Ultra-fast synthesis of hierarchical SAPO-11 molecular sieves using carbon materials under microwave radiation condition

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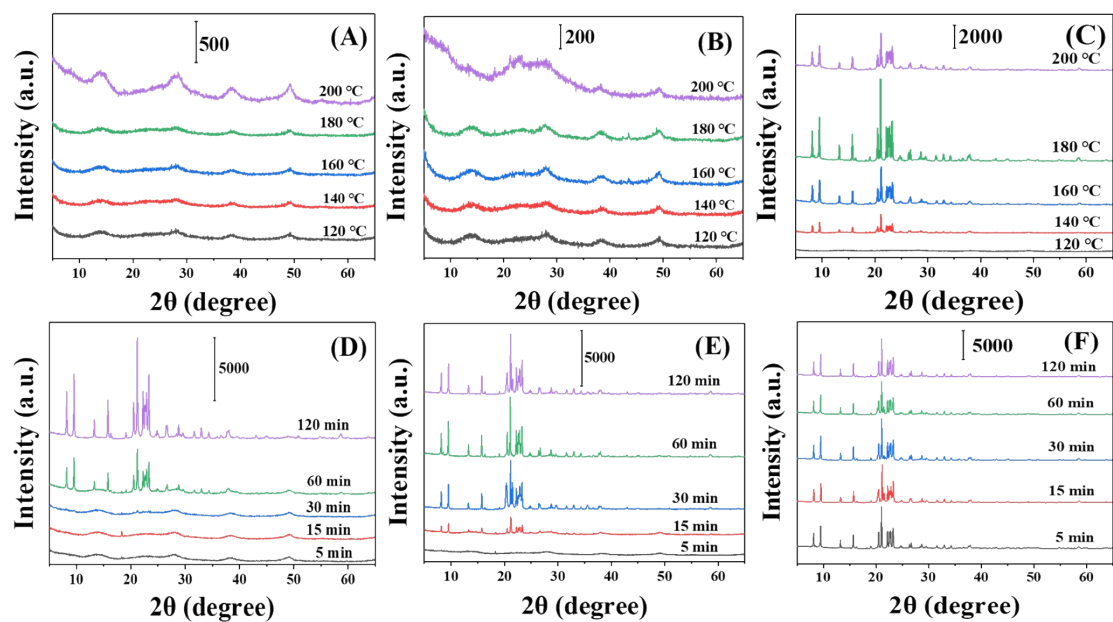*Corresponding author. E-mail addresses: liuyx@qust.edu.cn.

