

# Electronic Supplementary Information

## Water oxidation by manganese oxides, a new step towards a complete picture: Simplicity is the ultimate sophistication

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### Table of Contents

	Page
<b>The reactor set-up for oxygen evolution experiment</b>	2
<b>The XRD patterns</b>	3-6
<b>SEM Images</b>	7-20
<b>TEM Images</b>	21-23

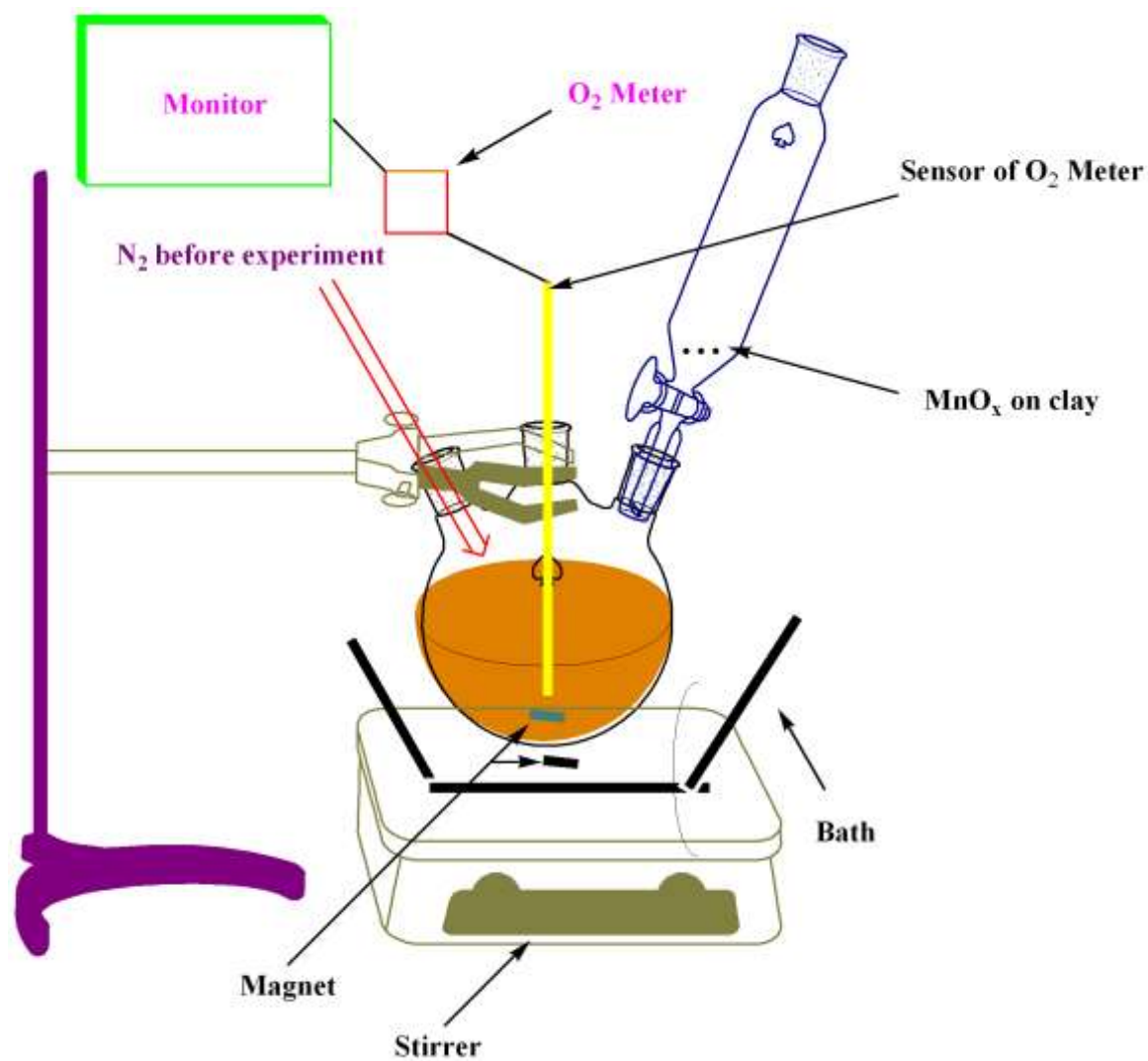


Figure S1. The reactor set-up for oxygen evolution experiment in the presence of Ce(IV).

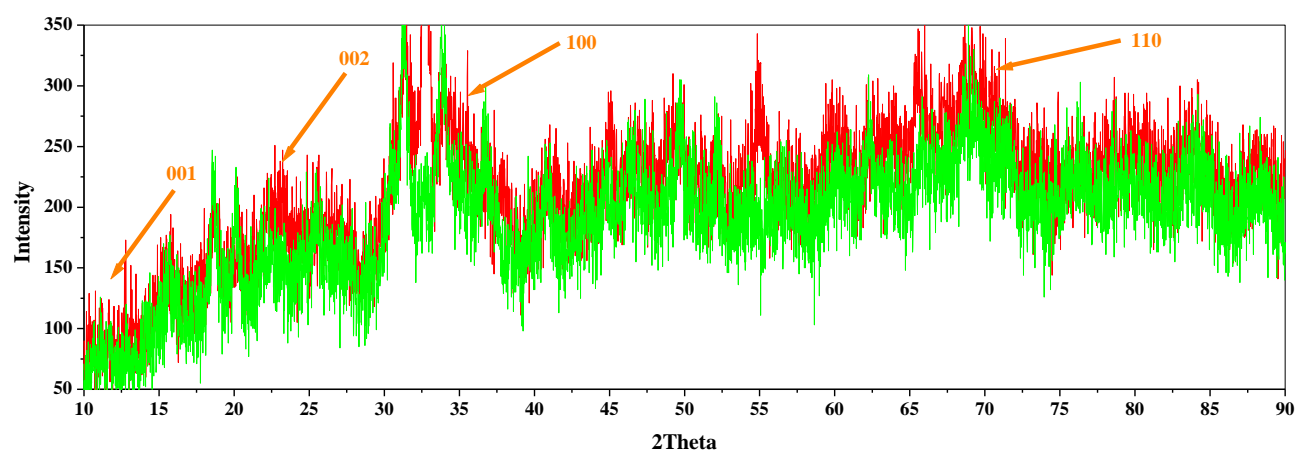


Figure S2. The XRD patterns show that both Mn<sub>2</sub>O<sub>3</sub> and CaMn<sub>3</sub>O<sub>6</sub> compounds after reaction with Ce(IV) convert to the same compound with layered structure.

