Electronic Supplementary Material (ESI) for New Journal of Chemistry

Support Information

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Water oxidation by nano-layered manganese oxides in the presence of cerium (IV) ammonium nitrate: Important factors and a proposed self-repair mechanism

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Water oxidation

Oxygen evolution from aqueous solutions in the presence of $(NH_4)_2Ce(NO_3)_6$ (Ce(IV)) was measured using an HQ40d portable dissolved oxygen meter connected to an oxygen monitor with digital readout. The reactor was maintained at 25.0 ºC in a water bath. In a typical run, the instrument readout was calibrated against air-saturated distilled water stirred continually with a magnetic stirrer in the air-tight reactor. After ensuring a constant baseline reading, the water in the reactor was replaced with Ce(IV) solution. Without catalyst, Ce(IV) was stable in this condition and oxygen evolution was not observed. After deaeration of Ce(IV) solution with argon, manganese oxides as several small particles were added, and oxygen evolution was recorded with the oxygen meter under stirring (Fig. S1, ESI†). The formation of oxygen was followed, and oxygen formation rates per manganese site were obtained from linear fits of the data. Only the dissolved Oxygen can be measured by the oxygen meter.

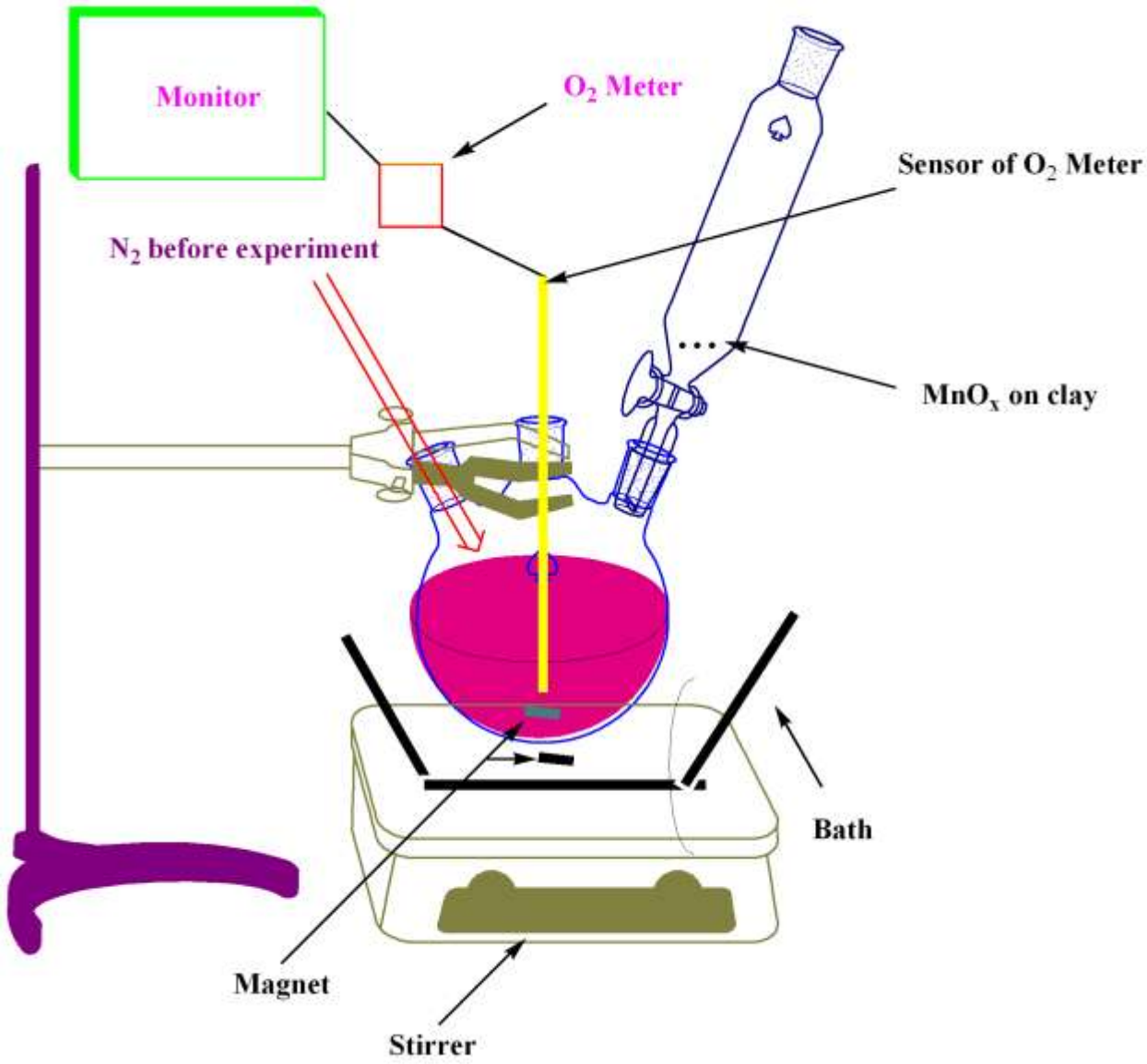
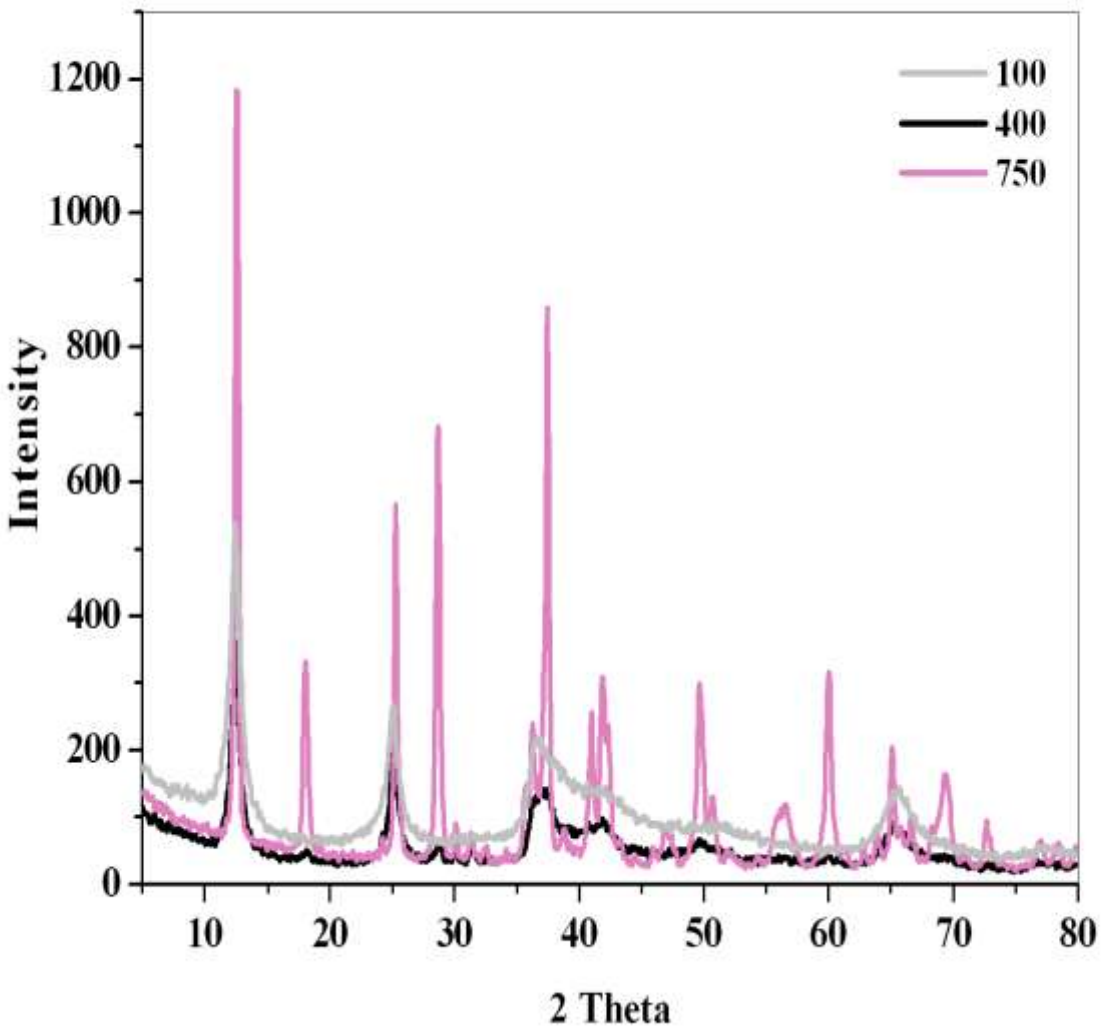
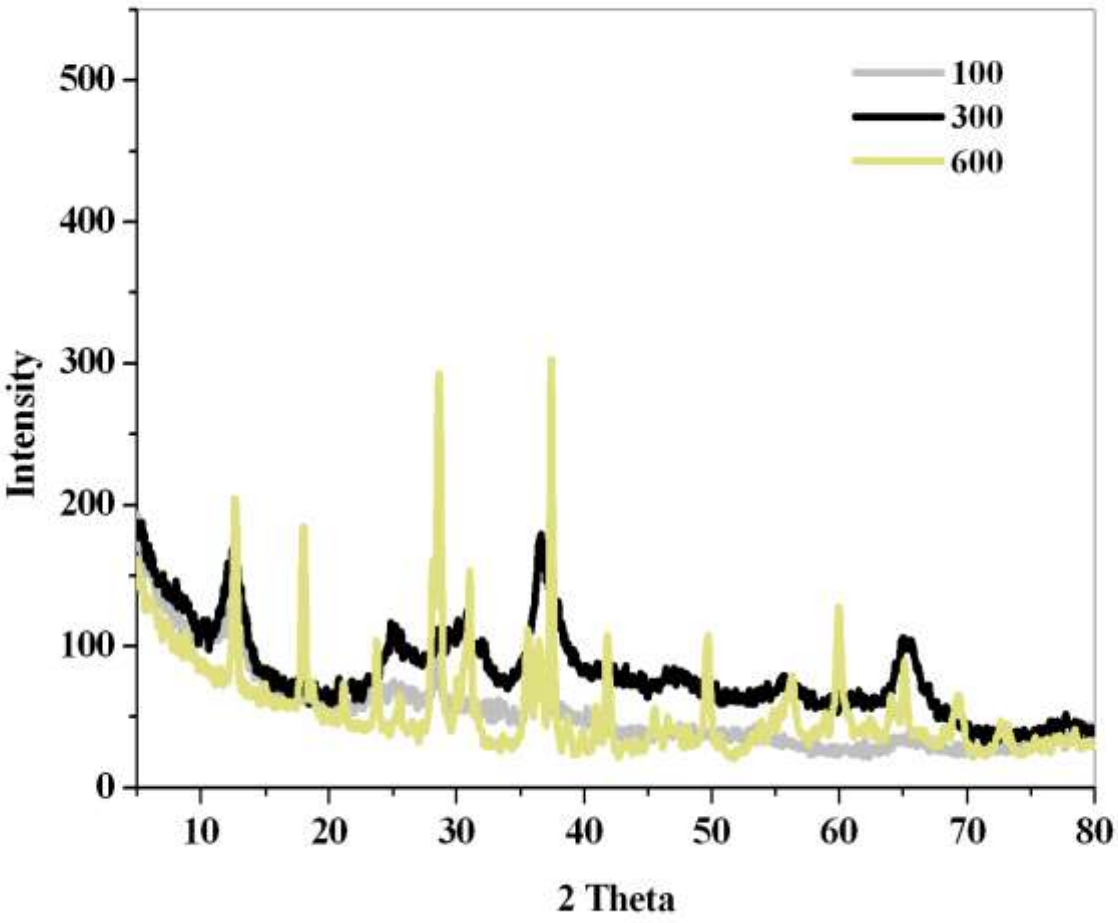


Fig. S1. The reactor set-up for oxygen evolution experiment in the presence of Ce(IV).

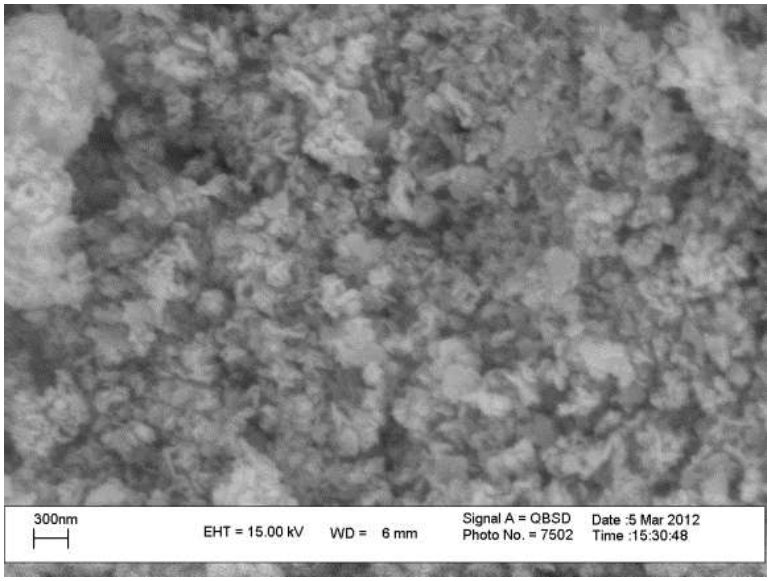


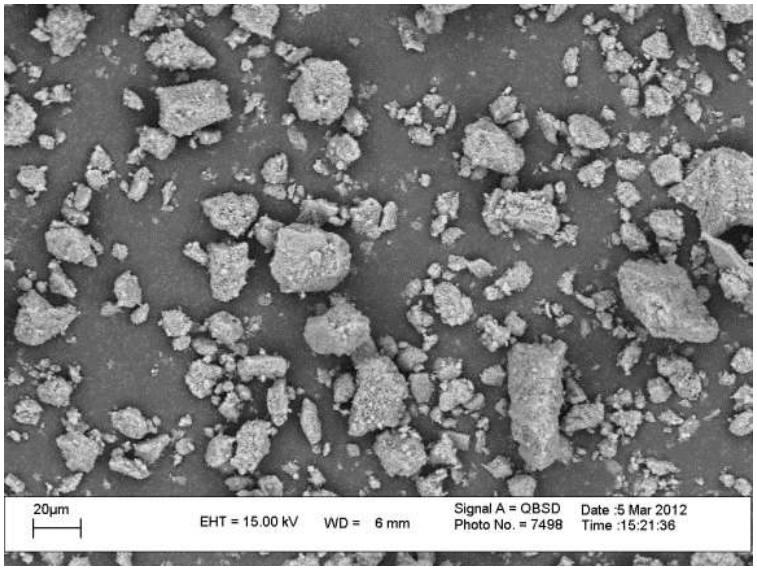
(a)

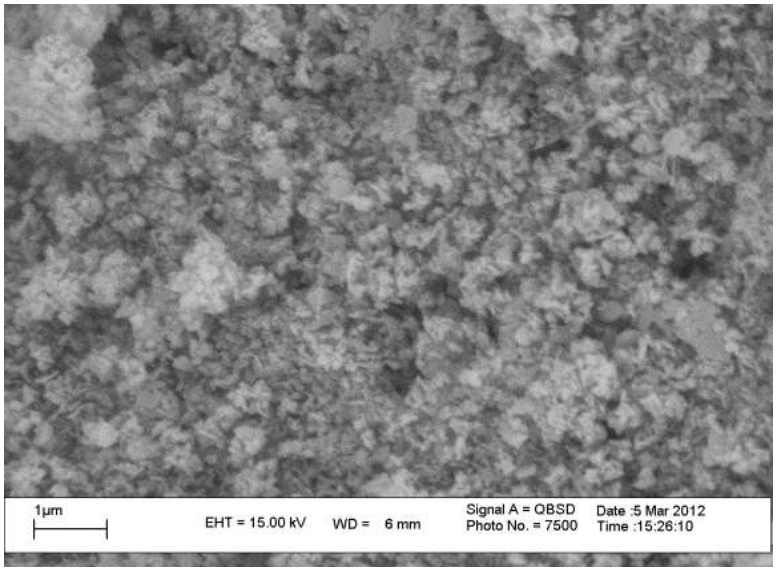


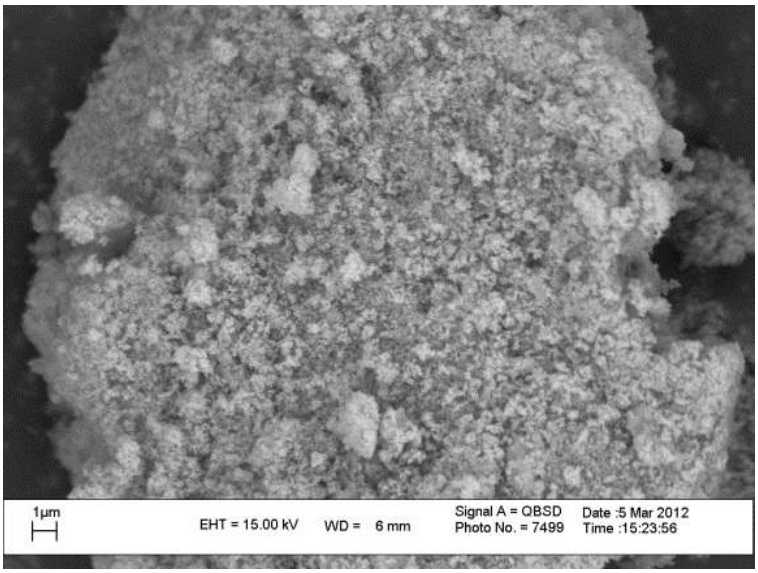
(b)

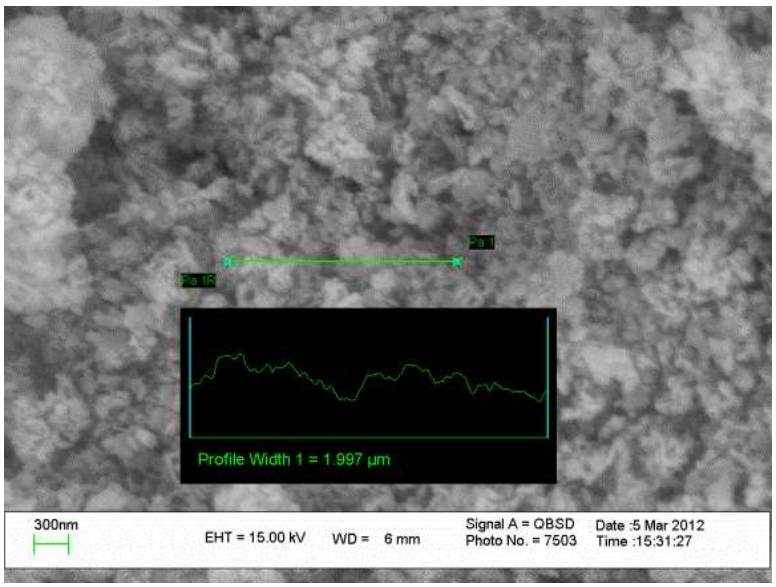
Fig. S2 XRD patterns for the best catalysts:, $Mg_{0.16}MnO_2$ (a) and $Cd_{0.16}MnO_2$ (b) Mn Oxide prepared at shown temperatures.

