Electronic Supplementary Material (ESI) for Green Chemistry

Highly Active, Stable, and Recyclable Magnetic Nano-size Solid Acid Catalysts: Efficient Esterification of Free Fatty Acid in Grease to Produce Biodiesel

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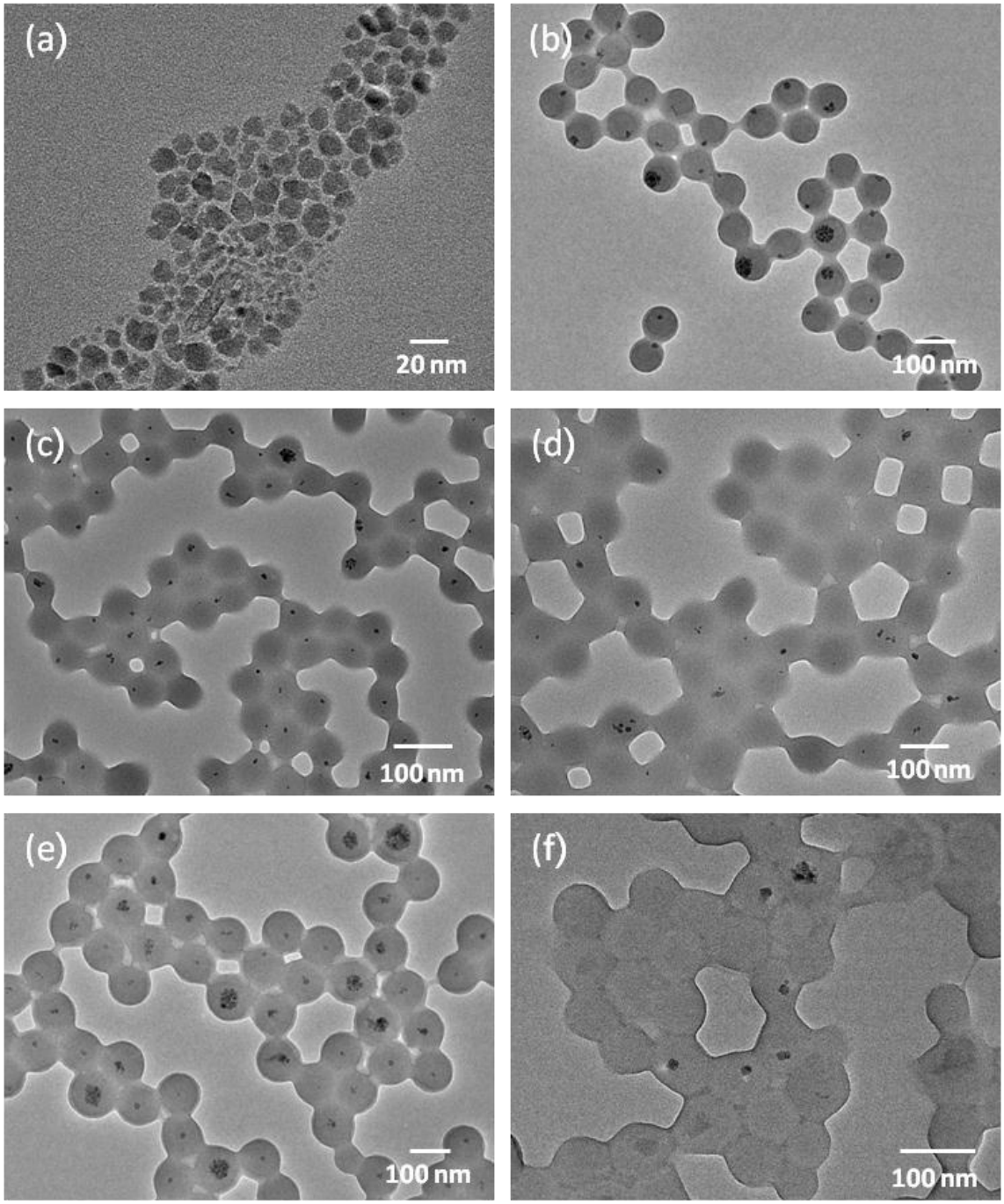
1. Characterization of particles by TEM or FESEM



