Supporting Information

Nano-sized manganese oxide: A proposed catalyst for water oxidation in the reaction of some manganese complexes and cerium (IV) ammonium nitrate

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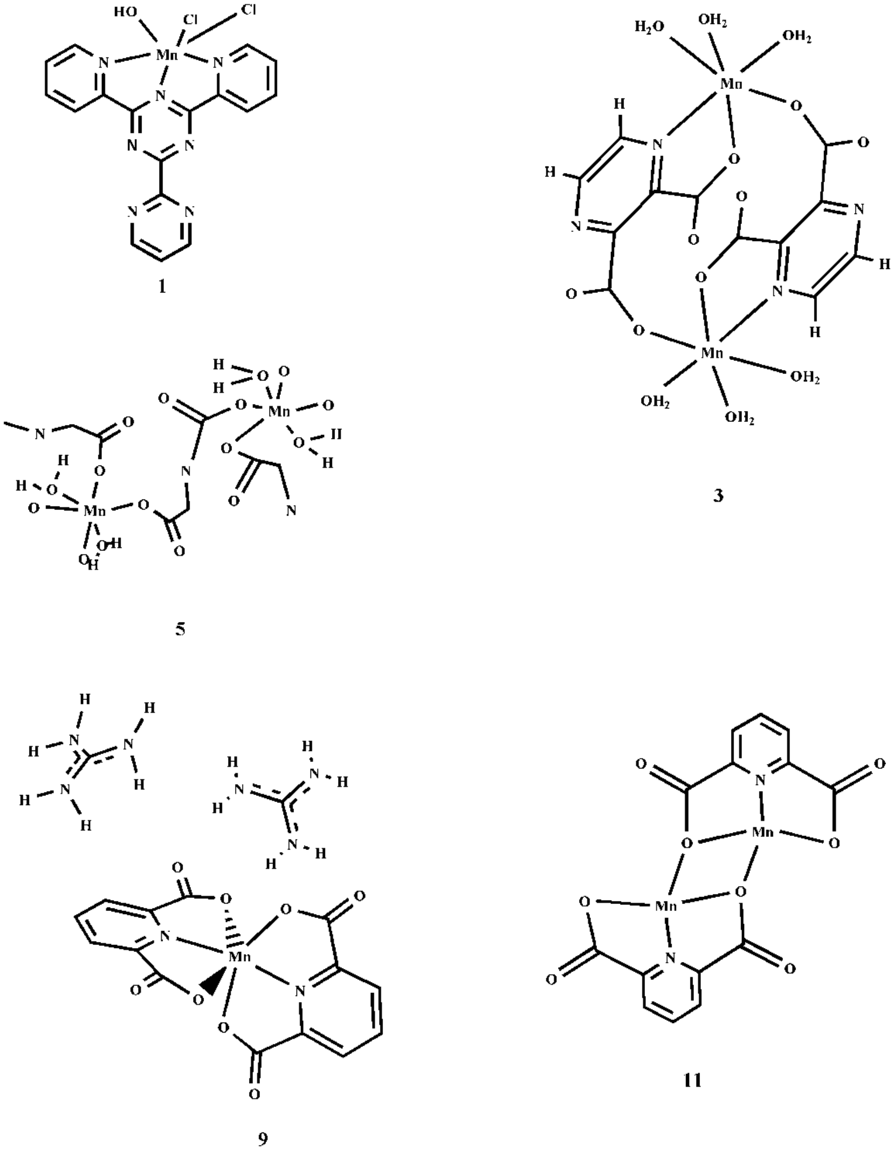


1

3

5

9

11

Scheme S1. The structures of synthesized manganese complexes studied in this paper.

Preparation of complexes

All complexes were synthesized by previously reported procedures:

Complex 1 [Mn(tptz)$Cl_2(OH_2)$, tptz: 2,4,6-tris(2-pyridyl)-1,3,5-triazine] [1]: The complex was prepared by dissolving manganese (II) chloride (1 mmol, 126 mg) and tptz (1 mmol, 312 mg) in water (30 ml); the mixture was stirred for about 1 h at room temperature under nitrogen. The solution was then evaporated on a steam bath to 10 mL and cooled to room temperature. Orange crystals separated and were filtered off, washed with 5 mL of cooled water and then dried in air. IR (cm^{-1}): 3445 (b), 3360 (s), 1,526 (s), 1,480 (m), 1379 (s), 1045 (w), 809 (s).

