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Nanoparticles synergistically stable pH-switched Pickering emulsion as an efficient reaction system for utilizing ammonia borane for organic conversion

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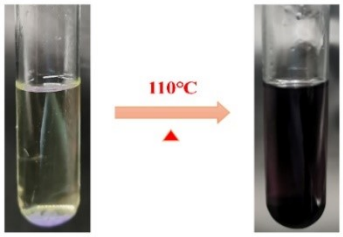
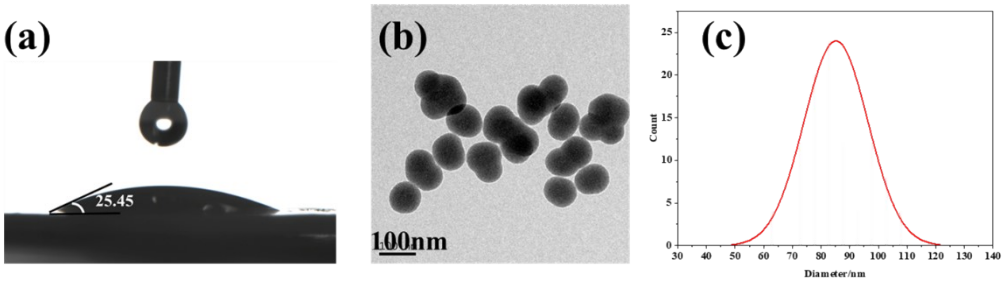
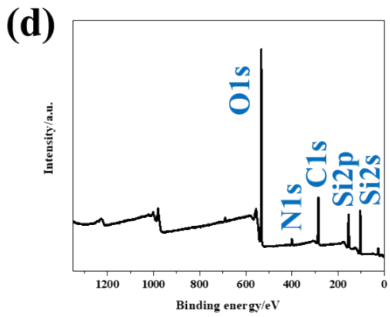


Fig.S1 The chromogenic reaction of SN-NH_2.

When the ninhydrin buffer solution and SN-NH_2 solution were heated at 110℃ for 15 min, the amino group was decomposed and the ninhydrin was reduced to form a blue-purple substance, which proved that -NH graft was successful.





(e)

Material	C	O	Si	N
SN-NH_2	28.79	45.87	22.82	2.52

Fig.S2 (a)Contact angles, (b)TEM image, (c)particle size distribution, (d)XPS test results and (e)elemental distribution of SN-NH_2.

As shown in Figure S2, the contact angle increased from 10.67° to 25.45° after the silicon oxygen coupling agent was grafted on SN surface.TEM images showed that the shape of SN-NH_2 was almost the same as SN, with a particle size of 85.19 nm. The XPS test results also confirmed the successful grafting of -NH, and the atomic percentage of N was 2.52%.