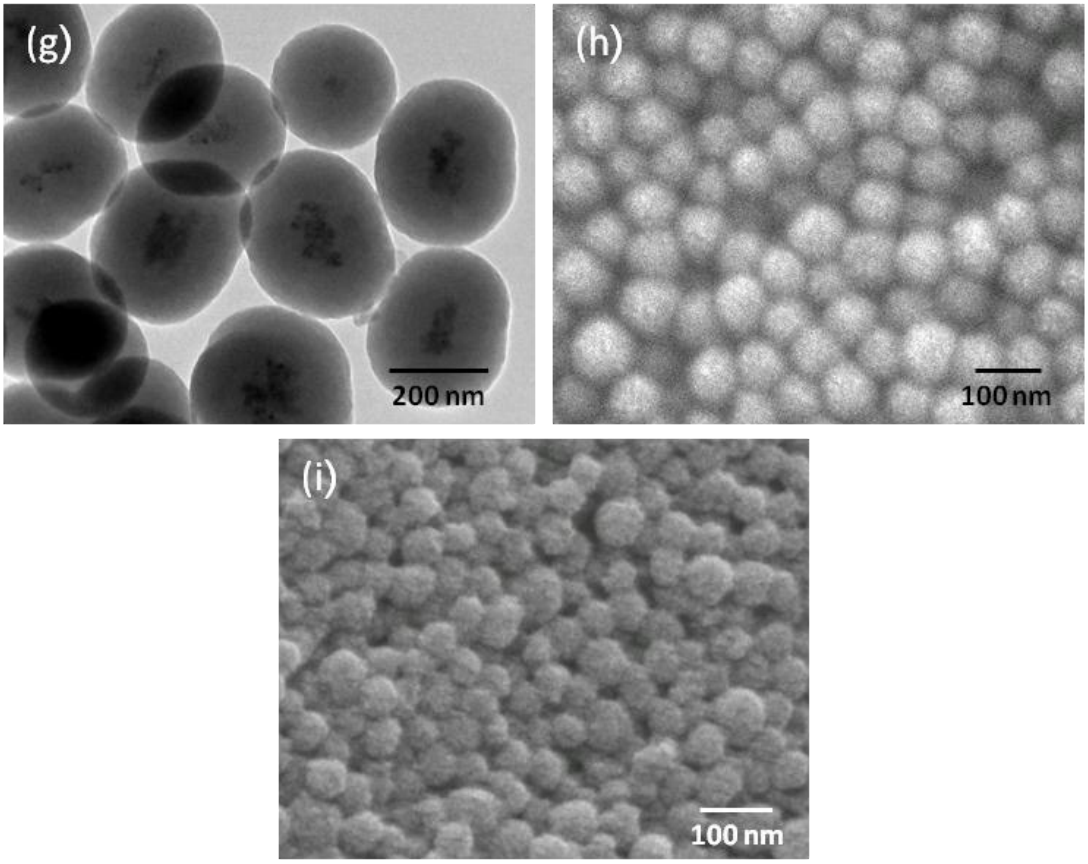


Fig. S1 TEM image of (a) OA-MNPs; (b) PGMA-MNPs; (c) PGMA-cat **8**; (d) PGMA-cat **9**; (e) PS-MNPs; (f) PS-cat **12**; (g) Si-MNPs; High-magnification SEM image of (h) PGMA-cat (m) **15**; (i) PS-cat (m) **16**.

2. Synthesis of PS-cat using aqueous H_2SO_4 at different concentration

Table S1 Preparation of PS-cat at different sulfonation conditions[a] and characterization of the PS-cat

Entry	[Sulfonation agent] (M)	Catalyst	Size	Acid capacity[b] (mmol H^+ g^{-1})	Separation[c]
1	3	PS-cat **a**	80 nm	0.1	Easy
2	4	PS-cat **b**	80 nm	0.1	Easy
3	5	PS-cat **c**	80 nm	0.1	Easy
4	6	PS-cat **13**	80 nm	0.2	Easy

[a] Sulfonation of PS-MNPs by aqueous H_2SO_4 were performed at 75 °C for 24 h. [b]Calculated by titration experiment. [c]Conducted by permanent magnet (neodymium, BH_{max} = 31 MGsOe).

