## **Supporting Information**

## Hot Pickering emulsion interfacial catalysis accelerates polyethylene terephthalate (PET) glycolysis

Qinan Chen<sup>a,c</sup>, Shuyao Wu<sup>a,b,\*</sup>, Po Zhang<sup>a</sup>, Xi-Ming Song<sup>a</sup> and Zhining Song<sup>a,\*</sup>

- <sup>a</sup> Liaoning Key Lab for Green Synthesis and Preparative Chemistry of Advanced Materials, College of Chemistry, Liaoning University, Shenyang 110036, China.
  E-mail: sywu@lnu.edu.cn, songzhining@lnu.edu.cn
- <sup>b</sup> Center for Analysis and Testing, College of Chemistry, Liaoning University, Shenyang 110036, China
- ° North Huajin Chemical Industries Group Corporation, Panjin 124021, China

## **SI Contents**

- Figure S1. SEM images of M-ANNs with different CTAB/Silane (g/g) ratios.
- Figure S2. SEM image and contact angle of M-NSPs.
- Figure S3. Microscopic photographs of the HPEIC system constructed by M-ANNs at

190 °C for different times.

- Figure S4. <sup>1</sup>H-NMR, HRMS, FT-IR, HPLC, DSC and XRD of the product BHET.
- Figure S5. The yield of product BHET at different temperatures with different reaction times.
- Figure S6. Microscopic photographs and droplet size distribution of the HPEIC system with different amounts of M-ANNs.
- Figure S7. The droplets size of emulsions with different amounts of M-ANNs.
- Figure S8. Conversion of PET and yield of BHET with different amounts of Zn(OAc)<sub>2</sub> in the HPEIC system.

Figure S9. Microscopic photograph of the HPEIC system after six catalytic cycles.

- Scheme S1. Mechanism of PET glycolysis catalyzed by Zn(OAc)<sub>2</sub> according to the literature.
- Table S1. Synthesis parameters of M-ANNs with different CTAB/Silane ratios.
- Table S2. Synthesis parameters of M-ANNs with different toluene/water ratios.
- Table S3. XRD parameters of product BHET.
- Table S4. Emulsion parameters of the HPEIC system with different amounts of M-ANNs.
- Table S5. The amount of Zn enriched on M-ANNs in EG.



**Figure S1.** SEM images of M-ANNs with the CTAB/Silane (g/g) ratio of (a) 0.9×10<sup>-2</sup>, (b) 1.1×10<sup>-2</sup>, (c) 1.3×10<sup>-2</sup>, (d) 1.5×10<sup>-2</sup>, (e) 2.0×10<sup>-2</sup>, and (f) 2.5×10<sup>-2</sup>.



**Figure S2.** SEM image and contact angle (inset) of M-NSPs. The average diameter is 35 nm. Its contact angle is about 110°. For the detailed preparation method of M-NSPs, please see No. 48 in Notes and references of the main text.



**Figure S3.** Microscopic photographs of the HPEIC system constructed by M-ANNs at 190 °C for different times (inset). EG was stained with eosin Y for better display in the microscopic photograph. Emulsion conditions: 1.5 g PET dispersed in 30 g BP, 0.5 g Zn(OAc)<sub>2</sub> dissolved in 30 g EG, 30 mg M-ANNs.



Figure S4. (a) <sup>1</sup>H-NMR, (b) HRMS, (c) FT-IR, (d) HPLC, (e) DSC and (f) XRD of the PET

depolymerization product. Reaction conditions: 1.5 g PET, 0.5 g Zn(OAc)<sub>2</sub>, 30 g EG + 30 g BP, 30 mg M-ANNs, reaction temperature 190 °C, reaction time 5 min.

As shown in the DSC curve of Figure S4e, the product BHET has a sharp endothermic peak at 112 °C, which is consistent with the melting point of BHET reported in the literature.<sup>1</sup> As shown in the XRD patterns of Figure S4f, PET exhibits a typical diffraction pattern due to its polyester crystalline structure, with broader peaks at  $2\theta$  = 16.3°, 17.5°, 22.7°, and 26.0°. In contrast, the diffraction peaks of product BHET are narrower and have higher relative intensity, which indicates that the product BHET has high crystallinity, and its XRD pattern is consistent with literature reports.<sup>1</sup>



**Figure S5.** The yield of product BHET at (a) 190 °C, (b) 180 °C, (c) 170 °C, (d) 160 °C, and (e) 150 °C with different reaction times. Reaction conditions: 1.5 g PET, 0.5 g Zn(OAc)<sub>2</sub>, 60 g EG (heterogeneous system)/30 g EG + 30 g NMP (homogeneous system)/30 g EG + 30 g BP + 30 mg M-ANNs (HPEIC system).



