Electronic Supplementary Information (ESI)

Phosphotungstic acid-functionalized magnetic nanoparticles as efficient and recyclable catalyst for one-pot production of biodiesel from grease *via* esterification and transesterification

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1. Preparation of HPW-PGMA-MNPs *via* one-step immobilization of HPW to PGMA-MNPs

A mixture of H_3PO_4 (3.33 µL), $Na_2WO_4.2H_2O$ (33.3 mg), HCl (26.67 µL), and PGMA-MNPs (60 mg) in DI water (5 mL) was stirred at 80 °C for 1 h. The resulting particles were repeatedly washed by DI water and freeze-dried.

EDX measurement revealed that the Fe, P, and W content of the resulting particles were 0.17, 0.07, and 2.62 wt%, respectively. Titration measurement revealed that the acidity of the particles was 0.4 mmol g^{-1} .

2. Preparation of phosphate-functionalized PGMA-MNPs by using different reagents

Entry	Support	Phosphonation conditions ^a			Size	Elemental composition ^b (wt%)		Magnetic property ^c
		Reagent	[Reagent]	Time	(nm)	Fe	Р	
			(M)	(h)				
1	PGMA-MNPs	H ₃ PO ₄	0.5	3	90	0.03	1.06	Poor
2	PGMA-MNPs	H_3PO_4	0.8	3	90	0	1.19	Poor
3	PGMA-MNPs	H ₃ PO ₄	1.0	3	90	0	1.86	Poor
4	PGMA-MNPs	Na ₃ PO ₄	0.1	24	90	1.95	0.06	Good
5	PGMA-MNPs	Na ₃ PO ₄	0.5	24	90	1.44	0.06	Good
6	PGMA-MNPs	Na ₃ PO ₄	1.0	24	90	0.72	0.04	Good
7	PGMA-MNPs	NaH ₂ PO ₄	0.1	3	90	1.23	0.10	Good
8	PGMA-MNPs	NaH ₂ PO ₄	0.1	24	90	1.03	0.08	Good
9	PGMA-MNPs	NaH ₂ PO ₄	0.5	24	90	0.62	0.04	Good
^a T = 80 °C. ^b Measured by EDX. ^c Tested by using permanent magnet (neodymium, BH _{max} = 31								
MGsOe).								

Table S1 Preparation and characterization of phosphate-functionalized PGMA-MNPs

3. Characterization of magnetic iron oxide nanoparticles



Fig. S1 XRD patterns of OA-MNPs, PGMA-MNPs, H₂PO₄-PGMA-MNPs 5, and HPW-PGMA-MNPs 11.



Fig. S2 EDX spectrum of PGMA-MNPs.



Fig. S3 (a) TEM image of OA-MNPs; (b) FESEM and TEM (inset) image of PGMA-MNPs.

4. Preparation of FAME standard from grease via two-step reaction

In the first step, esterification of FFA in grease was performed. Novozyme $435^{\text{\ensuremath{\mathbb{R}}}}$ (0.1 g) was added into 5 g of grease and 0.395 mL of methanol (methanol/grease molar ratio of 3.5:1). The reaction mixture was stirred at 30 °C for 19 h. After reaction, the mixture was centrifuged at 16700 g for 10 min to separate the Novozyme $435^{\text{\ensuremath{\mathbb{R}}}}$ from the pretreated grease. Then, the pretreated grease was taken for FFA content determination and the result showed that its FFA content decreased from 21.3 wt% to 0.45 wt%.

In the second step, transesterification of the remaining triglyceride in grease was performed. 68 mg of KOH was added into 4 g of pretreated grease and 1.122 mL of methanol (methanol/grease molar ratio of 6:1). The reaction mixture was stirred at 65 °C for 18 h. After reaction, the product mixture was centrifuged at 16700 g for 10 min to separate the glycerol by-product. Then, the product mixture was subjected to rotary evaporation to remove the excess methanol, washed with 0.2% HCl solution to neutralize the KOH, and washed with DI water until the washing water reached neutral pH. MgSO₄ was then mixed with the product for overnight. Finally, the mixture was centrifuged at 16700 g for 10 min and the FAME standard in the supernatant (3.52 g, corresponds to 88% isolated yield) was collected.

5. Determination of FAME yield by GC analysis

The FAME concentration in the product was determined 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 Technologies, 30 m × 0.25 mm × 0.25 μ m). The temperature of injector and detector were set at 240 °C and 280 °C, respectively, and the column temperature was raised from 150 to 225 °C at 15 °C/min, 225 to 260 °C at 5 °C/min, and kept at 260 °C for 3 min.^{S1}

Calibration curve of each fatty acid methyl esters was established by using GLC-10 FAME mix analytical standard. The GC sample was prepared by mixing the sample (5 μ L) with *n*-hexane containing 2 mM *n*-hexadecane as internal standard (995 μ L). GC chromatogram of the FAME produced from grease with HPW-PGMA-MNPs **11** is shown in Fig. S4. Retention time: 3.818 min for *n*-hexadecane, 7.176 min for palmitic acid methyl ester, 8.780 min for linoleic acid methyl ester, 9.006 min for oleic acid methyl ester, and 9.440 min for stearic acid methyl ester. The FAME yield was calculated by comparing the FAME concentration of the product and the standard FAME samples prepared from grease *via* two-step reaction.^{S1}



Fig. S4 GC chromatogram of FAME produced from grease *via* esterification of FFA and transesterification of triglyceride in one pot with HPW-PGMA-MNPs **11**. Reaction conditions: methanol/grease molar ratio of 33:1, catalyst loading of 4 wt% (referred to grease), 122 °C, and 24 h.

6. Determination of triacetin conversion by GC analysis

The triacetin concentration in the product was determined 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 Technologies, 30 m × 0.25 mm × 0.25 μ m). The temperature of injector and detector were set at 240 °C and 280 °C, respectively, and the column temperature was raised from 150 to 225 °C at 15 °C/min, 225 to 260 °C at 5 °C/min, and kept at 260 °C for 3 min.^{S1}

The GC sample was prepared by mixing the sample (5 μ L) with *n*-hexane containing 2 mM *n*-hexadecane as internal standard (995 μ L). GC chromatogram of the product sample from transesterification of triacetin with HPW-PGMA-MNPs **11** is shown in Fig. S5. Retention time: 3.887 min for *n*-hexadecane and 6.378 min for triacetin. The triacetin conversion was calculated by comparing the initial and the final triacetin concentration.



Fig. S5 GC chromatogram of the product sample from transesterification of triacetin with HPW-PGMA-MNPs 11. Reaction conditions: methanol/triacetin molar ratio of 6:1, catalyst loading of 4 wt% (referred to triacetin), 60 °C, and 30 min.

7. One-pot transformation of grease to FAME by using HPW-PGMA-MNPs 11 at different reaction temperature



Fig. S6 One-pot transformation of grease to FAME by using HPW-PGMA-MNPs **11** at different reaction temperature. Reaction conditions: methanol/grease molar ratio of 33:1, catalyst loading of 4 wt% (referred to grease), and 24 h.

Reference

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