Complex 2a [Mn(phen)$_2$]$Cl_2.2H_2O$) [2]: The complex was prepared by reacting of manganese (II) chloride (2.0 mmol, 252 mg) and 1,10-phenanthroline (4.0 mmol, 720 mg) in 20 ml EtOH. This solution yielded yellow crystals of the complex after 4 h. Anal. Yellow crystals separated and were filtered off, washed with 5 mL of cooled water, 5 mL EtOH and then dried in air. IR (cm^{-1}): 3413 (b), 1631 (m), 1583 (m), 1422 (s), 1096 (m), 1030 (m), 849 (s), 724 (s).

Complex 2b ([Mn(phen)$_3$]Cl_2 [3]: The complex was prepared by reacting of manganese (II) chloride (2.0 mmol, 252 mg) and1,10-phenanthroline (3.0 mmol, 0.54 g). This solution yielded yellow crystals of the complex after 24 h. Yellow crystals separated and were filtered off, washed with 5 mL of cooled water, 5 mL EtOH and then dried in air. IR (cm^{-1}): 3413 (b), 1632 (m), 14422 (s), 1093 (s), 1027 (s), 849 (s), 805 (w), 725 (s).

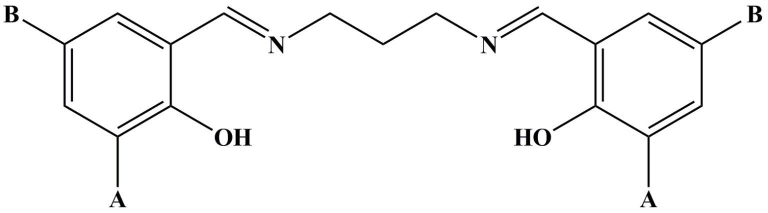
Complex 3 [MnPzdc$(H_2O)_4$, PzdcH =2,3-Pyrazinedicarboxylic acid][4]**:** A 10 ml amount of an aqueous solution of manganese (II) chloride (1.0 mmol, 126 mg) was added to 10 ml of an aqueous of $PzdcH_2$ (1.0 mmol, 168 mg) and stirred for about 3 h at 50 ^{o}C. The pale yellow prism crystals which formed after 2 d. Pale yellow crystals separated and were filtered off, washed with 5 mL of cooled water, 5 mL EtOH and then dried in air. IR (cm^{-1}): 3426 (b), 1634 (s), 1448 (s), 1374 (s), 1119 (s), 886 (s), 446 (m).

Complex 4 [$Mn_2^{III/IV}O_2(bpy)_4](ClO_4)_3$(**9**) [5]: A solution of 4.3 g of $Mn(CH_3COO)_2.4H_2O$ (17.5 mmol) in 60 mL of H_2O was added to 8.2 g of 2,2'-bipyridyl (52.5 mmol) in 30 mL of acetone. Eighty milliliters of 1 M acetate buffer (pH 4.5) was added to the yellow solution, and the pH adjusted to 4.5 with glacial acetic acid. After the solution was cooled to 0 "C in an ice bath 1.18 g of $KMnO_4$ (7.5 mmol) in 50 mL of

H_2O was added dropwise with stirring. The resulting green solution was stirred for 15 min at 0 "C after addition was complete before it was filtered and concentrated sodium pcrchlorate solution added to precipitate the product as a green powder. The product was collected on a medium frit and washed with ethanol and diethyl ether. IR (cm^{-1}): 3424 (b), 1601 (s), 1439 (s), 1090 (s), 1022 (m), 808 (s), 623 (s).

Complex 5 [6]: The complex was prepared by dissolving iminodiacetatic acid (4 mmol, 532.4mg) and manganese (II) perchlorate (2 mmol, 736 mg) in water (20 ml); The mixture was stirred for about 10 min at room temperature under nitrogen. Then calcium hydroxide (1 mmol, 74 mg) was added to this solution and stirred for about 3 h at room temperature under nitrogen. This solution yielded colourless crystals of the complex after 10 days. IR (cm^{-1}): 3423 (b), 1584 (s), 1408 (s), 1323 (m), 1266 (m), 1123 (m), 1008 (w), 924 (m), 874 (w), 797 (w), 724 (w), 704 (w), 596 (w), 528 (w).