Fig. S1. XRD patterns of SAPO-11 synthesized at different crystallization temperatures heated by oven (A), microwave (B), and microwave with carbon (C); XRD patterns of SAPO-11M/W synthesized with microwave radiation power of 0 W (D), 300 W (E), and 600 W (F) for various time. (All samples are uncalcined)
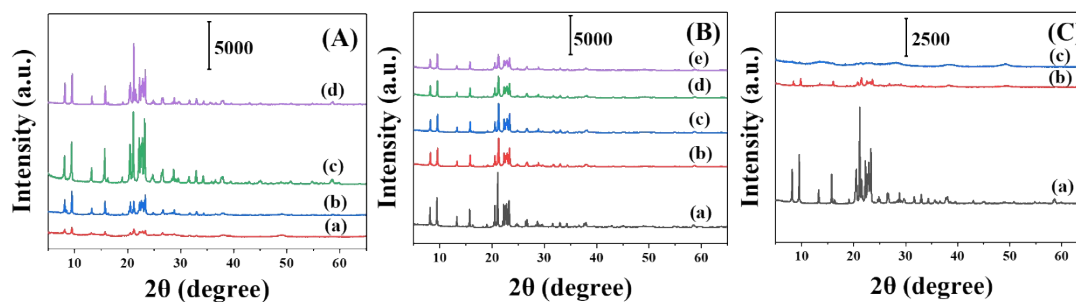
Fig. S2. XRD patterns of SAPO-11 synthesized with different carbon (A) of (a) Graphene, (b) Graphene oxide, (c) Activated carbon and (d) Biochar. The weight ratio between carbon materials and Pseudoboehmite is 1:110. Effect of hydroxyl radical quencher (i.e., tert-butanol) on the phase structure of SAPO-11 (B). The amount of tert-butanol is controlled by the volume ratio of tert-butanol: silicon sol: (a) 0, (b) 2, (c) 4, (d) 8, and (e) 16 mL. Effect of synthesis atmosphere on the phase structure of SAPO-11 (C): synthesized in air atmosphere (a), synthesized in N_2 atmosphere (b) and synthesized in N_2 atmosphere with hydroxyl radical quencher (weight ratio between hydroxyl radical quencher and silicon sol= 10:1) (c). (All samples are uncalcined)
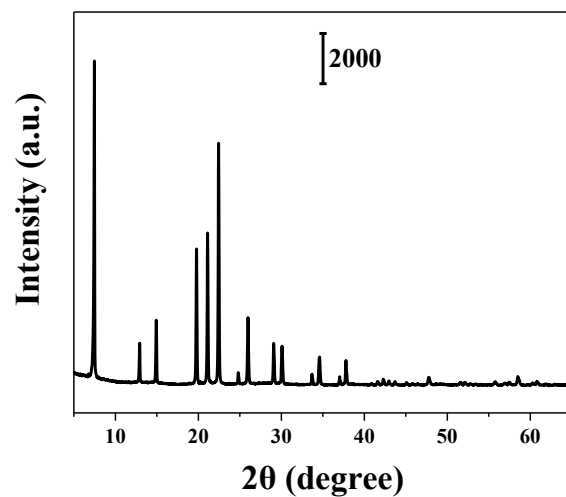
Fig. S3. XRD patterns of SAPO-5 synthesized by adding biochar under 180 ℃ for 5 min. (Samples are uncalcined)
