Supporting Information for

pH-Responsive Gas-Water-Solid Interface for Multiphase Catalysis

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Chemicals. *p*-Nitrophenol (AR), *cis*-2-butene-1,4-diol (98%), *o*-nitrophenol (AR), 2-hydroxybenzyl alcohol (98%), 4-hydroxybenzyl alcohol (97%), 3,5-dihydroxybenzyl alcohol (98%), 3-hydroxybenzyl alcohol (98%, Aladdin) and allylalcohol (AR) were purchased from Aladdin (China). $(MeO)_3SiCH_2CH_2CH_2(NHCH_2CH_2)_2NH_2$ (98%) and $(MeO)_3Si(CH_2)_7CH_3$ (98%) were obtained from Beijing J&K Company (China). $Pd(OAc)_2$ (Ac = acetate, 99%) and $HAuCl_4$ (99.9%) were purchased from Shanghai Boka Company (China). Cyclohexane (AR), *n*-hexanol (AR), tetraethyl orthosilicate (TEOS, AR) and ammonia ($NH_3{\cdot}H_2O$, 25 wt%) were purchased from Sinopharm Chemical Reagent Co., Ltd, (China). Triton X-10 (TX-10, 98%) was obtained from Guangzhou Reagent Company (China). Water used in this study was deionized water.

Preparation of silica nanoparticles (SN). Silica nanoparticles were prepared according to the reported method.[1] 5.1 mL of water, 24 mL of *n*-hexanol, 115 mL of cyclohexane and 28.5 mL of TX-10 were mixed together to form a microemulsion system. After stirring for 30 min at room temperature, 9.8 g of TEOS were added and stirred for 5 h. Then 1.5 mL of $NH_3{\cdot}H_2O$ were added with stirring. After further stirring for 18 h, the microemulsion system was destroyed by adding 15 mL of ethanol. The resultant solid was isolated through centrifugation. After being washed with ethanol and dried at 100 °C for 2 h, the desired silica nanoparticles (**SN**) were obtained.

Preparation of SN-O and SN-N nanoparticles. The synthesis of SN-O and SN-N is the same as the SN-ON(x) described except for the the used organosilane modifier**.** For SN-O, 1.5 mmol of $(MeO)_3Si(CH_2)_7CH_3$ was used solely as modifier. For SN-N, 1.5 mmol of $(MeO)_3SiCH_2CH_2CH_2(NHCH_2CH_2)_2NH_2$ was used solely as modifier.

Hydrogenation in the conventional three-phase systems. A mixture of 0.4 mL of *iso*propyl alcohol and 2.1 mL of deionized water was used as solvent. The composition of reaction systems including water, catalysts, SN-ON(*x*) particles and reactant was the same as in the microbubble systems. The procedure is the same as that used in the microbubble reaction systems.

Oxidation in the conventional (bubble-free) multiphase systems. 5.0 mL of deionized water was used as solvent. The composition of the other components including water, catalysts, SN-ON(*x*) particles and reactant was the same as in the microbubble systems. The procedure is also the same as that used in the microbubble reaction systems.

Table S1. Results of elemental analysis of various functionalized silica particles. [a]

Particle code	N/wt.%	C/wt.%
SN-O	0.10	3.29
SN-N	3.03	9.17
SN-ON(5)	0.28	4.47
SN-ON(10)	0.52	4.50
SN-ON(15)	0.84	5.21
SN-ON(20)	0.84	4.95
SN-ON(25)	1.00	5.28

[a] Assuming that there is a residual CH_3O- (unreacted) for each organosilane molecule.

Table S2. Results of *p*-nitrophenol hydrogenation in the microbubble systems with [Pd/SN-ON(*x*) + SN-ON(*x*)] or [Pd/SN-N + SN-N]. [a]

Particle code	Conversion/%
SN-N	11.0
SN-ON(5)	40.5
SN-ON(10)	97.2
SN-ON(15)	100.0
SN-ON(20)	75.2
SN-ON(25)	59.7

[a] Reaction conditions: 2.5 mL water, 1 mmol *p*-nitrophenol, 0.0469 g Pd/SN-ON(*x*) or Pd/SN-N, 0.1409 g SN-ON(*x*) or SN-N, 0.9 MPa, 25 °C, 1200 rpm, 50 min.

Table S3. Results of *p*-nitrophenol hydrogenation in bulk methanol over different catalysts. [a]

Particle code	Conversion/%
SN-N	52.2
SN-ON(5)	42.0
SN-ON(10)	48.5
SN-ON(15)	43.5
SN-ON(20)	36.2
SN-ON(25)	32.3

[a] Reaction conditions: 0.1839 g *p*-nitrophenol, 2.5 mL methanol, 0.0469 g Pd/SN-ON(*x*) or Pd/SN-N, 0.1409 g SN-ON(*x*) or SN-N, 0.5 h, 0.9 MPa, 25 °C.

