Electronic Supplementary Material (ESI) for ChemComm.

# Supporting Information for

## *Tuning the wettability of mesoporous silica for enhancing the catalysis efficiency of aqueous reactions*

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## 1 . Chemicals

Cetyltrimethylammonium chloride (CTAC), Tetramethoxy silane (TMOS) and various olefins were purchased from Aladdin Company. n-Octyltrimethoxysilane was obtained from Shanghai Chemical Reagent Company of Chinese Medicine Group. $Pd(OAc)_2$ was purchased from Shanghai Boka Company (China). All solvents were of analytical quality.

## 2. Catalyst preparation and catalysis reactions

**The synthesis of octyl-functionalized MSS.** 3.52 g CTAC was dissolved into a solution containing 400 mL of deionized water, 505 mL of methanol and 2.2 mL NaOH (1mol $L^{-1}$) at room temperature. After stirring 30 min, 8.08 mmol of TMOS was added dropwise to the above solution and stirred vigorously for the sufficient hydrolysis of TMOS. After for 90 min, the mixture of n-octyltrimethoxysilane (2.02*$x$/100 mmol) and TMOS [2.02*(1-$x$/100) mmol] dissolved in methanol were dropwise added into the above mixture, where $x$ represent the molar fraction of n-octyltrimethoxysilane in the total silane in the second step, and stirred for another 10 h and standed for another 24 h. The resultant material was filtered, washed with water and ethanol, and then dried at room temperature.

**Loading Pd on octyl-functionalized MSS.** 0.5 g of the above synthesized material was added to a toluene solution containing 10.5 mg of $Pd(OAc)_2$. After stirring for 4 h, the colorless toluene solution and was removed by filtration. The Pd-adsorbed solid was reduced with $NaBH_4$ in a mixture of toluene and ethanol (V/V =20/1). After being washed with ethanol and being dry, the catalyst with a Pd loading of 1wt% was obtained. The Uv-vis spectroscopy measurement of the $Pd(OAc)_2$ concentration in solution before and after adsorption revealed that $Pd(OAc)_2$ was completely adsorbed by the solid materials. The template was extracted twice (1.0 g material : 150 mL ethanol : 0. 3 g $NH_4NO_3$) under the refluxing conditions. The obtained Pd cataysts were denoted as Pd/MSS-C$x$ [$x$=0, 5, 10, 15 20 and 25, representing the molar fraction (%) of $(MeO)_3Si(CH_2)_7CH_3$ in the total silicon procurers of the second step].

**Hydrogenation.** The catalytic performacnes were tested with aqueous hydrogenation ofolefins. Typically, 10.5 mmol of substrate, 0.03 mol% of catalyst (with respect to substrate) were mixed with 3.1 mL of water in a 10 mL reaction vial. The mixture was vigrously stirred (2000 rpm) for 3 min. Then, the vial was placed in an atoclave. After being purged four times with $H_2$ (99.99%), the $H_2$ pressure was elevated to 0.35 MPa. The autoclave was heated with a water bath. Hydrogenations were conducted with magnetic stirring under a stirring input power of 12.5 w. At the end of reaction, the mixture was analyzed with GC to determine conversion and selectivity.

**Catalyst recycling.** At the end of reaction, the reaction mixture was transfered into a tuble for centrifugation. After centrifugation, the upper layer of organic product was removed. The recovered solid catalyst was washed with methol and dried under vaccum for next reaction cycle. The other procedures are the same as the first reaction cycle.

