From single atoms to nanoparticles: size effect on Pd/C-catalyzed hydrogenation of 2,5-furandicarboxylic acid

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Materials

The materials, which include $PdCl_2$ (purity of Pd>59%), Na_2PdCl_4 (purity>99.99%), activated carbon, Na_2CO_3, 2,5-tetrahydrofurandicarboxylic acid, 2,5-furandicarboxylic acid, and heptanedioic acid were purchased from Shanghai Maclin Biochemical Technology Co., Ltd. All chemicals used are of analytical grade and can be used directly without further purification.

Preparation of catalysts

Herein, nano Pd/C catalysts were prepared via the impregnation-reduction method, whereas the single-atom Pd_{SA}/C catalysts were prepared by the deposit-precipitation method.

To prepare the nano Pd/C catalyst, 1 g of activated carbon carrier was evenly dispersed in 35 mL of deionized water. Subsequently, a specific amount of $PdCl_2$ aqueous solution was added to the above suspension, stirred at room temperature for 10 h, and dried at 110 °C overnight. Finally, the obtained solid was reduced at 200 °C for 2 h in an atmosphere with H_2 and N_2 flows of 80 mL/min, respectively, to obtain the nano Pd/C catalyst.

To obtain a Pd_{SA}/C catalyst, 200 mg of activated carbon carrier was dispersed in 30 mL of deionized water and placed in a 100 °C oil bath after ultrasonic treatment. The pH of the mixture was adjusted to 10 with a 0.25 M Na_2CO_3 solution. Subsequently, a specific amount of Na_2PdCl_4 aqueous solution was added to the above mixture drop by drop, stirred at 100 °C for 1 h, and centrifuged. The resulting solid was washed in deionized water, vacuum dried at 60 °C for 12 h, and subsequently reduced at 30 mL/min in an H_2 atmosphere at 200 °C for 1 h to obtain the catalyst.

Characterization of the catalysts

The Pd content in the Pd/C catalyst was determined using the PerkinElmer 8300 inductively coupled plasma atomic emission spectrometer/mass spectrometry (ICP-AES/MS). Powder X-ray diffraction (XRD) analysis was performed using a Bruker D8 FOCUS diffractometer, operating at a current of 40 mA and voltage of 40 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on a FEI Talos F200S electron microscope operated at 200 kV. Aberration-corrected HAADFSTEM images were obtained using a JEM-ARM30F equipped with a spherical aberration corrector working at 200 keV. The metal dispersion was measured using CO chemisorption on a Micromeritics Autochem II 2920 instrument. The 100 mg sample was dried and pre-treated at a rate of 10 °C/min from room temperature to 100 °C, reduced in 10% H_2/Ar for 1 h. The

sample was then cooled to room temperature, and surface H_2 was removed using He gas (50 mL/min) until the baseline was stable. CO pulse titration was performed until saturation, and the dispersion and particle size of the metal were determined. X-ray photoelectron spectroscopy (XPS) was obtained on the Escalab 250Xi spectrometer from Thermo Scientific in the United States.

Evaluation of catalytic performance

The FDCA hydrogenation reaction catalyzed by Pd/C was performed in a 50 mL high-pressure reactor. Once the reactor containing FDCA, water, and Pd/C catalyst has attained the expected pressure, it is heated to a predetermined temperature and reacts for a specific duration. Following the reaction, the reactor was allowed to cool to room temperature naturally, and the catalyst and reaction solution were centrifuged. The reaction products were analyzed through liquid chromatography (Waters e2695) using the internal standard method. Notably, the internal standard is heptanelic acid, and the chromatographic conditions were as follows: SB-Aq C18 column, 30 °C, 1 mL/min, and the mobile phase was a phosphoric acid aqueous solution with a pH of 2.2. The FDCA conversion and THFDCA yield is represented in equations (1)-(2):

$$Y_{THFDCA} = \frac{moles\ of\ THFDCA\ produced}{moles\ of\ FDCA\ in\ feed} \cdot 100\% \#(1)$$

$$X_{FDCA} = \frac{moles\ of\ FDCA\ converted}{moles\ of\ FDCA\ in\ feed} \cdot 100\% \#(2)$$

TOF values were calculated based on Equation (3):

$$TOF\ (min^{-1}) = \frac{moles\ of\ FDCA\ converted}{(moles\ of\ Pd) \times dispersion \times reaction\ time} \#(3)$$

