

## Supporting Information

### An amphiphilic organosilicon framework (AOF) : a new solid

#### Pickering catalyst carrier

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#### Experimental Section

##### Synthesis

**2,5-Bis(trimethylsilylethynyl)pyridine.** A suspension of 2,5-diiodopyridine (10 g, 30.2 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.85 g, 1.21 mmol) and CuI (0.12 g, 0.60 mmol) in iPr<sub>2</sub>NH (120 ml) and THF (40 ml) was cooled with an ice bath, and then to this suspension was added trimethylsilylacetylene (11.8 g, 121 mmol) under an argon atmosphere. The reaction mixture was stirred at room temperature for 16 h. The resulting mixture was filtered to remove insoluble matter, and the filtrate was concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/AcOEt = 10:1) to give 2,5-bis(trimethylsilylethynyl)pyridine (7.4 g, 90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.26 (9 H, s), 0.27 (9 H, s), 7.38 (1 H, d, J = 8.24 Hz), 7.68 (1 H, dd, 8.24 Hz), 8.62 (1 H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ -0.1, 0.0, 97.3, 100.5, 101.4, 103.6, 119.8, 126.7, 139.0, 141.9, 152.9. The <sup>1</sup>H and <sup>13</sup>C NMR data were identical to those reported in the literature.

**2,5-Diethynylpyridine.** To a THF (160 mL) solution of 2,5-bis(trimethylsilylethynyl)pyridine (7.4g, 27.1 mmol) was added n-Bu<sub>4</sub>NF (1.0 M THF solution, 60 mL, 60 mmol) and a few drops of H<sub>2</sub>O subsequently. The reaction mixture was stirred for 4 h at room temperature, concentrated, and diluted with ether/H<sub>2</sub>O. The separated ether layer was washed with brine, dried over MgSO<sub>4</sub>, and then the solvent was completely evaporated. The residue was chromatographed on silica gel (hexane/AcOEt = 3:1) to give 2,5-diethynylpyridine (3.0 g, 88%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.26 (1 H, s), 3.31 (1 H, s), 7.45 (1 H, dd, J = 7.32 Hz), 7.75 (1 H, dd, J = 10.52 Hz), 8.68-8.69 (1 H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 79.1, 79.9, 82.3, 82.4, 119.0, 126.7, 139.2, 141.5, 152.9. The <sup>1</sup>H and <sup>13</sup>C NMR data were identical to those reported in the literature.

**2,5-Bis[(E)-2-(triethoxysilyl)vinyl]pyridine .** To a CH<sub>3</sub>CN (27 mL) solution of 2,5-diethynylpyridine (0.30 g, 2.36 mmol), [Rh(cod)Cl]<sub>2</sub> (23 mg, 0.047 mmol), PPh<sub>3</sub> (50 mg, 0.19 mmol) was added triethoxysilane (1.55 g, 9.44 mmol) under an argon atmosphere. The reaction mixture was stirred at 100 °C for 24 h. After cooling to room

temperature, the reaction mixture was filtered through charcoal and Celite bed, and then the solvent was completely evaporated. The residue was purified by Kugelrohr distillation at 190–200 °C/30 Pa to give 2,5-Bis[(E)-2-(triethoxysilyl)vinyl]pyridine (0.47 g, 44%) as a yellow oil. IR (neat):  $\nu_{\max}$  2974, 2928, 2893, 1603, 1545, 1477, 1439, 1389, 1078, 960  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  1.25–1.29 (18 H, m), 3.86–3.92 (12 H, m), 6.27 (1 H, d,  $J = 19.68$  Hz), 6.70 (1 H, d,  $J = 19.68$  Hz), 7.19 (1 H, d,  $J = 19.68$  Hz), 7.28 (1 H, d,  $J = 19.20$  Hz), 7.40 (1 H, d,  $J = 8.24$  Hz) 7.77–7.79 (1 H, m), 8.64 (1 H, d,  $J = 2.28$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  18.2, 58.7, 120.9, 121.7, 123.3, 132.4, 133.5, 145.0, 147.9, 148.9, 155.1;

