Electronic Supplementary Information (ESI)

Nano-sized layered aluminium or zinc-manganese oxides as efficient and biomimetic water oxidizing catalysts†‡

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Material and methods

All reagents and solvents were purchased from commercial sources and were used without further purification. TEM and SEM were carried out with Philips CM120 and LEO 1430VP, respectively. The X-ray powder patterns were recorded with a Bruker, D8 ADVANCE (Germany) diffractometer (Cu-Kα radiation). Manganese atomic absorption spectroscopy (AAS) was performed on an Atomic Absorbtion Spectrometer Varian Spectr AA 110. Prior to analysis, the oxide (10.0 mg metal) were added to 1 mL of concentrated nitric acid and H_2O_2, left at room temperature for at least 1 h to ensure that the oxides were completely dissolved. The solutions were then diluted to 25.0 mL and analyzed by AAS.

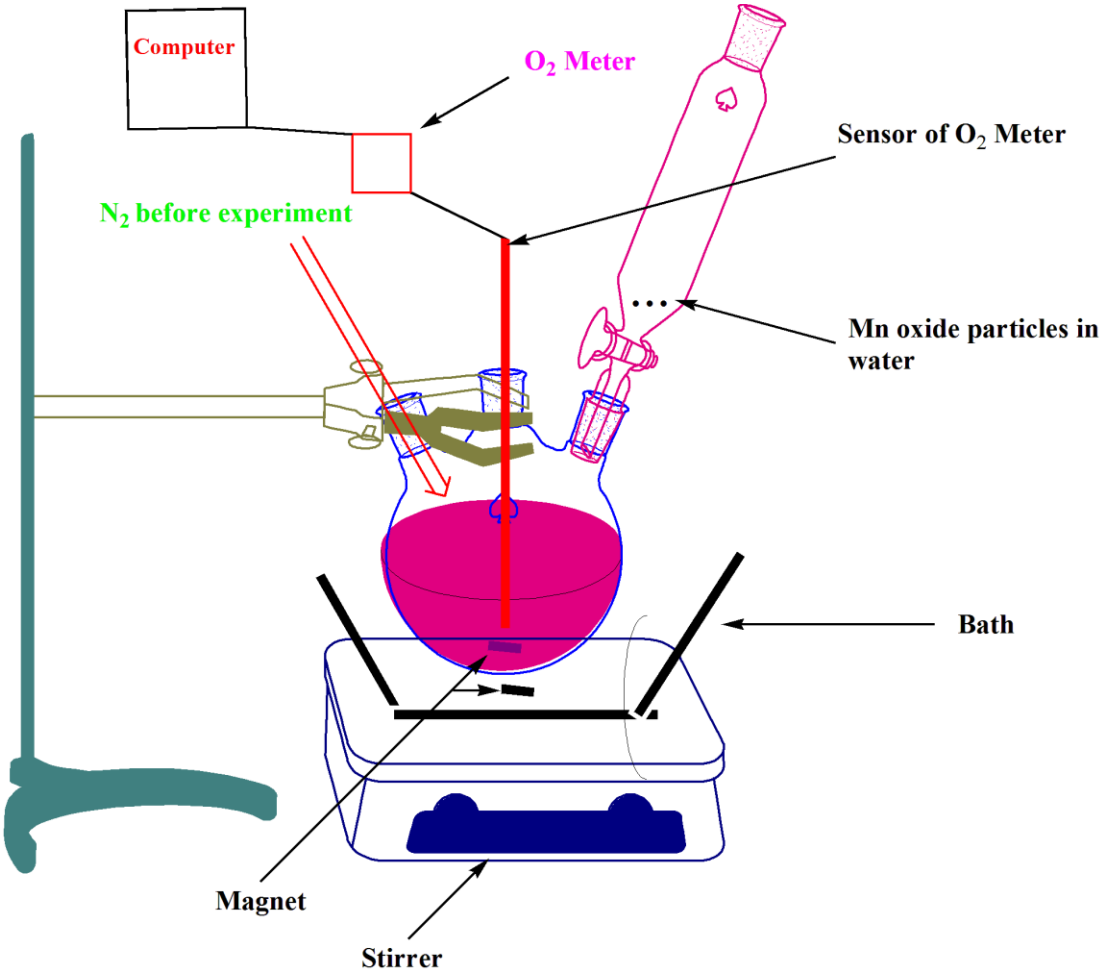
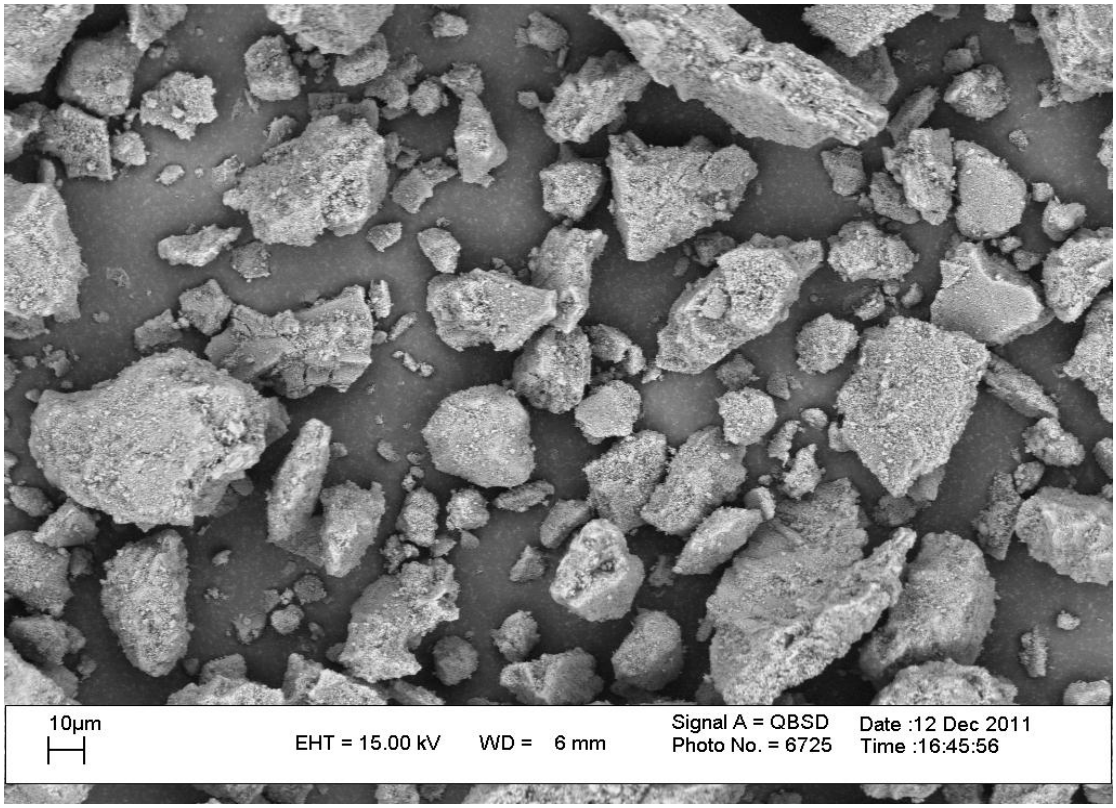


Fig. S1. The reactor set-up for oxygen evolution experiment in the presence of Ce(IV).



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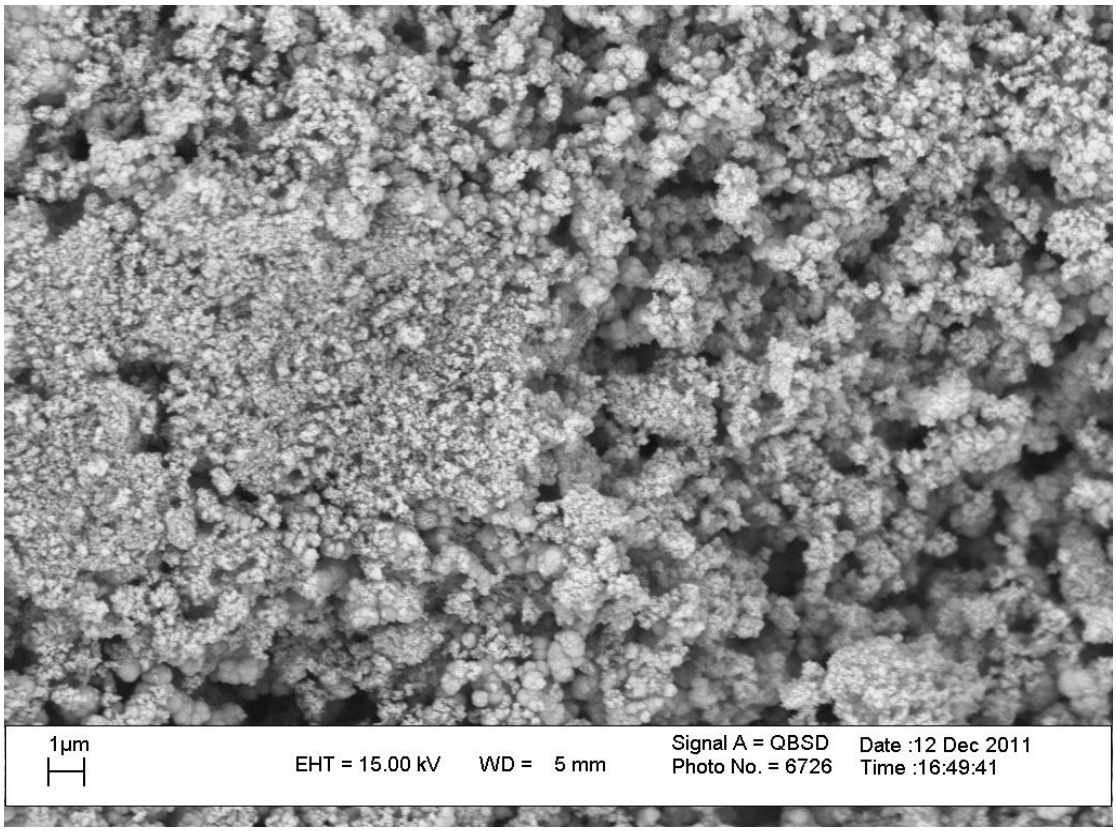

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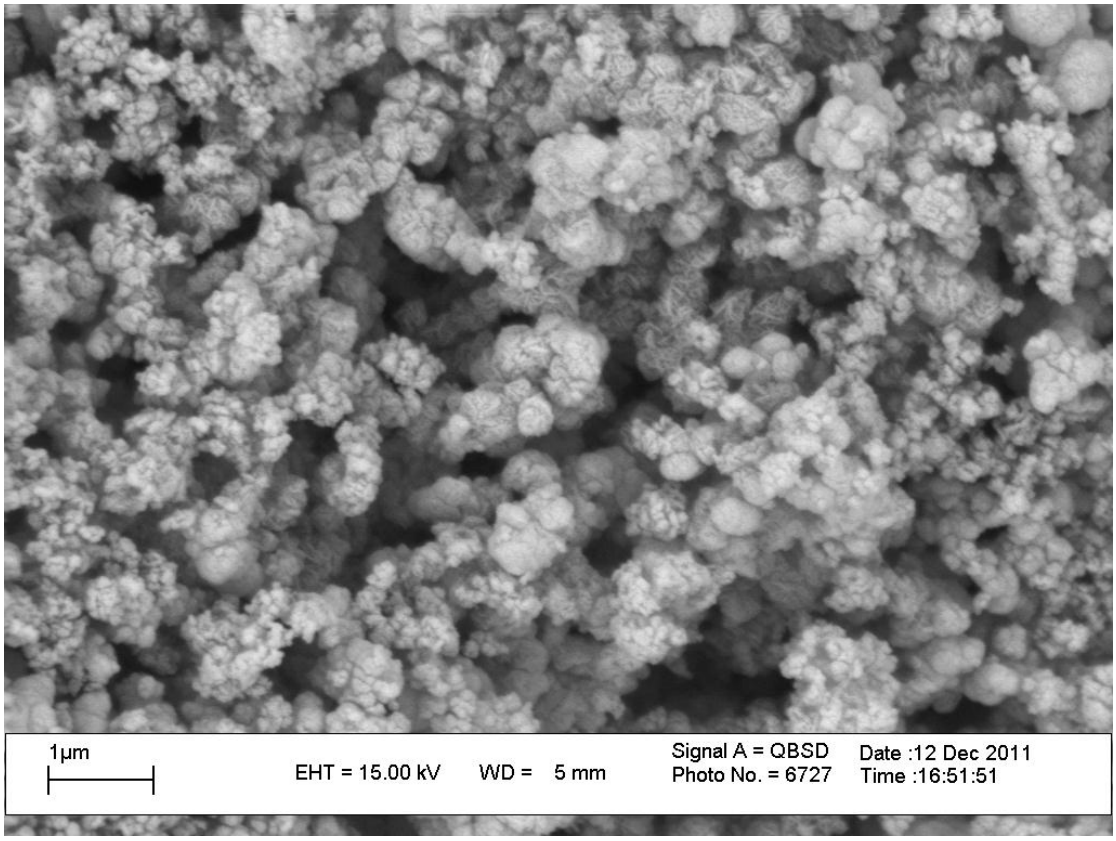

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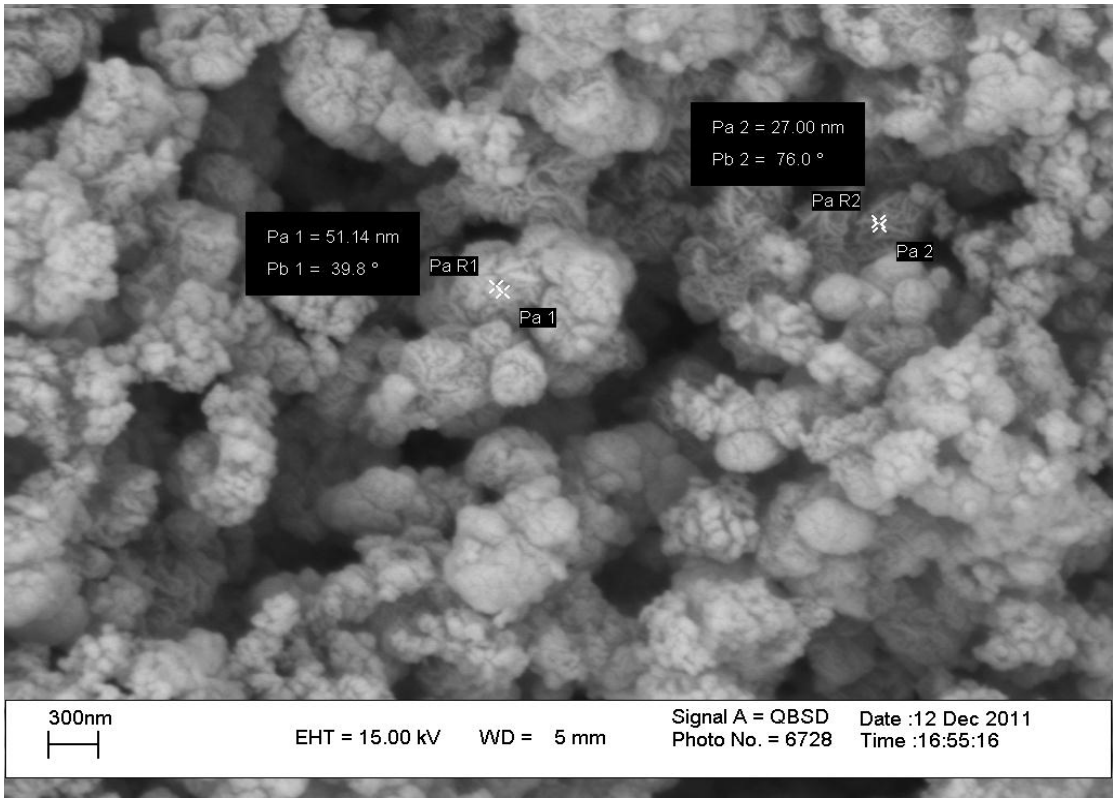

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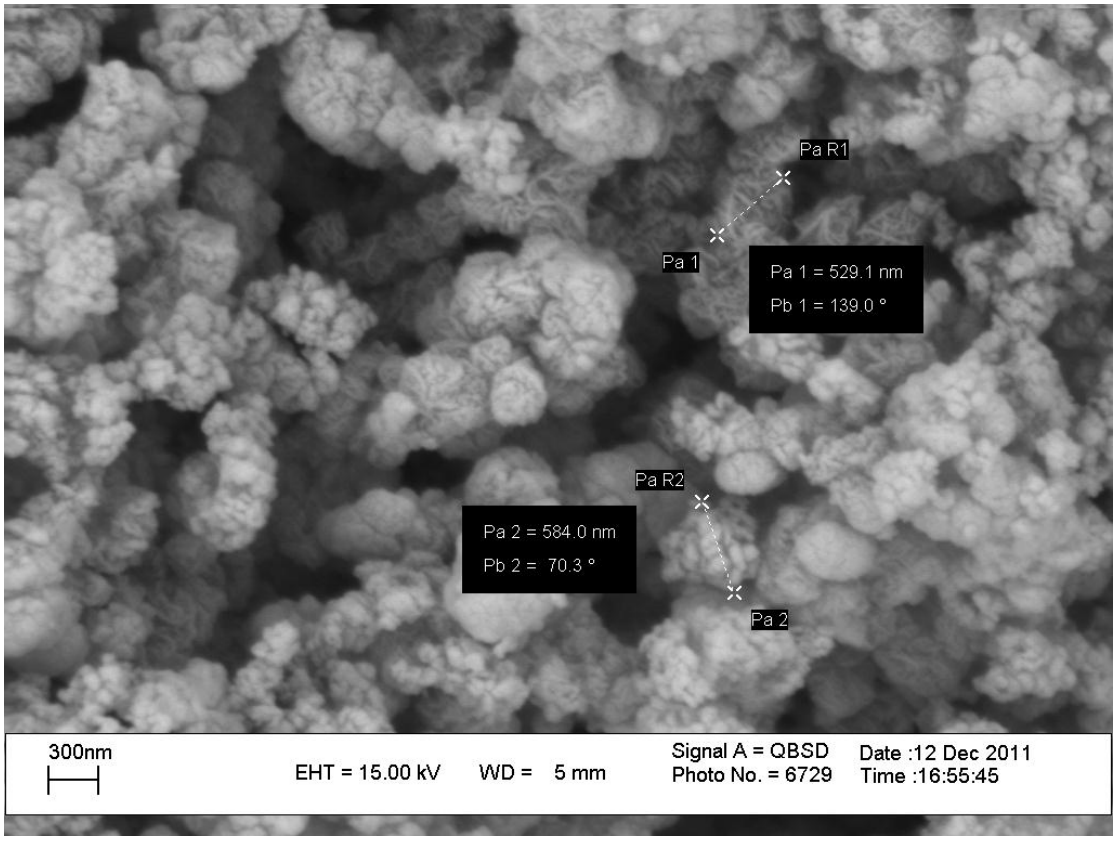
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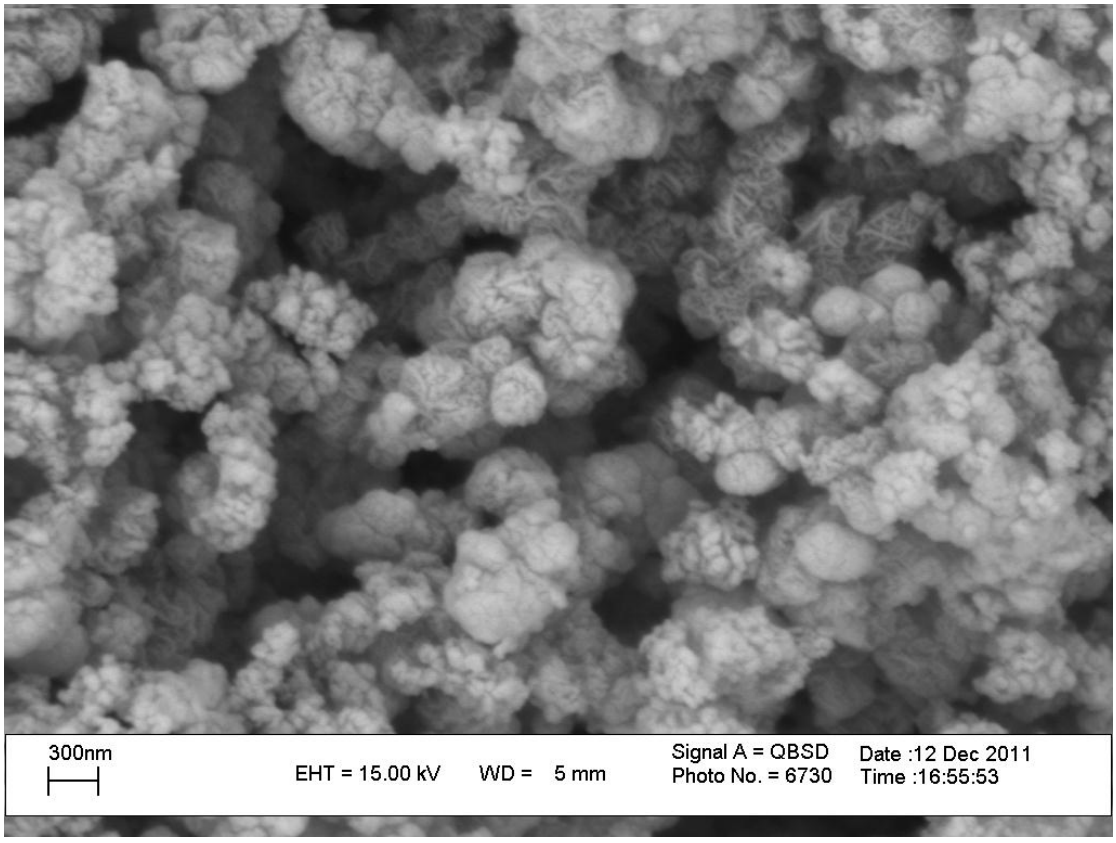
(e)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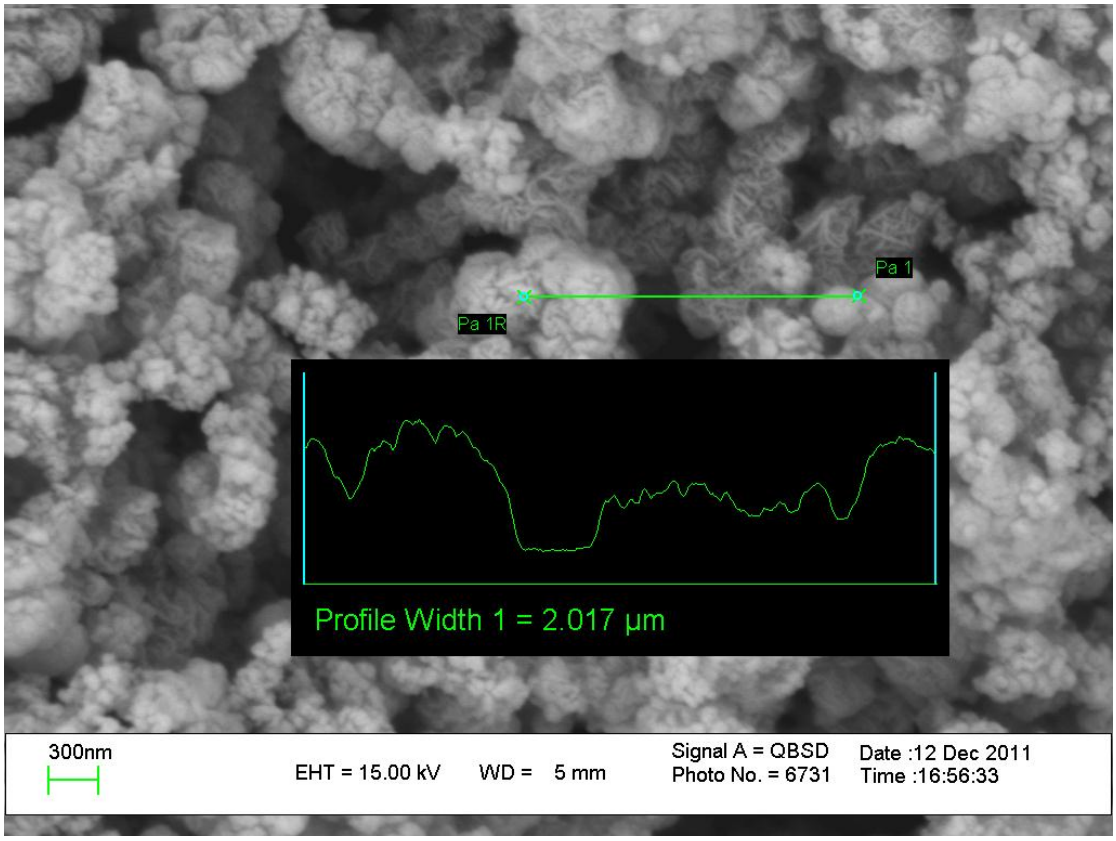
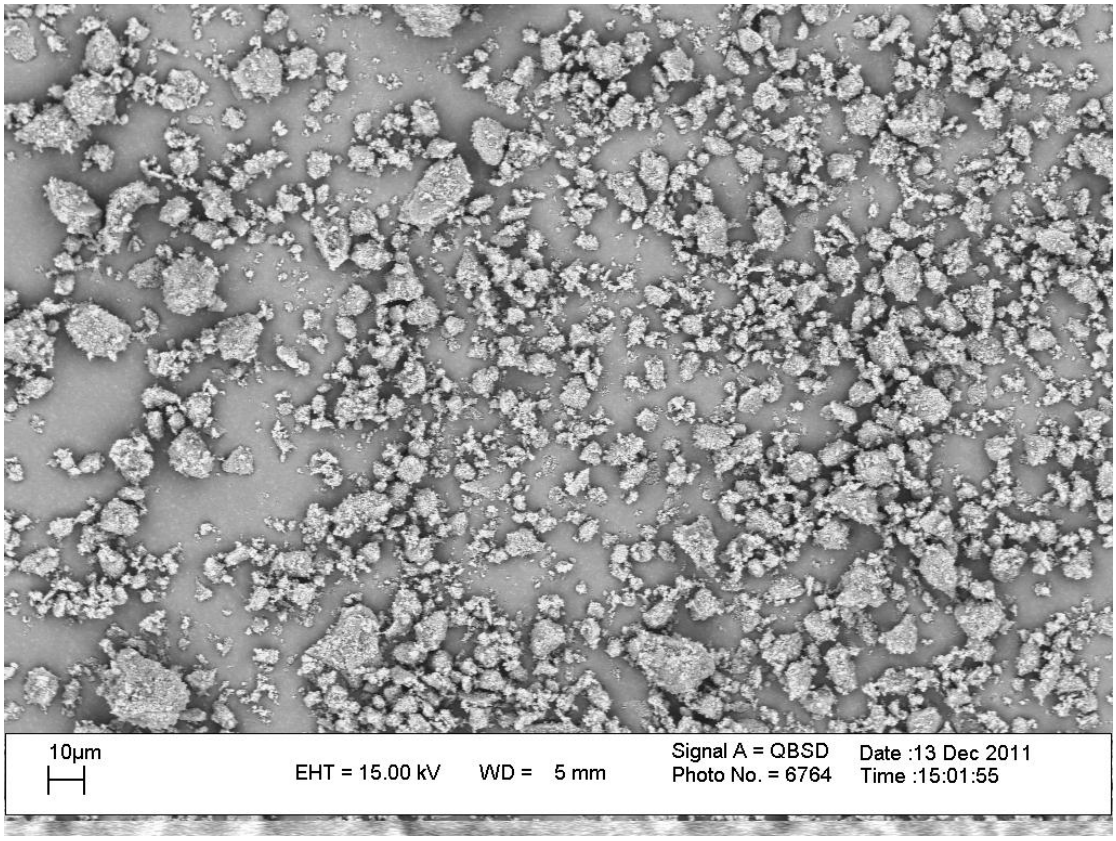
(f)



(g)