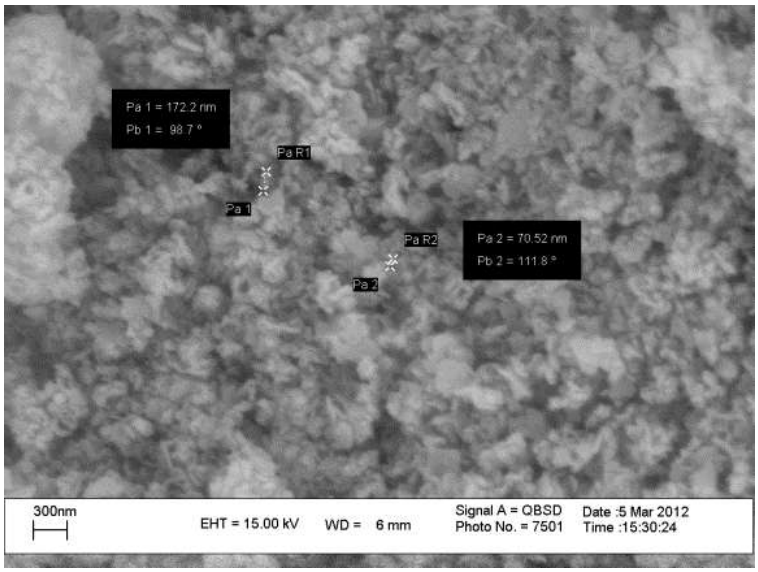












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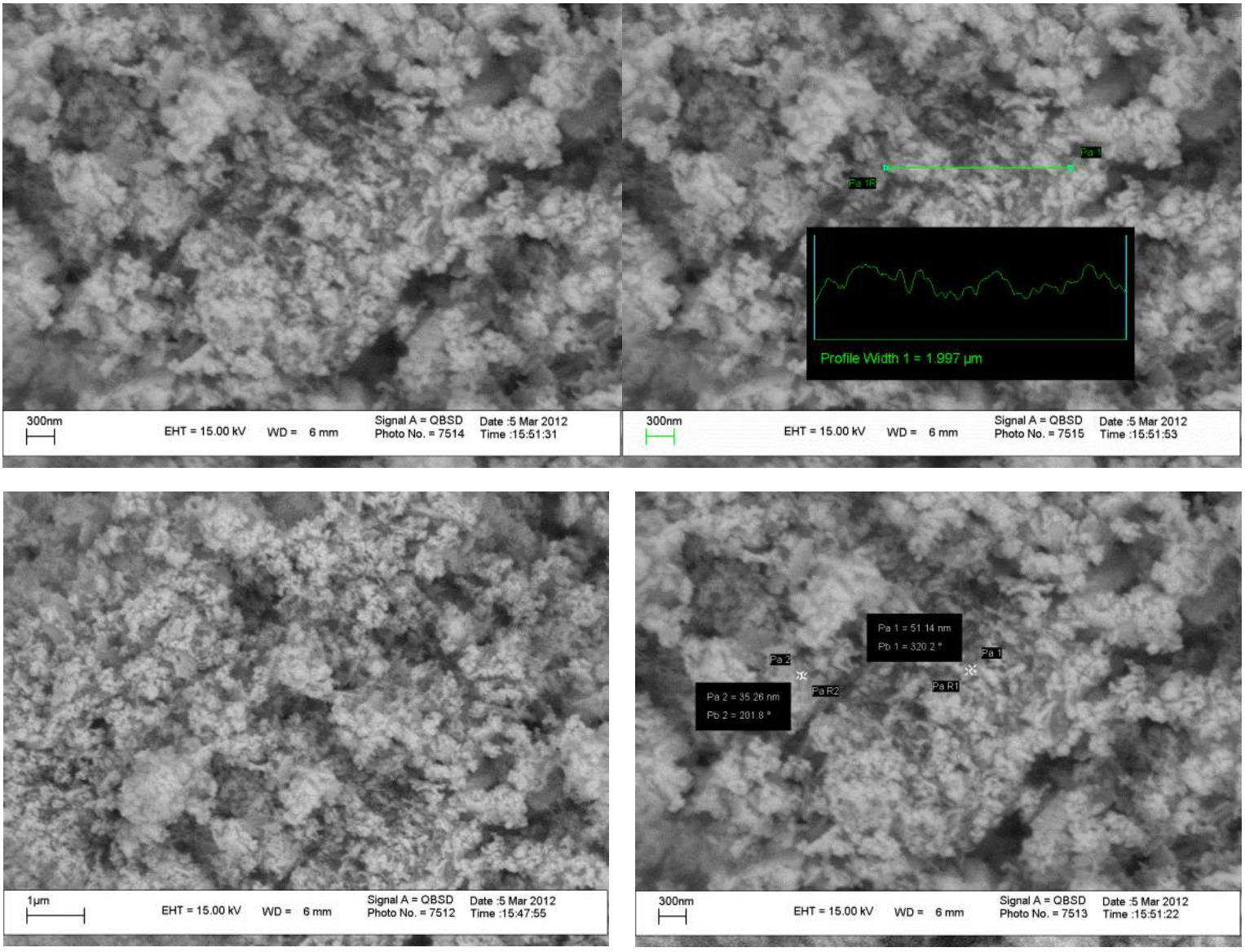

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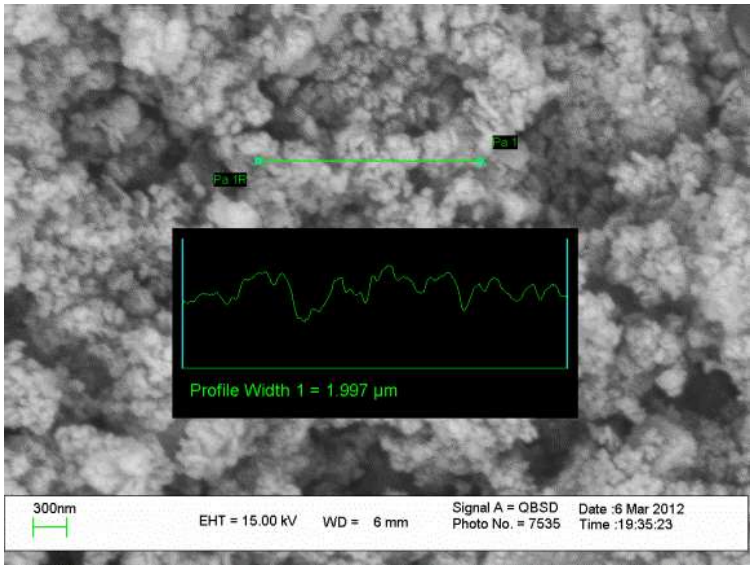

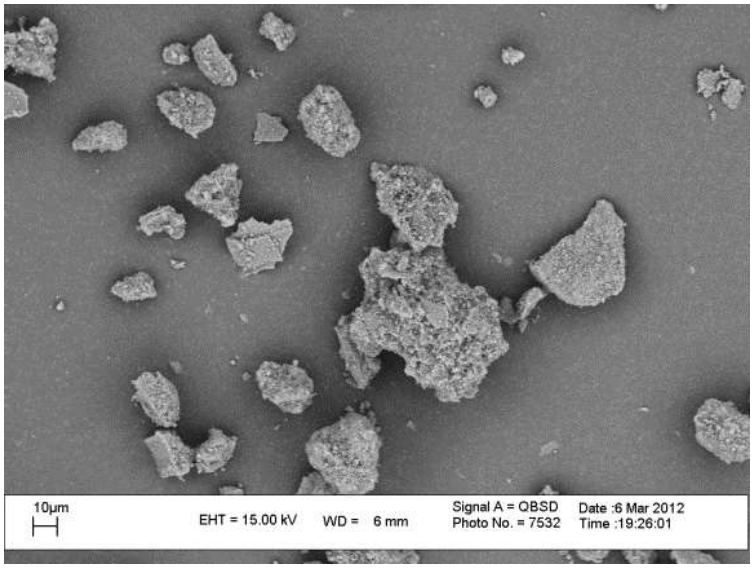

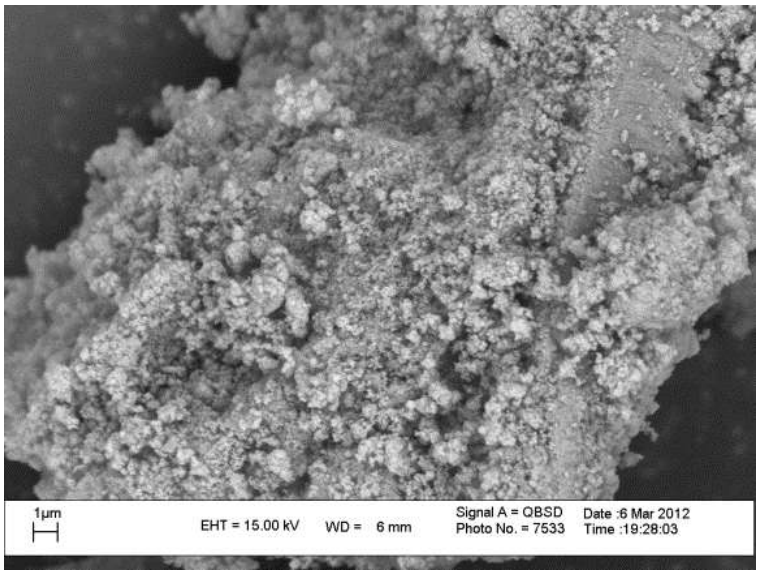

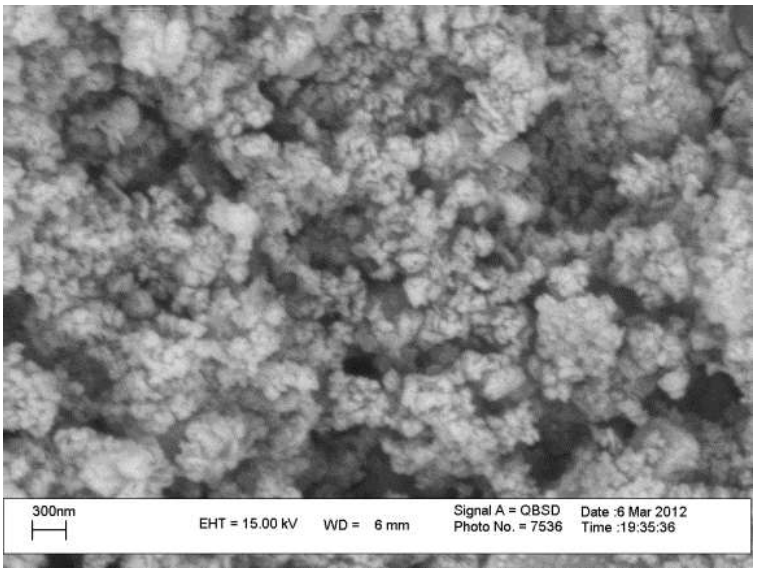

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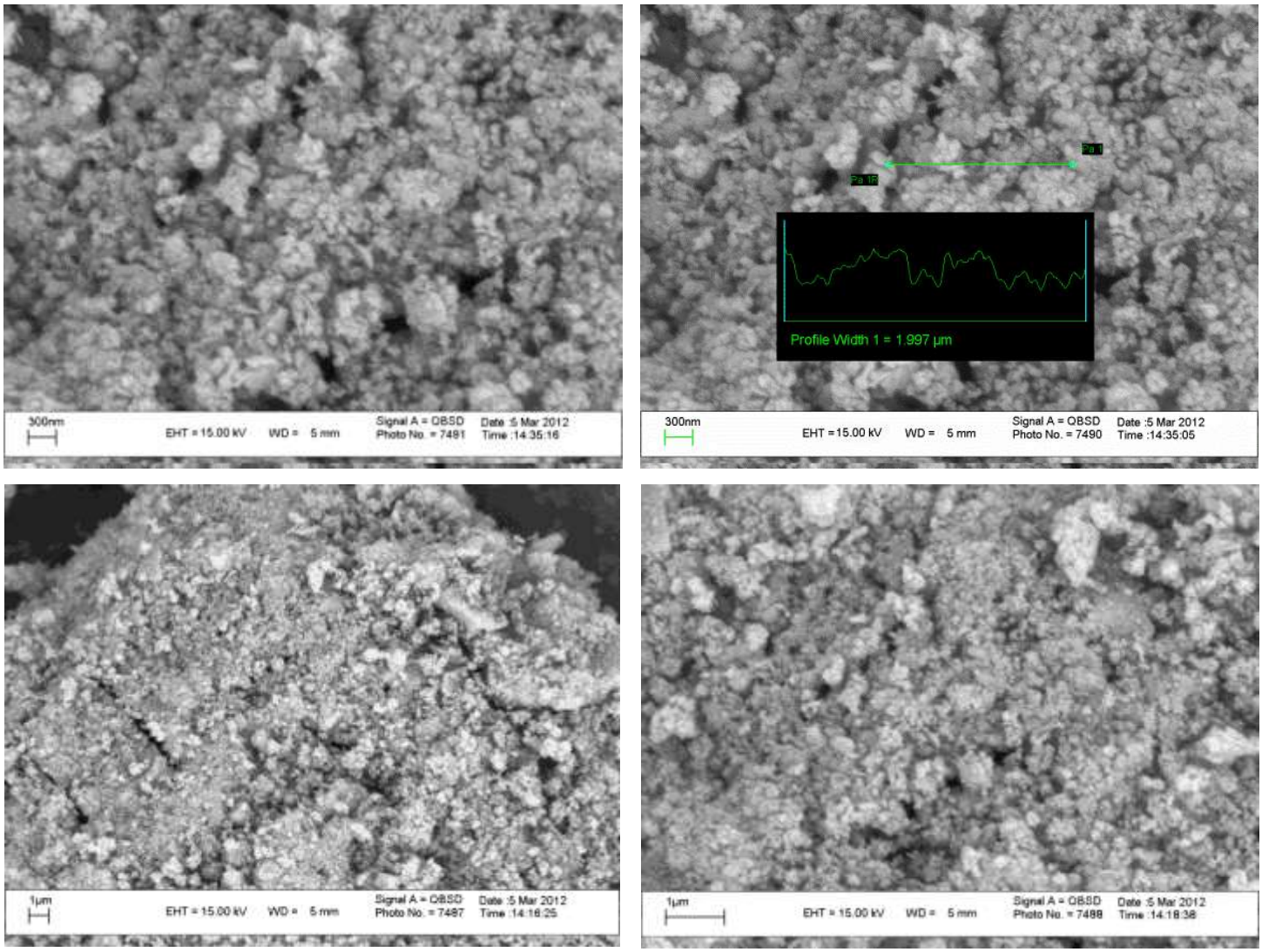

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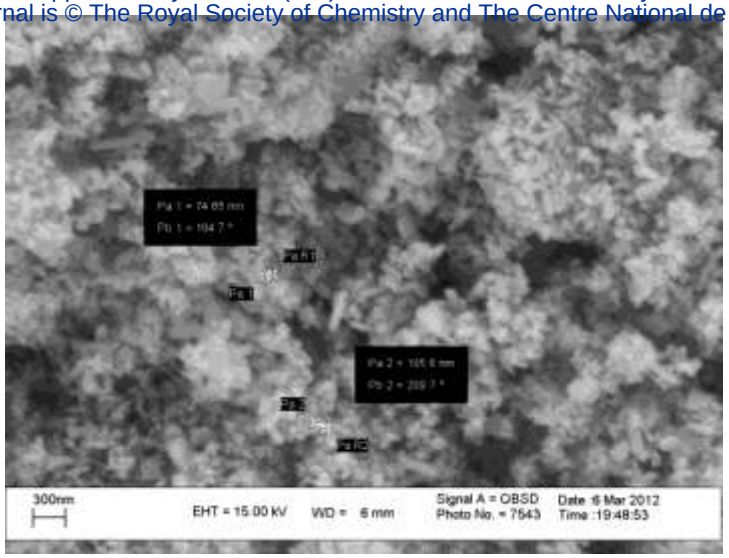

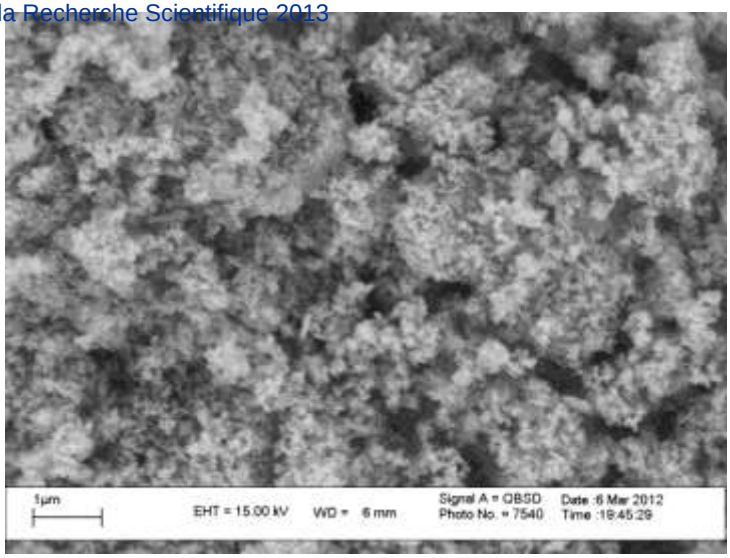

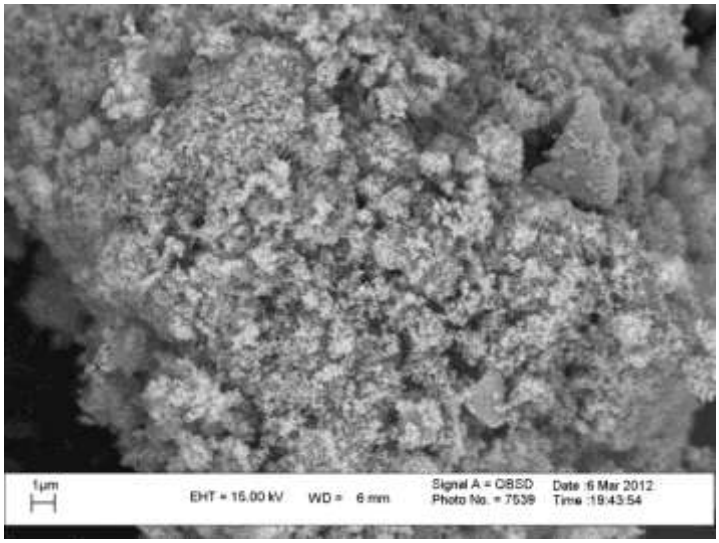

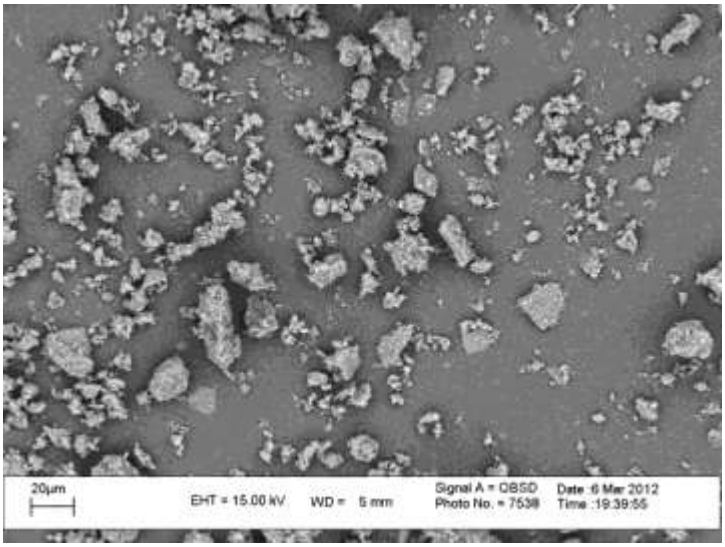

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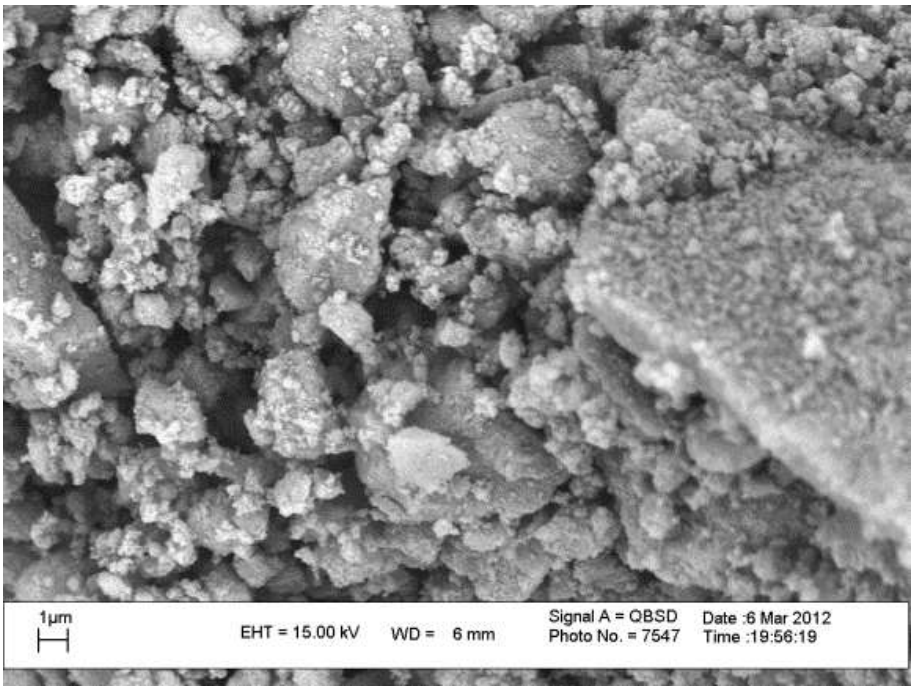