Table S4. Conversions for the 2-hydroxybenzyl alcohol oxidation in the microbubble system and in the conventional multiphase reaction at different stirring speeds. [a]

Stirring speed/rpm	400	600	800	900	1000
Microbubble system/%	78	87	89	90	89
Conventional multiphase system/%	21	33	46	45	47

[a] Reaction conditions: 5 mL water, 0.5 mmol substrate, 0.25 g Au/SN-ON(15) catalyst particles, 0.375 g SN-ON(15) particles. For the microbubble system, before reaction the system was stirred at 1600 rpm (at room temperature) for 10 min to produce catalyst particle-stabilized microbubbles.

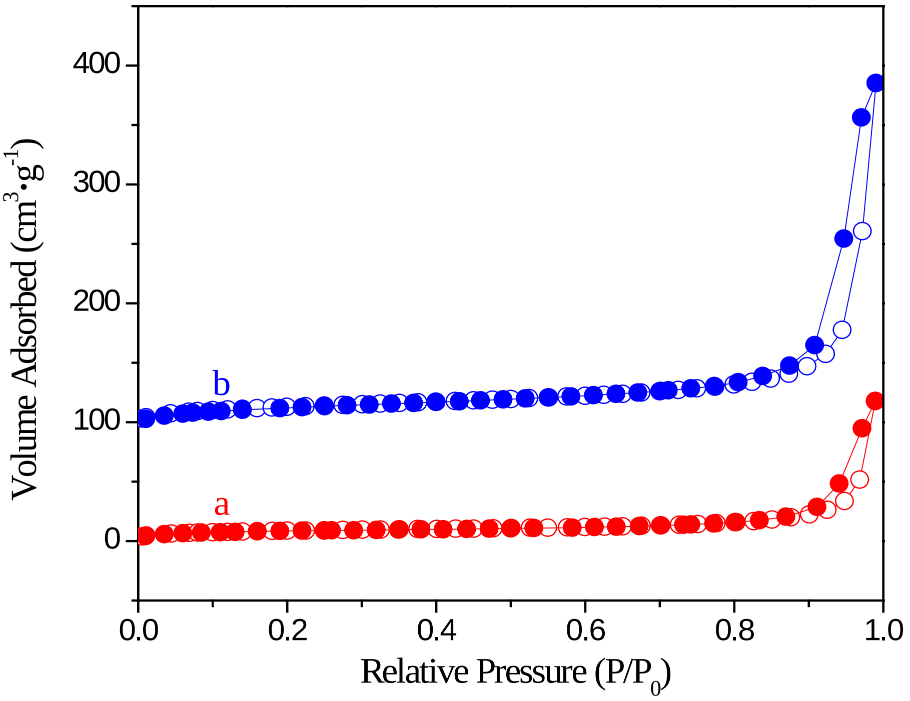


Figure S1. Nitrogen sorption isotherms of (a) unfunctionalized silica and (b) SN-ON(15) nanoparticles. Their specific surface areas are 32 and 50 m^2 g^{-1}, respectively. Open points adsorption; filled points desorption

