Supporting Information

Morphology-tuned MnO_x/TiO_2 nanocatalysts for recycling PET plastic waste with biomass-derived ethylene glycol

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1. Characterization studies of the catalysts and BHET monomer

The NMR spectra (^{1}H, ^{13}C, and DEPT 135°) were obtained using a Bruker Avance III 400 MHz/54 mm FT-NMR spectrophotometer to confirm the formation of BHET qualitatively. The molecular weight of the BHET monomer was confirmed by the high-resolution mass spectrum (HR-MS) instrument (Agilent 6538 UHD Q-TOF) in electron spray ionization mode contains the sodium metal ionization (Na^{+}) and potassium metals (K^{+}) at atmospheric pressure chemical ionization. Powder XRD analysis was conducted utilizing a Malvern PANalytical non-ambient XRD Empyrean-DY2584 equipped with 45 kW & 40 mA to elucidate crystal planes and phases of TiO_2 and MnO_x. The Ni-filtered Cu Kα radiation was used as the X-ray source. The TEM analysis of TiO_2 and MnO_x/TiO_2-NR materials was conducted on a JEOL (JEM F200) instrument with a 200 kV accelerating voltage electron beam to determine the particle size, shape, and dispersion of MnO_x and TiO_2 particles. A carbon-coated copper grid with a 200-mesh size was employed for TEM analysis. The specific surface areas, pore sizes, and pore volumes of pristine TiO_2 and MnO_x/TiO_2 catalysts were evaluated by N_2 adsorption-desorption analysis at -196 °C (liquid N_2 temperature). The measurements were performed on an Autosorb iQ Station 1 instrument, employing the Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) model. Before analysis, all samples underwent vacuum drying at 200 °C for 2 h to remove physisorbed species.

The XPS analysis was conducted under ultra-high vacuum conditions on an AXIS Supra with Al Kα radiation to determine the oxidation states of Mn, Ti, and O as well as the changes in their binding energies. The charge correction of the binding energies of Mn, Ti, and O of the catalysts was executed using the adventitious carbon at 284.6 eV. The CO_2-TPD measurements were carried out using a ChemBET Pulsar automatic chemisorption analyzer (MAKE Quantachrome Instruments), which was equipped with diffusion-type oxidation and CO_2-resistant TCD filaments. The fits were generated and analyzed by the in-built analyzer 'Quantachrome TPRWin v4.10'. The catalysts were pretreated at 120 °C for 30 min under a He flow and then cooled to 40 °C, followed by CO_2 adsorption with pure CO_2 (99.9% purity) at a flow rate of 50 mL min^{-1} for 20 min. The amount of basic sites was estimated by measuring the amount of CO_2 desorbed by increasing the temperature to 800 °C with ramping of 10 °C min^{-1}.

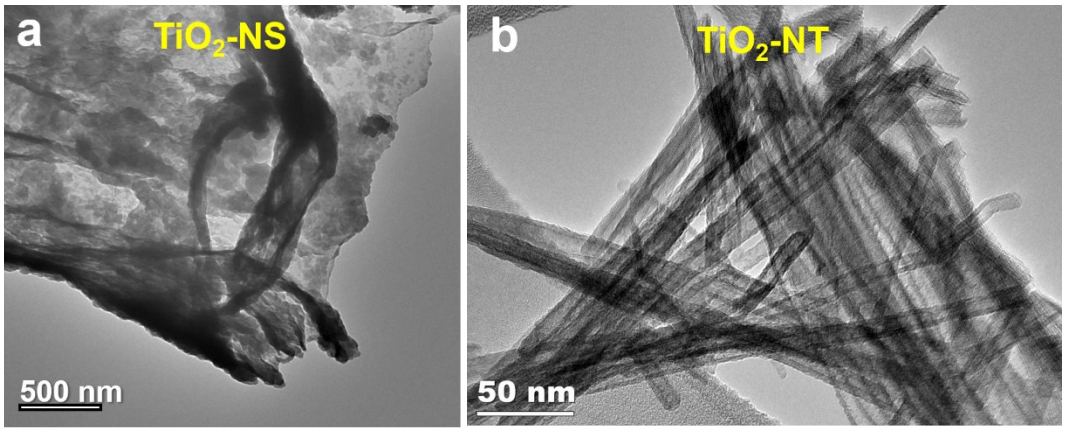


Fig. S1. TEM images of (a) TiO_2 nanosheets (NS) and (b) TiO_2 nanotubes (NT).