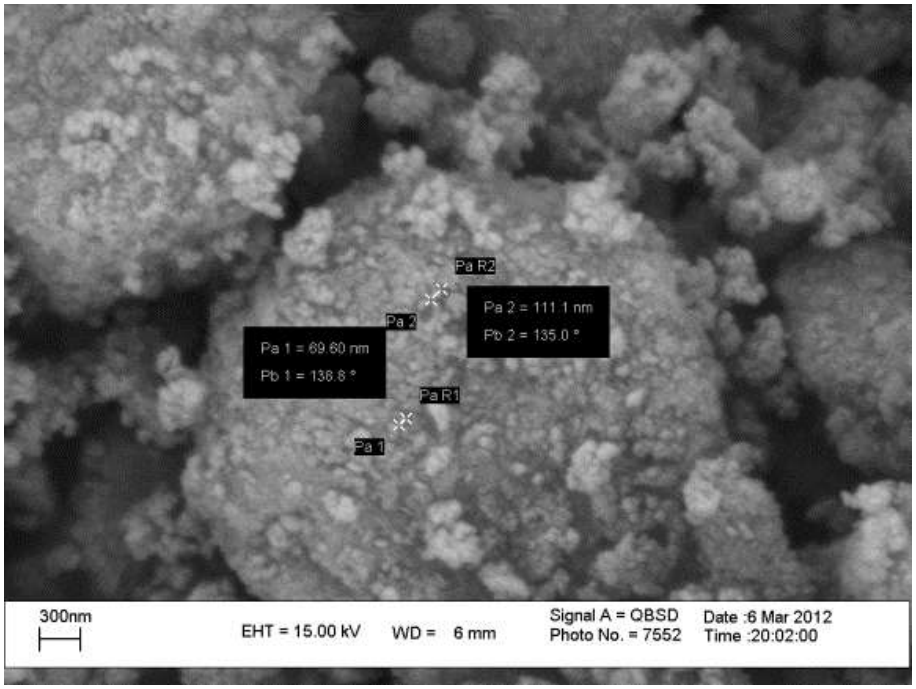

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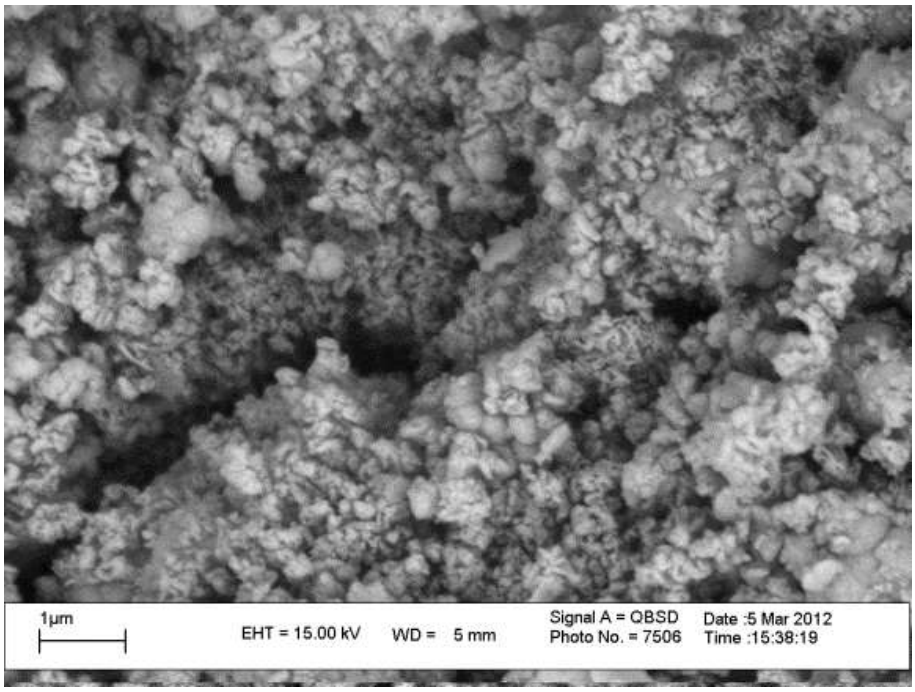

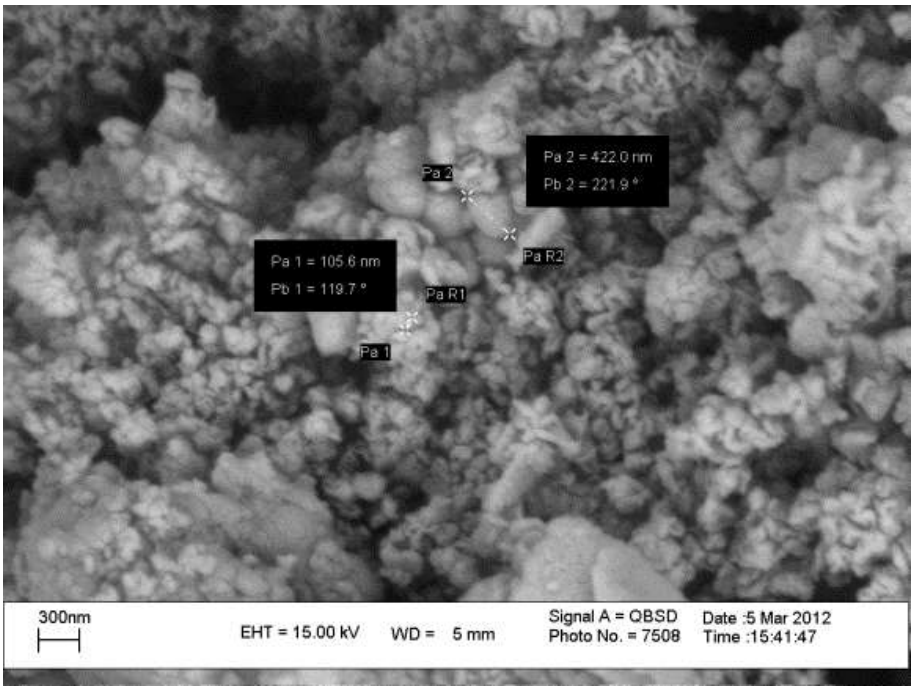

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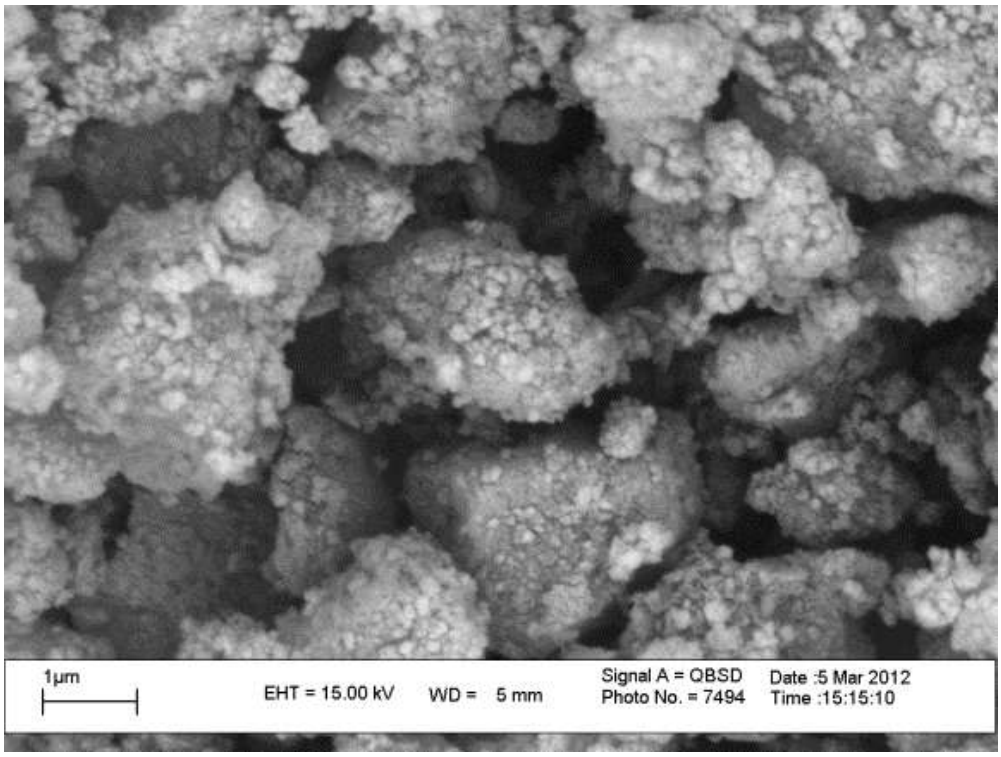

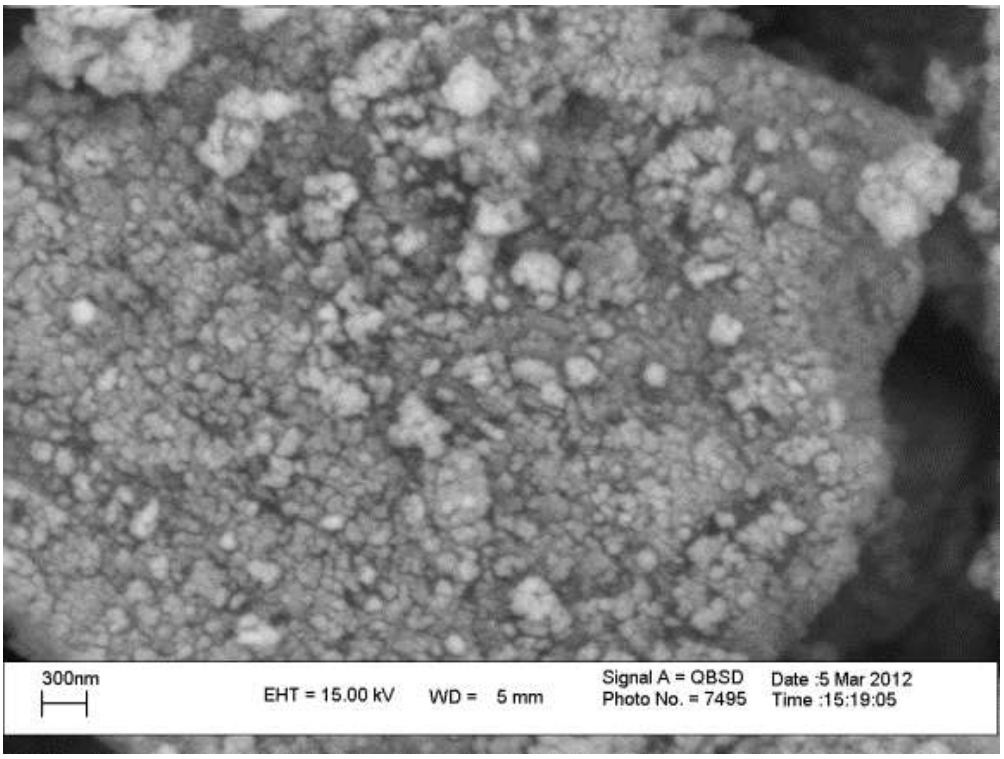

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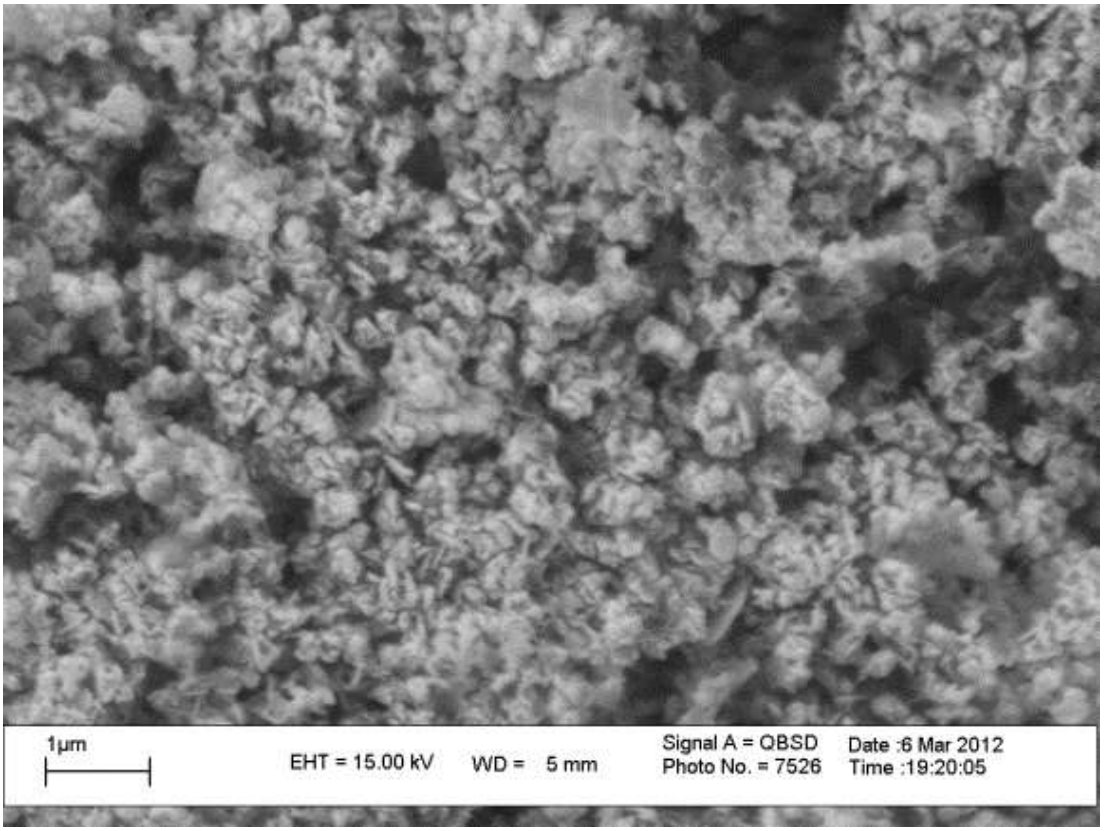

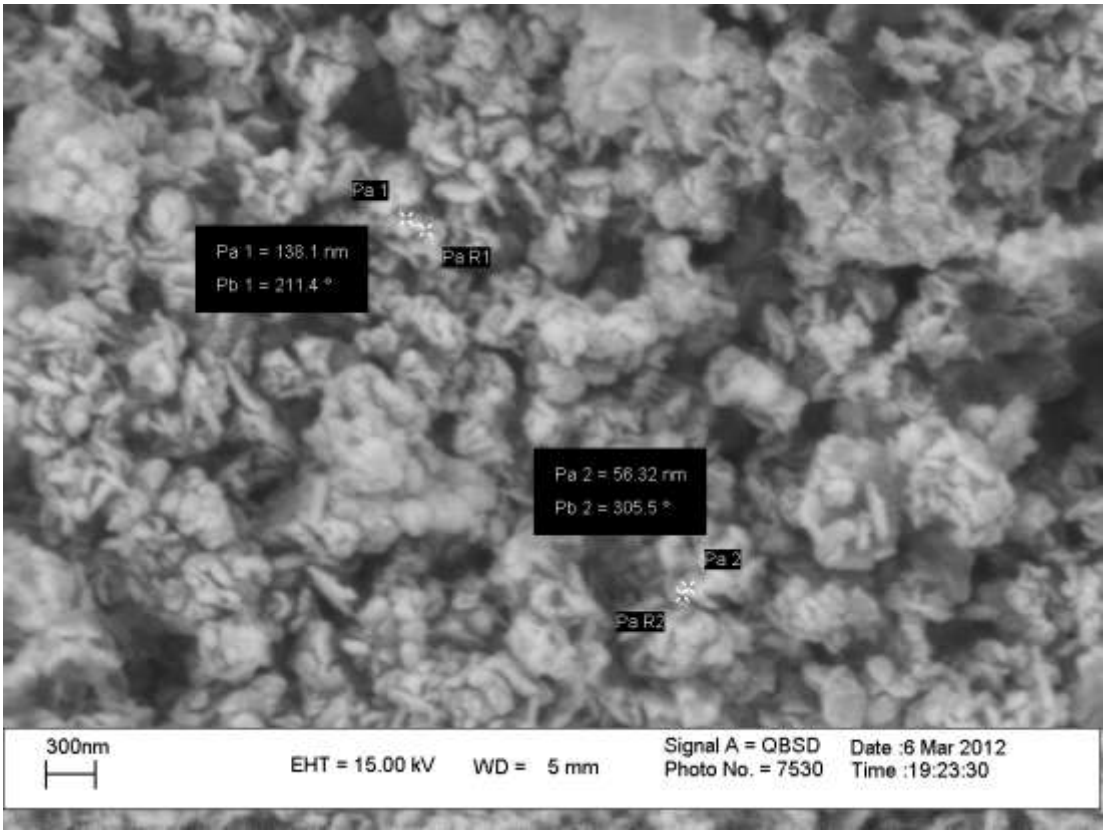

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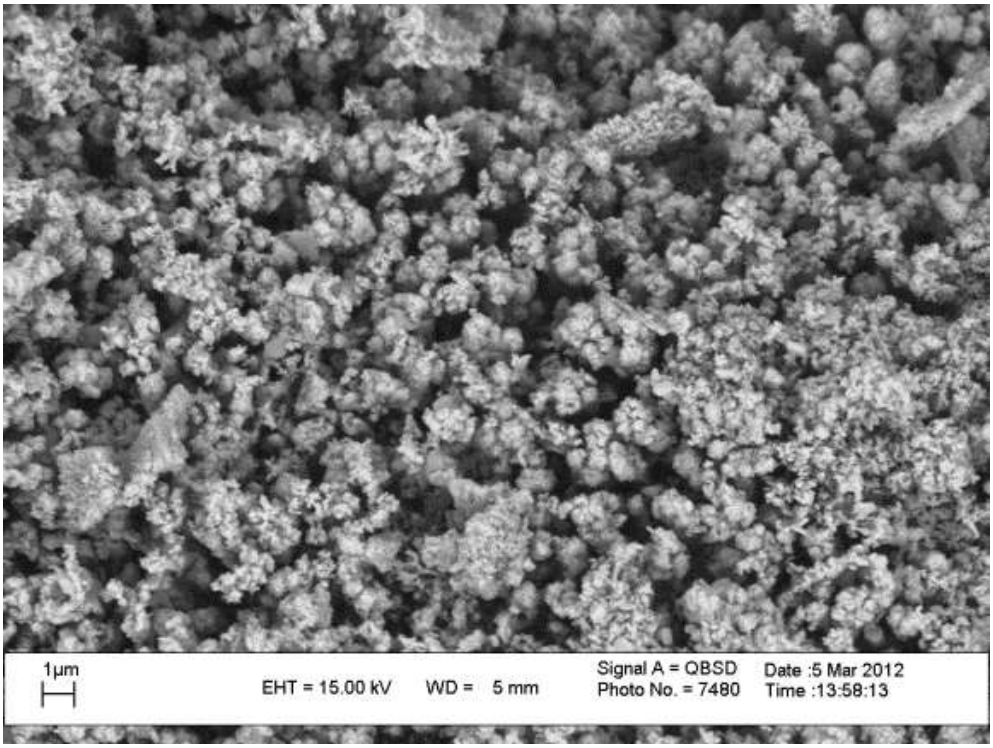