#### **1,4-bis-((E)-2-(triethoxysilyl)vinyl)-benzene**

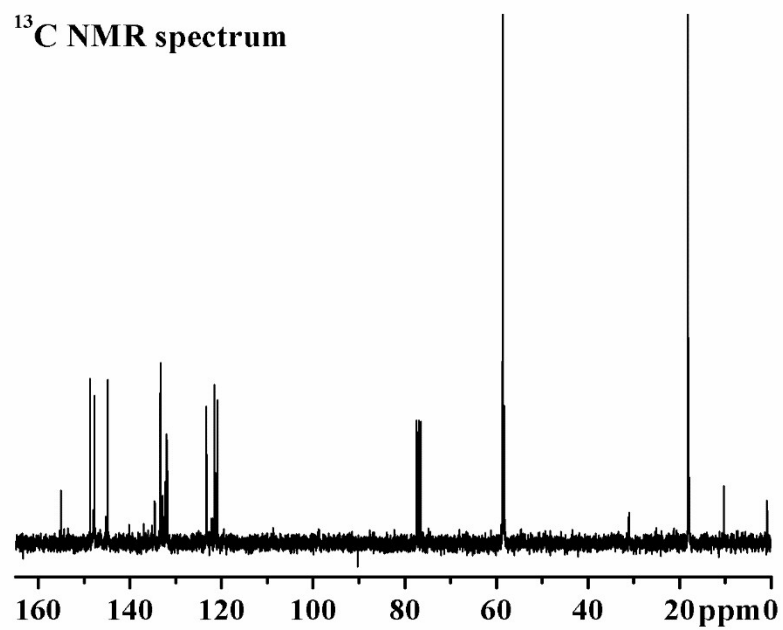
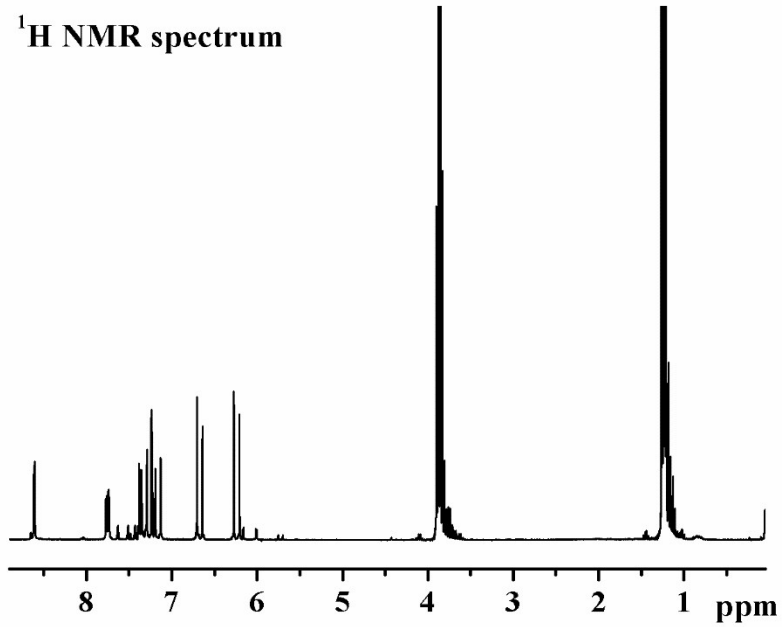
In a typical synthesis 30.12 g (0.128 mol) of 1,4-dibromobenzene was dissolved in 220 mL of dimethylformamide in a 500 mL three-necked-flask. To this solution 55 mL (0.261 mol) of vinyltriethoxysilane, 70 mL (0.512 mol) of triethylamine, and 0.493 g ( $4.27 \times 10^{-4}$  mol) of tetrakis(triphenylphosphine)-palladium were added. After the reaction mixture was stirred for 4d at 110 °C under an argon atmosphere, the resulting solution was cooled to 0 °C to complete the precipitation of the formed salt ( $\text{HNEt}_3\text{Br}$ ). After removal of the salt by filtration, the solvent was removed under reduced pressure. The obtained raw product was purified by kugelrohr distillation. For further purification of the precursor this distillation step was repeated twice: 41.7 g (0.092 mol, yield: 71%) of the organosilane precursor was obtained as a slightly yellow transparent liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.27 (t,  $J$ ) 6.89 Hz, 18 H), 3.89 (q,  $J$ ) 6.89 Hz, 12 H), 6.19 (d,  $J$ ) 19.2 Hz, 2 H), 7.20 (d,  $J$ ) 19.2 Hz, 2 H), 7.46 (s, 4 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  18.2, 58.5, 118.2, 126.9, 137.9, 148.3.