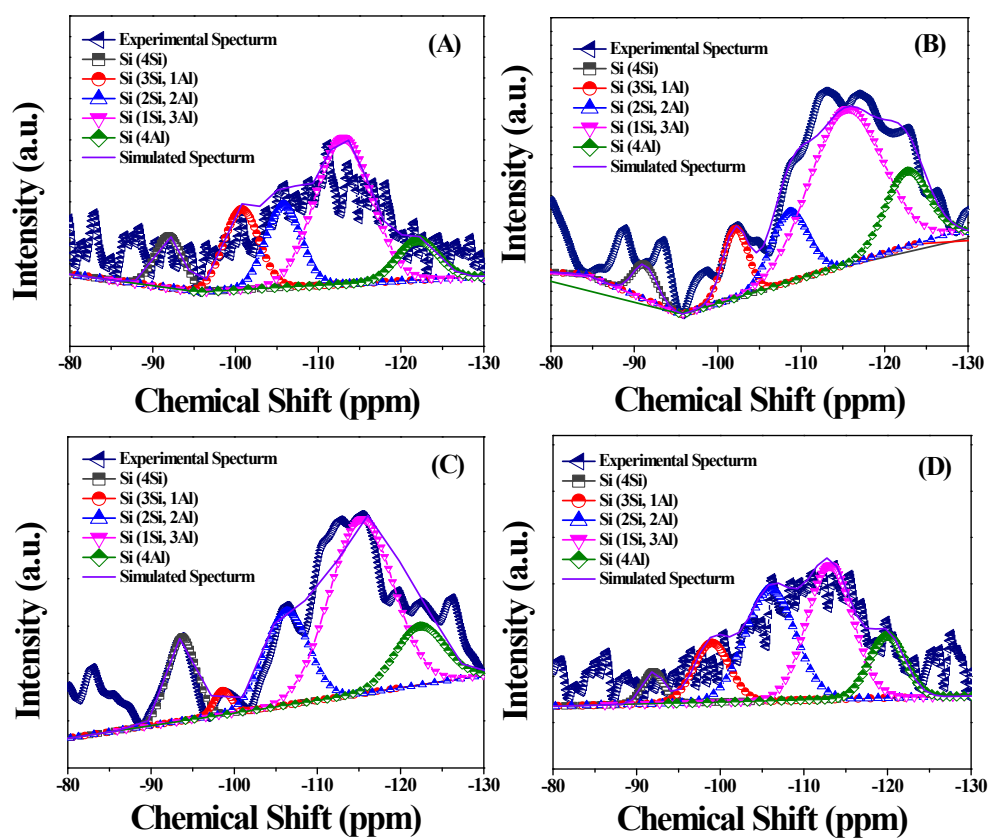
Fig. S4. ^{29}Si MAS NMR spectra of (a) SAPO-11M(B), (b) SAPO-11M(GO), (c) SAPO-11M(AC) and (d) SAPO-11M(G).
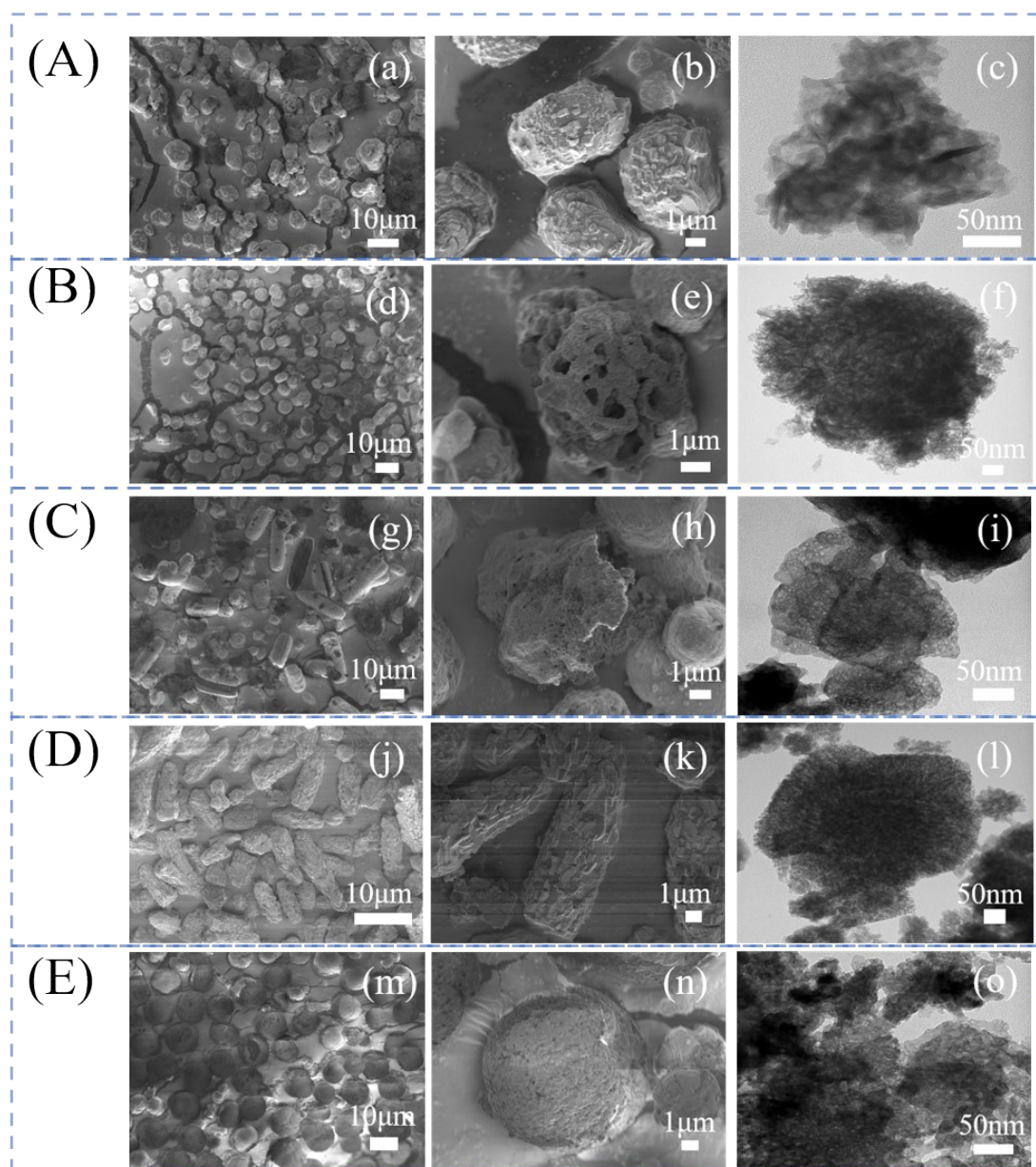
Fig. S5. SEM (a, b, d, e, g, h, j, k, m and n) and TEM (c, f, i, l and o) images of SAPO-11 prepared with adding different types of carbon of (A) carbon-free, (B) biochar, (C) graphene oxide, (D) activated carbon and (E) graphene.
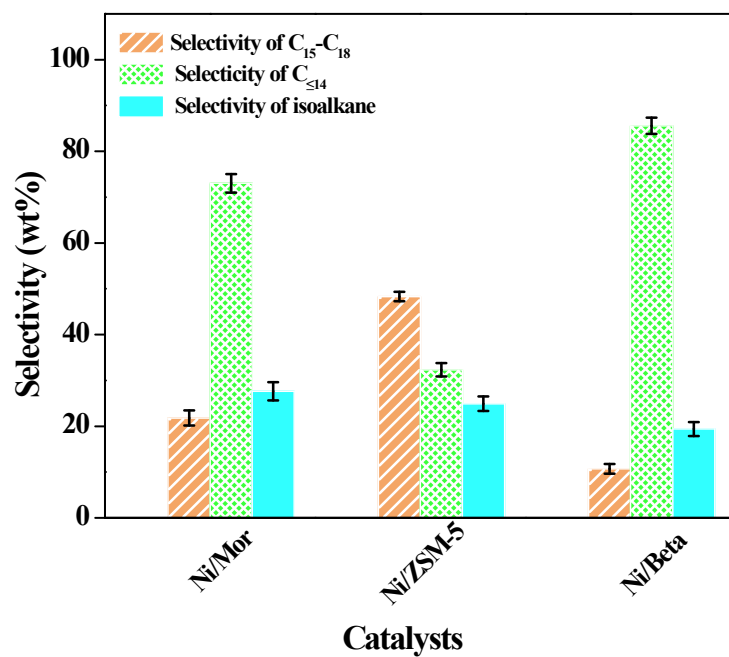
Fig. S6 Product distribution of stearic acid deoxygenation using different catalysts. Conversion of stearic

