Electronic Supplementary Information for

Morphology engineering of 2D Zn-catalysts to wrinkled particles using NaCl microcrystals: Enhanced recyclability for the synthesis of poly(caprolactone)s

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Experimental Section

Information on instruments: SEM images of materials were obtained using JSM-7100F and JSM-7800F instruments at the Chiral Material Core Facility Center, Sungkyunkwan University. TEM and EDS-elemental mapping images were acquired using a JEM-2100F instrument. PXRD patterns were recorded using a Rigaku MAX-2200 diffractometer. IR absorption spectra were measured with a Bruker VERTEX 70 spectrometer. Solid-state ^{13}C NMR spectra were collected in cross-polarization/total sideband suppression (CP/TOSS) mode using a 500 MHz Bruker AVANCE III HD spectrometer at the National Center for Inter-University Research Facilities of Seoul National University of Korea. ICP-AES analysis was performed with an OPTIMA 8300 instrument. TGA analysis was carried out using a Seiko Exstar 7300 instrument. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Ascend 500 MHz spectrometer at the Chiral Material Core Facility Center. HR-MS spectra were obtained using a Xevo G2-XS-UPC2 spectrometer at the same facility. GPC analysis was conducted using an Agilent Infinity 1260 instrument. Surface areas of materials were obtained by the analysis N_2 adsorption-desorption isotherm curves obtained at 77 K using a Micromeritics ASAP2020 instrument.

Preparation of M-NaCl

For the preparation of M-NaCl, NaCl (8.76 g, 0.150 mol) was dissolved in distilled water (50 mL) in a 50 mL Falcon tube. The NaCl aqueous solution (10 mL) was added dropwise to acetone (200 mL) in a 250 mL round-bottomed flask. The suspension was stirred for 30 min at room temperature. The precipitates (M-NaCl) were separated by centrifugation and dried under vacuum.

Synthesis of W-Zn-Gal NP and control Zn-Gal

For the preparation of W-Zn-Gal NP, after M-NaCl (1.0 g), zinc acetate dihydrate (0.307 g, 1.40 mmol), and distilled DMF (40 mL) were added to a 100 mL Schlenk flask, the mixture was sonicated for 30 min at room temperature. After gallic acid monohydrate (0.264 g, 1.40 mmol) was dissolved in distilled DMF (40 mL) in a 70 mL vial, the solution was added to the suspension. After being stirred at 50 ^{o}C for 48 h, the reaction mixture was cooled to room temperature. The M-NaCl@Zn-Gal composites were separated by centrifugation, washed with distilled DMF (10 mL) four times and acetone (12.5 mL) once, and dried at 80 ^{o}C under vacuum overnight. The resulting composites were washed with distilled water (20 mL) four times and acetone (20 mL) once and dried at 80 ^{o}C under vacuum overnight. For the preparation of control Zn-Gal,[1] the same synthetic procedures of W-Zn-Gal NP were applied without using the M-NaCl and without water washing steps. The control Zn-Gal(H_2O) was prepared by the same synthetic procedures of W-Zn-Gal NP without using the M-NaCl and with water washing steps. For the preparation of the partially etched M-NaCl@Zn-Gal, the M-NaCl@Zn-Gal was washed with a mixture of ethanol and water.

Experimental procedures of catalytic studies of the synthesis of PCL

For the synthesis of PCL (Entries 6 and 16 in Table 1 in text), ε-CL (0.500 mL, 4.51 mmol), distilled water (initiator, 1.6 μL, 90 μmol), and W-Zn-Gal NP (8.76 mg, 1.00 mol% Zn, 5.14 mmol Zn/g based on the ICP-AES analysis) or control Zn-Gal (6.98 mg, 1.00 mol% Zn, 5.73 mmol Zn/g based on the ICP-AES analysis) were added to a 10 mL Schlenk flask. After being stirred at 160 ^{o}C for 24 h, the reaction mixture was cooled to room temperature. The catalysts were retrieved by centrifugation from the reaction mixture. The remaining solution was filtered using a syringe filter (Advantech Co, 0.45 μm and 13 mm) and additional anhydrous methylene chloride. After evaporating volatile solvent, the mixture was redissolved in anhydrous methylene chloride (1 mL). After adding distilled methanol (19 mL), the mixture stood at 0 ^{o}C in a refrigerator to form PCL precipitates. The PCL precipitates were separated by centrifugation, washed with distilled methanol (20 mL) four times, and dried under vacuum. The characterization data of isolated PCL matched well with those reported in the literature.[2] Characterization data of isolated PCL: an isolated yield of 91%, ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.05 (t, J = 6.7 Hz, 2H), 3.64 (t, J = 6.5 Hz, end group), 2.35 (t, J = 7.3 Hz, end group), 2.30 (t, J = 7.5 Hz, 2H), 1.70 – 1.59 (m, 4H), 1.38 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ = 173.7, 64.3, 34.3, 28.5, 25.7, 24.7 ppm. $M_{n\text{-}NMR}$ values of PCLs were obtained through the ^{1}H NMR-based end group analysis of isolated PCLs; ^{1}H peaks at 4.05 ppm (2H, -OCH_2-) of polymer chains and 3.64 ppm (2H, -CH_2-OH) of end groups were used in the analysis. The $M_{n\text{-}GPC}$ values of PCLs were obtained by the GPC analysis using THF as eluent. It can be noted that M_n values have been corrected by the following equation: $M_{n\text{-}NMR} = 0.56M_{n\text{-}GPC}$, for PCL based on the Mark-Houwink correction.[3]

For the recyclability test, the separated catalysts were washed with acetone (8 mL) three times, dried under vacuum overnight, and used for the next run.

References

1 Y. Yang, K. Sung, J. D. Lee, J. Ha, H. Kim, J. Baek, J. H. Seo, S. -J. Kim, B. Y. Lee, S. U. Son, B. -S. Kim, Y. Kim, J. -Y. Park and H. -Y. Jang, *ACS Sustainable Chem. Eng.* 2024, **12**, 3933-3940.

