SUPPLEMENTARY INFORMATION

Electronic Supplementary Information (ESI) for ***New Journal of Chemistry.***

Nanoparticle cages as microreactor for producing acrolein from glycerol in liquid phase

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Materials.

The commercially available hydrophobic fumed silica nanoparticles (designated as SN-C, HB-220; purity ≥ 99.8%, the BET surface area is about 200 m^2/g) was purchased from Aladdin Company. The water in all experiments was distilled water. Glycerol, $KHSO_4$, toluene, isobutanol (all of 99.5% purity), hydroquinone (purity ≥ 90%), 1,4-dioxane (99% purity with 10 ppm BHT (butylated hydroxytoluene)) and dodecane (purity: 98%) were purchased from Sinopharm Chemicals Reagent Co., Ltd, Acrolein (95 - 98% purity) was purchased from Xiya Reagent Co, Ltd. Decane (purity: 98%), tetradecane (purity: 99%) tetradecane (purity: 99%), hexadecane (purity: 99%) and ethyl oleate (purity: 75%) were purchased from Shanghai Macklin Biochemical Co., Ltd. Peony seed oil (first grade) was supplied by Shanxi lu'an zhihua agricultural and forestry technology Co., Ltd. Flaxseed oil (edible grade) was supplied by Datong huajian oil Co., Ltd. Soybean oil (edible grade) was supplied by Cofco jiayue (Tianjin) Co., Ltd. Extra virgin olive oil (edible grade) was supplied by China Europe natural food Co., Ltd.

Characterization methods.

Yield of acrolein.

The collected acrolein was analyzed by Gas chromatography (GC, Shimadzu GC2010-Plus AFAPC) with an FID detector. Before the GC analysis, the collected oil and water were diluted 10 times by 1, 4-dioxane, and 0.10 g of isobutanol was added as the internal standard. For the GC analysis, the FID detector and the inlet

temperatures were set at 240 and 260 °C, respectively. Acrolein was analyzed by the following oven-heat procedure: the temperature was ramped from 40 °C to 100 °C at a rate of 10 °C/min and kept at 100 °C for 2 min, and then ramped from 100 °C to 200 °C at a rate of 10 °C/min and kept at 200 °C for 5 min.

Conversion of glycerol.

The conversion of glycerol was detected by a high-performance liquid chromatography (HPLC, Shimadzu LC-10AT) equipped with a RID-10A detector (refractive index detector) and a reversed-phased C18 column (200 × 4.6 mm) at 40 °C. The mobile phase was the 0.1 wt% acetic acid aqueous solution at 0.5 mL/min.

The Kinematic viscosity of oil phase.

The Kinematic viscosity of oil phases were tested by Herzog HVM 472 viscosity-analyzer at 40 °C.

Calculation of average emulsion droplet size (diameter).

The average droplet sizes of the Pickering emulsions were calculated by the following equation (1):

$$\bar{D} = \sum_{i=1}^{n} x_i D_i \quad (1)$$

Where x_i is the ratio of droplets with diameter D_i in Fig. S4.

Table S1. Glycerol dehydration to acrolein in the literature

Catalyst	T (°C)	Pressure (MPa)	Conv. (%)	Yield (%)	Ref.
WO_3/ZrO_2@SiC	250	not mentioned	100	71.1	[1]
HZMS-5(Si/Al=25)	300	not mentioned	99	80	[2]
ZrO_2/SBA-15	275	not mentioned	78	71	[3]
$ZnSO_4$	360	25	50	37.5	[4]
H_2SO_4	300	34.5	92	74	[5]
HY	250	7	89	88.1	[6]
$AlPO_4$ (650 °C)	270	0.1	not mentioned	23	[7]
[Bmim]HPO_4	270	0.1	100	57.4	[8]
$KHSO_4$	180	0.1	100	84.6	This work

[1] Q. Xie, S. Li, R. Gong, G. Zheng, Y. Wang, P. Xu, Y. Duan, S. Yu, M. Lu, W. Ji, Y. Nie, J. Ji, Microwave-assisted catalytic dehydration of glycerol for sustainable production of acrolein over a microwave absorbing catalyst, Appl. Catal. B: Environ. 243 (2019) 455-462.

[2] T.M. Neves, J.O. Fernandes, L.M. Lião, E. Deise da Silva, C. Augusto da Rosa, V.B. Mortola, Glycerol dehydration over micro- and mesoporous ZSM-5 synthesized from a one-step method, Micropor. Mesopor. Mat. 275 (2019) 244-252.