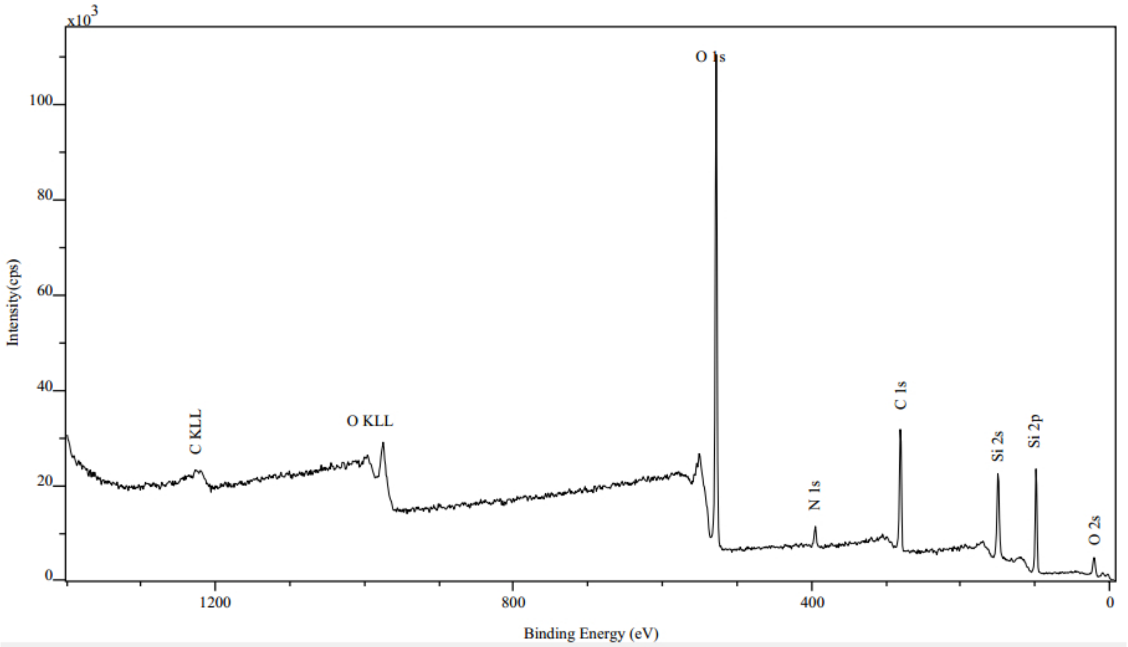


Figure S2. X-ray photoelectron spectroscopy (XPS) spectrum of SN-ON(15) particles.

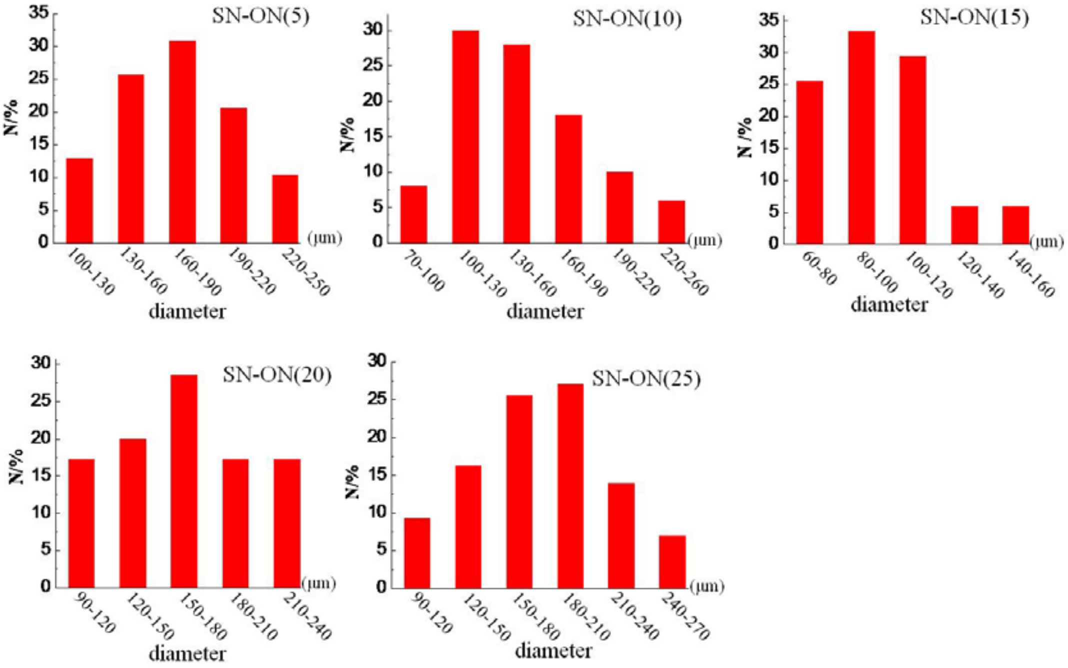
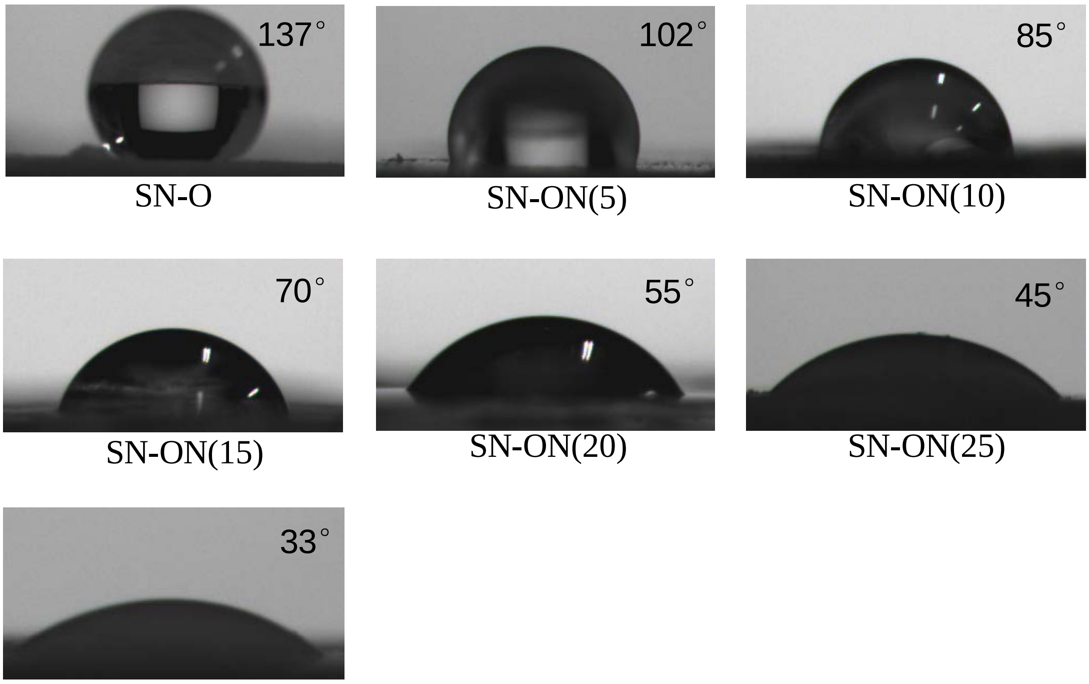