2 J. D. Lee, Y. -J. Ko, S. M. Lee, H. J. Kim and S. U. Son, *ACS Appl. Nano Mater.* 2022, **5**, 12401-12406.

3 F. Zhou, M. Lin, L. Li, X. Zhang, Z. Chen, Y. Li, Y. Zhao, J. Wu, G. Qian, B. Hu and W. Li, *Organometallics* 2011, **30**, 1283-1286.

Fig. S1 SEM images of (a) M-NaCl (b) M-NaCl@Zn-Gal, (c, e, f) partially NaCl-etched M-NaCl@Zn-Gal, and (d) W-Zn-Gal NP. composites. TEM images of (g, h) partially NaCl-etched M-NaCl.

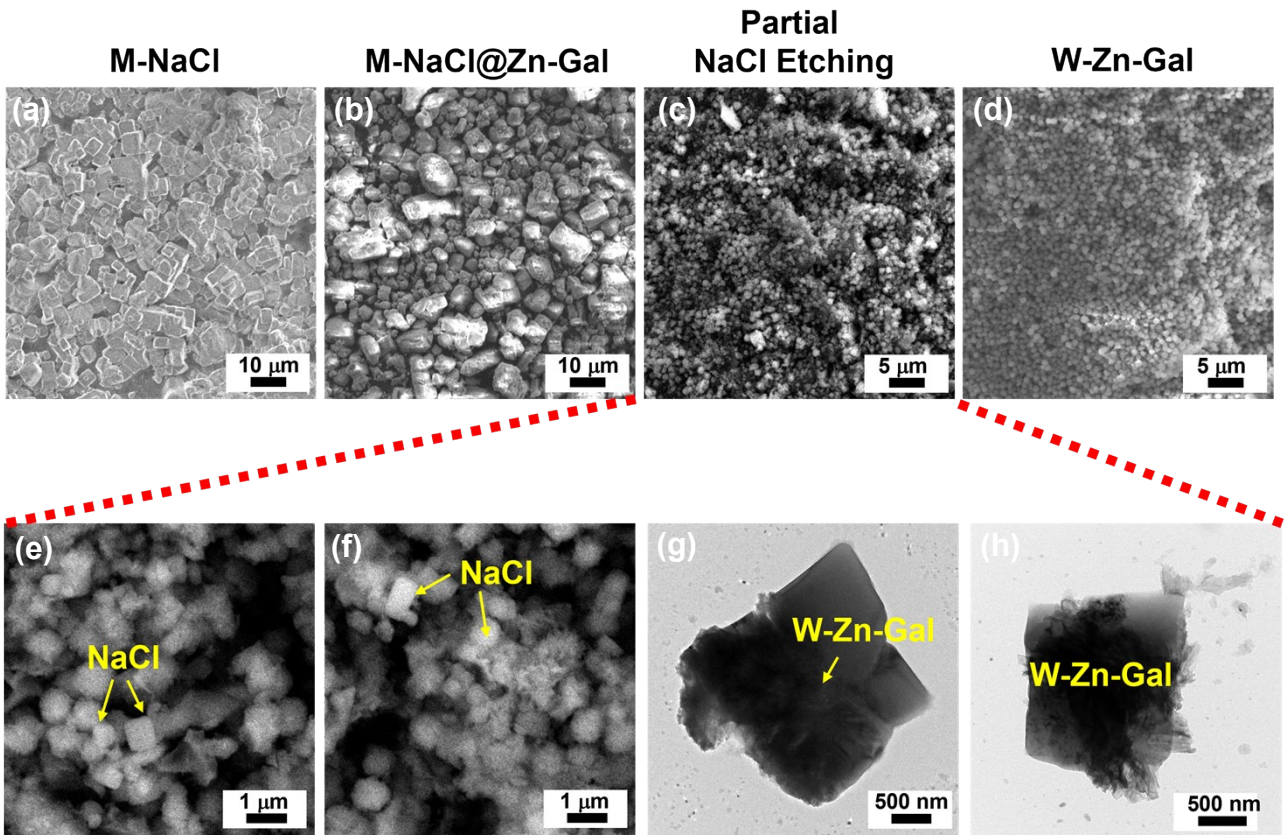


Fig. S2 Size distribution diagrams of (a) commercial NaCl, (b) M-NaCl, and (c) W-Zn-Gal NP.

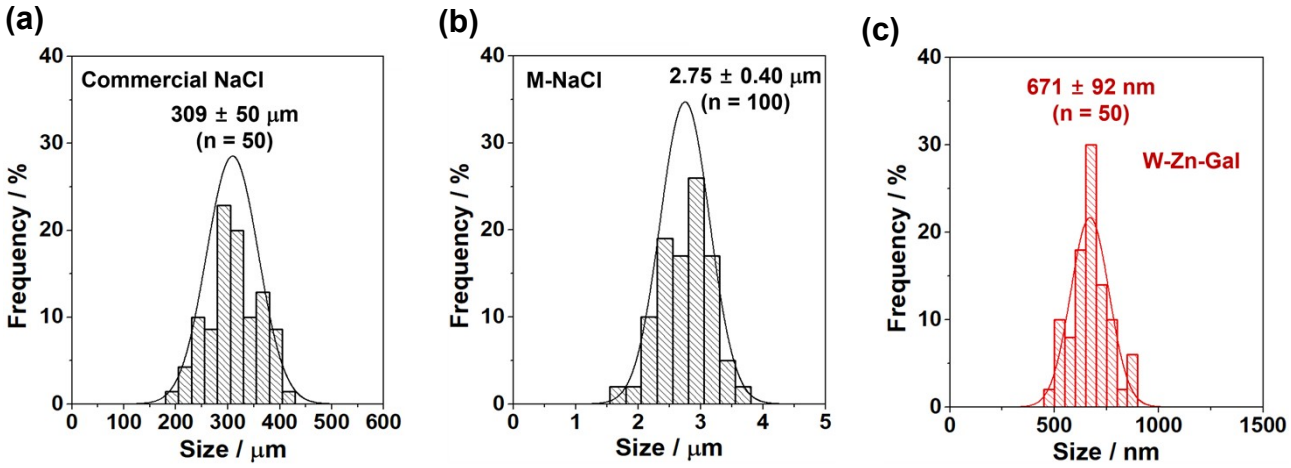


Fig. S3 (a) A SEM image of Zn-Gal aggregates and (b-d) TEM images of the dispersed Zn-Gal materials.

