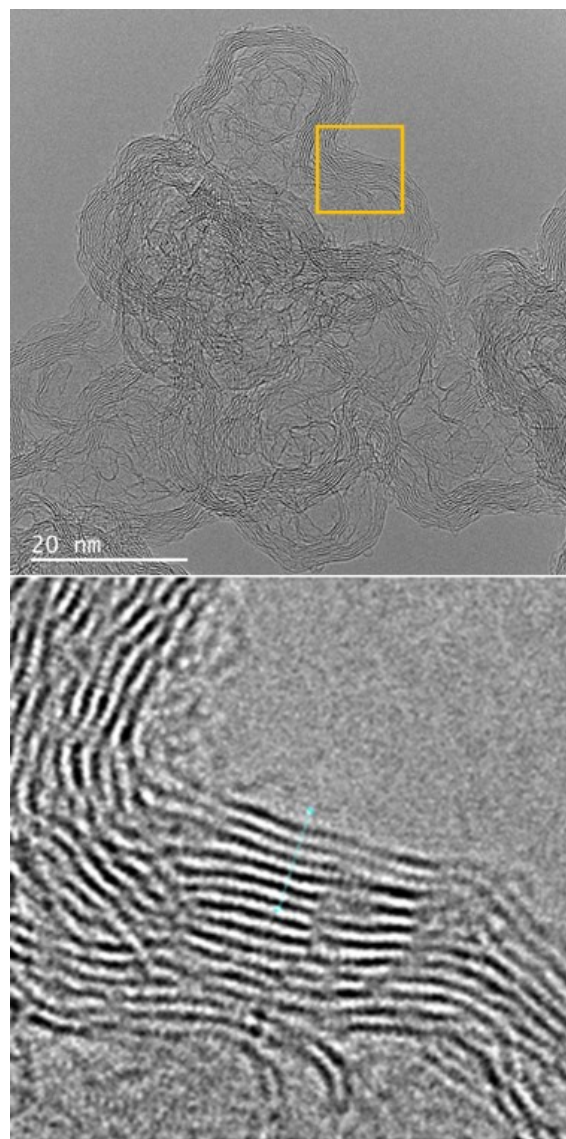


Figure S1. HR-TEM image of GC prepared at 1700 °C for 2 h under N₂ atmosphere.

Table S1. Characteristics of Co@CN/GC obtained from XPS N1s peak.

	BE [eV]	FWHM	at. %
Pyridinic- N	398.55	1.374	27.8
Pyrrolic-N and/or pyridone-N	400.18	2.389	37.0
Quaternary-N	401.12	3.026	19.3
Pyridinic-N ⁺ -O ⁻	403.70	4.991	15.9

Table S2. Characteristics of Co@CN/GC and CB obtained from XPS C1s peak.

	Co@CN/GC			CB		
	BE [eV]	FWHM	at. %	BE [eV]	FWHM	at. %
graphitic	284.59	0.803	67.7	284.29	0.892	64.4
defect	285.36	0.811	9.8	285.09	1.599	20.4
amine	286.02	1.014	4.0	-	-	-
alcohol and ether	286.54	1.793	8.2	286.57	1.377	4.0
carbonyl	288.01	1.317	2.4	287.98	2.293	4.3
carboxyl	289.11	1.314	1.9	289.09	2.861	1.1
carbonate	290.37	1.448	2.4	290.29	2.075	4.6
π - π^* shake-up satellite	291.52	1.874	3.6	291.58	1.47	1.1

