Supplementary Information

For

A Comprehensive Assessment of Catalytic Performances of Mn_2O_3 Nanoparticles for Peroxymonosulfate Activation during Bisphenol A Degradation

Li Chen [1,2], Wanyi Fu [1,3,*], Congyu Hou [1,2], Yulong Yang[1,2] and Xihui Zhang[1,2,*]

1   Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen 518055, Guangdong, China

2   School of Environment, Tsinghua University, Beijing 100084, China

3   Tsinghua-Berkeley Shenzhen Institute, Tsinghua University, Shenzhen 518055, Guangdong, China

*Corresponding authors: X. Zhang, zhangxh@sz.tsinghua.edu.cn; W. Fu, fu.wanyi@sz.tsinghua.edu.cn

2.1 Reagents

Bisphenol A (BPA, ≥99%, GC grade), Potassium peroxymonosulfate (PMS, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), Erythromycin, Ofloxacin, Naproxen, Paracetamol, furfuryl alcohol (FFA), *tert*-butanol (TBA), *p*-benzoquinone (*p*-BQ), 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO), 2,2,6,6-tetramethyl-4-piperidinol (TMP), sodium pyrophosphate (PP), ammonia, manganese acetate $(Mn(OAC)_3)$, humic acid, sodium hydroxide (NaOH), sodium sulfate (Na_2SO_4), sodium nitrate $(NaNO_3)$, sodium chloride (NaCl), calcium chloride $(CaCl_2)$ were purchased from Shanghai Aladdin Chemistry Co., Ltd., China. Anhydrous manganese sulfate $(MnSO_4)$ and magnesium chloride $(MgCl_2)$ were obtained from Shanghai Macklin Biochemical Co., Ltd., China. Hydrochloric acid (HCl) and nitric acid (HNO_3) were purchased from Dongguan Dongjiang Chemical reagent Co., Ltd (Guangdong, China). Methanol (99.9%) was supplied by Merck KgaA (Germany). Formic acid (100%) was obtained by Honeywell (Fluka, Germany). Isopropanol (≥ 99.9%) and acetonitrile (≥ 99.9%) were supplied by Saan Chemical Technology Co., Ltd (Shanghai, China). Methanol (MeOH), isopropanol, acetonitrile, formic acid, and ammonia used for HPLC-MS/MS analysis are of HPLC grade. All the other chemicals and reagents were at least of analytical grade and used

without further purification. Ultrapure water (UPW) was produced using a Milli-Q system (Millipore, USA).
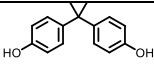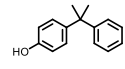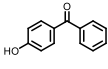
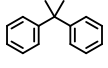**Table S1.** Water quality parameters of real waters.
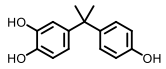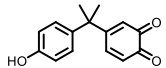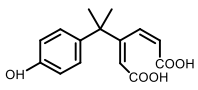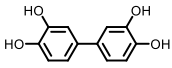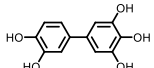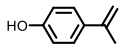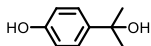
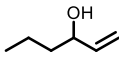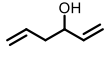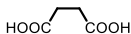| Parameters	Ultrapure water (UPW)	River water (RW)	Secondary effluent (SE)	Tap water (TW)
pH	6.83	8.17	7.05	6.96
COD (mg L^{-1})	-	29.26	38.40	6.03
SS (mg/L)	-	29.50	4.50	2.50
TOC (mg/L)	-	5.75	9.48	0.74
UV$_{254}$ (cm^{-1})	-	0.06	0.11	0.02
NH$_3$-N(mg/L)	-	0.19	0.11	0.05
TN (mg/L)	-	1.67	9.09	0.15
TP (mg/L)	-	0.07	0.16	0.05
Cl$^-$ (mg/L)	-	7.89	89.45	7.50
Turbidity	-	10.50	0.67	0.12
DO (mg/L)	6.82	9.26	5.74	7.59

Note: "-" stands for undetected.