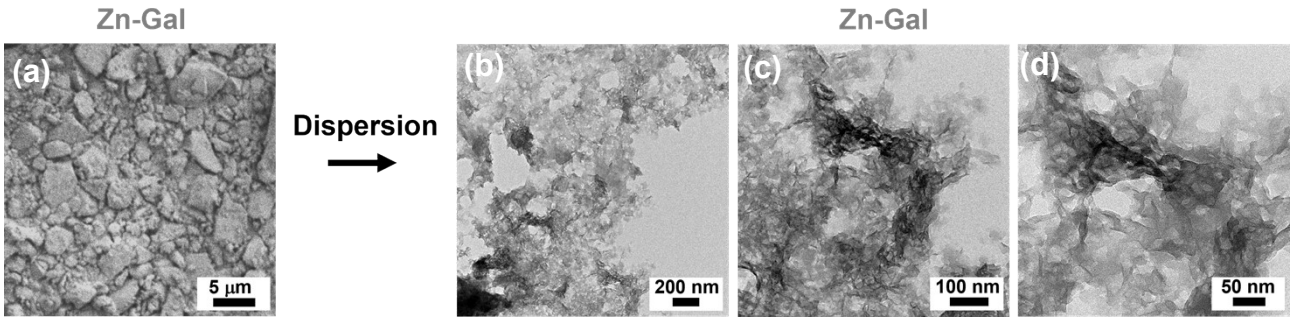


Fig. S4 SEM images of (a-c) commercial NaCl, (d) commercial NaCl@Zn-Gal, and (e) W-Zn-Gal obtained using commercial NaCl (C-W-Zn-Gal). (f) A TEM image of C-W-Zn-Gal.

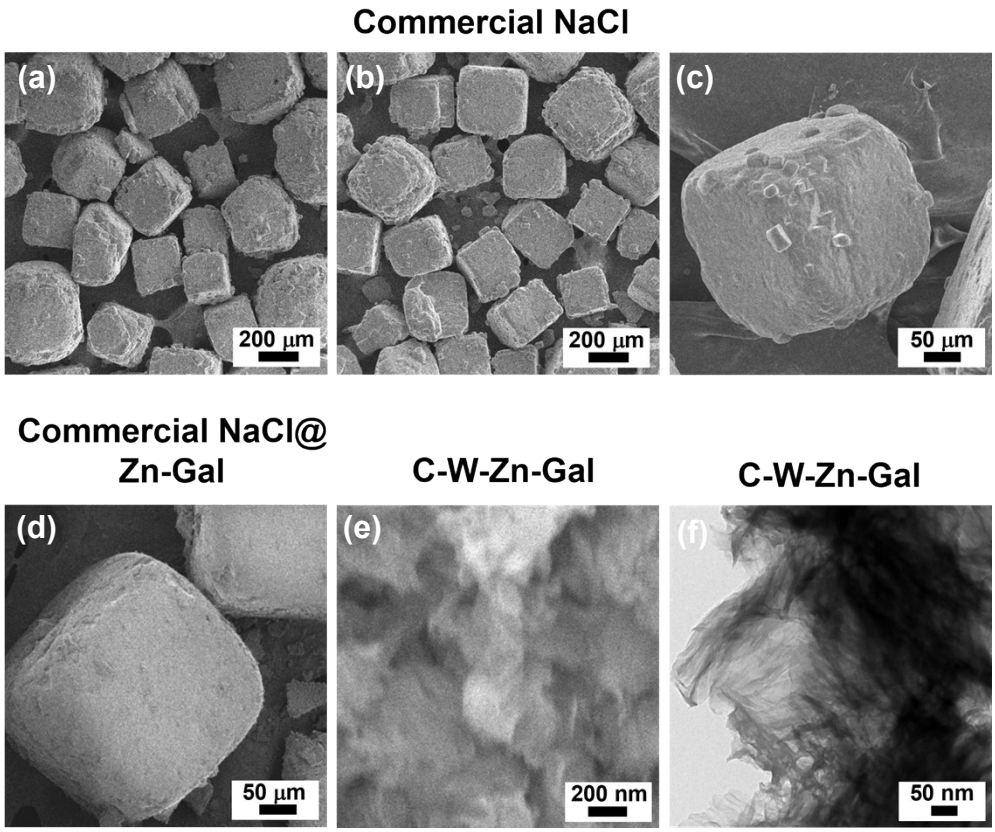


Fig. S5 EDS-based elemental mapping images of (a) M-NaCl, (b) M-NaCl@Zn-Gal, and (c) W-Zn-Gal NP (Zn-mapped images correspond to the Zn Kα line. The Na-mapped image of W-Zn-Gal NP corresponds to the Zn Lα line, not Na Kα line).

