

Supporting Information

A pH-switched Pickering emulsion catalysis system: high reaction efficiency and facile catalyst recycling

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EXPERIMENTAL SECTION

Chemicals. *p*-Methylenzaldehyde (97%), butyl methacrylate (GR, 99%), isopropenylbenzene (99%), phenylacetylene (97%), styrene (AR, 98%) and benzaldehyde (99%) were purchased from Aladdin (China). *N*-benzylideneaniline (98%) was purchased from Tokyo Chemical Industry Co., Ltd. (Japan). Methyl acrylate (CP, 98%), (MeO)₃SiCH₂CH₂CH₂(NHCH₂CH₂)₂NH₂ (98%) and (MeO)₃Si(CH₂)₇CH₃ (98%) were obtained from Beijing J&K Company (China). Pd(OAc)₂ (Ac = acetate, 98%) was purchased from Shanghai Boka Company (China). Cyclohexane (AR), *n*-Hexanol (AR), Tetraethyl orthosilicate (TEOS, AR) and ammonia (NH₃ • H₂O, 25wt%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Triton X-10 (TX-10, 98%) was obtained from Guangzhou Reagent Company (China). Deionized water was used in this study.

SiO₂ nanospheres (SN). SiO₂ nanospheres 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 NH₃•H₂O 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 obtained SiO₂ nanoparticles (SN) were obtained.

SN-ON nanospheres. 1.0 g of as-synthesized SiO₂ nanospheres (dried at 125 °C for 4 h) was dispersed into toluene (5 mL). A mixture of (MeO)₃SiCH₂CH₂CH₂(NHCH₂CH₂)₂NH₂ and (MeO)₃Si(CH₂)₇CH₃ were added this suspension. After refluxing at 110 °C for 4 h under N₂ atmosphere, the material obtained was isolated by centrifugation, washed five times with toluene and dried. The total amount of these two organosilanes was kept at 1.5 mmol, the molar fraction of triamine silane in this mixture was 10% (the molar fraction of octyl organosilane was 90%). The modified silica nanospheres material is denoted as SN-ON.

SN-N or SN-O nanospheres. For SN-N, 1.5 mmol of (MeO)₃SiCH₂CH₂CH₂(NHCH₂CH₂)₂NH₂ was used solely as modifier. For SN-O, 1.5 mmol of (MeO)₃Si(CH₂)₇CH₃ was used in presence 1.5 mmol of N(CH₂CH₃)₃ as catalyst. Other procedures are the same as the SN-ON.

Pickering emulsion preparation and demulsification. 4 mL of deionized water and 4 mL of ethyl acetate were added into a vial containing 0.04 g of solid emulsifier. Vigorous stirring with a magnetic bar (10 mm in length) at 800 rpm for 3 min led to Pickering emulsions.

A few drops of HCl solution (1 M) was added into Pickering emulsions. After further stirring gently for 3 min, Pickering emulsion was completely destroyed and the SiO₂ nanospheres were transferred to the water phase. A few drops of NaOH solution (1 M) were added to the demulsified systems and the pH was adjusted to ca. 7-8. After vigorously stirring at 800 rpm for 3 min Pickering emulsion formed again.

Pd/SN-ON. 1 g of SN-ON was dispersed into 5 mL of toluene containing 0.0211 g of Pd(OAc)₂. After Pd(OAc)₂ was fully absorbed by the particles (UV-Vis spectroscopy was used to monitor the absorbance of the solution), the solid material was isolated out through centrifugation. The Pd-adsorbed solid was further reduced with NaBH₄ dissolved in 5 mL of a mixture of toluene and ethanol (*V/V*=20:1). After stirring for 4 h at room temperature, the solid was isolated by centrifugation and washed four times with ethanol. After being dried under vacuum, the solid catalyst was achieved, which was denoted as Pd/SN-ON. The Pd loading for each catalyst was kept at 1 wt%, confirmed by ICP-AES determinations.

Catalytic reaction in Pickering emulsion system. 5.6 mL of deionized water and 5.6 mL of ethyl acetate were added into a glass vial containing 0.056 g of Pd/SN-ON particles. A given amount of reactant was then added into this bottle. The vial was placed in an autoclave (100 mL). After being purged four times with H₂ (99.99%), the H₂ pressure was elevated to the desired pressure. Hydrogenation was conducted under stirring at rate of 800 rpm (a magnetic stirring bar with length of 10 mm). At the end of reaction, the autoclave was de-pressurised and the pH was adjusted to 3-4 using HCl solution (1M). The Pickering emulsion system was destroyed under gentle stirring.