## 3. Characterization

The small-angle X-ray powder diffraction analysis was performed on Rigaku D/max rA X-Ray diffractometer (at 40 kV and 30 mA with CuKα radiation). $N_2$ physical adsorption was measured by using an ASAP2020 volumetric adsorption analyzer. Before measuring, all samples were outgassed at 120 $^{o}$C under vacuum for 6 h. Surface area was calculated from the adsorption branch in the relative pressure range of 0.05–0.15 using Brunauer-Emmett-Teller (BET) equation. Pore diameters were determined from the adsorption branch. The total pore volume was calculated at a relative pressure of $P/P_o>0.99$. FT-IR spectra were performed on Thermo-Nicolet-Nexus 470 infrared spectrometer. Transmission electron microscope (TEM) images were obtained on a JEM-2000EX (operated at 200 kV). 300 MHz spectrometer: for $^{13}$C 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 $^{13}$Si MAS NMR experiments, 79.6 MHz resonant frequency, 4 kHz spin rate, 4.0 s pulse delay, TMS as a reference compound. Pd content was analyzed with an inductively coupled plasma-atomic emission spectrometry (ICP-AES, AtomScan16, TJA Co.). C and N content analysis was conducted on Vario EL (Elementar). Metal content analysis was carried out on an inductively coupled plasma-atomic emission spectrometry (ICPAES, AtomScan16, TJA Co.). Water contact angles were measured on KRUSS DSA100 by using contact mode (the images was taken after 0.03 second for all the samples). Before measurement, the powder sample was pressed into flakes under 4 MPa. GC analysis was conducted on Agilent 7890A.

**Table 1.** Textural parameters of the prepared catalysts.

| Materials | $S_{BET}$ $^{a}$ ($m^2 \cdot g^{-1}$) | $V_P$ $^{b}$ ($cm^3 \cdot g^{-1}$) | Pore size $^{c}$ (nm) |
|---|---|---|---|
| Pd/MSS | 400 | 0.24 | 2.2 |
| Pd/MSS-C5 | 593 | 0.31 | 1.8 |
| Pd/MSS-C10 | 440 | 0.23 | 1.7 |
| Pd/MSS-C15 | 499 | 0.26 | 1.7 |
| Pd/MSS-C20 | 441 | 0.24 | 1.7 |
| Pd/MSS-C25 | 423 | 0.24 | 1.7 |

[a] BET surface area; [b] Single point pore volume determined at relative pressure of $P/P_0$= 0.99; [c] Pore size, BJH method from desorption branch.

**Table 2.** The elemental analysis results of the prepared catalysts .

| Samples | N (wt%) | C (wt%) |
|---|---|---|
| MSS | 0.40 | 8.32 |
| Pd/MSS-C5 | 0.20 | 6.80 |
| Pd/MSS-C10 | 0.20 | 7.34 |
| Pd/MSS-C15 | 0.22 | 9.13 |
| Pd/MSS-C20 | 0.27 | 10.23 |
| Pd/MSS-C25 | 0.11 | 10.04 |

**Table 3.** Recycling results of Pd/MSS-C20 in the styrene hydrogenation in Pickering emulsion system [a].

| Run | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Conv.(%) | 99.8 | >99.9 | >99.9 | >99.9 | >99.9 |

[a] Reaction conditions: 10.5 mmol of styrene, 3.1 mL of water, 0.35 MPa of $H_2$ pressure, 40 $^{o}$C, 0.031g of solid catalysts, 65 min.

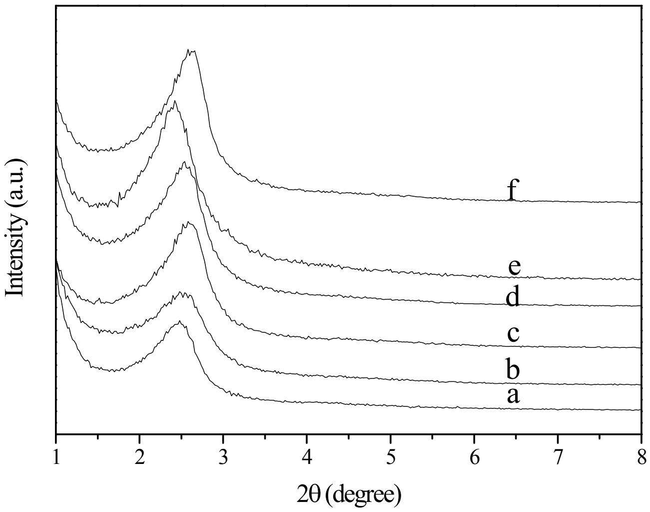

**Fig.S1.** The XRD patterns of the prepared catalysts: (a) Pd/MSS-C0; (b) Pd/MSS-C5; (c) Pd/MSS-C10; (d) Pd/MSS-C15; (e) Pd/MSS-C20; (f) Pd/MSS-C25.