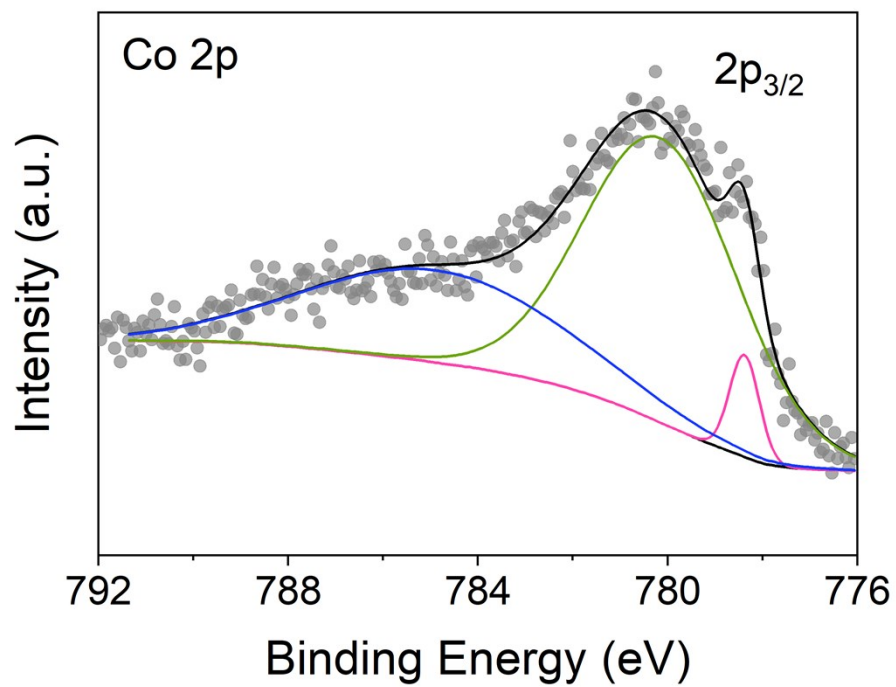


Figure S2. Co 2p XPS spectra of PtCo/NGC

Table S3. Characteristics of PtCo/NGC obtained from XPS Co 2p peak.

	PtCo/NGC		
	BE [eV]	FWHM	at. %
Co ⁰	778.38	0.734	4.2
Co(II)	780.14	3.843	62.0
Satellites	784.90	6.611	33.9