**Yolk-shell TS-1@PMO<sub>2</sub>** In a typical process, 100 mg of TS-1@PS, 0.12g of CTAB, 22 mL of deionized water, 11 mL of ethanol and 1.0mL of ammonium hydroxide aqueous solution were mixed together. After stirred for 1 h, 0.125 mL of 1,4-bis-((E)-2-(triethoxysilyl)vinyl)-benzene was added into the solution and stirred for further 24 h to fabricate TS-1@PS@PMO<sub>2</sub> core-shell particles with mesopores. The yolk-shell structured NPs were formed by dispersing TS-1@PS@PMO<sub>2</sub> particles into hot ethanol and THF to remove the CTAB and PS core, respectively.

**Yolk-shell TS-1@PMO<sub>1</sub>** In a typical process, 100 mg of TS-1@PS, 0.12g of CTAB, 22 mL of deionized water, 11 mL of ethanol and 1.0mL of ammonium hydroxide aqueous solution were mixed together. After stirred for 1 h, 0.125 mL of BTSB was added into the solution and stirred for further 24 h to fabricate TS-1@PS@PMO<sub>1</sub> core-shell particles with mesopores. The yolk-shell structured NPs were formed by dispersing TS-1@PS@PMO<sub>1</sub> particles into hot ethanol and THF to remove the CTAB and PS core, respectively.

#### **Supplementary Figures and Legends**

**$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 2,5-bis[(E)-2-(triethoxysilyl)vinyl]pyridine**



<sup>1</sup>H and <sup>13</sup>C NMR spectra of 1,4-bis-((E)-2-(triethoxysilyl)vinyl)-benzene

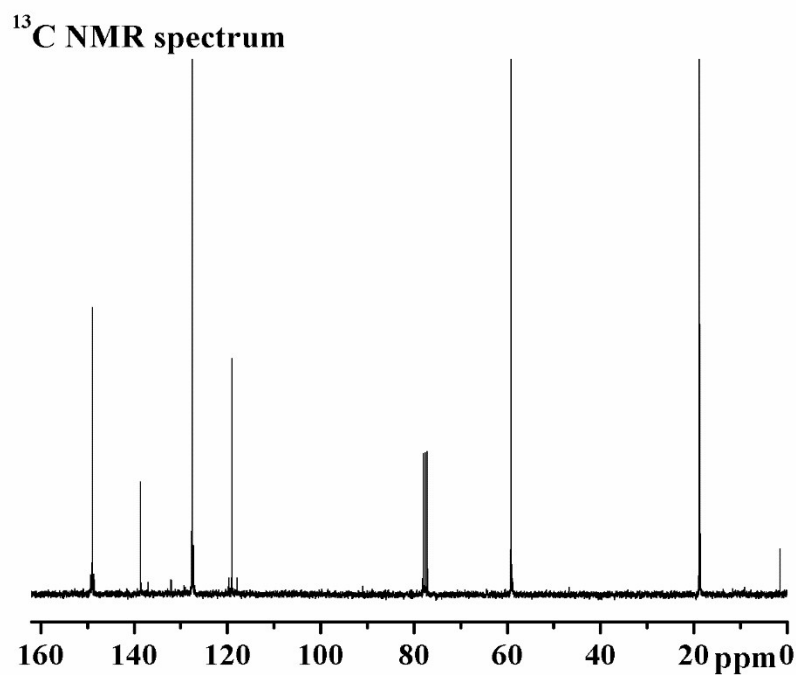
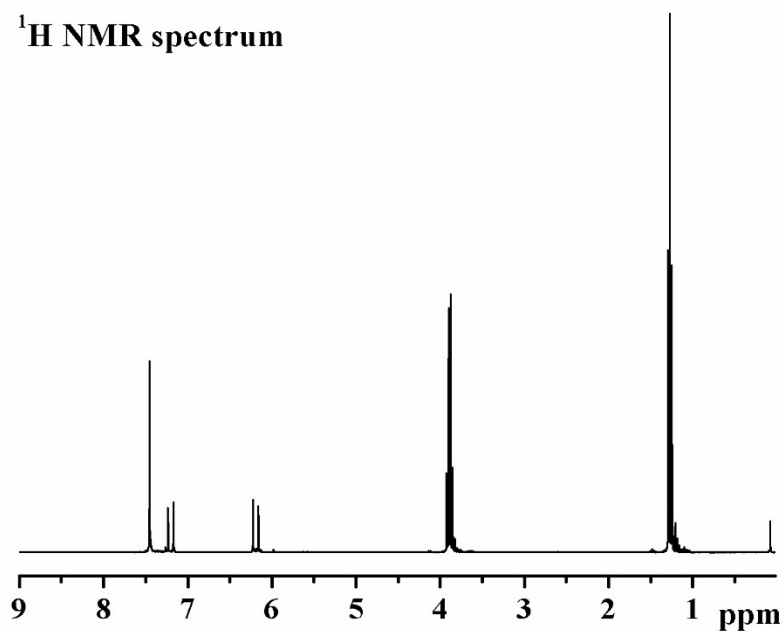
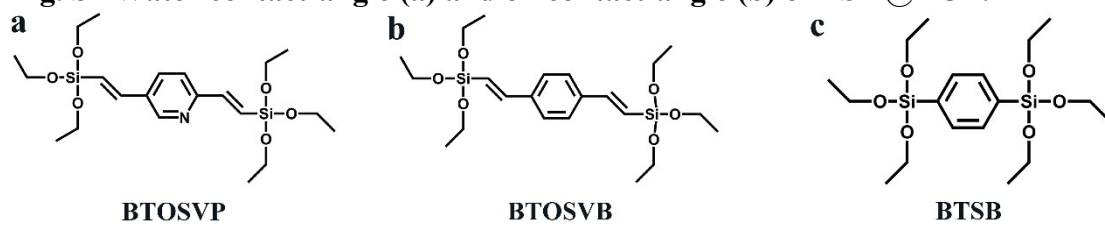