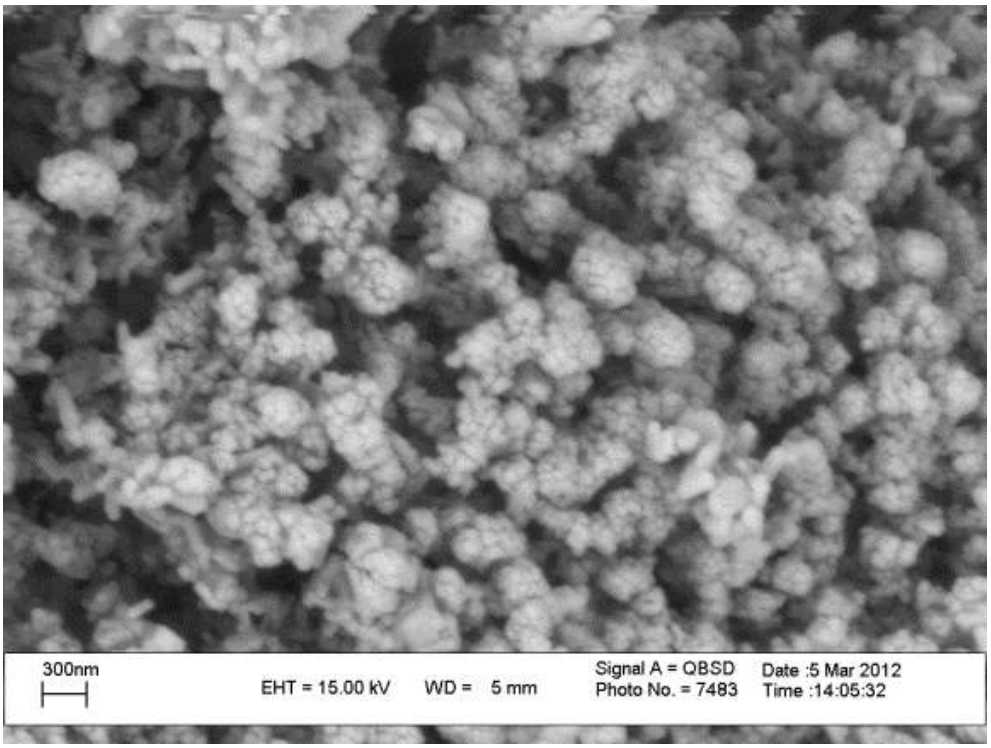

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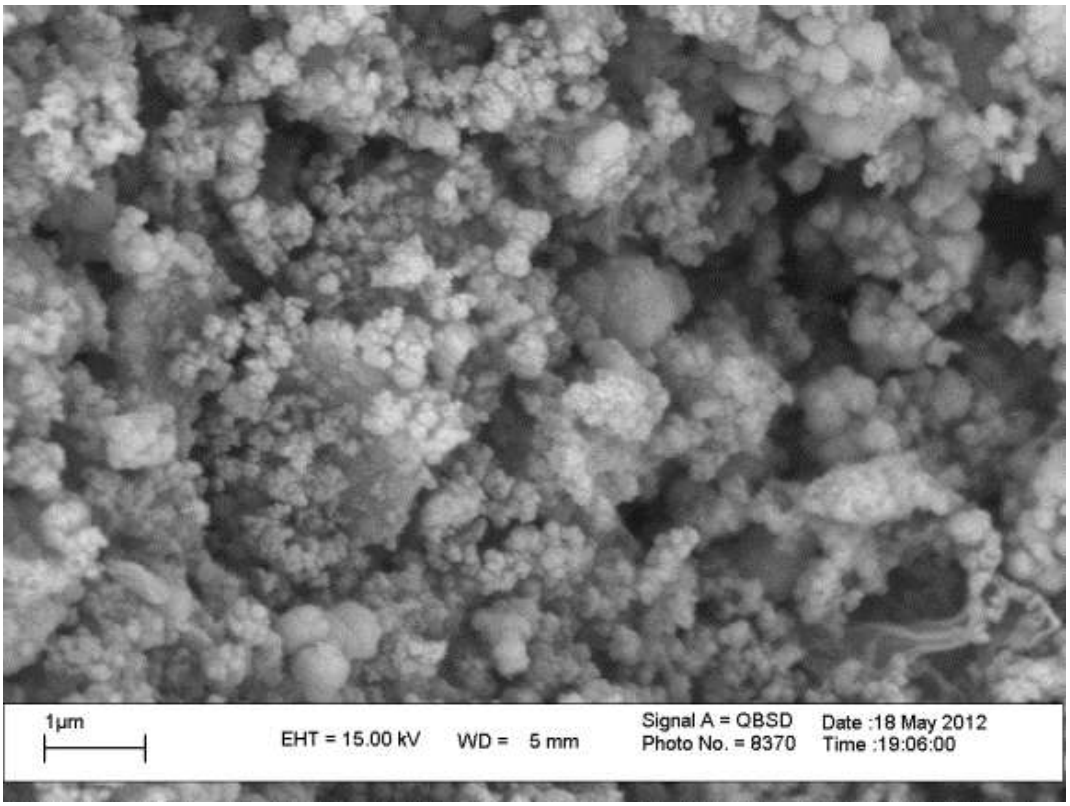

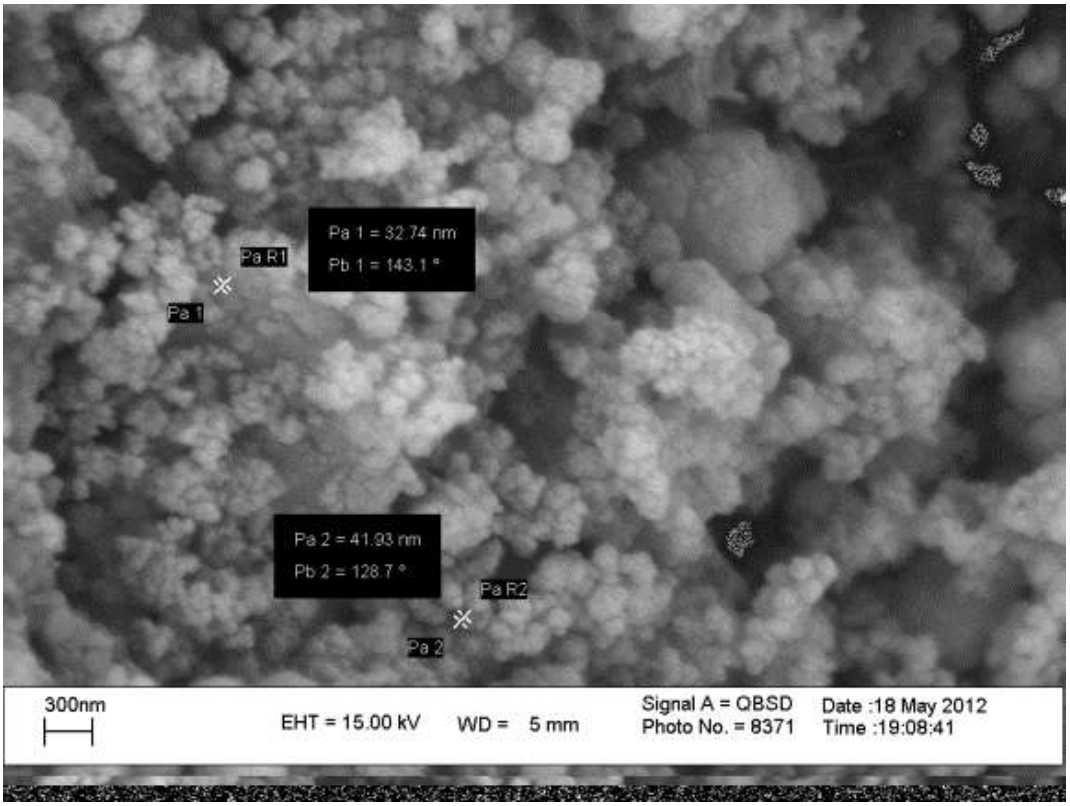

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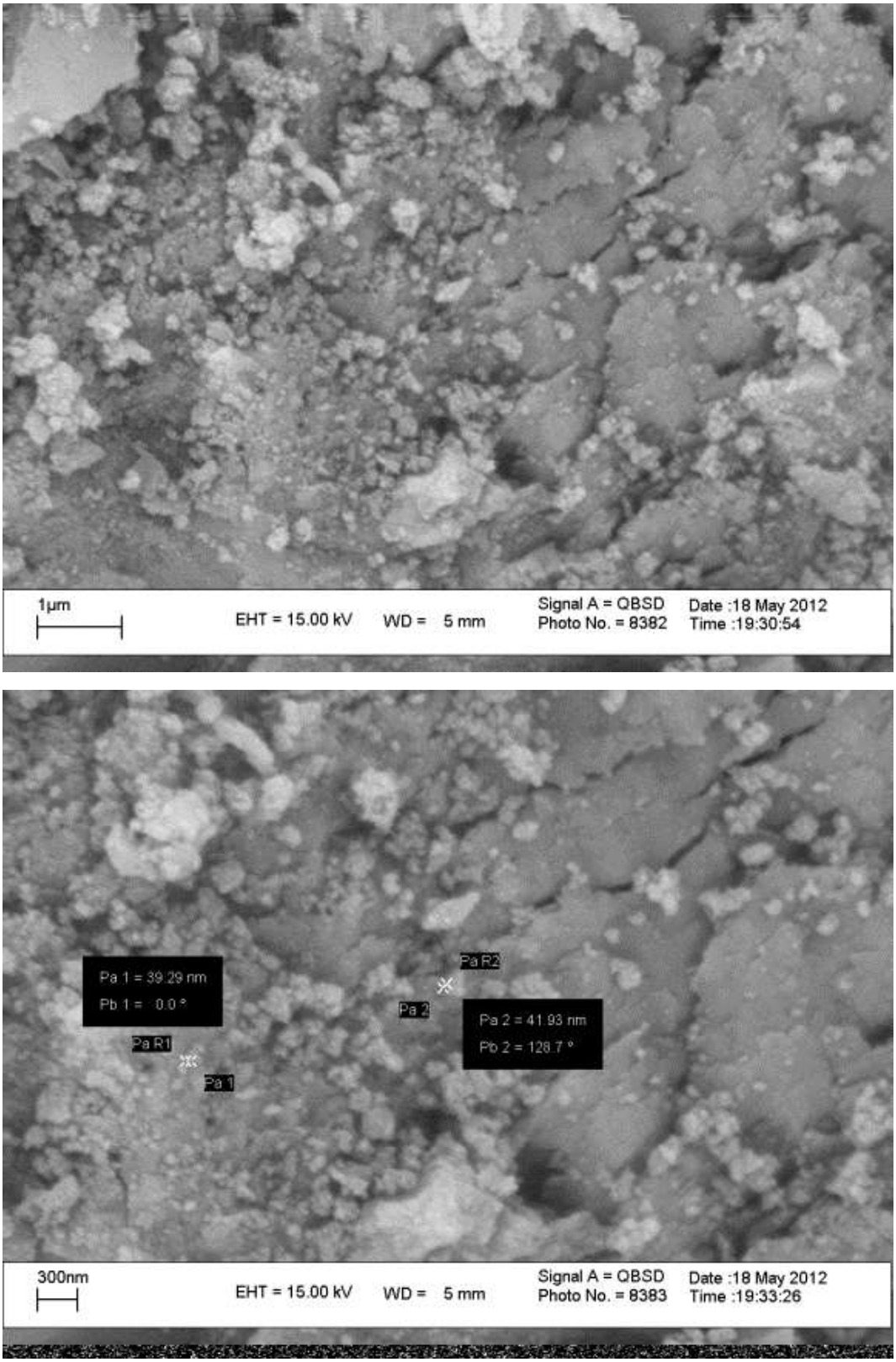

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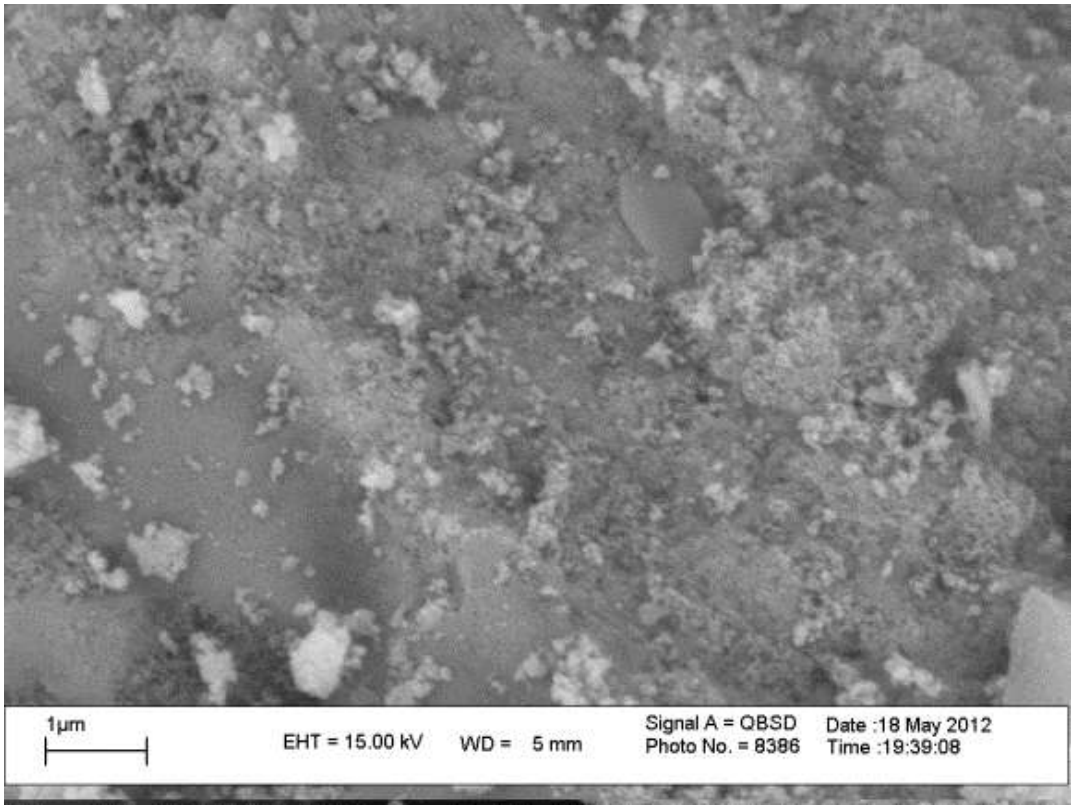

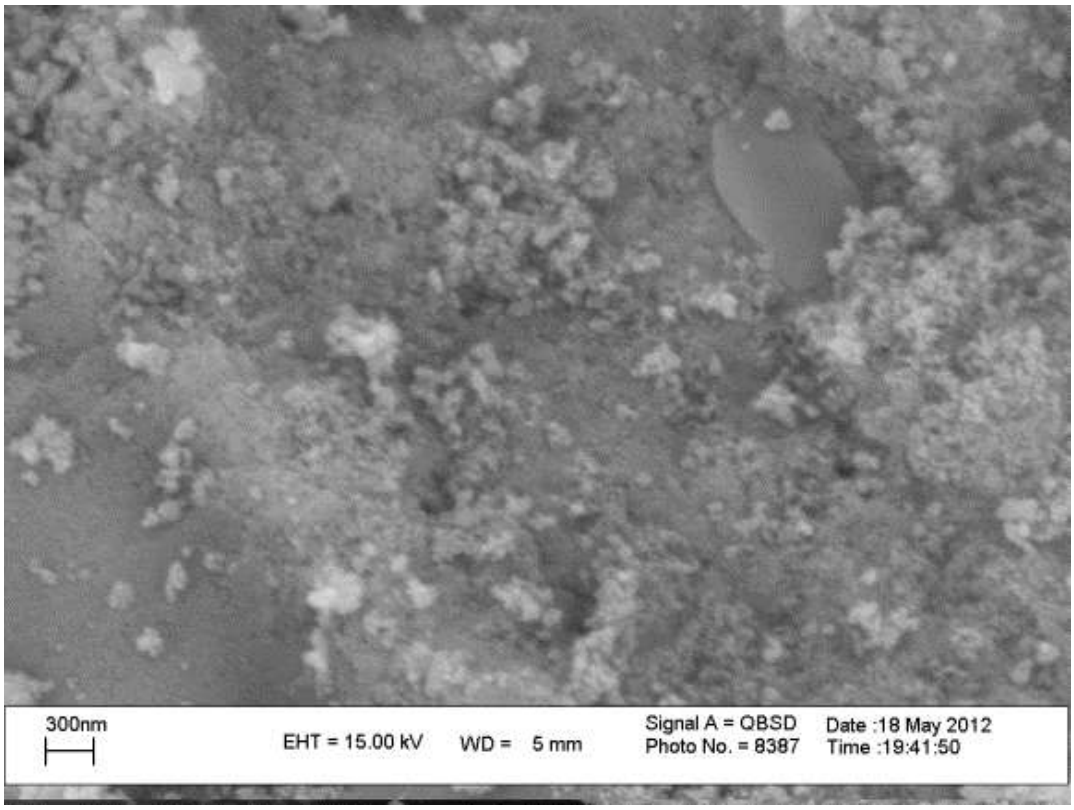

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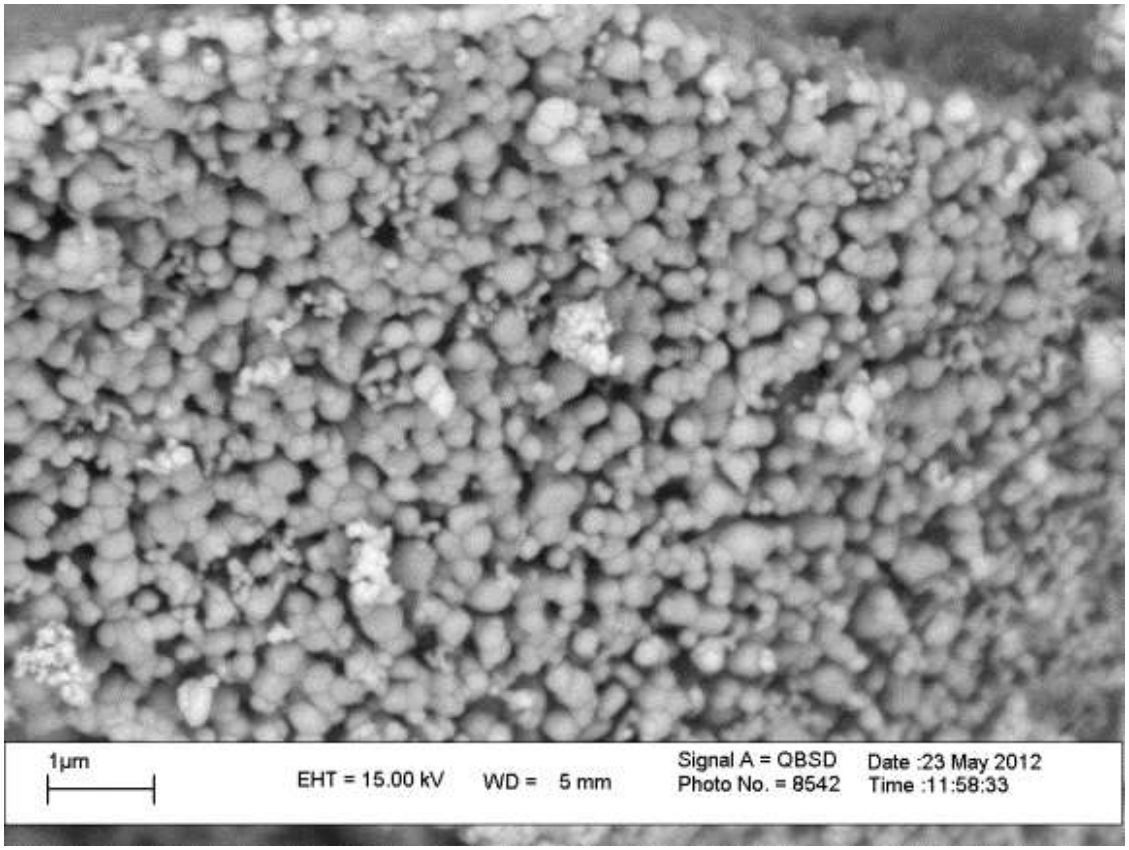