The isolated organic phase was analysis with GC analysis.

Hydrogenation in the conventional biphasic System. A mixture of 1.6 mL of isopropyl alcohol and 4 mL of deionized water was used to replace 5.6 mL deionized water. The other conditions were the same as those of Pickering emulsion systems.

Catalyst Recycling. At the end of the hydrogenation reaction of styrene, the autoclave was de-pressurised and the pH was adjusted to 3-4 using HCl solution (1 M). After gentle stirring 3-5 min, the Pickering emulsion was demulsified and the solid catalyst was held in water phase. The resolved organic phase was completely removed. In the next reaction cycle, 5.6 ml of fresh ethyl acetate and a given amount of styrene were added into the water containing catalyst and the pH was adjusted to 7-8 using NaOH solution (1M). The other procedure is the same as that in the first reaction cycle. At the beginning of the third, sixth, ninth, twelfth and fifteenth reaction cycles, the aqueous phase of the reaction systems was replaced with an equal volume of fresh water to prevent the buildup of salt.

Characterization. Samples for transmission electron microscope (TEM) observations were prepared by dispersing the sample powder in ethanol using ultrasound and then allowing a drop of the suspension to evaporate on a copper grid covered with a holey carbon film. TEM images of silica particles were obtained on a JEOL-JEM-2000EX instrument (operated at 120 kV). The electron energy loss energy (EELS), TEM images and X-ray energy dispersive spectroscopy (EDS) were achieved on a field emission transmission electron microscope equipped with an energy dispersive spectrometer (FEI Tecnai G2 F20, 200 kV). N₂ physisorption was measured by using an ASAP2020 volumetric adsorption analyzer. Before measuring, all samples were outgassed at 120 °C under vacuum for 6 h. The surface area was calculated from the adsorption branch in the relative pressure range of 0.05–0.15 using the Brunauer–Emmett–Teller (BET) method. Photographs were observed on an optical microscope (XSP-8CA, Shanghai, China). The emulsions were mounted on a glass slide and were observed with a digital camera. C and N contents were determined on a Vario EL instrument (Elementar). Solid state NMR spectra were recorded on an Infinityplus 300 MHz spectrometer: for ¹³C CP-MAS NMR experiments, 75.4 MHz resonant frequency, 4 kHz spin rate, 4 s pulse delay, 1.0 ms contact time, hexamethyl benzene as a reference compound; for ¹³Si CP-MAS NMR experiments, 79.6 MHz resonant frequency, 4 kHz spin rate, 4.0 s pulse delay, TMS as a reference compound.

Reference

- 1 D. Y. Kong, C. M. Zhang, Z. H. Xu, G. G. Li, Z. Y. Hou and J. Lin, *J. Colloid Interface Sci.*, 2010, **352**, 278.

Table S1 Elemental analysis results of functionalized SiO₂ nanospheres.

modified SiO ₂ nanosphere	N/wt.% [Triamine (mmol/g)]	C/wt.% [Octly (mmol/g)]	Triamine /Octly ^b
SN-O	0.10 (--)	3.29 (0.306)	0
SN-N	3.03 (0.721)	9.17 (--)	∞
SN-ON	0.52 (0.123)	4.50 (0.308)	0.4

^aAssuming that there is a residual CH₃O- (unreacted) for each organosilane molecule. ^b The molar ratio of triamine to octyl group.