Fig. S2 SEM images of zinc - manganese oxides prepared at 100 ^{o}C (a-g).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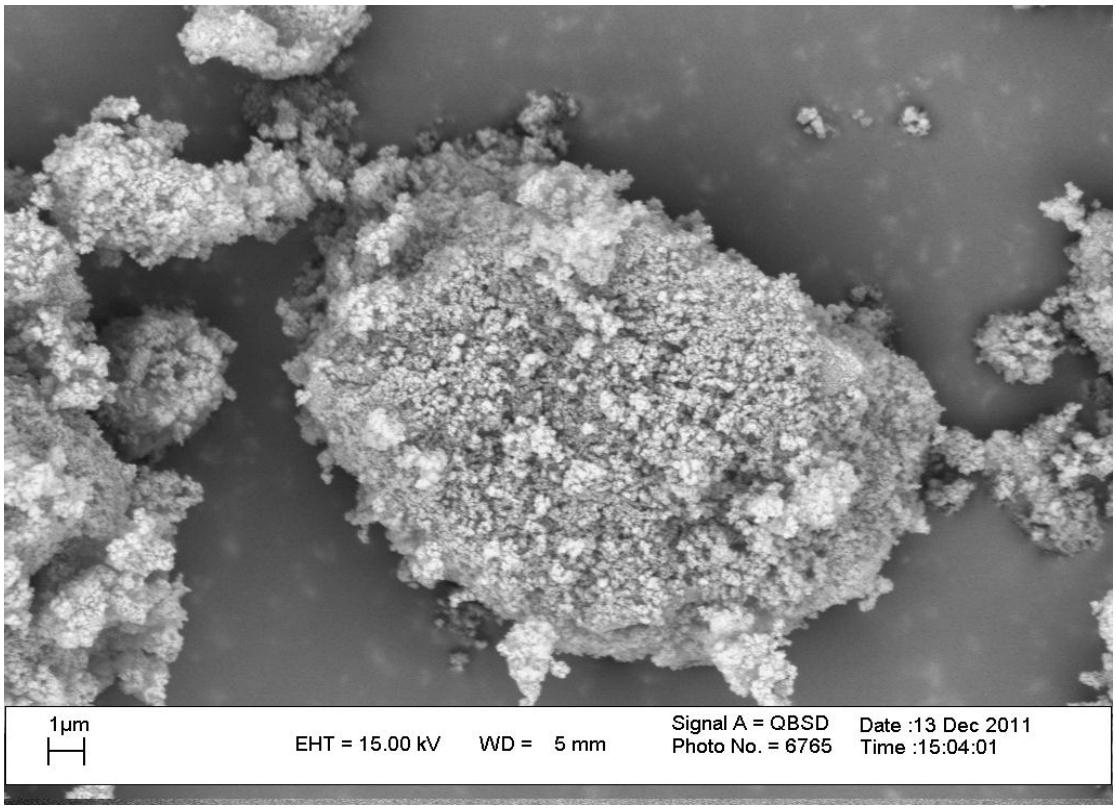
(a)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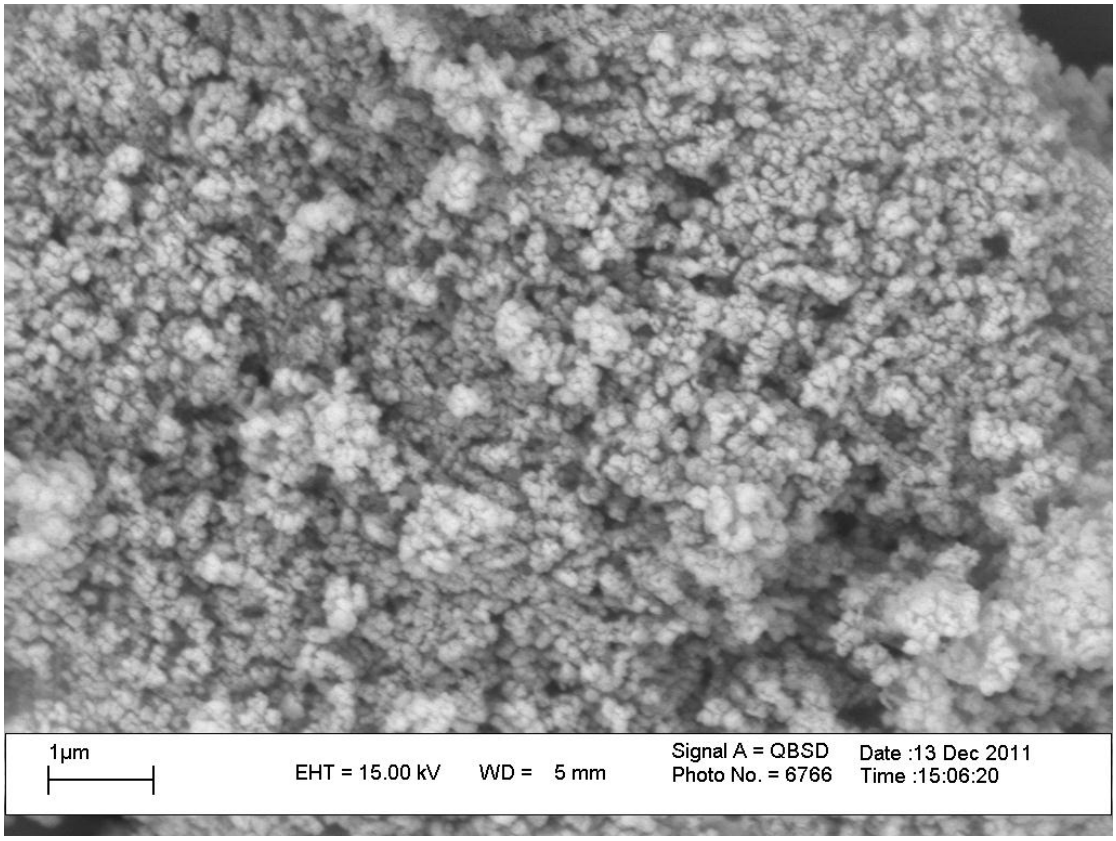
(b)



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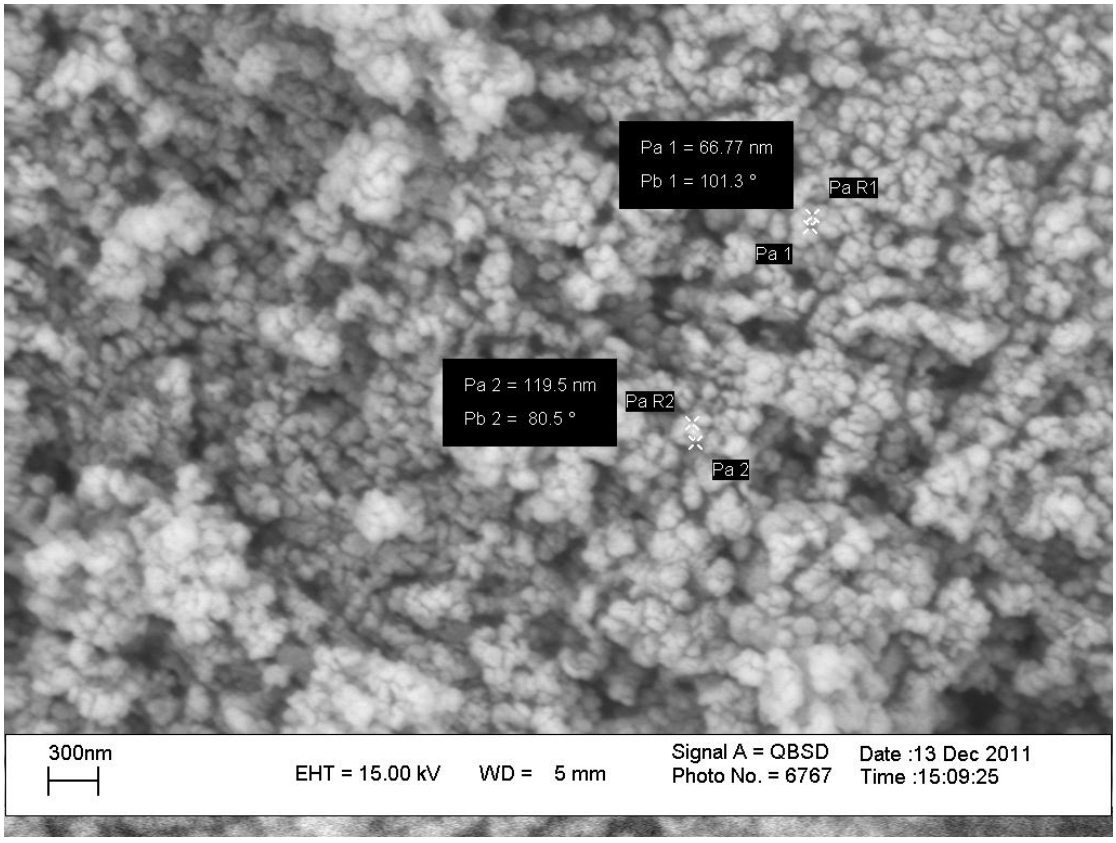

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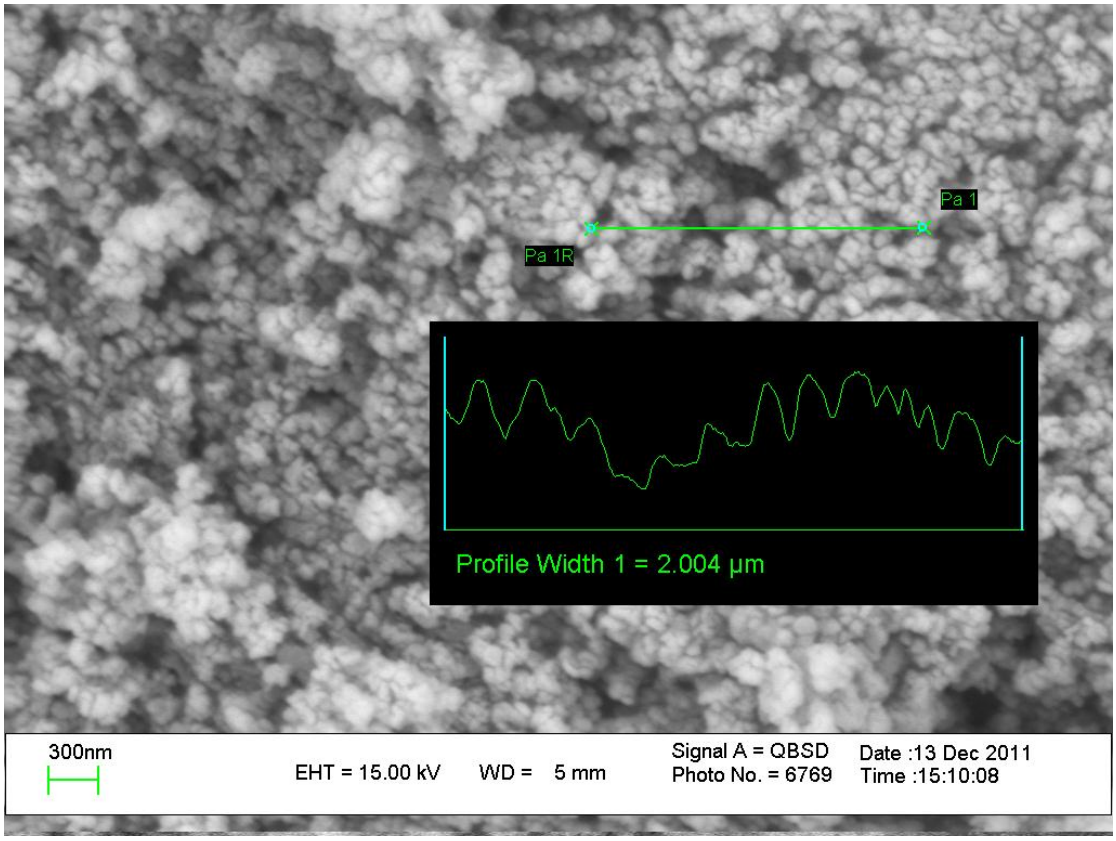

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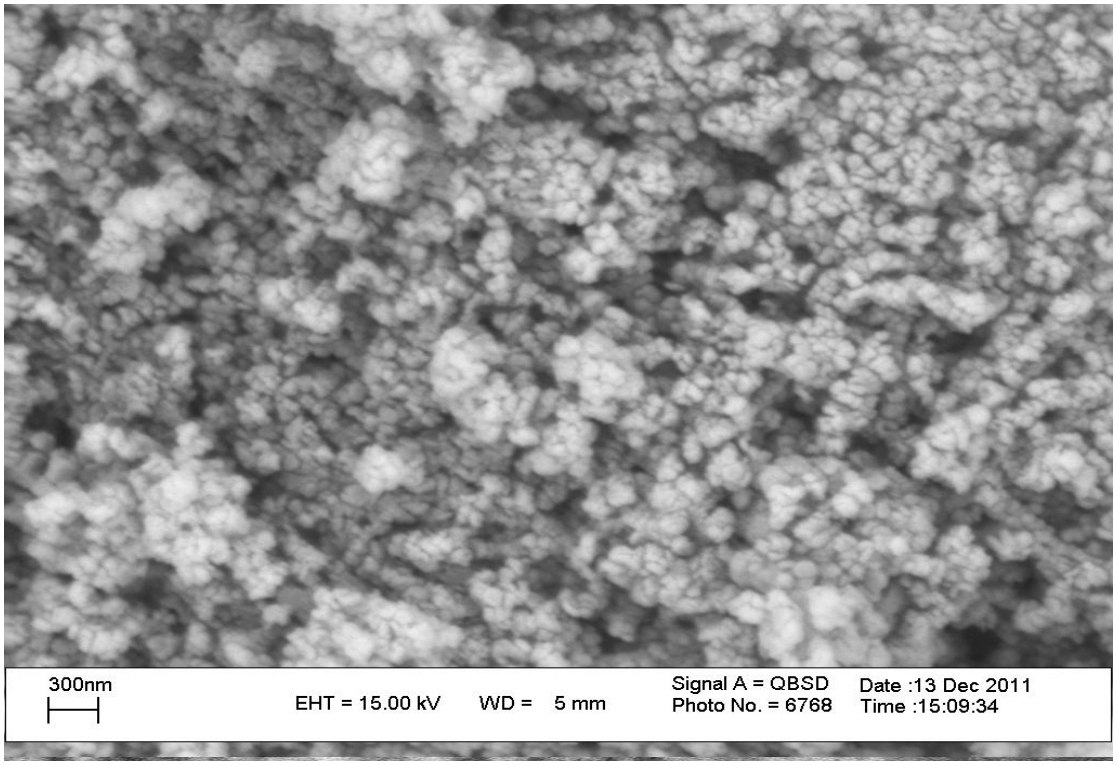
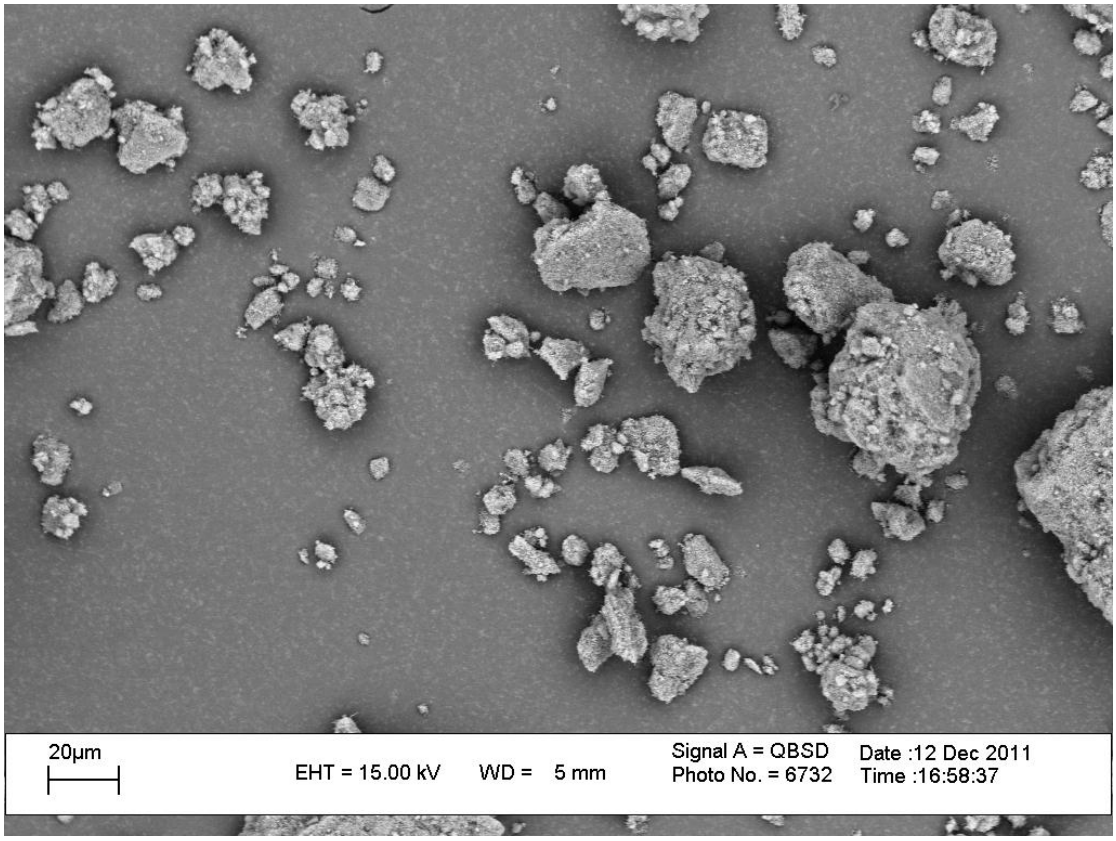


(f)

Fig. S3. SEM images of zinc - manganese oxides prepared at 300 ^{o}C (a-f).



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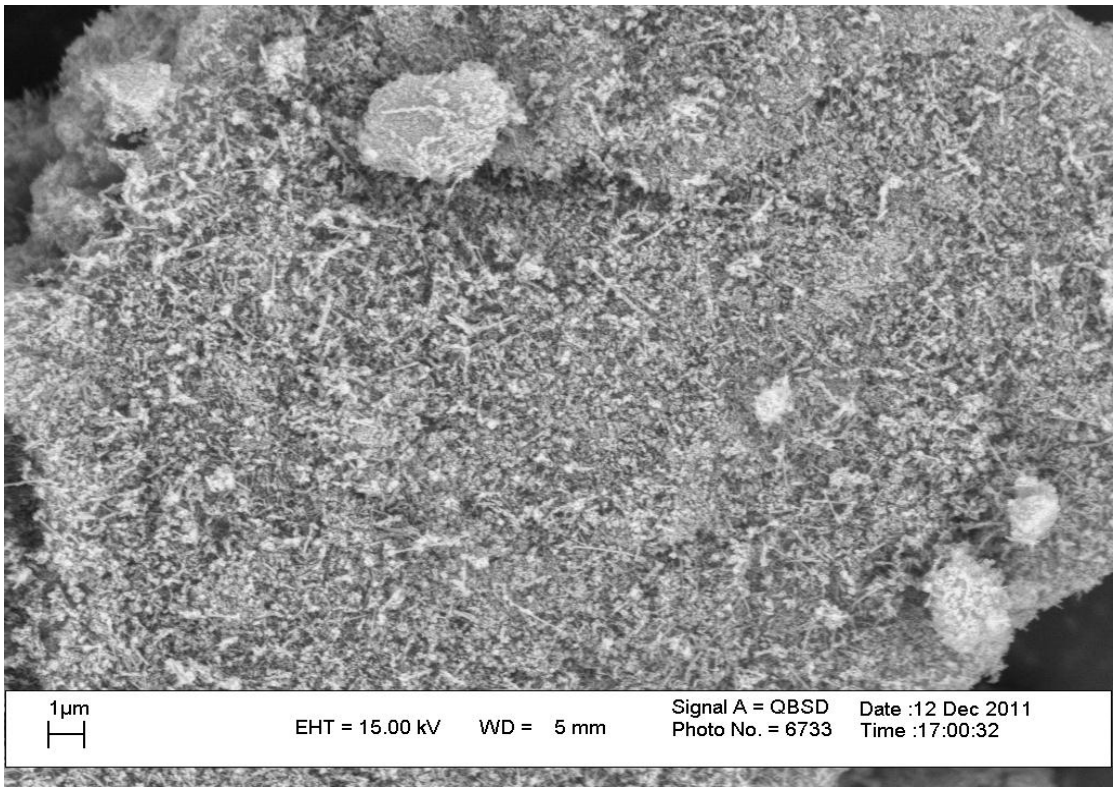

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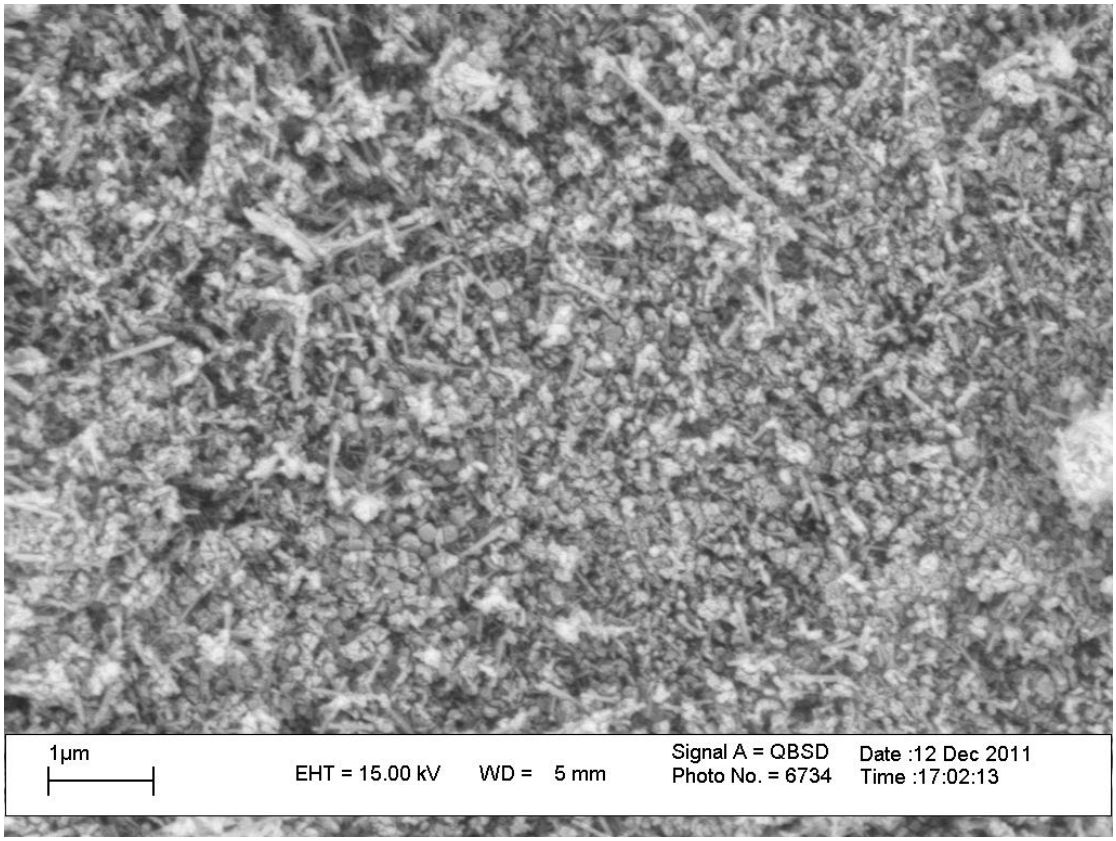
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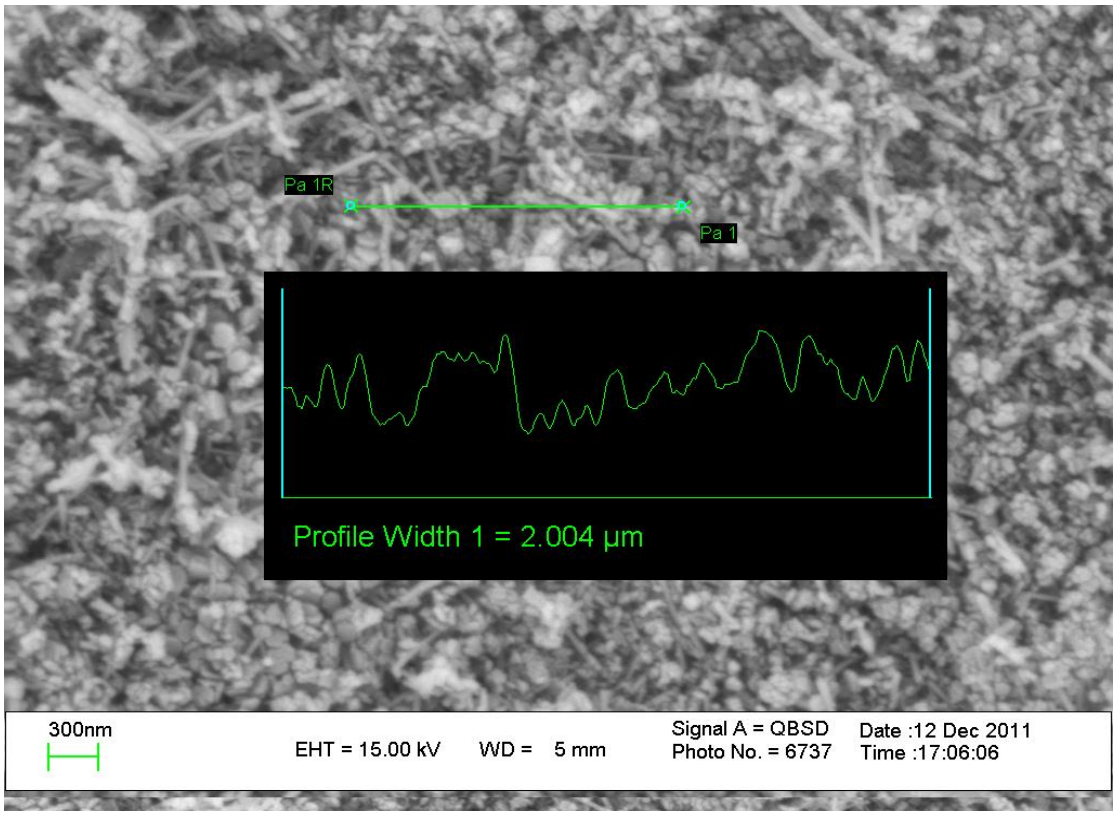
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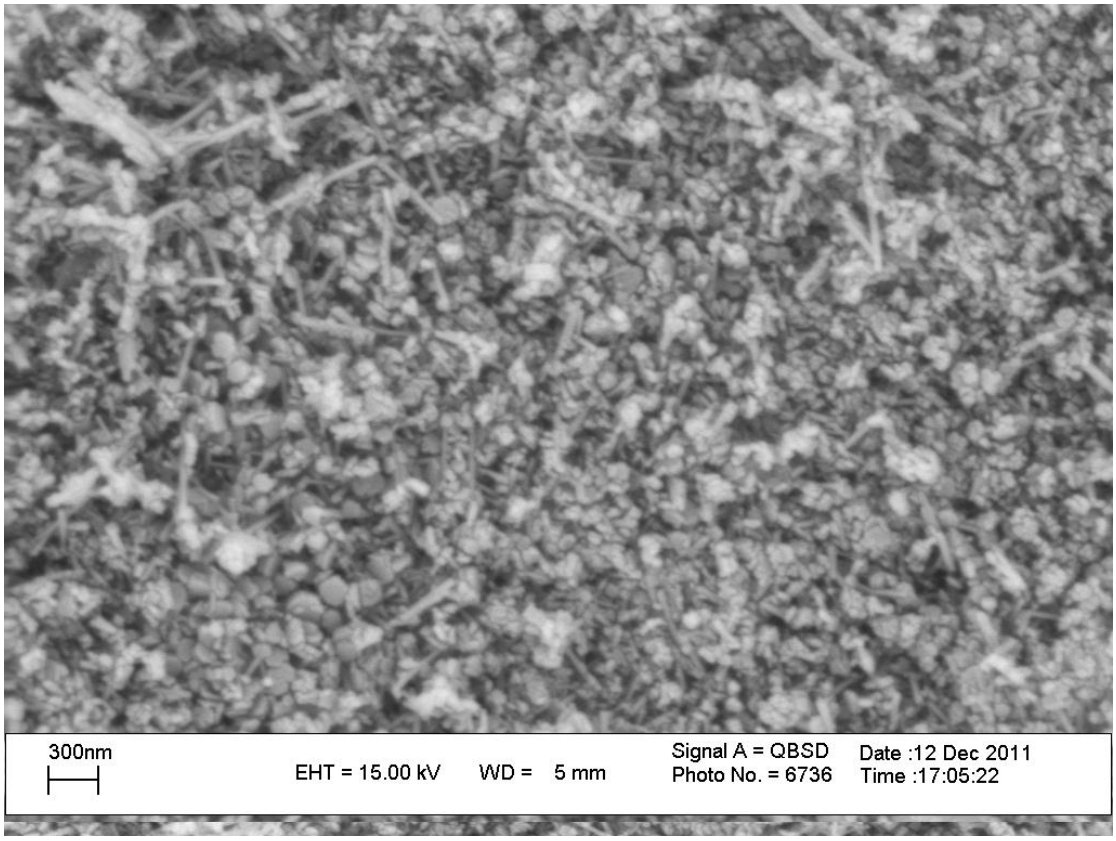