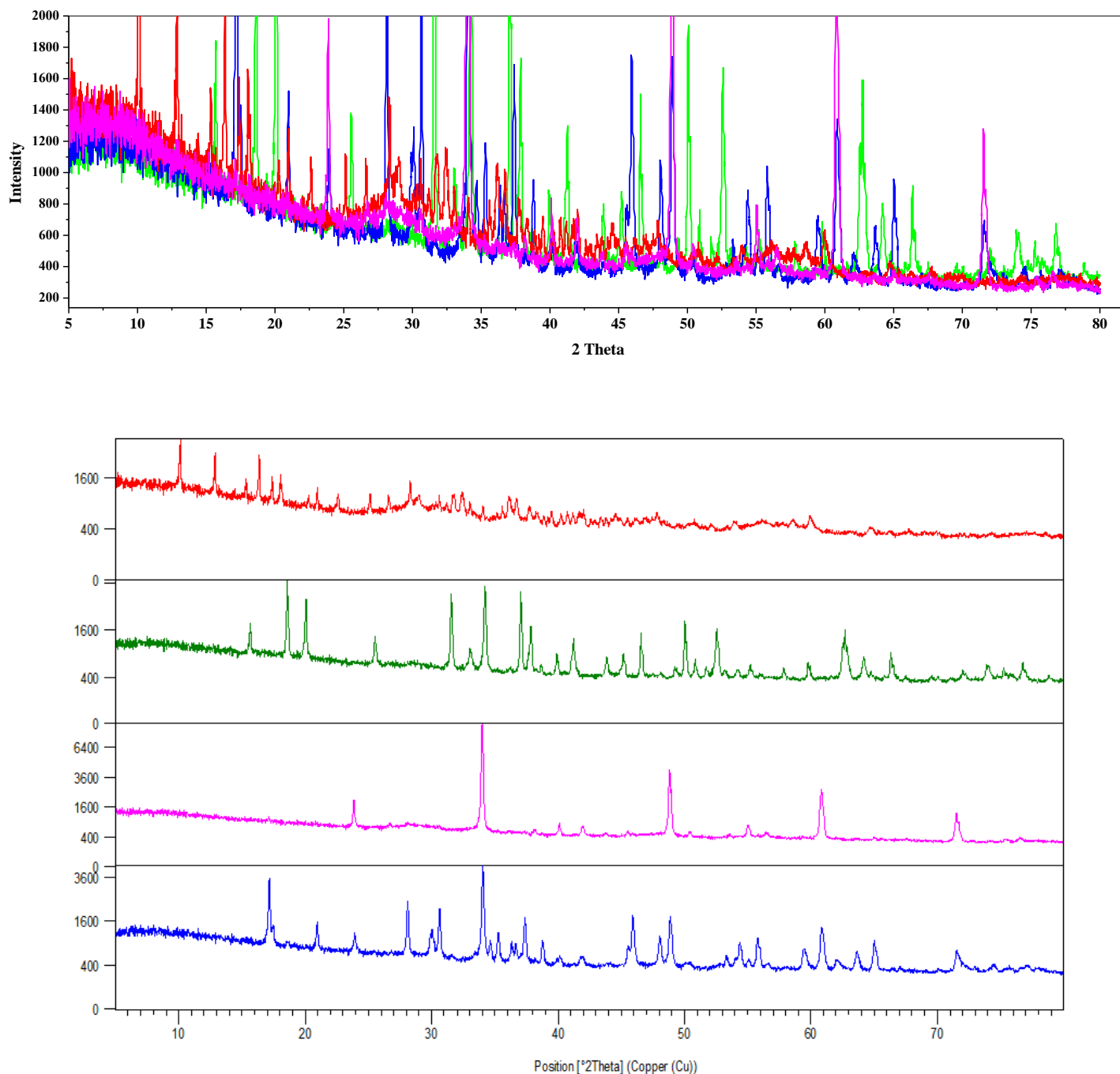
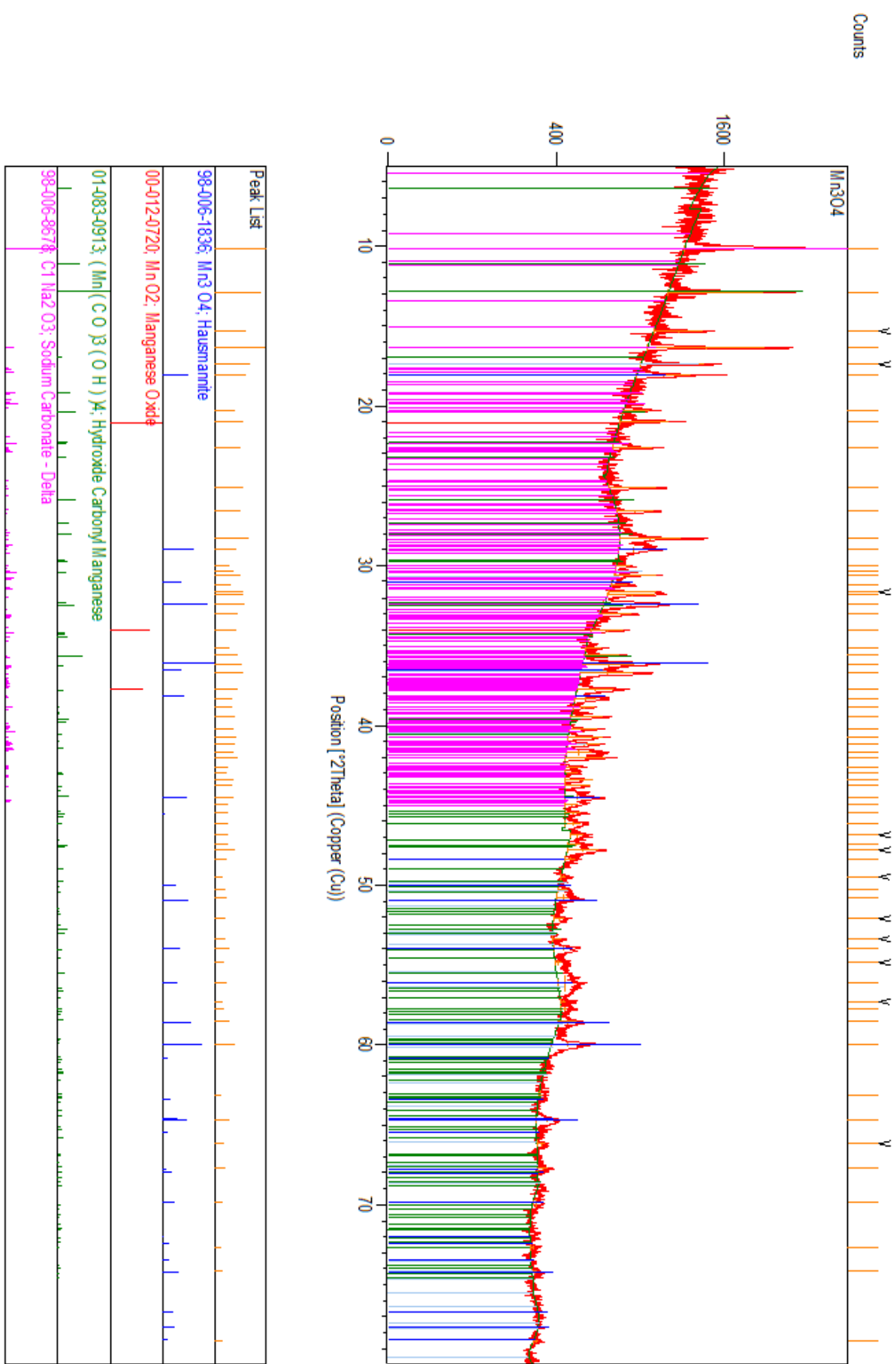
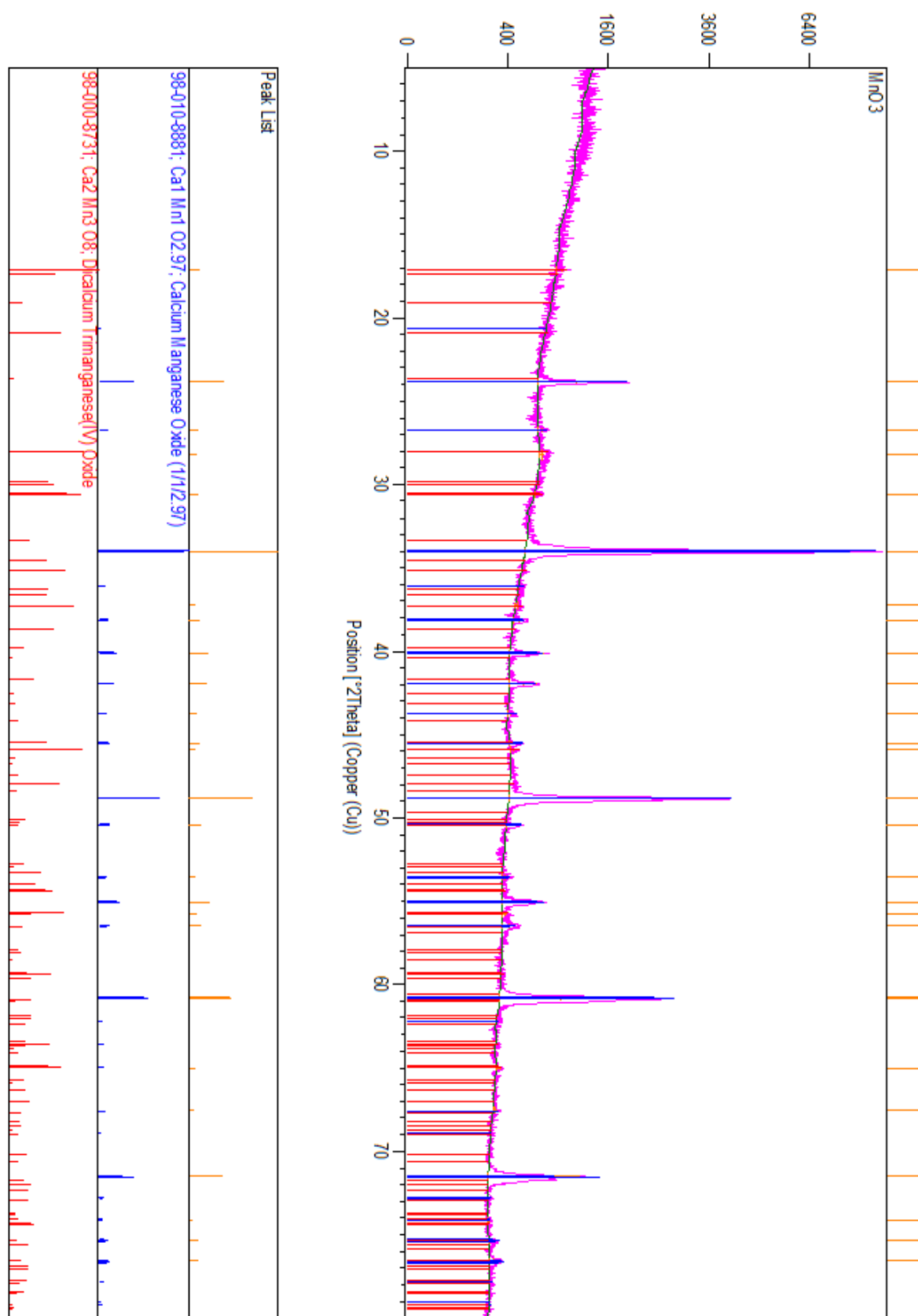


Figure S3. XRD patterns obtained from Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> (blue), CaMnO<sub>3</sub> (pink), CaMn<sub>4</sub>O<sub>8</sub> (green) and Mn<sub>3</sub>O<sub>4</sub> (red) after reaction by Ce(IV) (1.8 M, one months) by FFT method. FFT Filter Smoothing is a signal processing technique typically used to remove noise from signals. For more information see: <http://www.originlab.com/www/helponline/Origin/en/Category/Smoothing.html>.

Very careful analysis of XRD with FFT method shows that crystalline phases from many samples (Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>, CaMnO<sub>3</sub>, CaMn<sub>4</sub>O<sub>8</sub>) are not changed but convert to a layered phase with poor crystallinity.



(a)  
5



(b)

Figure S4. Details for XRD patterns obtained for Mn<sub>3</sub>O<sub>4</sub> (a) and CaMnO<sub>3</sub> (b).

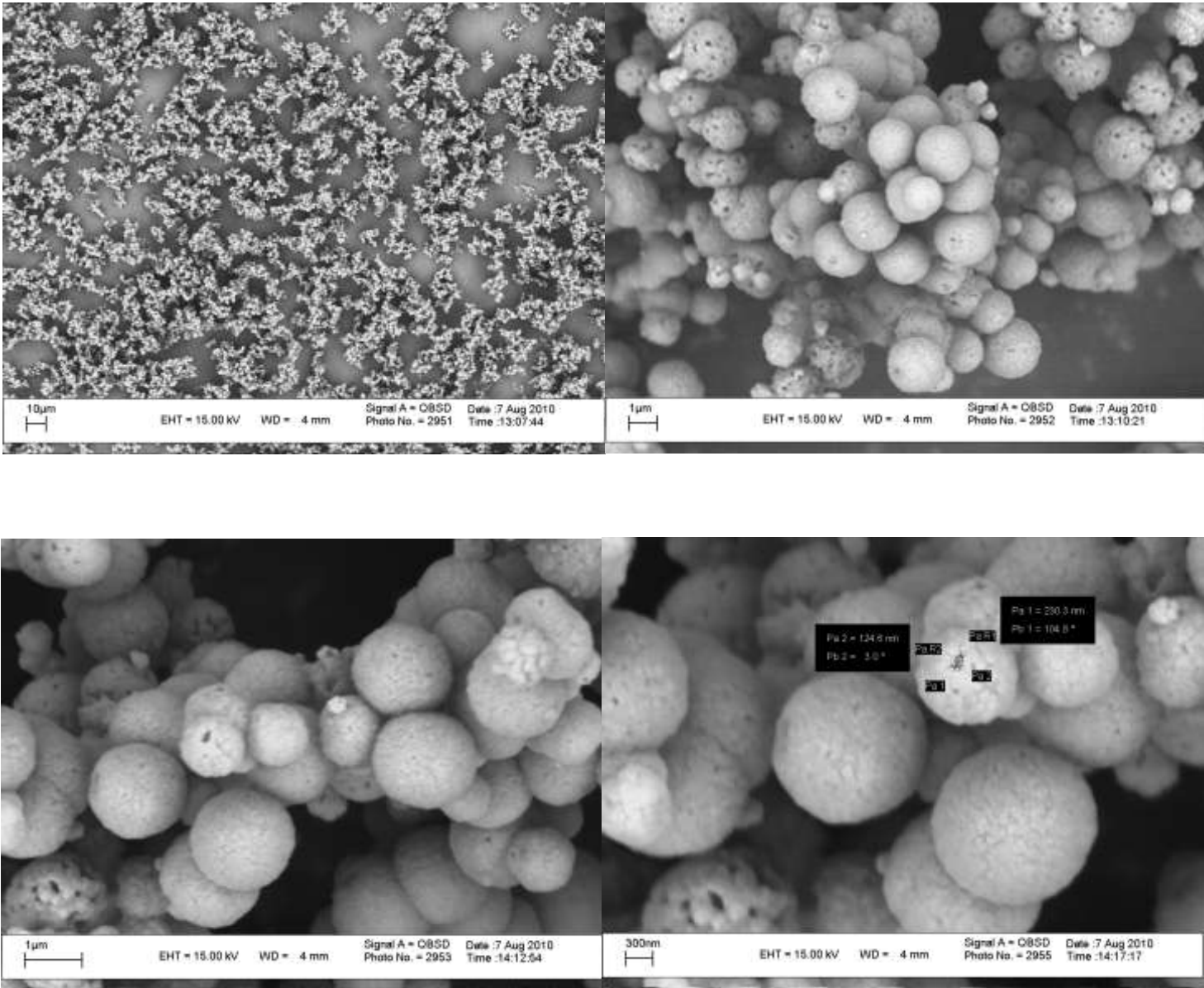


Figure S5. SEM images of  $\text{Ca}_2\text{Mn}_3\text{O}_8$ .