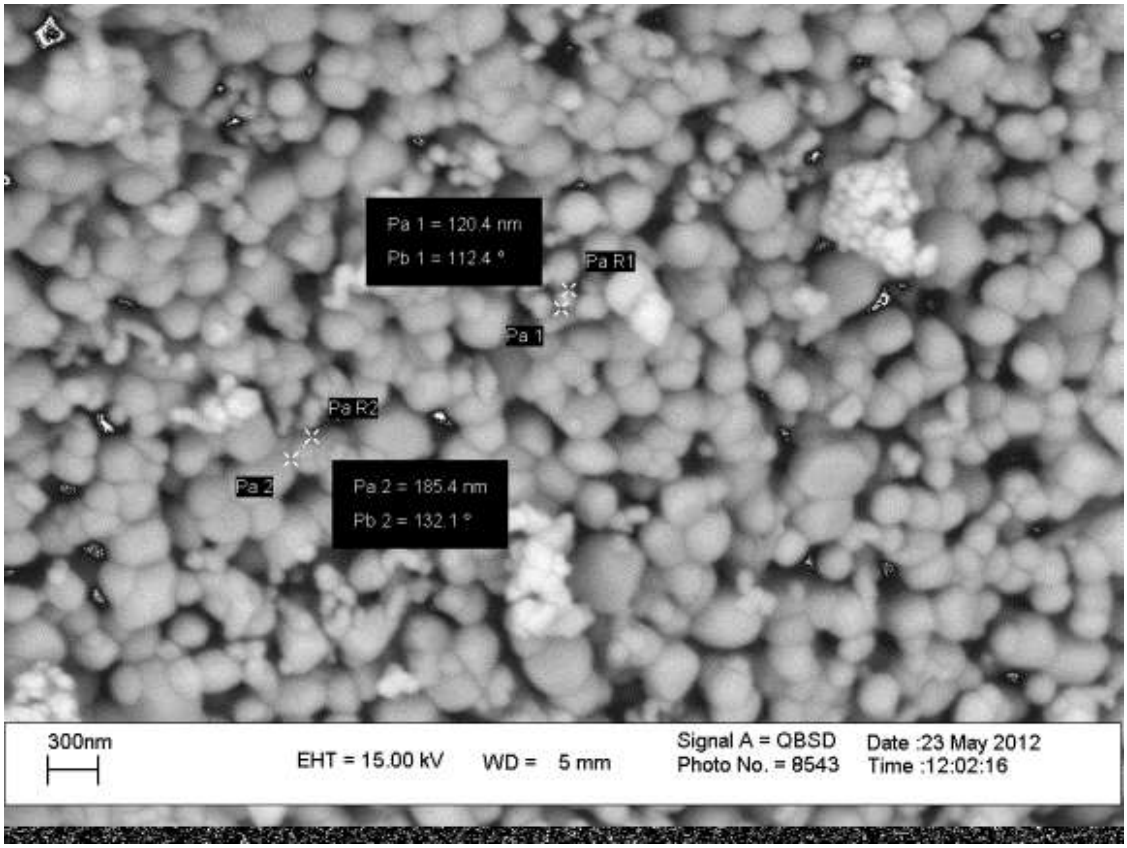

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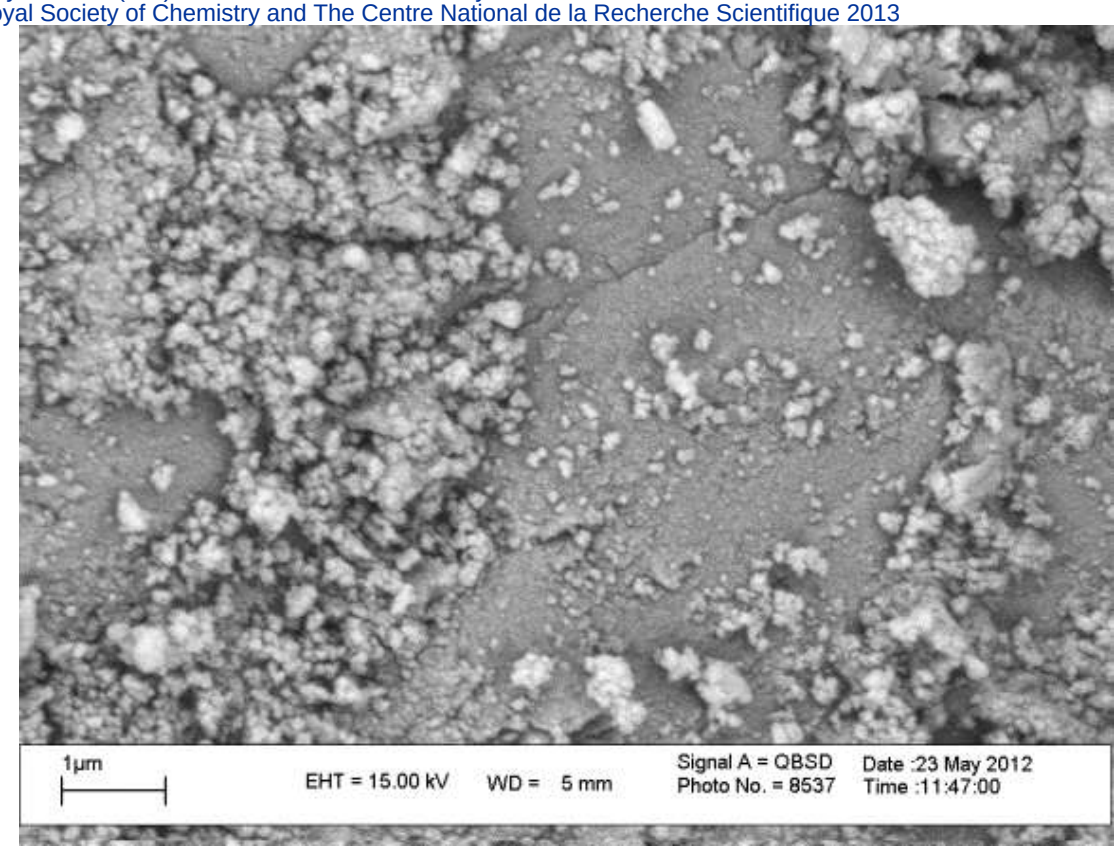

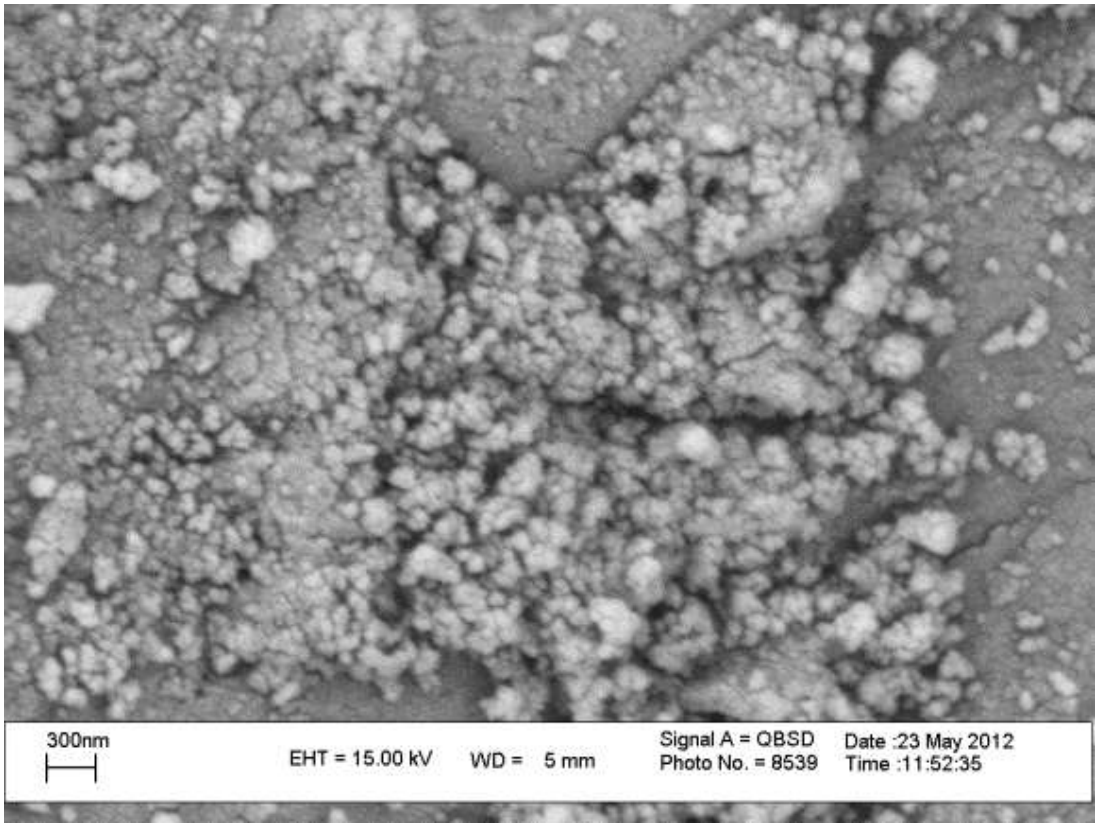

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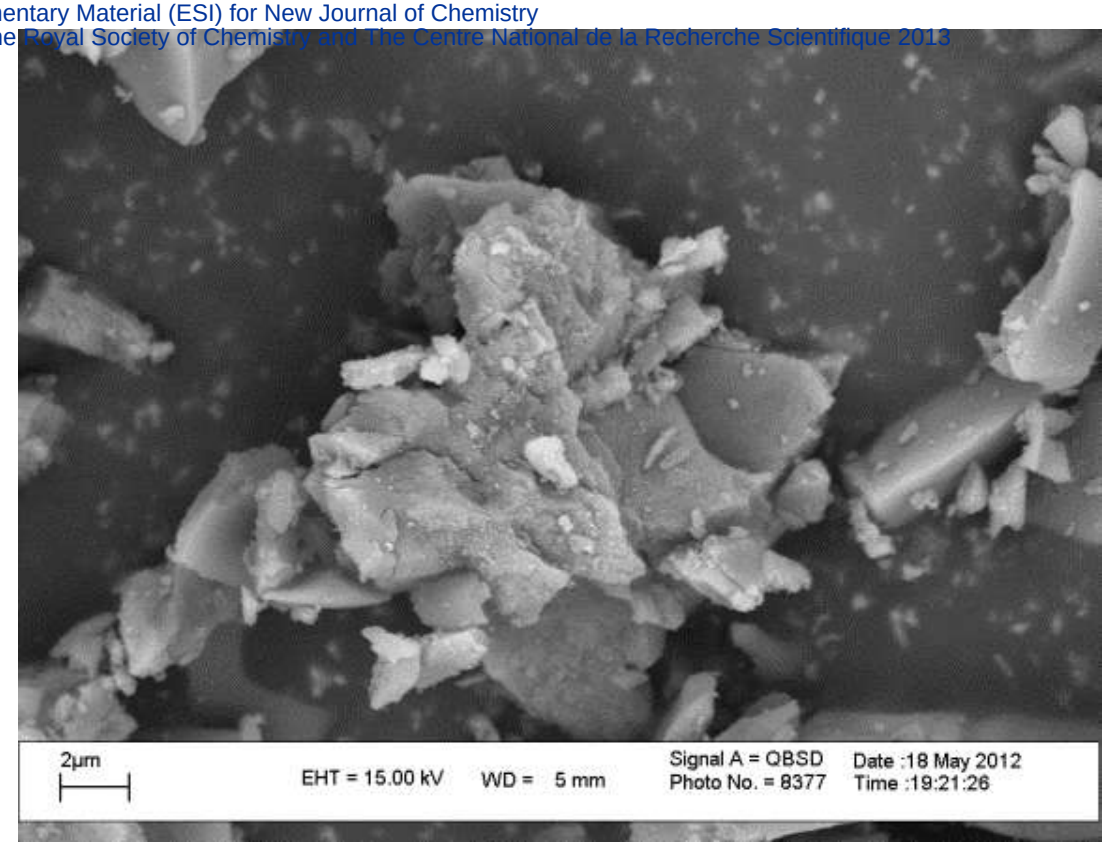