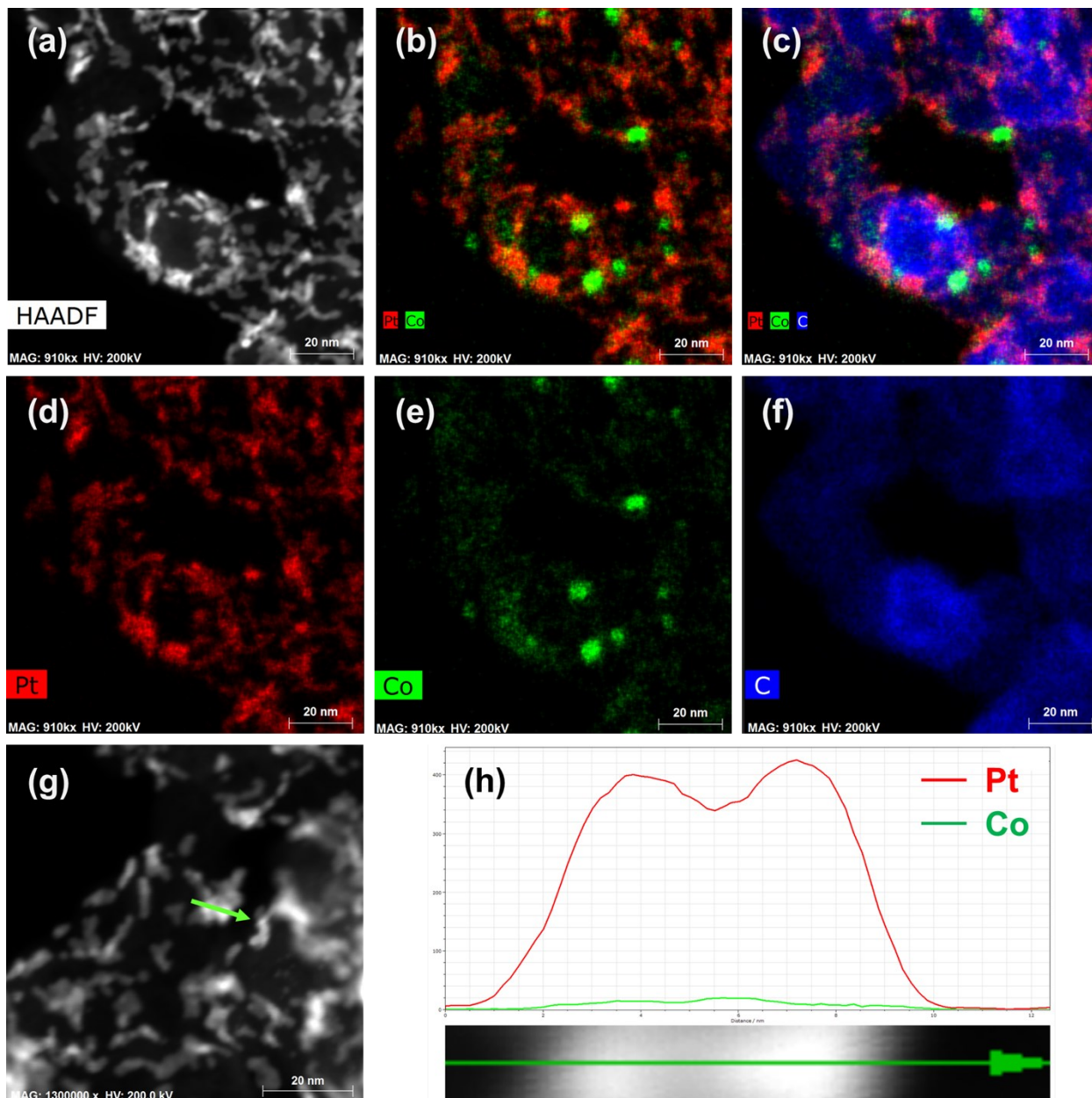


Figure S3. (a) HAADF-STEM image of Pt/Co@CN/GC. EDS elemental mapping images of Pt/Co@CN/GC: (b, c) overlap, (d) Pt, (e) Co, and (f) carbon. (g, h) EDS cross-sectional compositional line profile of Pt/Co@CN/GC.

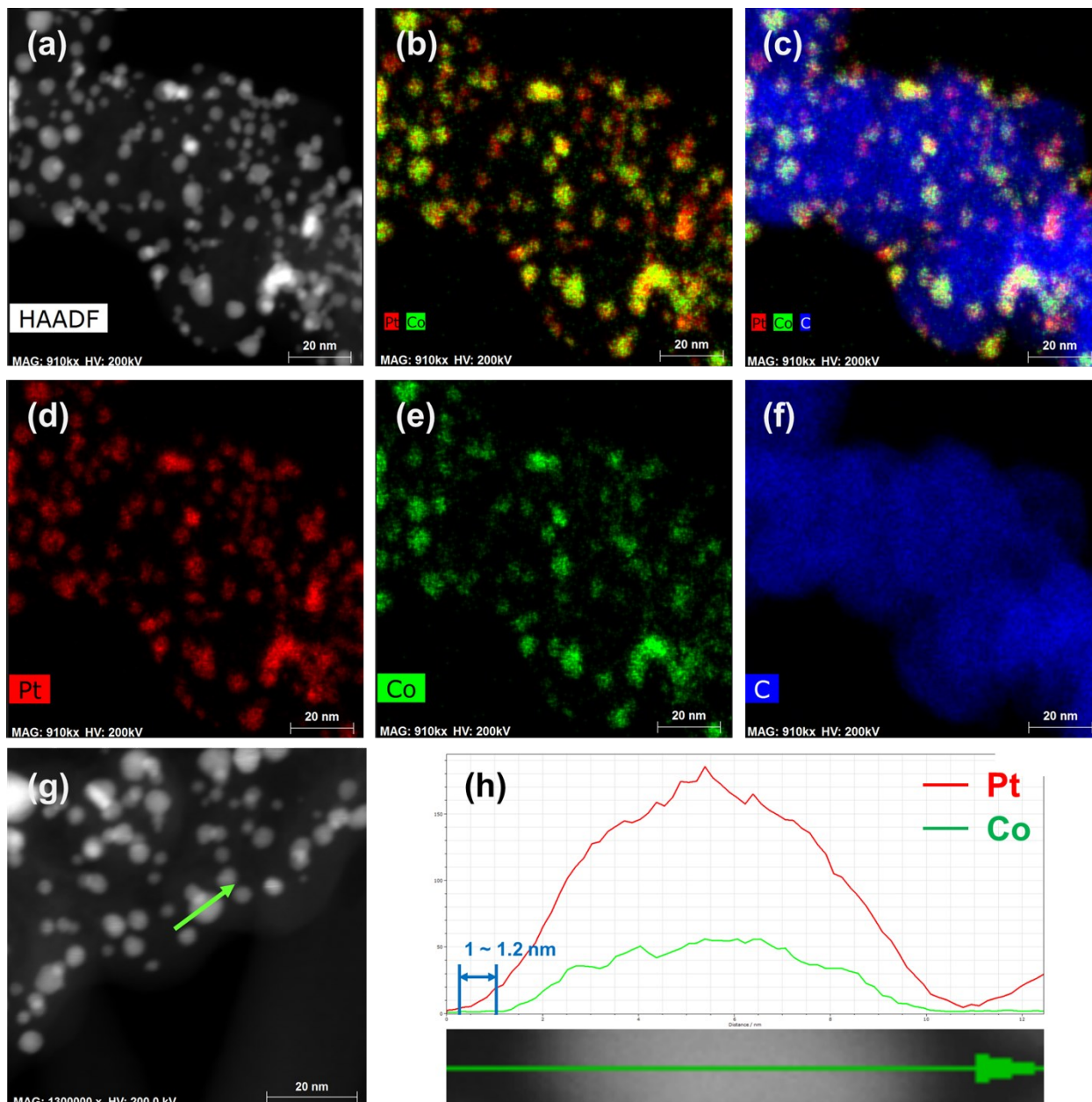


Figure S4. (a) HAADF-STEM image of PtCo/NGC which heat-treated the Pt/Co@CN/GC catalyst for 30 min. EDS elemental mapping images of PtCo/NGC (30 min): (b, c) overlap, (d) Pt, (e) Co, and (f) carbon. (g, h) EDS cross-sectional compositional line profile of PtCo/NGC (30 min).

