

## Supplementary Material

### **Facile and scalable synthesis of $\text{Ti}_6\text{Mn}_2$ oxo-cluster nanocrystals with flower-like morphology and excellent photocatalytic property**

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**Table S1.** Crystallographic data summary for **ST-Tb**, **ST-Mn** and **ST-Zn**.

	<b>ST-Tb</b>	<b>ST-Mn</b>	<b>ST-Zn</b>
CCDC number	1941080	1941081	1941082
Crystal Formula	C <sub>78</sub> H <sub>94</sub> O <sub>36</sub> Cl <sub>2</sub> P <sub>2</sub> Ti <sub>3</sub> Tb <sub>2</sub>	C <sub>33</sub> H <sub>33</sub> O <sub>17</sub> PTi <sub>3</sub> Mn	C <sub>66</sub> H <sub>70</sub> O <sub>36</sub> P <sub>2</sub> Ti <sub>6</sub> Zn <sub>2</sub>
Formula weight	2345.46	931.20	1919.16
crystal system	triclinic	monoclinic	tetragonal
space group	P-1	P 21/n	I 41/a
<i>a</i> [Å]	13.6150(14)	12.454(5)	31.7219(12)
<i>b</i> [Å]	13.6873(13)	22.161(8)	31.7219(12)
<i>c</i> [Å]	14.1064(17)	14.561(6)	15.9319(7)
$\alpha$ [°]	74.228(3)	90(6)	90
$\beta$ [°]	84.884(4)	104.660(10)	90
$\gamma$ [°]	62.691(3)	90(4)	90
V [Å <sup>3</sup> ]	2245.9(4)	3888(3)	16031.9(14)
Z	1	4	8
T[K]	293(2)	293(2)	293(2)
$\mu$ [mm <sup>-1</sup> ]	2.238	1.025	1.281
reflns coll.	23395	45697	62659
unique reflns	10222	15150	9161
GOF	1.090	1.346	1.171
$RI[I > 2\sigma(I)]^{[a]}$	0.0285	0.0703	0.0734
$wR2[I > 2\sigma(I)]^{[b]}$	0.0698	0.1679	0.2005

[a]  $RI = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ . [b]  $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ .

**Table S2.** Selected Bond Lengths (Å) and Angles (°) for **ST-Mn**.

Mn1-O1	2.204(6)	Mn1-O2	2.147(5)
Mn1-O5	2.275(5)	Mn1-O6	2.463(4)
Mn1-O15 <sup>1</sup>	2.255(4)	Mn1-O16 <sup>1</sup>	2.387(4)
Ti1-O3	2.096(4)	Ti1-O4	1.870(4)
Ti1-O9	1.947(4)	Ti1-O10	2.052(4)
Ti1-O13 <sup>1</sup>	1.956(4)	Ti1-O14	1.817(4)
Ti2-O6	2.045(4)	Ti2-O7	1.877(4)
Ti2-O8	1.970(4)	Ti2-O9	1.921(4)
Ti2-O10	1.966(4)	Ti2-O11	1.895(4)
Ti3-O8 <sup>1</sup>	2.053(4)	Ti3-O9 <sup>1</sup>	1.960(4)
Ti3-O12	1.966(4)	Ti3-O14	1.794(4)
Ti3-O16	2.157(4)	Ti3-O17	1.855(4)