Figure S3. Size distribution of the air-filled microbubbles stabilized with the different types of SN-ON(*x*) particles. Particle concentration is 7.5 wt.% in water.



SN-O SN-ON(5) SN-ON(10)

SN-ON(15) SN-ON(20) SN-ON(25)

SN-N

Figure S4. Advancing contact angle measurements through water of water drops in air on disks of functionalized silica particles.

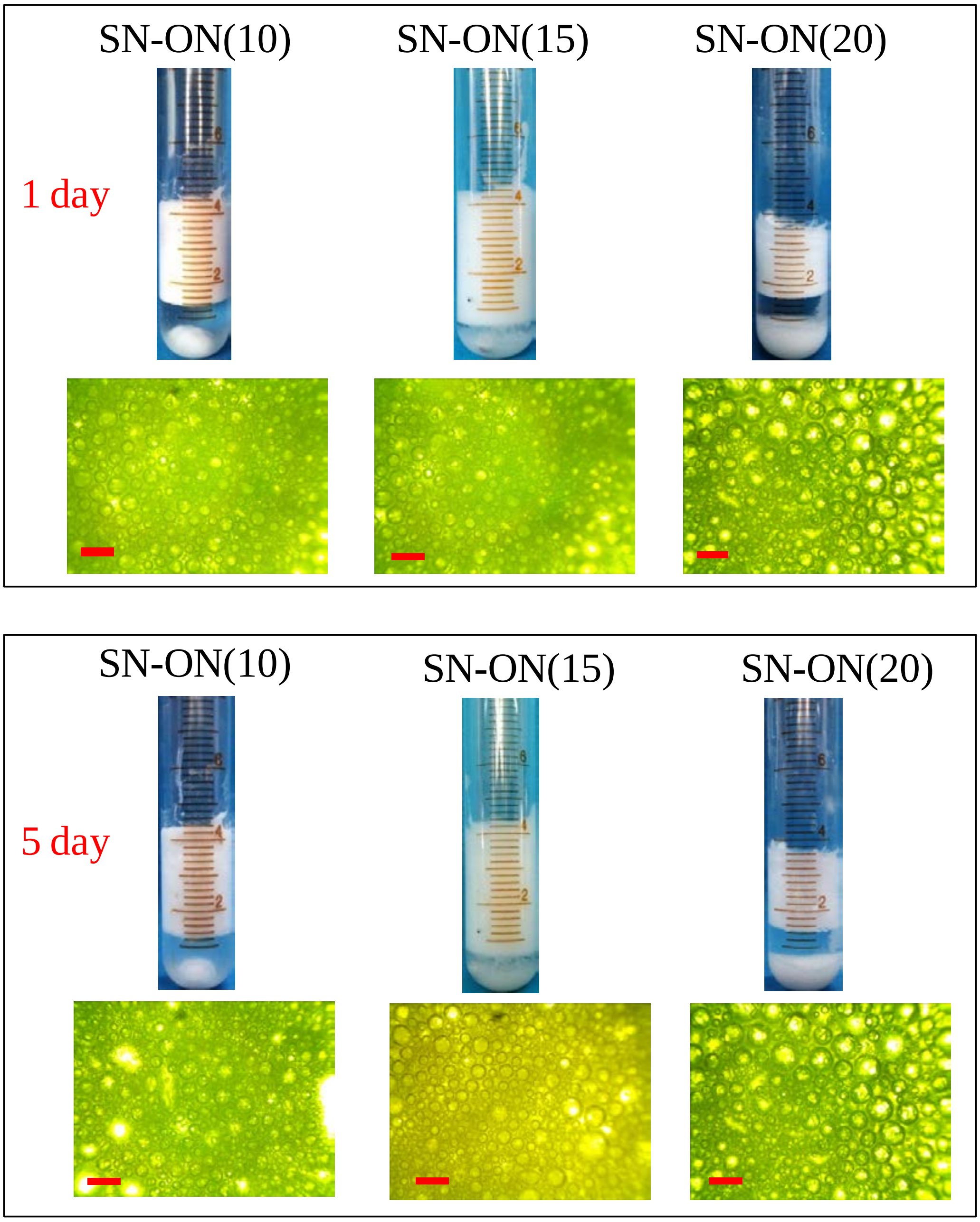