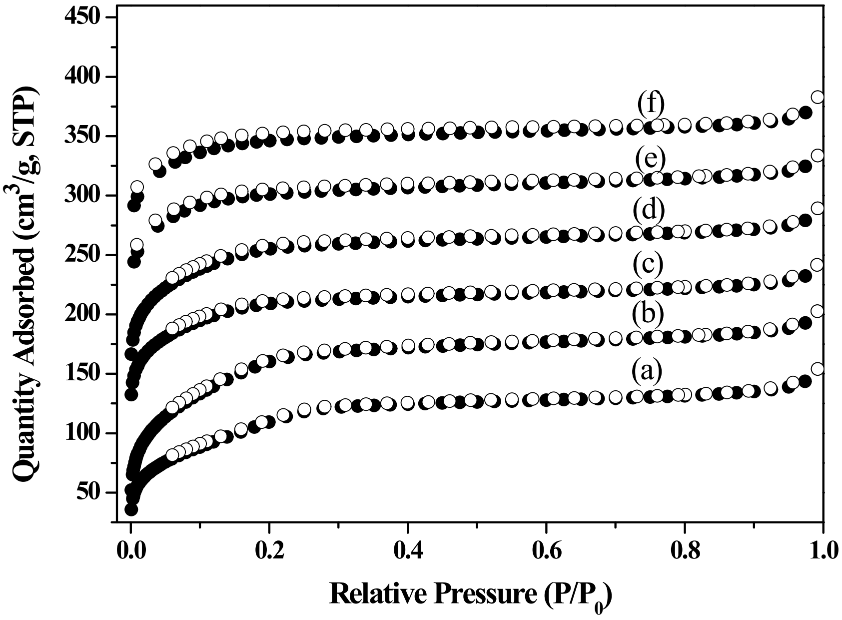

**Fig. S2.** $N_2$ adsorption-desorption isotherms of the prepared catalysts: (a) Pd/MSS-C0; (b) Pd/MSS-C5; (c) Pd/MSS-C10; (d) Pd/MSS-C15; (e) Pd/MSS-C20; (f) Pd/MSS-C25.