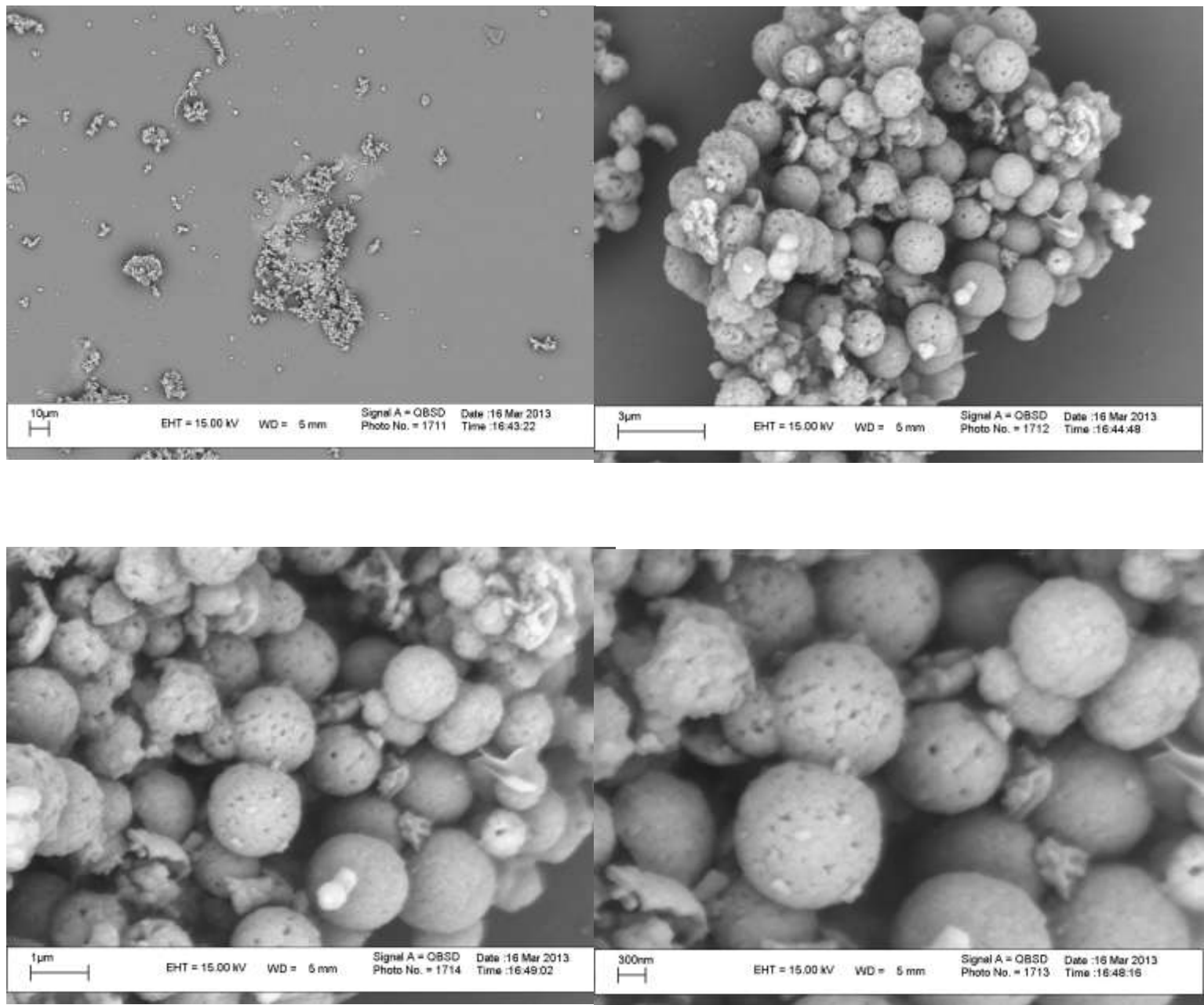


Figure S6. SEM images of  $\text{Ca}_2\text{Mn}_3\text{O}_8$  after treating with  $\text{Ce(IV)}$  (1.8 M, for one month).



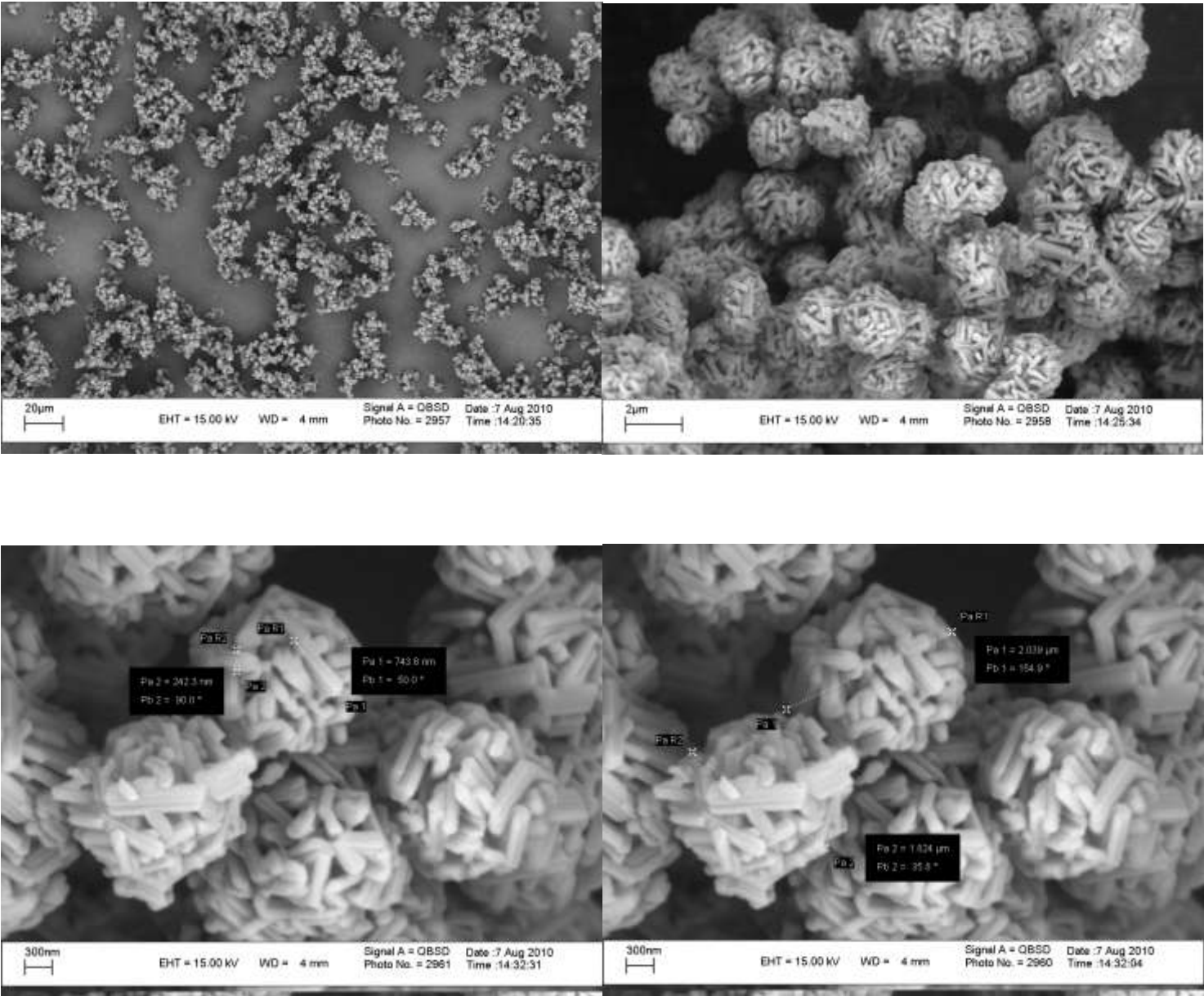


Figure S7. SEM images of  $\text{CaMn}_3\text{O}_6$ .