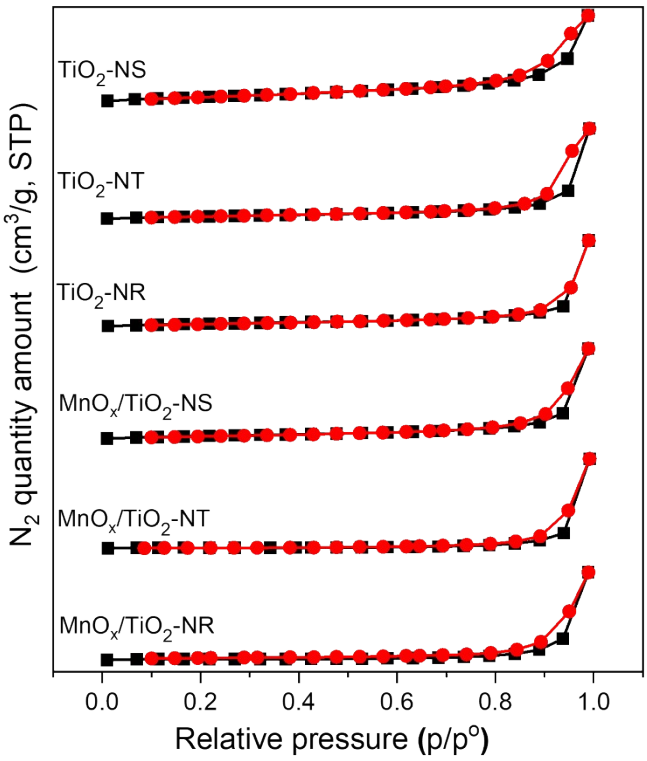


Fig. S2. N_2 adsorption-desorption isotherms of TiO_2 and MnO_x/TiO_2 catalysts.

Table S1: BET surface area, average pore volume, and average pore size of TiO_2 and MnO_x/TiO_2 nanocatalysts.

S. No.	Catalyst	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
1	TiO_2-NS	198	0.604	26.13
2	TiO_2-NT	185	0.575	25.20
3	TiO_2-NR	129	0.414	25.11
4	MnO_x/TiO_2-NS	152	0.326	25.06
5	MnO_x/TiO_2-NT	138	0.288	25.14
6	MnO_x/TiO_2-NR	94	0.307	26.18