Fig. S1 Structural formula of 2,5-Bis[(E)-2-(triethoxysilyl)vinyl]pyridine (BTOSVP) (a), 1,4-bis-[(E)-2-(triethoxysilyl)vinyl]-benzene (BTOSVB) (b) and 1,4-Bis(triethoxysilyl)benzene (BTSB) (c).

Fig. S2 Water contact-angle (a) and oil contact-angle (b) of TS-1@AOF.



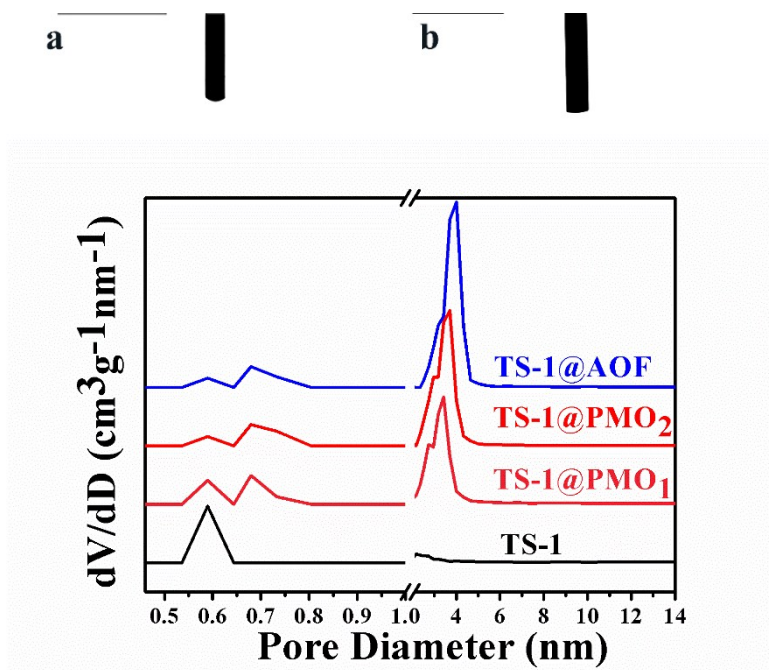


Fig. S3 The corresponding pore size distribution (PSD) of TS-1@AOF, TS-1@PMO<sub>2</sub> and PMO<sub>1</sub>.

Fig. S4 Wide-angle XRD spectra of the yolk-shell structured TS-1@AOF after five catalytic tests.

