Supplementary Material

Efficient hydrogen production from aqueous-phase reforming of biomass-derived oxygenated hydrocarbons over an ultrafine Pt nanocatalyst

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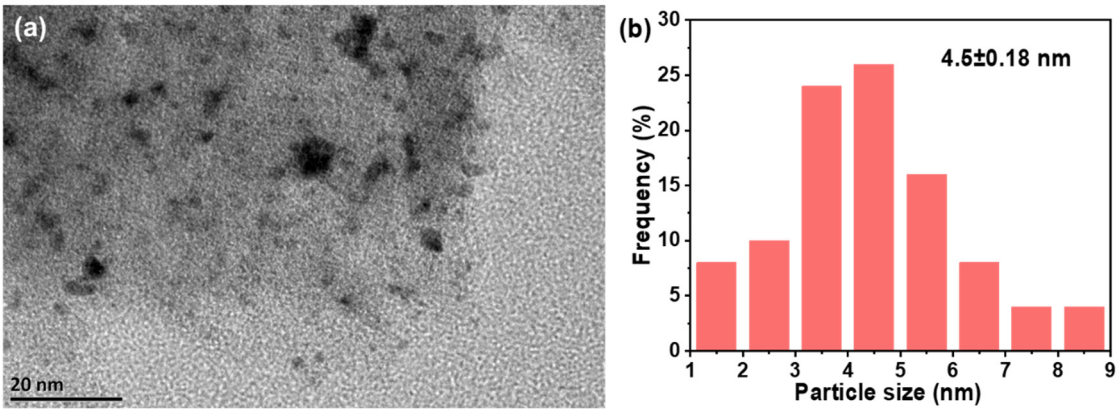

Figure S1. (a) TEM image of 20% Pt/C; (b) statistical distribution of Pt particle size of 20% Pt/C.