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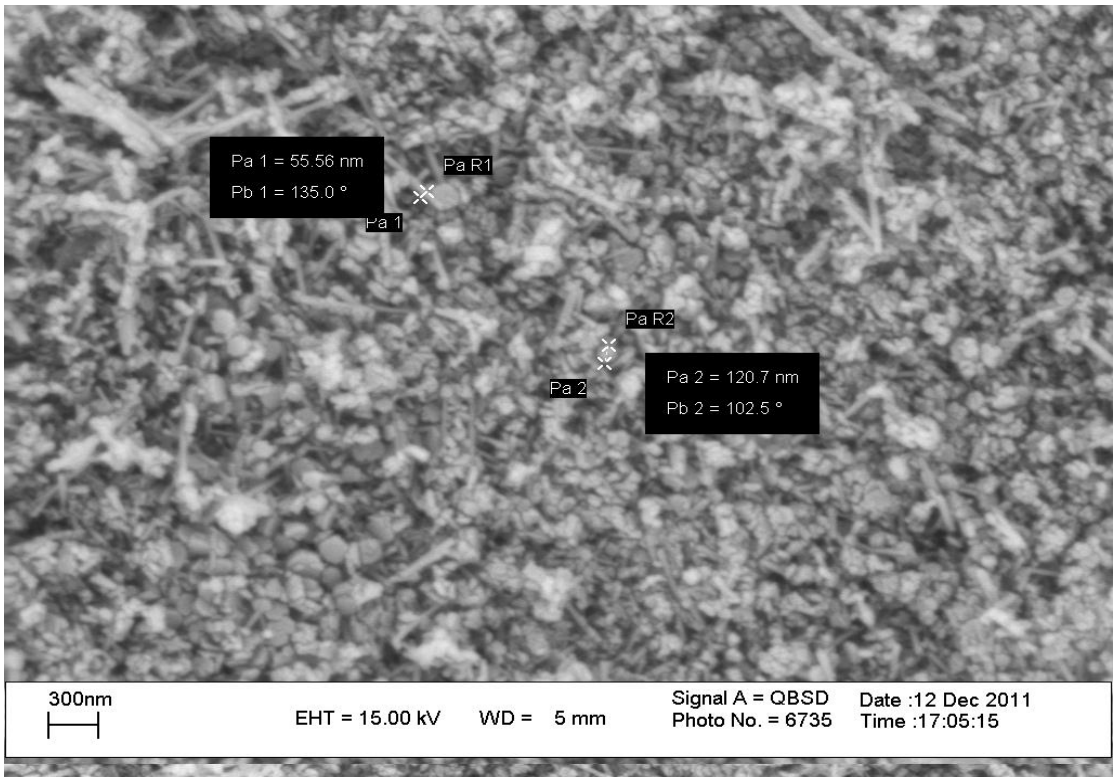
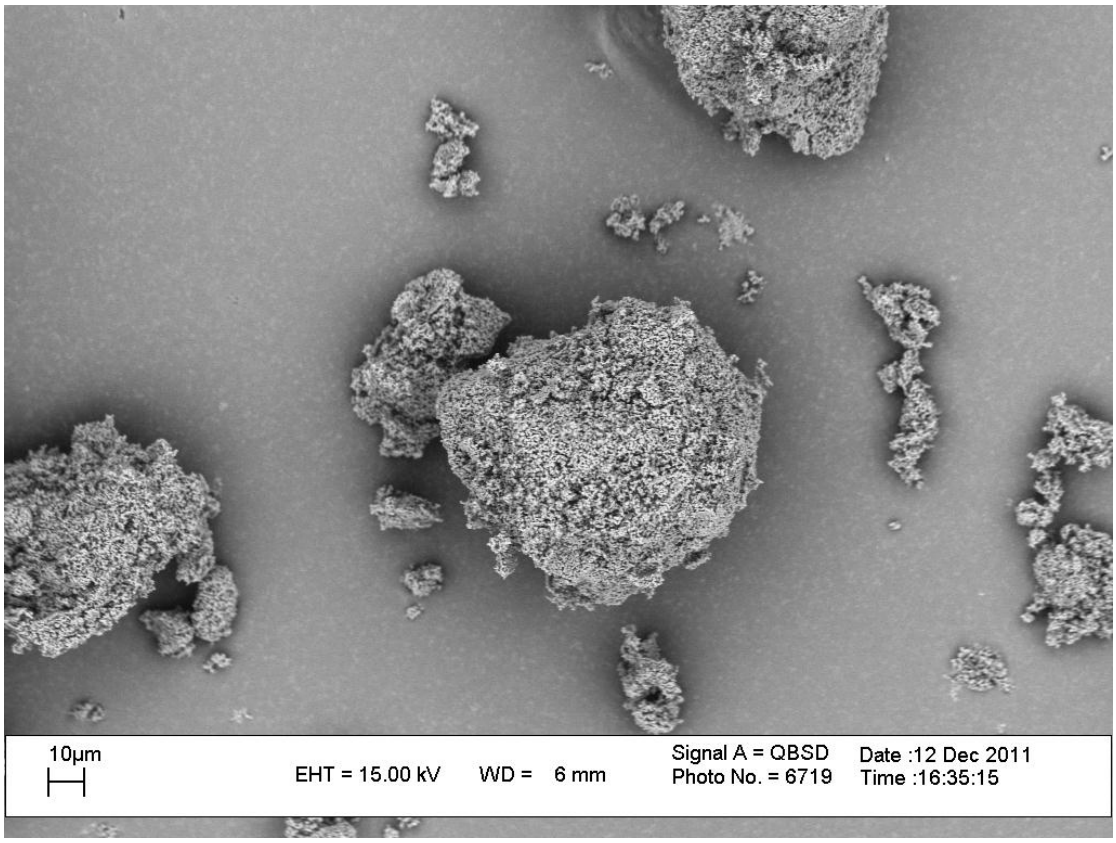
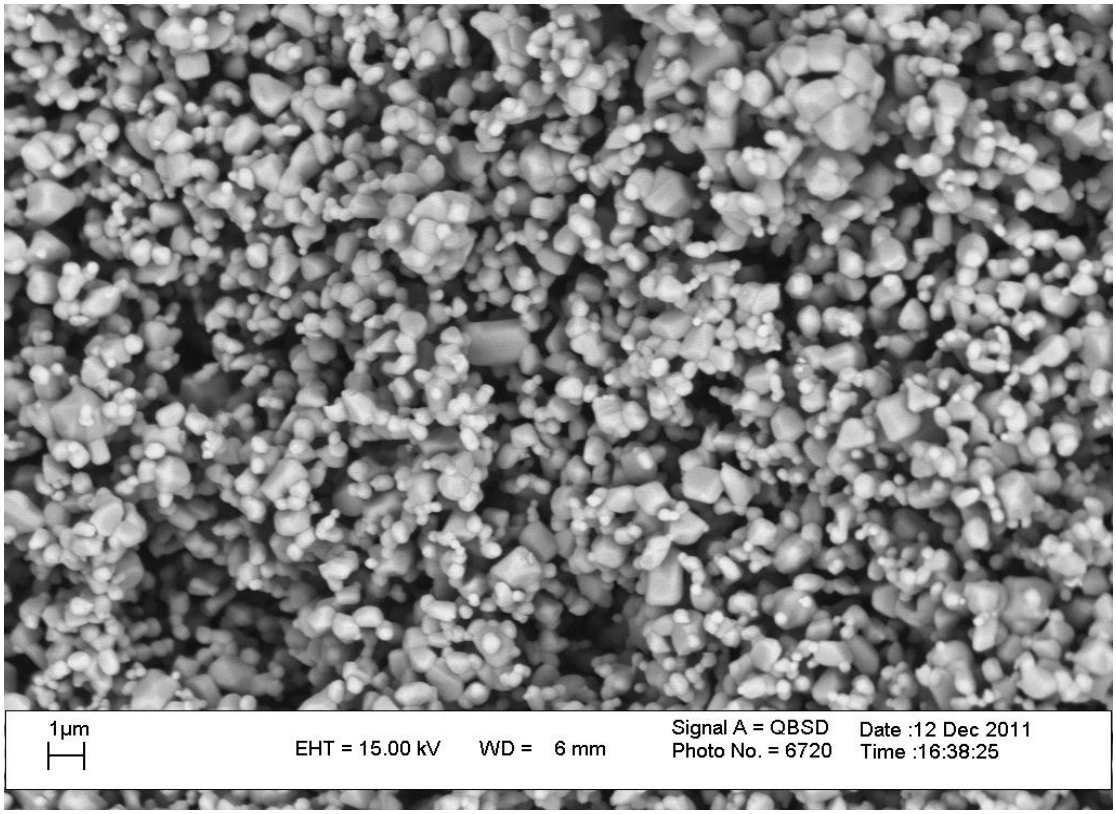


(f)

Fig. S4. SEM images of zinc - manganese oxides prepared at 600 ^{o}C (a-f).



(a)



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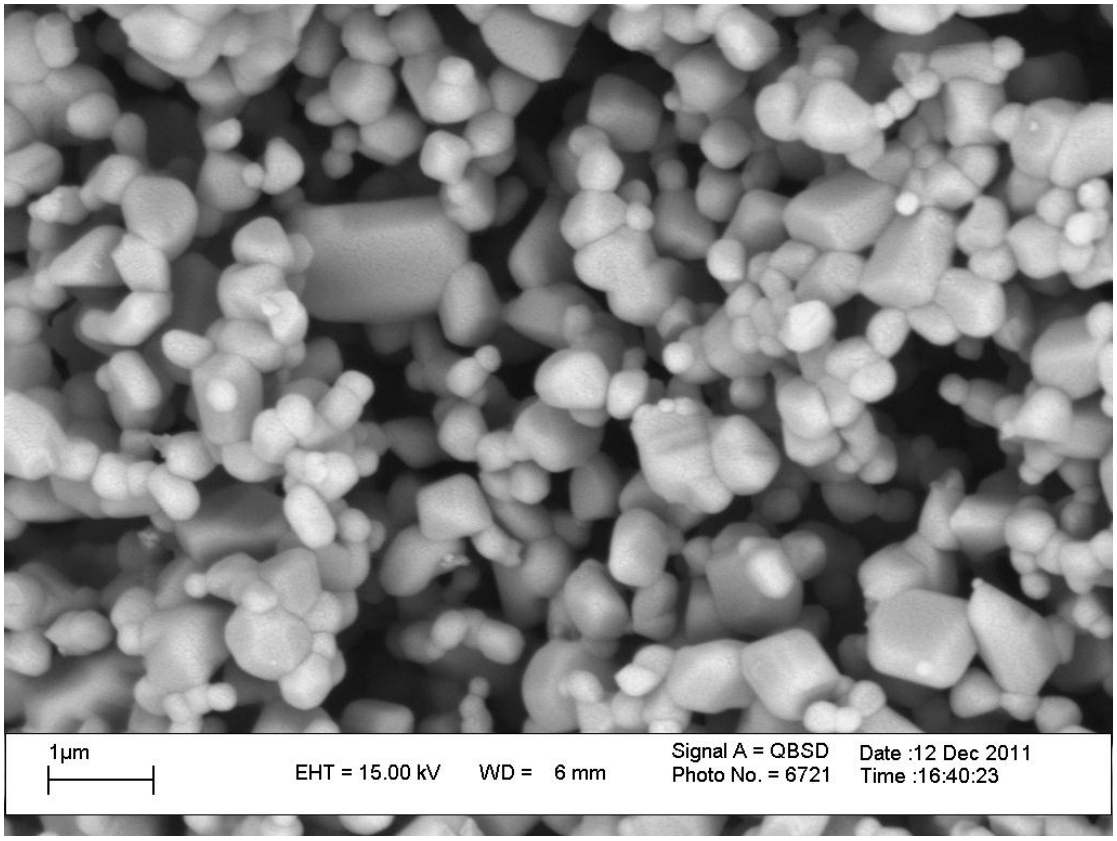

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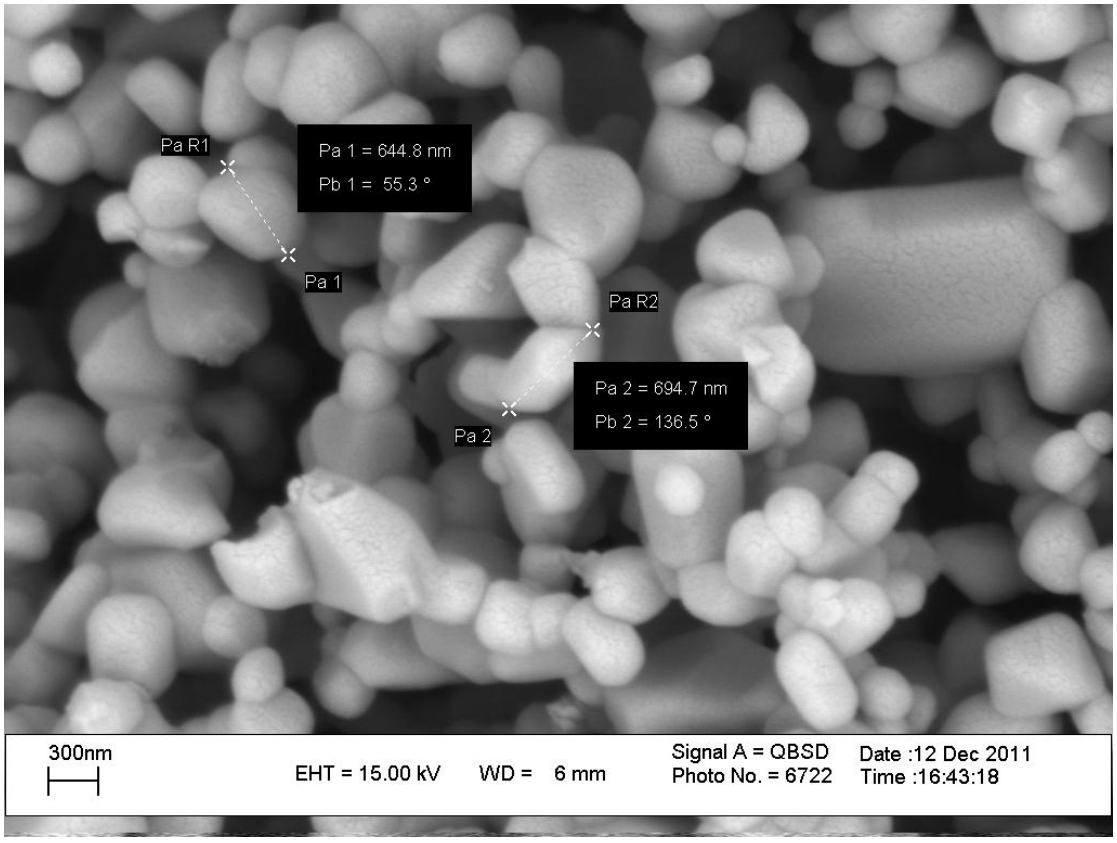

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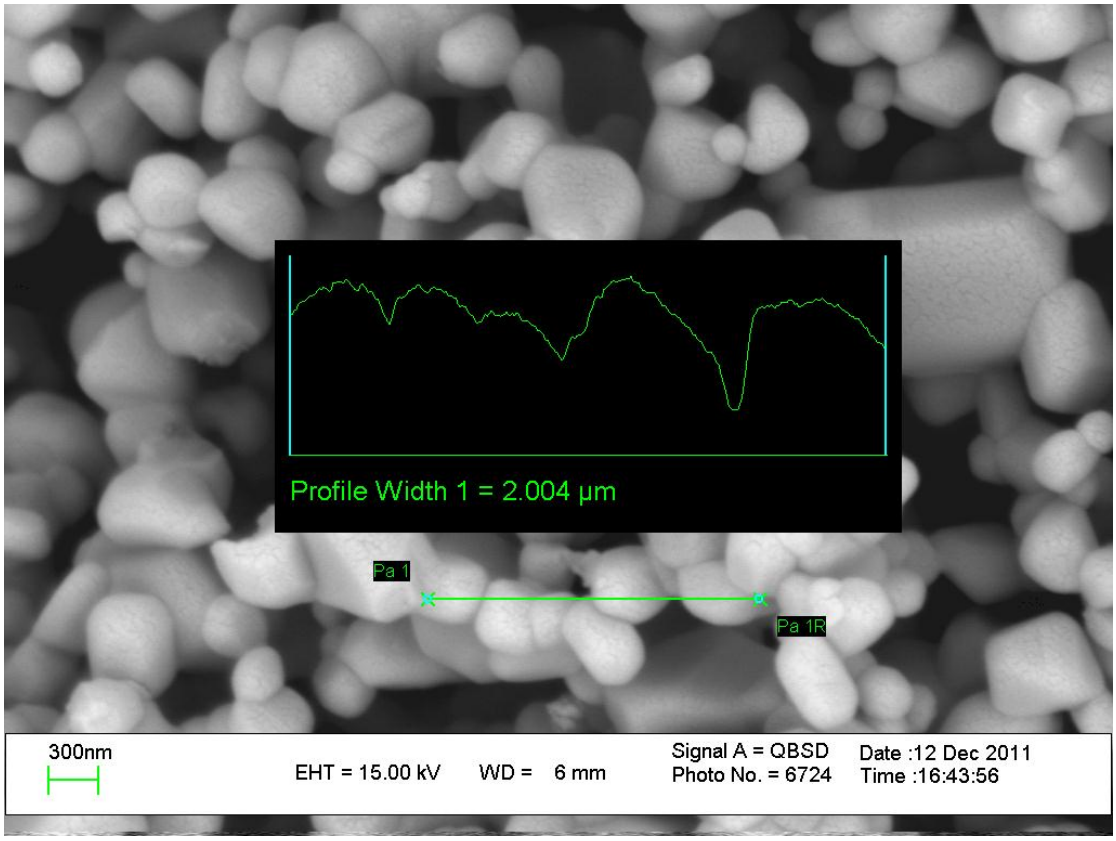

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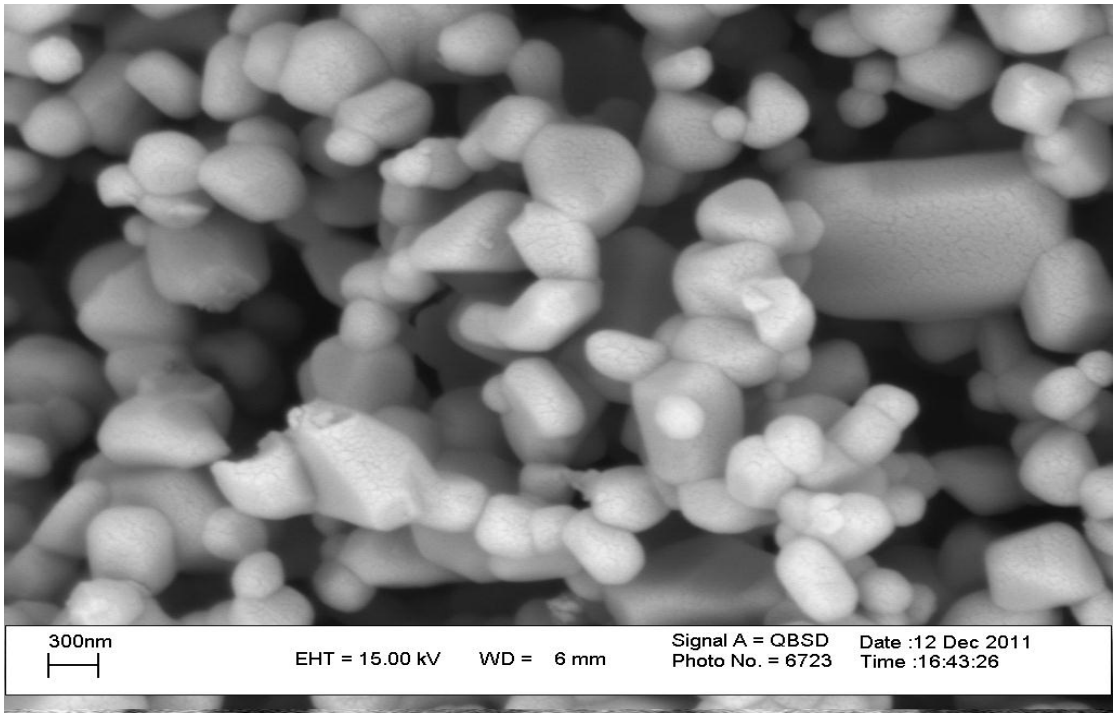
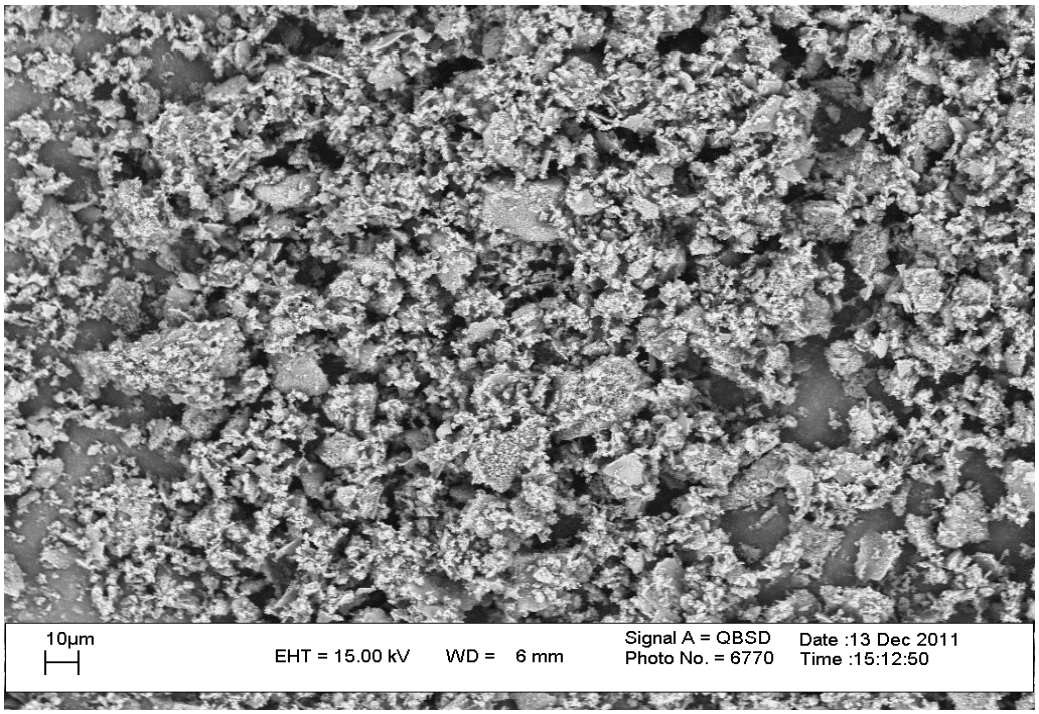
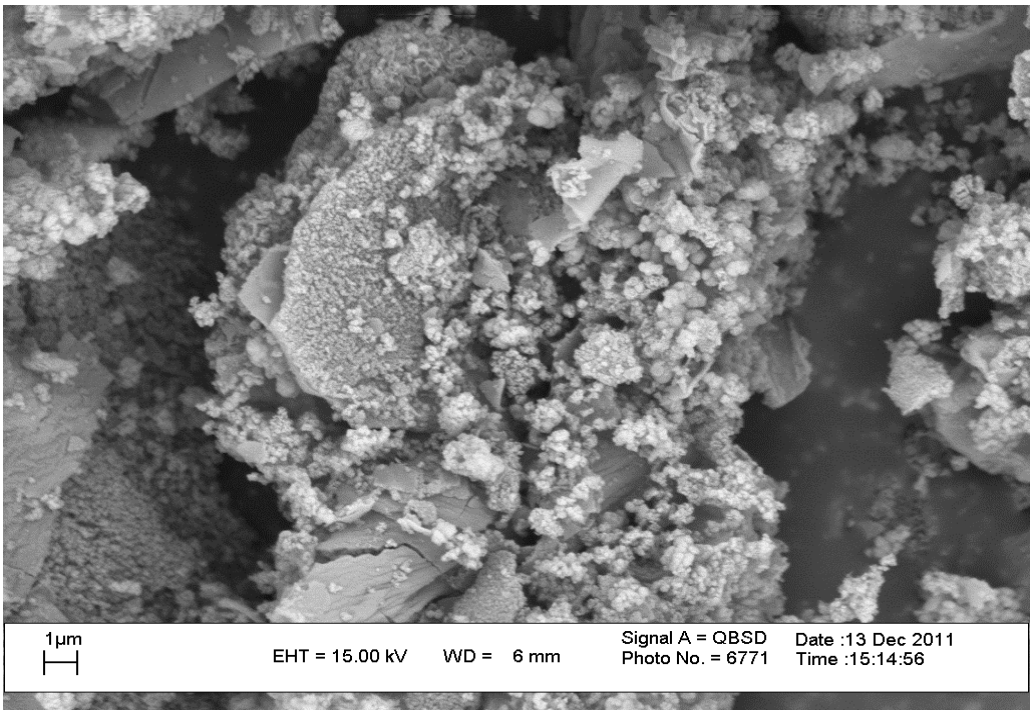


(f)

Fig. S5. SEM images of zinc - manganese oxides prepared at 1000 ^{o}C (a-g).



(a)



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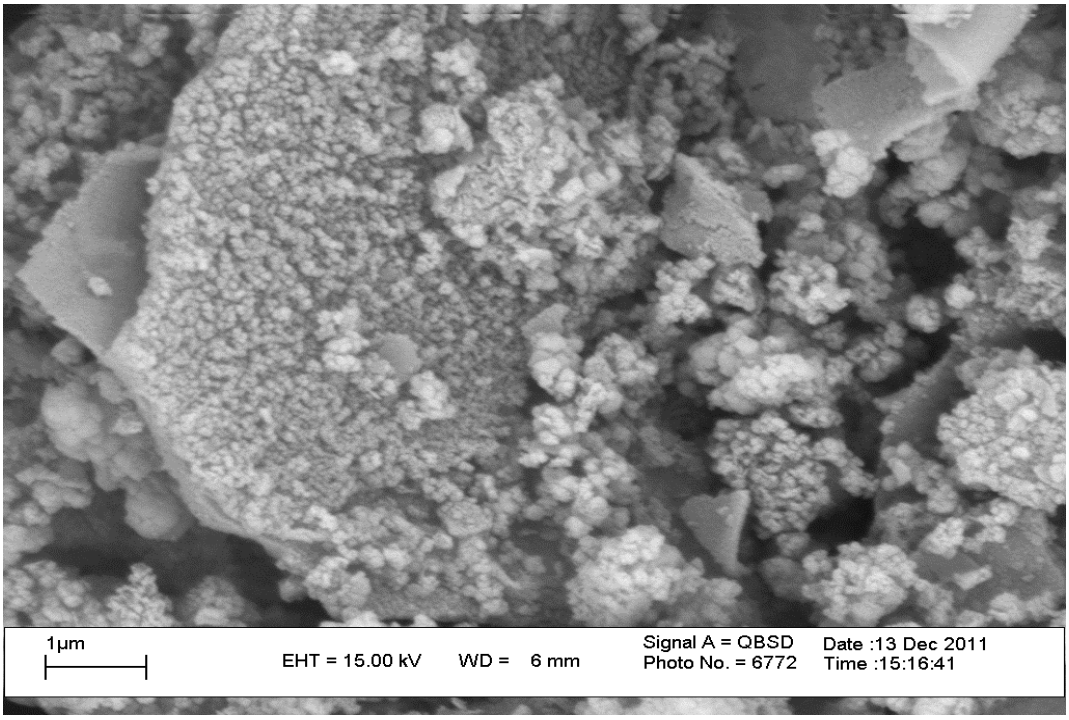

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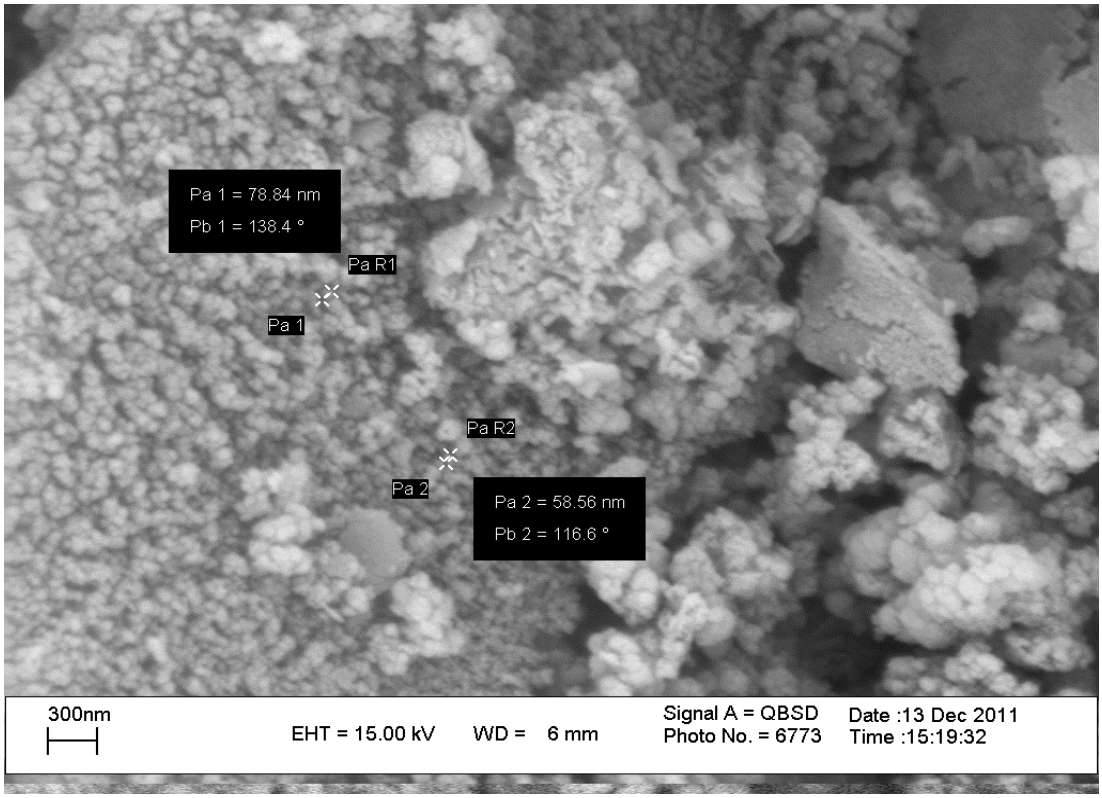