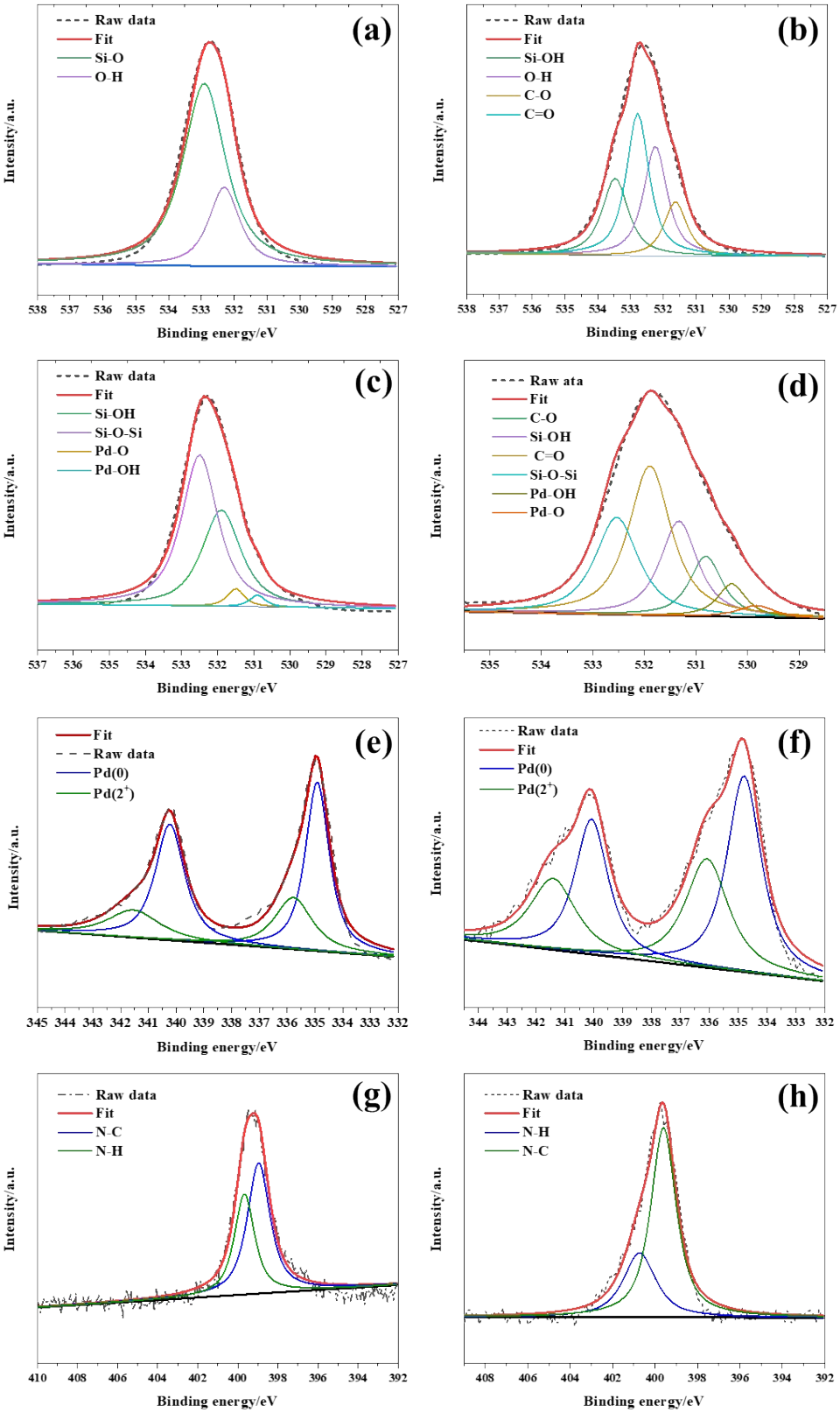


Fig.S3 XPS results of O in (a)SN, (b)SN-COOH, (c)Pd@SN and (d)Pd@SN-COOH. XPS results of (e-f) Pd and (g-h) N in Pd@SN or Pd@SN-COOH.

Tab.S1 elemental distribution of SN, SN-COOH, Pd@SN and Pd@SN-COOH.

Material	C	O	Si	N	Pd
SN	13.52	58.67	27.80		
SN-COOH	28.79	45.87	22.82	2.52	
Pd@SN	18.45	57.53	23.24		0.78
Pd@SN-COOH	38.09	42.40	15.66	2.62	1.23