[3] B. Katryniok, S. Paul, M. Capron, C. Lancelot, V. Bellière-Baca, P. Rey, F. Dumeignil, A long-life catalyst for glycerol dehydration to acrolein, Green Chem. 12 (2010) 1922.

[4] L. Ott, M. Bicker, H. Vogel, Catalytic dehydration of glycerol in sub- and supercritical water: a new chemical process for acrolein production, Green Chem. 8 (2006) 214-220.

[5] M. Watanabe, T. Iida, Y. Aizawa, T.M. Aida, H. Inomata, Acrolein synthesis from glycerol in hot-compressed water, Bioresour. Technol. 98 (2007) 1285-1290.

[6] A.S. de Oliveira, S.J.S. Vasconcelos, J.R. de Sousa, F.F. de Sousa, J.M. Filho, A.C. Oliveira, Catalytic conversion of glycerol to acrolein over modified molecular sieves: Activity and deactivation studies, Chem. Eng. J. 168 (2011) 765-774.

[7] R. Estevez, S. Lopez-Pedrajas, F. Blanco-Bonilla, D. Luna, F.M. Bautista, Production of acrolein from glycerol in liquid phase on heterogeneous catalysts, Chem. Eng. J. 282 (2015) 179-186.

[8] L. Shen, H. Yin, A. Wang, X. Lu, C. Zhang, F. Chen, Y. Wang, H. Chen, Liquid phase catalytic dehydration of glycerol to acrolein over Brønsted acidic ionic liquid catalysts, J. Ind. Eng. Chem. 20 (2014) 759-766.

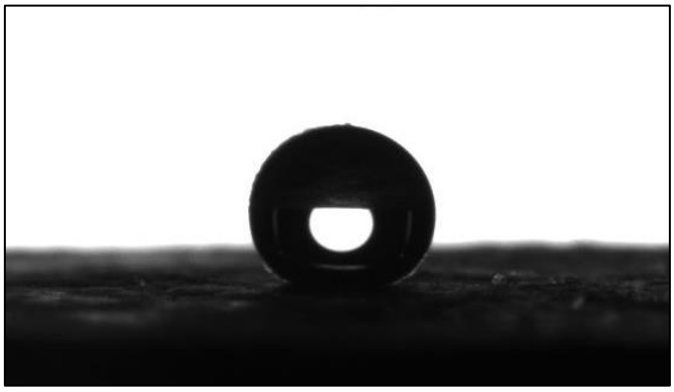

Fig. S1. The water contact angle of SN-C.

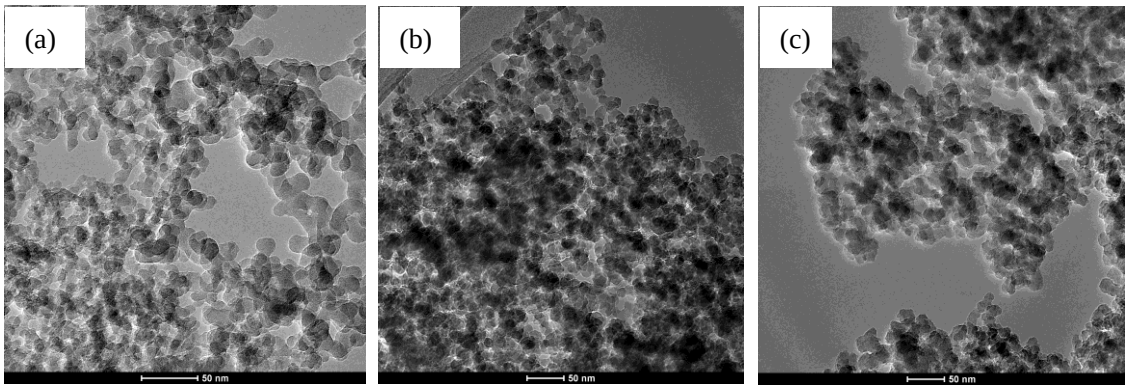

Fig. S2. TEM images of (a) SN-C, (b) SN, (c) SN-$C_{12\text{-}1.0}$. The length of the bar in all the images is 50 nm.