Mass transfer limitations: Internal-diffusion, Weisz-Prater criterion (C_{wp})

The Weisz-Prater criterion (C_{wp}) determines whether there is an internal mass transfer limit. The internal mass transfer limit can be ignored if C_{WP} is less than 1.

$$C_{WP} = \frac{r_{obs}\rho_c R_p^2}{D_{eff}C_s} \#(4)$$

$$D_{eff} = \frac{D_{AB}\varepsilon_p\sigma_c}{\tau} \#(5)$$

$$D_{AB} = \frac{7.4 \times 10^{-12} \times T \times \sqrt{\varphi \times M}}{\mu \times V_{FDCA}^{0.6}} \#(6)$$

Among them, ρ_c represents the solid density of the catalyst (kg/m^3), R_p represents the radius of the catalyst (m), C_s represents the concentration of FDCA in the solution (mol/m^3), D_{eff} represents the effective diffusivity (m^2/s), D_{AB} represents the diffusivity

(m^2/s), and Bird et al. 's method was used to estimate. ε_p is the porosity, r_{obs} is the observed reaction rate of FDCA, mol kg_{cat}^{-1} s^{-1}, T is the temperature (k), φ is the association parameter of the solvent, μ is the dynamic viscosity of the solvent (pa.s), and V_{FDCA} is summed by Le Bas table, which is 169.5 ($cm^3/$ mol).

$R_p \approx 1.7\times10^{-5}$ m (Catalyst particle radius).

ε_p= 0.4 (Pellet porosity)

σ_c = 0.8 (Constriction factor)

τ= 3 (Tortuosity)

φ=2.6

Mass transfer limitations: External diffusion, Mears' criterion (C_M)

The Mears criterion (C_M) determines whether there is an external mass transfer limit. The external mass transfer limit can be ignored if C_M is lower than 0.15.

$$C_M = \frac{r_{obs}\rho_b R_p n}{k_c C_S} \#(7)$$

$$k_c = \frac{D_{AB}}{R_p} + 0.31 \times N_{SC}^{-\frac{2}{3}}\left(\frac{\Delta\rho\mu g}{\rho_c^2}\right)^{\frac{1}{3}} \# (8)$$

$$N_{SC} = \frac{\mu}{\rho_c D_{AB}} \# (9)$$

Among them, ρ_b = 400 kg m^{-3} (Bulk density of catalyst). $R_p \approx 1.7\times10^{-5}$ m (Catalyst particle radius). g represents the acceleration of gravity (m/s^2), $\Delta\rho$ represents the density difference between the SCER and the solution (g/ml), N_{SC} stands for Schmidt number.

The calculation results displayed in Table 3 indicate that C_{wp} is below 1 and C_M is below 0.15. Hence, the influence of both internal and external diffusion can be ignored.

Reaction kinetics fitting

The kinetics of FDCA hydrogenation catalyzed by Pd/C with different sizes were calculated based on the conversion of FDCA at different times and temperatures. Ignoring the influence of internal and external diffusion, the rate equation of the hydrogenation reaction can be expressed as follows:

$$r = -dC_A/dt = kC_A^\alpha \#(10)$$

$$C_A = C_{A0}(1-X)\#(11)$$

If the preset reaction order α=1, then

$$r = \frac{-dC_A}{dt} = \frac{-dC_{A0}(1-X)}{dt} = -C_{A0}\frac{d(1-X)}{dt} = C_{A0}\frac{dX}{dt}\#(12)$$

$$r = kC_A = kC_{A0}(1-X)\#(13)$$

Then $$\frac{dX}{dt} = \frac{r}{C_{A0}} = k(1-X) \# (14)$$

By integrating it, we can obtain:

$$-ln(1-X) = kt \#(15)$$

Where X is the FDCA conversion, C_A is the FDCA concentration, C_{A0} is the initial FDCA concentration, k is the rate constant, and t is the reaction time.