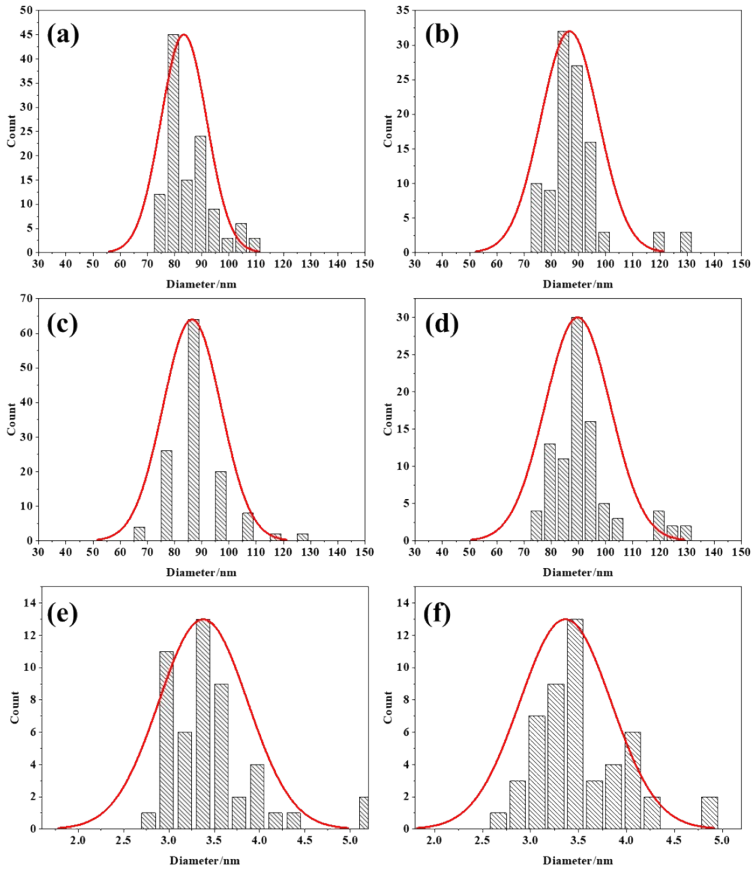


Fig.S4 Particle sizes distribution of nanoparticles. (a) SN, (b) SN-COOH, (c) Pd@SN and (d) Pd@SN-COOH. particle sizes distribution of Pd in (e) Pd@SN and (f) Pd@SN-COOH.

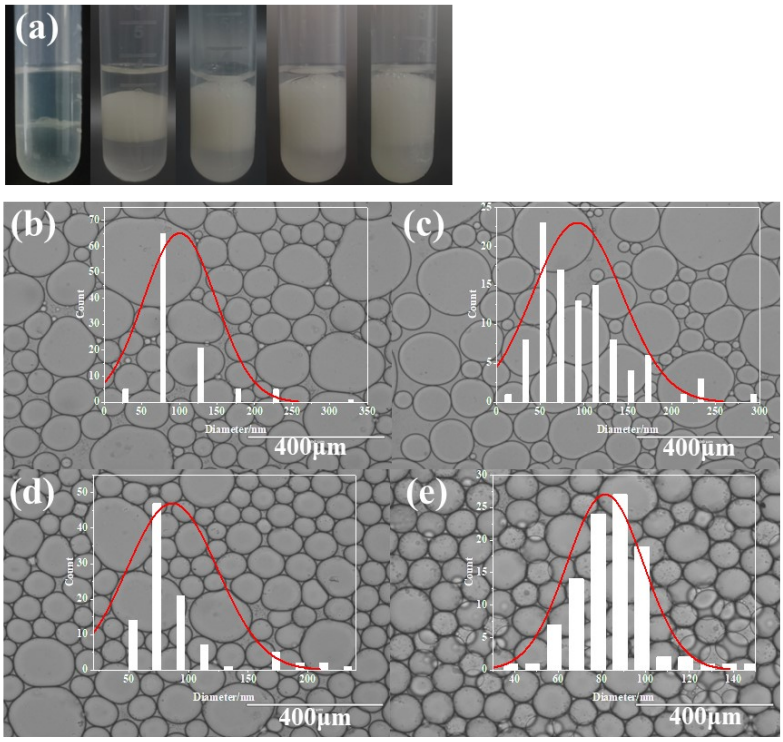


Fig.S5 Optical, micrograph and particle size distribution of Pickering emulsion stabilized by SN-COOH. The oil-water mass ratio is 1:1. (a) Optical photos of conventional Pickering emulsion by SN-COOH. The concentration of SN-COOH from left to right: 0.1wt %, 0.25wt %, 0.5wt%, 0.75wt % and 1wt % respectively. (b-e) Microscopic images and particle size distribution of Pickering emulsions stabilized by SN-COOH. The concentration of SN-COOH: (b) 0.25 wt%, (c) 0.5 wt%, (d) 0.75 wt% and (e) 1 wt%.