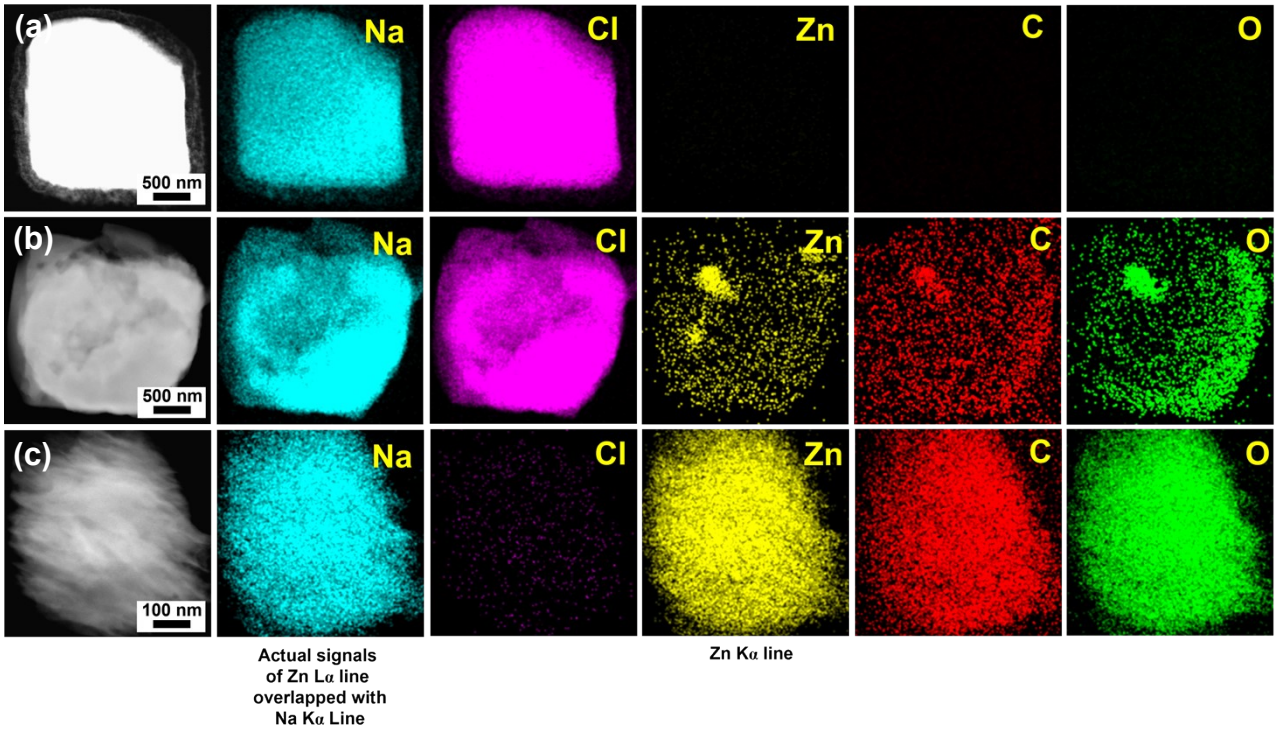


Fig. S6 TGA curves of W-Zn-Gal NP and control Zn-Gal.

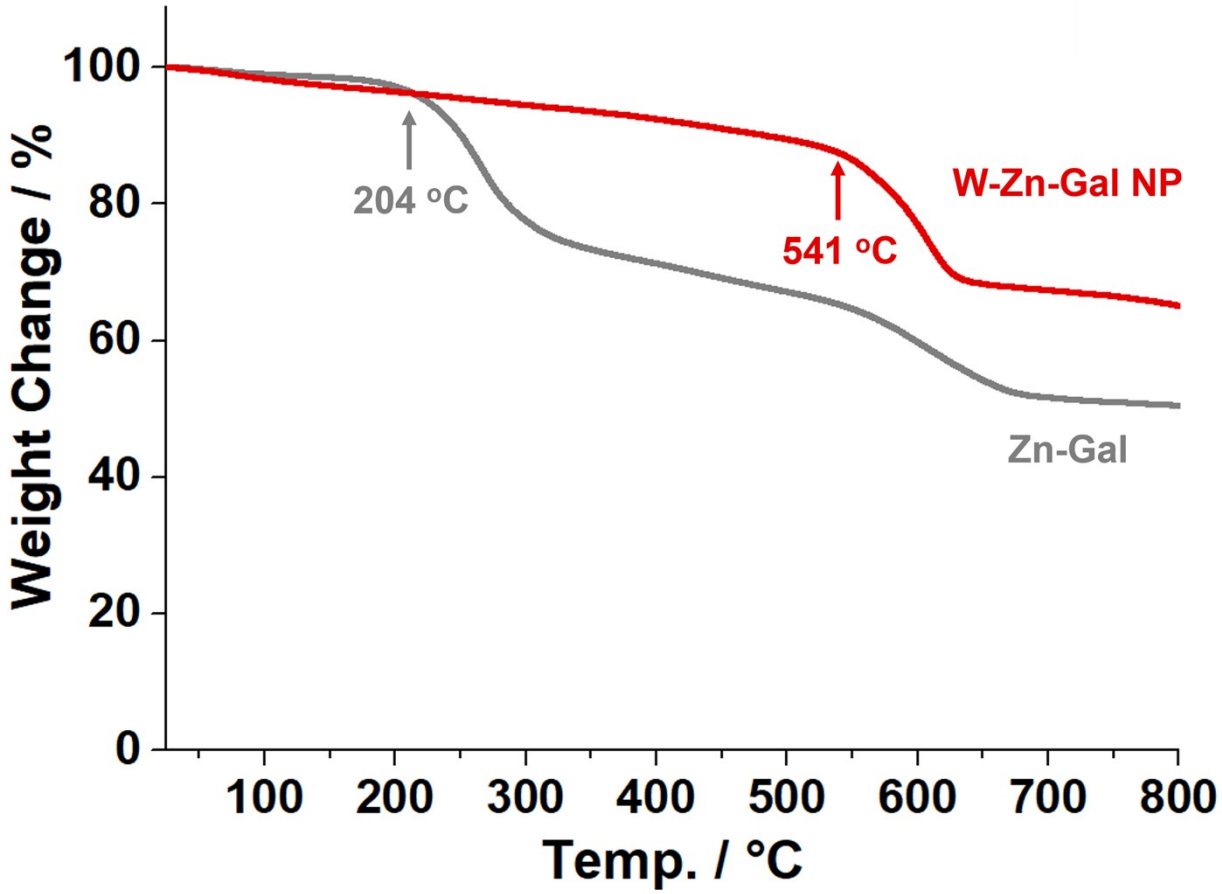


Fig. S7 ^{1}H and ^{13}C NMR spectra of isolated PCL.