3. Characterization of PS-MNPs and PS-cat 12 by FTIR

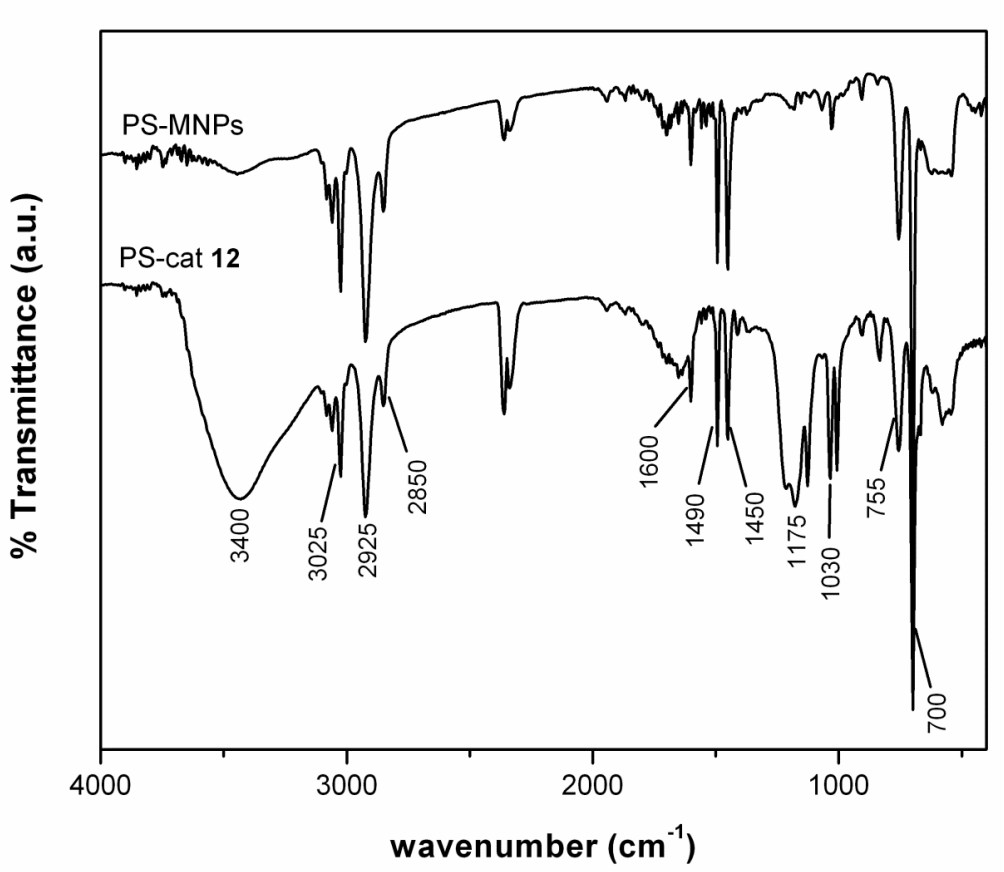


Fig. S2 FT-IR spectra of PS-MNPs and PS-cat **1**2.

No	Functional group	Absorption band (cm^{-1})	Particle
1	Benzene ring in polystyrene	700	PS-MNPs and PS-cat **12**
		755	PS-MNPs and PS-cat **12**
		1450	PS-MNPs and PS-cat **12**
		1490	PS-MNPs and PS-cat **12**
		1600	PS-MNPs and PS-cat **12**
		3025	PS-MNPs and PS-cat **12**
2	CH_2 stretch in polystyrene	2850	PS-MNPs and PS-cat **12**
		2925	PS-MNPs and PS-cat **12**
3	SO_3H group	1030	PS-cat **12**
		1175	PS-cat **12**
4	O-H stretch in SO_3H group	3400	PS-cat **12**