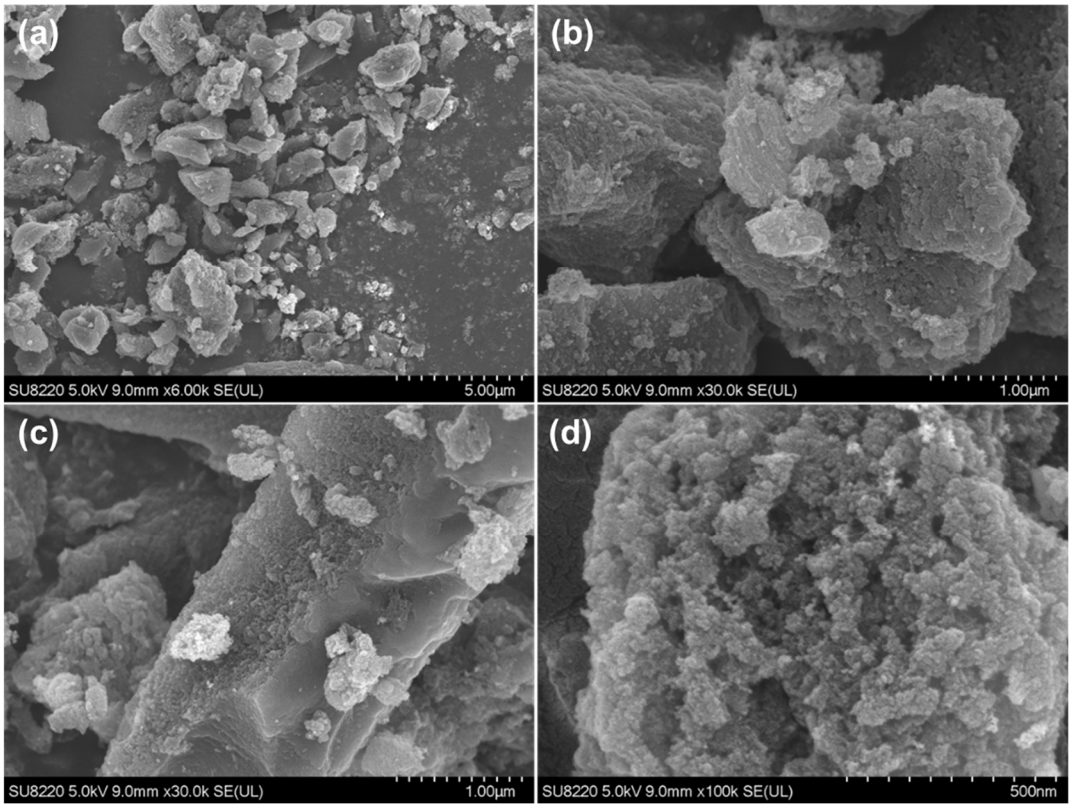

Figure S2. SEM images of 20% Pt/C catalyst.

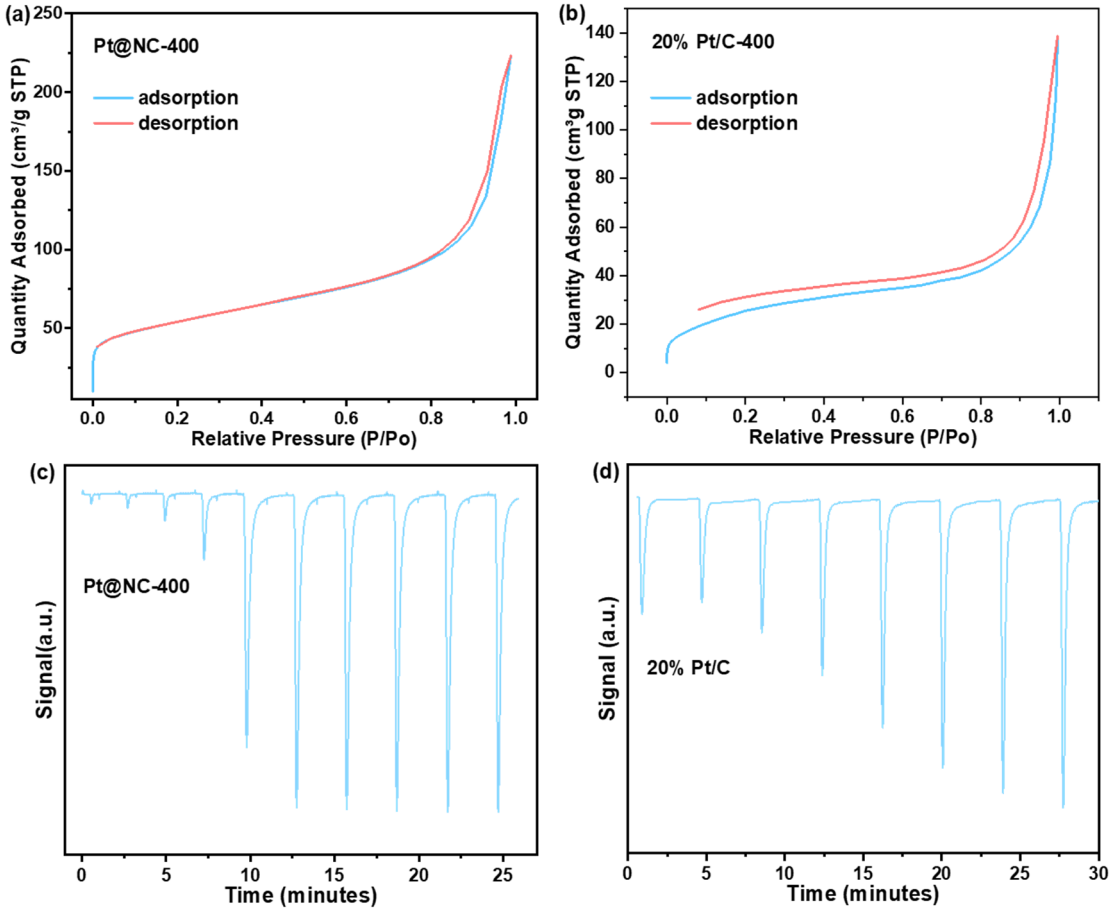

Figure S3. N_2 adsorption and desorption curves and the CO pulse chemisorption curves of Pt@NC-400 and 20% Pt/C catalysts.