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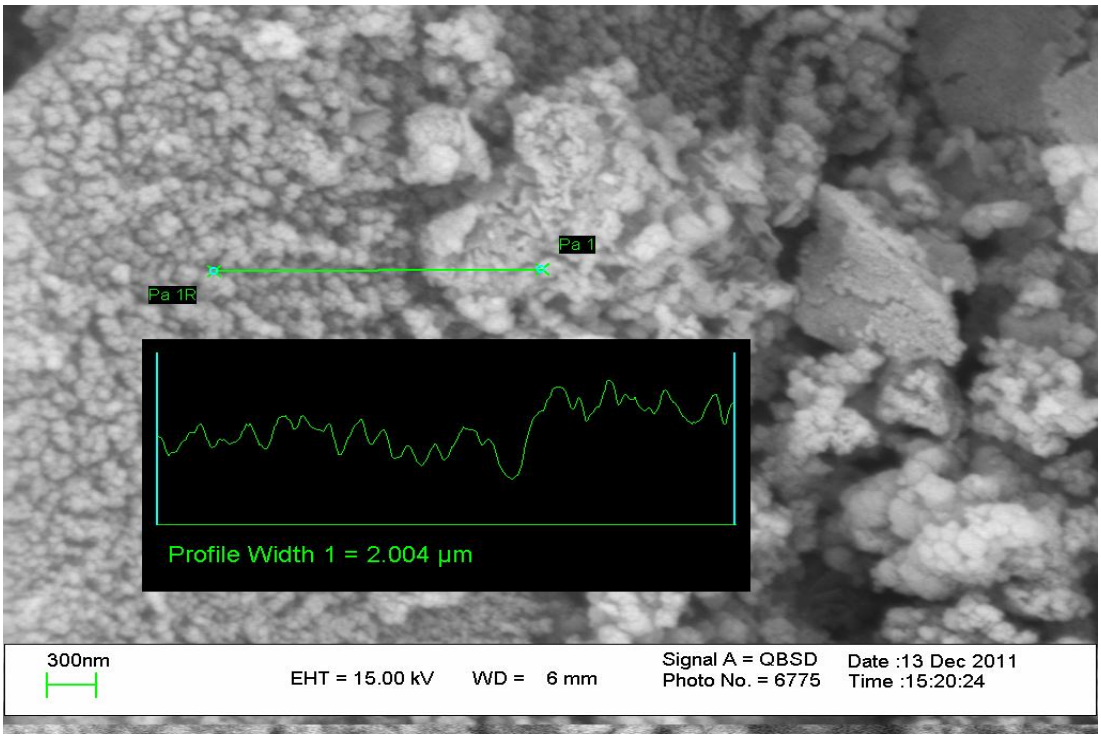

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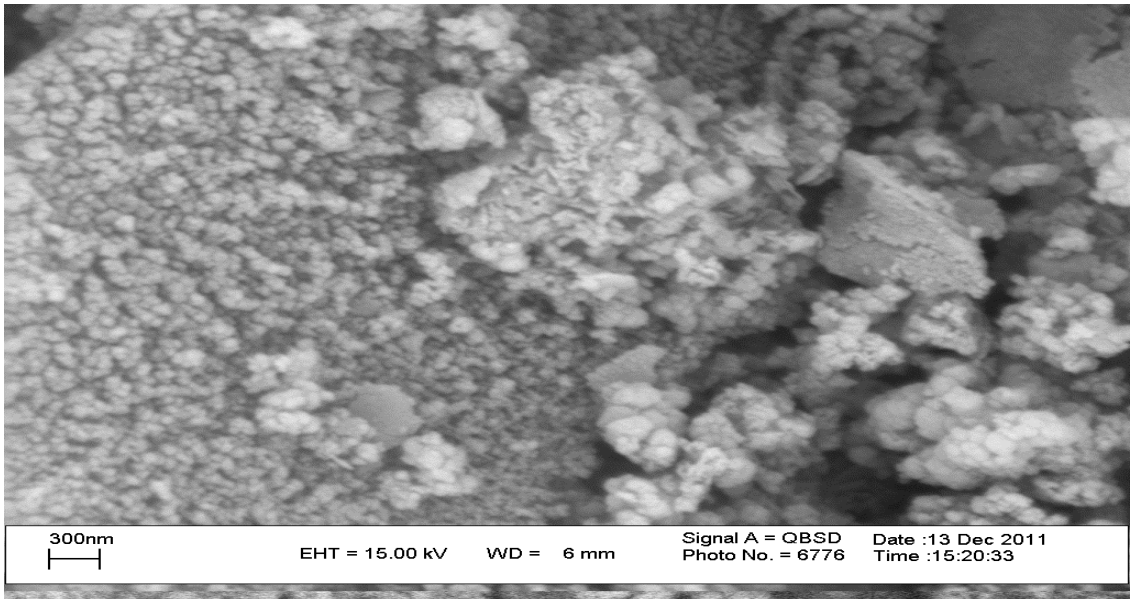
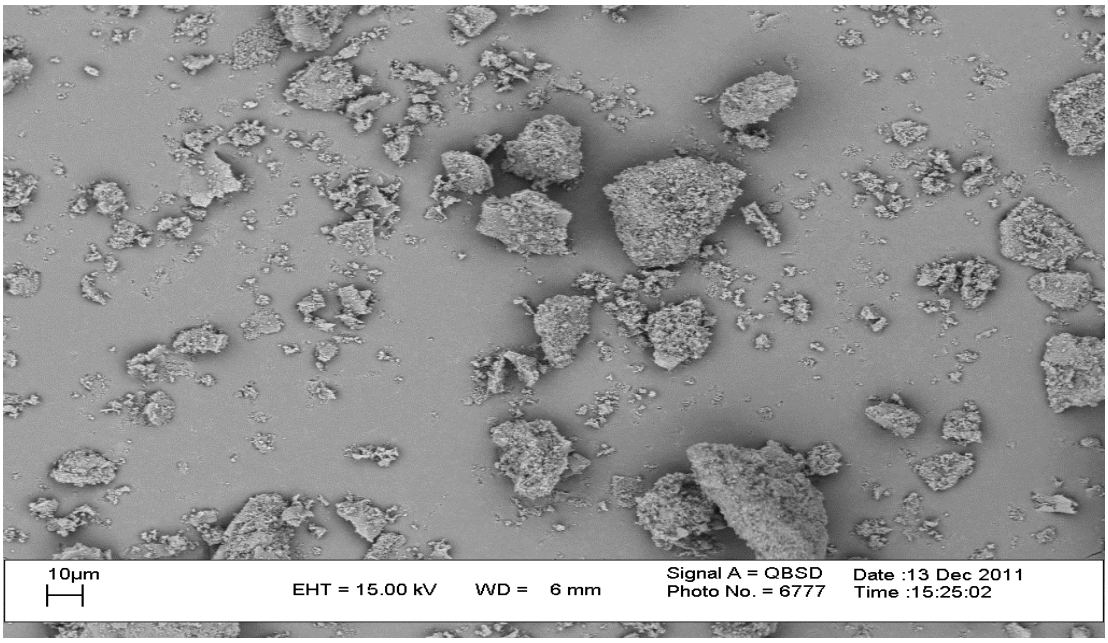
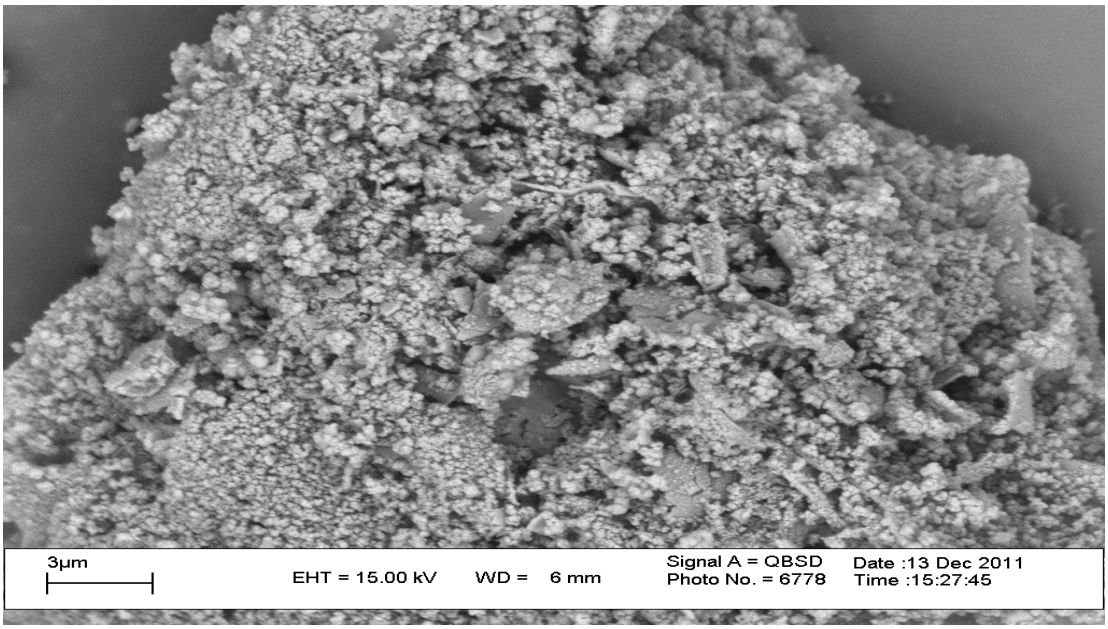


(f)

Fig. S6 SEM images of aluminium - manganese oxides prepared at 100 ^{o}C (a-g).



(a)



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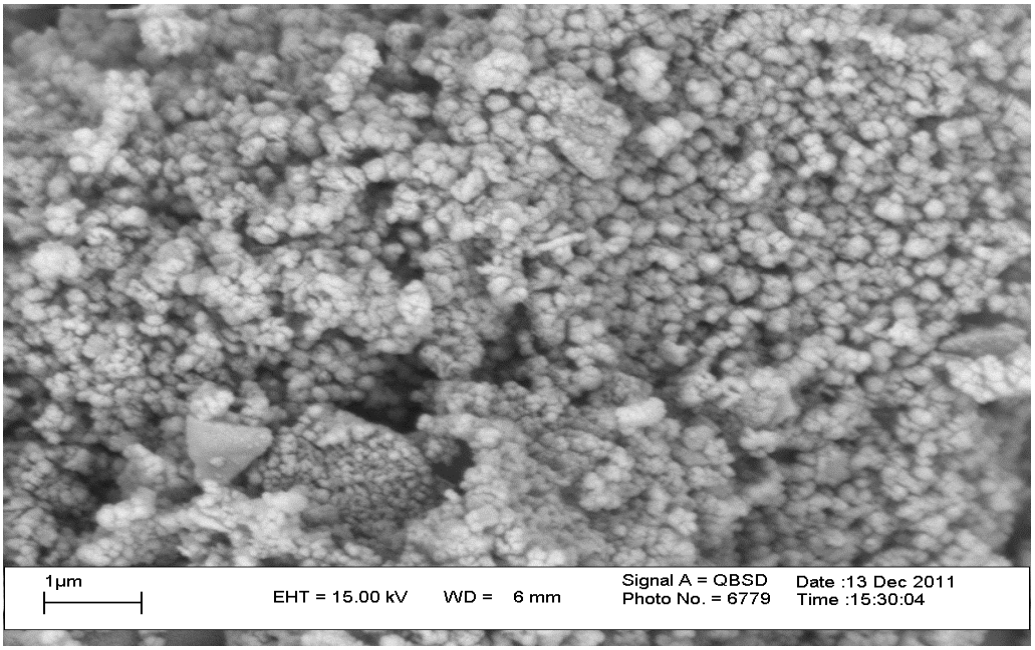
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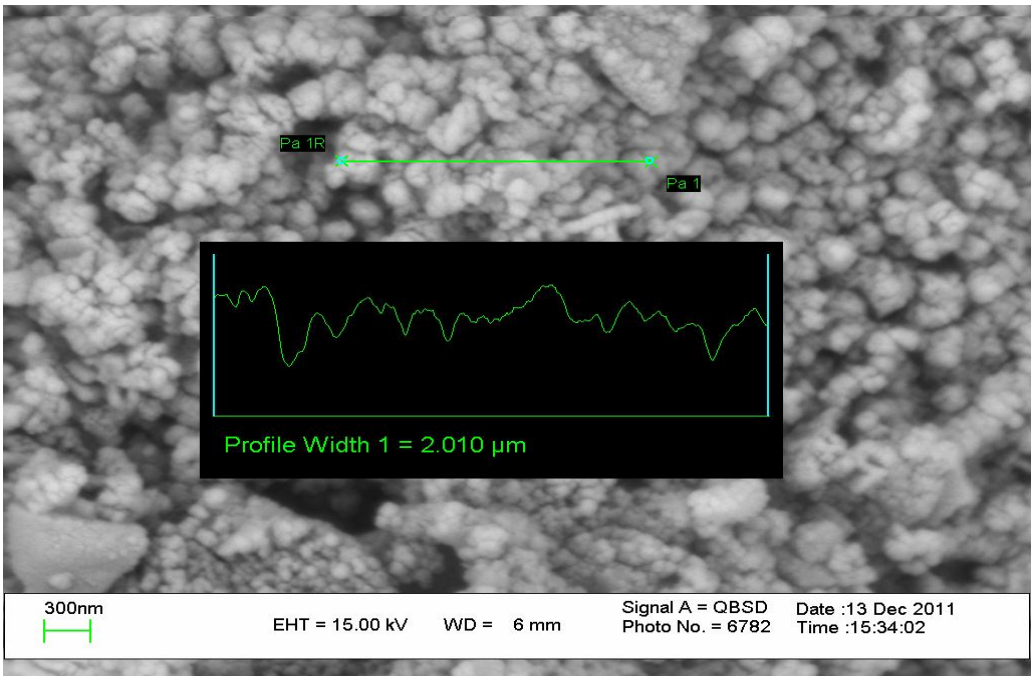
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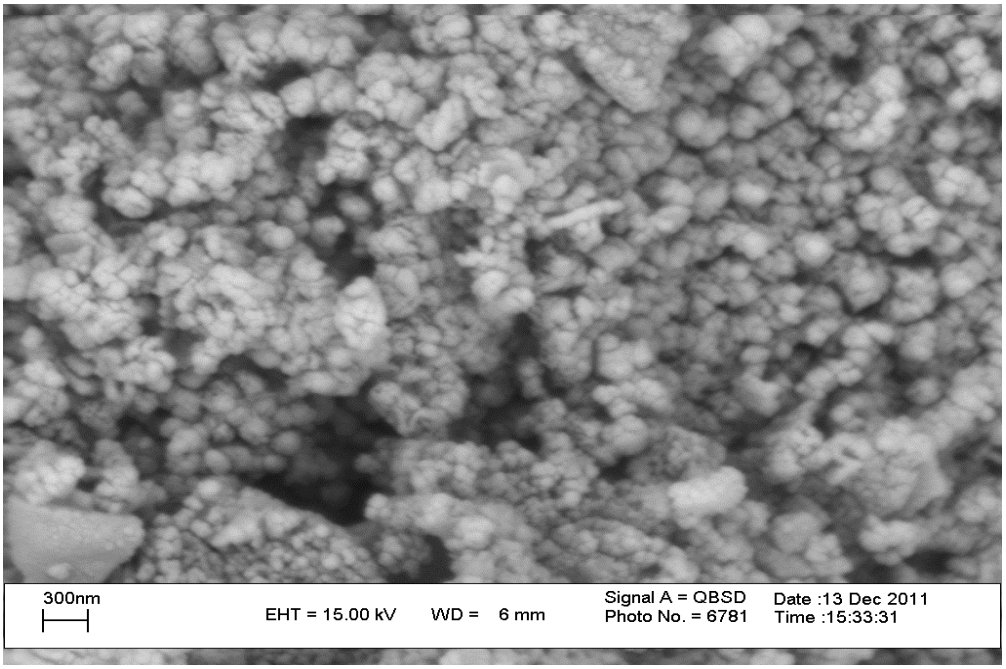

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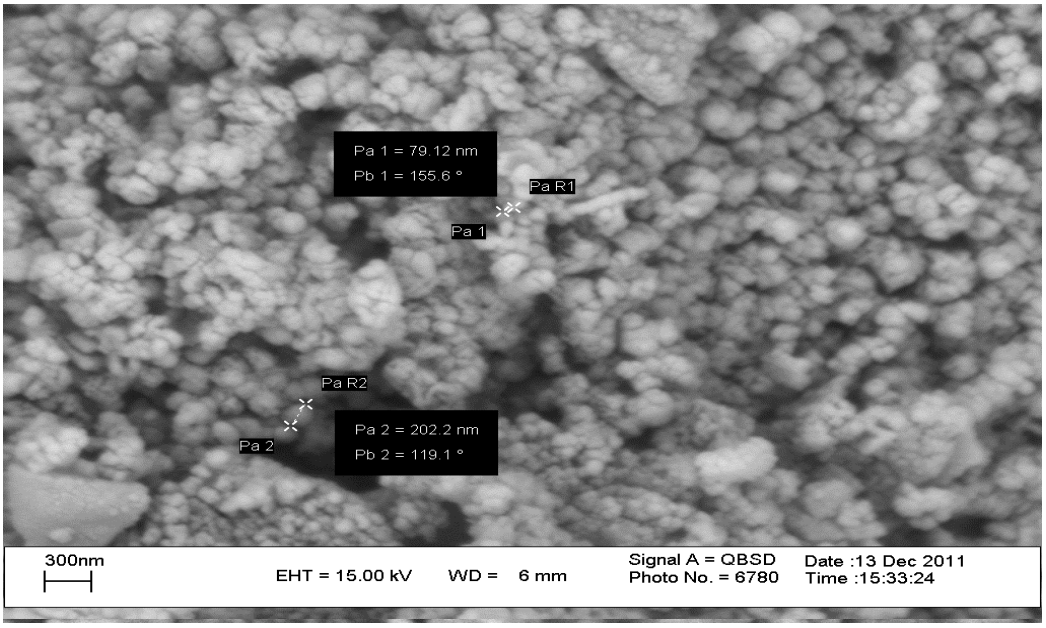
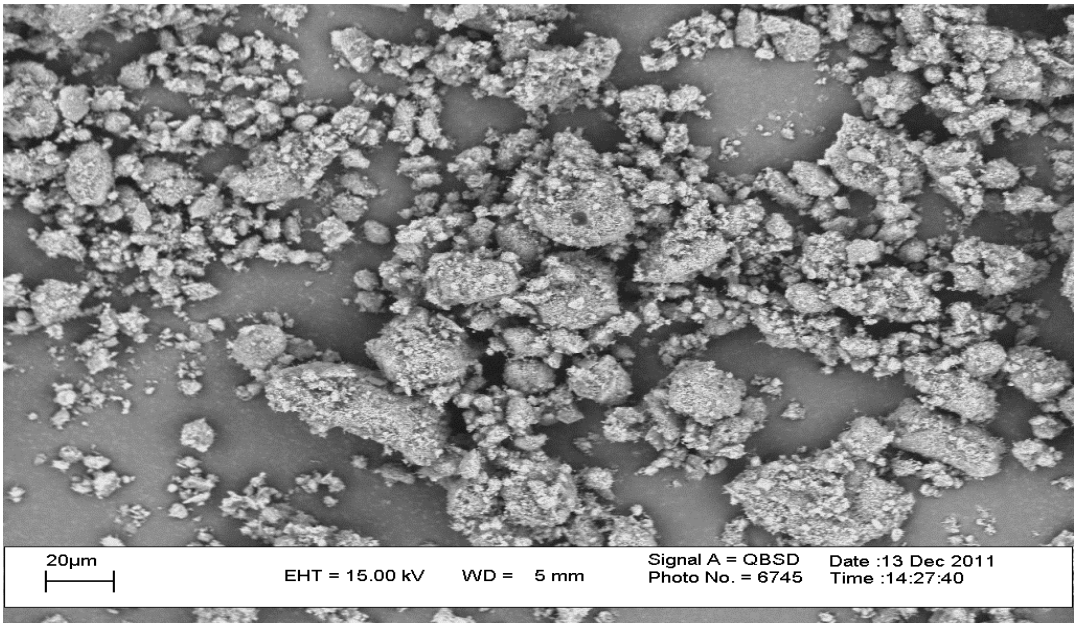


(f)

Fig. S7 SEM images of aluminium - manganese oxides prepared at 300 ^{o}C (a-f).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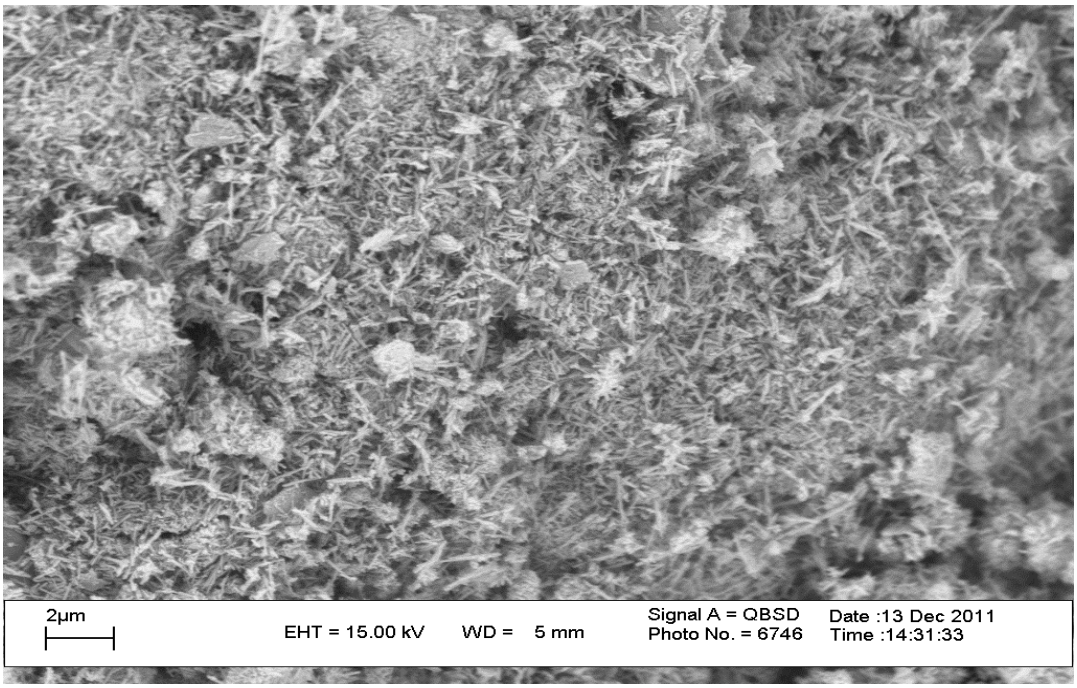
(a)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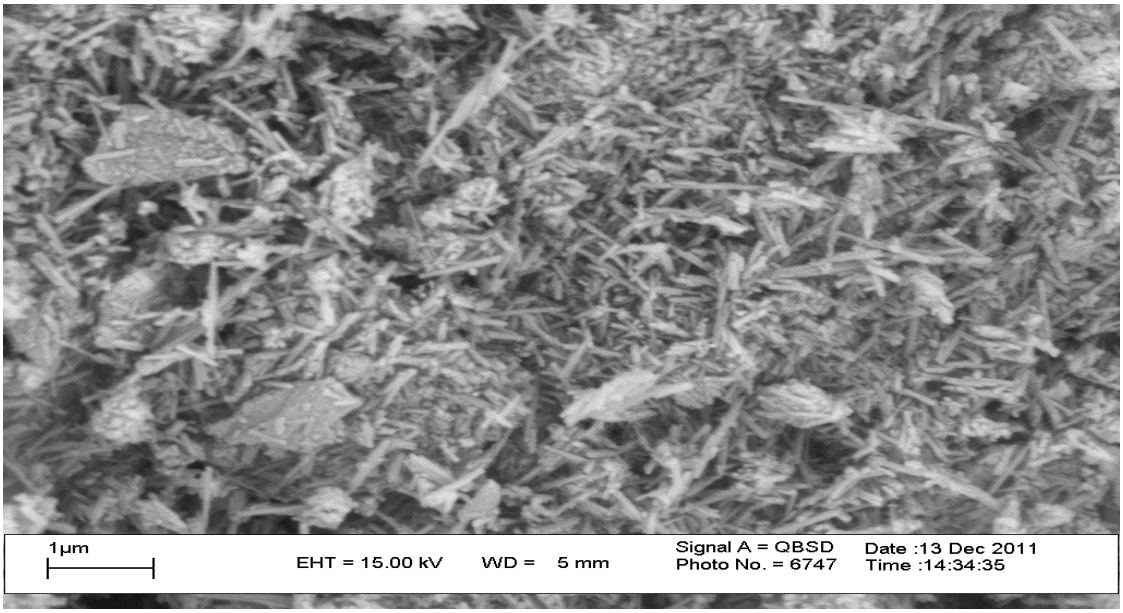
(b)



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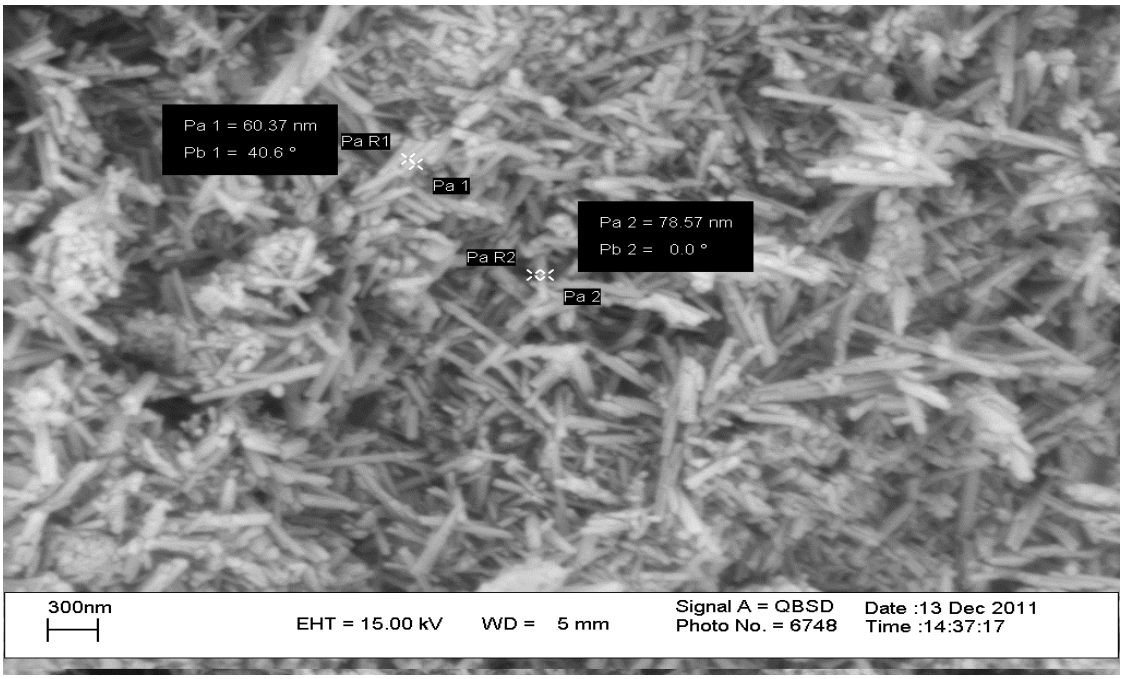

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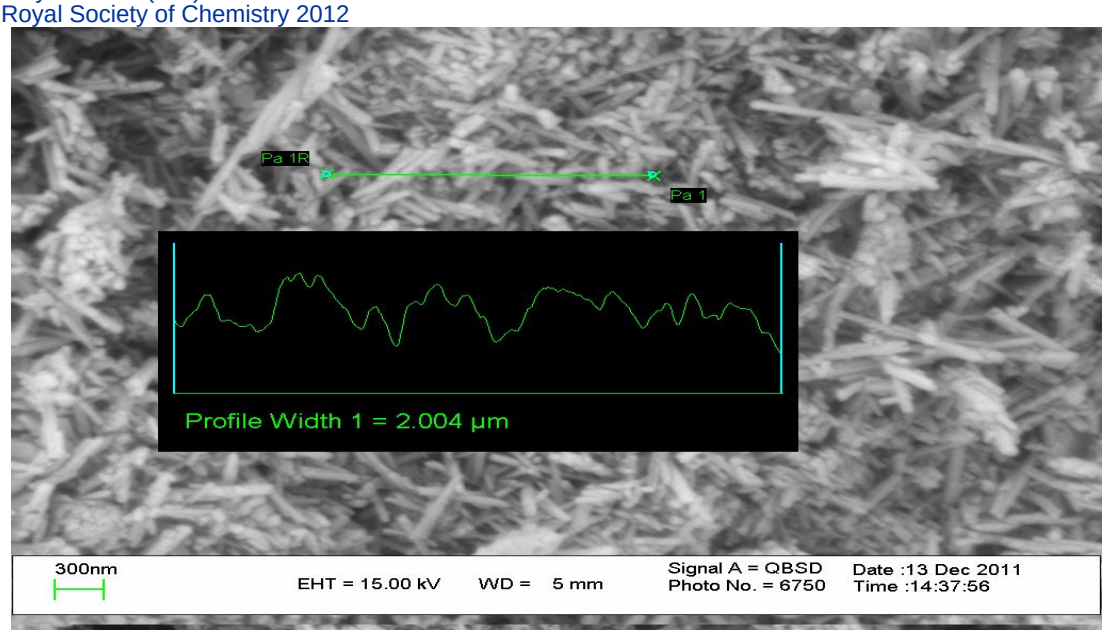