Table S2 Linear equations and R^2 of the reaction processes under different conditions

Different PMS dosages			Different Mn$_2$O$_3$ dosages		
Dosage (mM)	Equations	R^2	Dosage (g/L)	Equations	R^2
0.01	y =-0.0441x-0.1725	0.9276	0.01	y =-0.0070x-0.0132	0.9543
0.02	y =-0.0545x-0.0257	0.9236	0.05	y =-0.0553x+0.0259	0.9944
0.03	y =-0.0570x-0.1024	0.9791	0.1	y =-0.1088x-0.0483	0.9984
0.05	y =-0.0698x-0.1702	0.9685	0.2	y =-0.5402x-0.0557	0.9922
0.1	y =-0.1136x-0.0304	0.9973	0.3	y =-0.7500x+0.4852	0.9908
0.3	y =-0.1360x-0.1596	0.9369			
0.5	y = -0.0906x-0.195	0.9720			
Different initial pH			Different BPA concentrations		
Value	Equations	R^2	Concentration (mg/L)	Equations	R^2
4.0	y = -0.4391x+0.2119	0.9920	0.1	y = -0.7120x-0.5416	0.9320
7.0	y = -0.5402x-0.0557	0.9922	1.0	y = -0.6852x-0.0248	0.9974
9.0	y = -0.9287x+0.2548	0.9863	10	y = -0.5402x-0.0557	0.9922
10.8	y = -0.2315x-0.0604	0.9979	20	y = -0.1064x-0.1942	0.9849
			30	y = -0.0653x-0.2087	0.9776

Table S3. Identified main TPs of BPA by ESI analysis.