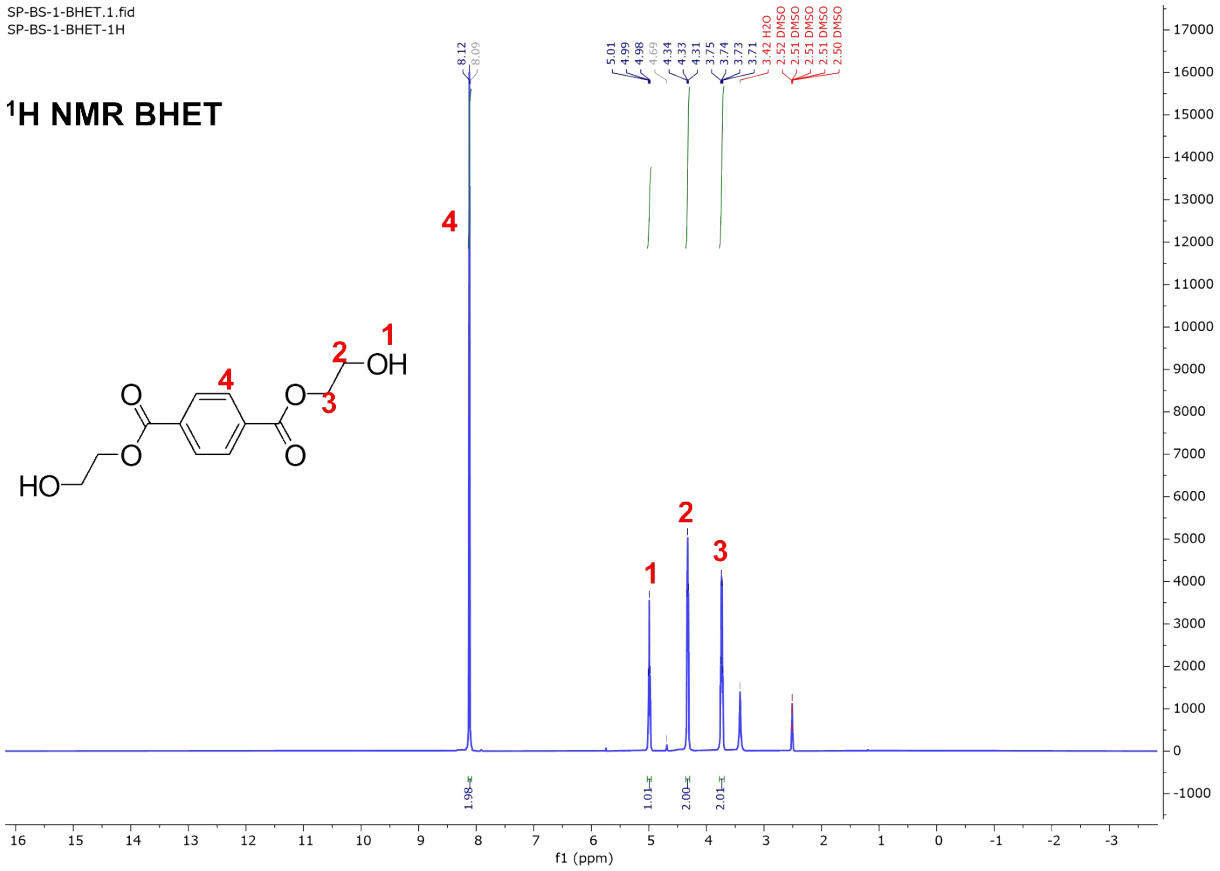


Fig. S3. ^{1}H NMR analysis of BHET monomer.