O1-Mn1-O5	150.31(18)	O1-Mn1-O6	154.44(18)
O1-Mn1-O15 <sup>1</sup>	80.26(19)	O1-Mn1-O16 <sup>1</sup>	86.63(19)
O2-Mn1-O1	89.0(2)	O2-Mn1-O5	95.7(2)
O2-Mn1-O6	96.0(2)	O2-Mn1-O15 <sup>1</sup>	160.15(18)
O2-Mn1-O16 <sup>1</sup>	140.42(16)	O5-Mn1-O6	54.19(14)
O5-Mn1-O16 <sup>1</sup>	140.42(16)	O15 <sup>1</sup> -Mn1-O5	85.92(18)
O15 <sup>1</sup> -Mn1-O6	100.90(15)	O15 <sup>1</sup> -Mn1-O16 <sup>1</sup>	56.08(13)
O16 <sup>1</sup> -Mn1-O6	73.58(14)		
O4-Ti1-O3	83.40(16)	O4-Ti1-O9	160.12(16)
O4-Ti1-O10	92.03(17)	O4-Ti1-O13 <sup>1</sup>	101.45(17)
O9-Ti1-O3	81.54(15)	O9-Ti1-O10	74.43(15)
O9-Ti1-O13 <sup>1</sup>	90.13(16)	O10-Ti1-O3	87.42(16)
O14-Ti1-O3	178.88(18)	O14-Ti1-O4	96.19(17)
O14-Ti1-O9	99.10(16)	O14-Ti1-O10	93.64(16)
O14-Ti1-O13 <sup>1</sup>	90.13(16)	O13 <sup>1</sup> -Ti1-O3	85.09(17)
O13 <sup>1</sup> -Ti1-O10	163.69(16)		
O7-Ti2-O6	82.48(17)	O7-Ti2-O8	99.46(18)
O7-Ti2-O9	169.52(17)	O7-Ti2-O10	106.14(18)
O7-Ti2-O11	88.70(18)	O8-Ti2-O6	89.46(16)
O9-Ti2-O6	87.69(15)	O9-Ti2-O8	76.73(15)
O9-Ti2-O10	76.99(16)	O10-Ti2-O6	87.89(16)
O10-Ti2-O8	153.68(16)	O11-Ti2-O6	170.92(17)
O11-Ti2-O8	94.18(18)	O11-Ti2-O9	101.24(16)
O11-Ti2-O10	92.47(17)		
O8 <sup>1</sup> -Ti3-O16	85.42(16)	O9 <sup>1</sup> -Ti3-O8 <sup>1</sup>	73.98(15)
O9 <sup>1</sup> -Ti3-O12	88.54(16)	O9 <sup>1</sup> -Ti3-O16	83.87(14)
O12-Ti3-O8 <sup>1</sup>	161.50(17)	O12-Ti3-O16	86.75(16)
O14-Ti3-O8 <sup>1</sup>	93.09(17)	O14-Ti3-O9 <sup>1</sup>	98.66(16)
O14-Ti3-O12	95.55(17)	O14-Ti3-O16	176.61(17)
O14-Ti3-O17	95.26(17)	O17-Ti3-O8 <sup>1</sup>	96.28(17)
O17-Ti3-O9 <sup>1</sup>	163.36(16)	O17-Ti3-O16	81.90(16)

<sup>1</sup>1-X,1-Y,1-Z

**Table S3.** Selected Bond Lengths (Å) and Angles (°) for **ST-Zn**.

Zn1-O1	2.050(4)	Zn1-O2	2.171(4)
Zn1-O3	1.993(4)	Zn1-O131	2.118(4)
Zn1-O161	2.038(4)		
Ti1-O4	2.076(3)	Ti1-O5	1.878(3)