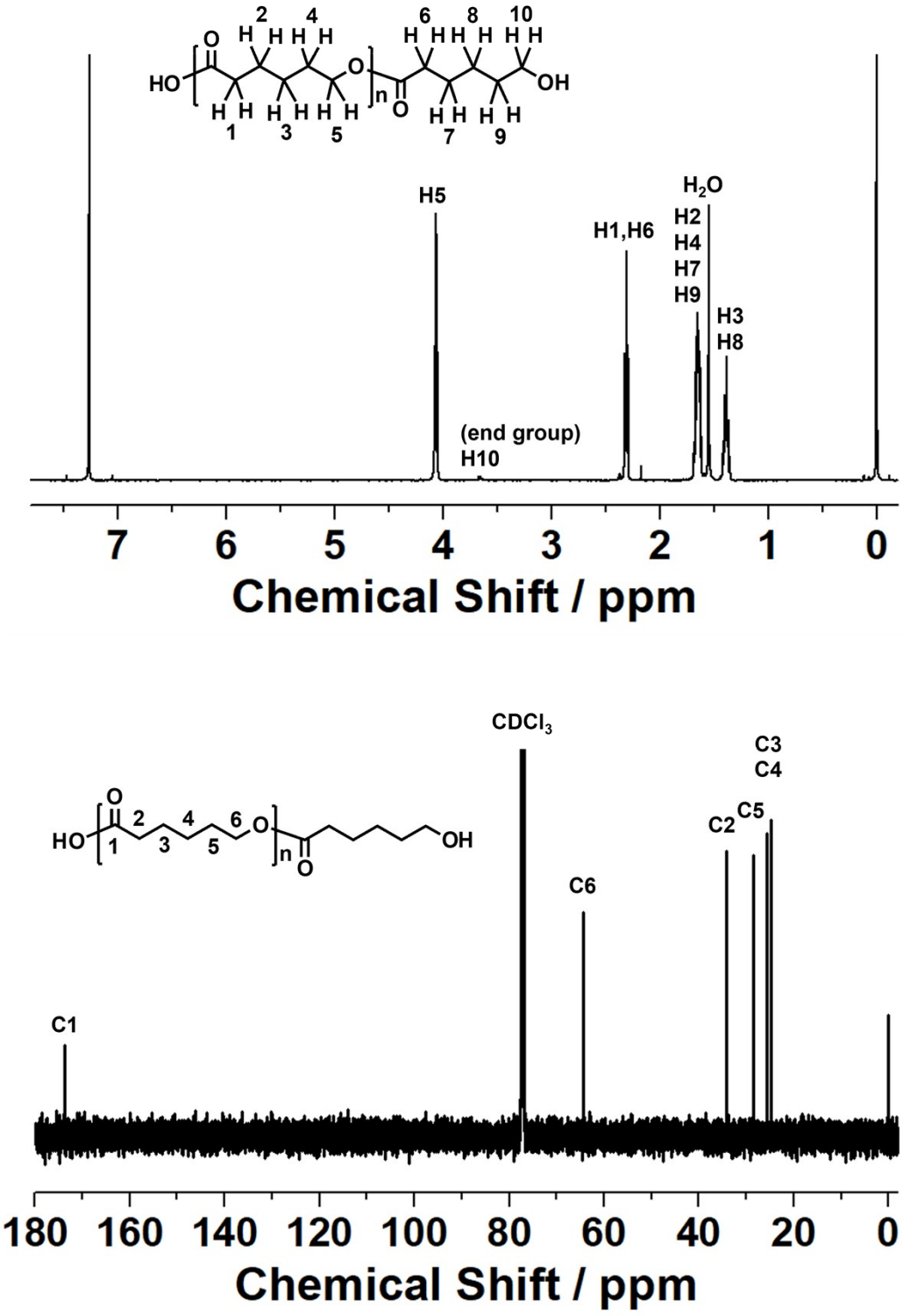


Fig. S8 IR spectrum of isolated PCL.