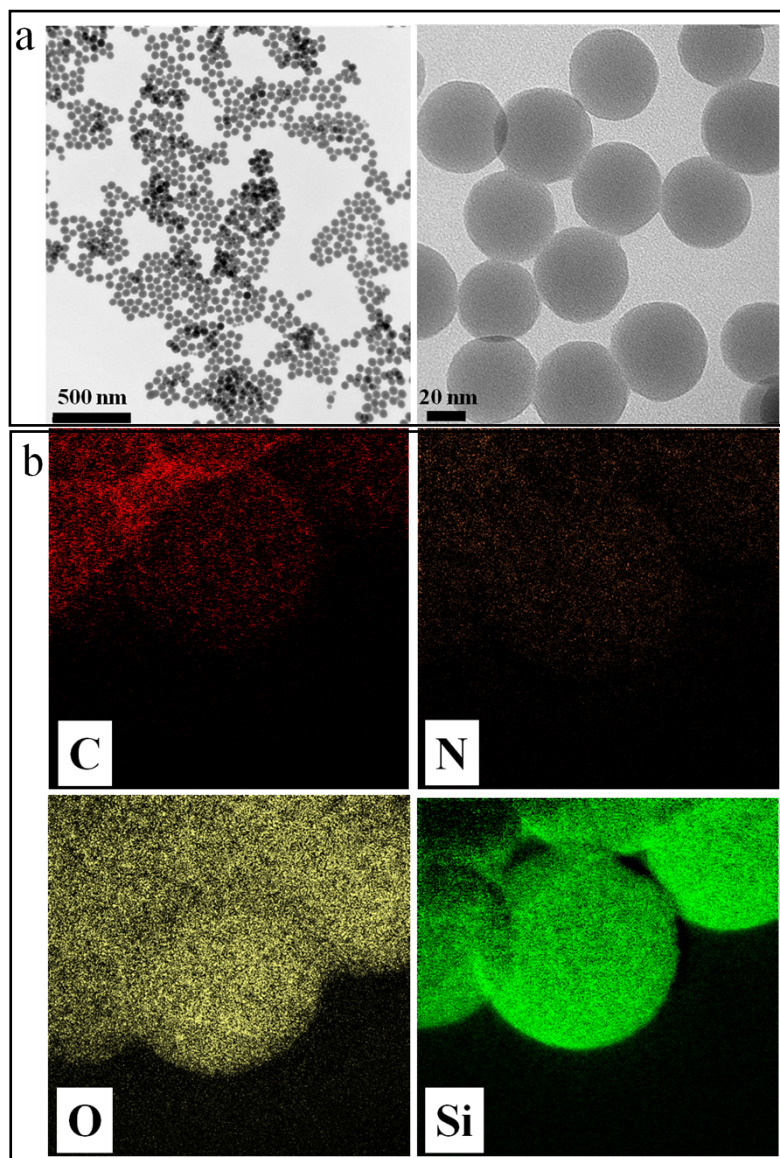


Fig. S1 TEM images and electron energy loss energy (EELS) mapping of SN-ON.

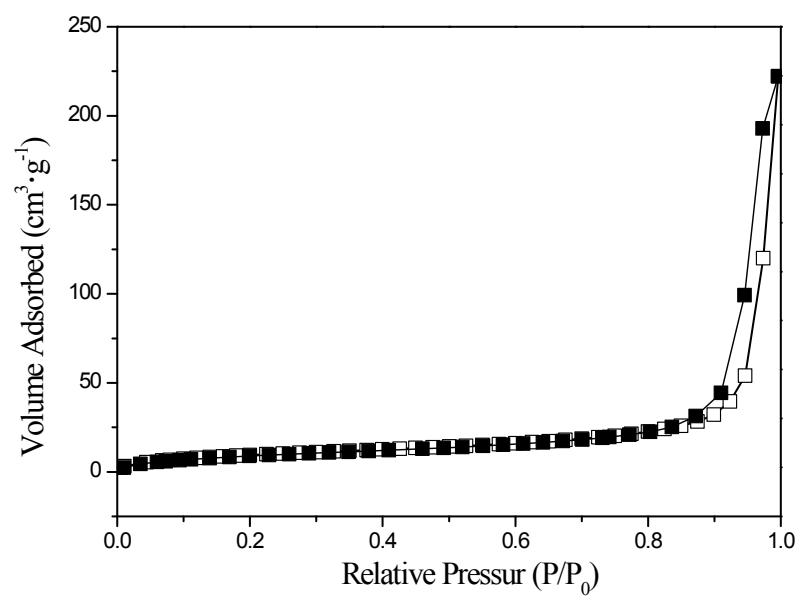


Fig.S2 N₂ sorption isotherm of SN-ON.