Figure S5. Appearance of the air-filled microbubbles stabilized with SN-ON(10), SN-ON(15) or SN-ON(20) particles after standing for 1 and 5 days, and their corresponding optical micrographs. Scale bar = 200 μm.

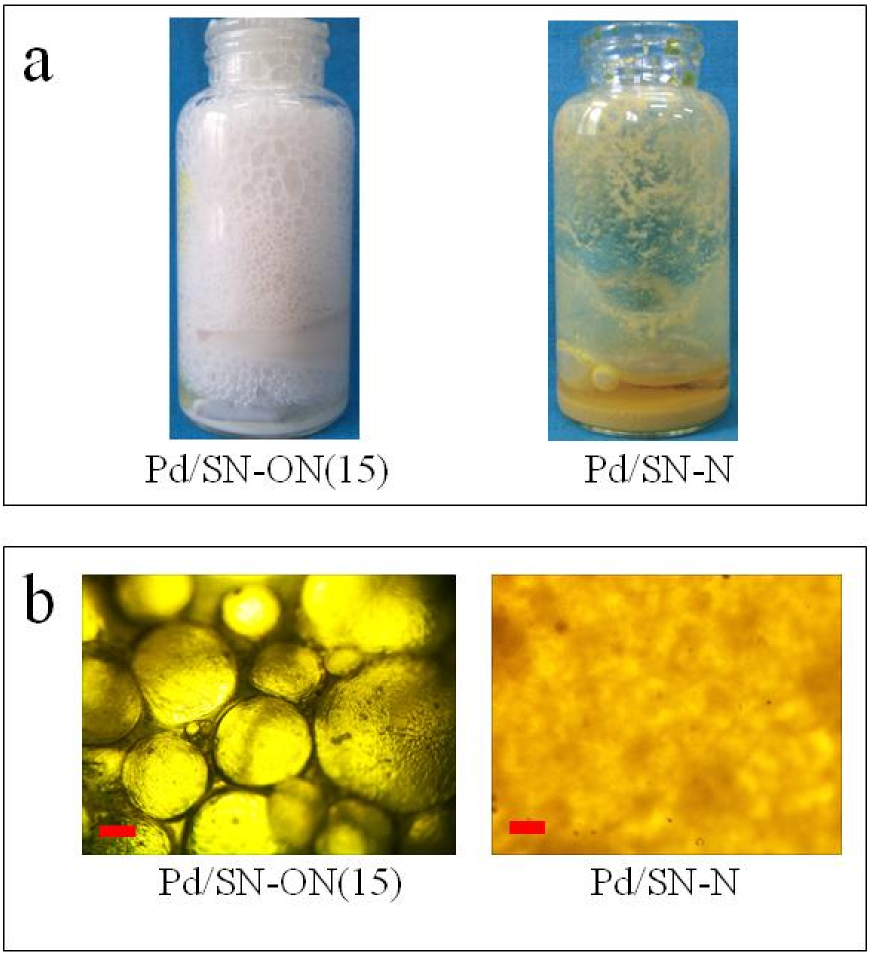


Figure S6. (a) Appearance of the hydrogenation reaction systems with Pd/SN-ON(15) + SN-ON(15) catalyst particles (left) and Pd/SN-N + SN-N catalyst particles (right) at the end of reaction; (b) their corresponding optical micrographs. Scale bar = 200 μm.