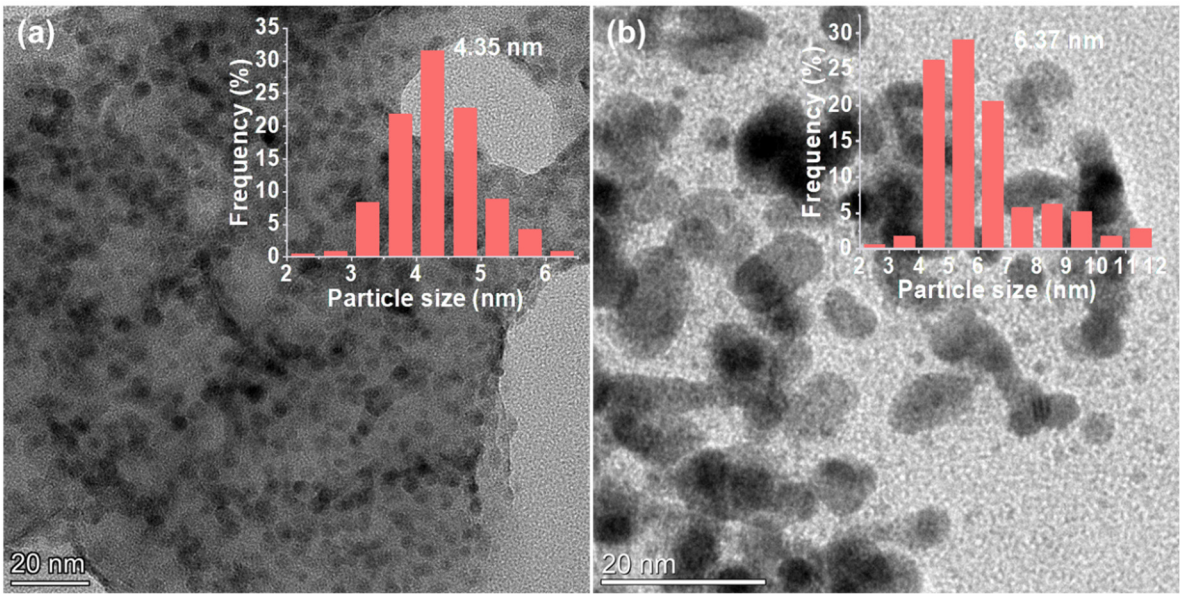

Figure S4. TEM images and particle size distributions of the spent Pt@NC-400 (a) and 20% Pt/C (b) catalysts after 8 times of in-situ cycling reaction.

Table S1. The particle size of Pt@NC-X catalysts.

Catalysts	Particle size [a] (nm)	Carbonization temperature (°C)
Pt@NC-300	3.4	300
Pt@NC-400	3.6	400
Pt@NC-500	4.3	500
Pt@NC-600	11.2	600
Pt@NC-700	24.8	700

[a] Pt particle sizes were calculated by Scherrer formula using XRD data.

Table S2. Main physiochemical properties of Pt@NC-400 and 20% Pt/C catalysts.

Samples	Pt loading [a] (wt. %)	S_{BET} [b] ($m^2 g^{-1}$)	V_p [b] ($cm^3 g^{-1}$)	d_p [b] (nm)	Pt metallic surface area [c] ($m^2 g^{-1}$)	Pt dispersion [c] %
Pt@NC-400	32.2	135.3	0.31	14.4	11.6	14.6
20% Pt/C	22.9	105.6	0.24	10.5	6.8	12.0

[a] Pt loading in the calcined catalysts were examined by inductively coupled plasma optic emission spectrometry (ICP-OES). [b] The BET surface area, pore volume and pore size were obtained from N_2 physisorption. [c] Pt metallic surface area and Pt dispersion of the reduced catalysts were determined by CO chemisorption.