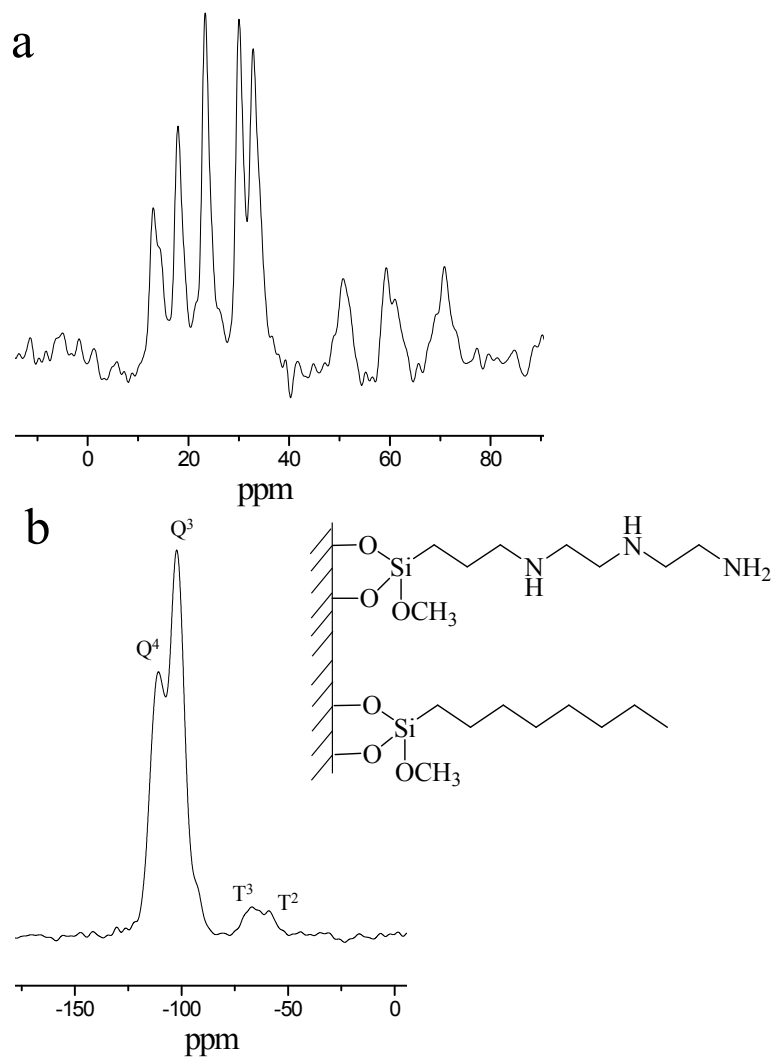


Fig. S3 Solid state ^{13}C CP-MAS NMR spectrum and solid state ^{29}Si CP-MAS NMR spectrum of SN-ON.

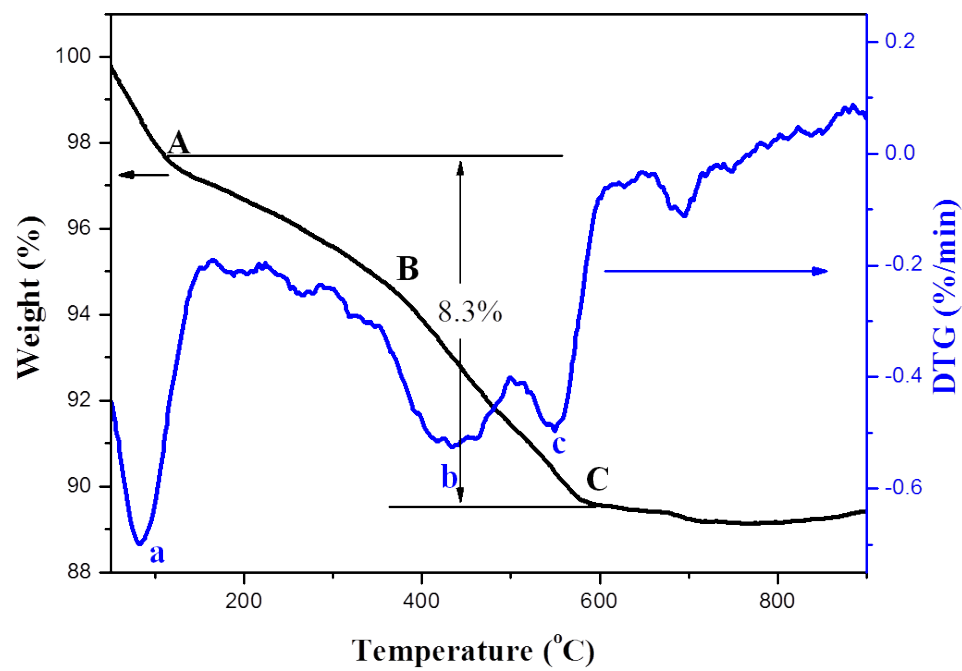


Fig. S4 TG and DTG curves of SN-ON.