acids is >99%. Impregnation amount of nickel is similar (5 wt%) in catalysts.

Ni 2p   **(A)**

2p 1/2   2p 3/2 Ni^{2+} 856.4 eV

Statellite 861.9 eV

Ni^{0} 853.0 eV

Intensity (a.u.)

Binding energy (eV)

885 880 875 870 865 860 855 850

Ni 2p   **(B)**

2p 1/2   2p 3/2 Ni^{2+} 856.5 eV

Statellite 862.3 eV

Ni^{0} 852.9 eV

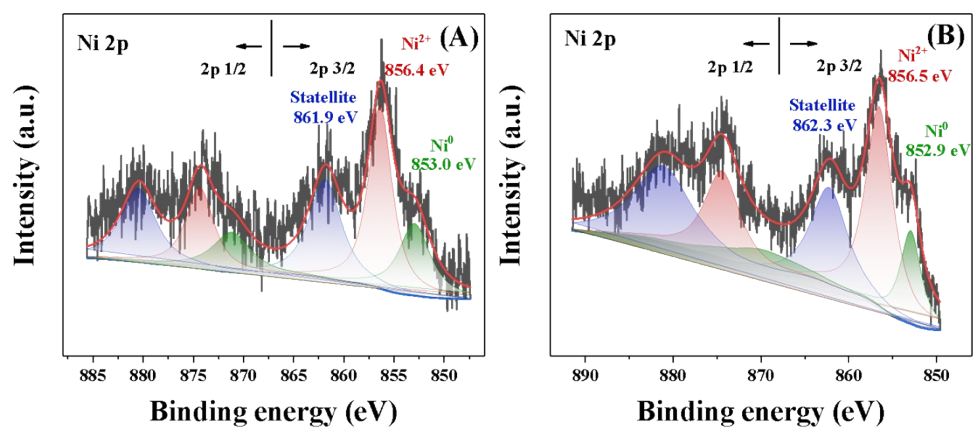Intensity (a.u.)

Binding energy (eV)

890 880 870 860 850

Fig. S7 Ni 2p orbit XPS spectra of (A) Ni/SAPO-11W and (B) Ni/SAPO-11M(B) catalysts.
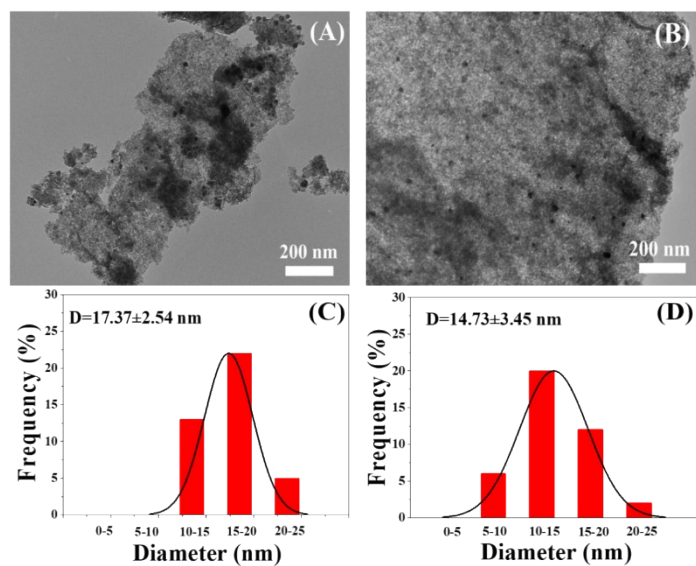
Fig. S8. TEM images (A and B) and particle size distributions (C and D) of nickel in Ni/SAPO-11W (A and C) and Ni/SAPO-11M(B) (B and D).
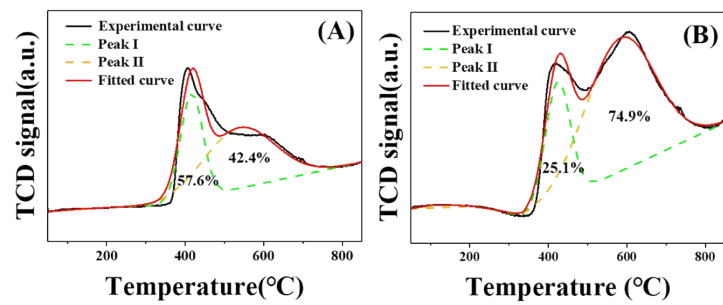
Fig. S9. H$_2$-TPR fitted curves of (A) Ni/SAPO-11W and (B) Ni/SAPO-11M(B).

Table S1. Textural Properties of SAPO-11W, SAPO-11M(B), SAPO-11M(GO), SAPO-11M(AC) and SAPO-11M(G).