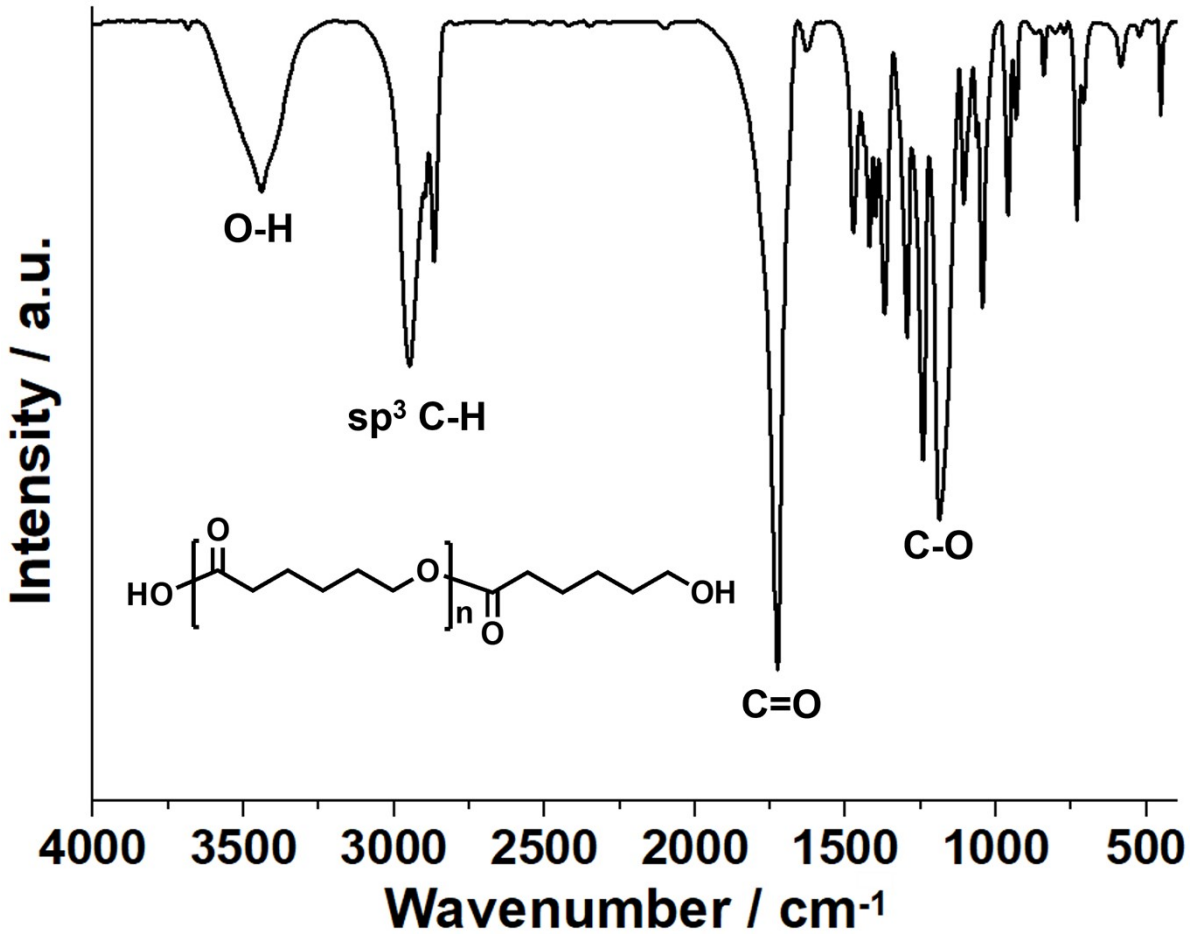
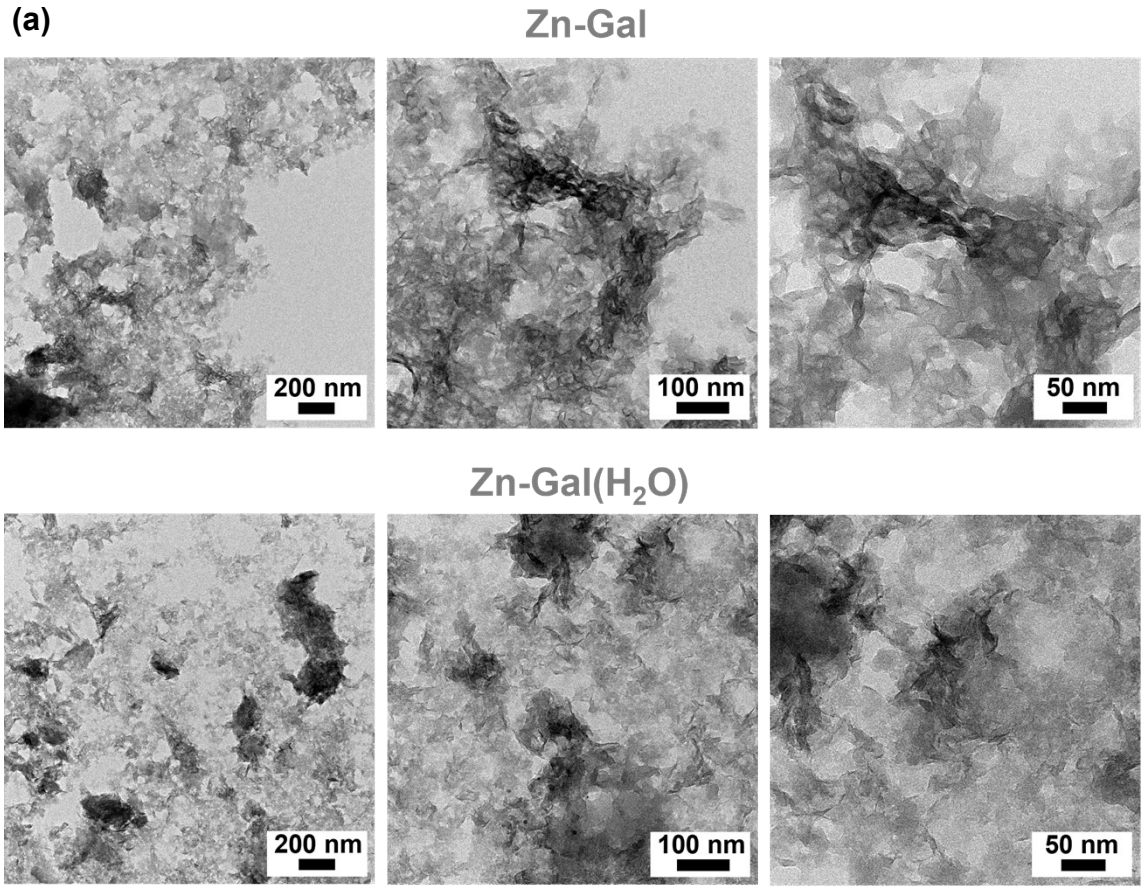
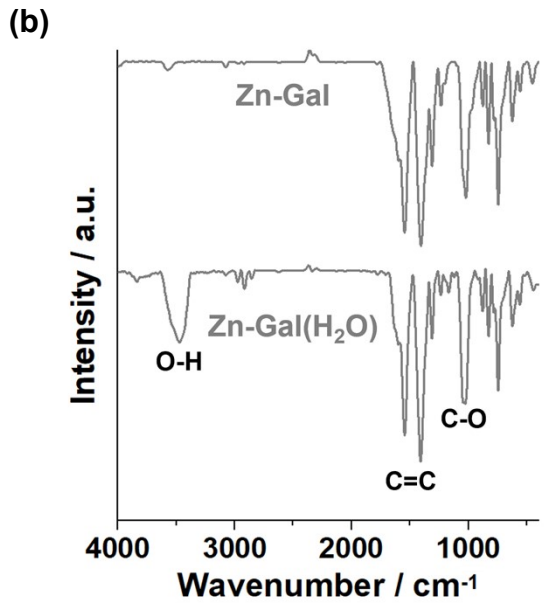


Fig. S9 (a) TEM images, (b) IR spectra, (c) PXRD patterns of Zn-Gal and Zn-Gal(H_2O).