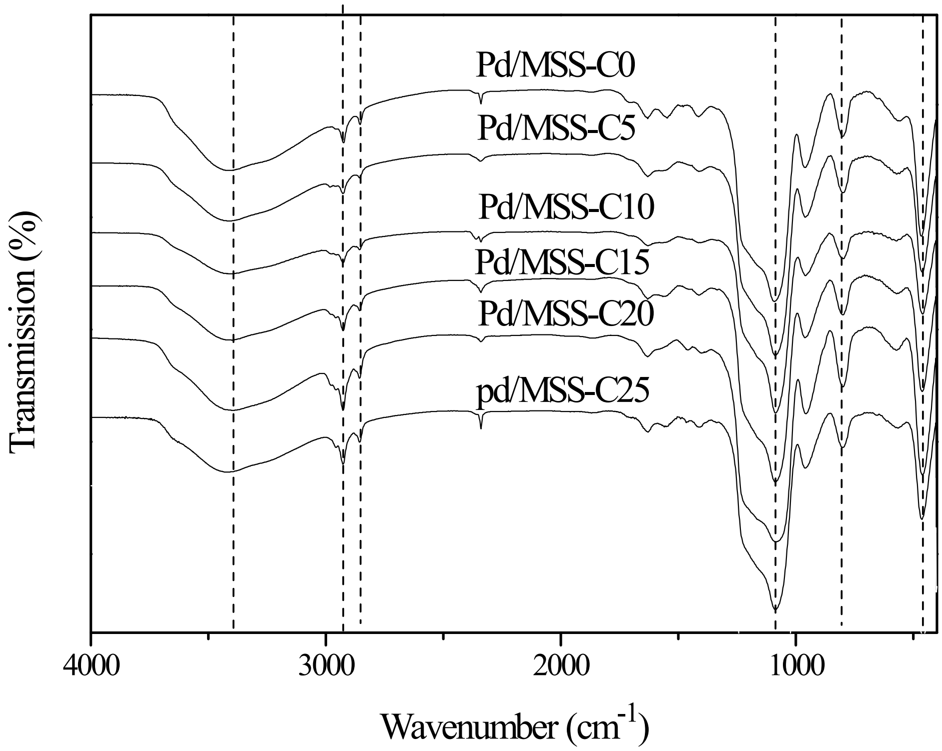

**Fig. S3.** FT-IR spectra of the prepared catalysts.

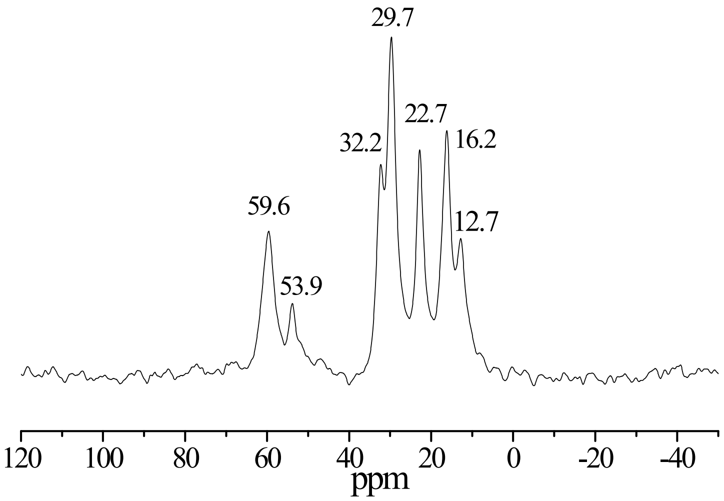

**Fig.S4.** Solid state $^{13}$C CP-MAS NMR spectrum of Pd/MSS-C20.

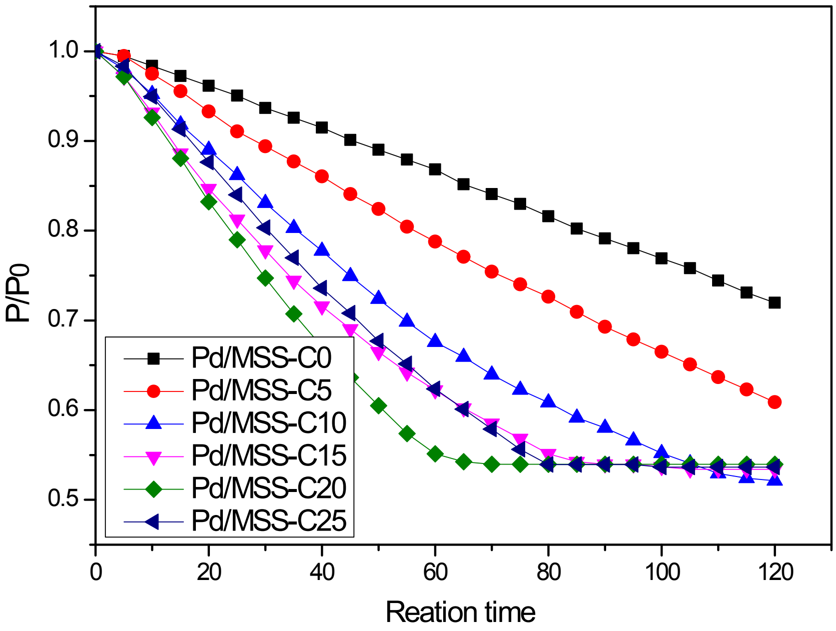