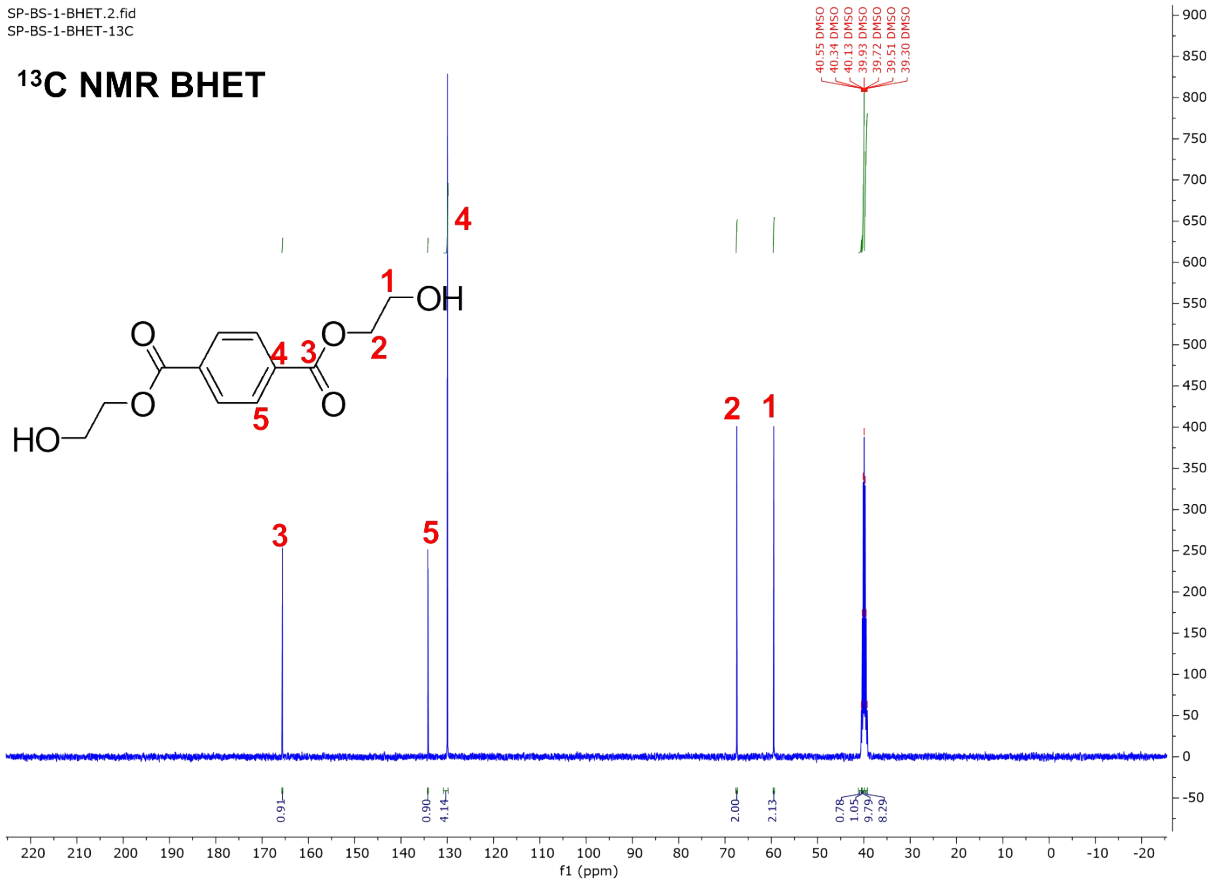


Fig. S4. ^{13}C NMR analysis of BHET monomer.