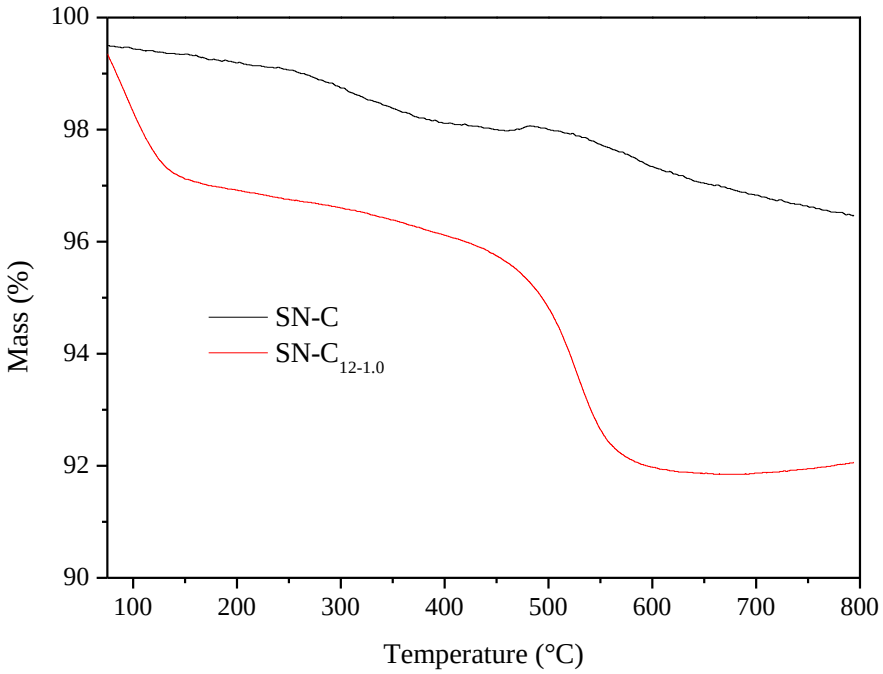

Fig. S3. TG curves of SN-C and SN-$C_{12\text{-}1.0}$.