Samples	S_{BET} (m²/g)	S_{Micro} (m²/g)	V_{Micro} (cm³/g)	V_{Meso} (cm³/g)	V_{Total} (cm³/g)
SAPO-11W	171	112	0.05	0.12	0.17
SAPO-11M(B)	224	101	0.05	0.23	0.28
SAPO-11M(GO)	241	119	0.06	0.24	0.30
SAPO-11M(AC)	194	84	0.05	0.22	0.27
SAPO-11M(G)	227	111	0.06	0.23	0.29

Table S2. Catalytic performance of catalysts

Catalysts	Loading amount of nickel (wt%)	Conv. (%)	C_{15}-C_{18} paraffin selec. (%)
1	1 wt%	83.5	78.9
2	3 wt%	92.4	87.0
3	5 wt%	99.6	98.1
4	7wt%	99.8	95.2

Reaction conditions:290 °C, 3 h, 4 MPa H_2

Table S3. Catalytic performance of catalysts

Catalysts	Conv. (%)	C_{15}-C_{18} selec. (%)
Ni/SAPO-11H*	99.3±0.2	92.2±0.2
Ni/SAPO-11M(B)*	99.6±0.2	98.1±0.1
Ni/SAPO-11M(AC)*	99.3±0.1	97.5±0.3
Ni/SAPO-11M(GO)*	99.6±0.2	95.9±0.2
Ni/SAPO-11M(G)*	99.6±0.1	93.9±0.2
Ni/SAPO-11H#	87.5±1.3	29.6±2.2
Ni/SAPO-11M(B)#	94.4±0.6	53.9±1.7
Ni/SAPO-11M(AC)#	93.2±0.5	43.0±2.4
Ni/SAPO-11M(GO)#	95.2±0.8	40.1±1.9
Ni/SAPO-11M(G)#	92.9±1.3	44.2±2.3

Notes:

*Reaction temperature 290 ºC; Reaction duration: 3h; Loading amount of Ni: 5wt%

#Reaction temperature 230 ºC; Reaction duration: 3h; Loading amount of Ni: 5wt%

Table S4. Concentration of nickel in Ni/SAPO catalysts

Sample	Ni/SAPO-11W	Ni/SAPO-11M(B)
Concentration of nickel (wt%)[*]	4.3	4.1

*detected by ICP-MS.

Table S5 Concentration of surface metallic particles determined by CO chemisorption

Catalyst	Concentration of surface metallic particles(%)
Ni/SAPO-11W	35.2
Ni/SAPO-11M(B)	48.3

Table S6. Comparison of catalytic performance between published results and current research

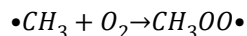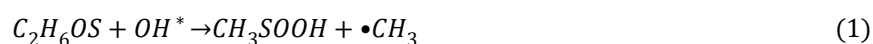| Catalysts	Reaction conditions	Conv. (%)	C_{15}-C_{18} paraffin selec. (%)	Iso-paraffins selec. (%)	Ref.
Ni/SAPO-11	300 ℃, 4.0 MPa H_2, 3h	96.2	93.0	9.8	1
Ni/SAPO-11	290 ℃, 4.0 MPa H_2, 3h	97.6	92.2	10.3	2
Ni/SAPO-11	290 ℃, 2.0 MPa H_2, 3h	92.4	98.4	7.9	3
Ni/SAPO-11M(B)	290 ℃, 4.0 MPa H_2, 3h	99.6	98.1	8.9	Current research

References:

1 Y. Wu, J. Duan, X. Li, K. Wu, J. Wang, J. Zheng, S. Li, D. Wang, Z. Zheng, *Renew. Energ.*, 2023, **218**, 119372.

2 Y. Liu, D. Zheng, H. Yu, X. Liu, S. Yu, X. Wang, L. Li, J. Pang, X. Liu, Z. Yan, *Micropor. Mesopor. Mat.*, 2020, **303**, 110280.