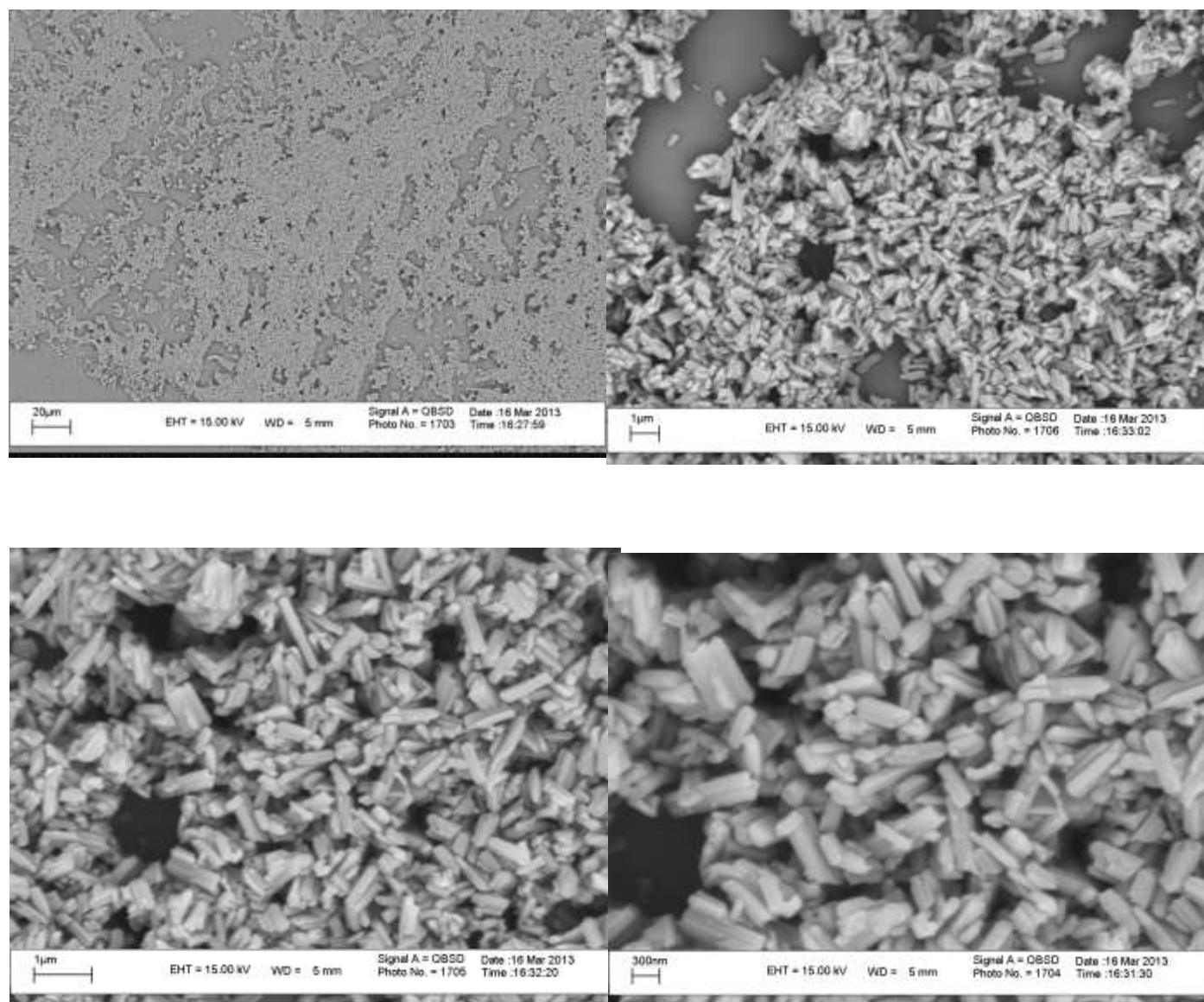


Figure S8. SEM images of  $\text{CaMn}_3\text{O}_6$  after treating with  $\text{Ce(IV)}$  (1.8 M, for one month).

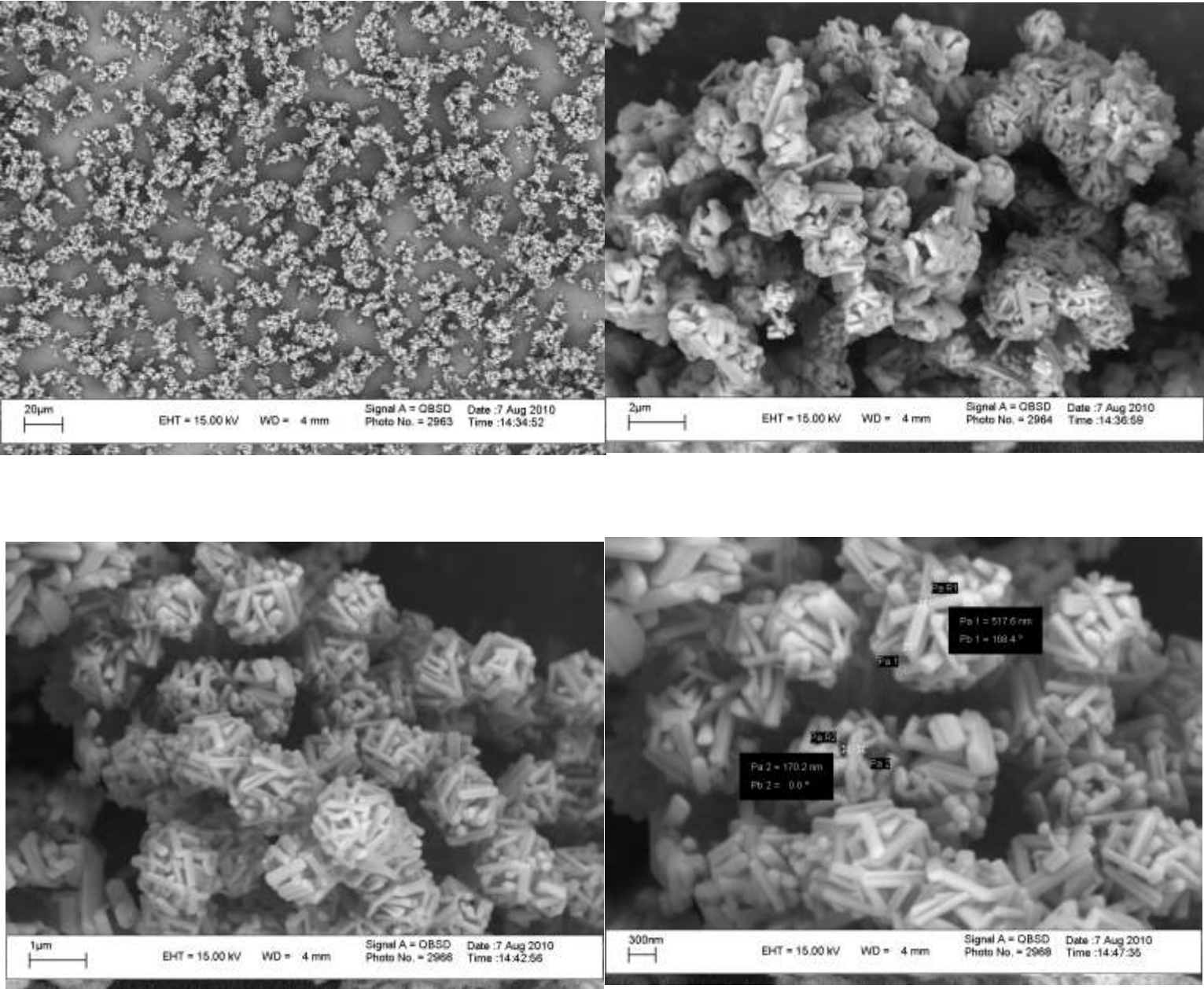


Figure S9. SEM images of  $\text{CaMn}_4\text{O}_8$ .



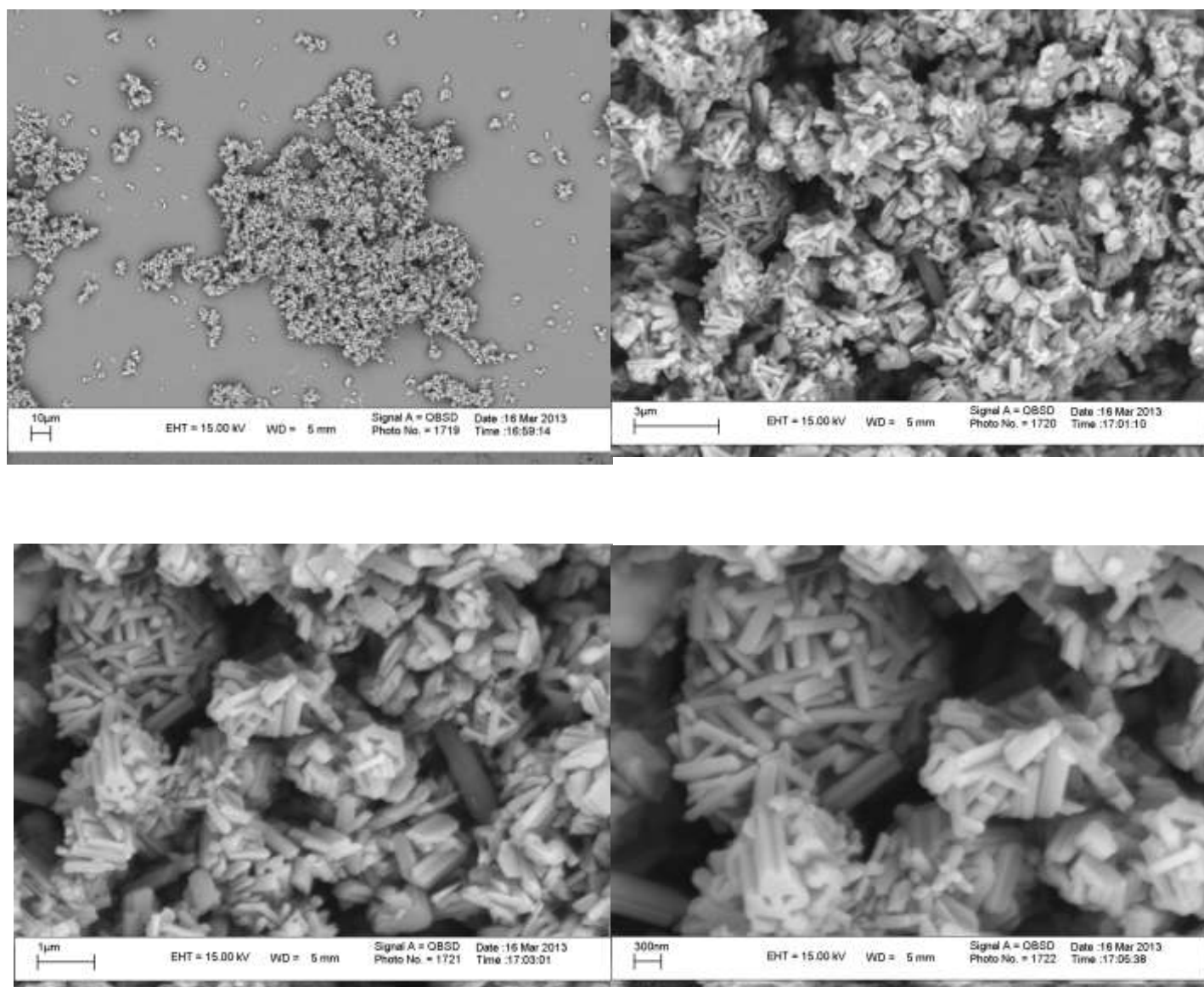


Figure S10. SEM images of  $\text{CaMn}_4\text{O}_8$  after treating with  $\text{Ce(IV)}$  (1.8 M, for one month).