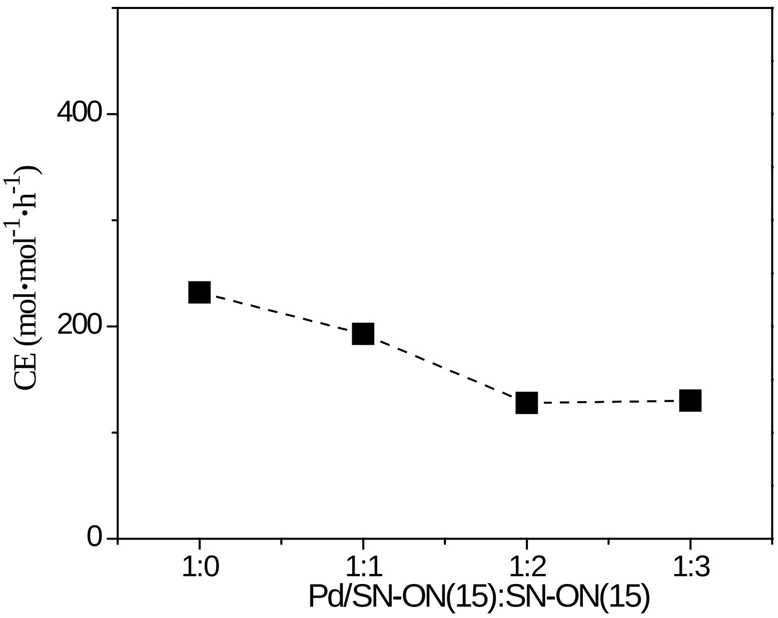


Figure S7. Catalysis efficiency during hydrogenation *versus* the mass ratio of Pd/SN-ON(15) particles to SN-ON(15) particles in conventional multiphase bubble-free systems. A mixture of 0.4 mL of *iso*propyl alcohol and 2.1 mL of water was used as solvent; other reaction conditions are the same as those of microbubble systems.

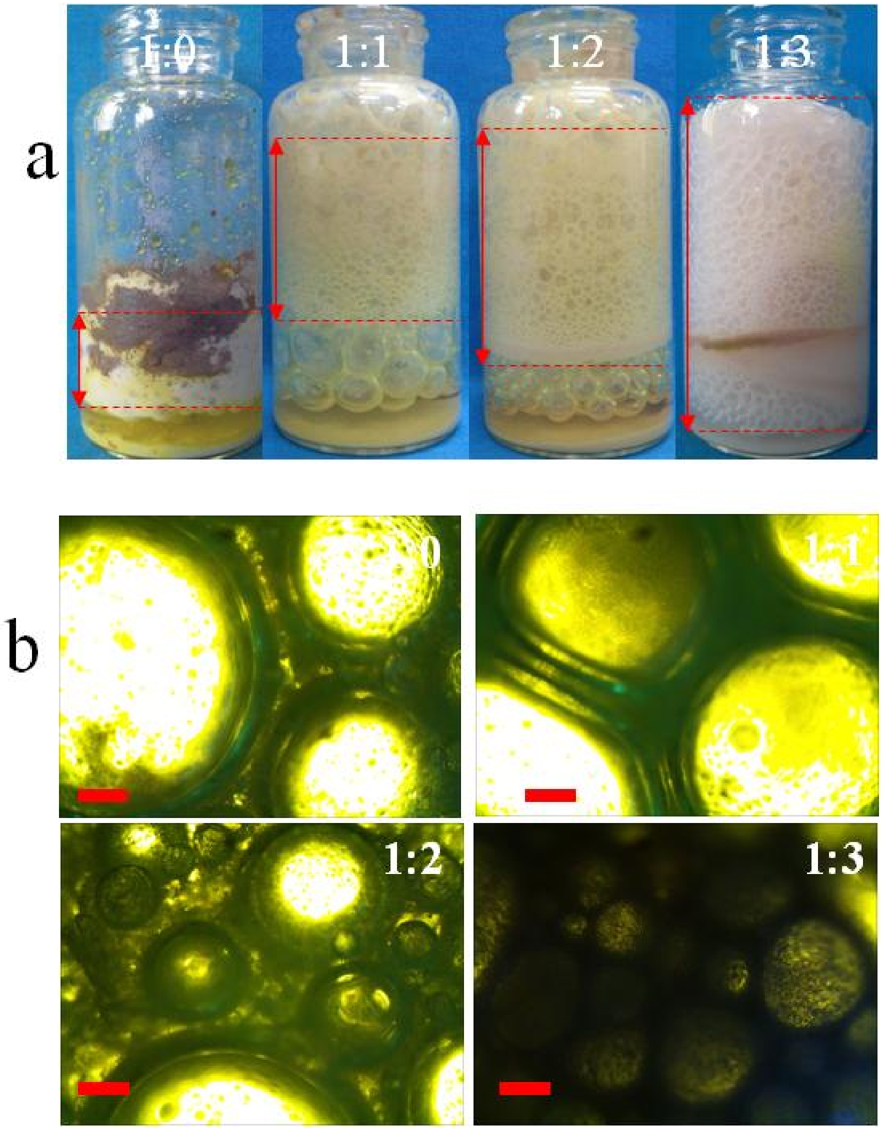


Figure S8. (a) Appearance of the hydrogenation reaction systems using a mixture of Pd/SN-ON(15) catalyst particles and SN-ON particles at the end of reaction; (b) their corresponding optical micrographs. Scale bar = 200 μm. The mass ratio of Pd/SN-ON(15) to Pd/SN-ON is given on the vessels and micrographs.