Table S3. Relative atomic ratios of the elements C, N, and Pt in the Pt@NC-400 catalyst measured by EDS.

Z	Element	Family	Atomic Fraction (%)
6	C	K	61.0
7	N	K	9.2
78	Pt	L	29.8

Table S4. Data statist ics for the Pt 4f spectrum of Pt@NC-400 catalysts. [a.]

Species	Peak position (eV)	Percentage (%)
Pt^{4+}	72.8	1.2
Pt^0	71.3	98.8

[a] Data in this table was obtained from the XPS experiment.

Table S5. APRM performance of Pt-based catalysts at different pyrolysis temperatures.

Catalyst	Pyrolysis temperatures (℃)	H_2 production rate ($\mu mol_{H2}/g_{cat.}/s$)	ATOF (h^{-1})
Pt@NC-300	300	391.6	1639.1
Pt@NC-400	400	1013.4	4242.1
Pt@NC-500	500	363.5	1521.4
Pt@NC-600	600	323.6	1354.7
Pt@NC-700	700	186.0	778.7

Reaction conditions: 5 mL of methanol solution ($n(CH_3OH)/n(H_2O)$ = 1:3), 2 mg of catalyst, 2 MPa of N_2, reaction at 210 ℃ for 1.25 h. The catalysts were reduced in H_2 at 200 ℃ for 2 h before reaction.

Table S6. Reproducibility test of APRM reaction catalyzed by Pt@NC-400.

Reaction times	H_2 production rate ($\mu mol_{H2}/g_{cat.}/s$)	Relative deviation (%)
1	1013.4	4.0
2	957.1	-1.8
3	936.0	-3.9
4	999.5	2.6
5	964.8	-1.0
Average H_2 production rate ($\mu mol_{H2}/g_{cat.}/s$)	974.2	-
Relative average deviation (%)	-	2.7

Relative deviation = $100\%*(x_i-\bar{x})/\bar{x}$, Relative average deviation = $100\%*|x_i-\bar{x}|/5$, where x_i is the hydrogen production rate for each reaction and $\bar{x}$ is the average hydrogen production rate. Reaction conditions: 5 mL of methanol solution ($n(CH_3OH)/n(H_2O)$ = 1:3), 2 mg of catalyst, 2 MPa of N_2, reaction at 210 ℃ for 1.25 h. The catalyst was reduced in H_2 at 200 ℃ for 2 h before reaction.

Table S7. APRM performance of Pt@NC-400 and 20% Pt/C catalysts at different reaction temperatures.

Catalyst	T (℃)	H_2 production rate ($\mu mol_{H2}/g_{cat.}/s$)	ATOF ($mol_{H2}/mol_{Pt}/h$)	CO selectivity (%)
20% Pt/C	170	34.8	266.4	40.16
	190	208.4	1595.3	1.63
	210	357.3	2734.9	3.20
	230	634.7	4792.4	0.33
	250	676.5	5177.8	0.30
Pt@NC-400	170	240.1	1256.2	10.99
	190	594.2	2487.4	4.43
	210	1013.4	4242.1	2.92
	230	1187.5	4970.9	0.66
	250	1536.6	6462.4	0.62

Reaction conditions: 5 mL of methanol solution ($n(CH_3OH)/n(H_2O)$ = 1:3), 2 mg of catalyst, 2 MPa of N_2, reaction at 170-250 ℃ for 1.25 h. The catalysts were reduced in H_2 at 200 ℃ for 2 h before reaction.

Table S8. Differences in APR catalytic performance between Pt@NC-400 and 20% Pt/C catalysts under different feedstocks.