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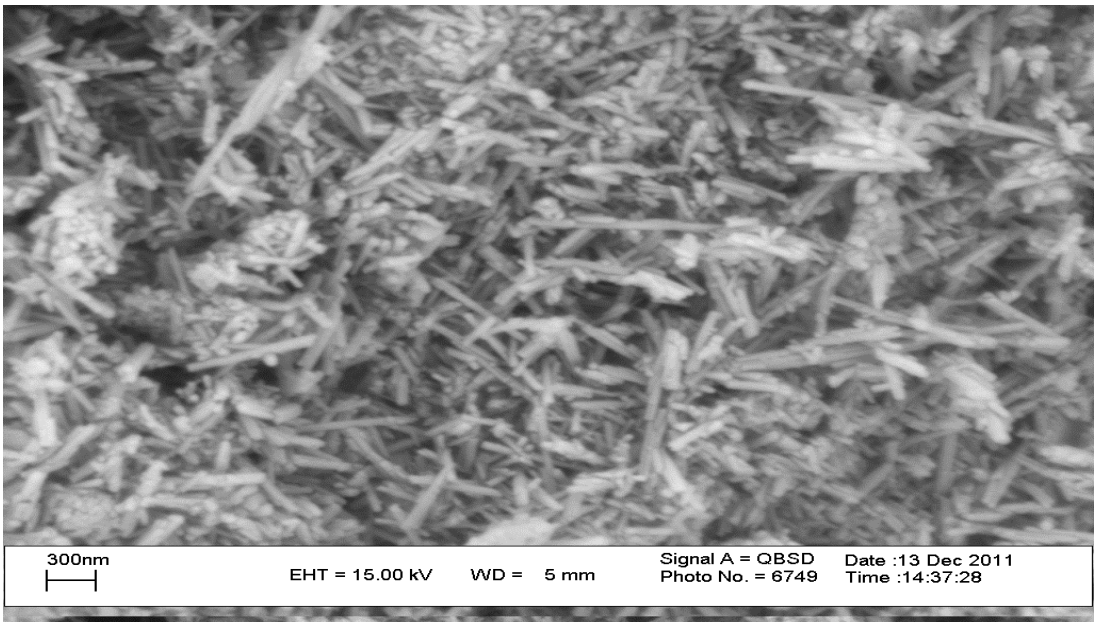
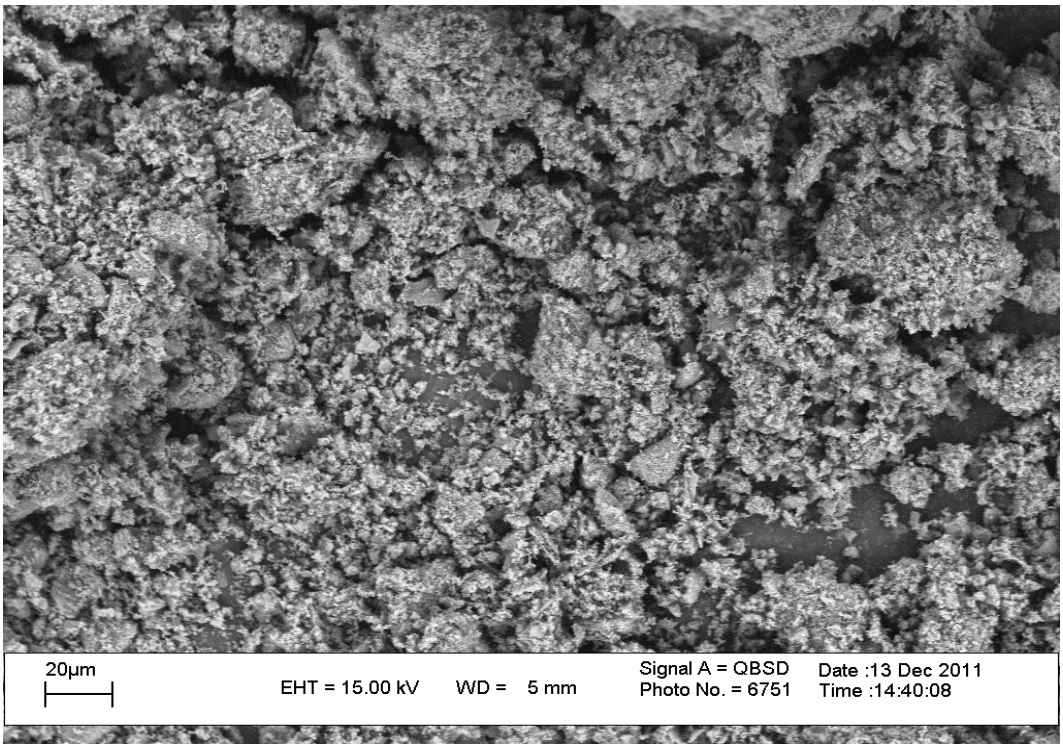
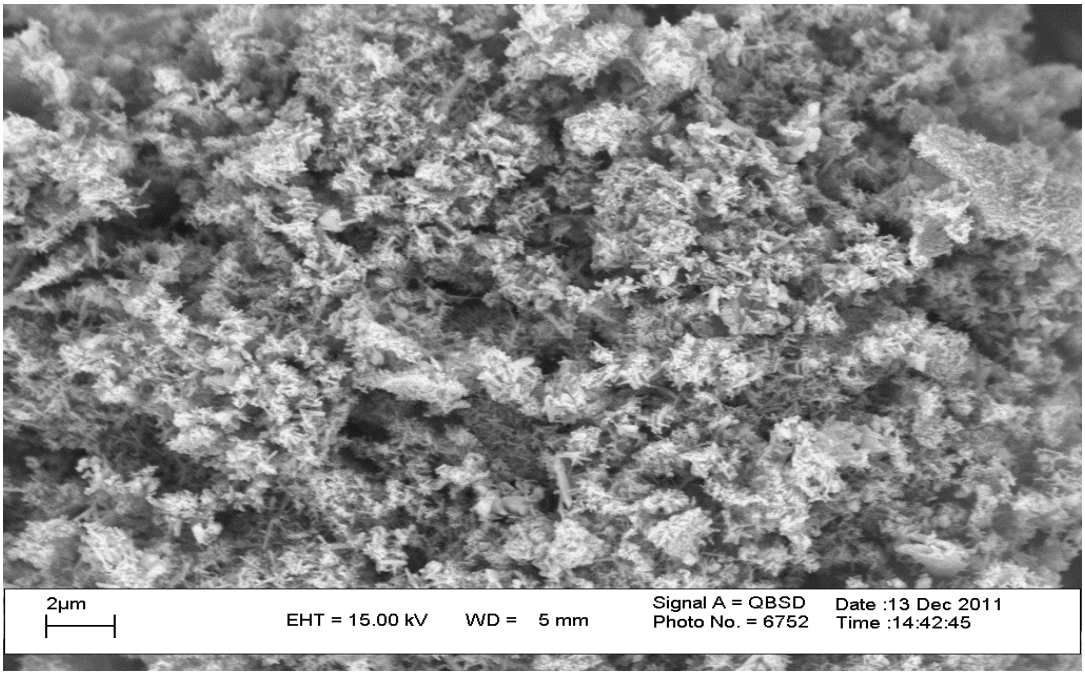


(f)

Fig. S8 SEM images of aluminium - manganese oxides prepared at 500 ^{o}C (a-f).



(a)



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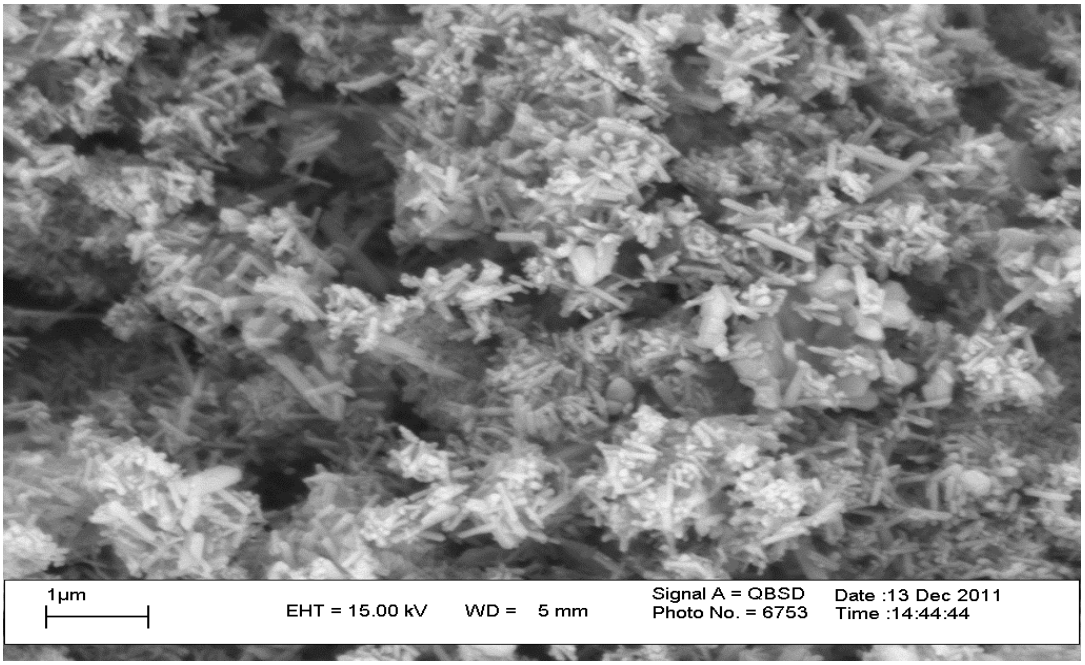
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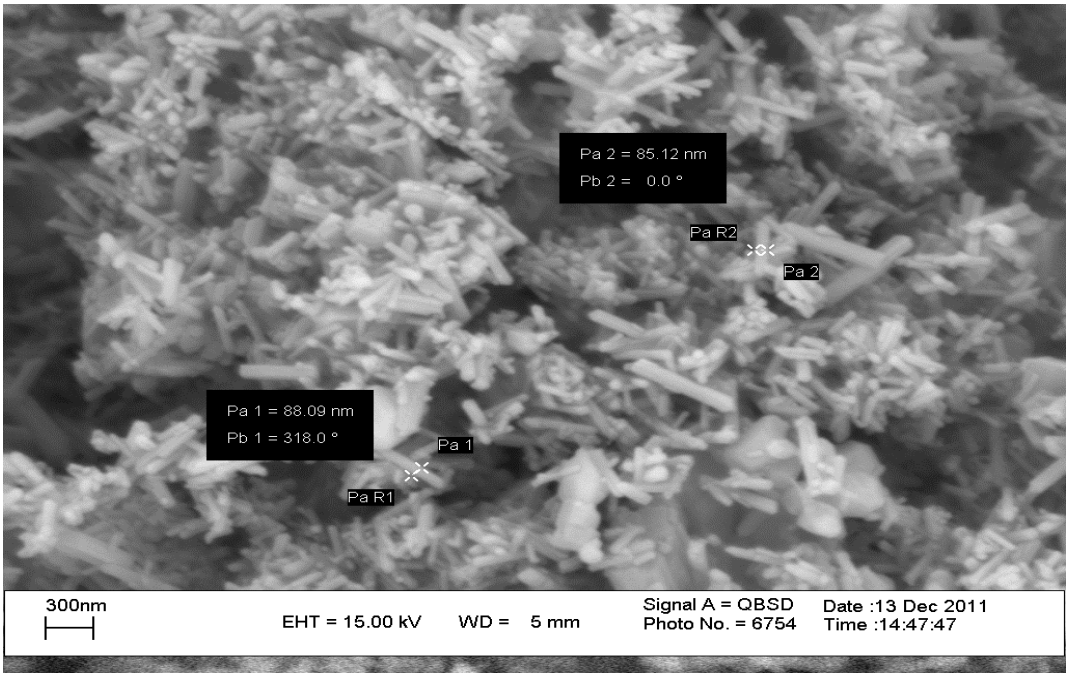
(c)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Pa R2
Pa 2
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Pb 1 = 318.0 °
Pa 1
Pa R1
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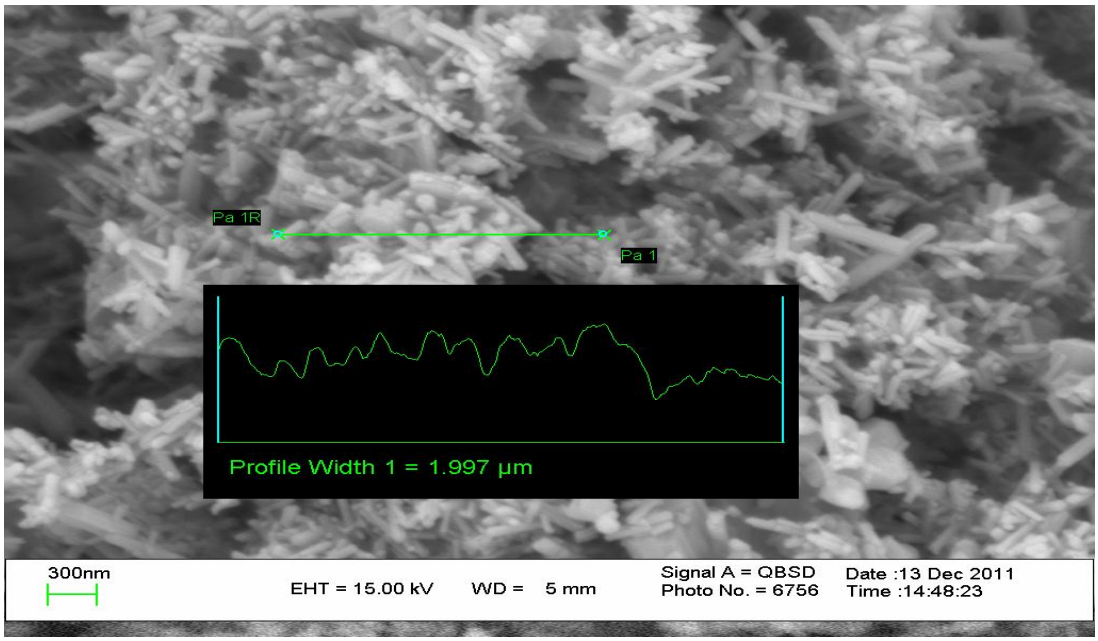
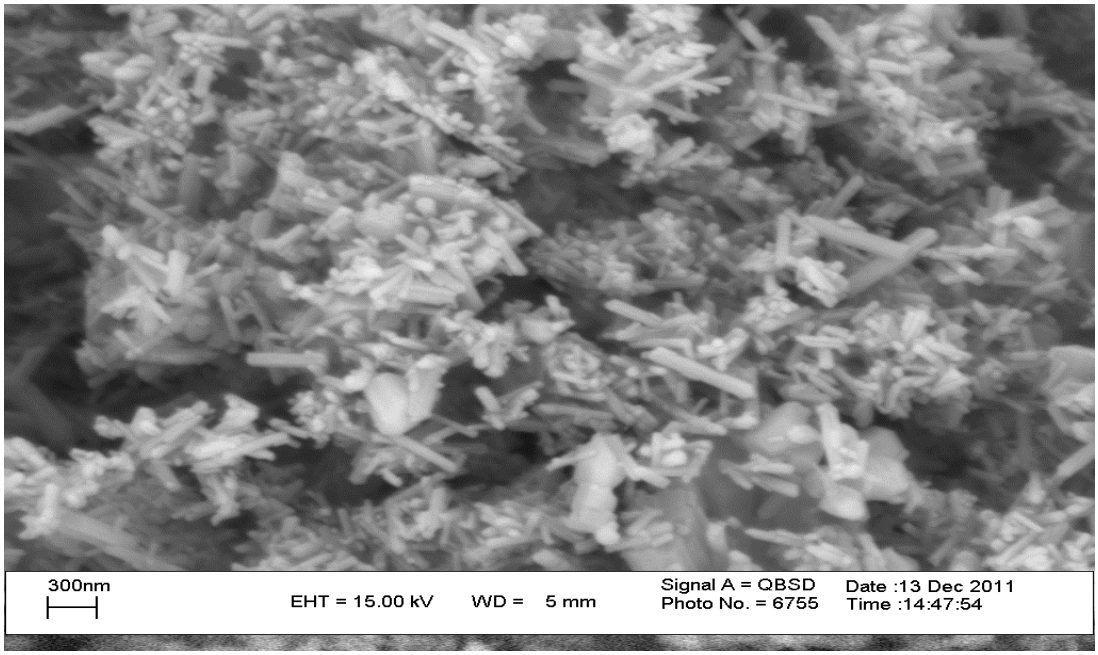
Time :14:47:47

(d)

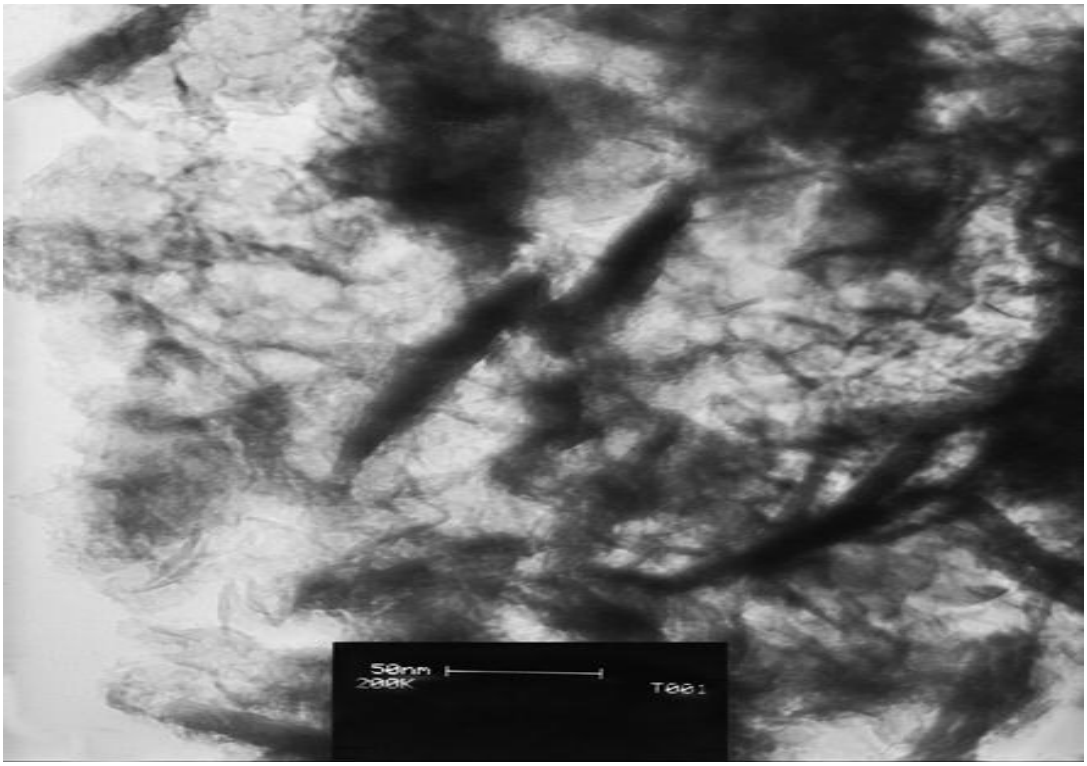


(e)

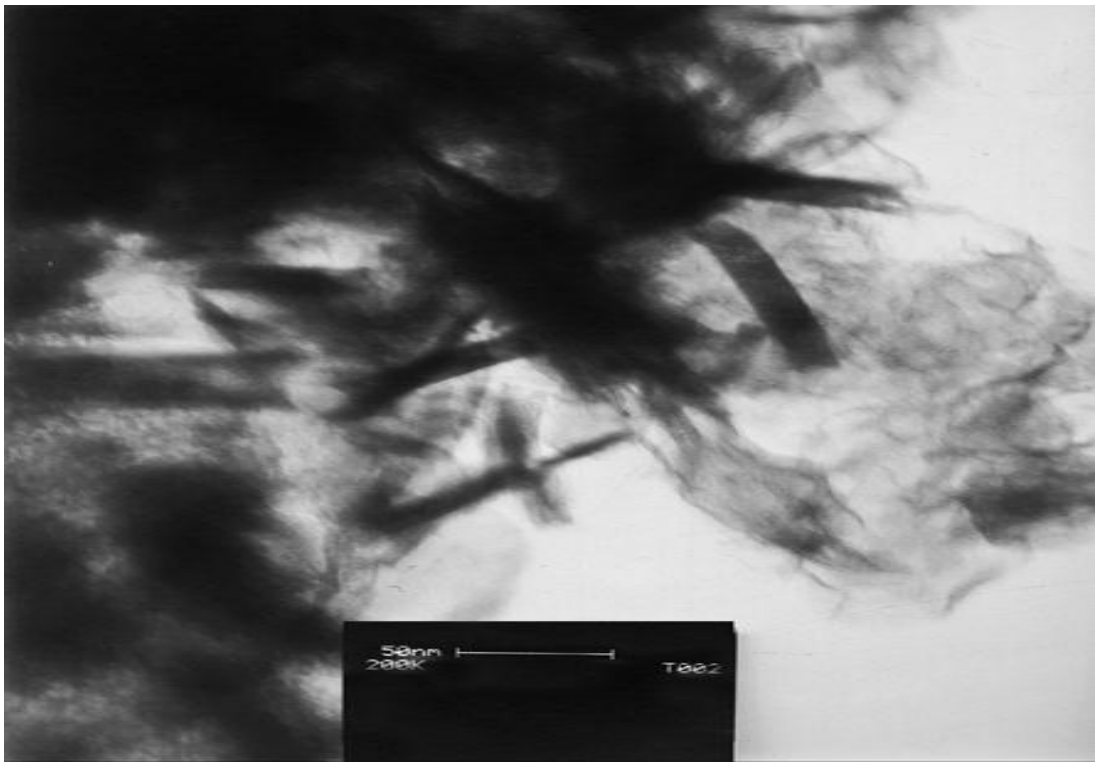


(f)

Fig. S9 SEM images of aluminium - manganese oxides prepared at 750 ^{o}C (a-f).

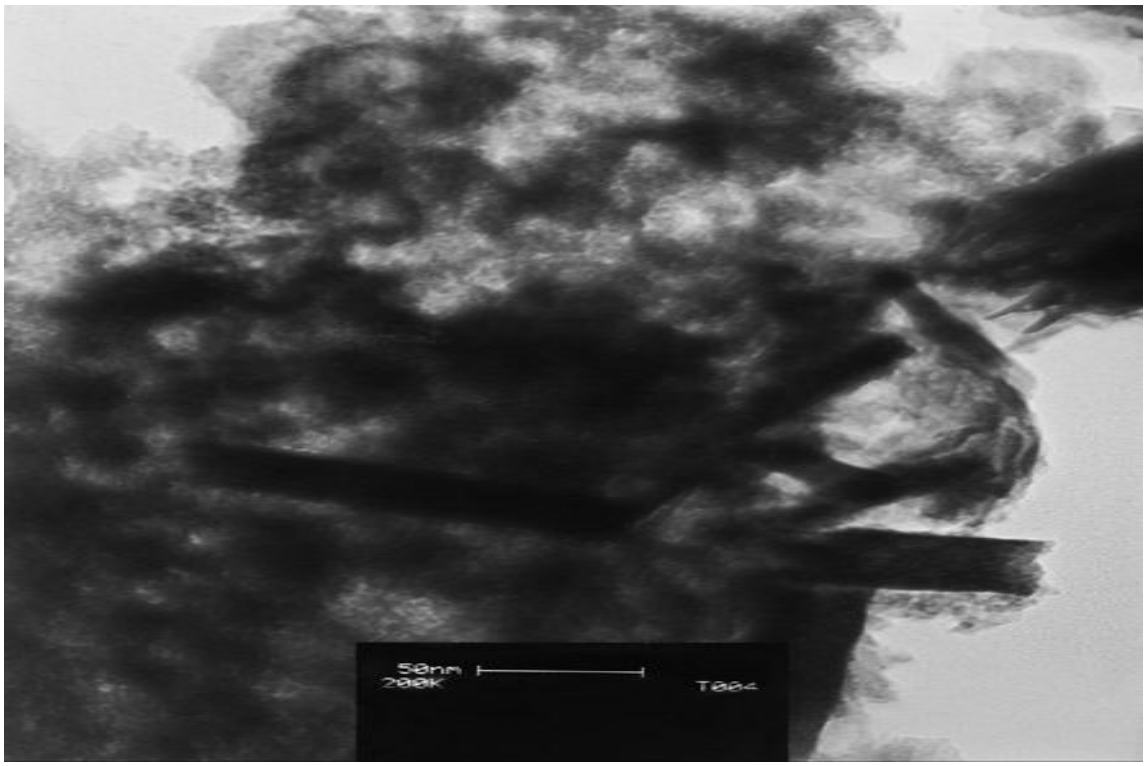


(a)

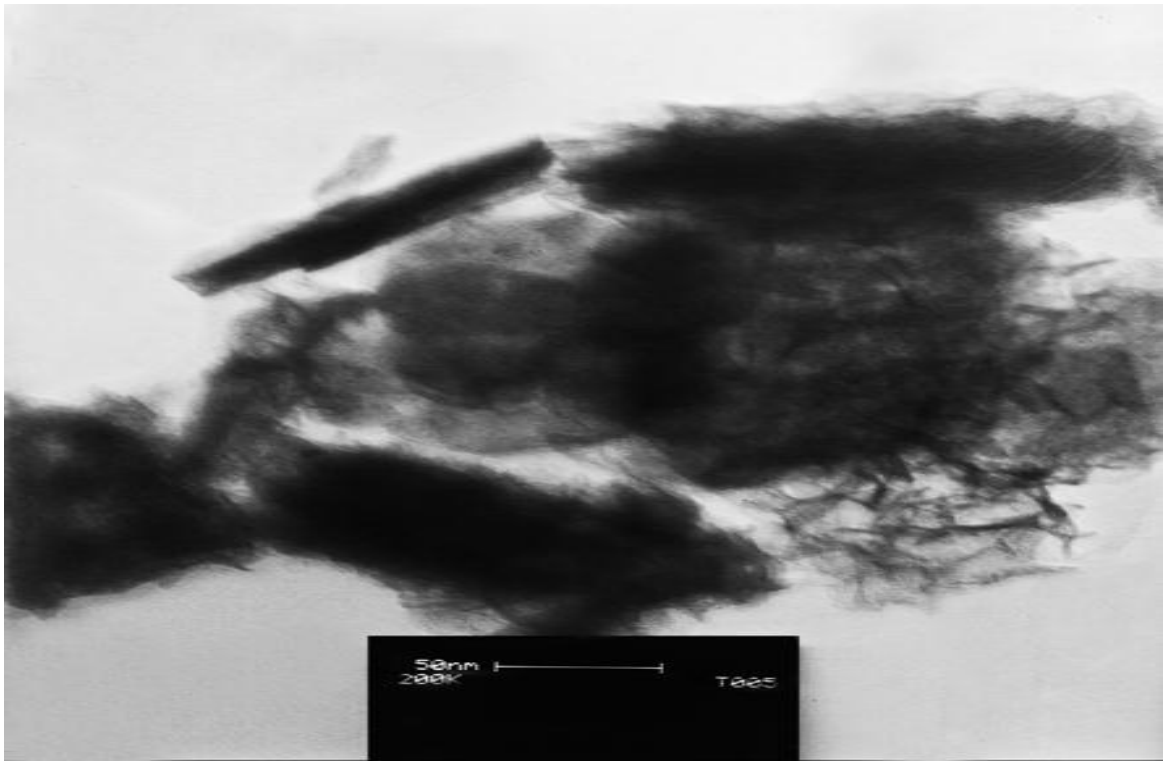


(b)

(c)

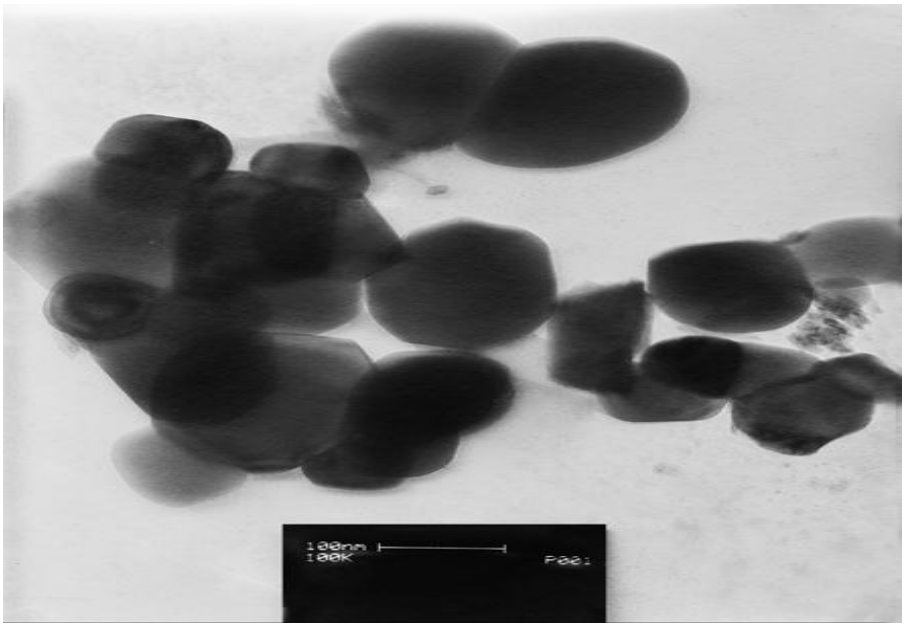


(d)

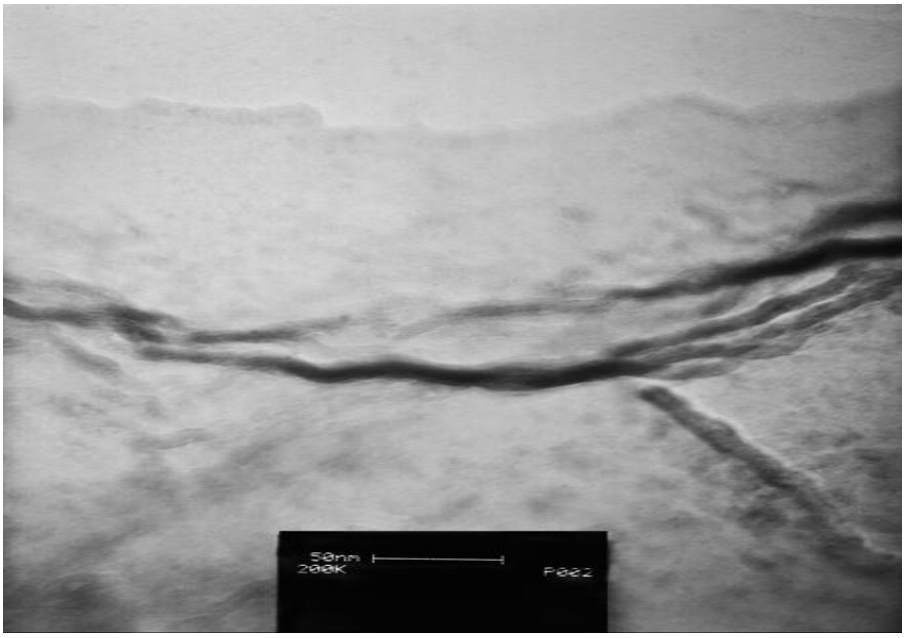


(e)

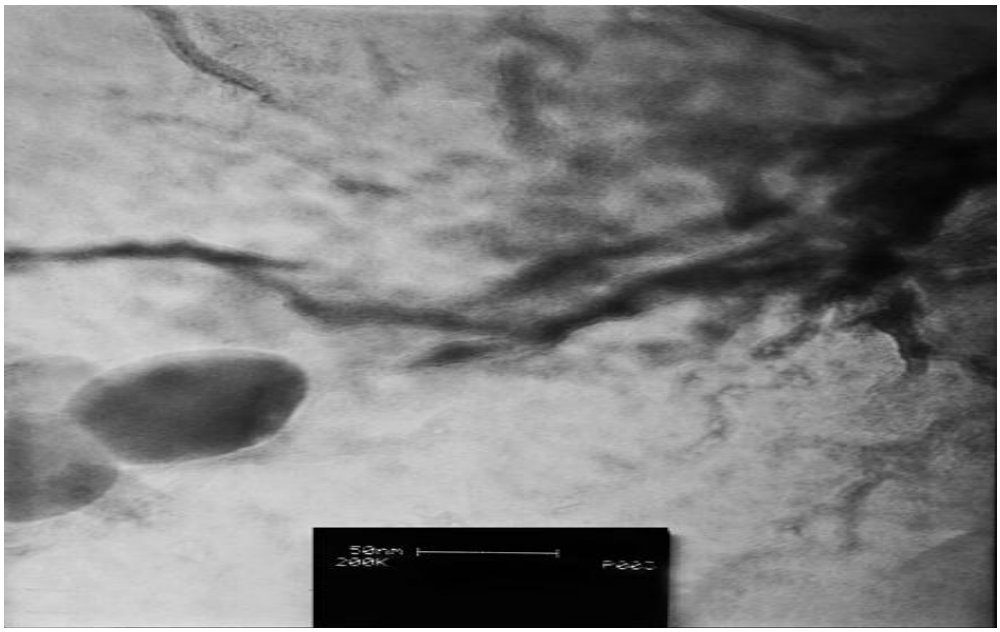
Fig. S10 TEM images of zinc - manganese oxides prepared at 300 ^{o}C (a-e).