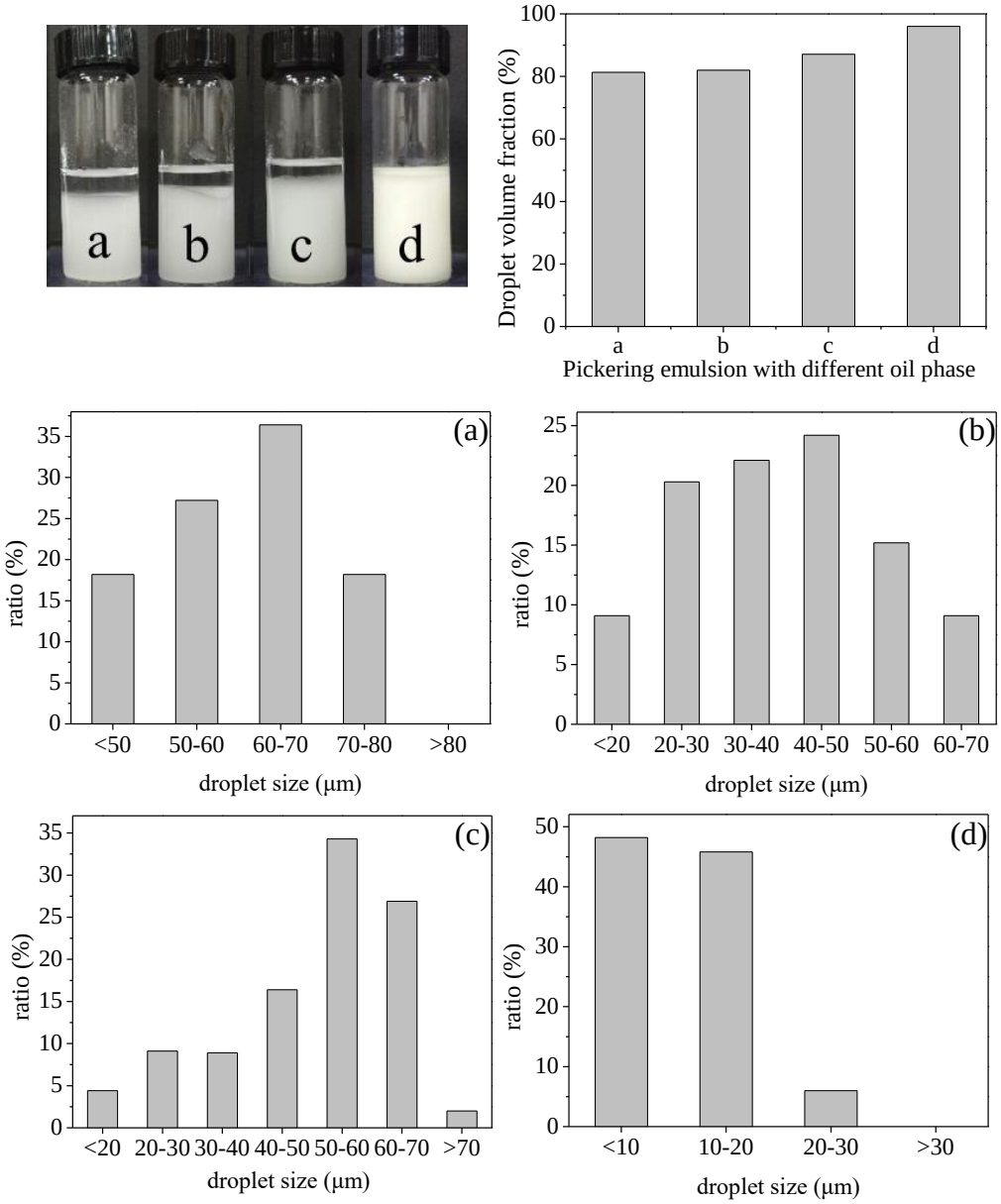

Fig. S4. The droplet size distribution of water-in-oil Pickering emulsion. From (a) to (d) are decane, hexadecane, ethyl oleate and peony seed oil, respectively. The droplet size means the diameter of droplet.

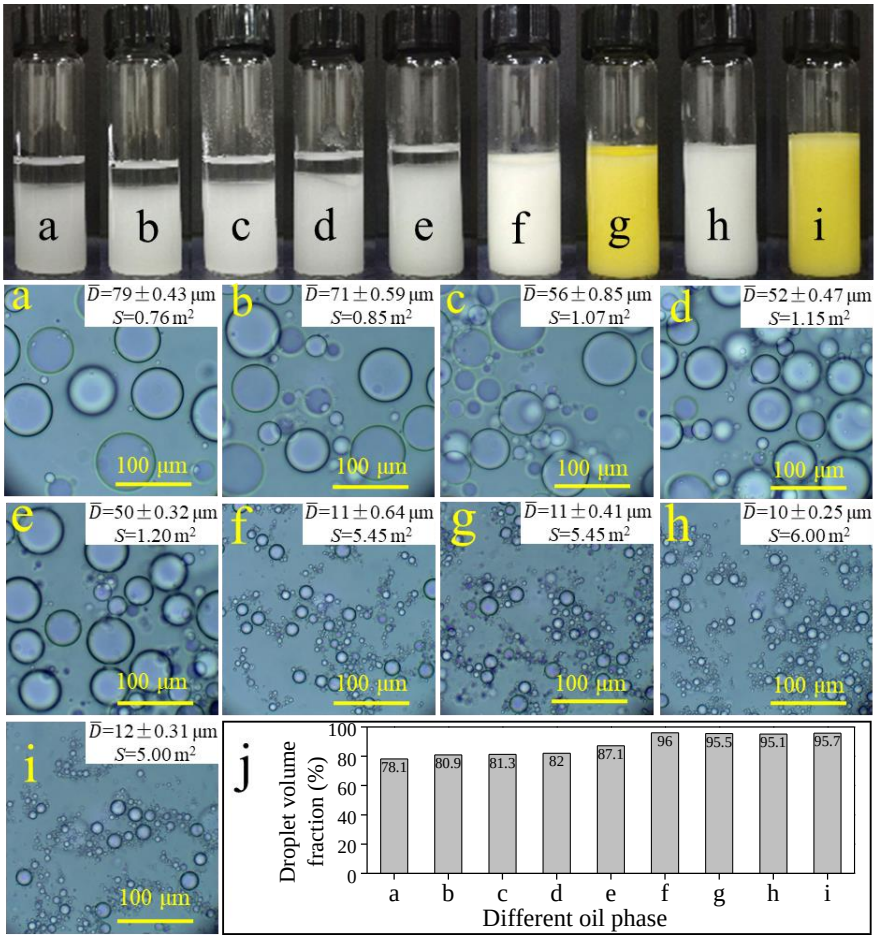

Fig. S5. The optical microscopic images (a-i) and the droplet volume fraction of water-in-oil Pickering emulsion stabilized by 3.5 wt% SN-C (j). The oil phase from (a) to (i) were decane, dodecane, tetradecane, hexadecane, ethyl oleate, peony seed oil, flaxseed oil, soybean oil and olive oil, respectively. The $\bar{D}$ values of droplet diameters means average of three measurements ± STD. The scale bar is 100 μm.