Ti1-O7	1.967(3)	Ti1-O9	1.817(3)
Ti1-O101	1.945(3)	Ti1-O111	2.045(3)
Ti2-O8	1.905(3)	Ti2-O10	1.929(3)
Ti2-O11	1.966(3)	Ti2-O12	1.979(3)
Ti2-O14	2.020(3)	Ti2-O15	1.876(3)
Ti3-O61	1.959(3)	Ti3-O9	1.801(3)
Ti3-O10	101.945(3)	Ti3-O12	2.050(3)
Ti3-O17	2.102(3)	Ti3-O18	1.879(3)
O1-Zn1-O2	91.19(17)	O1-Zn1-O131	94.26(15)
O3-Zn1-O1	98.25(18)	O3-Zn1-O2	91.09(19)
O3-Zn1-O131	91.01(16)	O3-Zn1-O161	170.30(14)
O131-Zn1-O2	173.83(15)	O161-Zn1-O1	91.21(17)
O161-Zn1-O2	86.55(18)	O161-Zn1-O131	90.42(15)
O5-Ti1-O4	82.14(14)	O5-Ti1-O7	103.48(14)
O5-Ti1-O101	161.10(14)	O5-Ti1-O111	91.72(13)
O7-Ti1-O4	85.32(13)	O7-Ti1-O111	162.19(13)
O9-Ti1-O4	176.02(14)	O9-Ti1-O5	94.09(15)
O9-Ti1-O7	94.36(14)	O9-Ti1-O101	99.49(14)
O9-Ti1-O111	93.75(13)	O101-Ti1-O4	84.48(13)
O101-Ti1-O7	88.62(13)	O101-Ti1-O111	74.41(12)
O111-Ti1-O4	87.66(13)		
O8-Ti2-O10	99.01(13)	O8-Ti2-O11	93.26(14)
O8-Ti2-O12	91.03(14)	O8-Ti2-O14	170.52(14)
O10-Ti2-O11	76.58(13)	O10-Ti2-O12	77.62(13)
O10-Ti2-O14	90.38(13)	O11-Ti2-O12	154.19(13)
O11-Ti2-O14	90.23(13)	O12-Ti2-O14	89.64(13)
O15-Ti2-O8	87.72(14)	O15-Ti2-O10	173.23(14)
O15-Ti2-O11	102.39(14)	O15-Ti2-O12	103.21(14)
O15-Ti2-O14	82.92(13)		
O61-Ti3-O12	163.84(14)	O61-Ti3-O17	84.44(13)
O9-Ti3-O61	94.65(14)	O9-Ti3-O10	99.09(14)
O9-Ti3-O12	93.01(13)	O9-Ti3-O17	178.50(14)
O9-Ti3-O18	96.63(15)	O10-Ti3-O61	89.18(13)
O10-Ti3-O12	75.56(13)	O10-Ti3-O17	82.11(13)
O12-Ti3-O17	88.17(13)	O18-Ti3-O61	101.82(14)
O18-Ti3-O10	160.00(14)	O18-Ti3-O12	91.38(14)
O18-Ti3-O17	82.40(14)		

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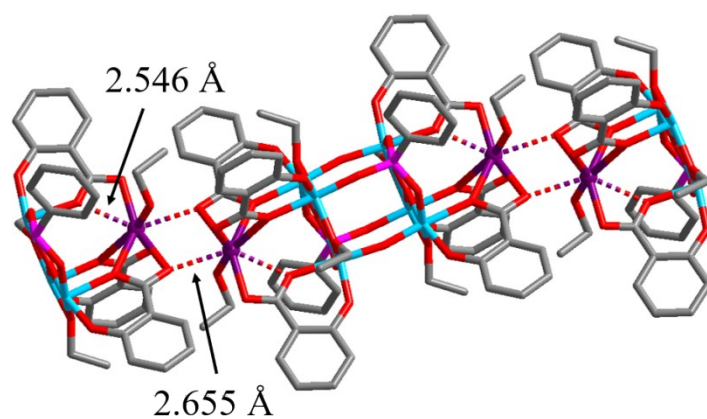
1-X,1-Y,1-Z