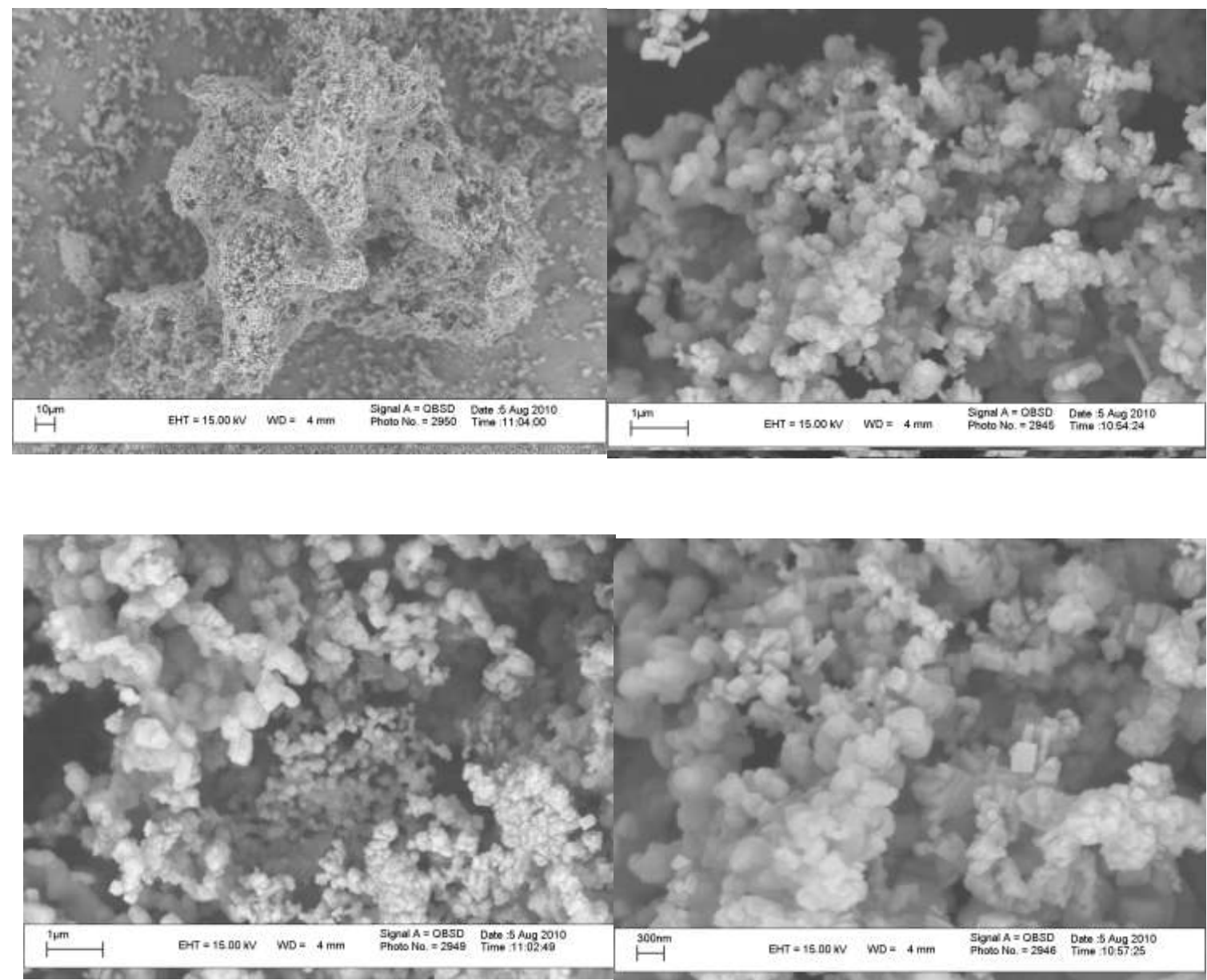


Figure S11. SEM images of  $\text{CaMnO}_3$ .

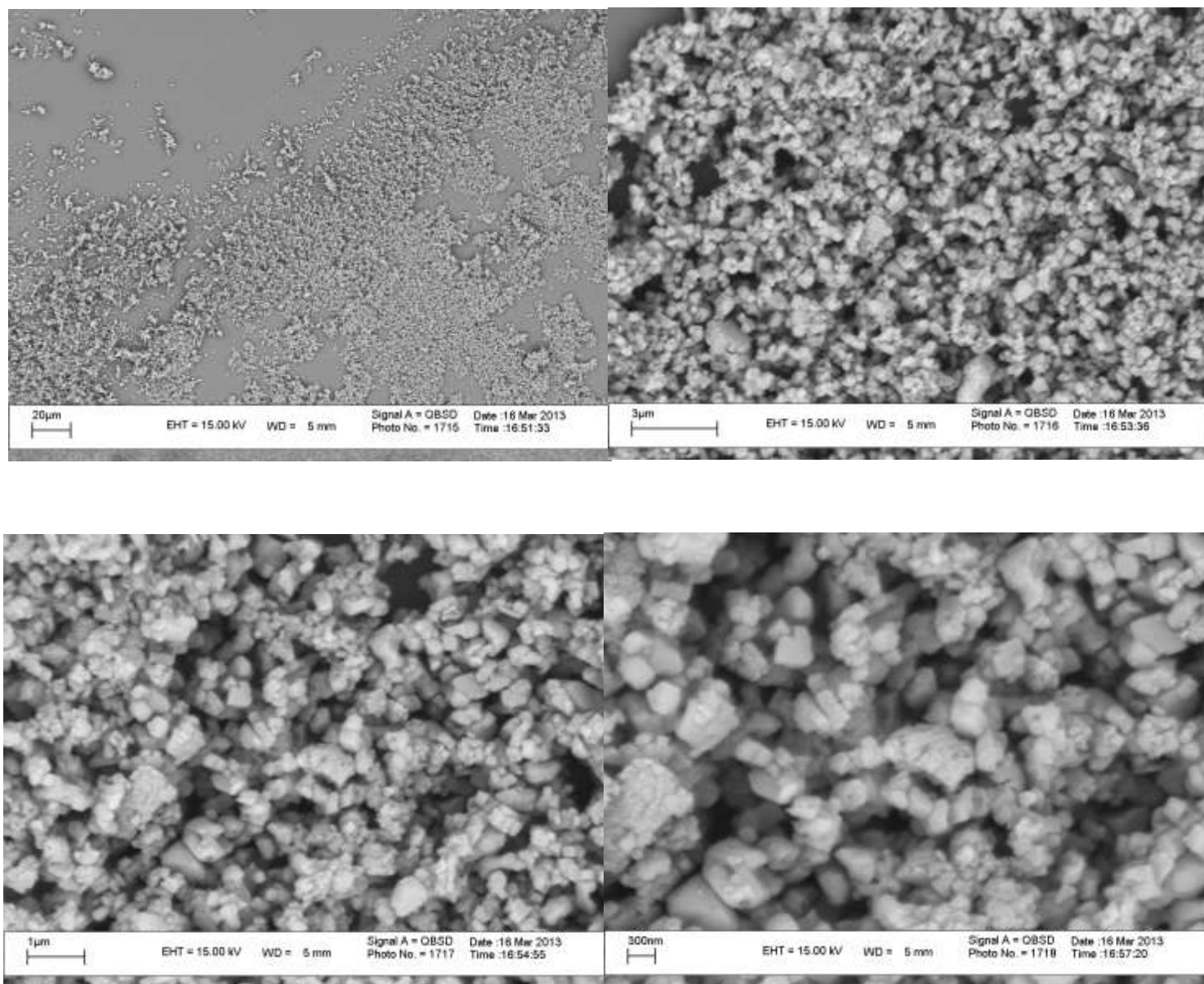


Figure S12. SEM images of  $\text{CaMnO}_3$  after treating with  $\text{Ce(IV)}$  (1.8 M, for one month).



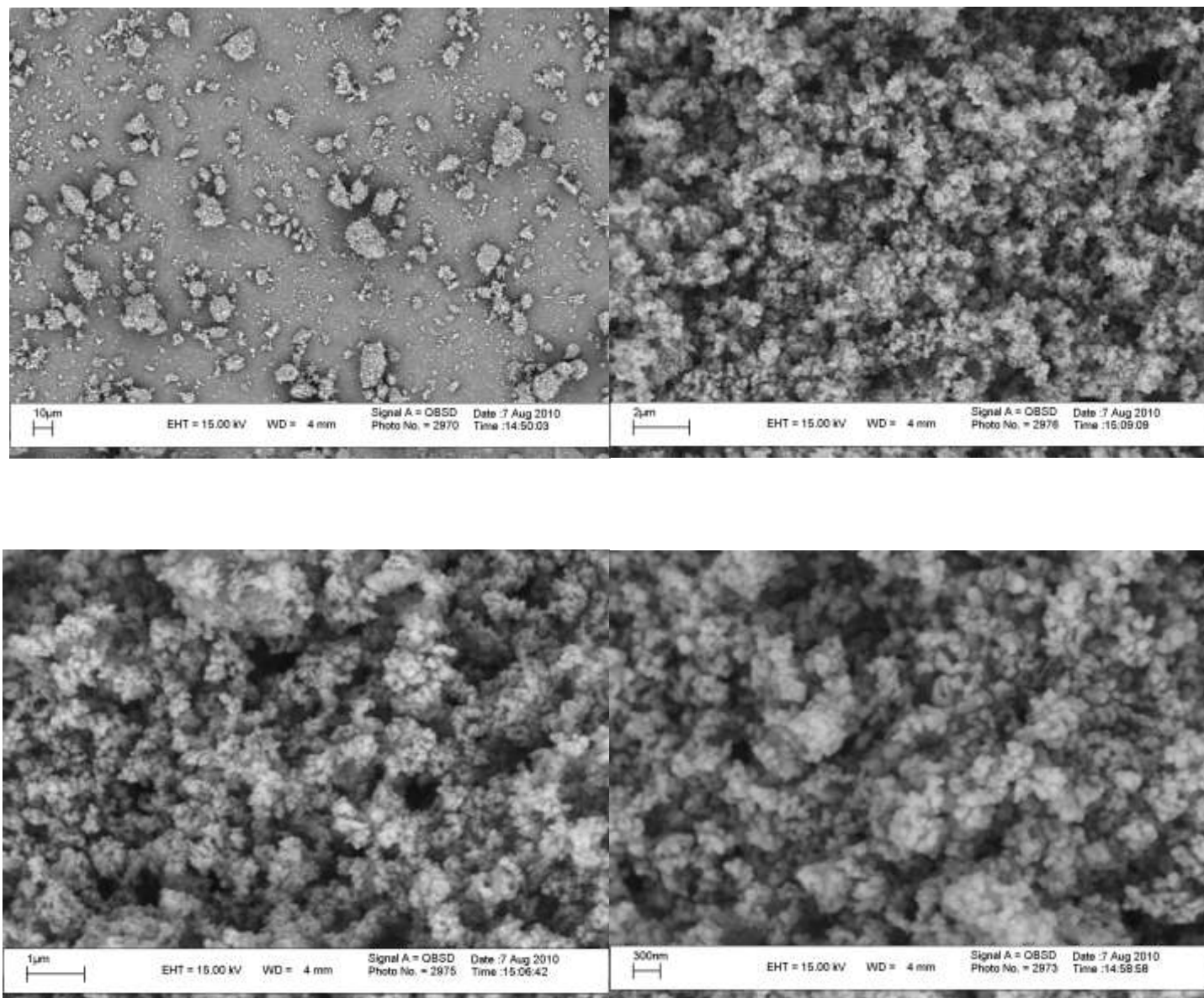


Figure S13. SEM images of  $\text{Mn}_2\text{O}_3$ .