| No.	Compound name	Tentative structure	Molecular weight (m/z)
P0	Bisphenol A		228
P1	4-(2-phenylpropan-2-yl)phenol		212
P2	(4-hydroxyphenyl)(phenyl)methanone		198
P3	propane-2,2-diyldibenzene		196
P4	2,2-diphenylethen-1-one		194
P5	4-(2-(4-hydroxyphenyl)propan-2-yl)benzene-1,2-diol		244
P6	4-(2-(4-hydroxyphenyl)propan-2-yl)cyclohexa-3,5-diene-1,2-dione		242
P7	(2E,4Z)-3-(2-(4-hydroxyphenyl)propan-2-yl)hexa-2,4-dienedioic acid		276
P8	[1,1'-biphenyl]-3,3',4,4'-tetraol		218
P9	[1,1'-biphenyl]-3,3',4,4',5-pentaol		234
P10	4-(prop-1-en-2-yl) phenol		134
P11	2-(4-hydroxypheny)-propanol-2-ol		152
P12	hex-1-en-3-ol		100
P13	hexa-1,5-dien-3-ol		98
P14	hexa-1,5-diene-3,4-diol		114
P15	succinic acid		118
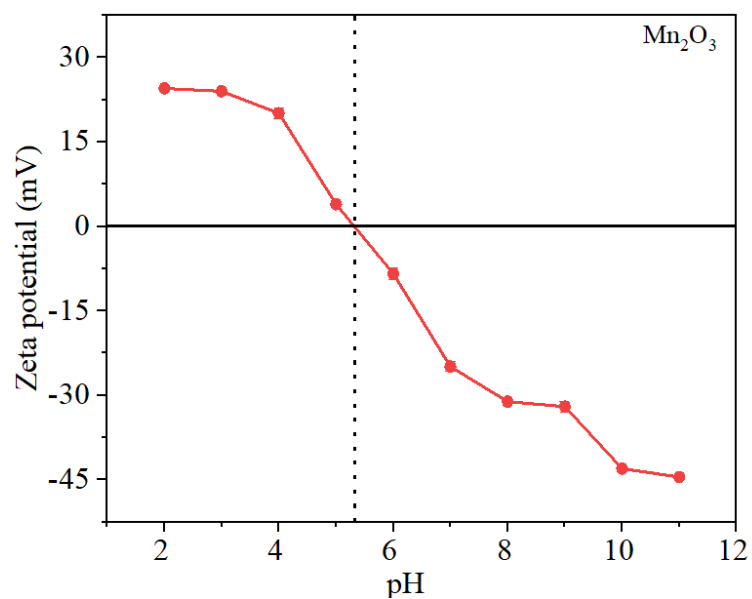
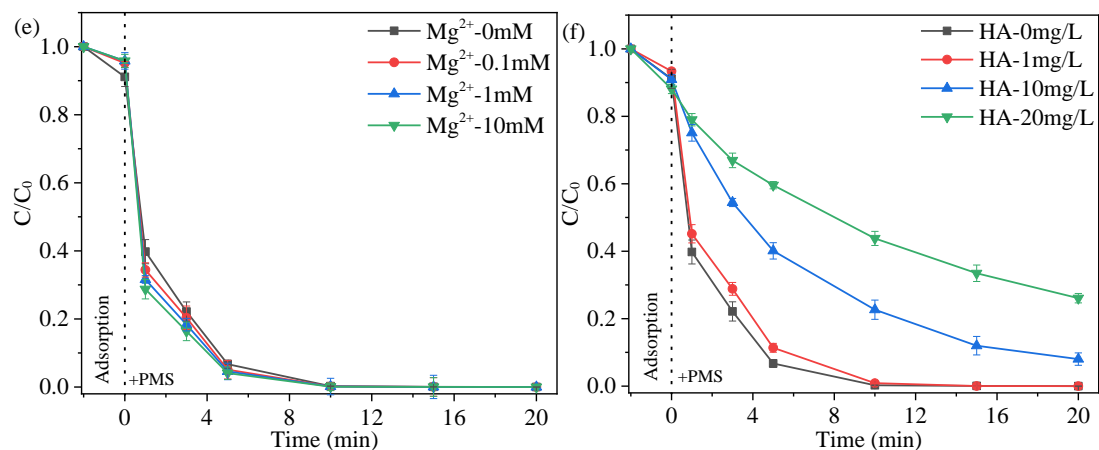**Fig. S1.** Zeta potential vs. pH curve of Mn_2O_3.
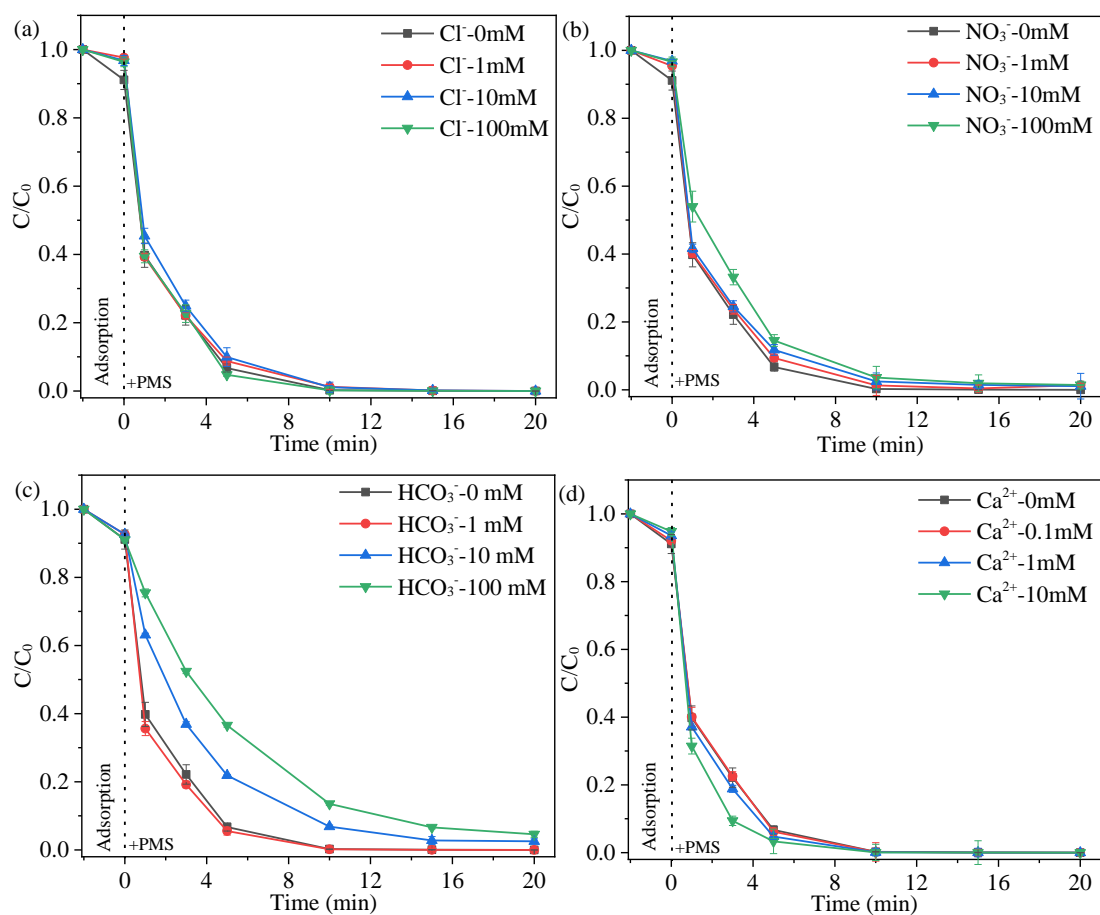
Fig. S2. Effects of (a) Cl^-, (b) NO_3^-, (c) HCO_3^-, (d) Ca^{2+}, (e) Mg^{2+} and (f) HA on BPA removal efficiency. Reaction condition: $[BPA]_0 = 10$ mg/L, $[PMS]_0 = 0.10$ mM, $[Mn_2O_3]_0 = 0.2$ g/L, initial pH = 7.0±0.2.
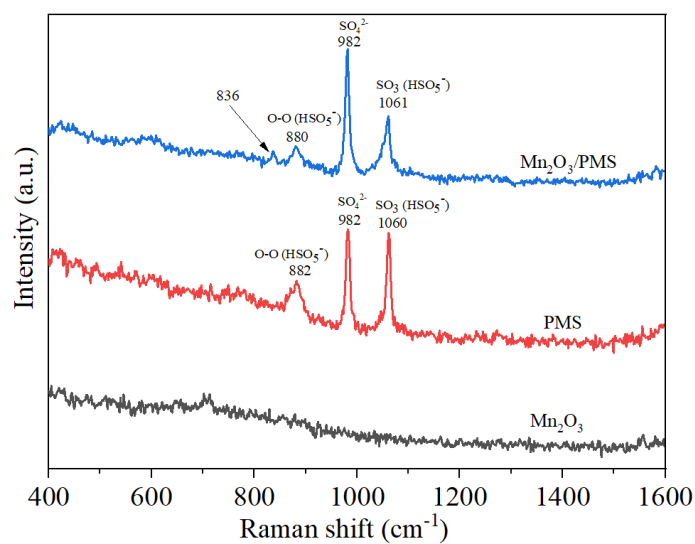