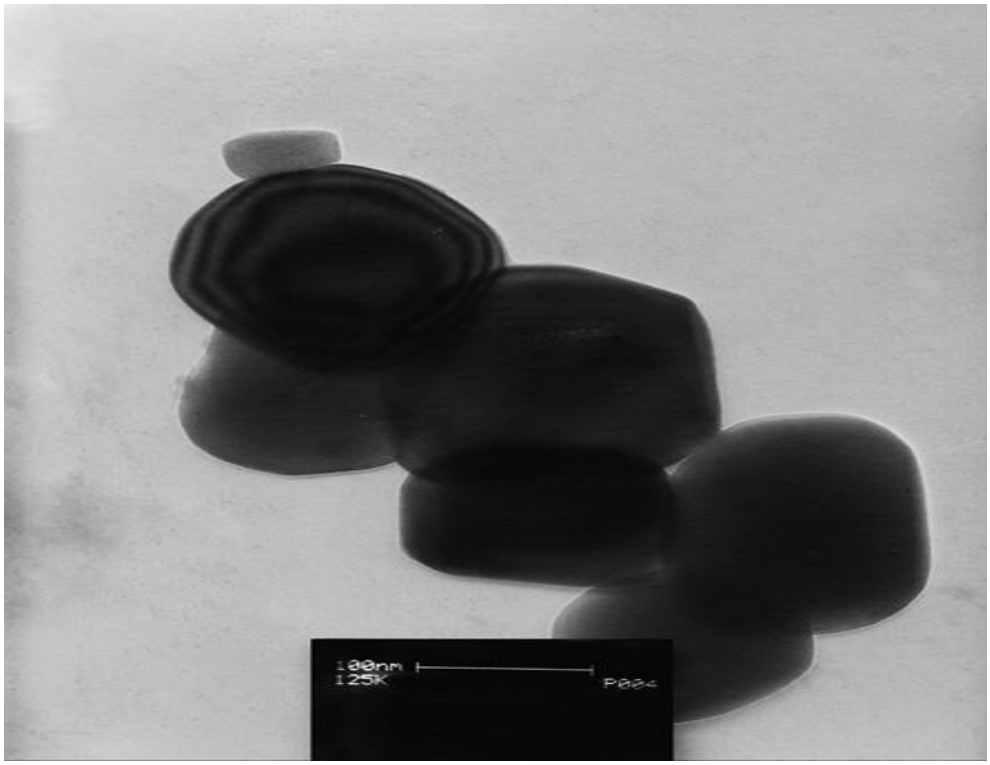
(a)



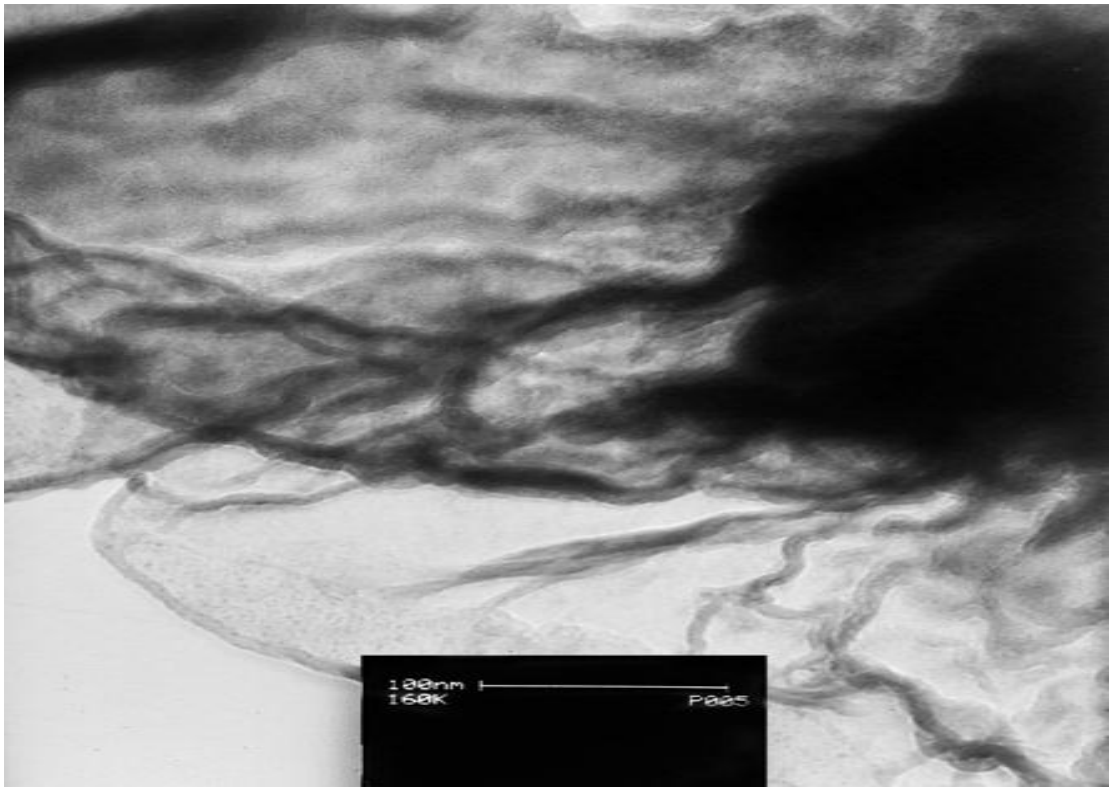
(b)



(c)

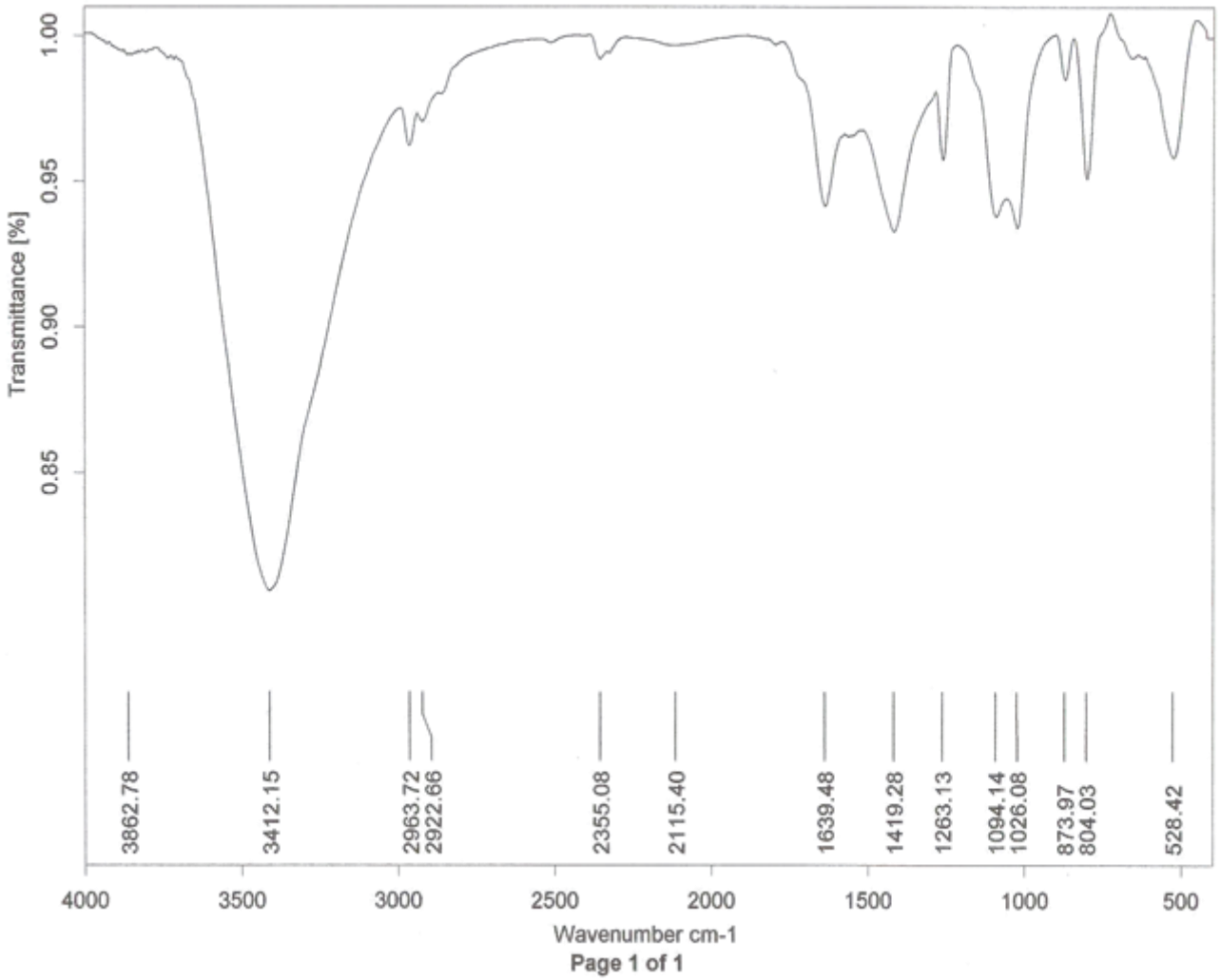


(d)

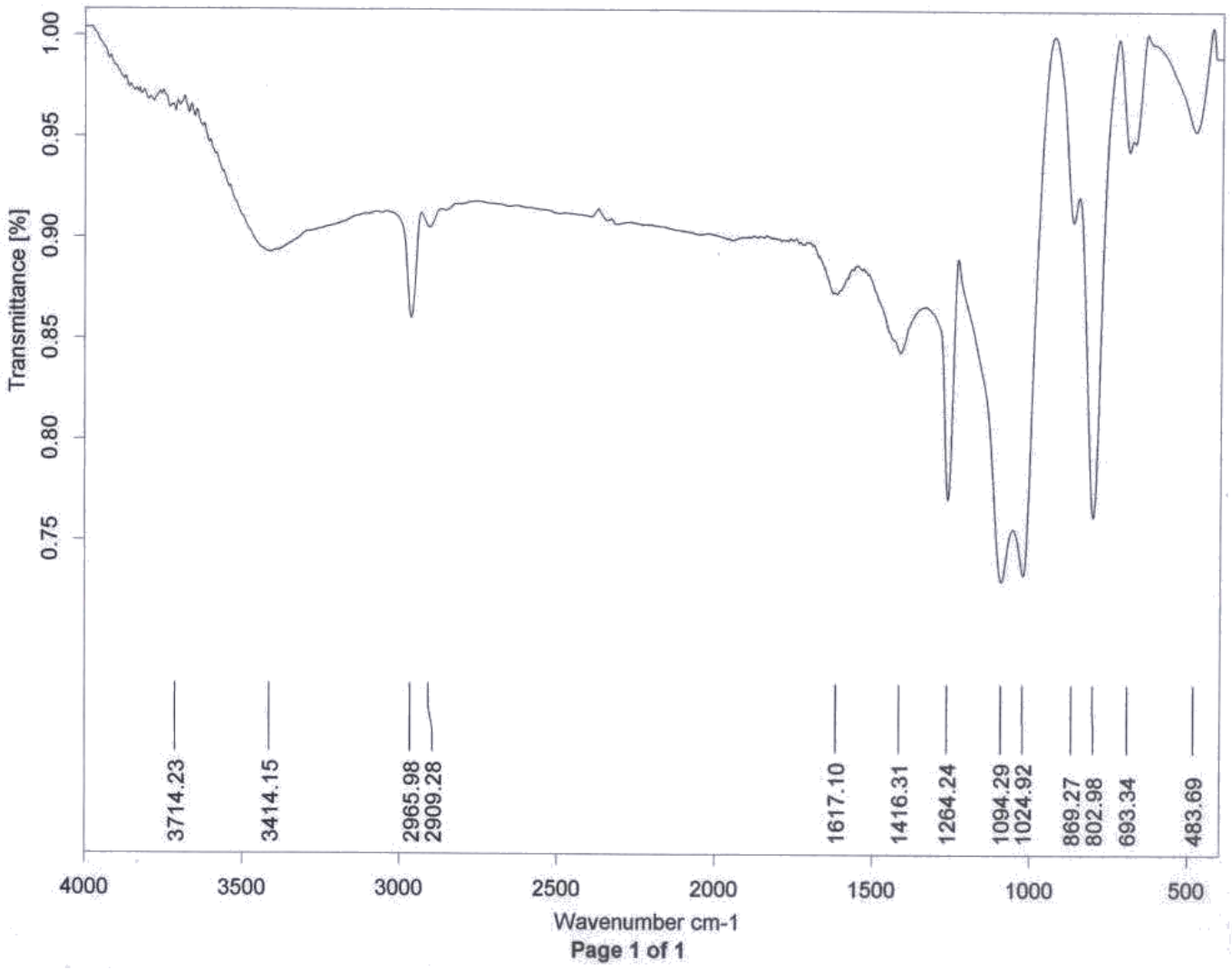


(e)

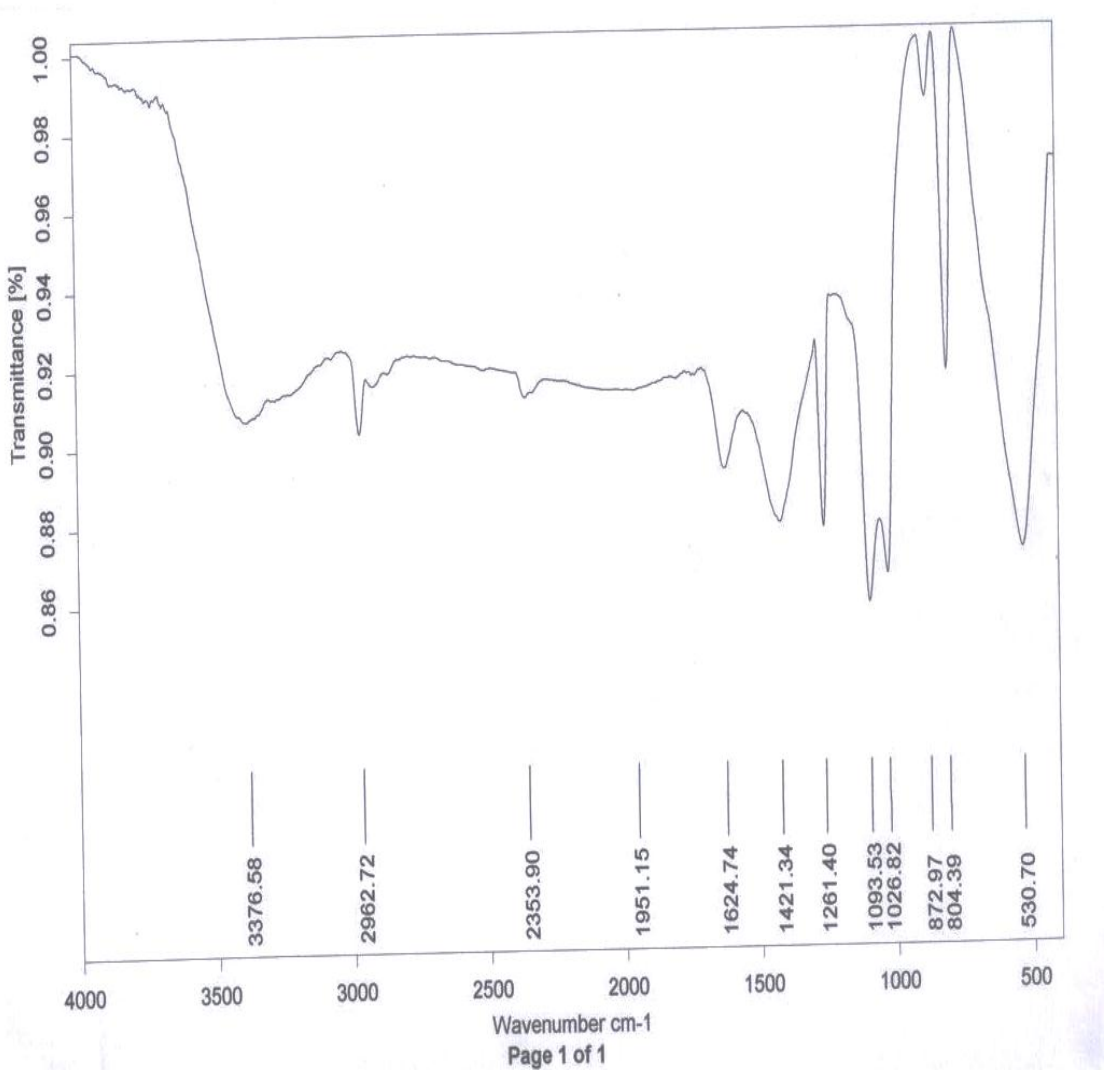
Fig. S11 TEM images of aluminium - manganese oxides prepared at 300 ^{o}C (a-e).



(a)


Transmittance [%]
1.00
0.95
0.90
0.85
0.80
0.75
3714.23
3414.15
2965.98
2909.28
1617.10
1416.31
1264.24
1094.29
1024.92
869.27
802.98
693.34
483.69
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
Page 1 of 1

(b)


Transmittance [%]
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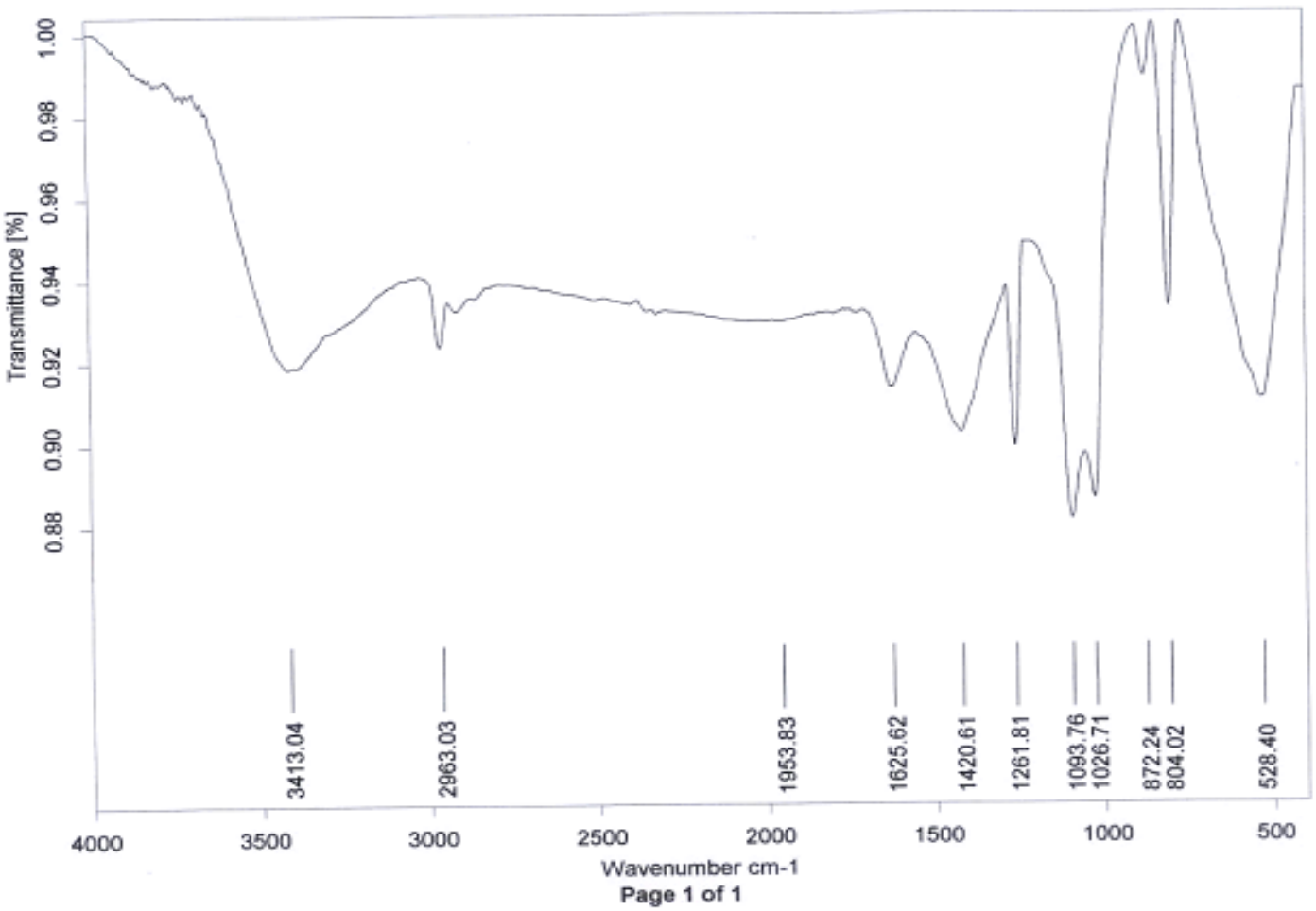
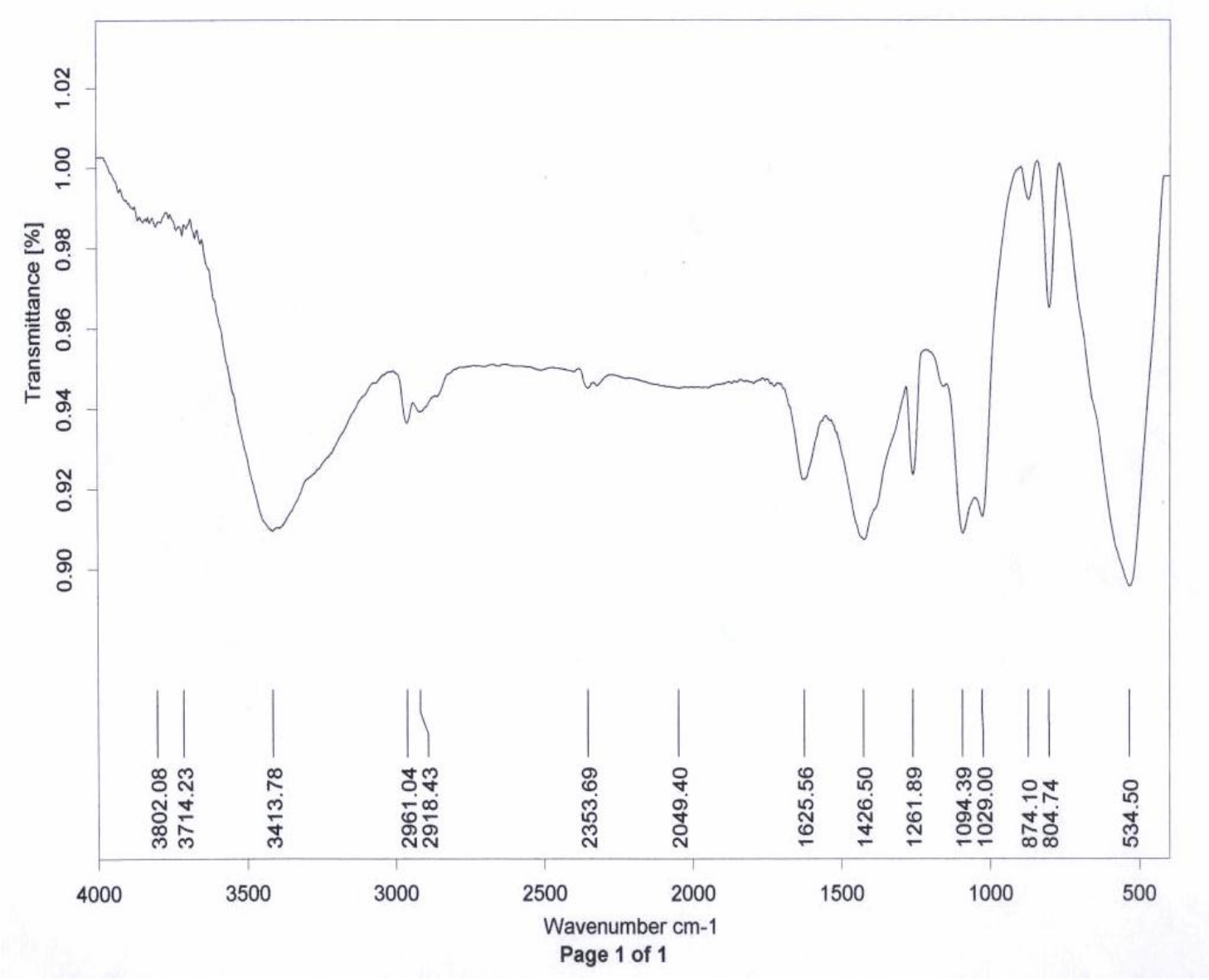
0.98
0.96
0.94
0.92
0.90
0.88
0.86
3376.58
2962.72
2353.90
1951.15
1624.74
1421.34
1261.40
1093.53
1026.82
872.97
804.39
530.70
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
Page 1 of 1

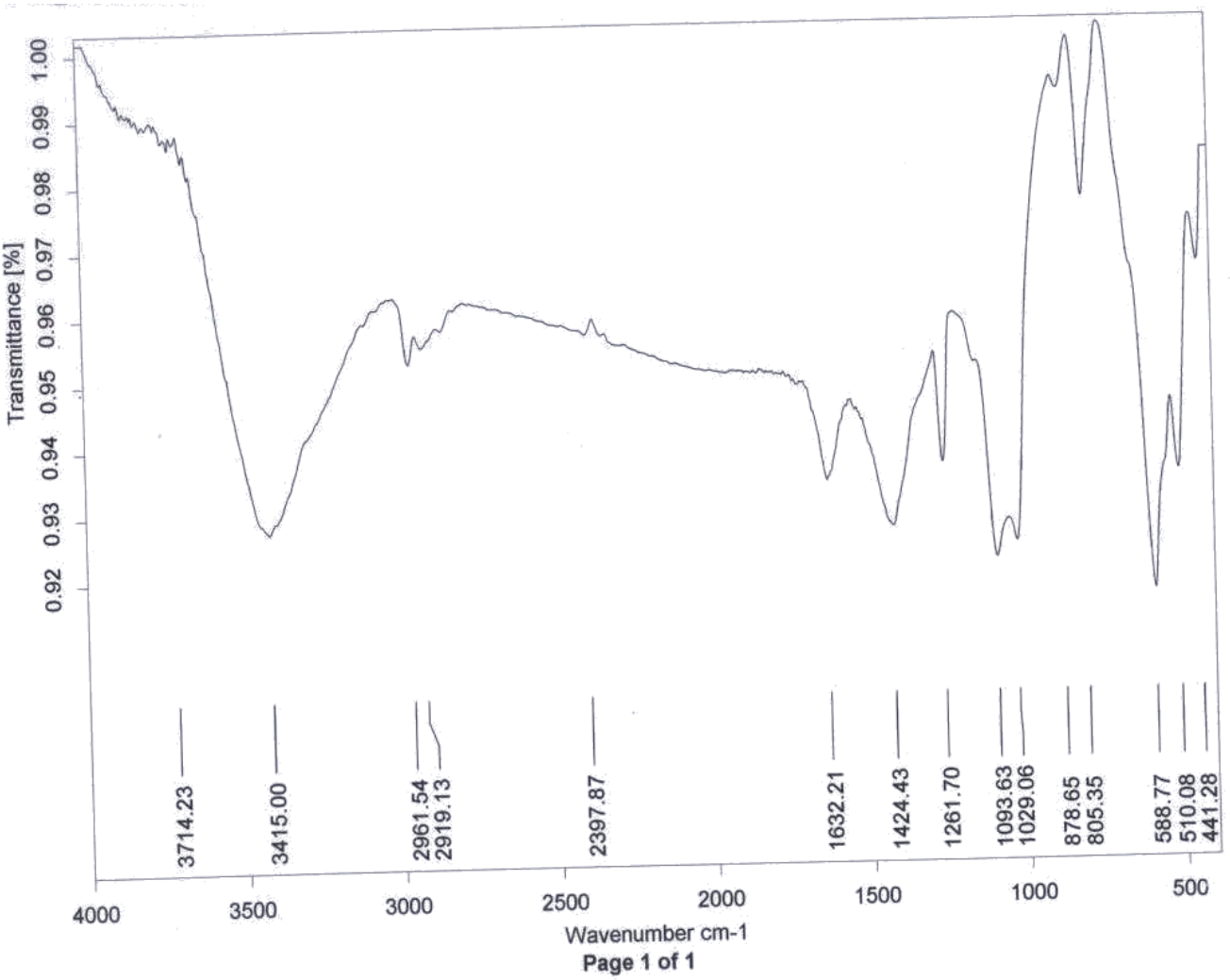
(c)