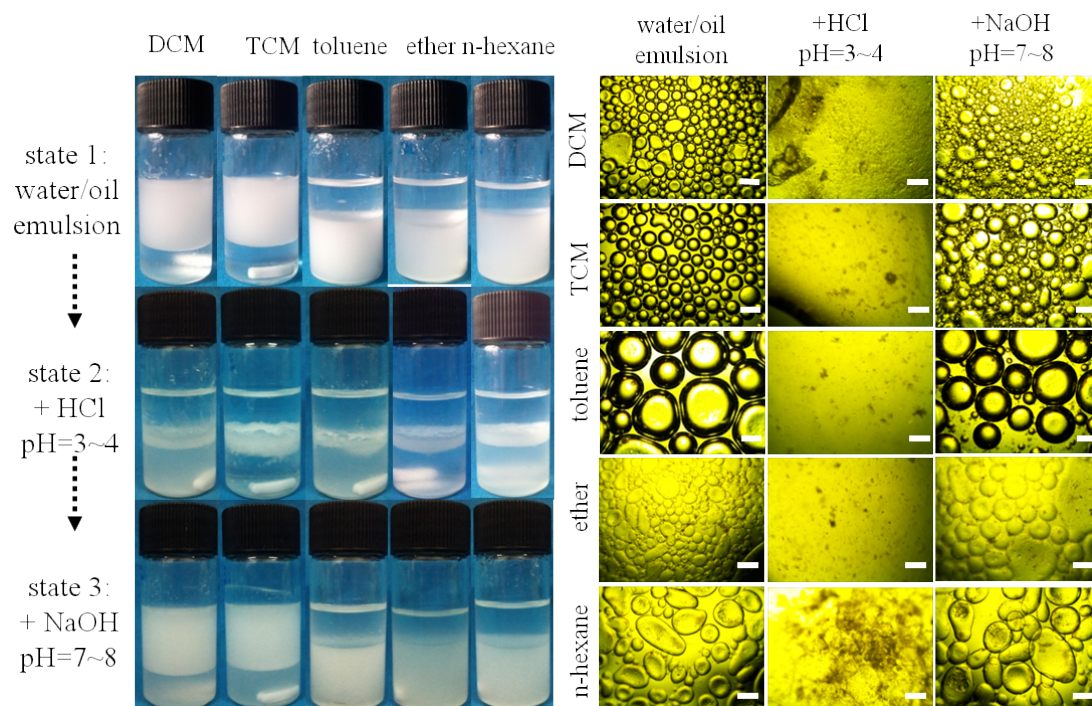


Fig. S5 Appearance and optical micrographs of biphasic systems in the presence of SN-ON. Every vial contains 4 mL organic solvent, 4 mL water, and 0.04 g silica nanosphere. State 1: before adding HCl; State 2: pH value is adjusted to 3-4 using HCl (1M); State 3: pH value is adjusted to 7-8 using NaOH (1M). Scale bar is 200 μm .