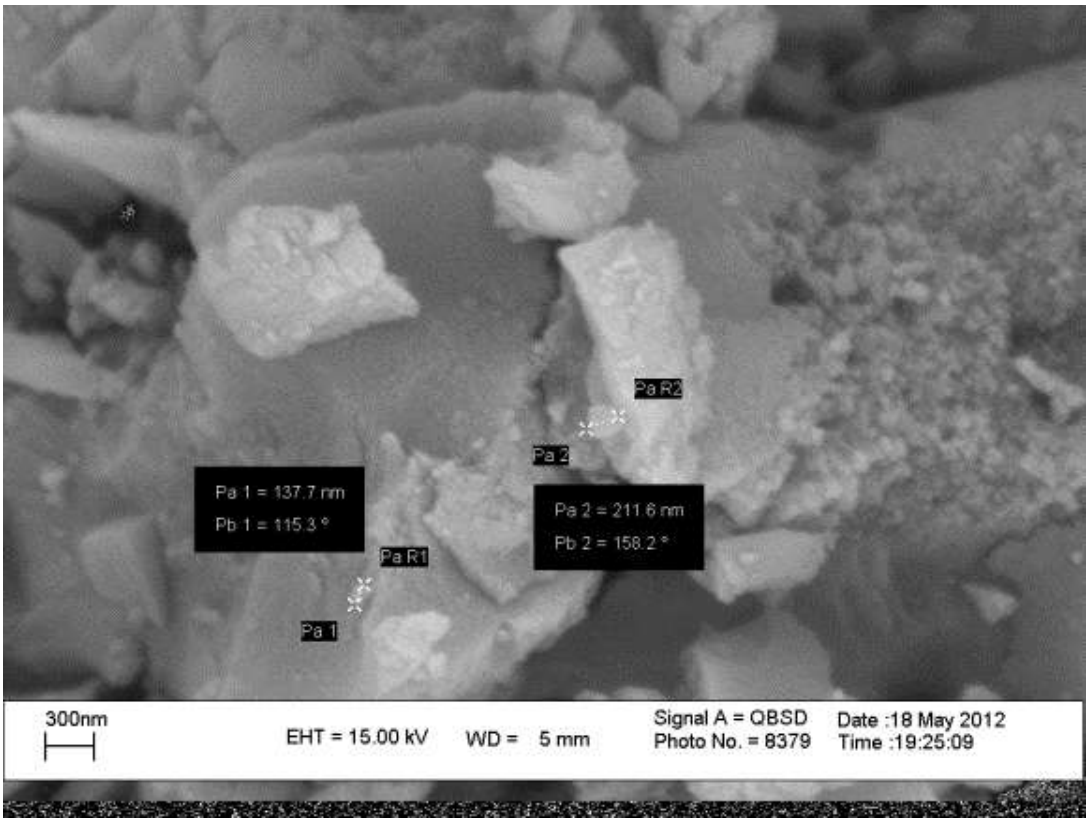

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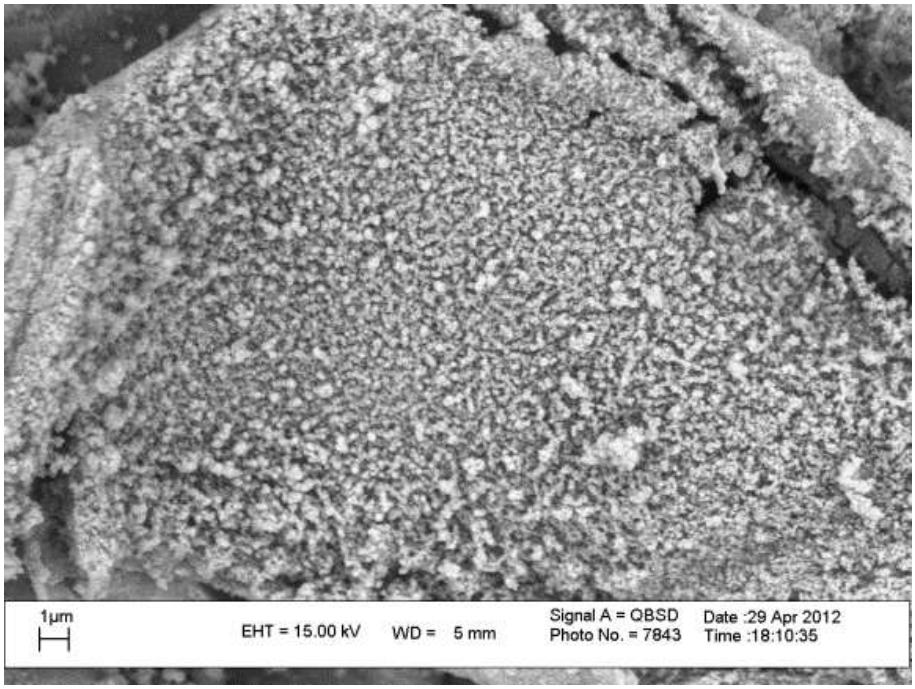
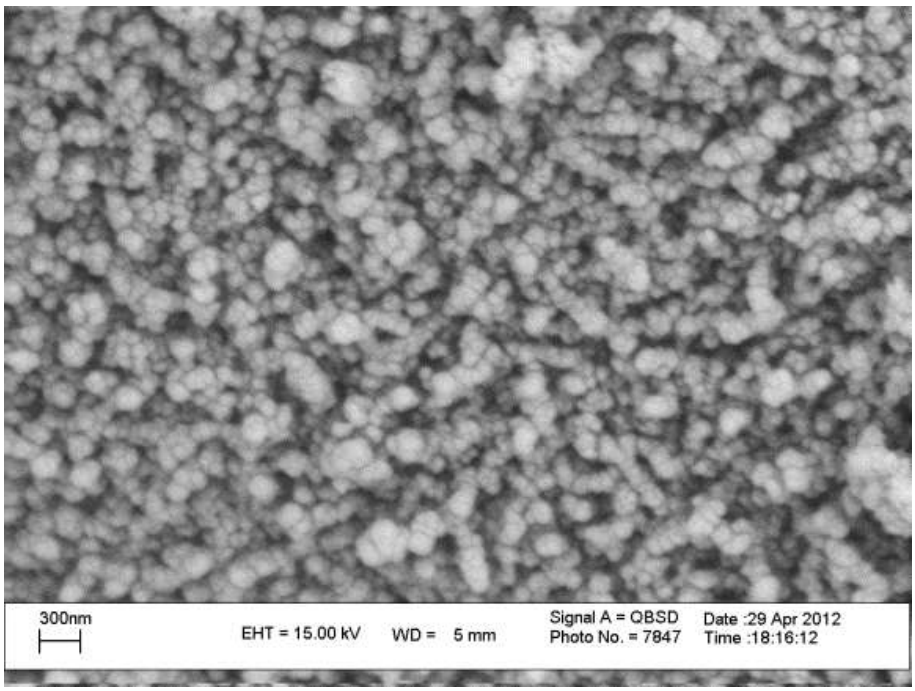
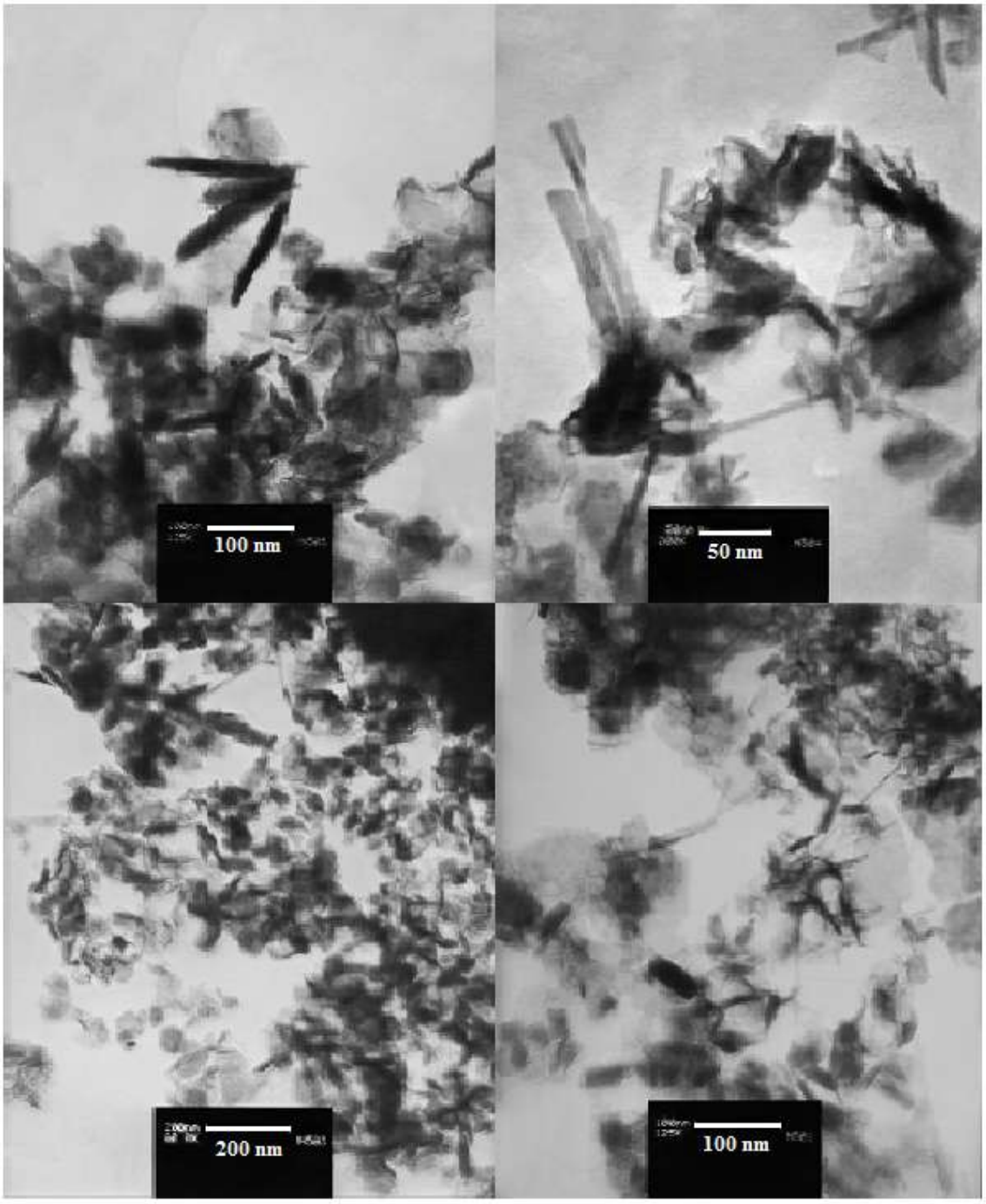


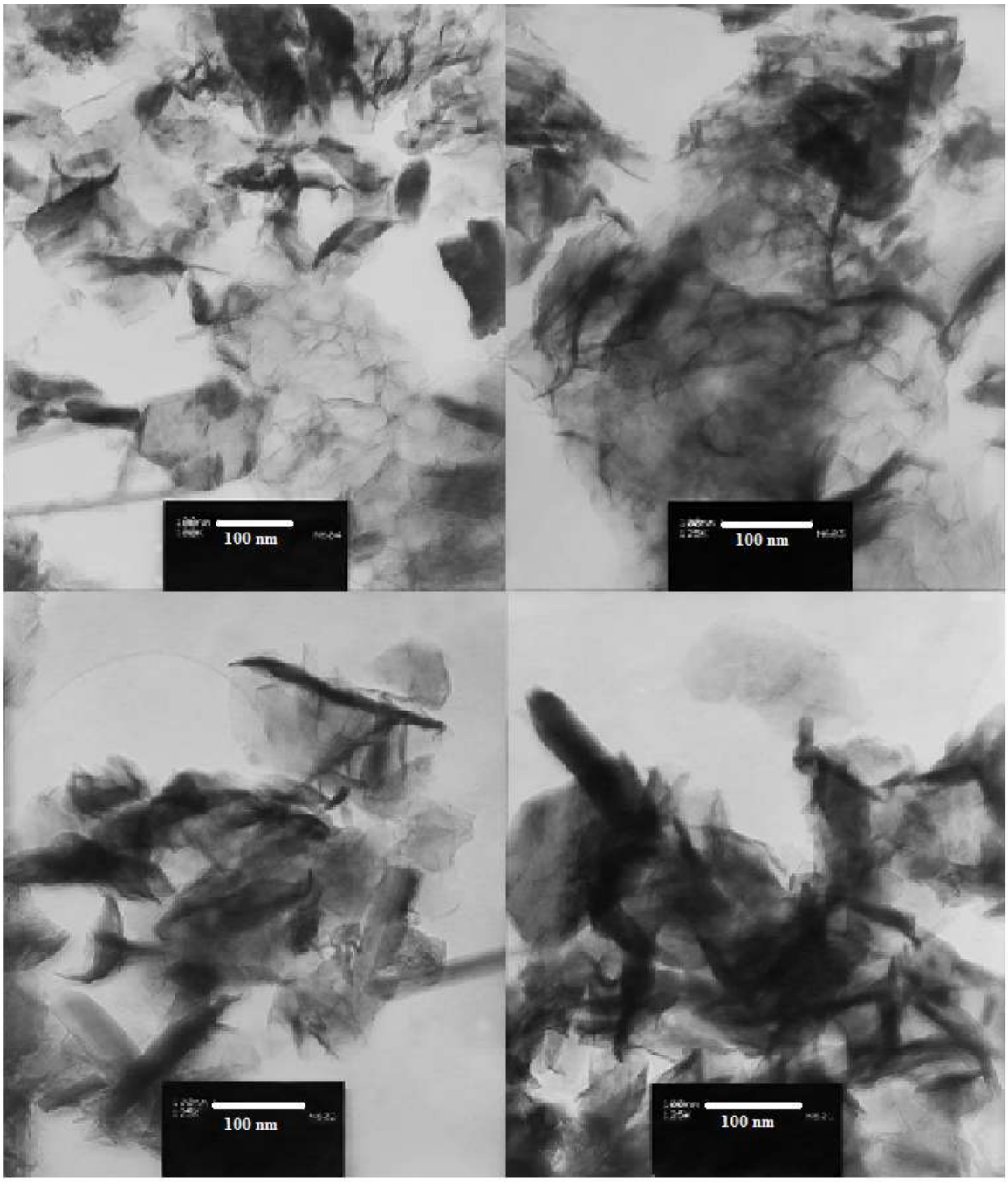


(q)

Fig. S3SEM images of Cd: Mn = 4 (mole ratio in solution 1 see text) (a), 30 (b), best catalysts (Cd: Mn = 0.16) prepared at 100 (c), 300 (d), 600 ^{o}C (e), Mg:Mn = 4 (mole ratio in solution 1 see text) (f), 30 (g), best catalysts (Mg: Mn = 0.16) prepared at 100 (h), 400 (i), 750 ^{o}C (j), K-Mn oxide prepared with 40 g KOH (k), at pH = 7 at 100(l), 400 (m), 700 (n), 60 (o), pH = 0 at 60 ^{o}C (p) and M-Mn oxide (q).



(a)



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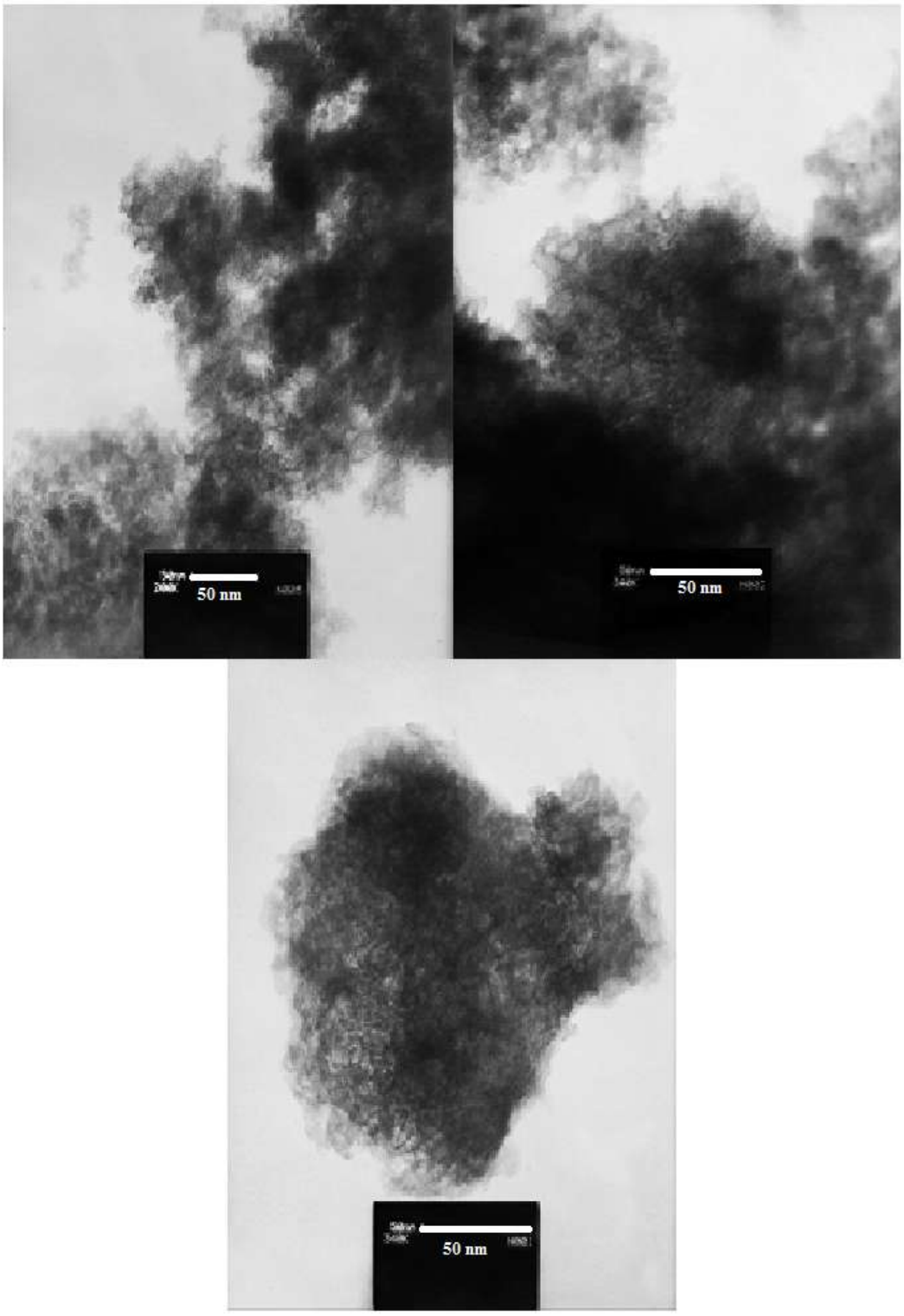

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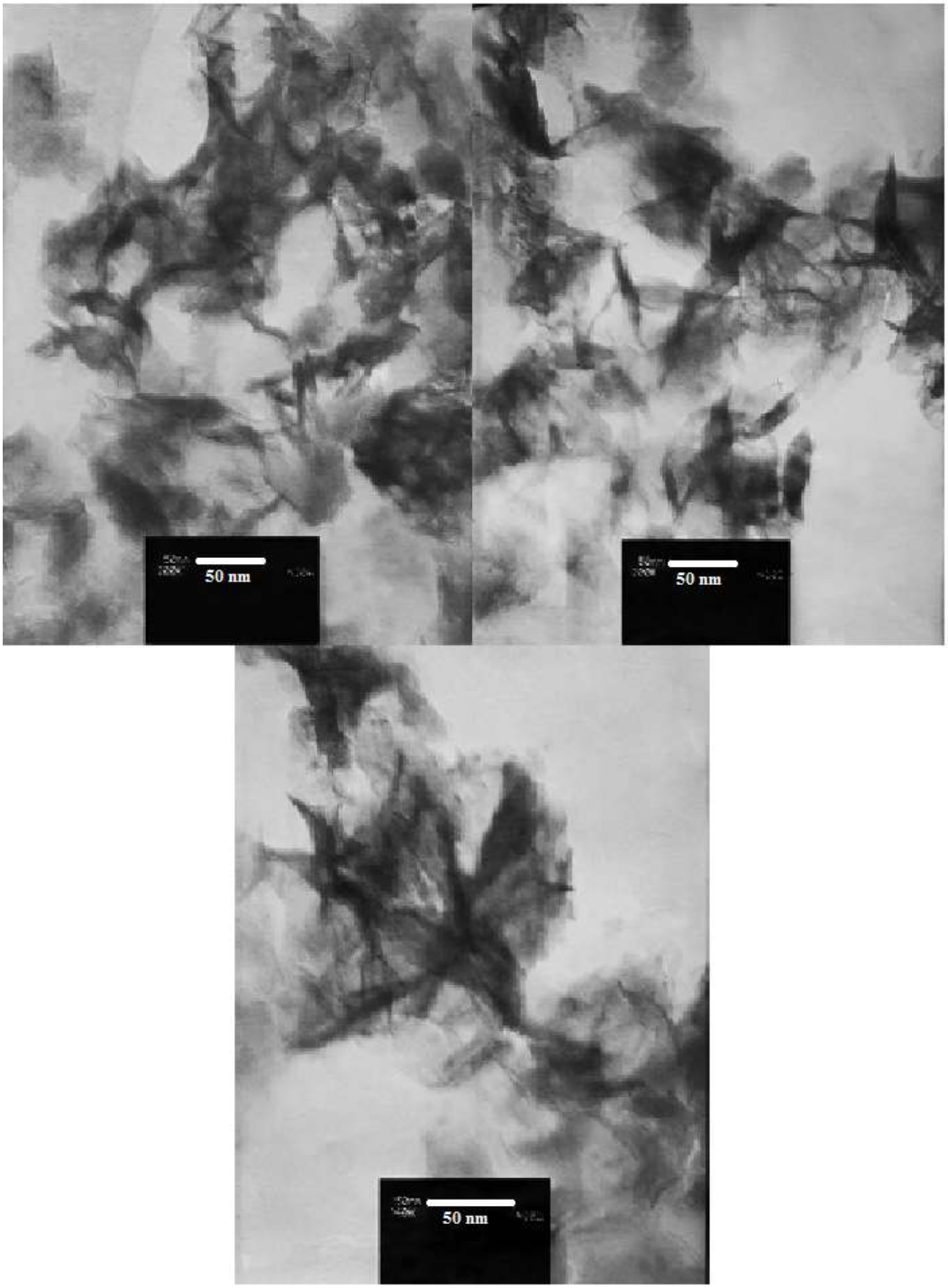
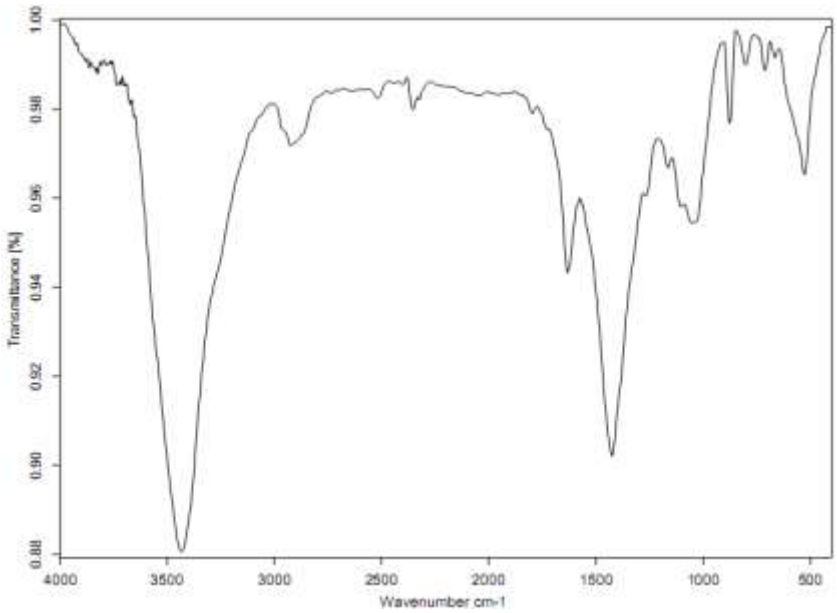
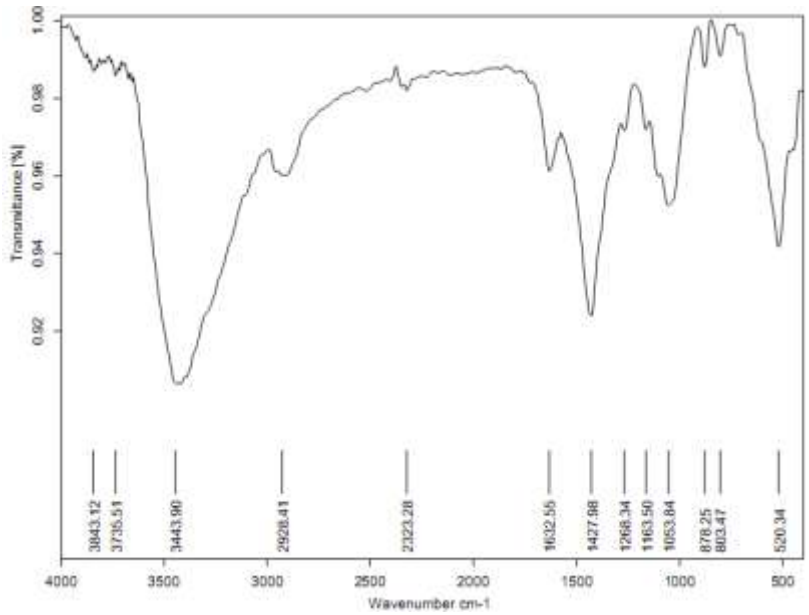


(d)

Fig S4. TEM images of the best catalysts (Cd: Mn = 0.16) prepared at 400 (a), (Mg: Mn = 0.16) prepared at 300 (b), (K:Mn: 0.2) prepared at 200 (c) and M-Mn oxide prepared at 200 ^{o}C (d).