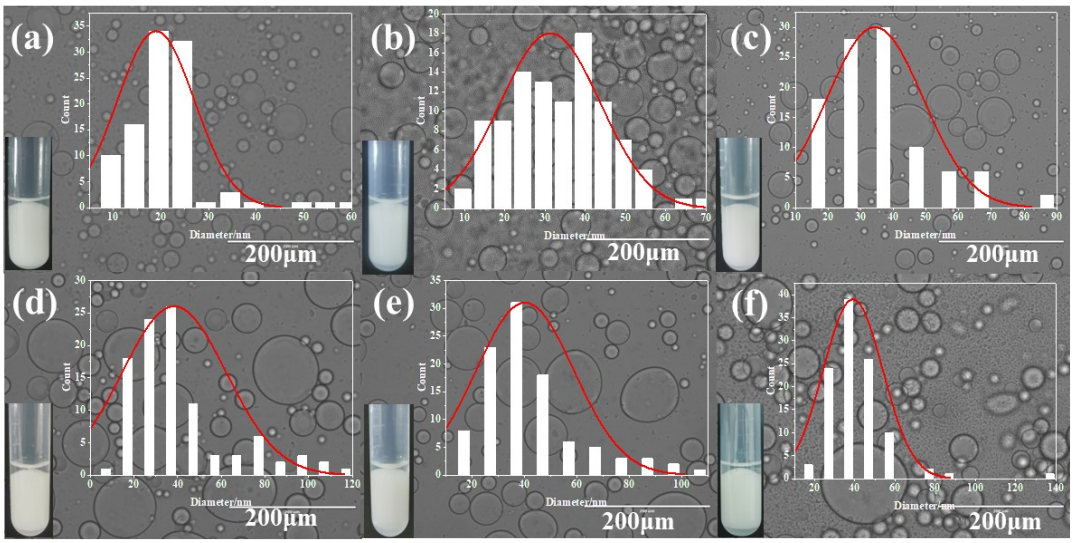


Fig.S6 Optical, micrograph and particle size distribution of Pickering emulsion stabilized by SN and SN-COOH. The oil-water mass ratio is 1:1. "A-B" indicates that the concentrations of SN-COOH are A wt% and the concentrations of SN are B wt%. (a) 0.5-0.5；(b) 0.25-0.25；(c) 0.1-0.1；(d) 0.05-0.05；(e) 0.025-0.025；(f) 0.01-0.01.