Catalysts	H_2 production rate ($\mu mol_{H2}/g_{cat.}/s$)	ATOF ($mol_{H2}/mol_{Pt}/h$)	CO selectivity (%)	Reaction mixture
20%Pt/C	357.3	2734.9	3.20	Methanol (1:3)
Pt@NC-400	1013.4	4242.1	2.92	
20%Pt/C	266.0	2035.8	1.52	Ethanol (1:3)
Pt@NC-400	779.0	3260.9	1.55	
20%Pt/C	239.1	1829.9	2.35	Propanol (1:5)
Pt@NC-400	546.9	2289.4	0.89	
20%Pt/C	850.9	6513.2	0.61	EG (1:2)
Pt@NC-400	1072.2	4488.1	0.94	
20%Pt/C	824.0	6306.8	0.34	1,2-PG (1:4)
Pt@NC-400	1766.5	7394.5	0.31	
20%Pt/C	201.6	1543.1	2.83	Sorbitol (1:6)
Pt@NC-400	555.6	2325.7	0.60	

Reaction conditions: 5 mL of alcohol solution, 2 mg of catalyst, 2 MPa of N_2, reaction at 210 ℃ for 1.25 h. The catalysts were reduced in H_2 at 200 ℃ for 2 h before reaction.

Table S9. Hydrogen production performance of ARP catalyzed by Pt-based catalysts in recent literature.

Catalysts	H_2 production rate ($\mu mol_{H2}/g_{cat.}/s$)	ATOF ($mol_{H2}/mol_{Pt}/h$)	CO selectivity (%)	Reaction condition	Reference
2%Pt/α-MoC	129.6	4134	0.06	190 ℃, n_{CH3OH}/n_{H2O} =(1:3), batch	2017[7]
1% Pt/$NiAl_2O_4$	7.3	-	0.05	210 ℃, 10 wt% methanol, continuous flow	2019[18]
2% Pt/Al_2O_3	30.7	1077	0.4	240 ℃, 10 wt% methanol continuous flow	2021[39]
1% Pt/γ-Al_2O_3	1.8	-	0.02	210 ℃, 10 wt% methanol, continuous flow	2019[18]
6% Pt/SiO_2	-	450000	undetected	210 ℃, 10 wt% ethylene glycol, continuous flow	2022[40]
5% Pt/Al_2O_3	11840.3	-	undetected	250 ℃, 10 wt% glycerol, continuous flow	2019[41]
Pt/$LaNiO_x$-2	5.3	-	0.2	210 ℃, 10 wt% methanol continuous flow	2022[42]
ZnO/Pt/Al_2O_3	-	26.4	undetected	250 ℃ 5 wt% 1-propanol continuous flow	2016[43]
Pt-Mn/C	-	1020	undetected	225 ℃ 10 wt% glycerol, continuous flow	2017[44]

Table S10. Catalytic stability performance of Pt@NC-400 and 20% Pt/C catalysts at 210 ℃.

Catalysts	Cycle times	H_2 production rate ($\mu mol_{H2}/g_{cat.}/s$)	ATOF ($mol_{H2}/mol_{Pt}/h$)	CO selectivity (%)
20% Pt/C	1	356.9	2734.9	0.0491
	2	279.9	2144.8	0.0903
	3	185.7	1423.0	0.0676
	4	169.8	1301.1	0.1020
	5	117.9	903.5	0.1313
	6	118.1	905.0	0.0850
	7	101.1	774.7	0.1168
	8	97.3	745.6	0.1186
Pt@NC-400	1	1013.4	4242.1	0.0470
	2	986.2	4128.3	0.0571
	3	815.3	3412.9	0.1026
	4	566.9	2373.0	0.1184
	5	545.6	2284.1	0.1297
	6	447.9	1874.8	0.1404
	7	412.6	1727.1	0.1668
	8	423.9	1774.6	0.1703

Reaction conditions: 5 mL of methanol solution ($n(CH_3OH)/n(H_2O)$ = 1:3), 2 mg of catalyst, 2 MPa of N_2, reaction at 210 ℃ for 1.25 h. The catalysts were reduced in H_2 at 200 ℃ for 2 h before reaction.