**Fig.S5** The results of styrene hydrogenations over different solid catalysts.

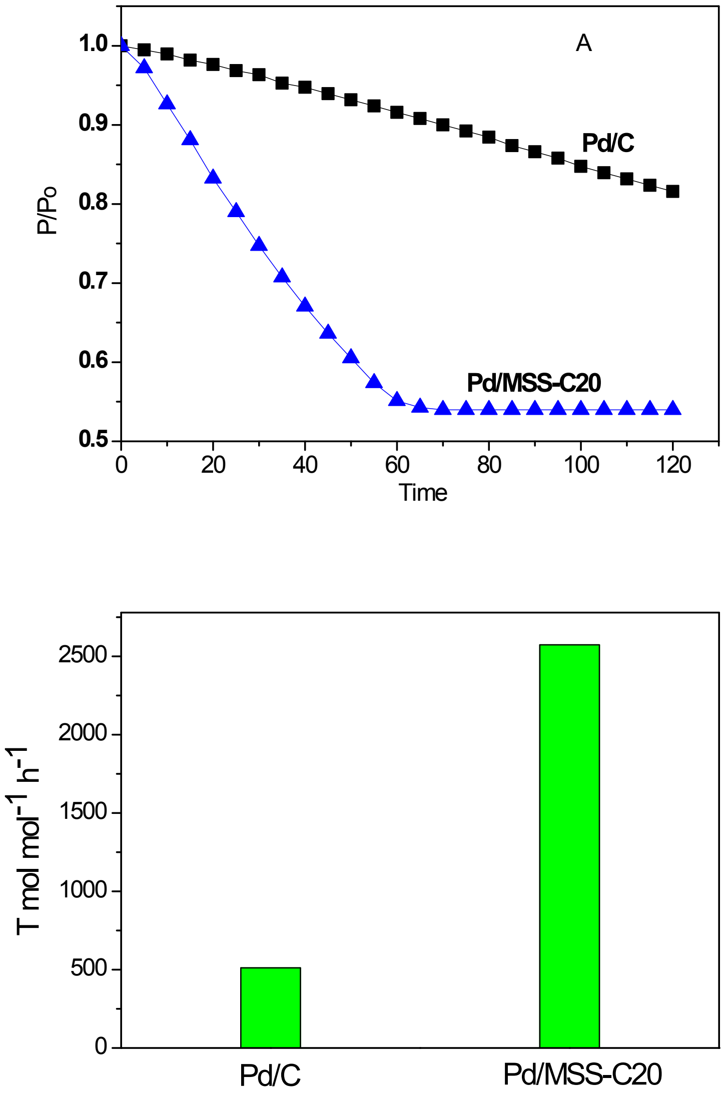

**Fig. S6.** Aqueous stryene hydrogenation efficiency of Pd/MSS-C20 and Pd/C. Reaction conditions: 10.5 mmol of styrene, 3.1 mL of water, 0.35 MPa of $H_2$ pressure, 40 $^{o}$C, 0.031g of solid catalysts.