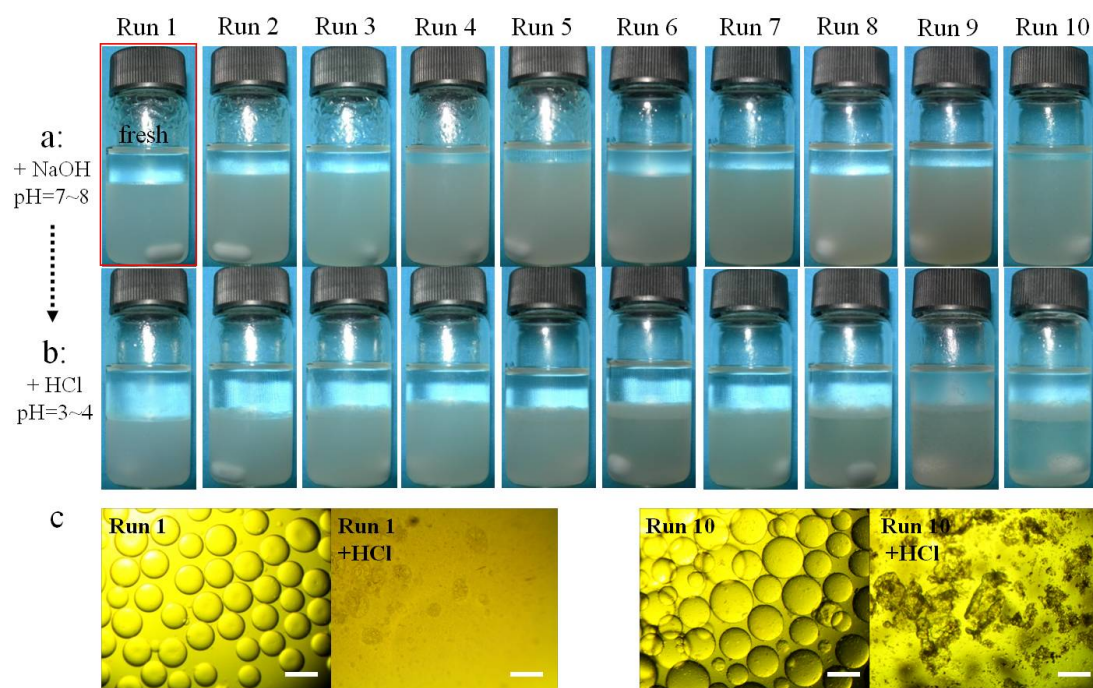


Fig. S6 Appearance for reversible switch and micrographs of the water/ethyl acetate system in the presence of SN-ON. (a) The biphasic system contains 4 mL ethyl acetate, 4 mL water, and 0.04 g SN-ON, the pH value is adjusted to 7-8 by adding NaOH except Run 1. (b) Adding a few drops of HCl to a, the pH value is adjusted to 3-4. Scale bar is 200 μm .