**Table S4.** Selected Bond Lengths (Å) and Angles (°) for **ST-Tb**.

Tb1-Cl1	2.6054(7)	Tb1-O1 <sup>1</sup>	2.386(2)
Tb1-O2 <sup>1</sup>	2.4820(17)	Tb1-O11	2.4680(19)
Tb1-O12	2.4963(17)	Tb1-O14	2.382(2)
Tb1-O15	2.4785(18)	Tb1-O17	2.366(2)
Ti1-O6	1.8846(18)	Ti1-O8	1.9710(18)
Ti1-O9	1.9792(18)	Ti1-O10	1.9045(17)
Ti1-O12	2.0892(18)	Ti1-O13	1.8682(18)
Ti2-O5 <sup>1</sup>	1.9573(18)	Ti2-O7	1.8102(18)
Ti2-O8	2.0500(18)	Ti2-O10	1.9549(18)
Ti2-O15	2.1548(18)	Ti2-O16	1.8564(18)
Ti3-O2	2.1463(18)	Ti3-O3	1.8454(19)
Ti3-O4	1.9755(18)	Ti3-O7	1.8064(18)
Ti3-O9 <sup>1</sup>	2.0599(18)	Ti3-O10 <sup>1</sup>	1.9658(18)
O1 <sup>1</sup> -Tb1-Cl1	89.83(6)	O1 <sup>1</sup> -Tb1-O2 <sup>1</sup>	53.27(6)
O1 <sup>1</sup> -Tb1-O11	80.61(7)	O1 <sup>1</sup> -Tb1-O12	94.02(7)
O1 <sup>1</sup> -Tb1-O15	145.35(6)	O2 <sup>1</sup> -Tb1-Cl1	86.84(4)
O2 <sup>1</sup> -Tb1-O12	72.45(6)	O11-Tb1-Cl1	156.96(5)
O11-Tb1-O2 <sup>1</sup>	103.58(6)	O11-Tb1-O12	51.91(6)
O11-Tb1-O15	112.66(6)	O12-Tb1-Cl1	150.51(5)
O14-Tb1-Cl1	98.32(6)	O14-Tb1-O1 <sup>1</sup>	160.52(7)
O14-Tb1-O2 <sup>1</sup>	144.36(6)	O14-Tb1-O11	85.20(7)
O14-Tb1-O12	87.57(7)	O14-Tb1-O15	53.34(6)
O6-Ti1-O8	92.55(8)	O6-Ti1-O9	91.17(8)
O6-Ti1-O10	100.82(8)	O6-Ti1-O12	173.85(7)
O8-Ti1-O9	155.81(8)	O8-Ti1-O12	89.59(8)
O9-Ti1-O12	89.22(8)	O10-Ti1-O8	77.94(7)
O10-Ti1-O9	77.88(7)	O10-Ti1-O12	85.26(7)
O13-Ti1-O6	92.21(8)	O13-Ti1-O8	103.65(8)
O13-Ti1-O9	100.08(8)	O13-Ti1-O10	166.82(8)
O13-Ti1-O12	81.69(7)		
O5 <sup>1</sup> -Ti2-O8	162.26(8)	O5 <sup>1</sup> -Ti2-O15	86.53(7)
O7-Ti2-O5 <sup>1</sup>	95.58(8)	O7-Ti2-O8	93.65(8)
O7-Ti2-O10	99.08(8)	O7-Ti2-O15	177.89(8)
O7-Ti2-O16	97.52(8)	O8-Ti2-O15	84.33(7)
O10-Ti2-O5 <sup>1</sup>	88.63(7)	O10-Ti2-O8	74.95(7)
O10-Ti2-O15	81.00(7)	O16-Ti2-O5 <sup>1</sup>	100.86(8)
O16-Ti2-O8	92.89(8)	O16-Ti2-O10	159.96(8)

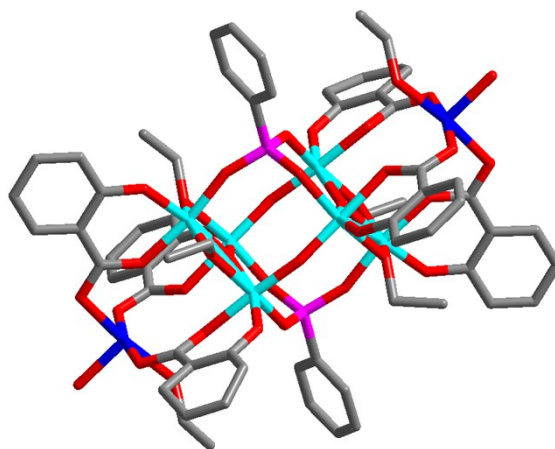
O16-Ti2-O15	82.00(8)	O3-Ti3-O2	81.75(8)
O3-Ti3-O4	100.02(8)	O3-Ti3-O9 <sup>1</sup>	94.77(8)
O3-Ti3-O10 <sup>1</sup>	160.16(8)	O4-Ti3-O2	86.14(7)
O4-Ti3-O9 <sup>1</sup>	161.91(7)	O7-Ti3-O2	178.79(8)
O7-Ti3-O3	98.84(8)	O7-Ti3-O4	94.79(8)
O7-Ti3-O9 <sup>1</sup>	93.17(8)	O7-Ti3-O10 <sup>1</sup>	98.46(8)
O9 <sup>1</sup> -Ti3-O2	85.72(7)	O10 <sup>1</sup> -Ti3-O2	80.79(7)
O10 <sup>1</sup> -Ti3-O4	88.12(7)	O10 <sup>1</sup> -Ti3-O9 <sup>1</sup>	74.63(7)