Fig. S4 depicts the linear relationship between -ln(1-X) and reaction time for Pd/C catalysts of different sizes in the temperature range of 90-120 °C. Notably, all experimental data fall on the corresponding straight lines within the error range, thereby exhibiting first-order reaction kinetics. The slope of the fitted line represents the apparent rate constant k at this temperature.
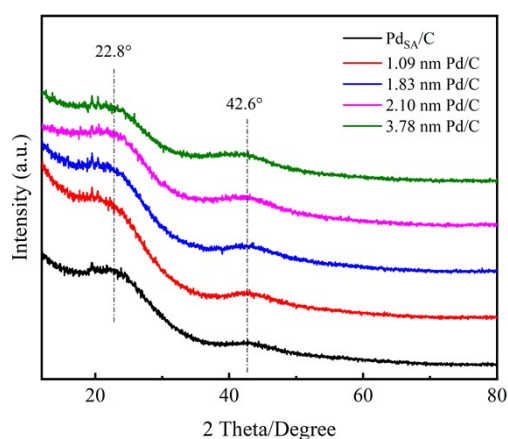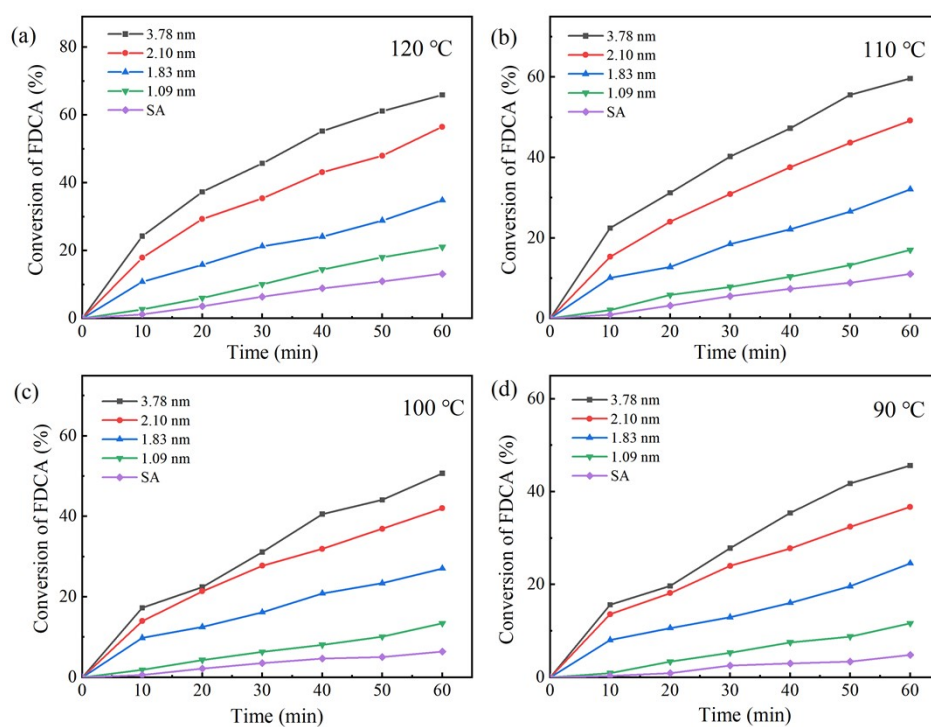