3 D. Zheng, D. Guo, Z. Wang, X. Wang, Y. Shan, X. Liu, Z. Yan, S. Yu, Y. Liu, *Chem. Eng. J.*, 2023, **451**, 138929.

Detection of hydroxyl radicals ($OH^\bullet$)

The method to determine the formation of hydroxyl radicals is based on previous publication. (C. Tai, J. Peng, J. Liu, G. Jiang, H. Zou, *Anal. Chim. Acta.*, 2004, **527**, 73-80.) Hydroxyl radicals react with DMSO to generate formaldehyde, which is reacted with 2,4-dinitrophenylhydrazine (DNPH) to generate corresponding hydrazone ($DNPH_0$), which is analyzed by the high performance liquid chromatography-ultraviolet detector forusing an external standard working curve method.

Assuming that DMSO consumes all hydroxyl radicals, the amount of $OH^\bullet$ produced is calculated based on equations (1-3). The concentration of $DNPH_0$ indirectly determines the concentration of hydroxyl radicals.

$$C_2H_6OS + OH^* \rightarrow CH_3SOOH + \bullet CH_3 \tag{1}$$

$$\bullet CH_3 + O_2 \rightarrow CH_3OO\bullet$$

$$2CH_3OO\bullet \rightarrow HCHO + CH_3OH + O_2 \tag{3}$$

Test methods

Mobile phase: acetonitrile/water=60/40(V/V), flow rate: 0.6 mL/min, column: Waters XBridge BEH C_{18} (4.6*150 mm, 2.7 μm), oven temperature: 25 °C, UV detector wavelength: 355 nm, injection volume: 20 μL.

The synthesis method is similar to 2.2 (main article), but it is necessary to add 8 mL of 250 mmol/L DMSO standard solutions to the Teflon-lined microwave autoclave before microwave heating, and then heat under microwave conditions. After the reaction is completed and the temperature drops to room temperature, take 2 mL of the suspension and filter it with a 0.45 μm

filter. Then add 2.5 mL of H_3PO_4 and NaH_2PO_4 buffer with pH 4.0, 0.2 mL of 6 mmol/L DNPH

standard solution and 0.3 mL of ultrapure water. The mixture was kept at room temperature for 30

minutes, and then detected by HPLC.

Establishment of standard working curve

Prepare a series of acetonitrile solutions of $DNPH_0$ with concentrations of 0.00036, 0.00072,

0.00108, 0.00144, and 0.0018 µg/mL. The standard solution was placed in an aqueous solution at

60 °C to react for 20 minutes. Take 20 µL of sample for analysis, and establish a standard working

curve of $DNPH_0$ peak area and concentration, as shown in Fig. S10. The results show that the

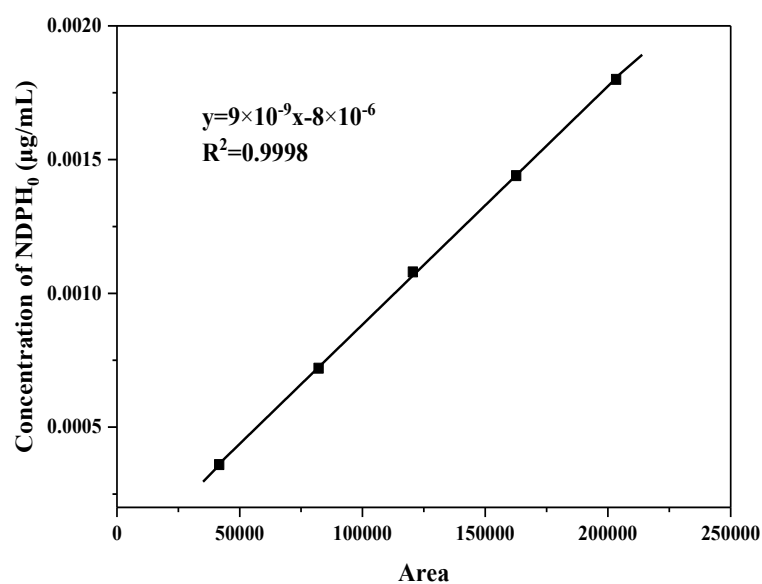standard curve has a good linearity in the concentration range of 0.00036-0.0018 µg/mL, R^2=0.9998.

Fig. S10. The relationship between $DNPH_0$ concentration and peak area