<sup>1</sup>1-X,-Y,1-Z

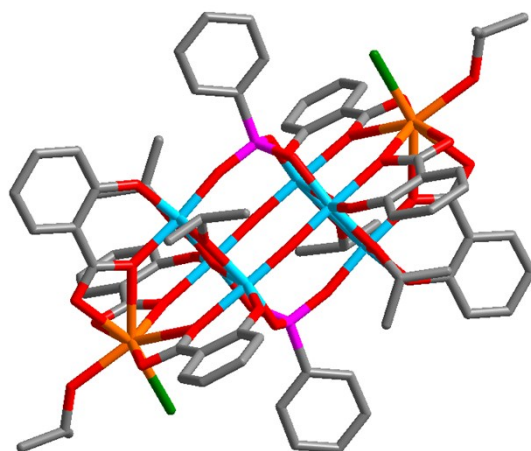


**Figure S1.** Structure of **ST-Mn** and the weak interactions between adjacent clusters

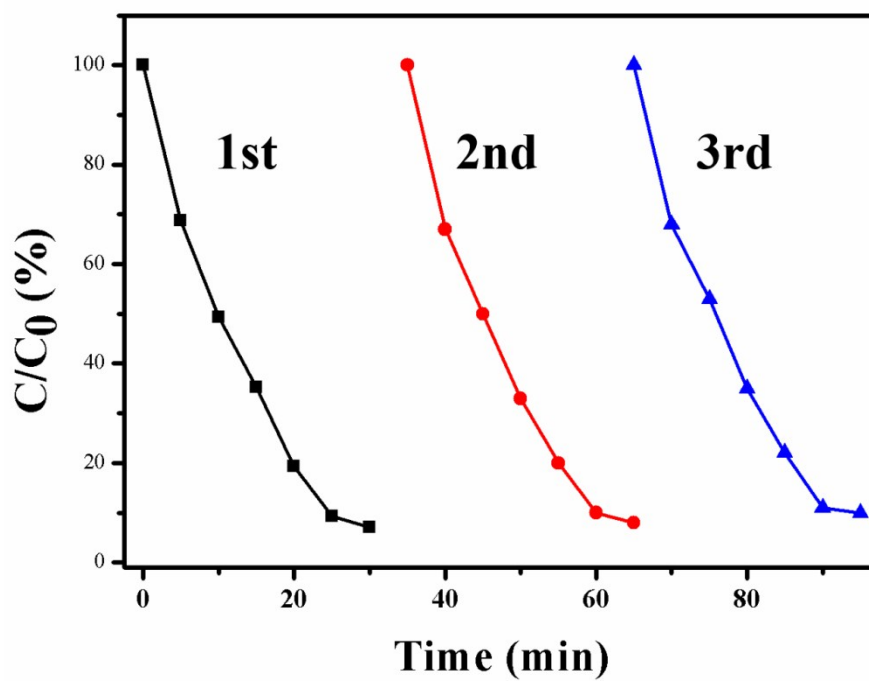
(H atoms are omitted for clarity).



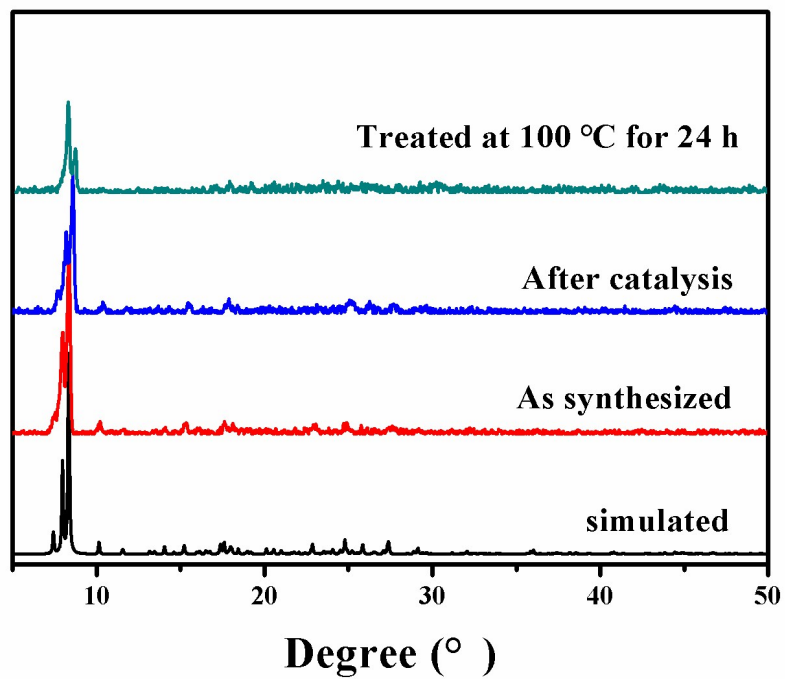
**Figure S2.** Structure of **ST-Zn** (H atoms are omitted for clarity).