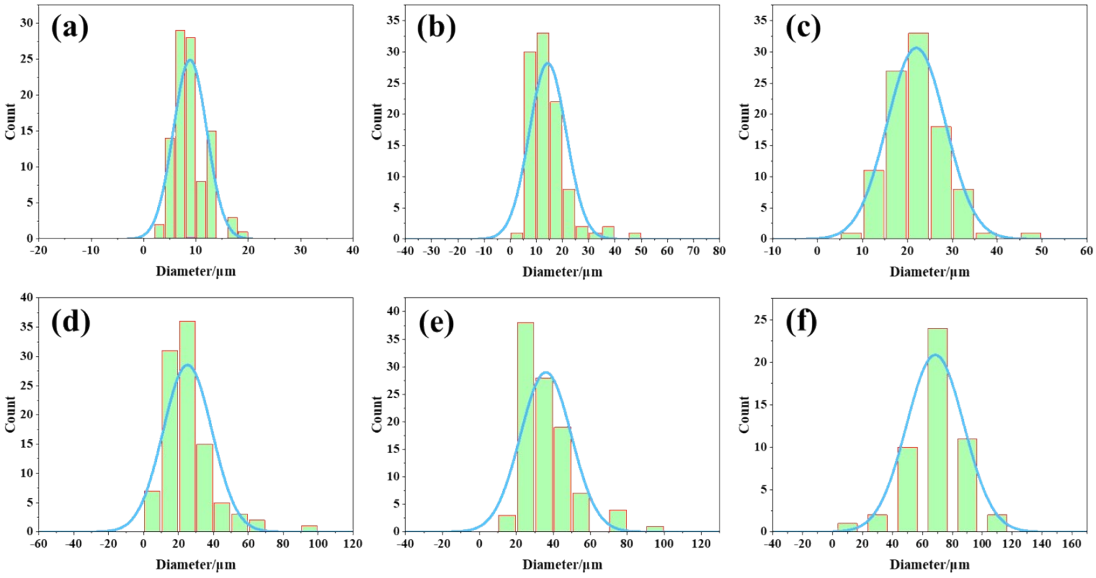


Fig.S7 Particle size distribution of Pickering emulsion stabilized by Pd@SN-COOH and Pd@SN. The oil-water mass ratio is 1:1. The concentrations of Pd@SN-COOH and Pd@SN both are (a) 0.5wt%, (b) 0.25wt%, (c) 0.1wt%, (d) 0.05wt%, (e) 0.025wt% and (f) 0.01wt%.

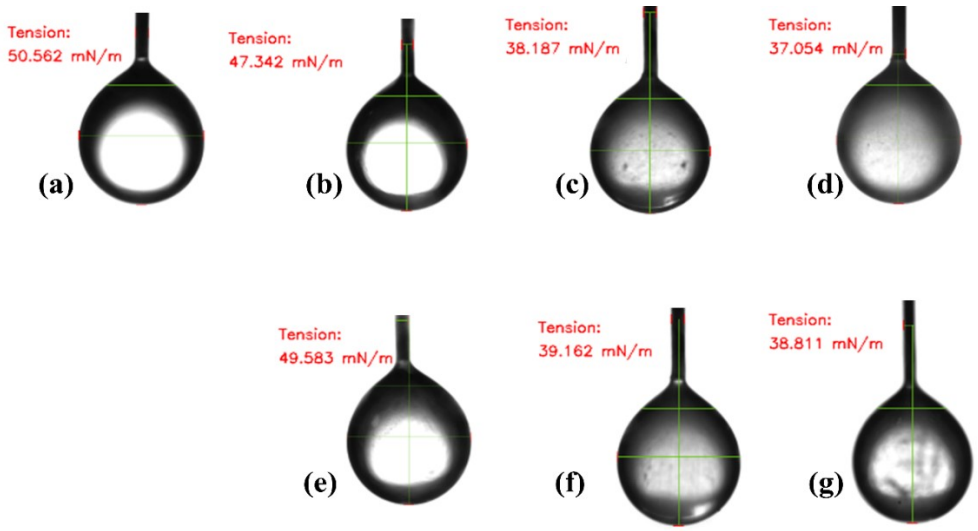


Fig.S8 Test results of interfacial tension. (a) Interfacial tension between water and n-heptane; (b) 0.1 wt% Pd@SN aqueous solution and n-heptane; (c) interfacial tension between 0.1 wt% Pd@SN-COOH aqueous solution and n-heptane; (d) interfacial tension between 0.1 wt% Pd@SN and 0.1 wt% Pd@SN-COOH aqueous solution and n-heptane; (e) interfacial tension between 0.1 wt% SN aqueous solution and n-heptane; (f) interfacial tension between 0.1 wt% SN-COOH aqueous solution and n-heptane; (g) interfacial tension between 0.1 wt% SN and 0.1 wt% SN-COOH aqueous solution and n-heptane.

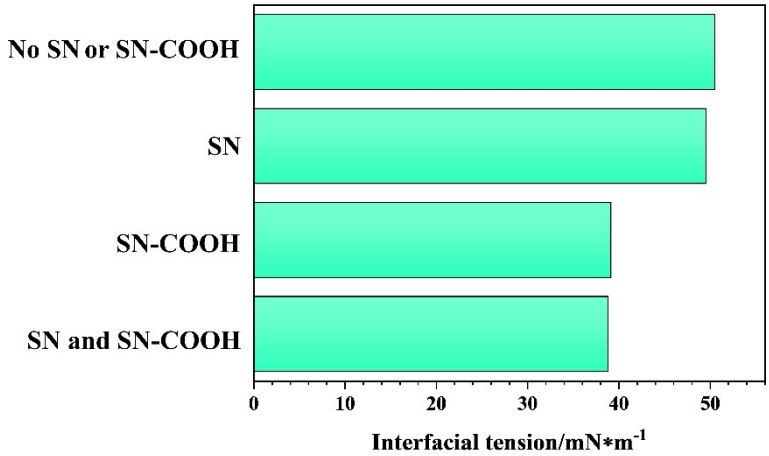


Fig.9 Oil-water interfacial tension. From top to bottom: Interfacial tension between water and n-heptane; interfacial tension between 0.1 wt% SN aqueous solution and n-heptane; interfacial tension between 0.1 wt% SN-COOH aqueous solution and n-heptane; interfacial tension between 0.1 wt% SN and 0.1 wt% SN-COOH aqueous solution and n-heptane.