4. Characterization of Si-MNPs, SH-Si-MNPs, and Si-cat 14 by FTIR

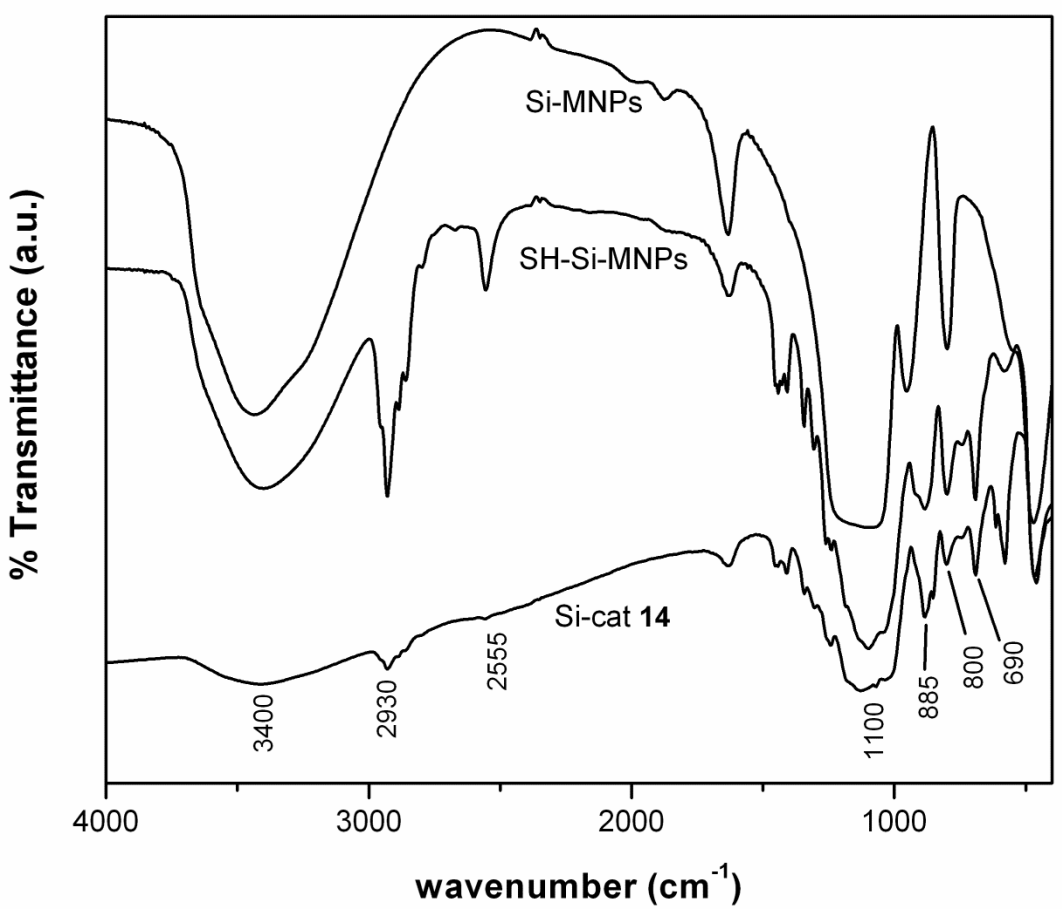


Fig. S3 FT-IR spectra of Si-MNPs, SH-Si-MNPs, and Si-cat **14**.

No	Functional group	Absorption band (cm^{-1})	Particle
1	Si-C stretch in silica	800	Si-MNPs, SH-Si-MNPs and Si-cat **14**
2	Si-O-CH_2 stretch in silica	885	Si-MNPs, SH-Si-MNPs and Si-cat **14**
3	Si-O-Si stretch in silica	1100	Si-MNPs, SH-Si-MNPs and Si-cat **14**
4	O-H stretch in silanol group	3400	Si-MNPs and SH-Si-MNPs
5	SH group	2555	SH-Si-MNPs
6	S-CH_2 stretch in mercaptopropyl or propyl sulfonic acid chain	690	SH-Si-MNPs and Si-cat **14**
7	CH_2 stretch in mercaptopropyl chain or propyl sulfonic acid chain	2930	SH-Si-MNPs and Si-cat **14**
8	O-H stretch in SO_3H group	3400	Si-cat **14**

5. Transesterification of the pretreated grease on 2 mL scale

After the FFA content in grease was reduced to less than 0.5 wt% with PGMA-cat **4**, the pretreated grease was used for the subsequent FAME production using the well-established base-catalyzed transesterification process.

0.025 g KOH was added into pretreated grease (1.5 g) and methanol (0.4 mL). The reaction mixture was stirred at 65 ºC for 2 h, yielding 1.32 g of FAME (corresponds to 88% isolated yield).

6. Determination of FAME purity by GC analysis

The resultant FAME (50 µL) was taken for FAME yield determination by gas chromatography (GC). To prepare the GC sample, 50 µL reaction mixture was washed with 50 µL DI water and centrifuged at 16700 g for 10 min. Finally, 5 µL oil from top layer was dissolved in 995 µL of hexane containing 2 mM of hexadecane as internal standard.