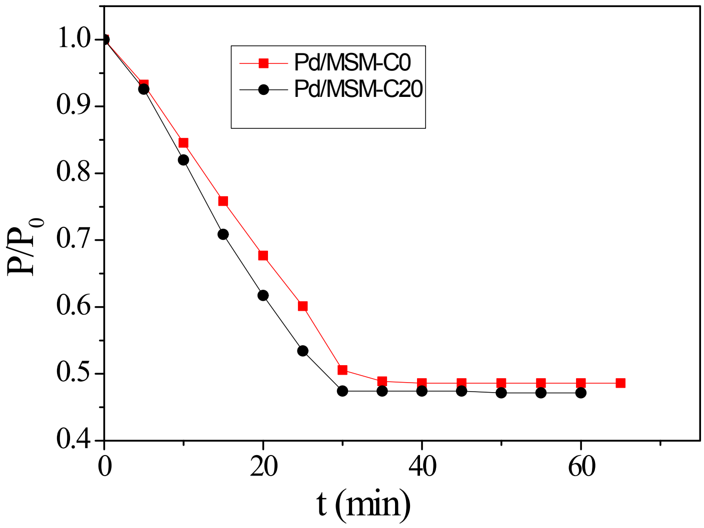

**Fig.S7.** Comparison of the styrene hydrogenations over Pd/MSS-C0 and Pd/MSS-C20 using ethyl acetate as reaction medium (10.5 mmol of styrene, 3.1 mL of **ethyl acetate**, 0.35 MPa of $H_2$ pressure, 40 $^{o}$C, solid catalyst containing 0.00292 mmol Pd).