(a)



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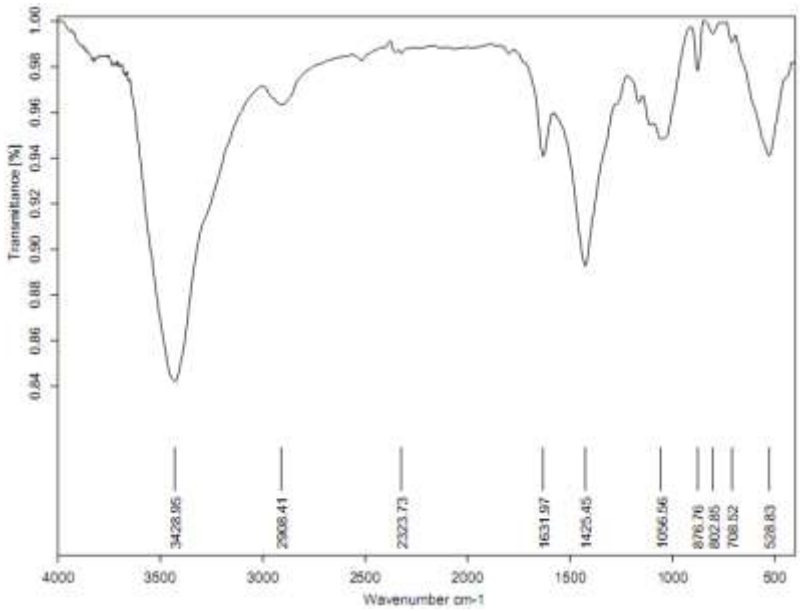

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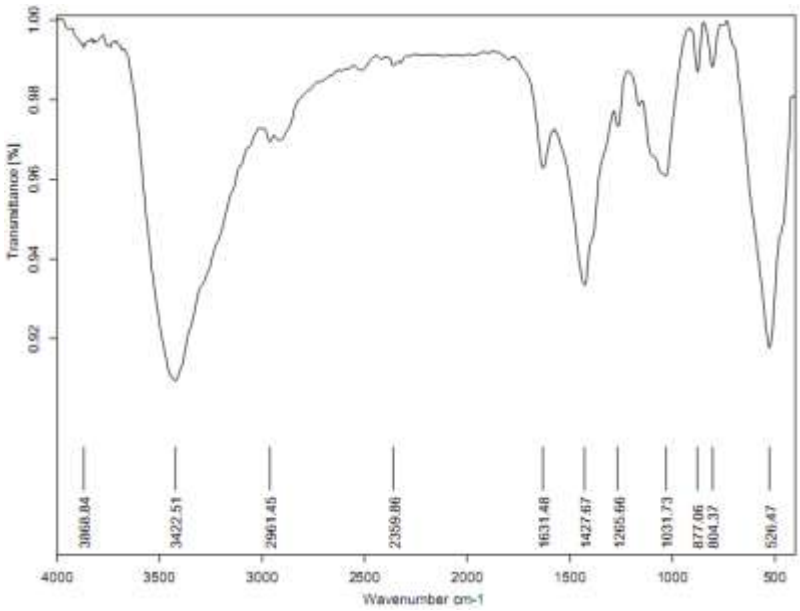

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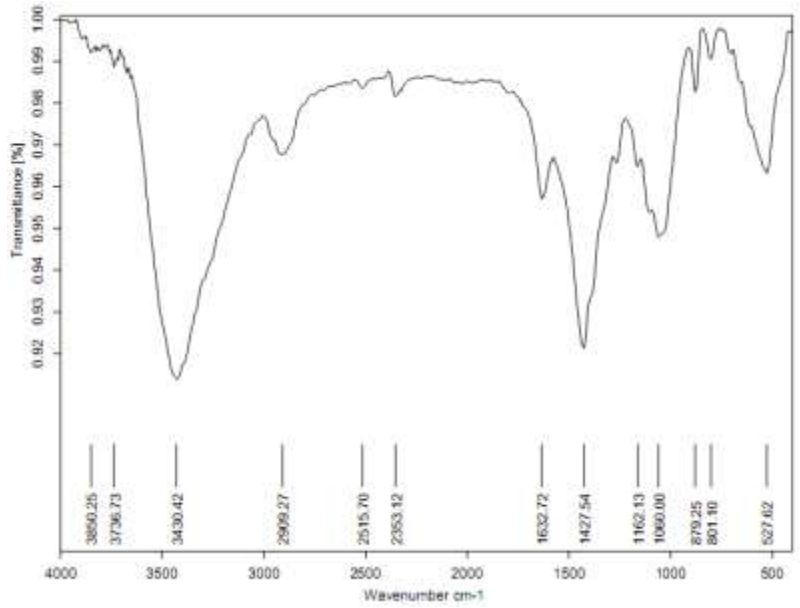

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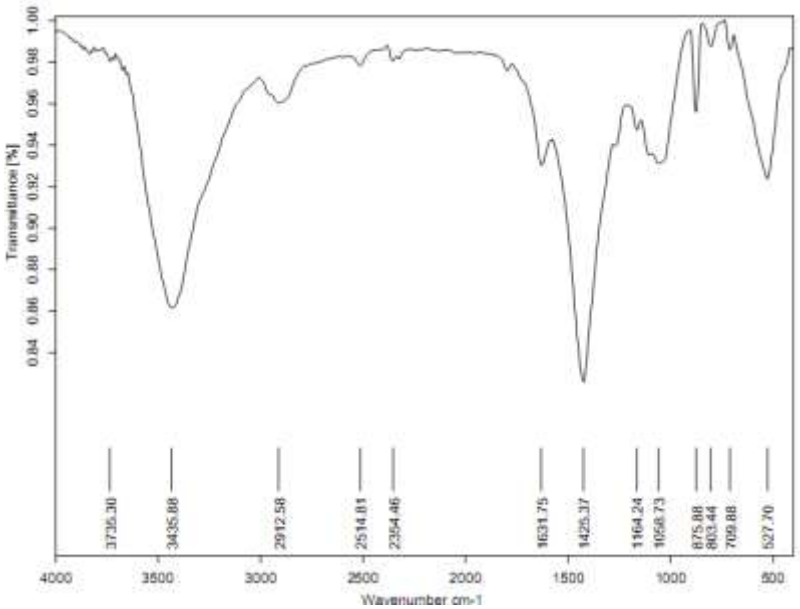

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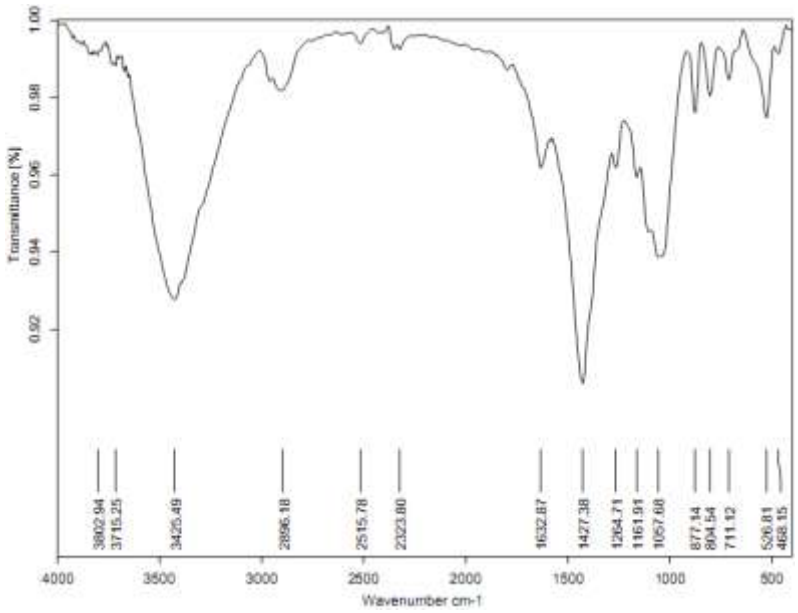

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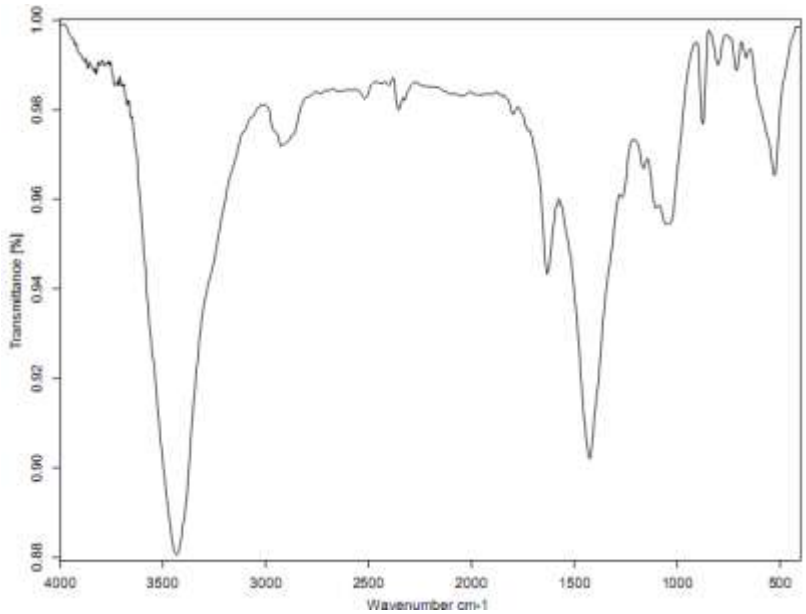

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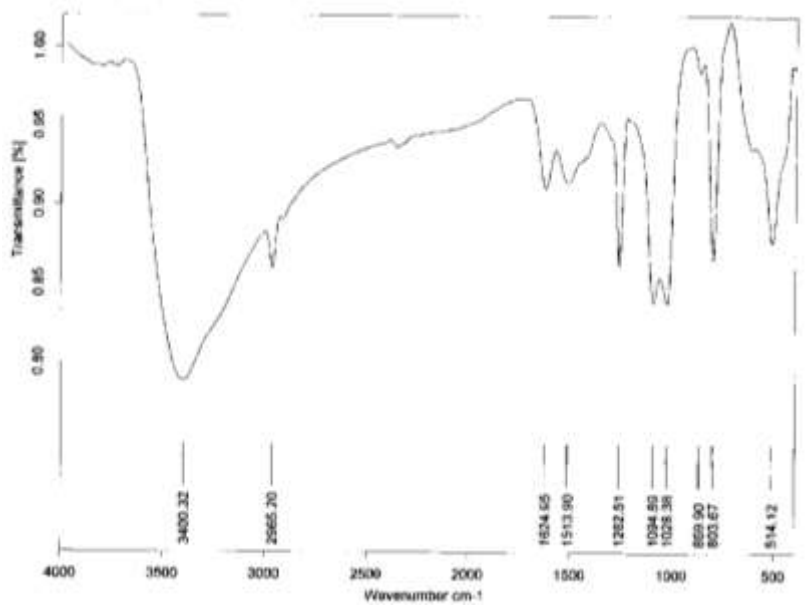
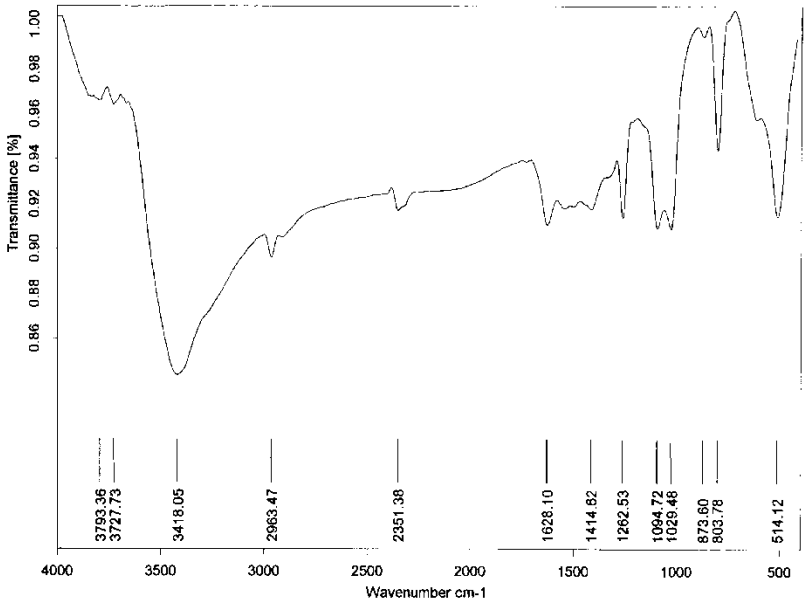
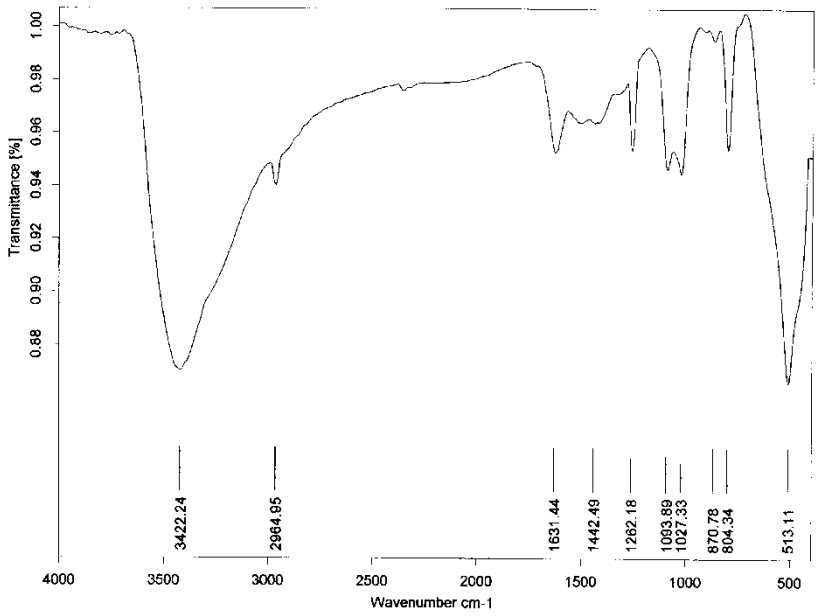


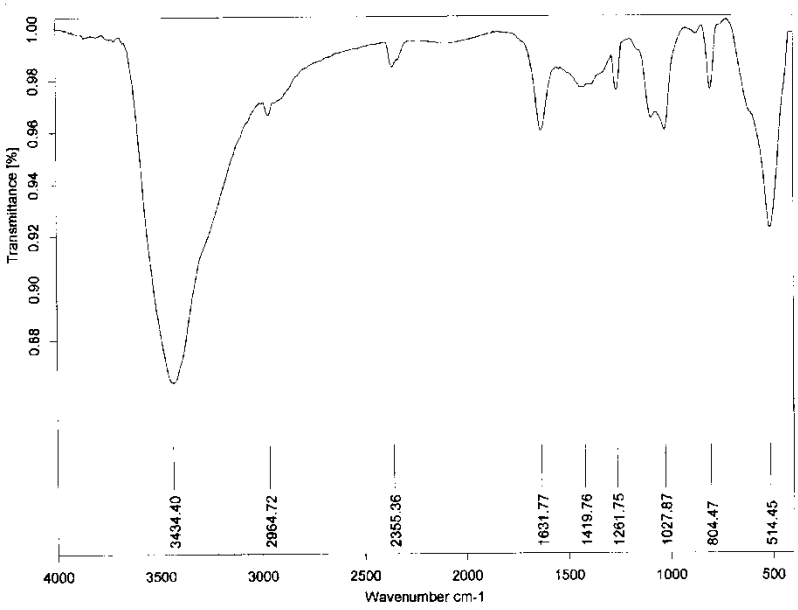
(i)



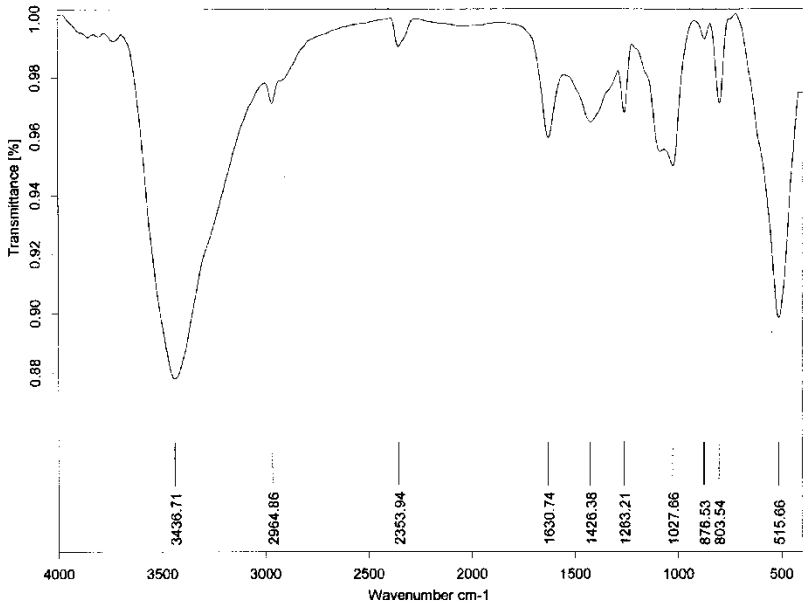
(j)