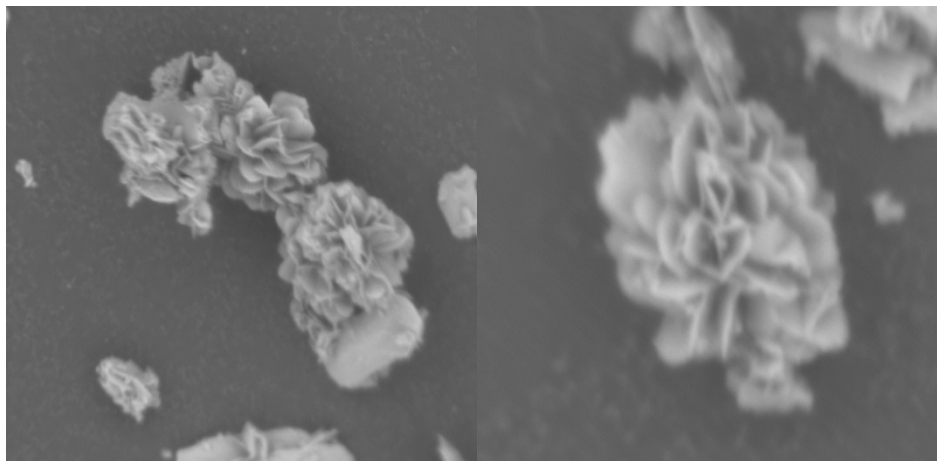
**Figure S3.** Structure of ST-Tb (H atoms are omitted for clarity).