Recycle	Run 1	Run 2	Run 3	Run 4	Run 5
Reaction time（Min）	40	60	80	110	140
Conv.%	96	100	100	81	91

Figure S9. Appearance of microbubble reaction systems for the consecutive hydrogenation of *p*-nitrophenol and the reaction results. The reaction conditions are the same as those stated in Table 2.

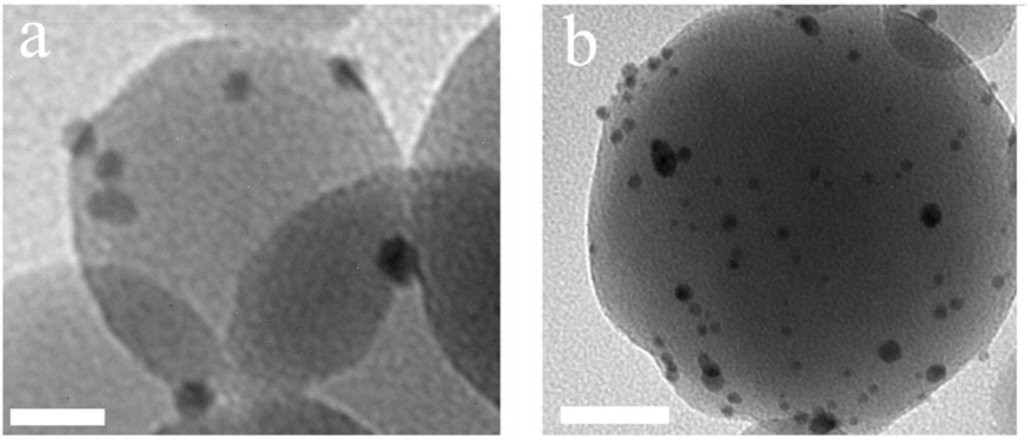


Figure S10. TEM images of the recycled (a) Pd/SN-ON(15) and (b) Au/SN-ON(15) catalysts. Scale bar = 20 nm. For Pd/SN-ON(15) recycled five times, the Pd loading is determined as 0.21 wt.%. For Au/SN-ON(15) recycled ten times, the Au loading is determined as 0.72 wt.%.