Complex 6 [7]: Mn Schiff base complexes: All the complexes (Fig. 1) were prepared and identified according to the literature [7]. In a typical reaction, the complexes were prepared by the reaction of the Schiff base (2.0 mmol) with manganese(III) acetate dihydrate, $Mn(III)(OAc)_3.2H_2O$ (0.27 g, 1.0 mmol) in methanol (100 mL) at 60 °C for 2 h. The resulting precipitates were filtered off. Yields ~ 47%.



Scheme 2S The structure of tetradentate Schiff base ligands in **1-6**: A: NO_2, B: Br for **1**, A: H, B: H for **2**, A: H, B: Br for **3**, A: OH, B: H for **4**, A: H, B: OMe for **5**, A: H, B: OEt for **6**.

Complex 7 [8]: Di-μ-sulfato-κ^3O,O':O"; κ ^{3}O,O':O"-bis{aqua[2,4,6-tris(2-pyridyl)-1,3,5-triazine- κ $^3N^1,N^2,N^6$]manganese (II)} tetrahydrate (5)[8]: The complex was prepared by dissolving manganese(II) sulphate (2 mmol, 338 mg) and tptz (2 mmol, 624mg) in water (20 ml); The mixture was stirred for about 4 h at 45°C. IR (cm^{-1}): 3436 (b), 1629 (m), 1535 (s), 1381 (s), 1107 (s), 780 (s).

Compound 8: A soluble form of nano-sized colloidal manganese (IV) oxide [9]: was synthesized by a similar method to the one described by Perez-Benito et al. [9]. Water-soluble colloidal manganese dioxide was prepared by reducing potassium permanganate with sodium thiosulfate in neutral aqueous solution and a stoichiometric ratio 8:3 [9].

Complex 9 [[Mn(dipic)$_2$][Gua]$_2$, Gua [10]: Guanidinium, dipic: Pyridine-2,6-dicarboxylate]: The complex was prepared [28] by dissolving guanidinium carbonate (4.0 mmol, 720 mg) and pyridine-2,6-dicarboxylic acid (2.0 mmol, 334mg) in water (20 ml); The mixture was stirred for about 1 h at room temperature. Then manganese (II) chloride (1.0 mmol, 126 mg) was added to this solution and stirred for about 3 h at room temperature. This solution yielded yellow crystals of the complex after 10 d. Yellow crystals separated and were filtered off, washed with 5 mL of cooled water, 5 mL EtOH and then dried in air. IR (cm^{-1})**:** 3424 (b), 3225 (b), 1650 (m), 1614 (m), 1456 (s), 1385 (s), 1345 (s), 1042 (m), 816 (m), 741 (m).

Complex 10 [2]: The complex was prepared by reacting of $Mn(NO_3)_2.2H_2O$ (2.0 mmol, 430 mg) and 2,2'-Bipyridine (4.0 mmol, 624 mg) in 20 ml EtOH/water (1/1). This solution yielded yellow crystals of the complex after 4 h. Anal. Yellow crystals separated and were filtered off, washed with 5 mL of cooled water, 5 mL EtOH and then dried in air. IR (cm^{-1}): 3423 (s), 3199 (s), 1621 (s), 1384 (s), 823 (m).

Complex 11: $Mn_2(dipic)_2(H_2O)_6.2H_2dipic]$ [11]: The complex was prepared by dissolving $Mn(ClO_4)_2.6H_2O$ (2 mmol, 736 mg) and dipic pyridine-2,6-dicarboxylic acid (5 mmol, 835 mg in water (100 ml); the mixture was stirred for about 2 h at room temperature. Then $HClO_4$ (0.01 mmol, 0.01 mL) was added to the solution. This solution yielded white crystals of the complex after 3 days (0.503 g, 57%

yield based on $Mn(ClO_4)_2.6H_2O$)). $C_{28}H_{28}Mn_2N_4O_{22}$ ($[Mn_2(dipic)_2(H_2O)_6$. 2H2dipic]). IR (cm^{-1}): 3412 (b), 1693 (s), 1617 (s), 1384 (s), 1237 (m), 1082 (s), 883 (s), 761 (m), 729 (s).

Complexes on clay

Na-montmorillonite clay (2.0 g) was added to an aqueous solution of complexes (~ 1.0 mM, 10 ml). After stirring for 30 min, the complex-clay hybrid was filtrated and then dried in air [12].