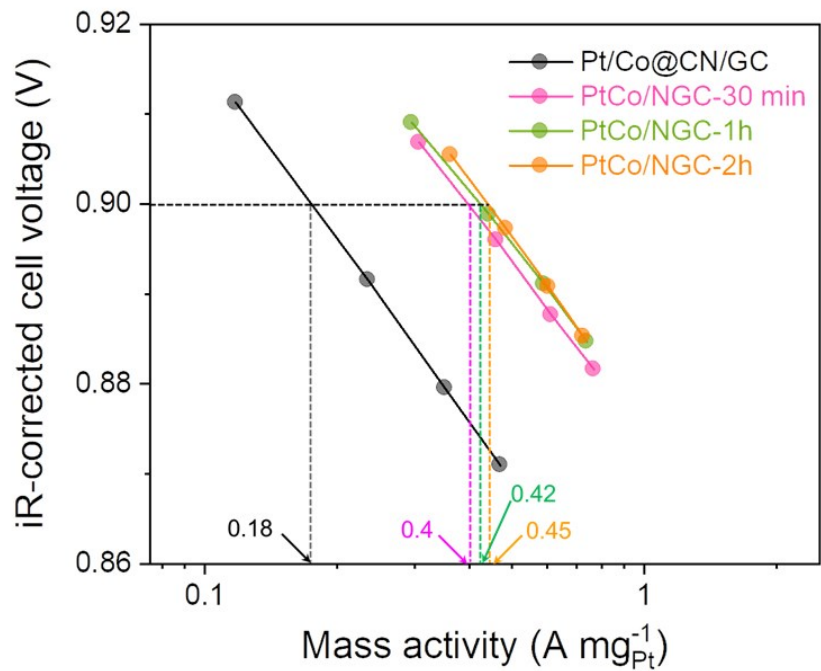


Figure S5. Mass activity of Pt/Co@CN/GC and PtCo/NGC with different heat-treatment duration time (30 min, 1 h and 2 h) at 800 °C. Commercial Pt/C (TEC10E50E, Tanaka Kikinzoku Kogyo K.K.) was used as a catalyst for the anode.