**Figure S4.** The recycling experiments of FST-Mn

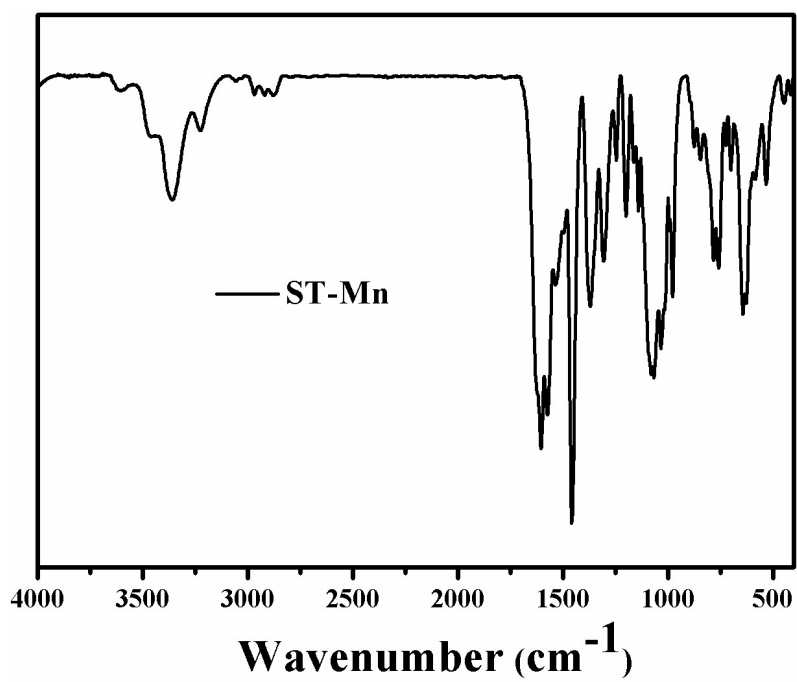


**Figure S5.** PXRD patterns of simulated, as synthesized, used and treated samples at 100 °C for 24 h of **FST-Mn**.

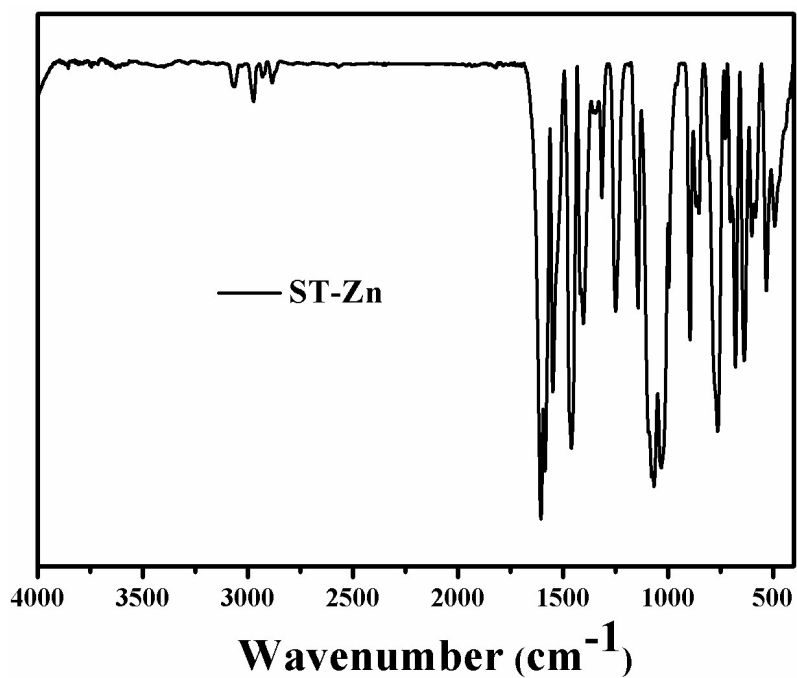


**Figure S6.** The SEM images of used samples of **FST-Mn**.

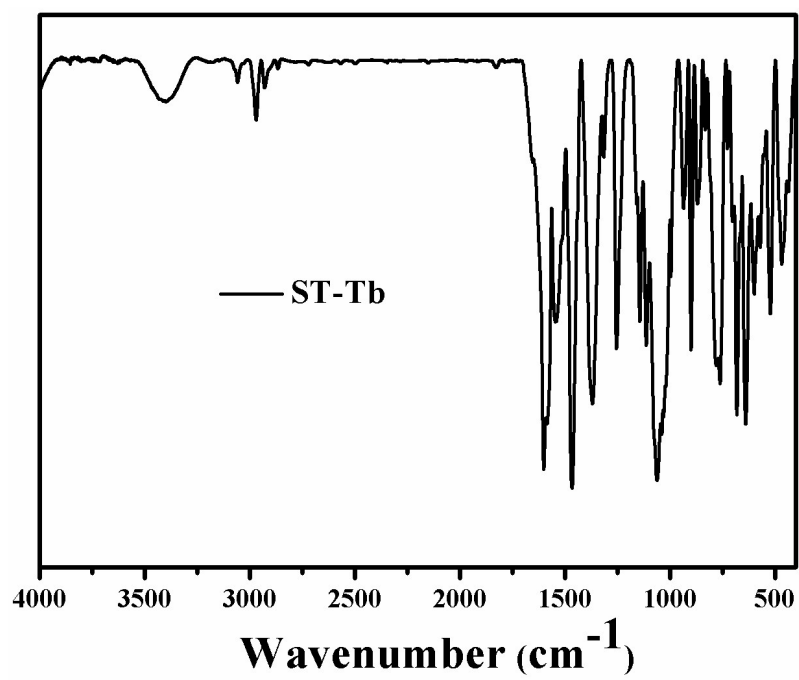




**Figure S7.** FT-IR spectra of ST-Mn.



**Figure S8.** FT-IR spectra of ST-Zn.



**Figure S9.** FT-IR spectra of ST-Tb.