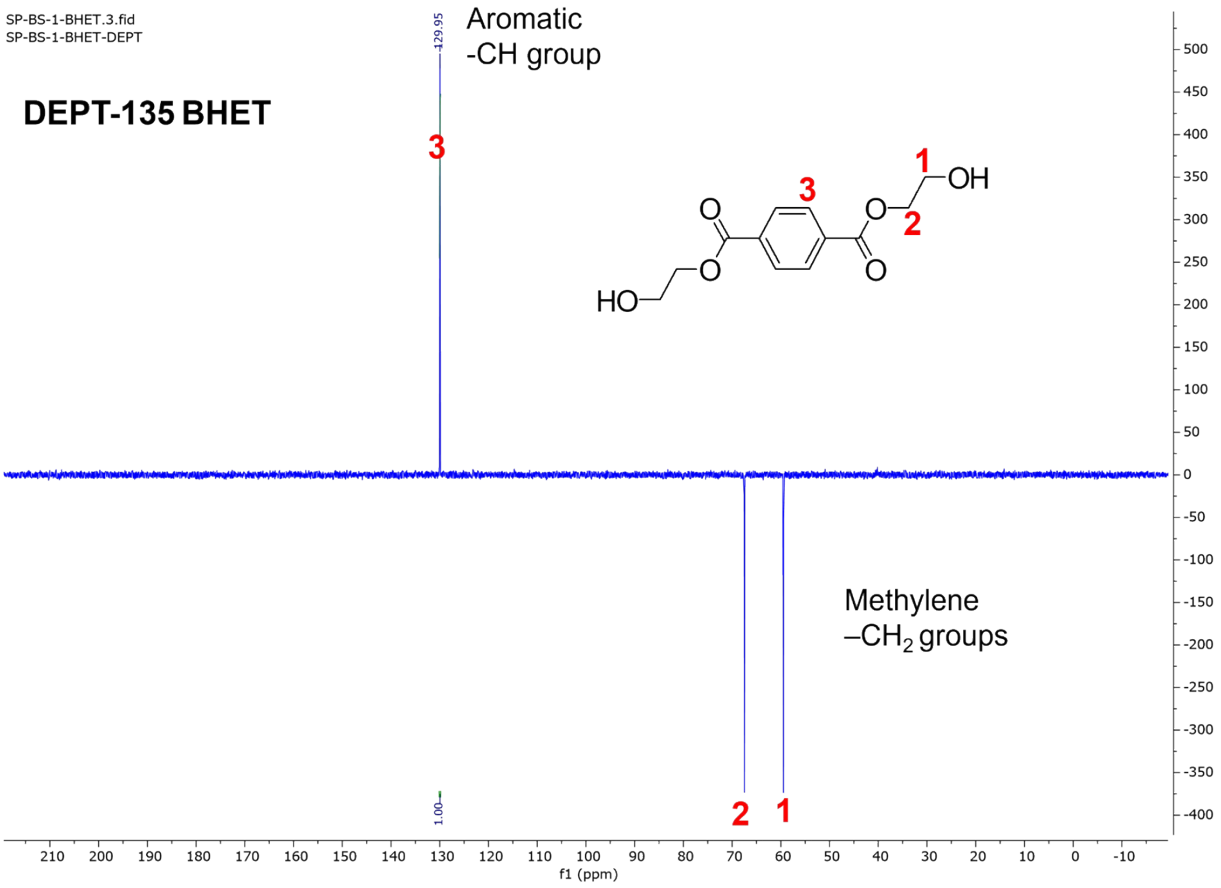
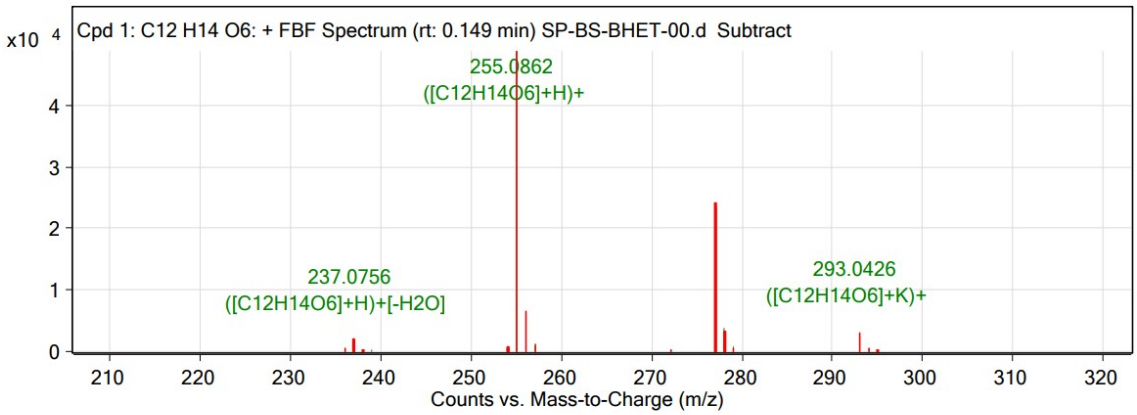


Fig. S5. DEPT-135 NMR analysis of BHET monomer.



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
236.0678	1	547.95	C12H14O6	M+[-H2O]
237.0756	1	1616.04	C12H14O6	(M+H)+[-H2O]
254.0857	1	653.1	C12H14O6	M+
254.0993	1	400.56	C12H14O6	(M+NH4)+[-H2O]
255.0862	1	48780.16	C12H14O6	(M+H)+
256.0901	1	5695.69	C12H14O6	(M+H)+
272.1111	1	289.55	C12H14O6	(M+NH4)+
277.068	1	23501.08	C12H14O6	(M+Na)+
278.0719	1	3738.86	C12H14O6	(M+Na)+
293.0426	1	2910.35	C12H14O6	(M+K)+

Fig. S6. HR-MS analysis of BHET monomer.