Figure S6. Microscopic photographs (left column) and droplet size distribution (right column) of the

HPEIC system (EG stained with eosin Y) with different amounts of M-ANNs. The amount of M-ANNs is (a,b) 30 mg, (c,d) 40 mg, (e,f) 50 mg, (g,h) 60 mg, and (i,j) 70 mg. Reaction condition: 1.5 g PET, 0.5 g Zn(OAc)<sub>2</sub>, 30 g EG + 30 g BP, reaction temperature 170 °C, reaction time 5 min.



**Figure S7.** The droplets size of emulsions with different amounts of M-ANNs according to the data in Figure S6.



**Figure S8.** The conversion of PET and the yield of BHET with different amounts of  $Zn(OAc)_2$  in the HPEIC system. Reaction condition: 1.5 g PET, 30 g EG + 30 g BP, 70 mg M-ANNs, reaction temperature 170 °C, reaction time 5 min.



**Figure S9.** Microscopic photograph of the emulsion constructed by M-ANNs after six catalytic cycles. EG was stained with eosin Y for better display in the microscopic photograph. Reaction condition: 1.5 g PET,  $0.5 \text{ g Zn}(\text{OAc})_2$ , 30 g EG + 30 g BP, 70 mg M-ANNs, reaction temperature  $170 \text{ }^{\circ}\text{C}$ .



Scheme S1. Mechanism of PET glycolysis catalyzed by Zn(OAc)<sub>2</sub> according to the literature.<sup>2</sup>

CTAB (mg)	TEOS (g)	APTMS (g)	CTAB/Silane (g/g)	water (g)	toluene (g)
17	1.65	0.25	0.9×10 <sup>-2</sup>	50	30
21	1.65	0.25	1.1×10 <sup>-2</sup>	50	30
25	1.65	0.25	1.3×10-2	50	30
29	1.65	0.25	1.5×10 <sup>-2</sup>	50	30
38	1.65	0.25	2.0×10 <sup>-2</sup>	50	30
48	1.65	0.25	2.5×10 <sup>-2</sup>	50	30

**Table S1.** Synthesis parameters of M-ANNs with different CTAB/Silane ratios (g/g) (Silane = TEOS + APTMS).

Table S2. Synthesis parameters of M-ANNs with different toluene/water ratios (g/g).

CTAB (mg)	TEOS (g)	APTMS (g)	water (g)	toluene (g)	toluene/water (g/g)
38	1.65	0.25	50	10	0.2
38	1.65	0.25	50	30	0.6
38	1.65	0.25	50	50	1.0
38	1.65	0.25	50	70	1.4
38	1.65	0.25	50	90	1.8
38	1.65	0.25	50	110	2.2

2θ (°)	d (nm)	I (%)
13.87	6.4	100.0
35.18	2.5	63.7
27.98	3.2	41.8
20.88	4.3	28.1
23.37	3.8	23.9
26.48	3.4	19.4
27.29	3.3	13.2
16.45	5.4	8.8

Table S3. XRD parameters of the product BHET.

Table S4. Emulsion parameters of the HPEIC system with different amounts of M-ANNs.\*

<i>w</i> (mg)	п	<i>d</i> (µm)	$A_{\rm s}/A_{\rm s0}$
30	86	46.8	1.00
40	111	42.9	1.08
50	118	42.5	1.13
60	124	42.1	1.16
70	125	42.0	1.18

\**w* is the weight of M-ANNs, *n* is the number of emulsion droplets, *d* is the average diameter of emulsion droplets,  $A_s$  is the surface area of emulsion droplets,  $A_s = n\pi d^2$ ,  $A_{s0}$  is the surface area of emulsion droplets when 30 mg of M-ANNs were added. Reaction condition: 1.5 g PET, 0.5 g Zn(OAc)<sub>2</sub>, 30 g EG + 30 g BP, reaction temperature 170 °C, reaction time 5 min.

$C_1 (mg/L)$	$C_1 (\mathrm{mg/L})$ $C_2 (\mathrm{mg/L})$		Zn/M-ANNs (mg/g)	
5654	5406	248	223	

Table S5. The amount of Zn enriched on M-ANNs in EG.\*

\* $C_1$  is the concentration of Zn in 30 g EG before adding M-ANNs,  $C_2$  is the concentration of Zn in EG after adding 30 mg of M-ANNs, which was determined by ICP-OES,  $\Delta C$  is the concentration of Zn enriched on M-ANNs, Zn/M-ANNs is Zn enriched on M-ANNs per unit of weight.

## References

- 1. Y. Liu, X. Yao, H. Yao, Q. Zhou, J. Xin, X. Lu and S. Zhang, *Green Chemistry*, 2020, **22**, 3122-3131.
- Y. Geng, T. Dong, P. Fang, Q. Zhou, X. Lu and S. Zhang, *Polymer Degradation and Stability*, 2015, 117, 30-36.