Fig. S3. *In-situ* Raman spectra of PMS, the commercial Mn_2O_3 and bulk Mn_2O_3/PMS.
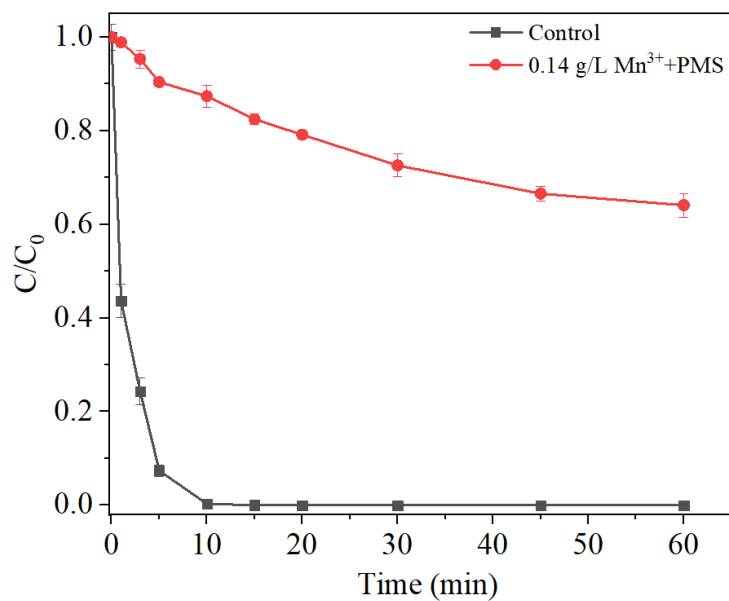
Fig. S4. Homogeneous and heterogeneous catalysis in the degradation of BPA.
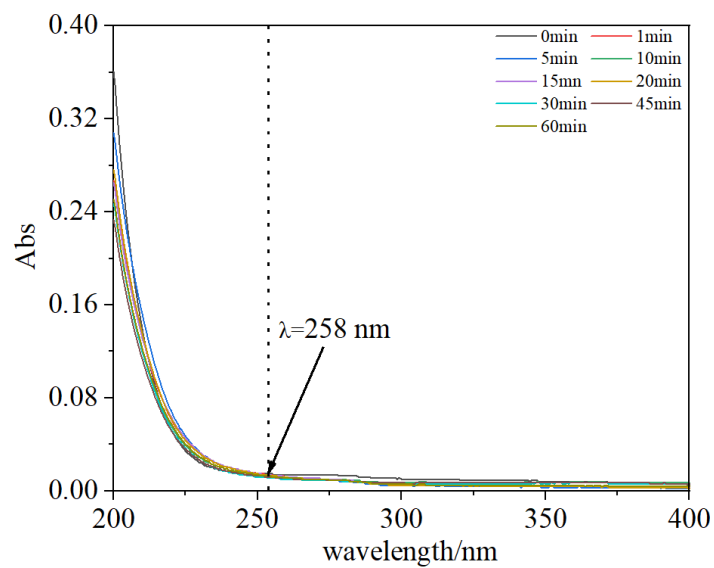