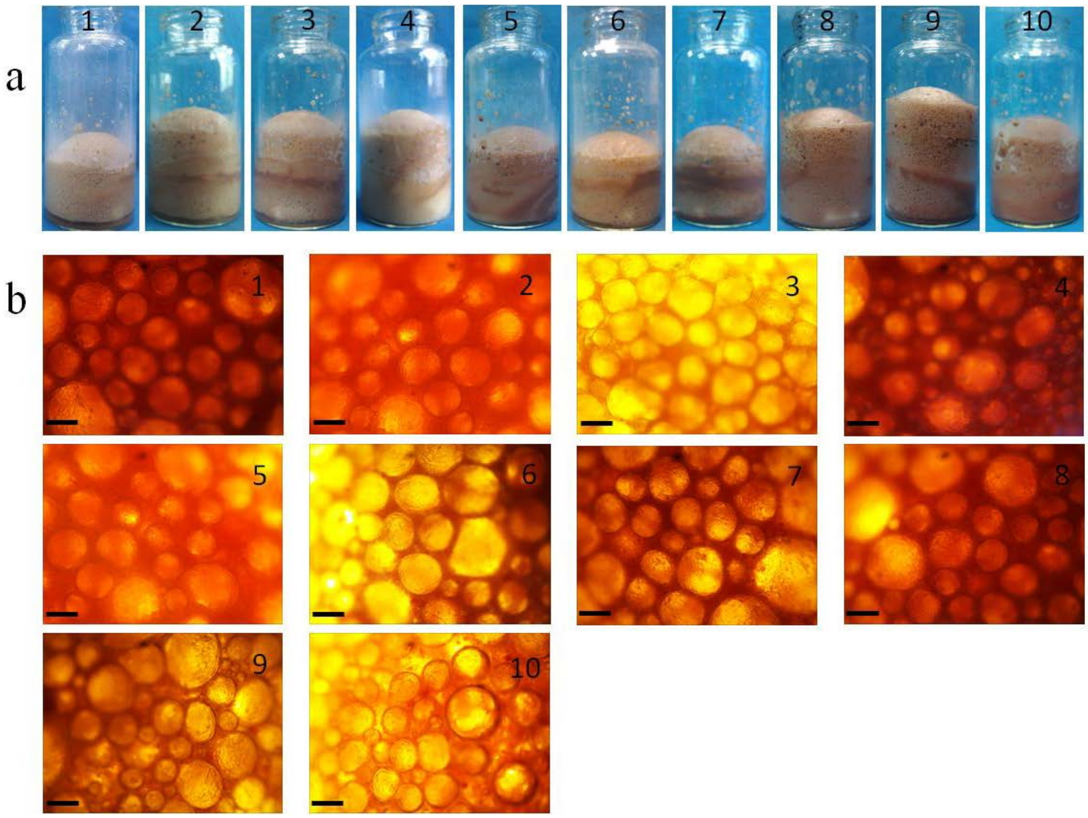


Figure S11. (a) Appearance of ten cycles of 2-hydroxybenzyl alcohol oxidation in the microbubble system using Au/SN-ON(15) catalyst particles; (b) their corresponding optical micrographs. Scale bar = 200 μm.

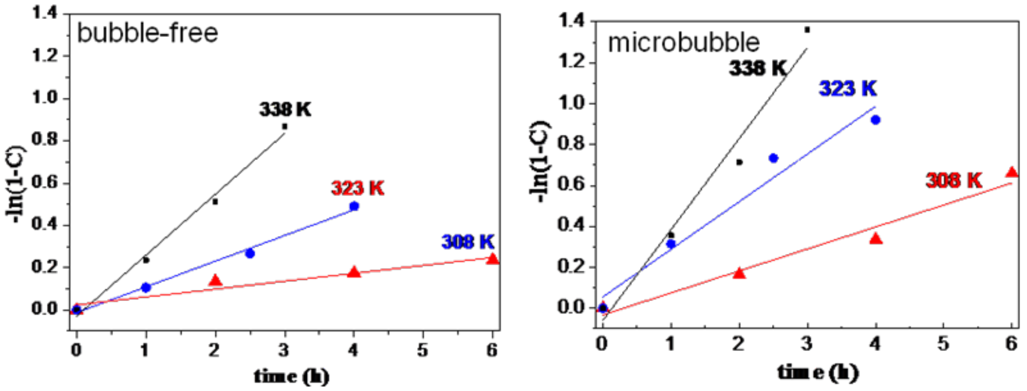
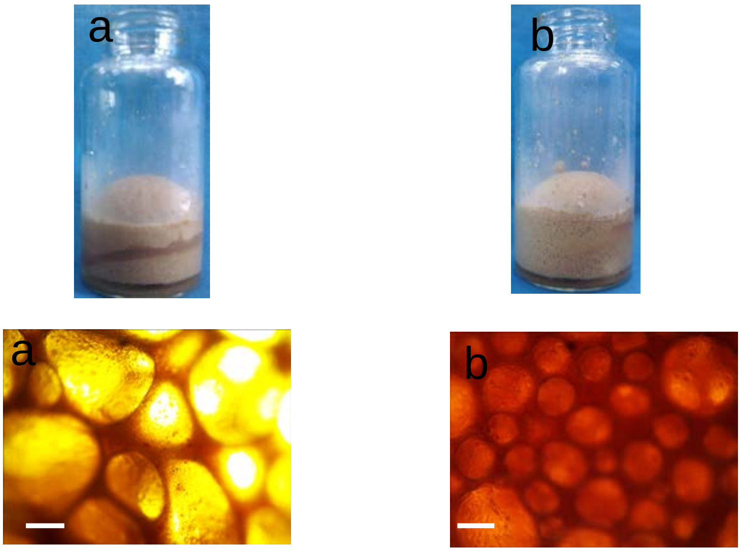


Figure S12. Time course of conversion for the conventional bubble-free multiphase oxidation system (left) and the microbubble oxidation system (right) at different temperatures. C is the substrate concentration (2-hydroxybenzyl alcohol) in M. The reaction shows pseudo-first order kinetics with respect to substrate concentration and ln(1-C) is plotted accordingly (ref. 57).



CE= 36 mol· mol^{-1}· h^{-1}

CE= 53 mol· mol^{-1}· h^{-1}

Figure S13. Appearance of the oxidation systems for different bubble sizes and their corresponding optical micrographs. Scale bar = 200 μm. (a) A mixture of 0.1250 g Au/SN-ON(15) catalyst particles and 0.0625 g SN-ON(15) particles; (b) a mixture of 0.1250 g Au/SN-ON(15) catalyst particles and 0.1875 g SN-ON(15) particles. The other conditions are the same as those described in Figure 8. CE = moles of converted substrate/moles of Pd × reaction time (h).