Fig. S1. XRD patterns of Pd/C

Fig. S2. Effects of Pd size on the conversion of FDCA.
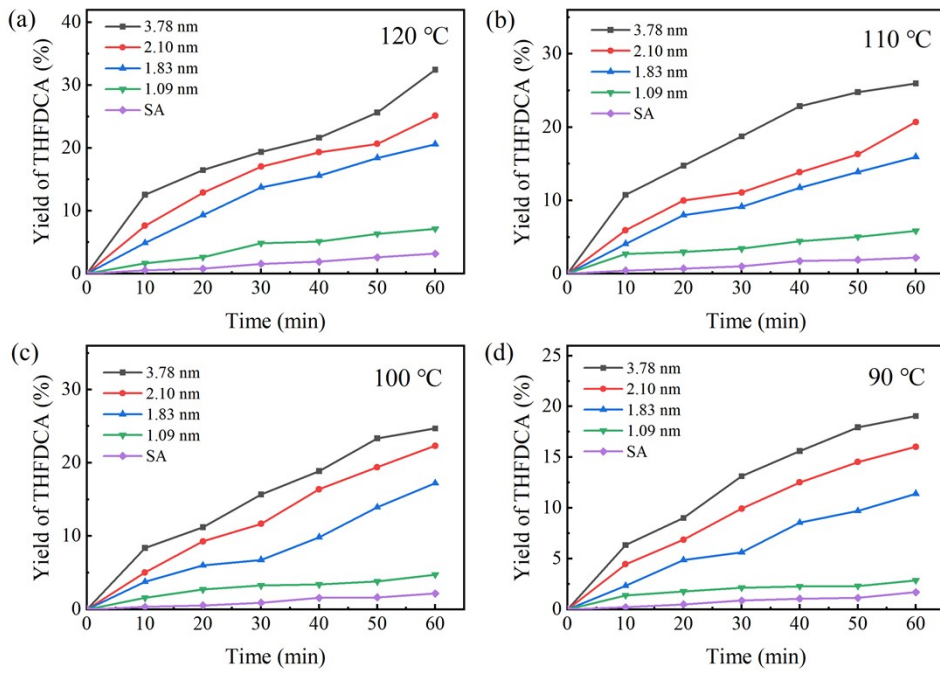
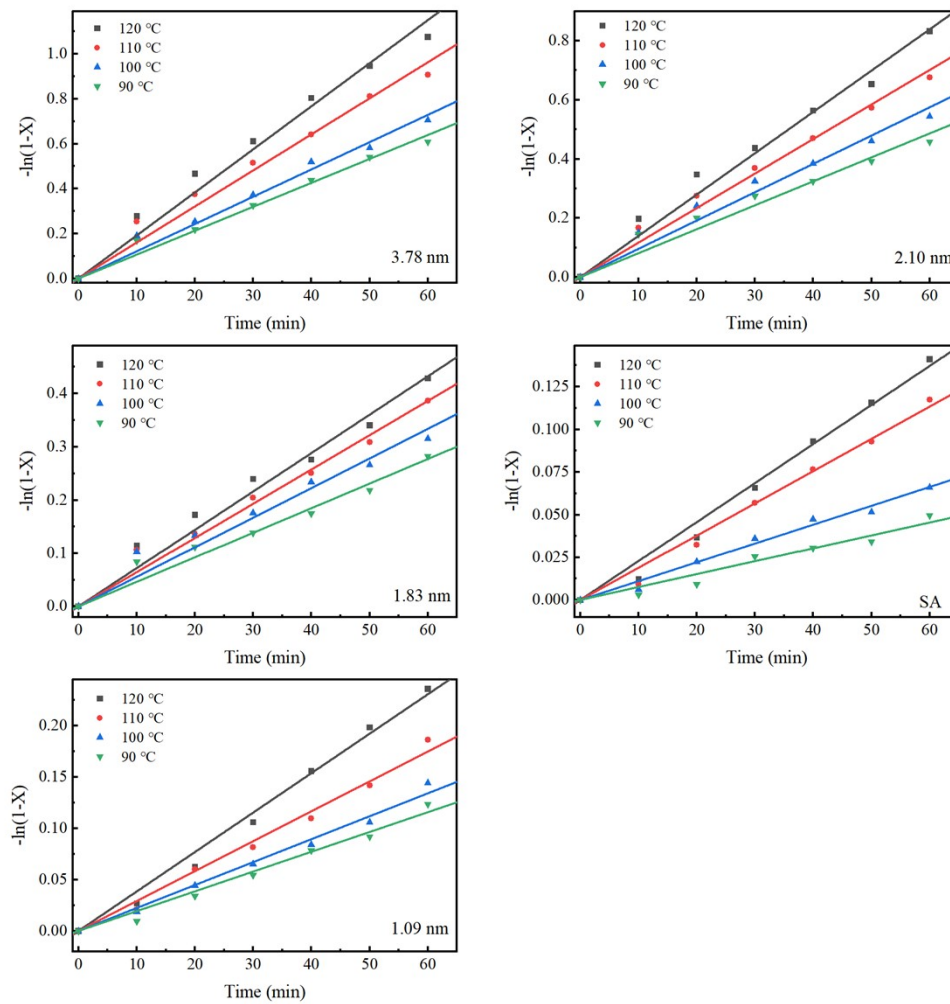**Fig. S3.** Effects of Pd size on the yield of THFDCA.