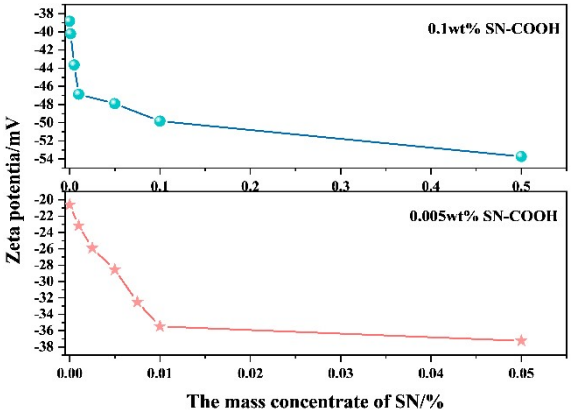


Fig.S10 Zeta potentials of 0.1wt% and 0.005wt% SN-COOH dispersed in water with different mass fractions of SN.

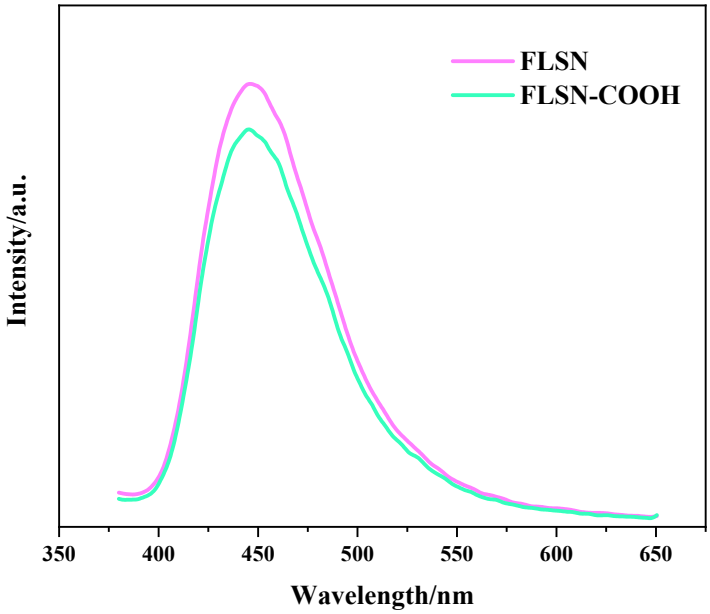


Fig.S11 The fluorescence emission spectra of FLSN and FLSN-COOH. The excitation wavelength is 360 nm.

Fluorescence labelling of SN

The fluorescence-labeled SN was prepared as previously reported[1]. 2 g of SN was dispersed in 250 mL pure water. 1.759 g citric acid monohydrate and 35 mL KH-792 were dissolved in 500 mL pure water and stirred for 5 min. The nano-SiO_2 particle dispersion was added to the above mixed solution and transferred to a

polytetrafluoroethylene autoclave, which was then put in a vacuum oven at 180 ℃ for 3 h. After cooling to room temperature, the dried particles were washed with pure water and ethanol three times. The fluorescence-labeled SN was named FLSN.

Fluorescence labelling of and SN-COOH

FLSN was used to synthesize FLSN-COOH. The synthesis procedure **was** consistent with SN-COOH.