Fig. S5. UV-Vis spectra for Mn^{3+}-PP in the reaction solution of the Mn_2O_3/PMS.
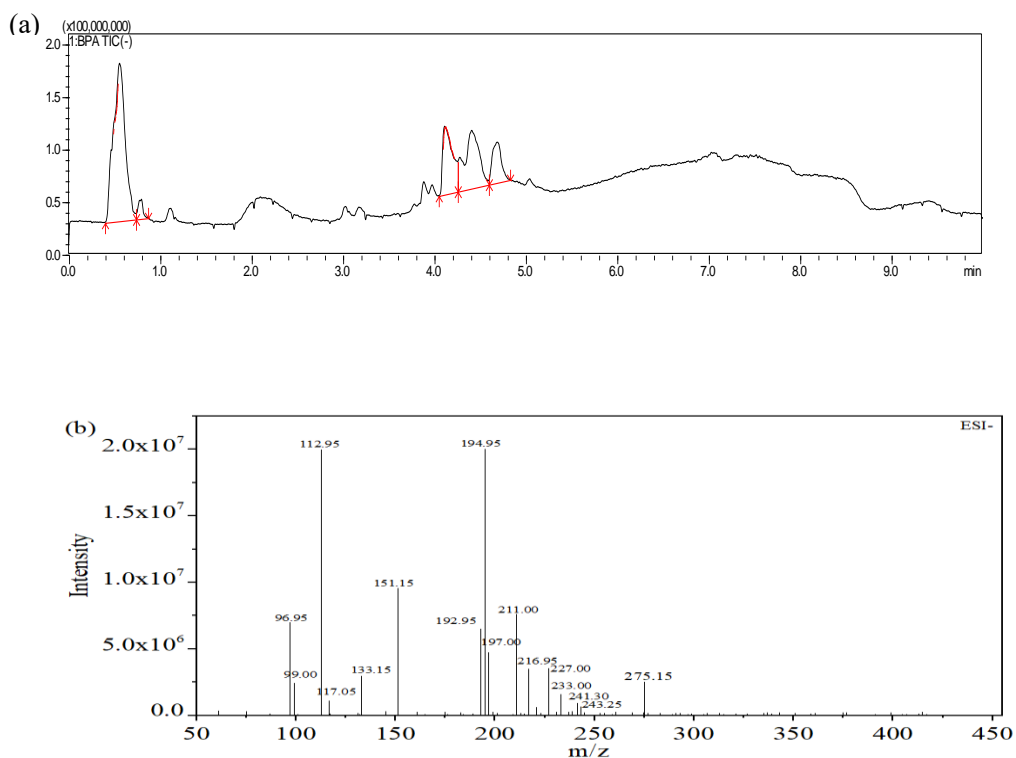
Fig. S6. The total ion current (TIC) chromatogram of TPs and BPA (a); mass spectra of the TPs of BPA detected in our study (b).
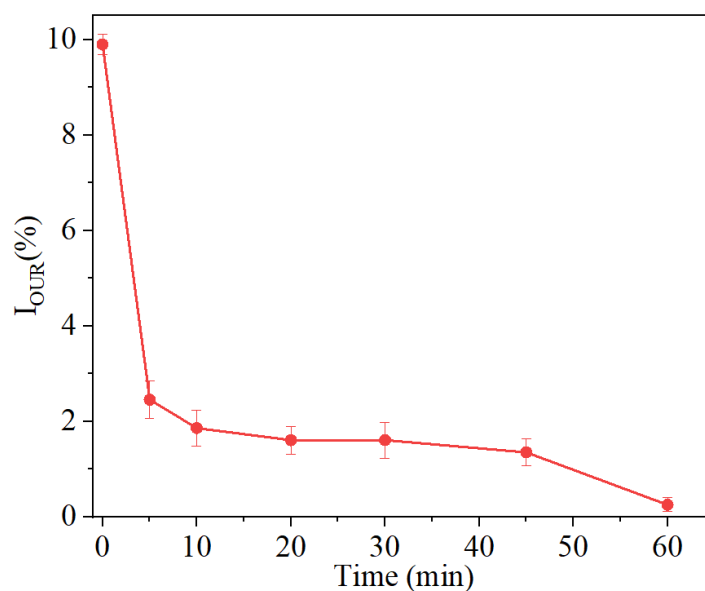