Fig. S4. Dynamics fitting of THFDCA conversion

Table S1 Hydrogenation performance of Pd/C catalyst

Entry	Particle size (nm)	Temperature (℃)	Pressure （MPa）	Time (h)	Catalyst amount (g)	Conversion (%)	Yield (%)
1-1	3.78	120	3	3	0.1	82.1	59.3
1-2	3.78	120	3	5	0.1	100	100
1-3	3.78	120	3	7	0.1	100	96.9
1-4	3.78	120	1	5	0.1	9.86	5.2
1-5	3.78	120	2	5	0.1	69.5	46.1
1-6	3.78	90	3	5	0.1	83.4	78.8
1-7	3.78	100	3	5	0.1	88.5	80.5
1-8	3.78	110	3	5	0.1	98.7	94.3
1-9	3.78	120	3	5	0.04	88.5	12.9
1-10	3.78	120	3	5	0.06	91.6	43.8
1-11	3.78	120	3	5	0.08	97.6	89.7
Entry	Particle size (nm)	Temperature (℃)	Pressure （MPa）	Time (h)	Catalyst amount (g)	Conversion (%)	Yield (%)
2-1	3.78	120	3	5	0.1	100	100
2-2	2.10	120	3	5	0.1	100	100
2-3	1.83	120	3	5	0.1	100	100
2-4	1.09	120	3	5	0.1	92.8	11.6
2-5	SA	120	3	5	0.1	86.7	3.8

Reaction conditions: FDCA 1mmol, water 15 mL

Table S2 physical properties of various Pd/C catalysts.

T (°C)	Pd particle size/nm	C_{WP}	C_M
	3.78	4.36E-04	5.69E-05
	2.10	2.75E-04	4.36E-05
120	1.83	1.47E-04	2.48E-05
	1.09	5.17E-05	7.24E-06
	SA	2.93E-05	5.18E-06
	3.78	3.82E-04	5.24E-05
	2.10	2.56E-04	3.59E-05
110	1.83	1.07E-04	1.80E-05
	1.09	4.48E-05	6.63E-06
	SA	2.53E-05	4.58E-06
	3.78	3.61E-04	4.09E-05
	2.10	2.18E-04	3.19E-05
100	1.83	1.01E-04	1.58E-05
	1.09	3.83E-05	5.78E-06
	SA	1.81E-05	3.21E-06
	3.78	2.88E-04	3.37E-05
	2.10	1.96E-04	2.76E-05
90	1.83	8.73E-05	1.41E-05
	1.09	3.32E-05	5.26E-06
	SA	1.19E-05	2.11E-06
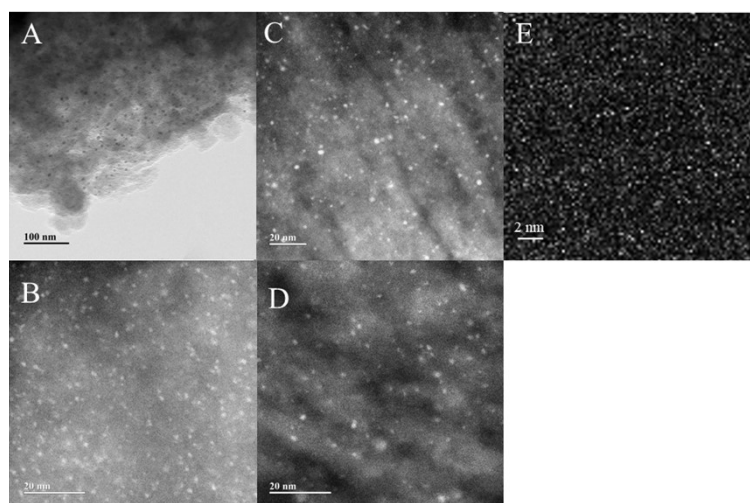
Fig. S5. HAADF-STEM and Aberration-corrected HAADF-STEM images of Pd/C catalysts
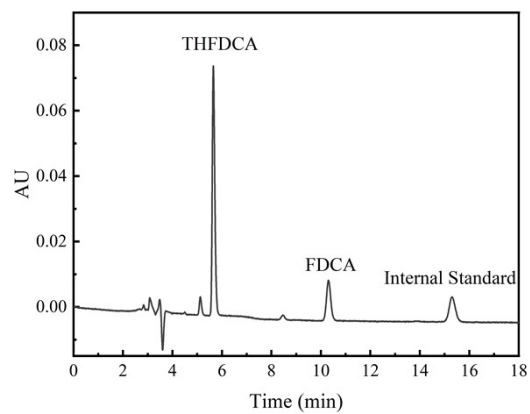
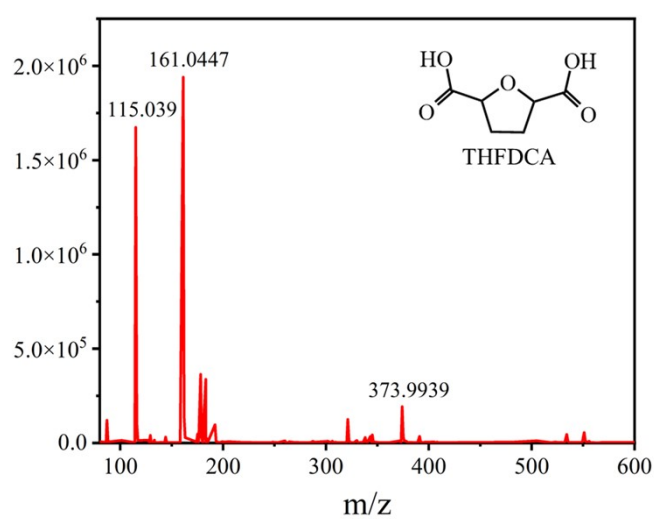**Fig. S6.** HPLC spectra of reaction solution
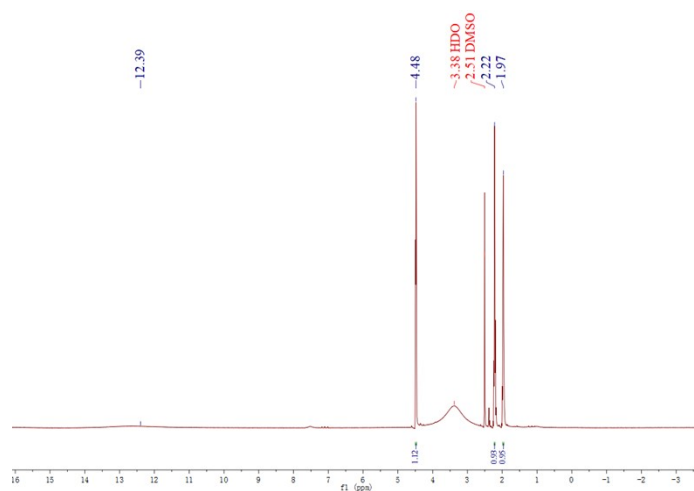