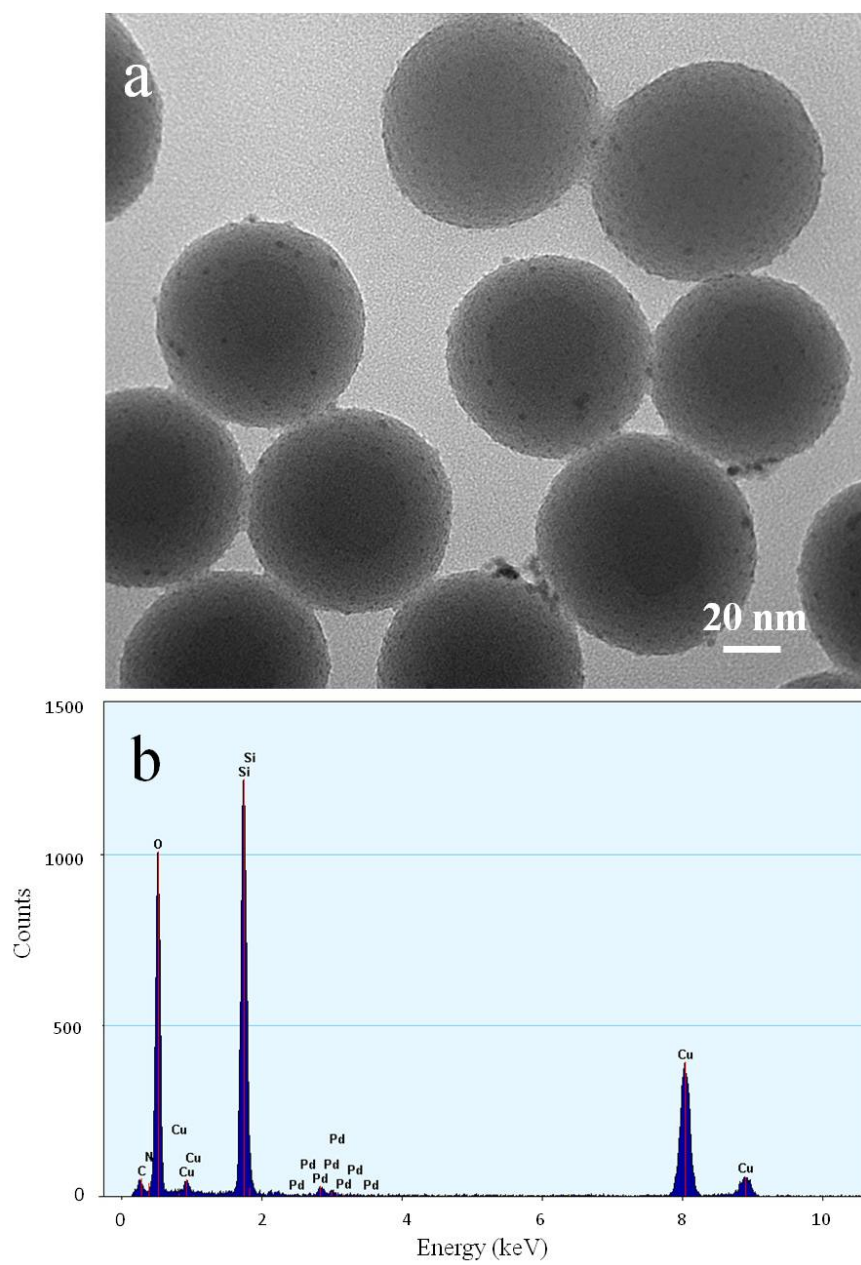


Fig. S7 TEM image and EDS spectrum of Pd/SN-ON.

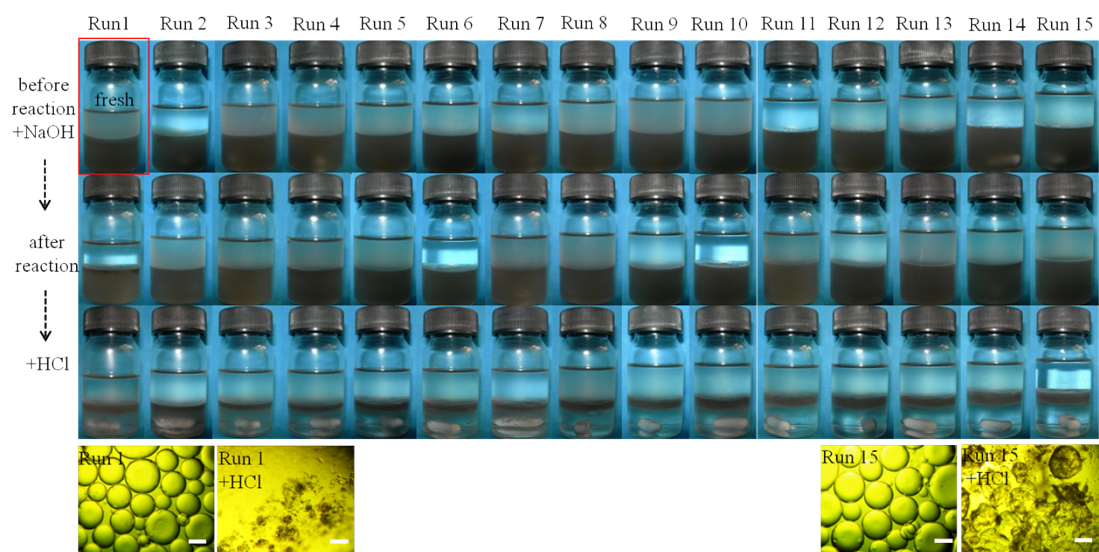


Fig. S8 Appearance for consecutive reaction cycles and micrographs of hydrogenation styrene.

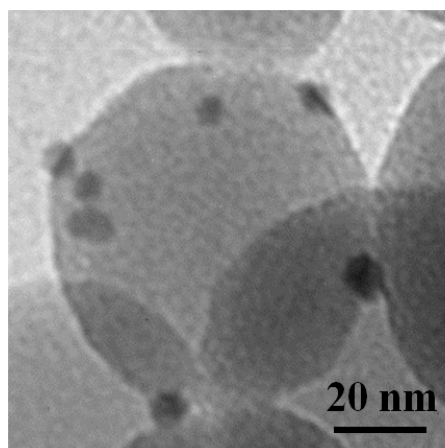


Fig. S9 TEM image of the fourth recycled Pd/SN-ON. The Pd loading is 0.82% with determined with ICP-AES.