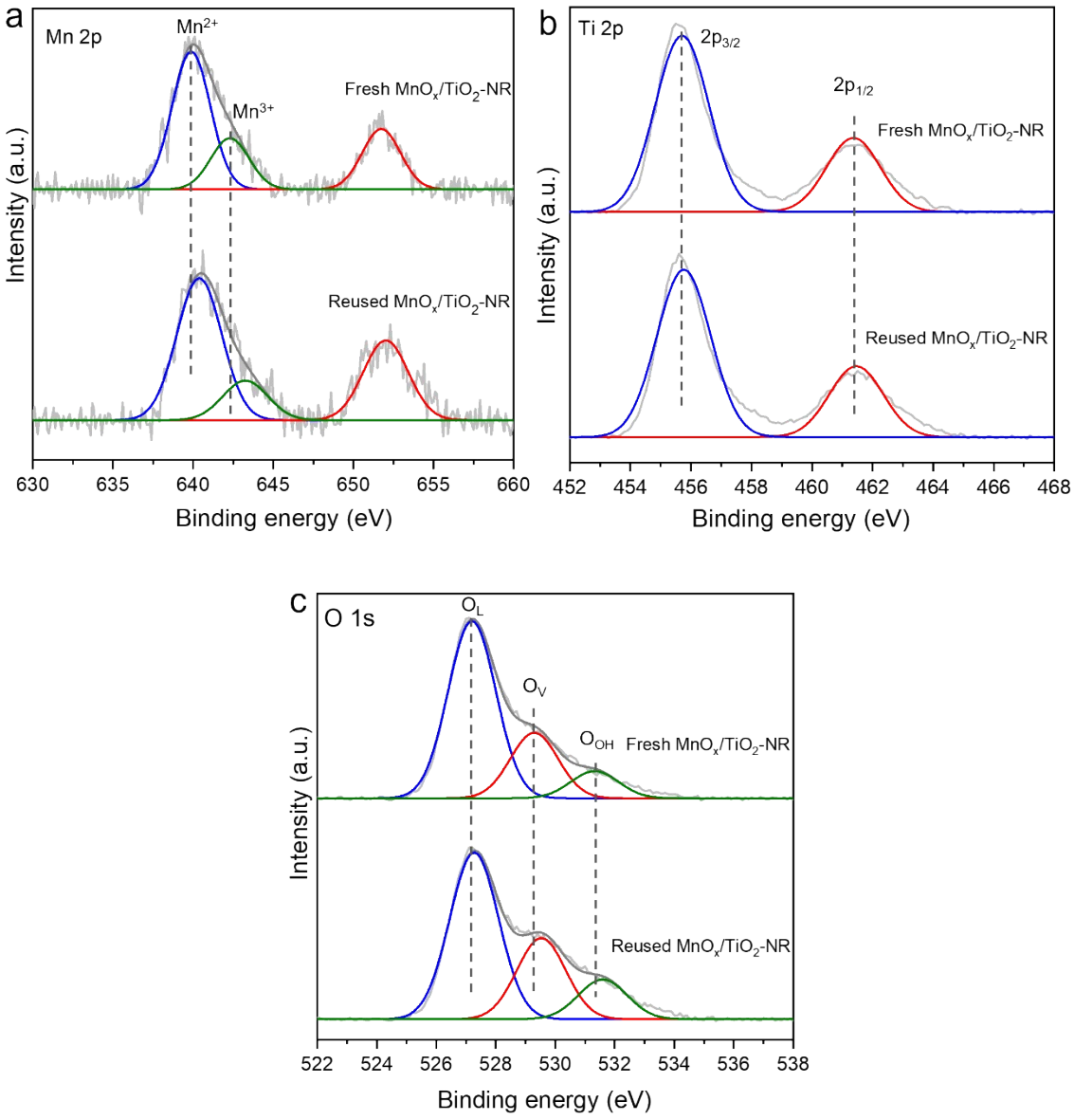


Fig. S7. (a) Mn 2p, (b) Ti 2p, and (c) O 1s XP spectra of fresh and reused MnO_x/TiO_2-NR catalysts.