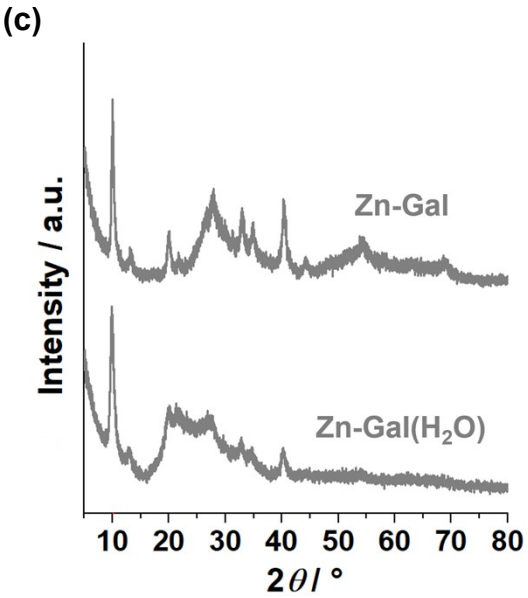


Fig. S10 TGA curves of Zn-Gal and Zn-Gal(H_2O).

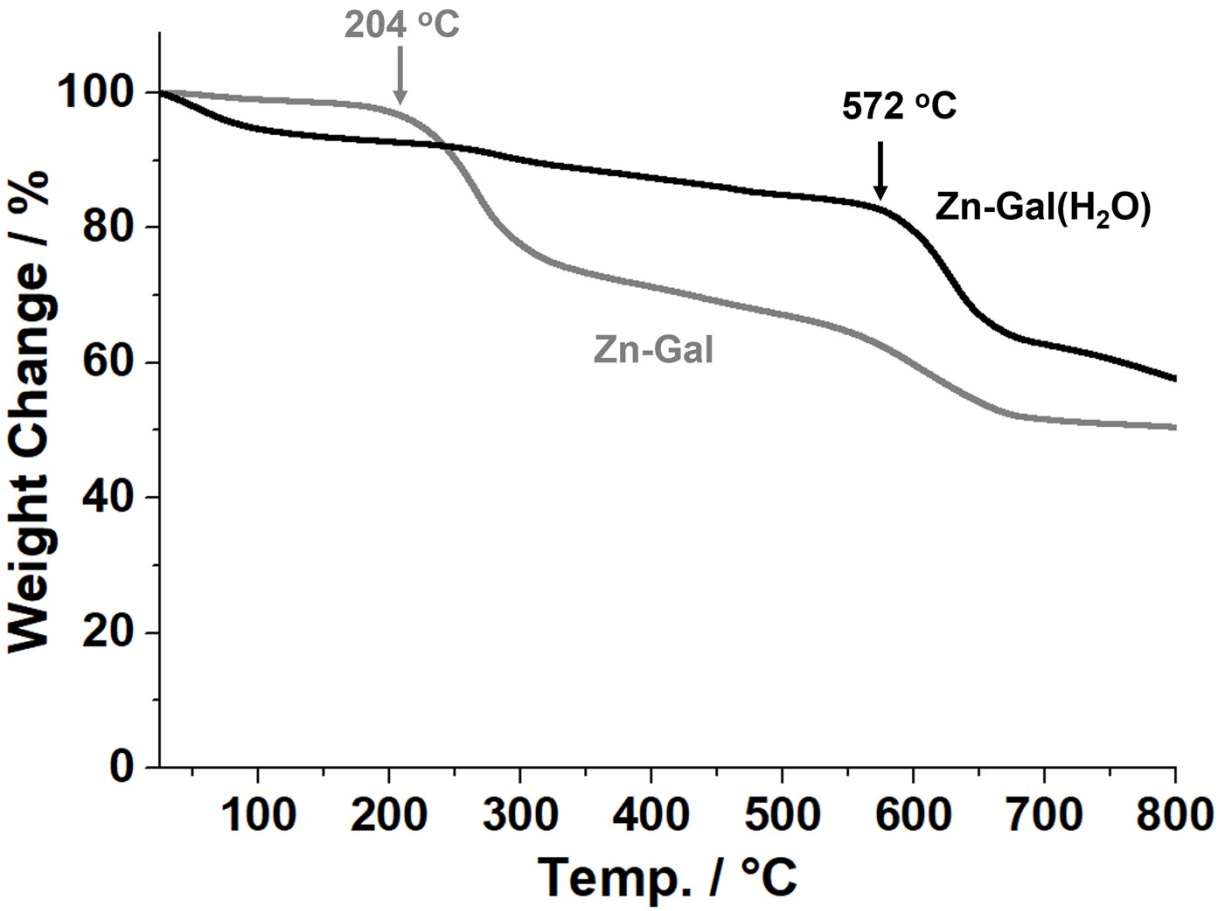


Fig. S11 Comparison recyclability of (a) Zn-Gal and (b) Zn-Gal(H_2O) catalysts for the ring-opening polymerization of ε-CL to PCL (Reaction conditions: ε-caprolactone (0.500 mL, 4.51 mmol), H_2O initiator (1.6 μL), Zn-Gal and Zn-Gal(H_2O) (1.00 mol% Zn), 24 h, and 160 °C). Conversion yields of ε-CL and isolated yields of PCL were displayed.