The FAME yield and purity were quantitatively analyzed by using Agilent 7890A Series GC system equipped with a split/splitless injection system, a flame-ionization detector (FID) and a capillary column (HP-INNOWax, Agilent Tecnologies, 30 m × 0.25 mm × 0.25 µm), and predetermined temperature program.[S1] The purity of FAME produced was determined as 100% by GC analysis (Fig S4. in the ESI†).

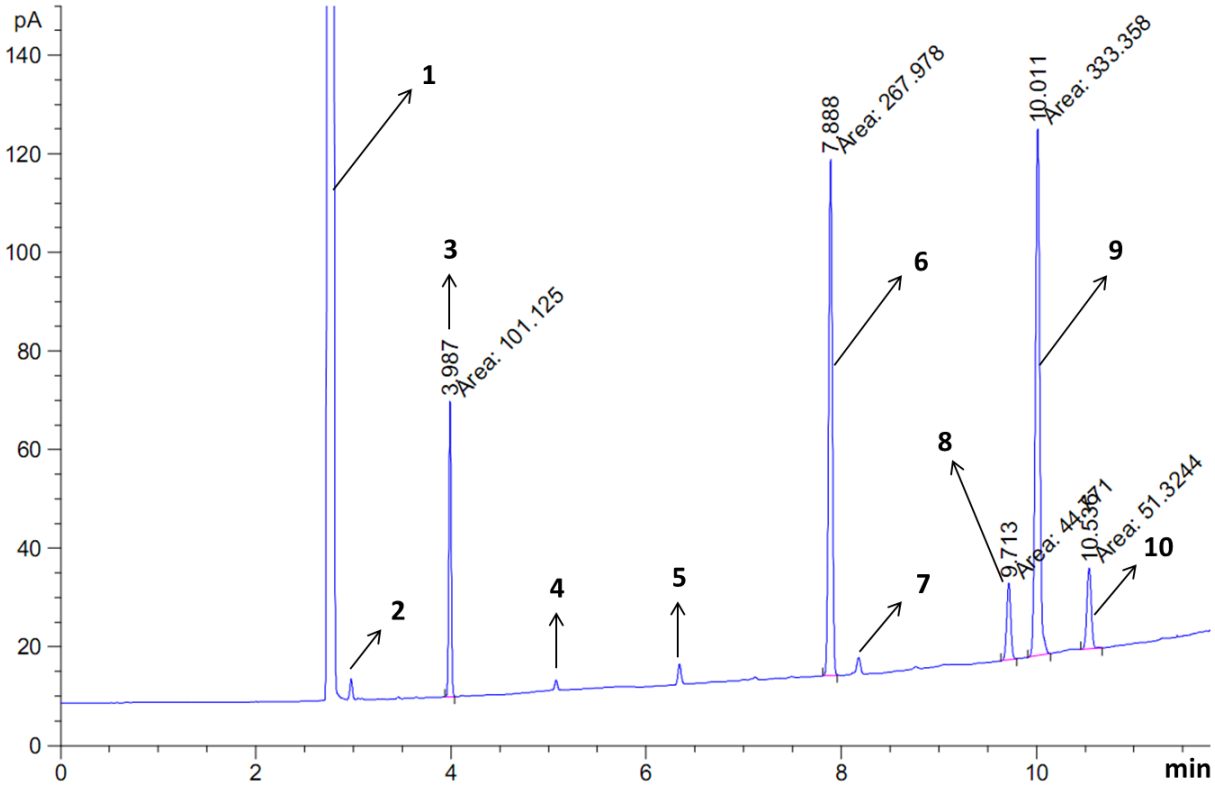


Fig. S4 GC chromatogram of FAME produced from transesterification of grease pretreated by PGMA-cat **4**. Reaction conditions: methanol:triglyceride molar ratio of 6:1, KOH loading of 1.7 wt% (referred to pretreated grease), 65°C and 2 h.

Peak no	Retention time (min)	Corresponding compound
1	2.75	*n*-hexane (solvent)
2	2.90	caprylic acid methyl ester
3	3.98	*n*-hexadecane (internal standard)
4	5.10	lauric acid methyl ester
5	6.35	myristic acid methyl ester
6	7.88	palmitic acid methyl ester
7	8.20	margaric acid methyl ester
8	9.71	linoleic acid methyl ester
9	10.01	oleic acid methyl ester
10	10.53	stearic acid methyl ester

Reference

S1. A. Li, T. P. N. Ngo, J. Yan, K. Tian and Z. Li, *Bioresour. Technol.*, 2012, 114, 725-729.