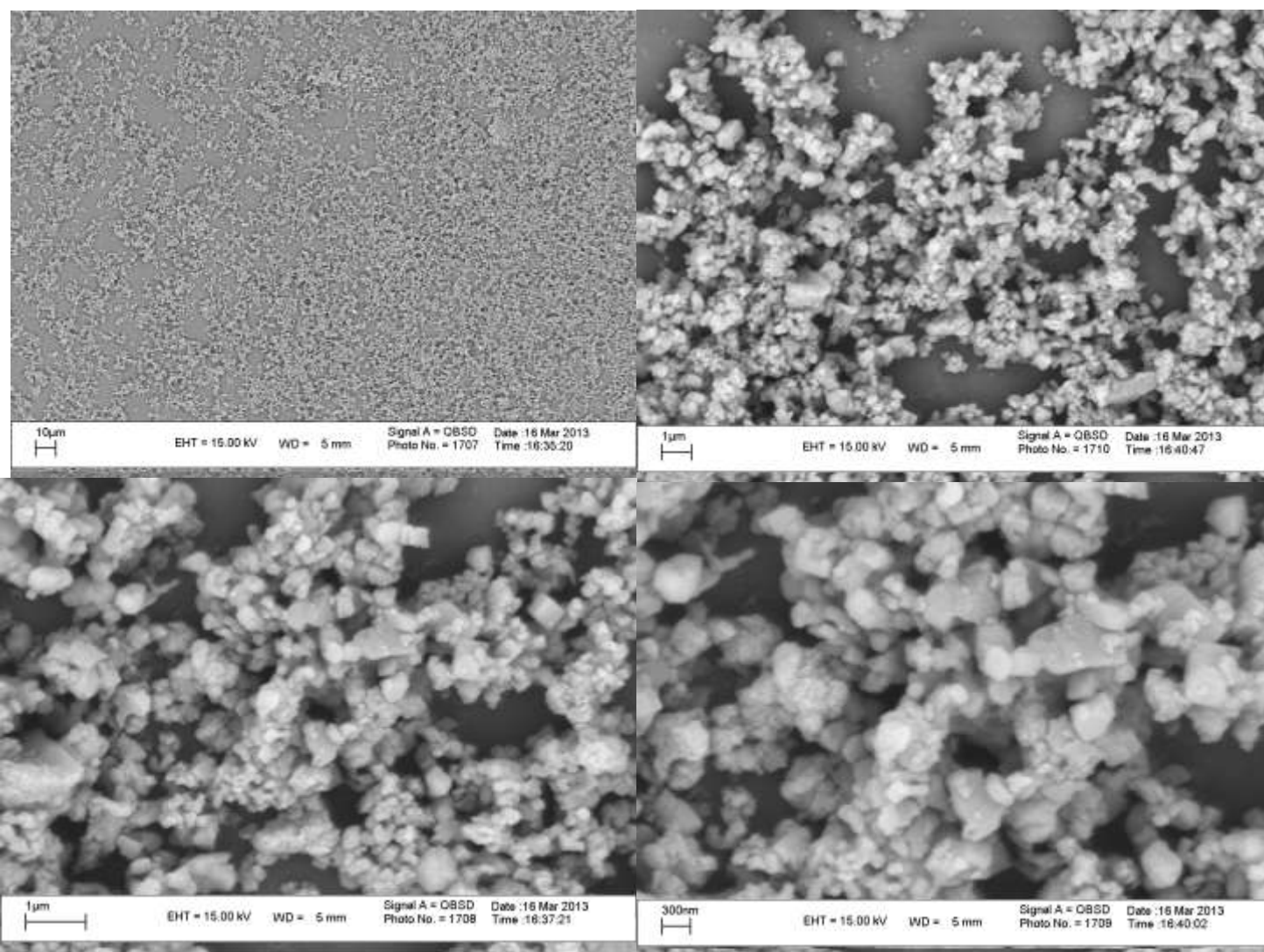


Figure S14. SEM images of  $\text{Mn}_2\text{O}_3$  after treating with  $\text{Ce(IV)}$  (1.8 M, for one month).



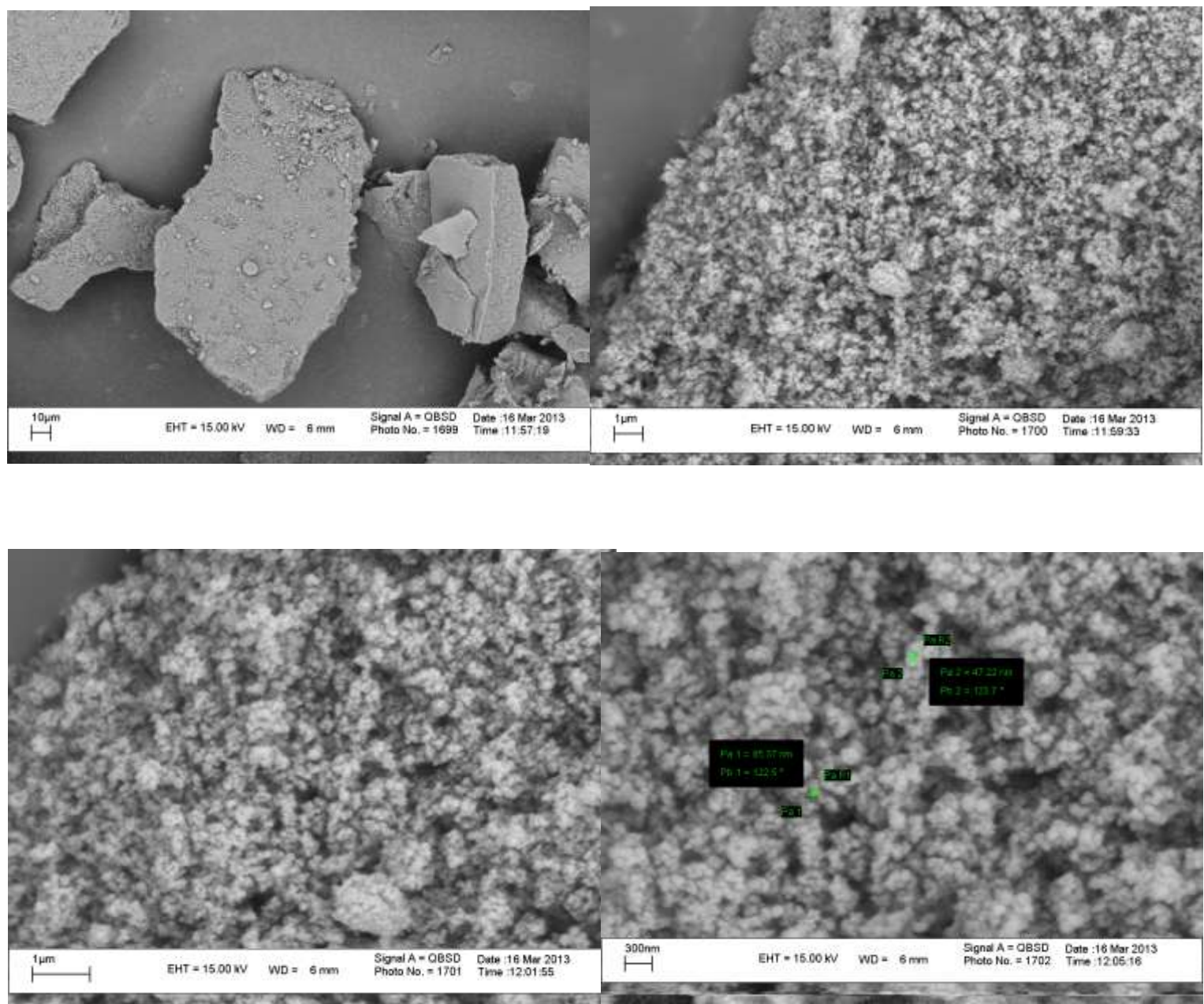


Figure S15. SEM images of  $\text{Mn}_3\text{O}_4$ .