Fig. S7. HPLC-MS spectra of THFDCA

Fig. S8. ^{1}H-NMR spectra of THFDCA (DMSO-d$_6$)
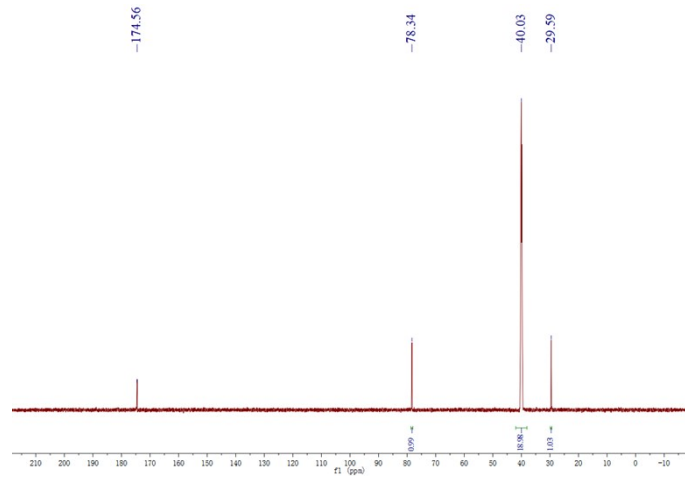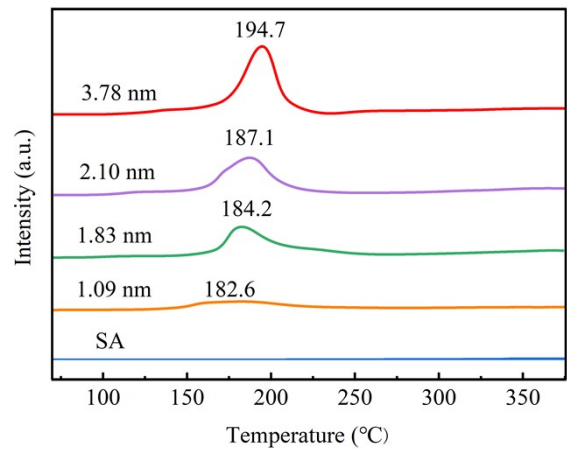
Fig. S9. ^{13}C-NMR spectra of THFDCA (DMSO-d$_6$)

Fig. S10. H$_2$-TPR curves of samples.