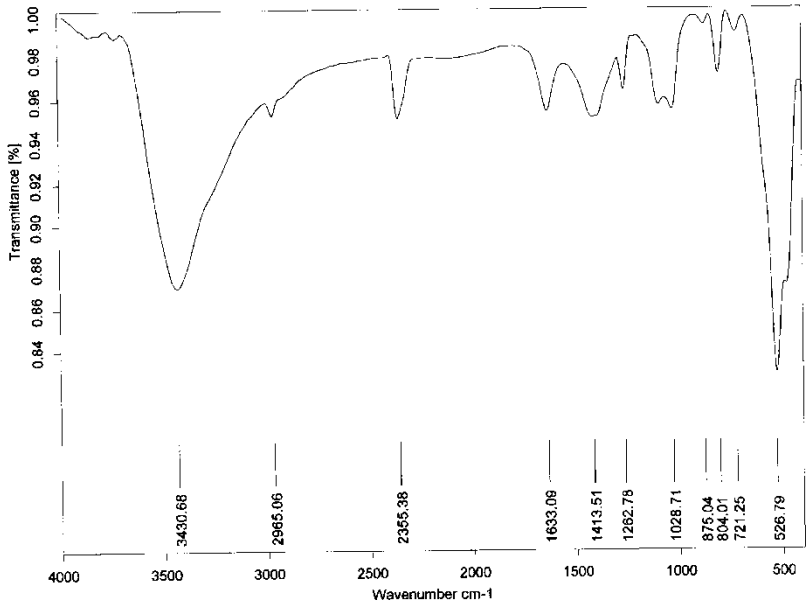
(k)



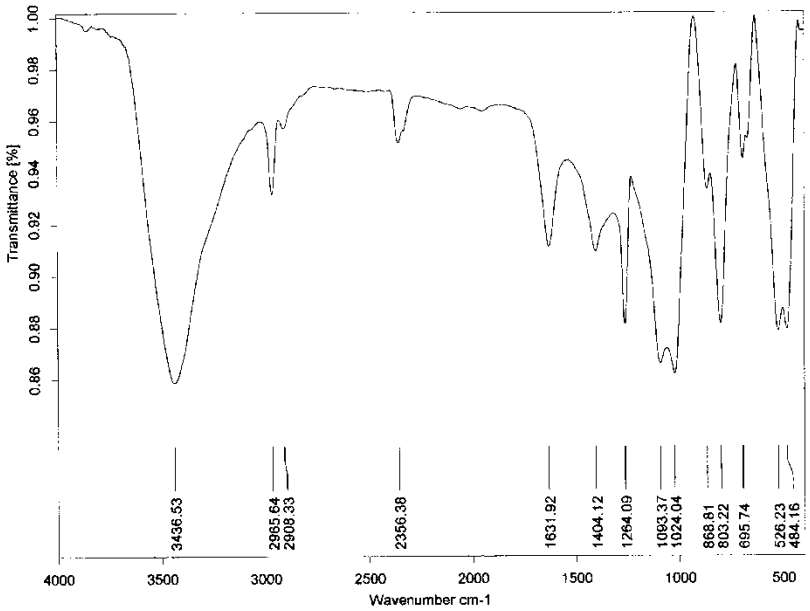
(l)



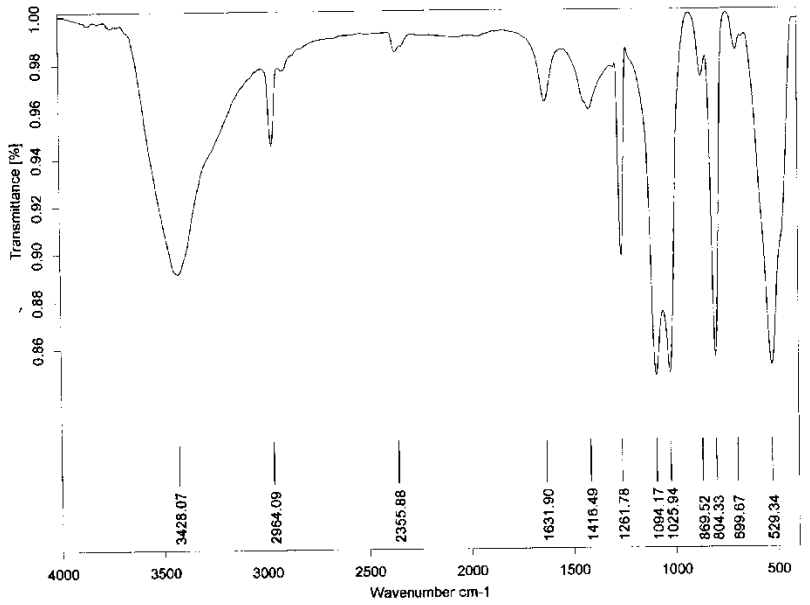
(m)



(n)

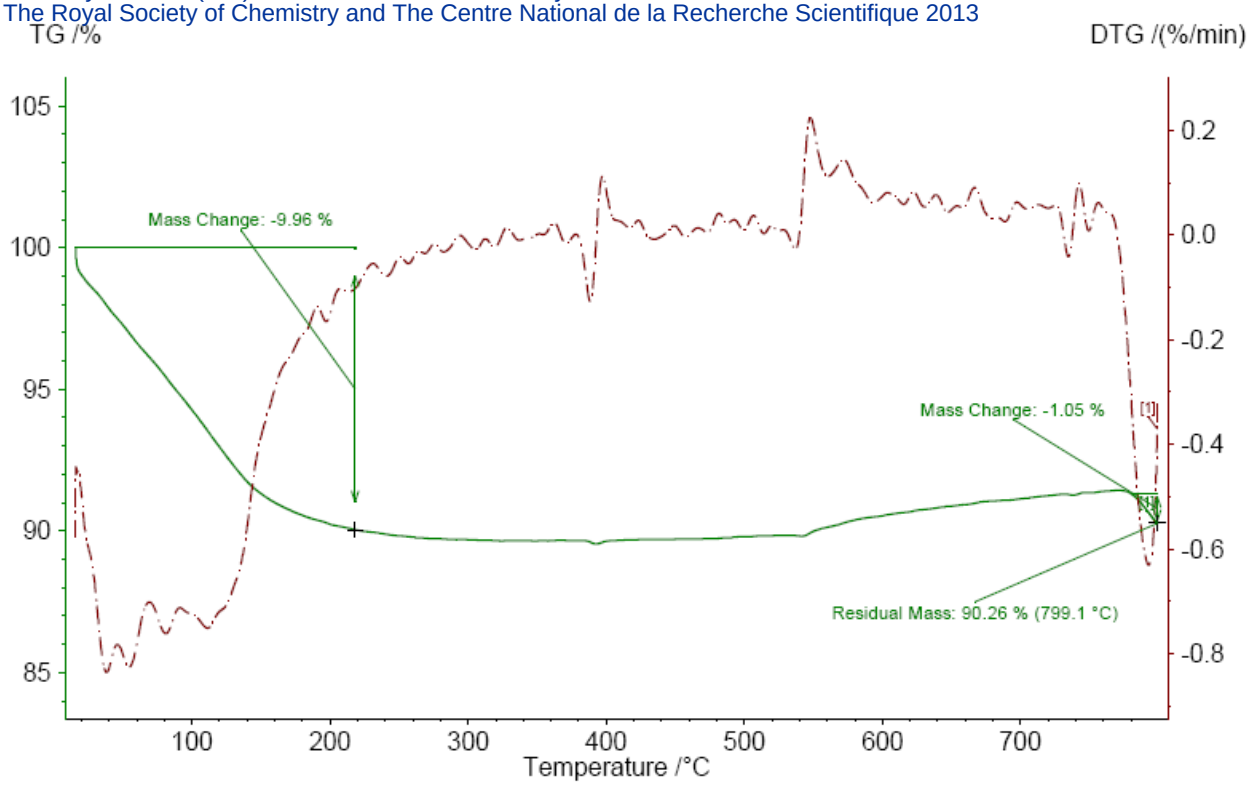


(o)

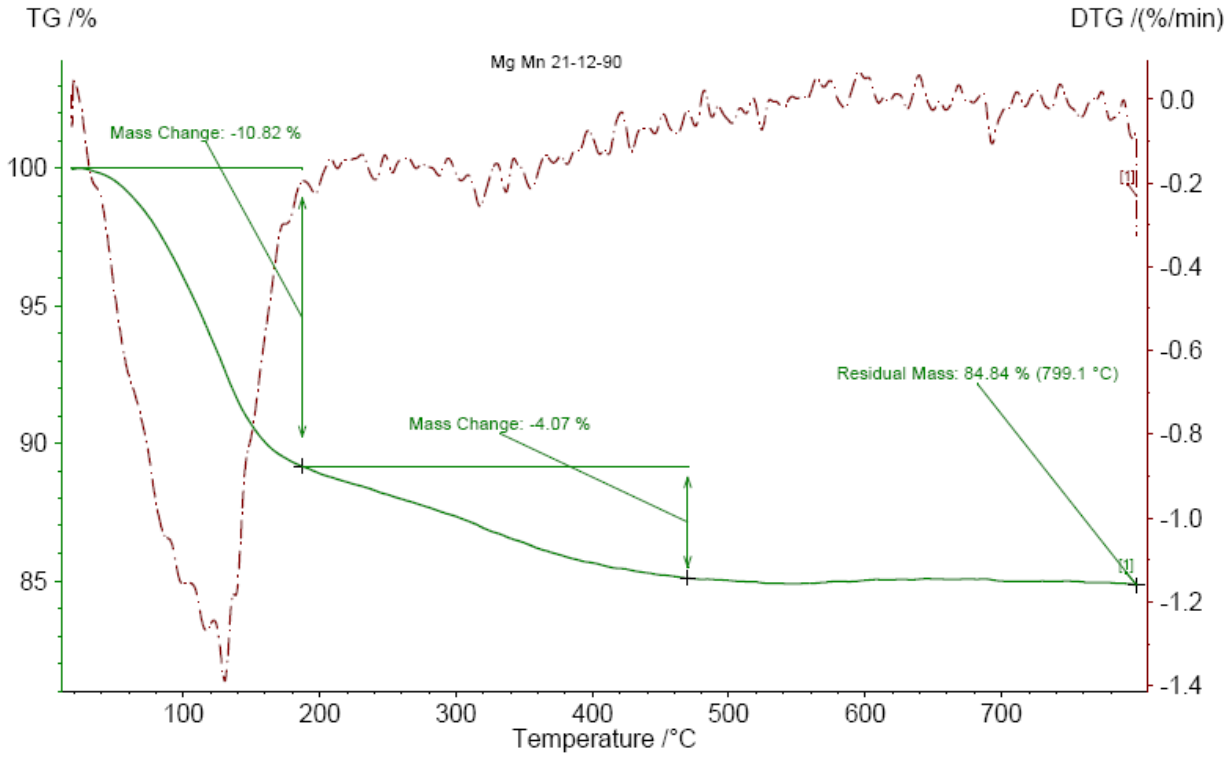


(p)

Fig S5. IR spectra of Cd: Mn (mole ratio in solution 1 see text) = 40 (a), 50 (b), best catalysts (Cd: Mn = 0.16) prepared at 100 (c), 150 (d), 200 (e), 300 (f), 500 (g), 600 ^{o}C (h), best catalyst (Mg: Mn = 0.16) prepared at 60 (i), 100 (j), 200 (k), 300 (l), 400 (m), 500 (n), 600 (o) and 750 ^{o}C (p). K-Mn oxide prepared with 40 g KOH (k), at pH = 7 at 100(l), 400 (m), 700 (n), 60 (o), pH = 0 at 60 ^{o}C (p).



a



b

Fig. S6 TGA and DTG of the $Cd_{0.16}MnO_2$ (a) $Mg_{0.16}MnO_2$ (b) prepared at 60 ^oC.

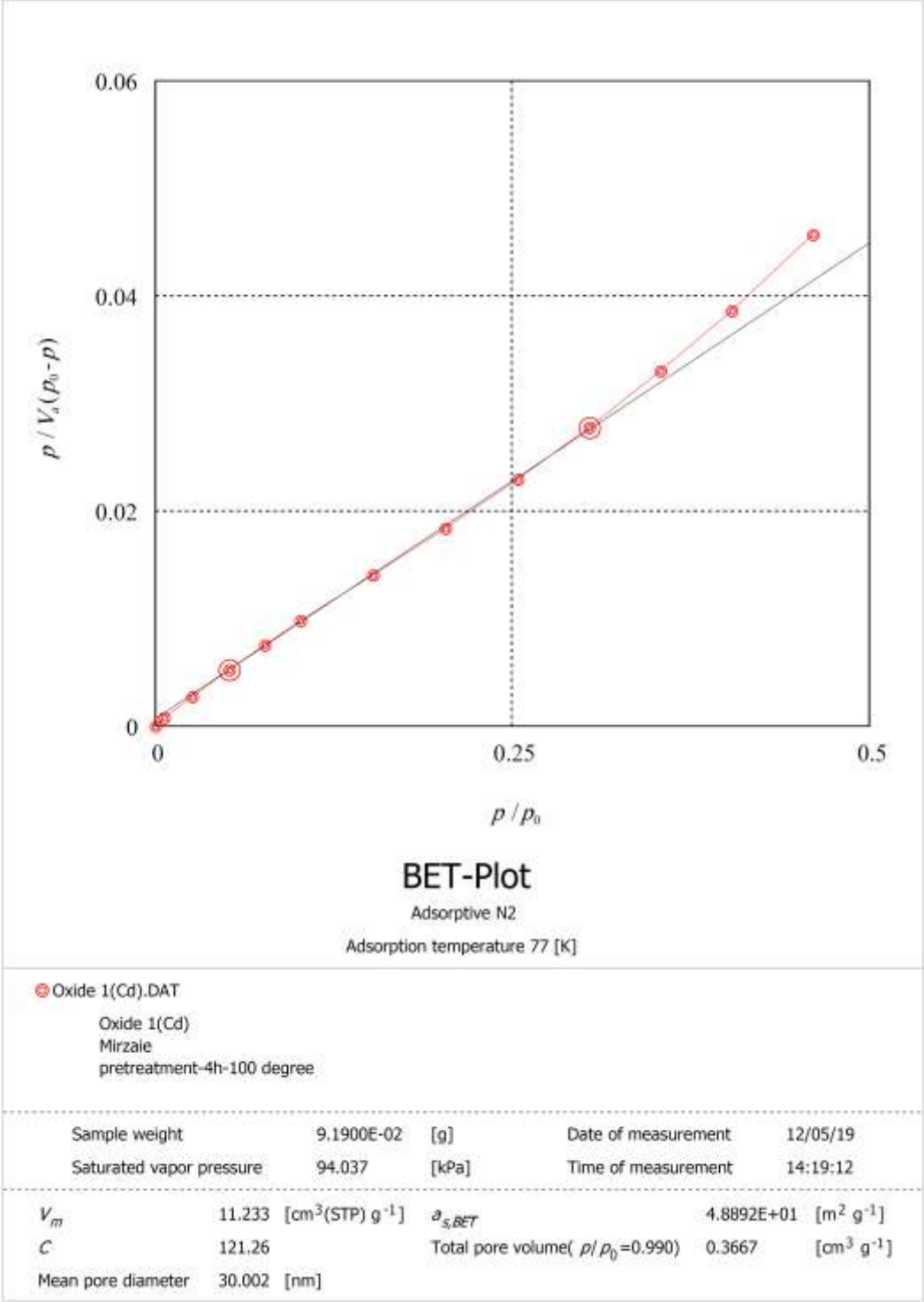


Fig. S7 BET diagram for the best Cd-Mn oxide (Cd:Mn = 0.16) prepared at 400 °C.

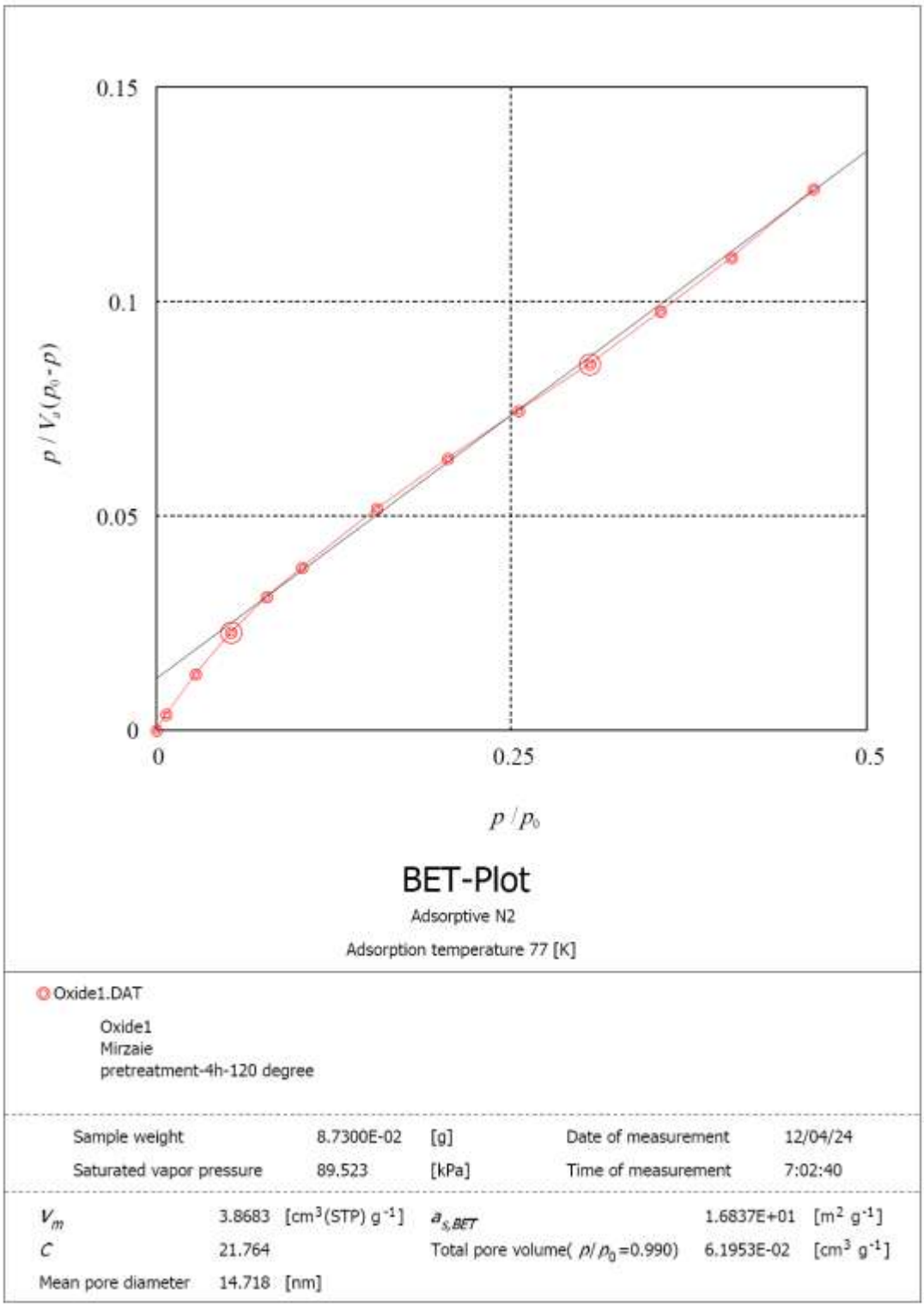


Fig. S8 BET diagram for the best Mg-Mn oxide (Mg:Mn = 0.16) prepared at 300 °C.