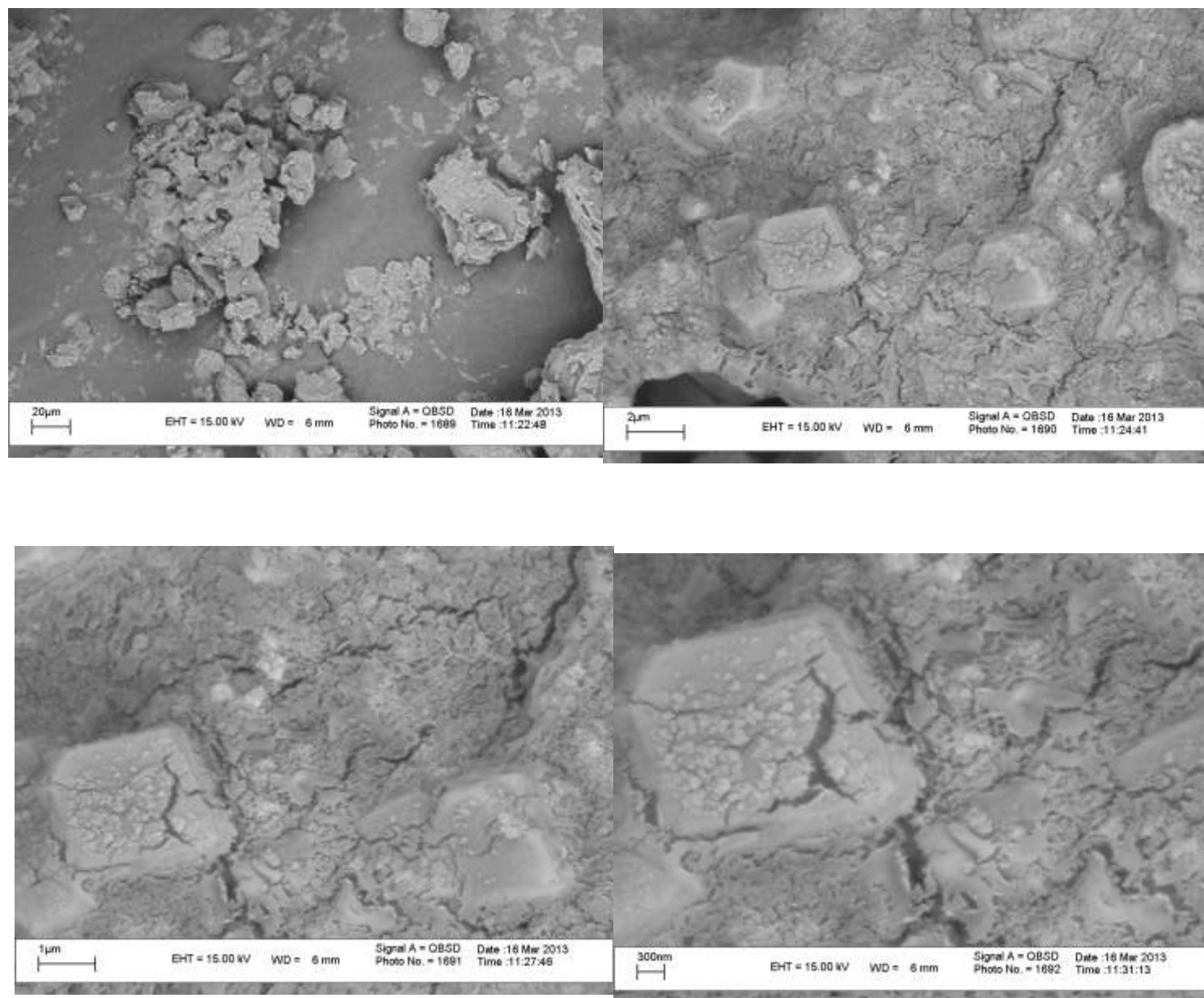


Figure S16. SEM images of  $\text{Mn}_3\text{O}_4$  after treating with  $\text{Ce(IV)}$  (1.8 M, for one month).

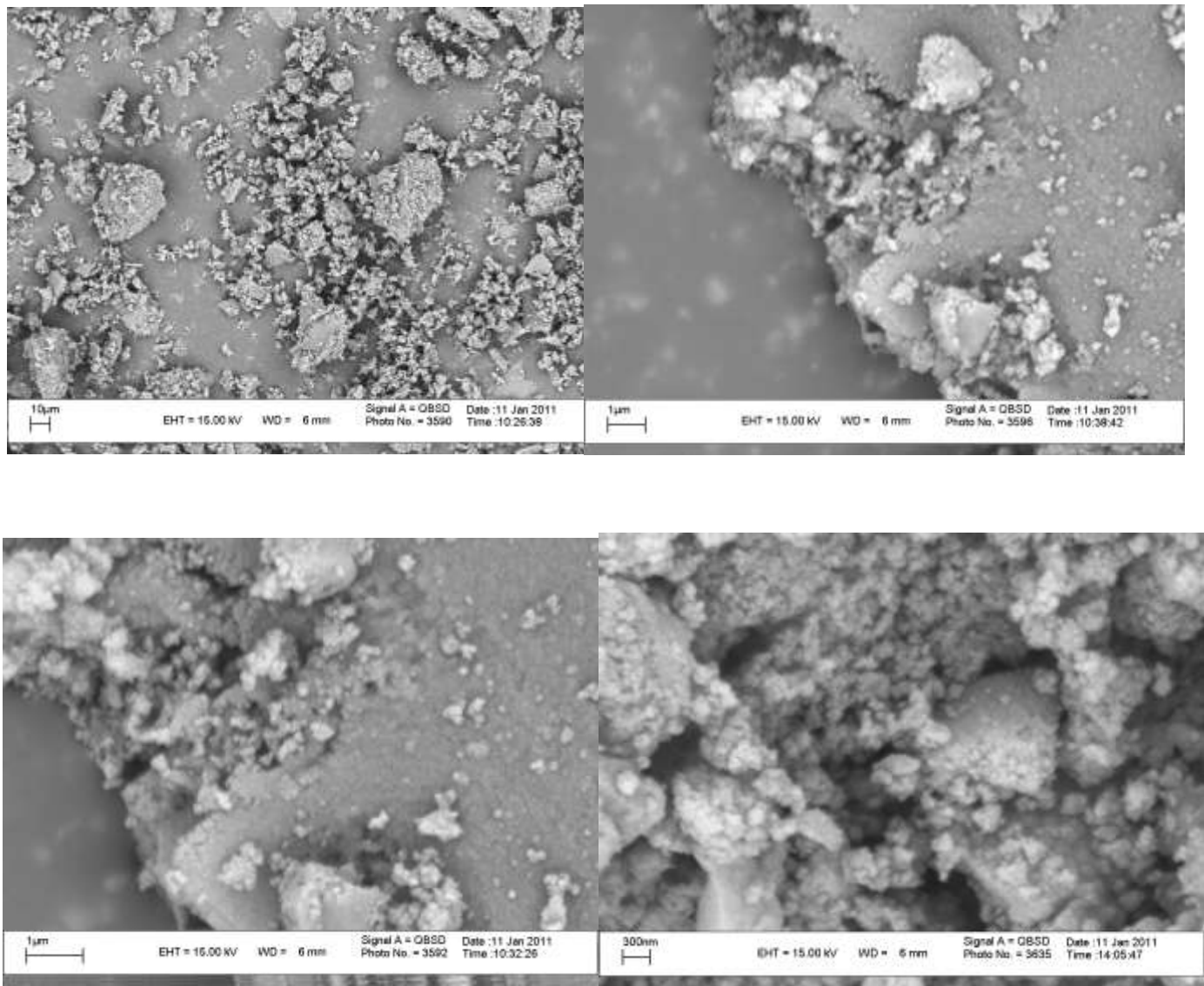


Figure S17. SEM images of layered Mn Oxide.