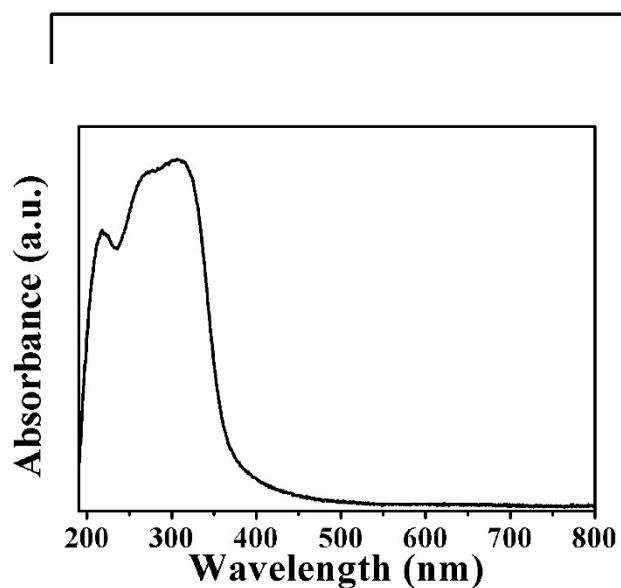
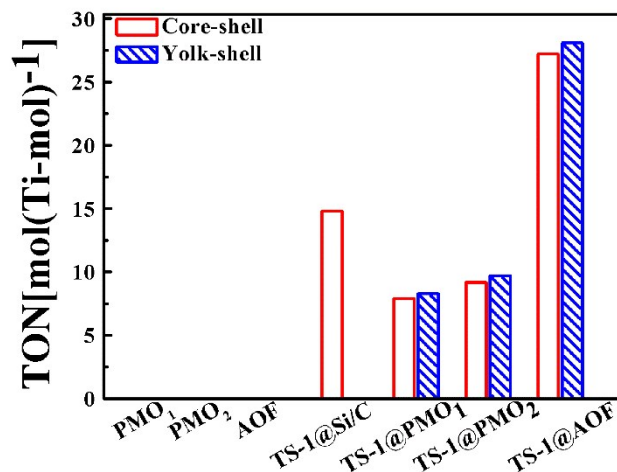


Fig. S5 UV-Vis spectra of the yolk-shell structured TS-1@AOF after five catalytic tests.