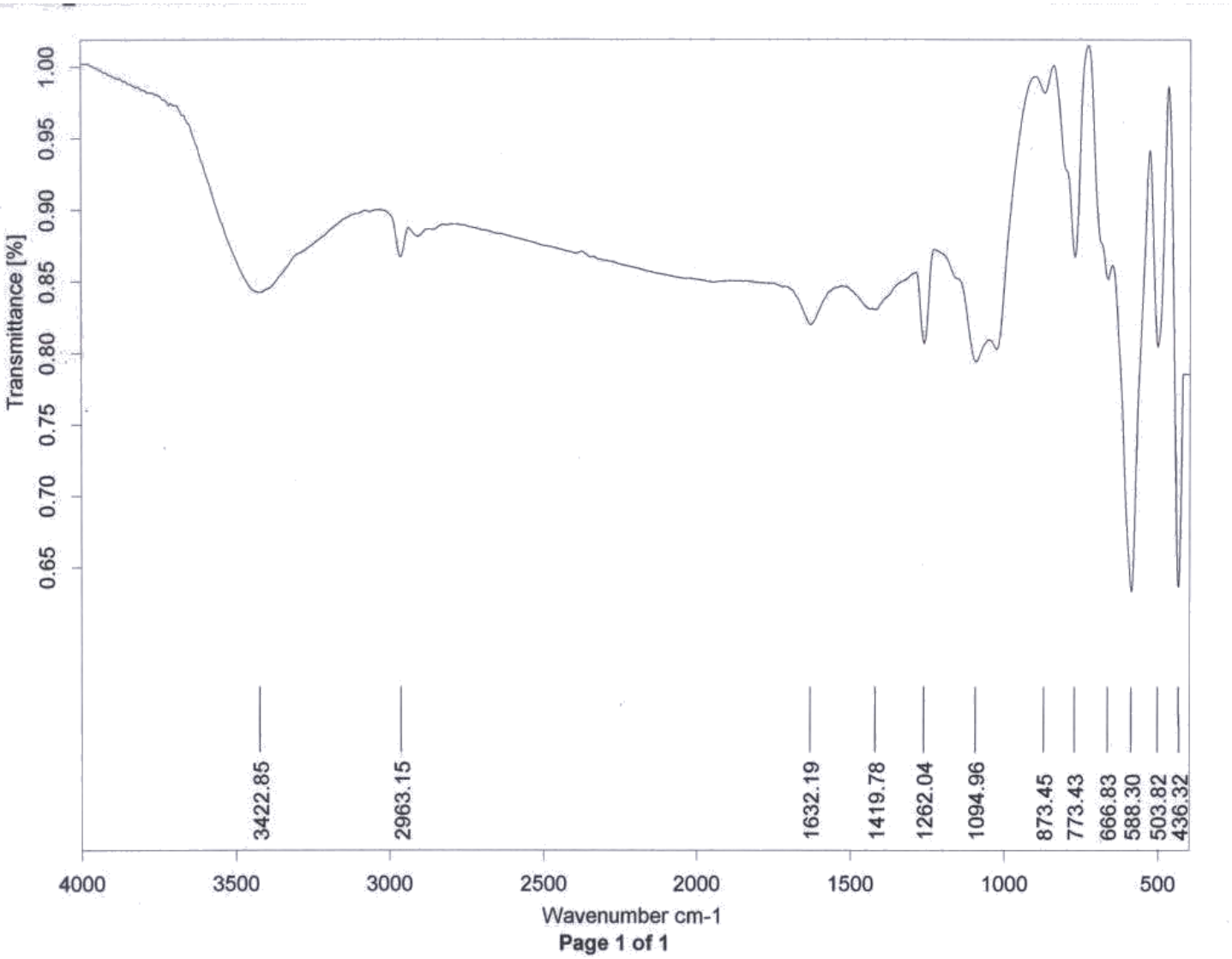
(d)


Transmittance [%]
0.90
0.92
0.94
0.96
0.98
1.00
1.02
3802.08
3714.23
3413.78
2961.04
2918.43
2353.69
2049.40
1625.56
1426.50
1261.89
1094.39
1029.00
874.10
804.74
534.50
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
Page 1 of 1

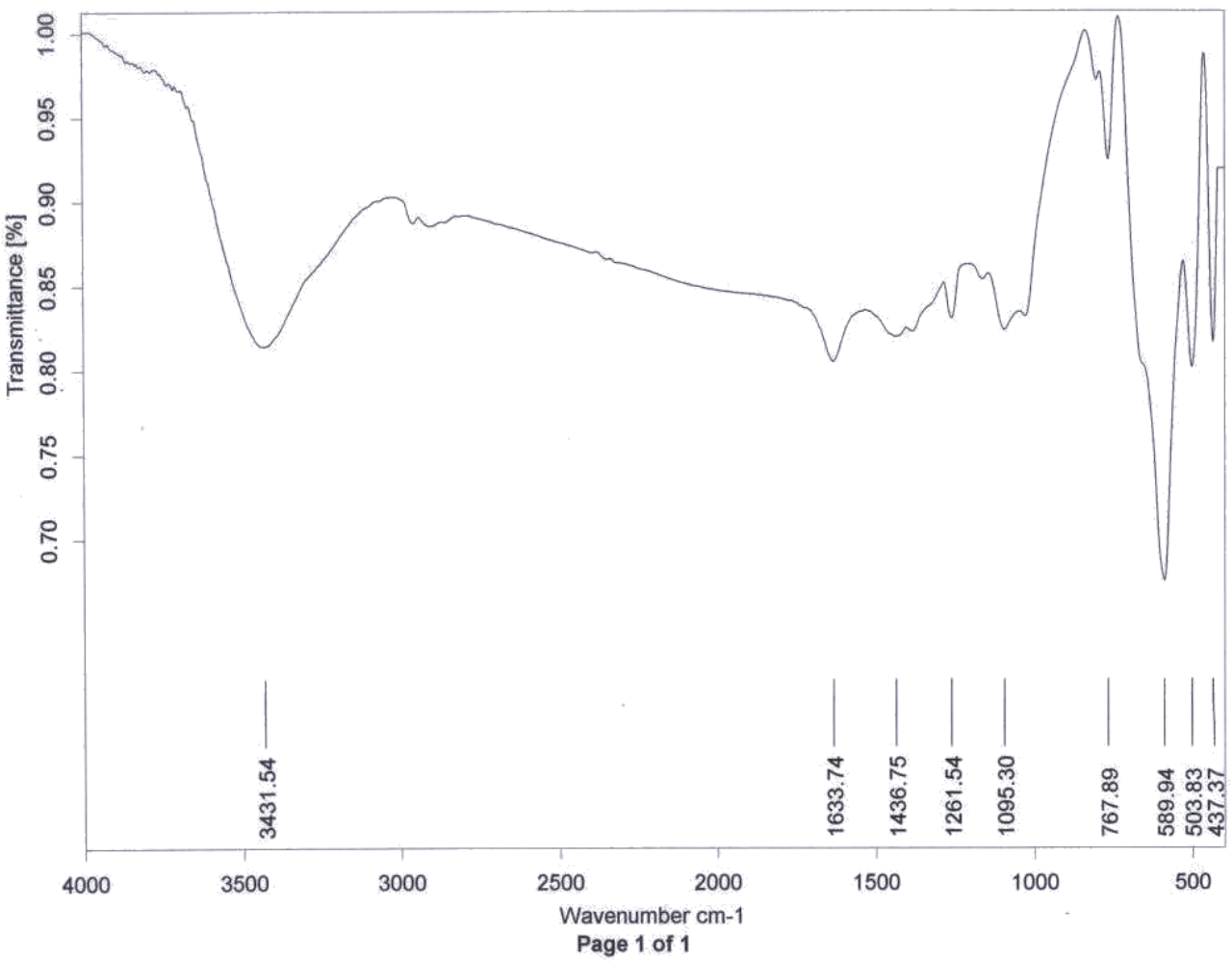
(e)



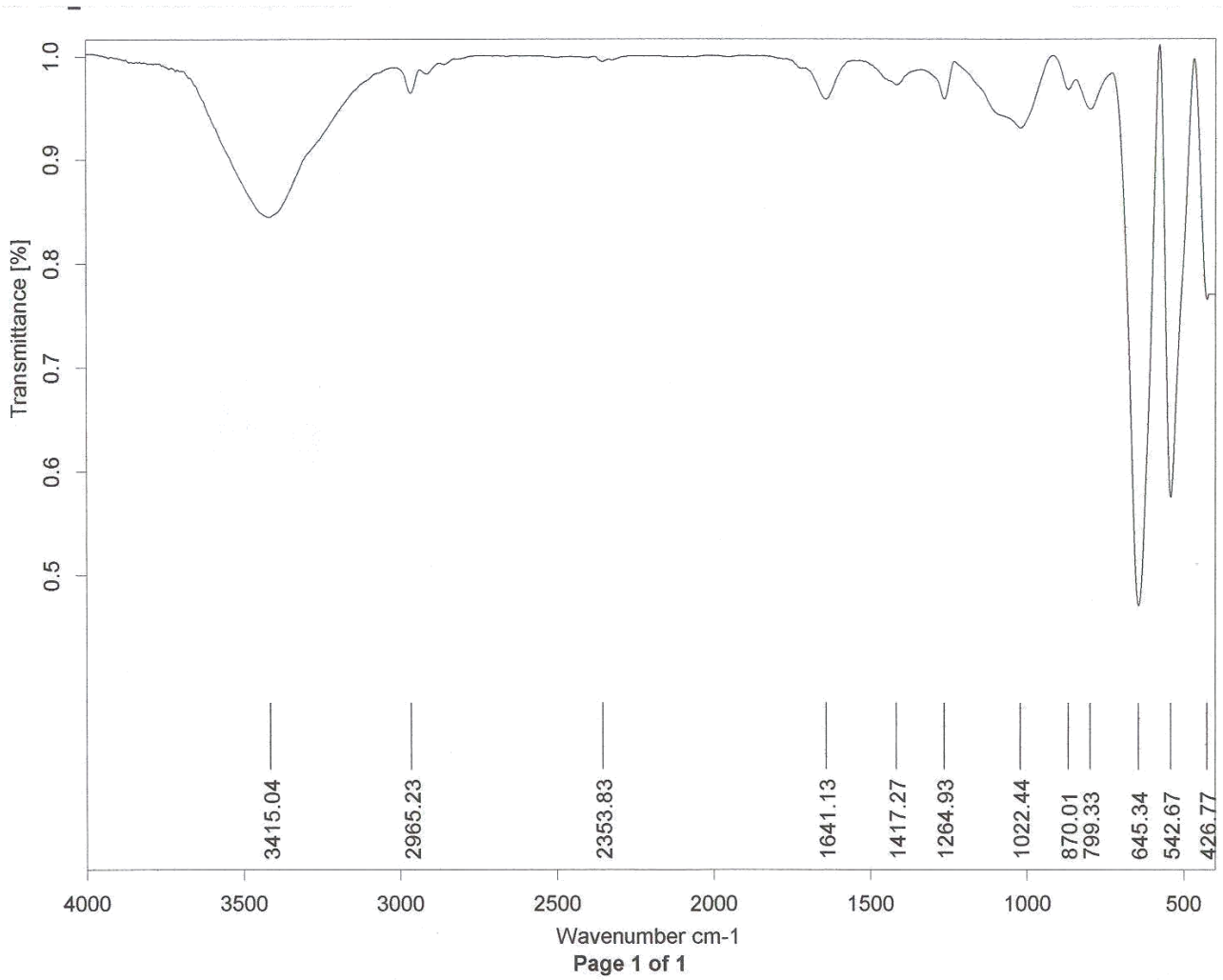
(f)



(g)

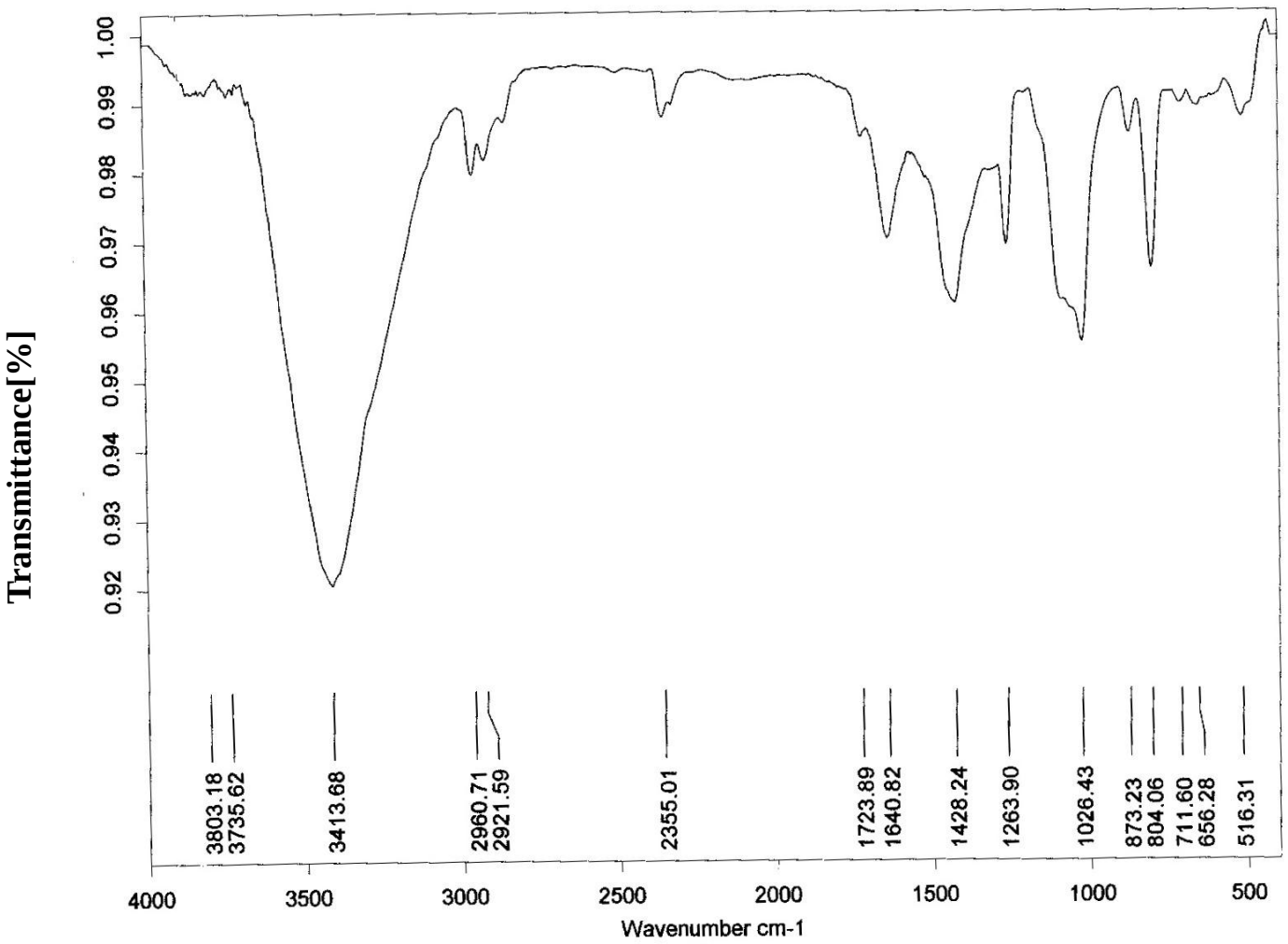


(h)

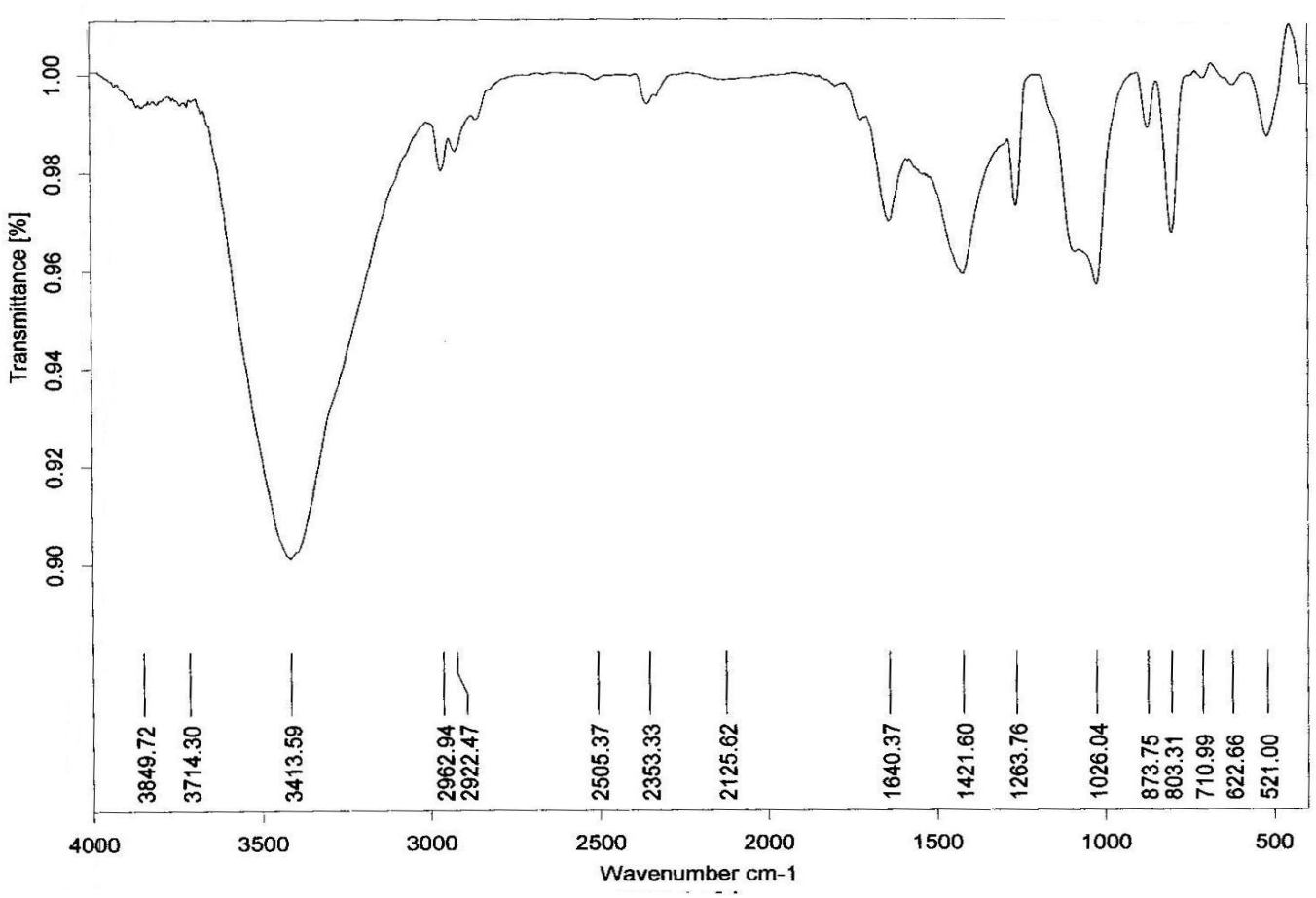


(k)

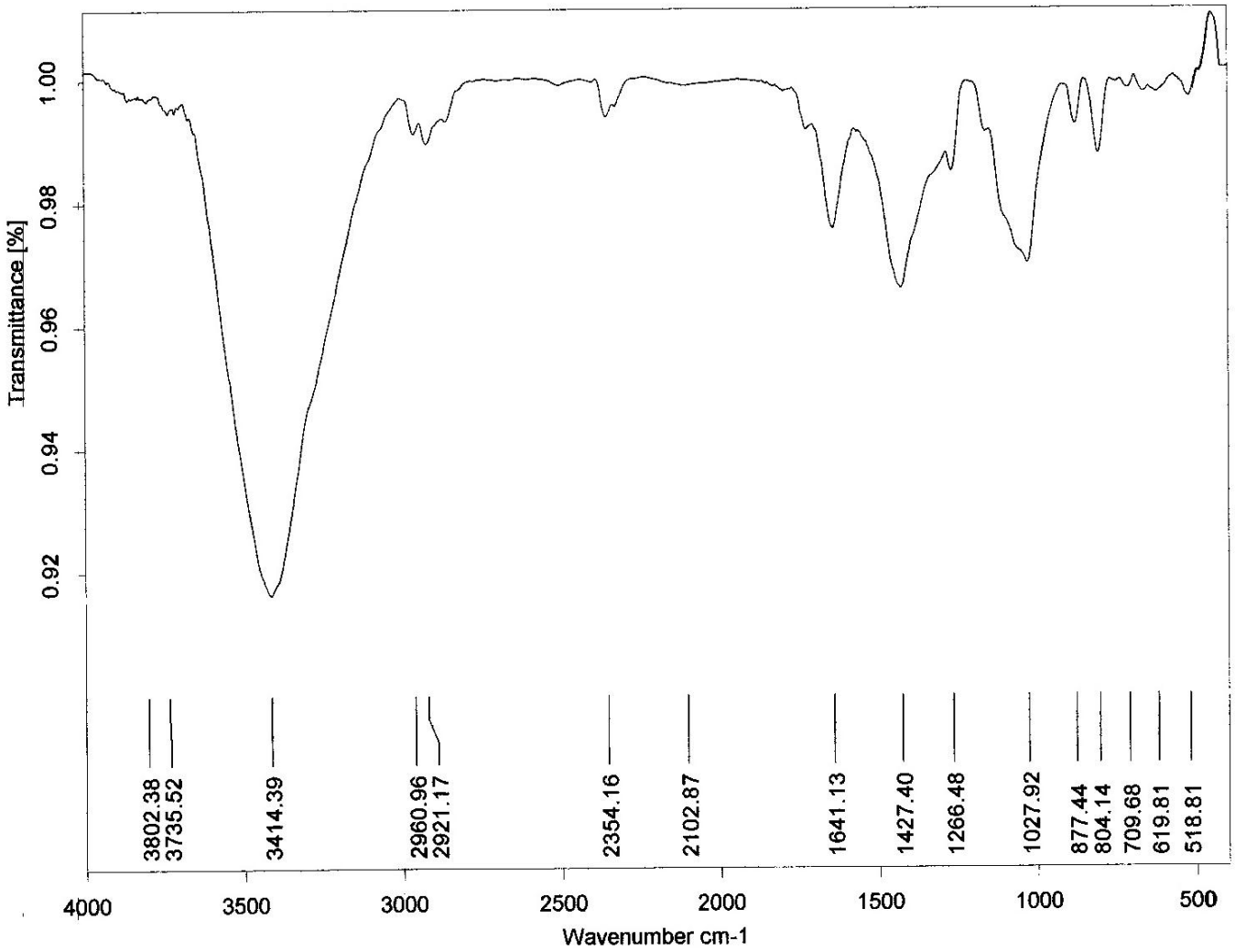
Fig. S12 FTIR spectra of zinc - manganese oxides prepared at 100 (a), 200 (b), 300 (c), 400 (d), 450 (e), 550 (f), 600 (g), 750 (h) and 1000 (k) ^{o}C.



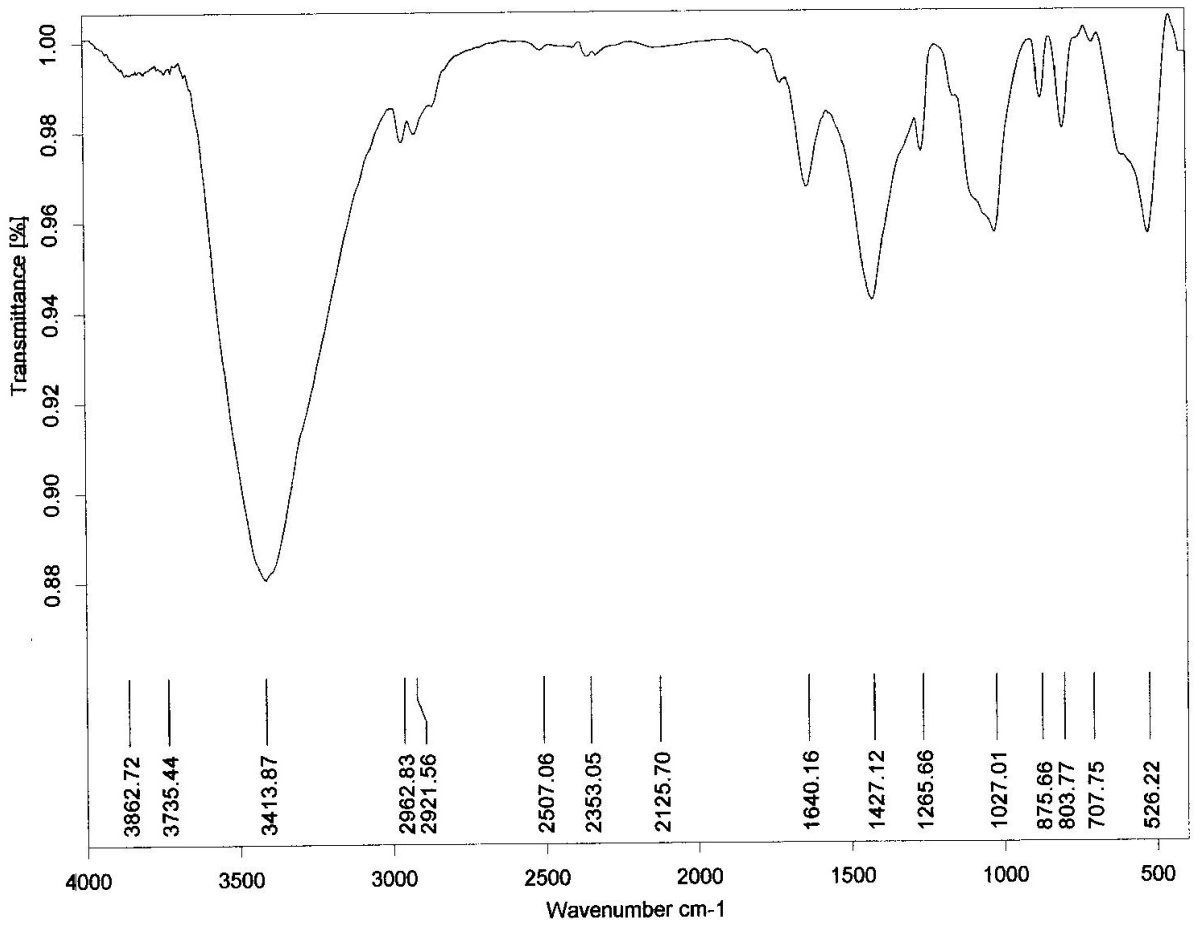
(a)