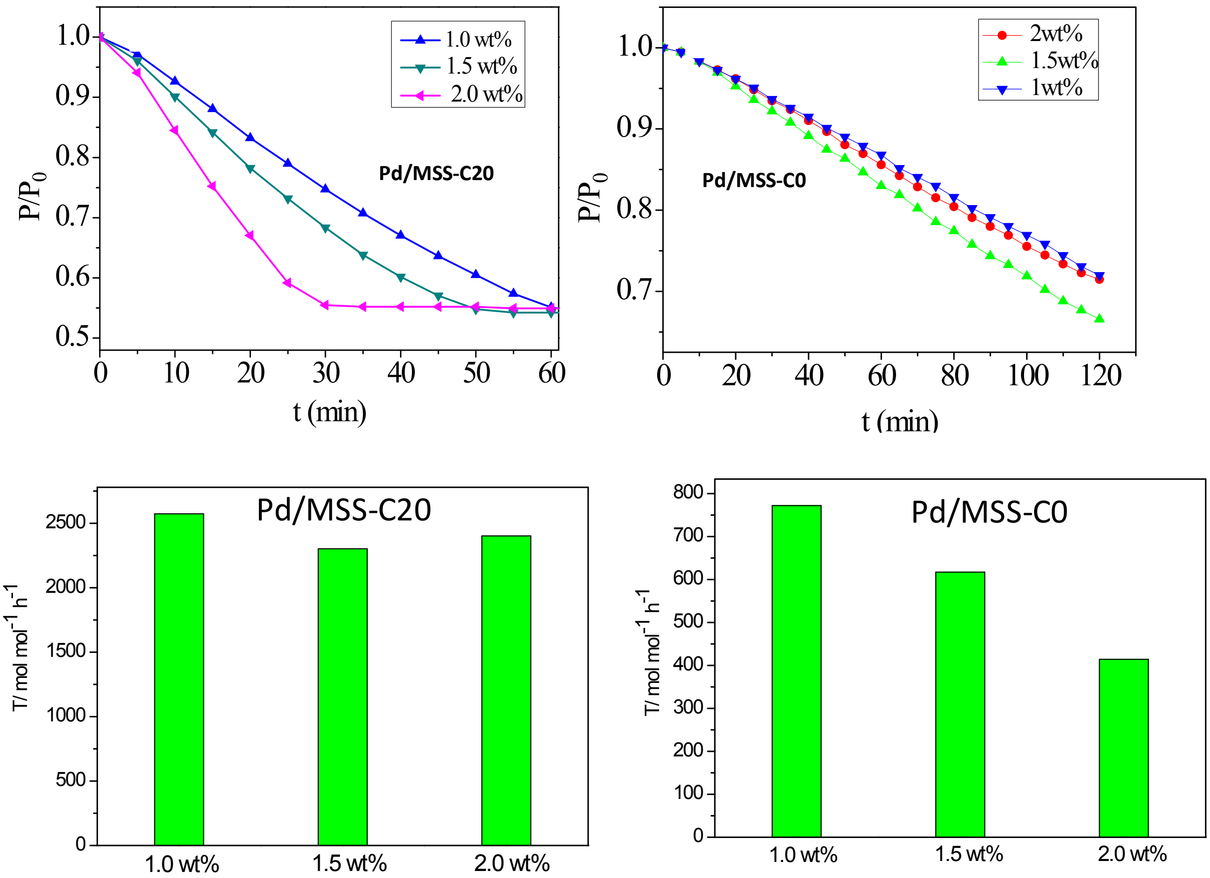

**Fig. S8.** The results of aqueous styrene hydrogenation with different amounts of Pd/MSS-C0 and Pd/MSS-C20. (A) The $H_2$ pressure drop plots with time for Pd/MSS-C0; (B) The $H_2$ pressure drop plots with time for Pd/MSS-C20; (c) Catalysis efficiency as function of the catalyst amount applied. Reaction conditions: 10.5 mmol of styrene, 3.1 mL of water, 0.35 MPa of $H_2$ pressure, 40 $^{o}$C, 0.031g of solid catalysts.

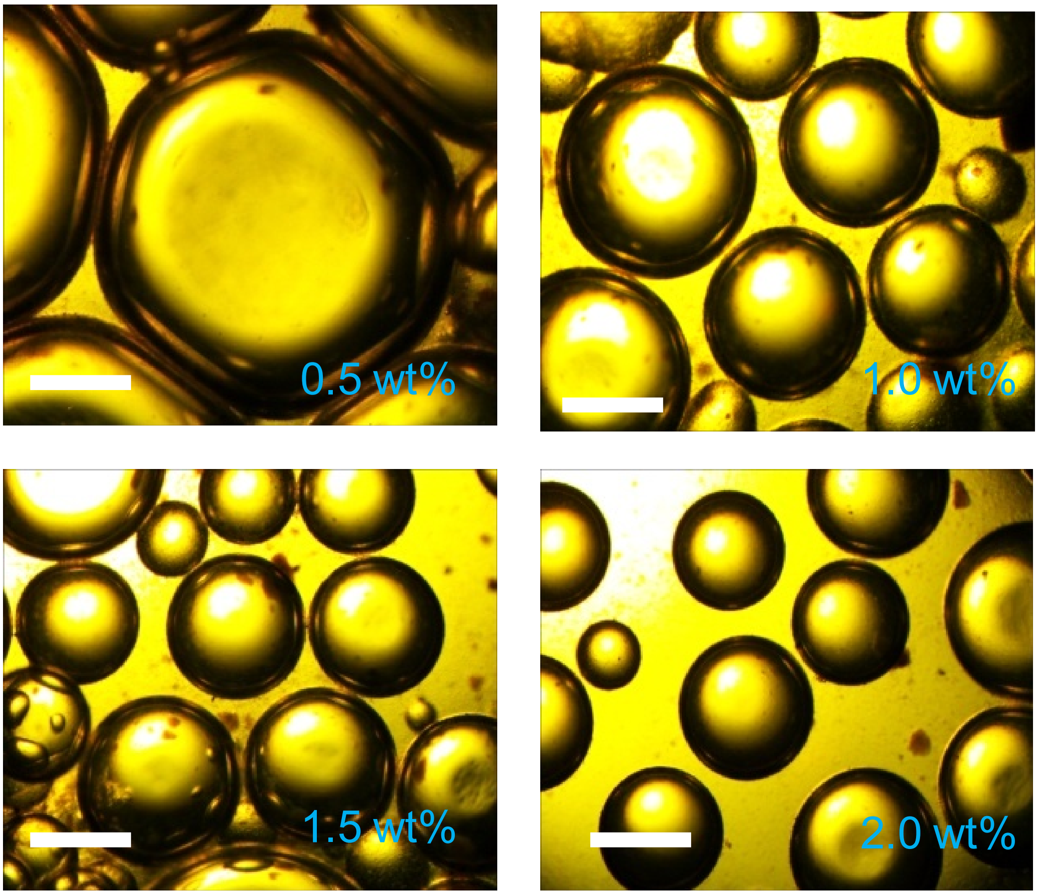

**Fig. S9.** The microscopic images of the Pickering emulsion system with different amount of Pd/MSS-C20. The scale bar is 200 μm.