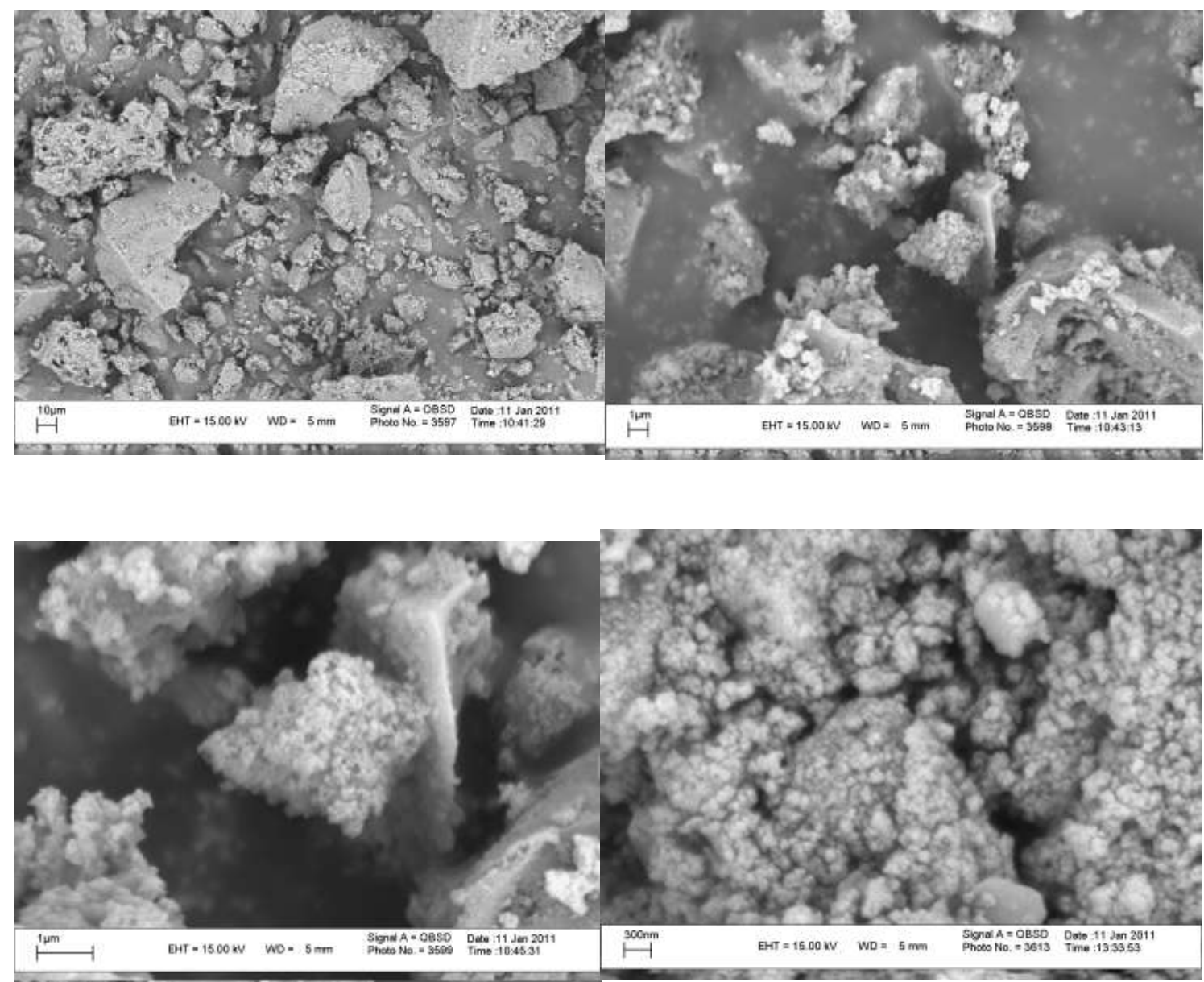
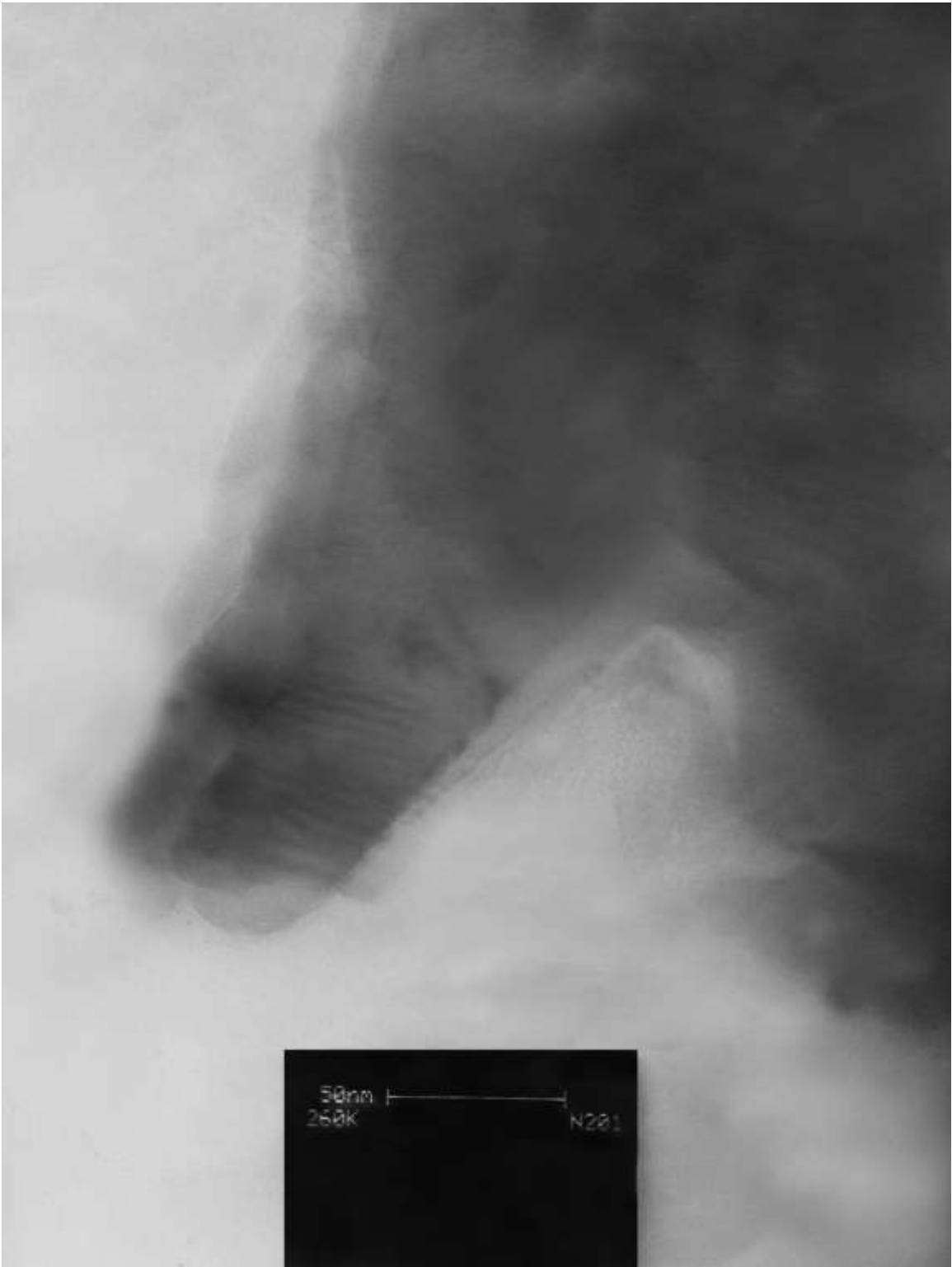
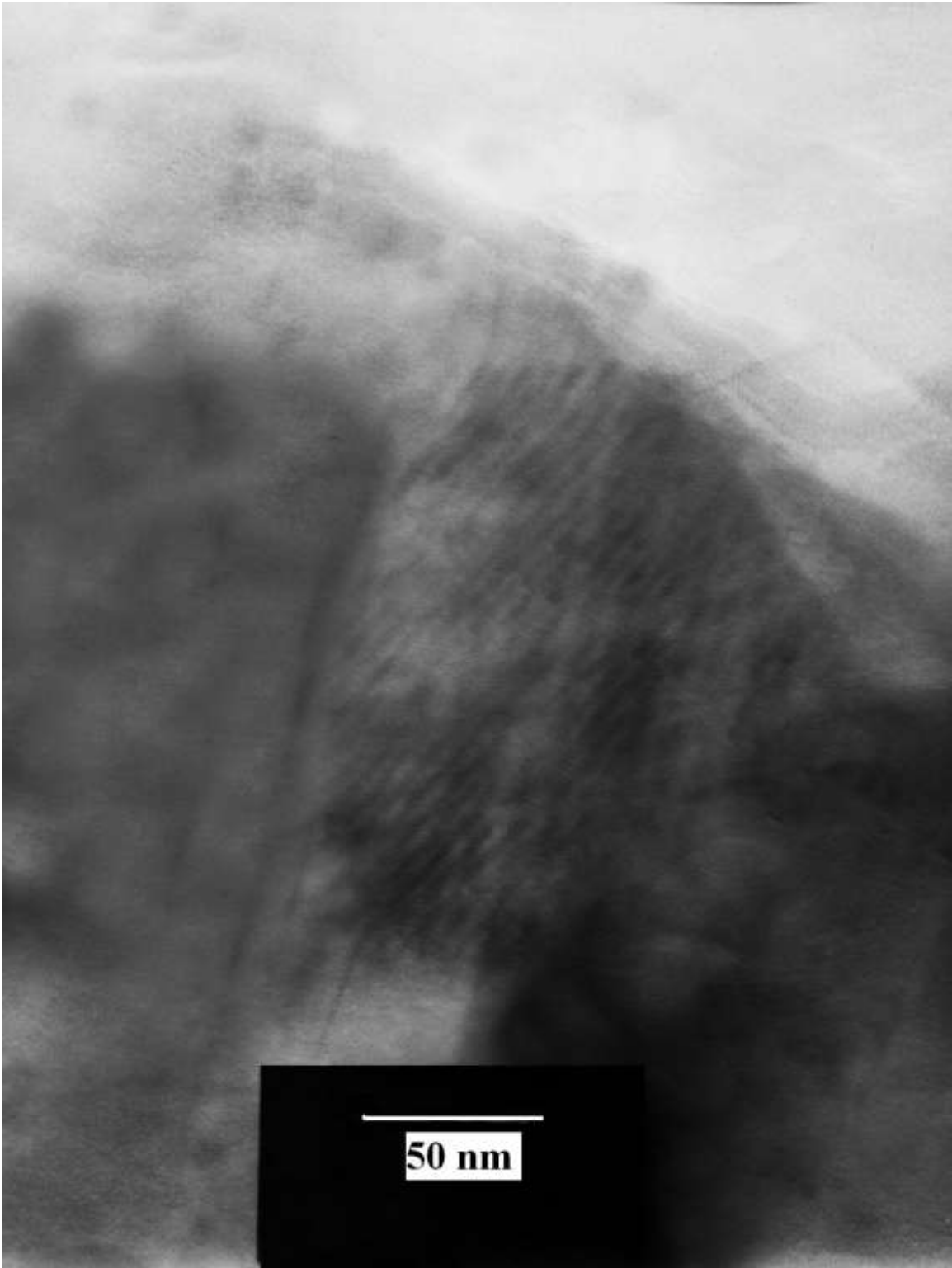


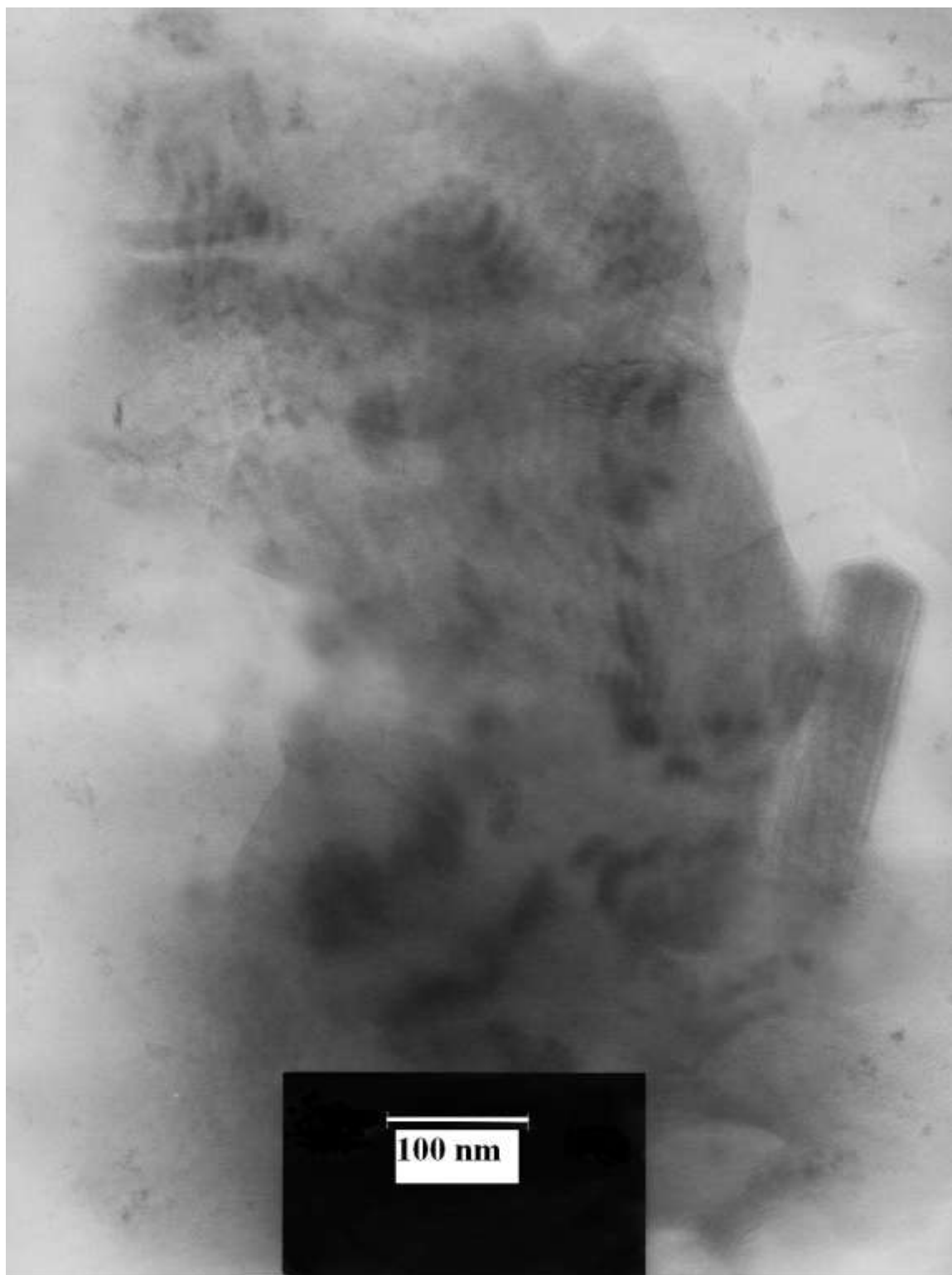
Figure S18. SEM images of layered Mn oxide after treating with Ce(IV) (1.8 M, for one month).



a



b



c

Figure S19. TEM images of layered Mn oxide after treating with Ce(IV) (1.8 M, for one month) (a-c).