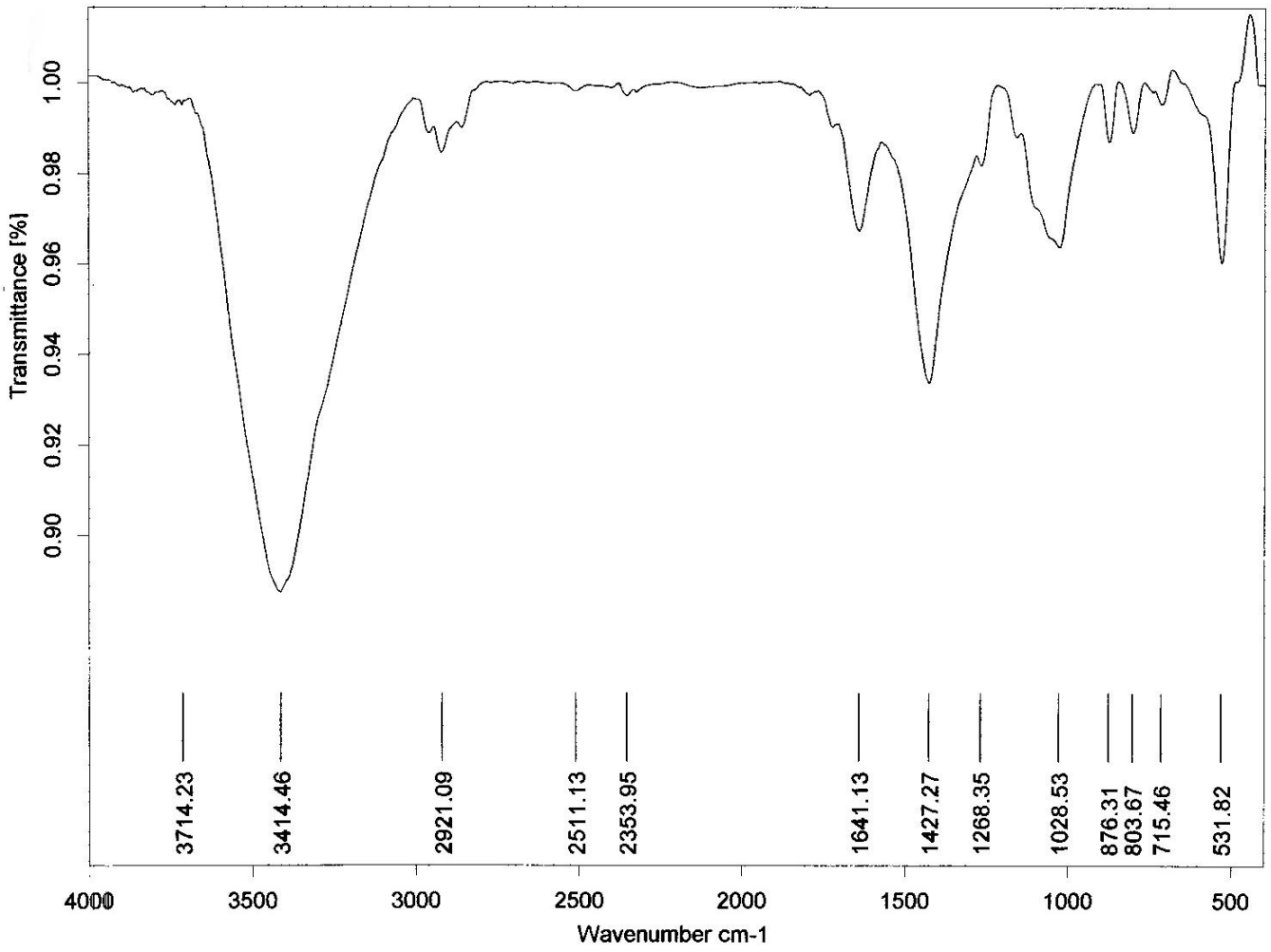
(b)


Transmittance [%]
1.00
0.98
0.96
0.94
0.92
3802.38
3735.52
3414.39
2960.96
2921.17
2354.16
2102.87
1641.13
1427.40
1266.48
1027.92
877.44
804.14
709.68
619.81
518.81
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

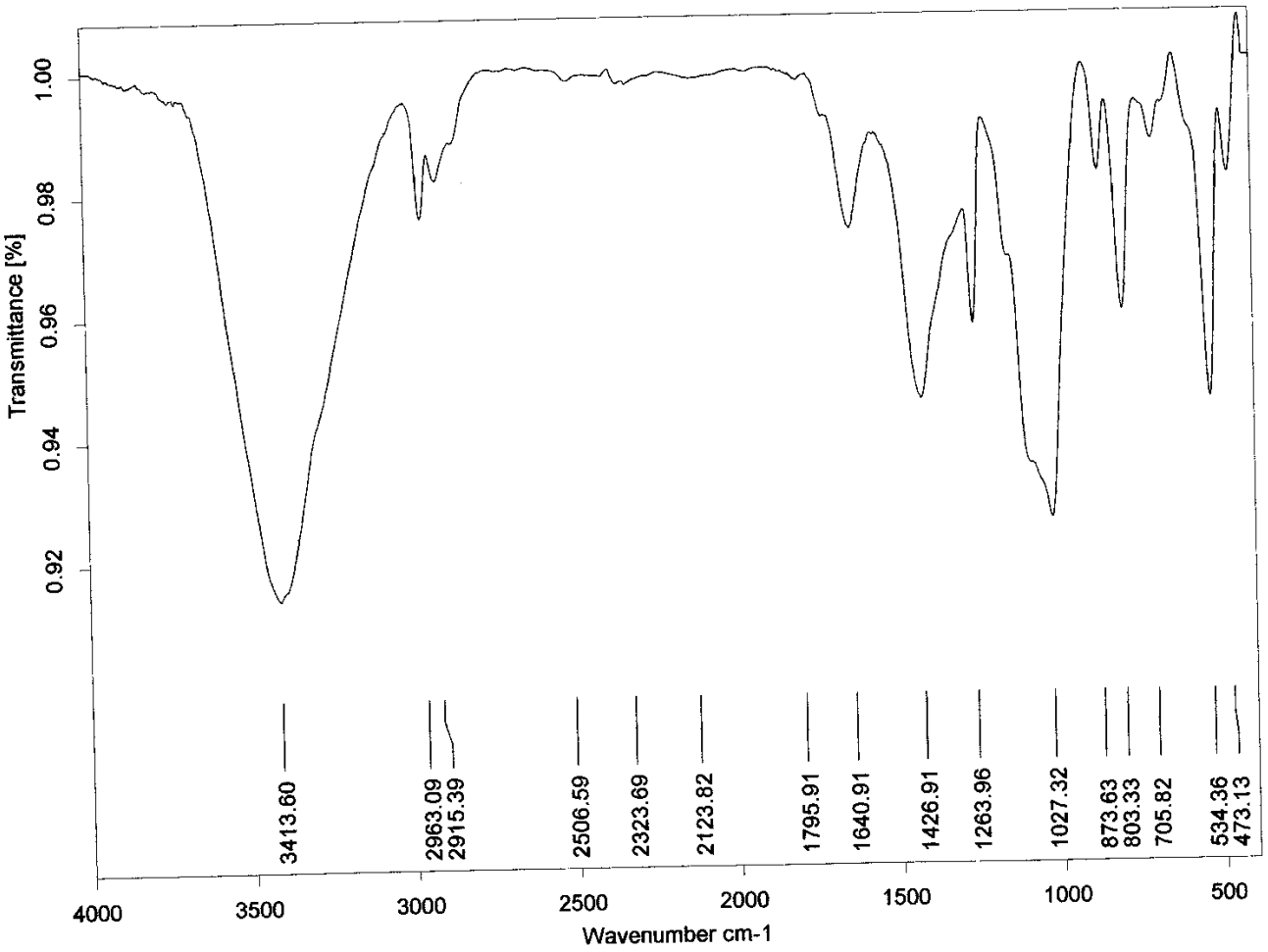
(c)



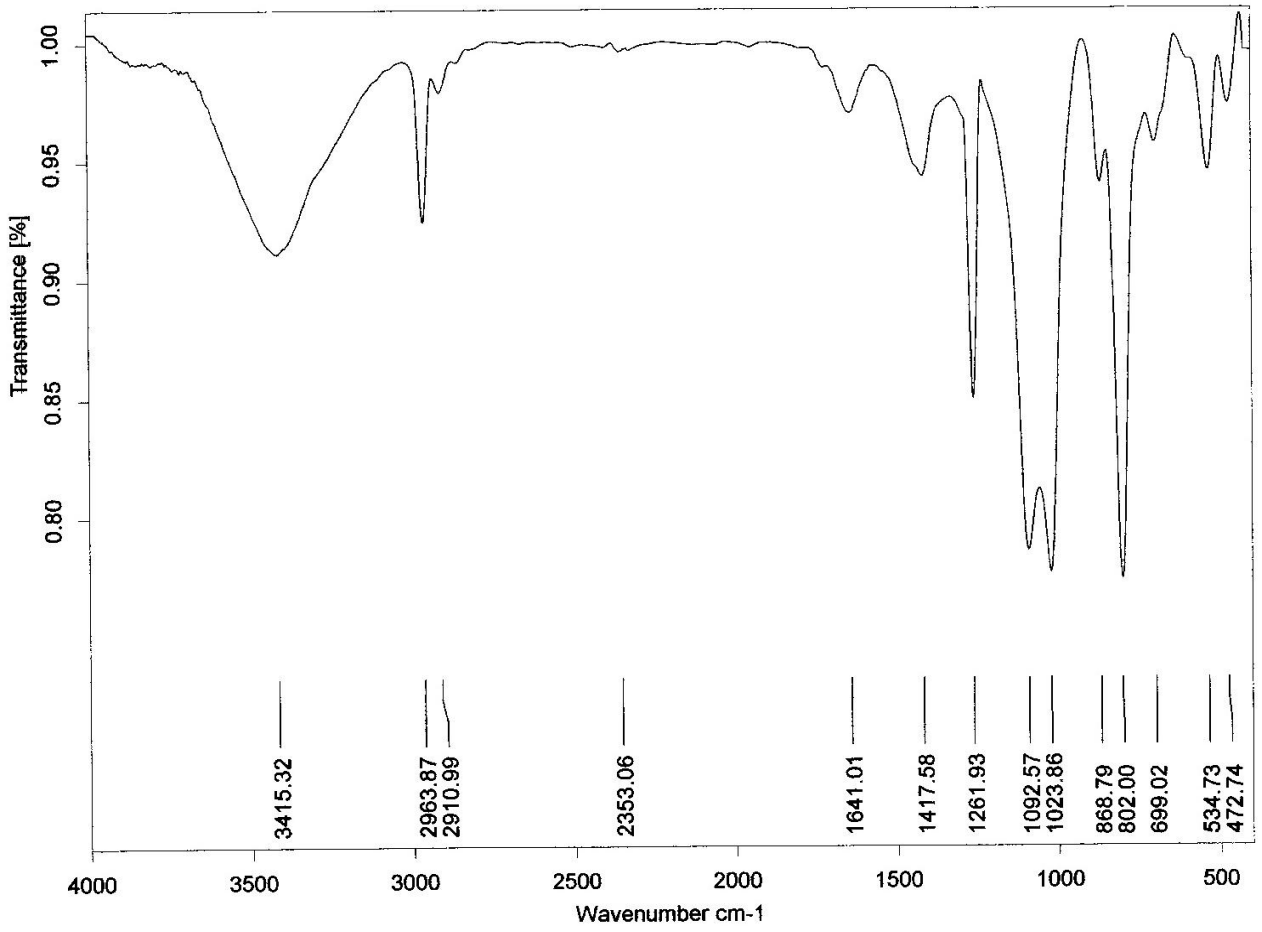
(d)



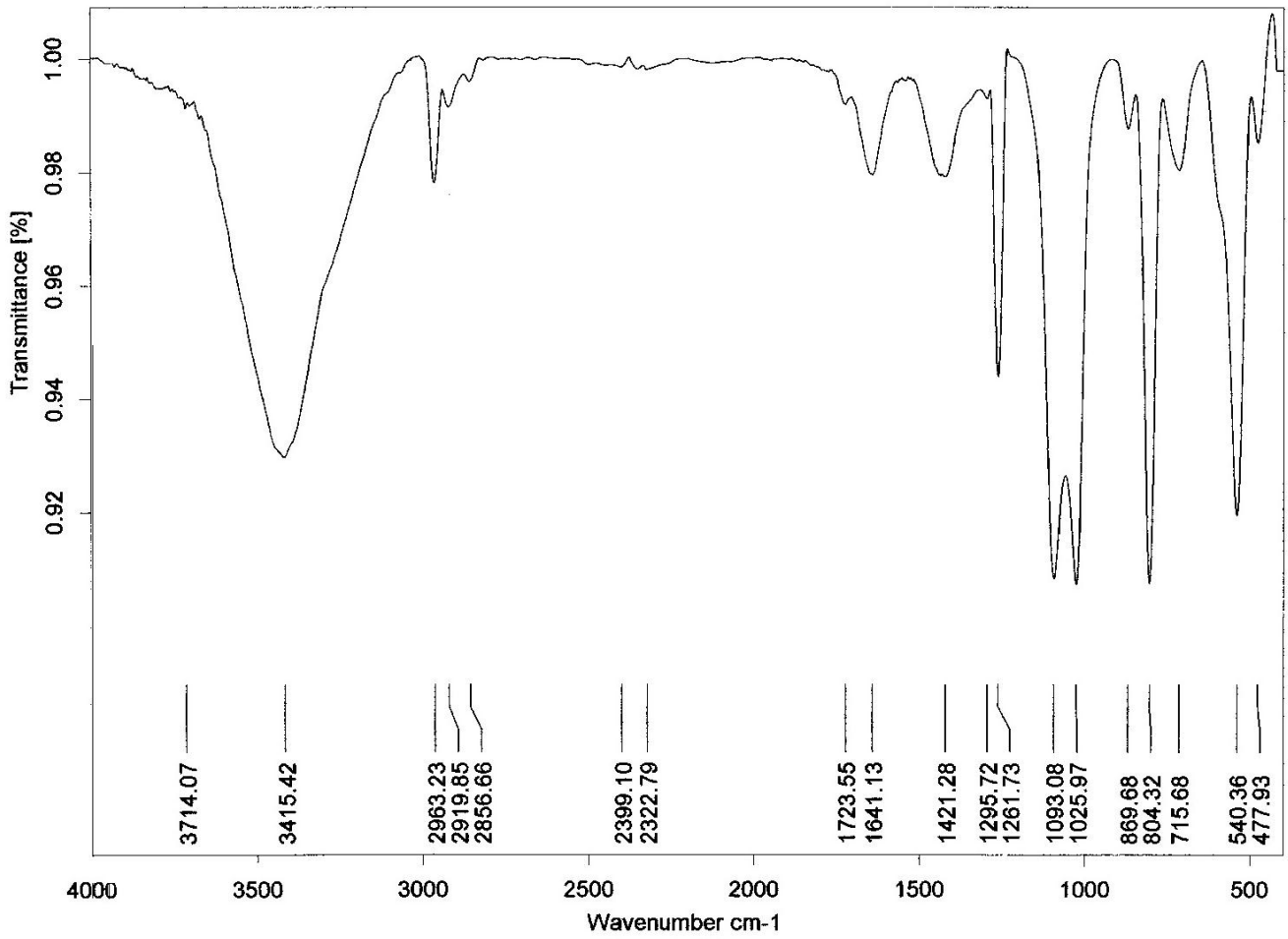
(e)


Transmittance [%]
1.00
0.98
0.96
0.94
0.92
3413.60
2963.09
2915.39
2506.59
2323.69
2123.82
1795.91
1640.91
1426.91
1263.96
1027.32
873.63
803.33
705.82
534.36
473.13
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

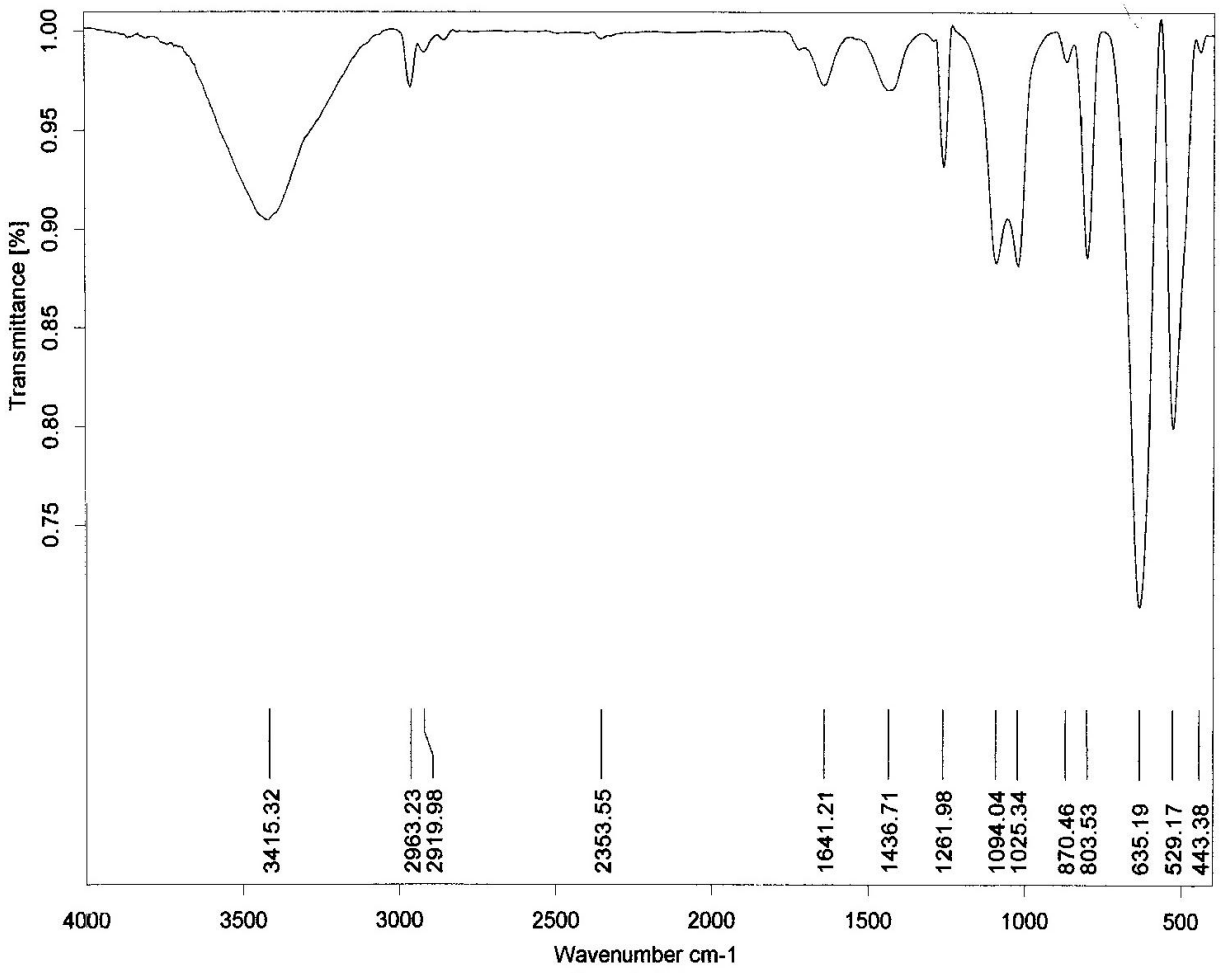
(f)



(g)

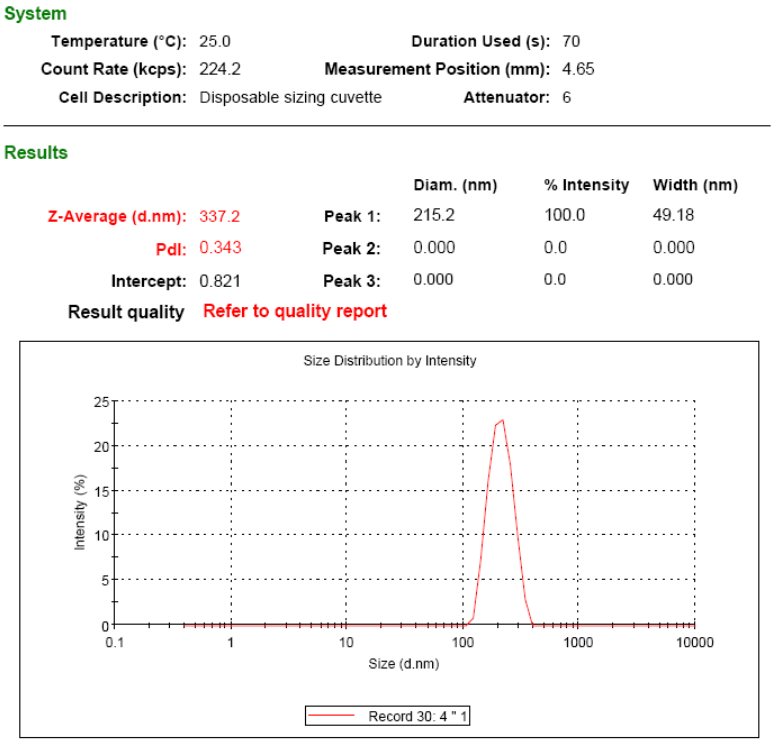


(h)

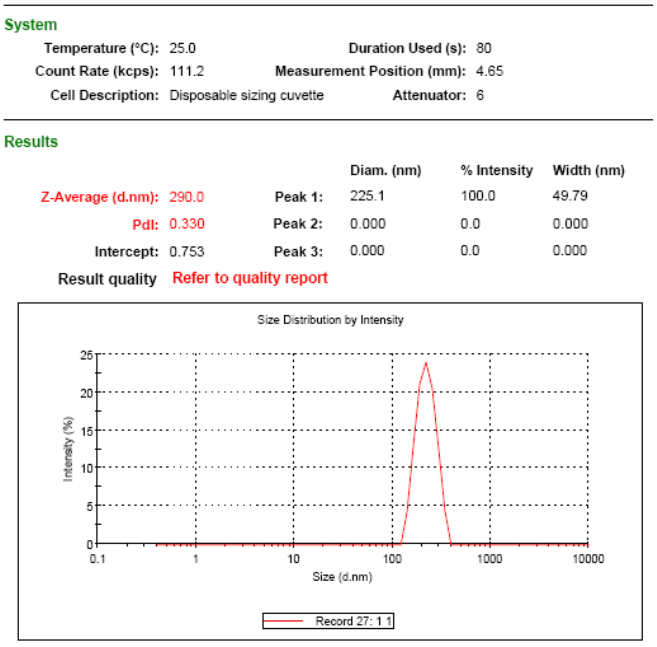


(k)

Fig. S13 FTIR spectra of aluminium - manganese oxides prepared at 100 (a), 200 (b), 300 (c), 400 (d), 450 (e), 550 (f), 600 (g), 750 (h) and 1000 (k) ^{o}C.



(a)



(b)

Fig. S14 DLS results for aluminium (a) or zinc (b) - manganese oxides prepared at 300 ^{o}C.

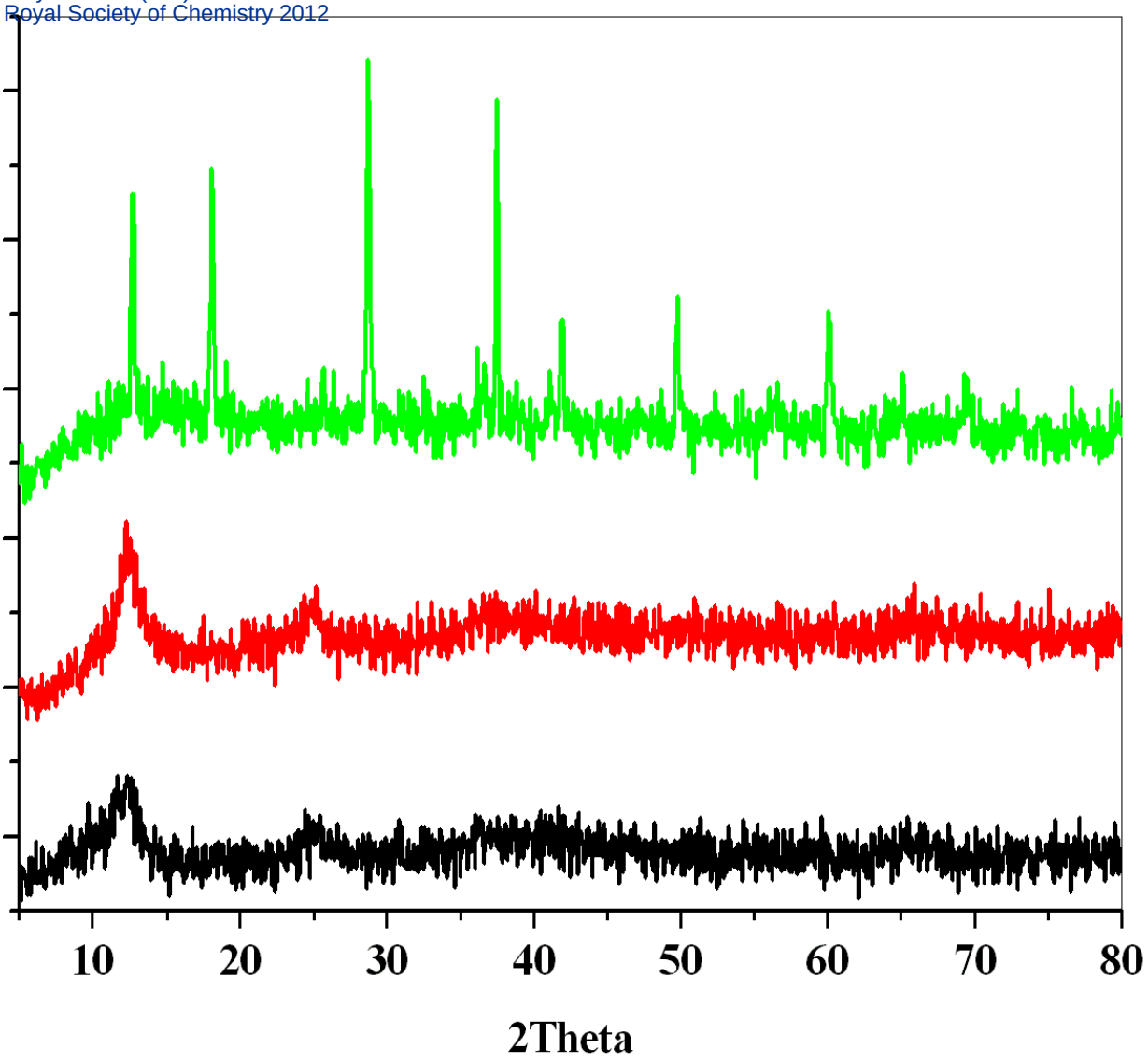


Fig. S15 **XRD patterns of the obtained nano-sized layered aluminium - manganese oxides prepared at 100 (black), 300 (red) and 750 (green) ^{o}C.**

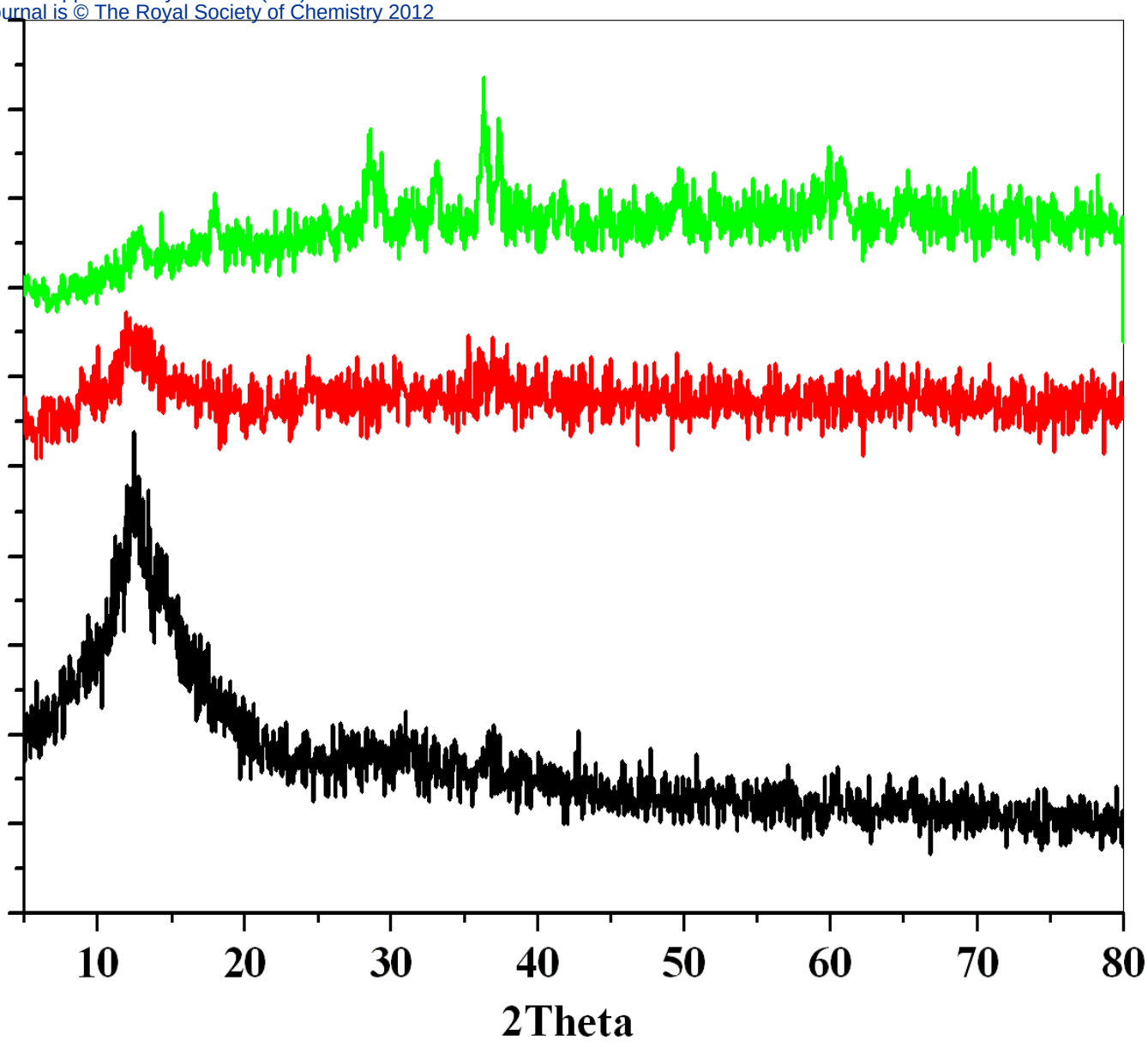


Fig. S16 **XRD patterns of the obtained nano-sized layered zinc - manganese oxides prepared at 100 (black), 300 (red) and 700 (green) ^{o}C.**