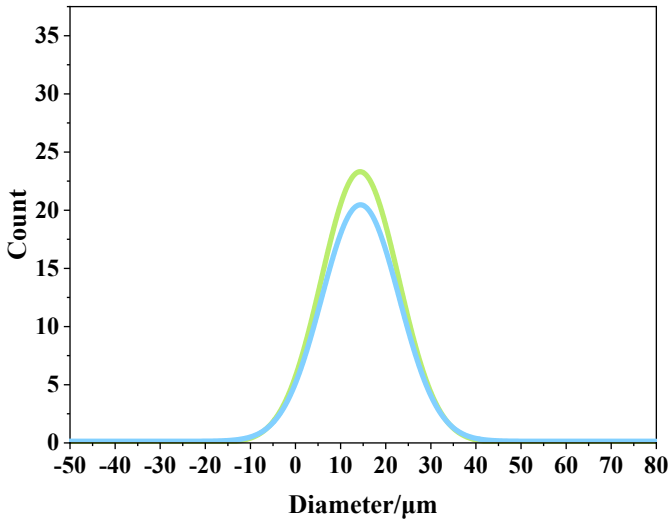


Fig.S12 Particle size of emulsion before and after alternately adding NaOH and HCl aqueous solutions (Pd@SN-COOH and Pd@SN both are 0.1wt%). The oil-water mass ratio is 1:1.

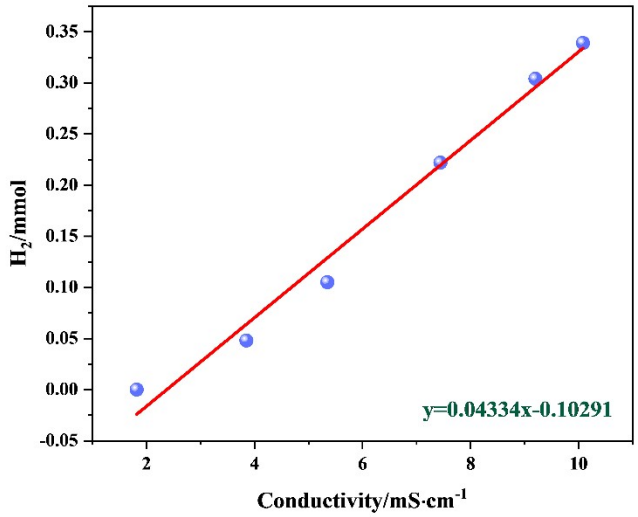


Fig.S13 The standard curves of the relationship between hydrogen evolution amount and conductivity.

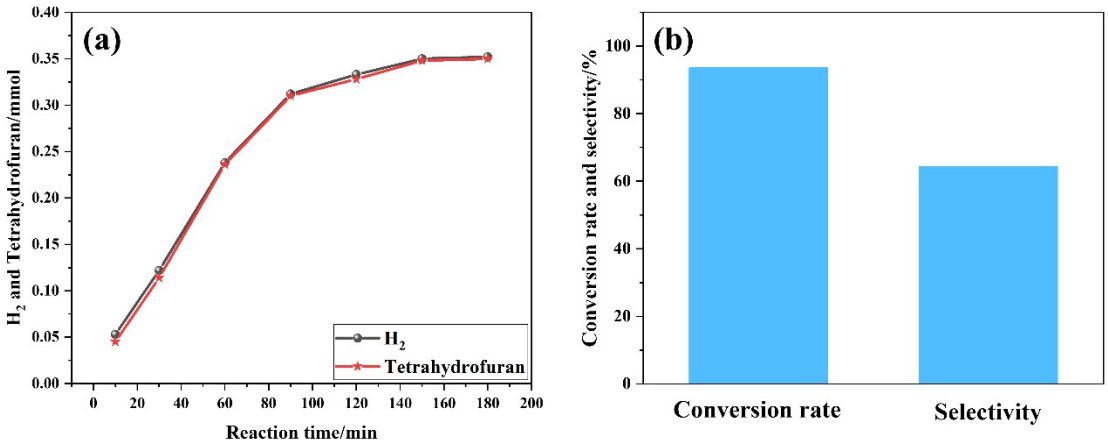


Fig.S14 (a) Kinetic study of hydrogen evolution of AB and hydrogenation reaction of 2,5-DHF in the typical reactor and typical reaction temperature. (b) Conversion of 2, 5-DHF and selectivity of tetrahydrofuran.

2,5-Dihydrofuran is prone to isomerization on Pd. The selectivity of the hydrogenation product tetrahydrofuran was 64.33%.