**Fig. S6 FT-IR spectra of the yolk-shell structured TS-1@AOF after five catalytic tests.**

**Fig. S7 TON values of catalysts under the PIC condition.**

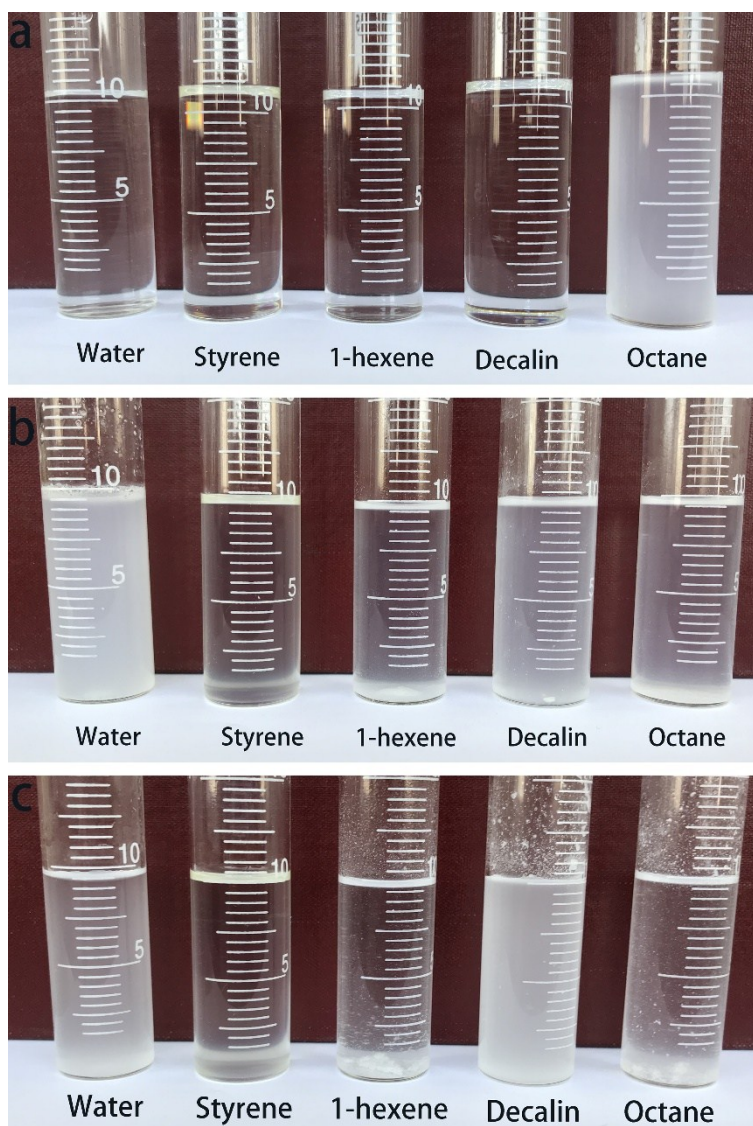


Reaction conditions: cat., 50 mg; 1-hexene, 12.1 mmol; H<sub>2</sub>O<sub>2</sub> (30 wt%), 15.0 mmol; temp., 333 K; time, 1 h; static conditions.

The catalytic experiments were carried out using the several catalysts in the Fig. S7. The activities of the single AOF and PMO materials were almost zero. The experimental results show that pure AOF shell and PMO shell will not play any catalytic role. The catalytic activity of TS-1@AOF, TS-1@PMO<sub>1</sub> and TS-1@PMO<sub>2</sub> with yolk-shell structure were 28.1, 8.3 and 9.7, respectively. The catalytic activities of TS-1@PMO<sub>1</sub>, TS-1@PMO<sub>2</sub> and TS-1@AOF with core-shell structure were 7.9, 9.2 and 27.2, respectively. The results showed that the yolk-shell structure did promote the activity of the catalyst. In addition, we made some comparison with other works reported in this field<sup>47</sup>. The amphiphilic core-shell structured TS-1@AOF catalyst has higher catalytic activity than the amphiphilic core-shell structured TS-1@Si/C catalysts (TON is 14.8) obtained by adjusting hydrophilic/hydrophobic ratio.

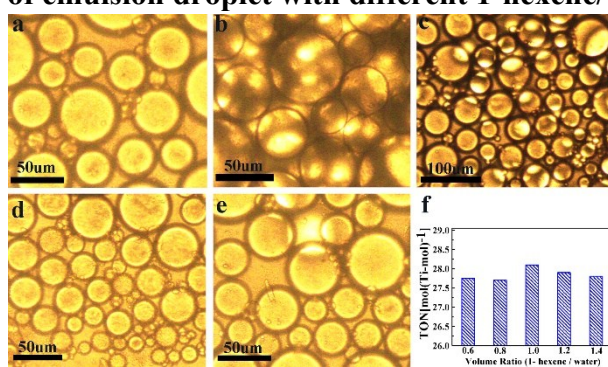
**Fig. S8 The dispersion pictures of TS-1@AOF and control samples in different solutions (water and organic solvent).**

Dispersion process of TS-1@AOF nanoparticles: 20 mg TS-1@AOF nanoparticles



were added into 10 ml water, styrene, 1-hexene, decalin and n-octane solution, respectively. After ultrasonic treatment for 5 minutes, the solution was placed for 3 hours before the phenomenon was observed ( Fig. S8a ). The dispersion process of TS-1@PMO<sub>2</sub> and TS-1@PMO<sub>1</sub> nanoparticles in water, styrene, 1-hexene, decalin and n-octane is the same as that of TS-1@AOF nanoparticles. The dispersion effects of TS-1@PMO<sub>2</sub> and TS-1@PMO<sub>1</sub> nanoparticles in water, styrene, 1-hexene, decalin and n-octane are shown as Fig. S8b and Fig. S8c.

**Fig. S9 Diameters of emulsion droplet with different 1-hexene/water volume ratio**



**and slightly changed TON values.**

The emulsion droplet pictures of 1-hexene / water with volume ratios of 0.6, 0.8, 1.0, 1.2 and 1.4 are (a), (b), (c) and (d), respectively. (f) Slightly changed TON values.