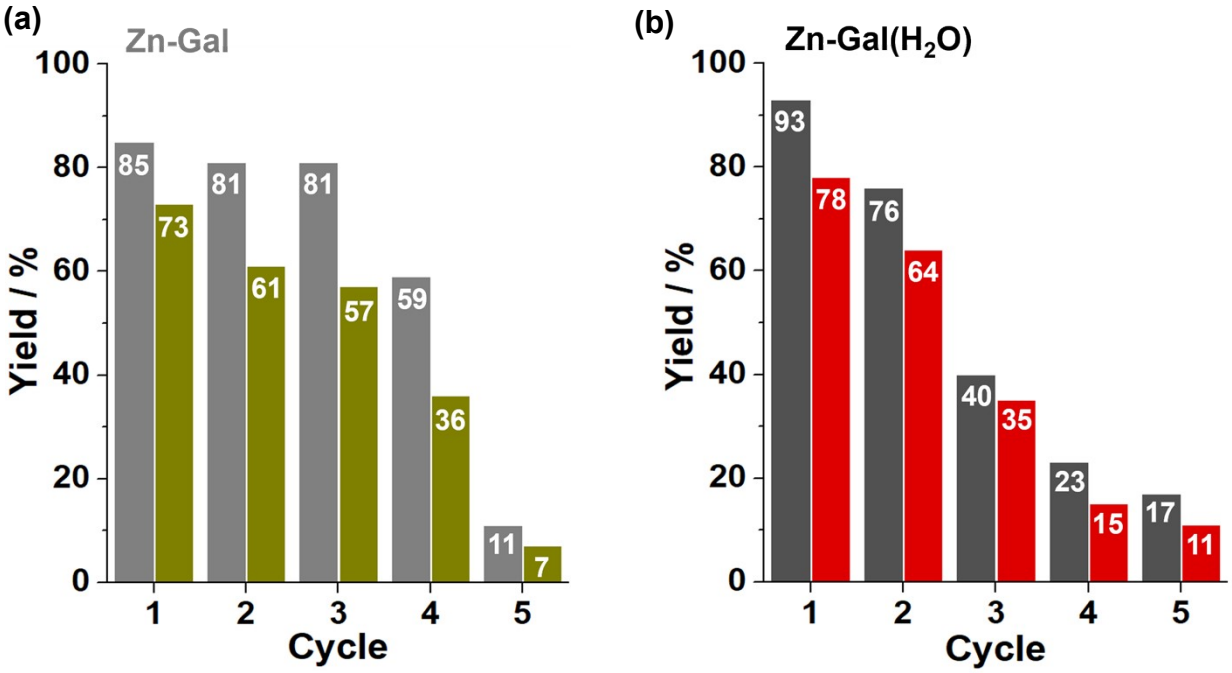


Fig. S12 PXRD patterns of W-Zn-Gal NP before and after five successive reactions.

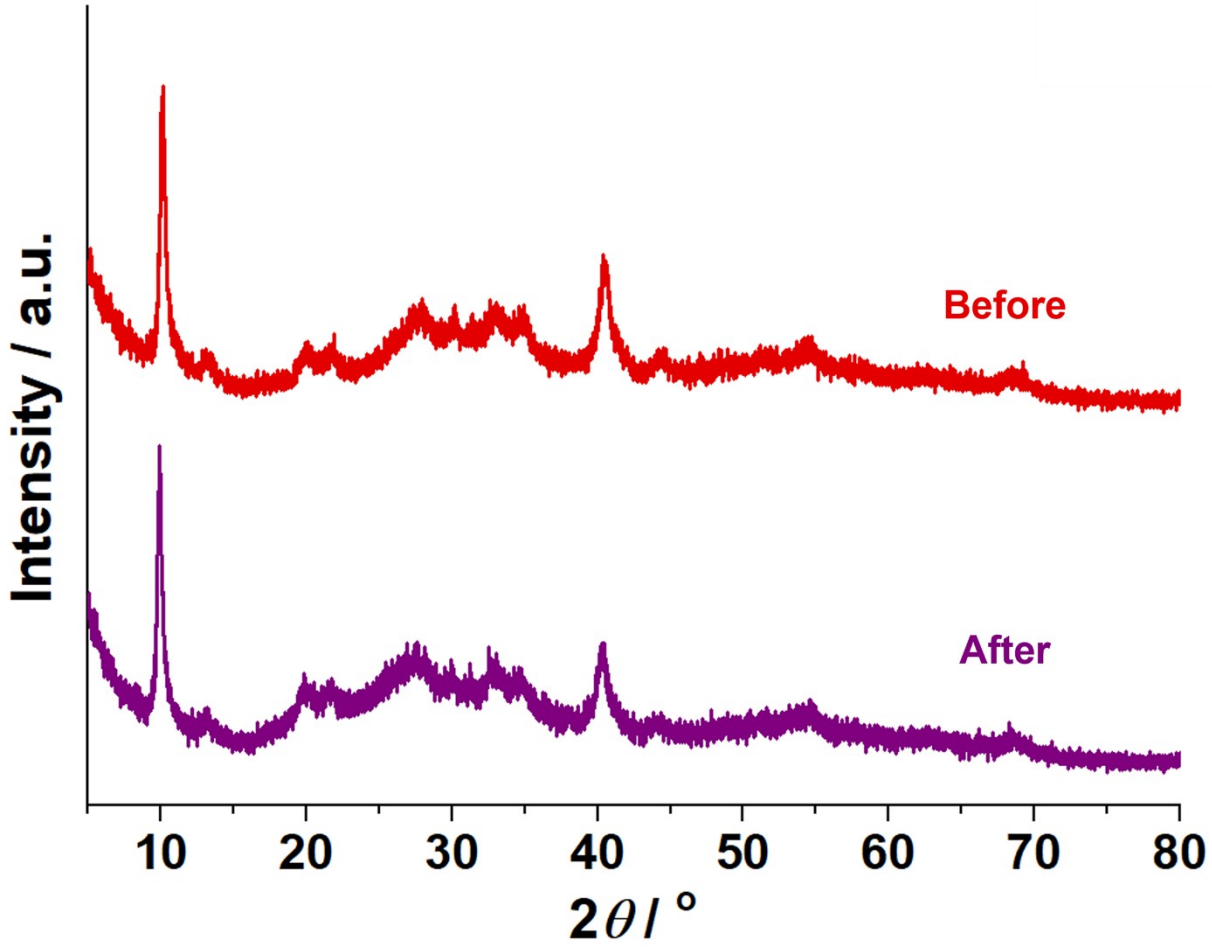


Fig. S13 N_2 adsorption-desorption isotherm curves (77 K) of (a) W-Zn-Gal NP and (b) Zn-Gal before and after five successive reactions.