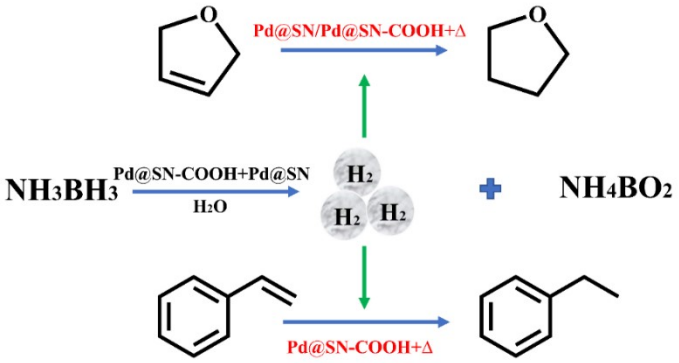


Fig.S15 Schematic Illustration for the conversion of styrene and 2,5-dihydrofuran.

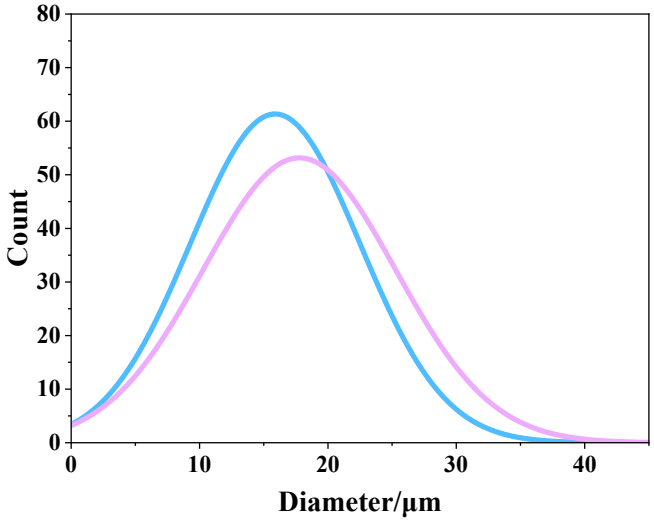


Fig.S16 The particle size distribution of emulsion before and after reaction in the fifth cycle. The blue line represents before reaction and the pink line represents after reaction.

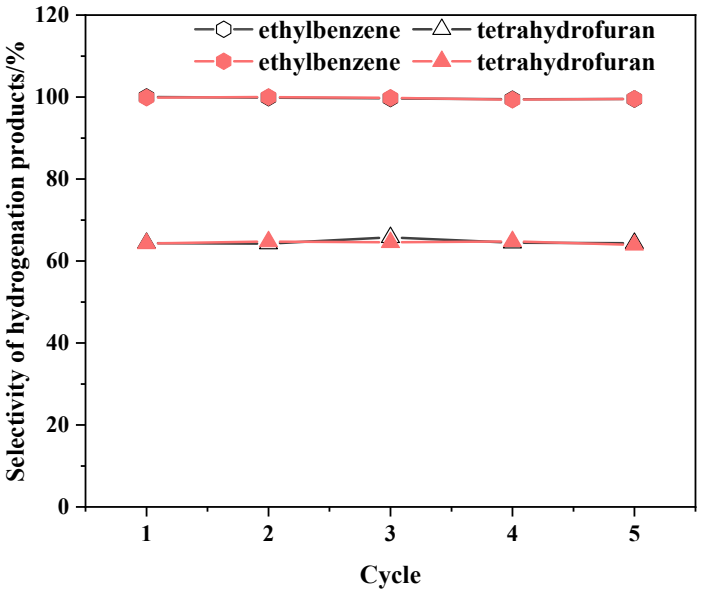


Fig.S17 The selectivity of ethylbenzene and tetrahydrofuran in 5 cycles. Black represent demulsification by NaOH and red represent demulsification by centrifugation.

References

1. J. Jiang, S. Yu, W. Zhang, H. Zhang, Z. Cui, W. Xia and B. P. Binks, *Angew. Chem. Int. Ed.*, 2021, **60**, 11793-11798.