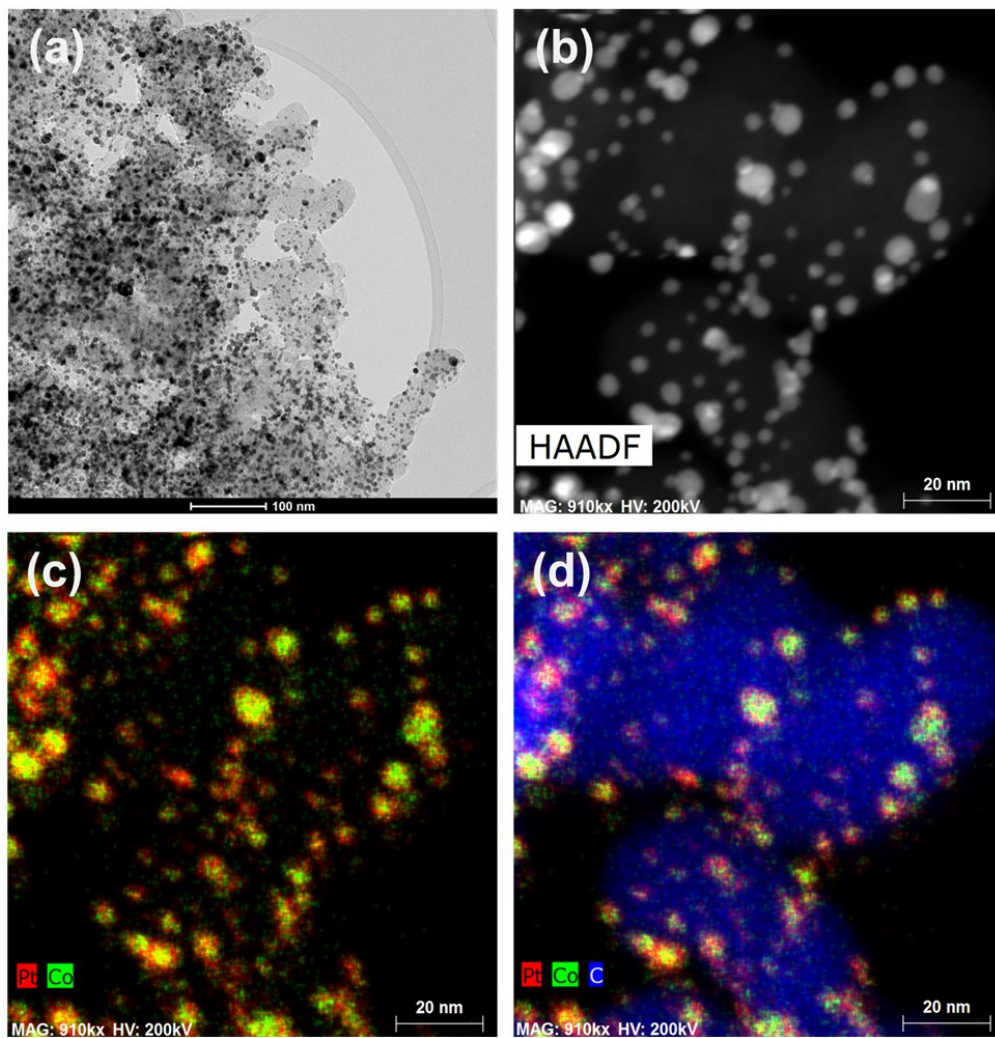


Figure S6. (a) HR-TEM and (b) HAADF-STEM images of PtCo/NGC after AST measurement. (c, d) Elemental mapping images of PtCo/NGC: Pt (red), Co (green), and Carbon (blue).

Table S4. Summary of the accelerated stress test (AST) results for oxygen reduction reaction in PEMFCs

Catalysts (Pt loading at cathode)	Cell Temp. [°C]	AST conditions (cycle No. and potential range)	Initial mass activity @ 0.9 V _{iR-free} [A mg ⁻¹]	Activity loss [%]	Initial ECSA [m ² g _{Pt} ⁻¹]	ECSA loss [%]	Performance loss	Ref No.
PtCo/NGC (0.1 mg cm ⁻²)	80	30,000 cycles (0.6 – 1.0 V)	0.45	53	74	27	34 mV at 800 mA cm ⁻²	This work
Pt _{2.6} Co TONs/C (0.1 mg cm ⁻²)	80	30,000 cycles (0.6 – 0.95 V)	0.294	24	99	17	-	Xia et al. (1)
PtNi@Pt/C (0.2 mg cm ⁻²)	80	30,000 cycles (0.6 – 1.0 V)	-	-	-	22	ca. 100 mV at 800 mA cm ⁻²	Lee et al.* (2)
Ga–PtNi/C (0.15 mg cm ⁻²)	65	30,000 cycles (0.6 – 1.0 V)	-	-	-	-	33% loss (current density) at 0.6 V	Cho et al. (3)
Pt/IrO ₂ -TiO ₂ (0.45 mg cm ⁻²)	80	10,000 cycles (0.6 – 1.0 V)	0.088	19	43	60	100 mV at 800 mA cm ⁻²	Kotz et al. (4)
Pd/C@Pt _{skin} (0.033 mg cm ⁻²)	65	30,000 cycles (0.6 – 1.0 V)	0.3	-	92.3	-	-	Hou et al. (5)
Dealloyed PtNi ₃ /C (0.1 mg cm ⁻²)	80	30,000 cycles (0.6 – 1.0 V)	0.5	0	37	29	-	Mukerjee et al. (6)
CNF/TiO ₂ -Pt (0.4 mg cm ⁻²)	75	-	0.282	-	44.97	-	-	Shul et al. (7)
GO coated Pt/C (0.2 mg cm ⁻²)		30,000 cycles (0.6 – 1.0 V)	-	-	48.8	33	-	Rafailovich et al. (8)
Pt on NbO _x /C (0.1 mg cm ⁻²)	80	30,000 cycles (0.6 – 0.95 V)	0.328	36	29	51	-	Xu et al. (9)
PtNi/C (0.1 mg cm ⁻²)	80	30,000 cycles (0.6 – 1.0 V)	-	58	42.4	59	ca.50 m V _{iR-free} at 800 mA cm ⁻²	Mustain et al.* (10)
PtCuCO/C (0.2 mg cm ⁻²)	80	30,000 cycles (0.5 – 1.0 V)	0.42	40.5	-	51	-	Strasser et al. (11)

* Performance loss represented here is estimated from V-i polarization curves.

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