Fig. S7. Changes in toxicity with reaction time in the Mn_2O_3/PMS system. Reaction condition: $[BPA]_0 = 10$ mg/L, $[PMS]_0 = 0.10$ mM, $[Mn_2O_3]_0 = 0.2$ g/L, initial pH = 7.00. I_{OUR} is the inhibition rate calculated by the formula as below:

$$OUR(mg/L \cdot h) = (DO_0 - DO_t)/t$$

$$I_{OUR}(\%) = \frac{OUR_b - OUR_s}{OUR_b} \times 100$$

where OUR is the oxygen uptake rate (mg/(L•h)), and DO_0 and Do_s are the concentrations of dissolved oxygen in the slurry at 0 min and t min. Moreover, the OUR_S are the OUR in the reaction samples, and the OUR_b stands for the OUR in the blank sample. I_{OUR} is the inhibition rate as expressed as a percentage.
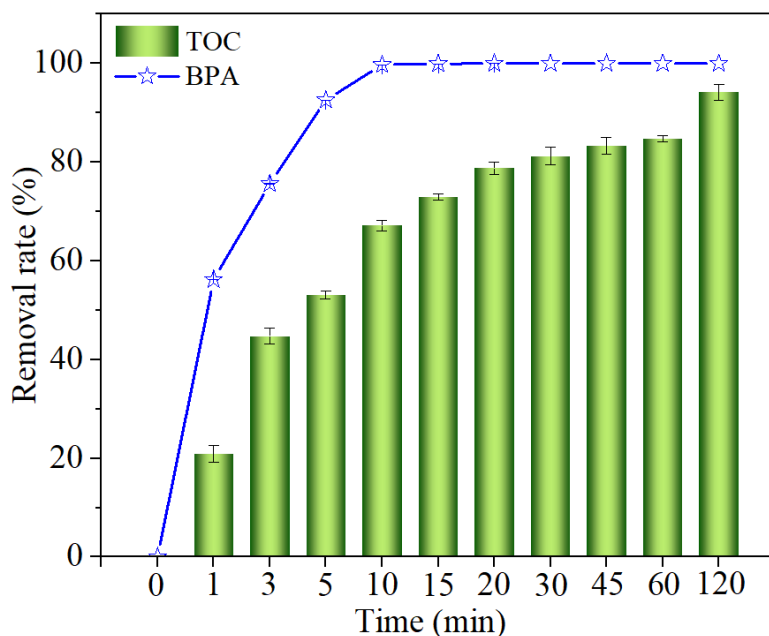

Fig. S8. TOC removal of BPA by Mn_2O_3/PMS system. Reaction condition: $[BPA]_0 = 10$ mg/L, $[PMS]_0 = 0.10$ mM, $[Mn_2O_3]_0 = 0.2$ g/L, initial pH = 7.00.
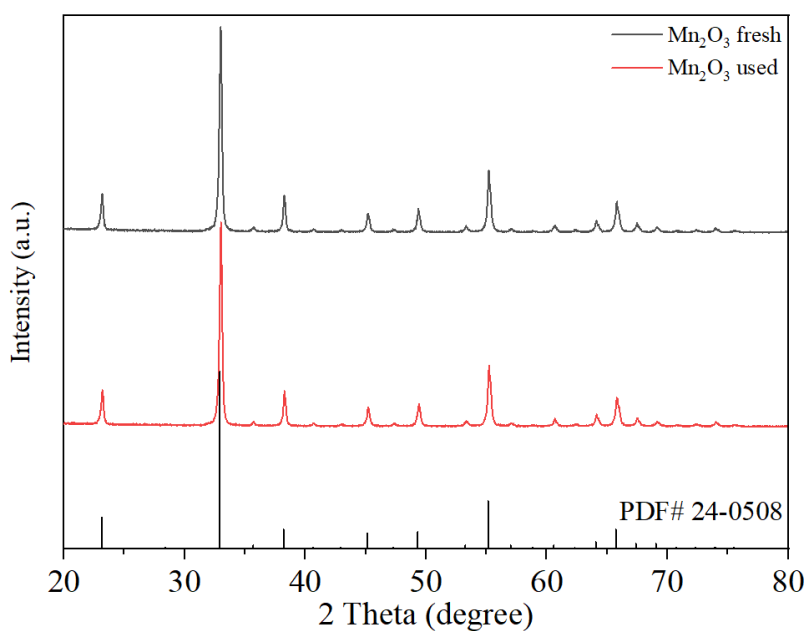

Fig. S9. XRD spectrum of the fresh and used commercial Mn_2O_3.