The reaction of manganese complexes with Ce(IV)

The complex as solid was added to a solution Ce(IV) in water (condition are reported in text or captions). The colloidal solution was used for DLS, SEM and TEM experiments. For XRD, EPR and FTIR experiments, the colloidal solution was centrifuged and particles were washed by water and dried in air at room temperature.

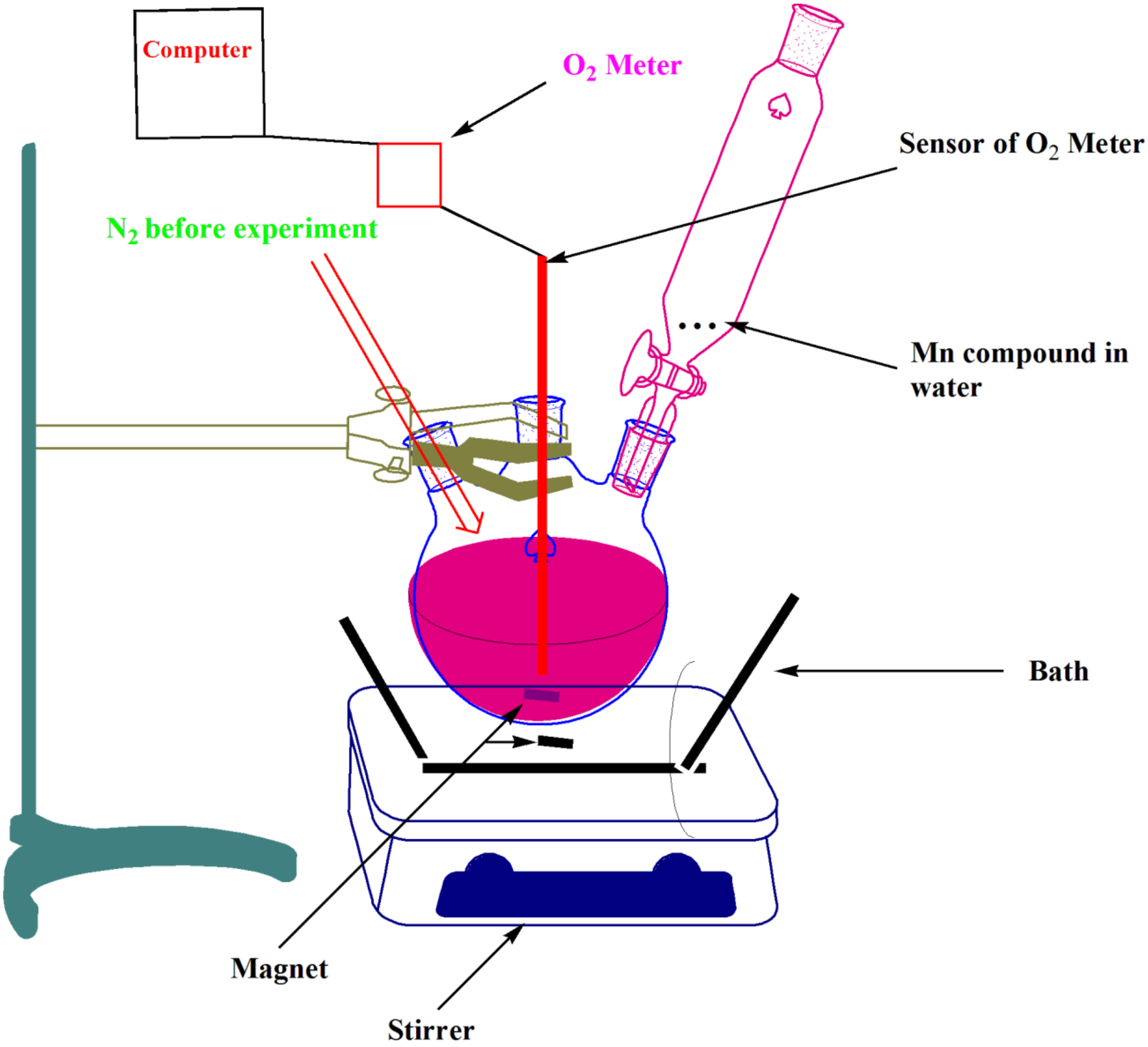
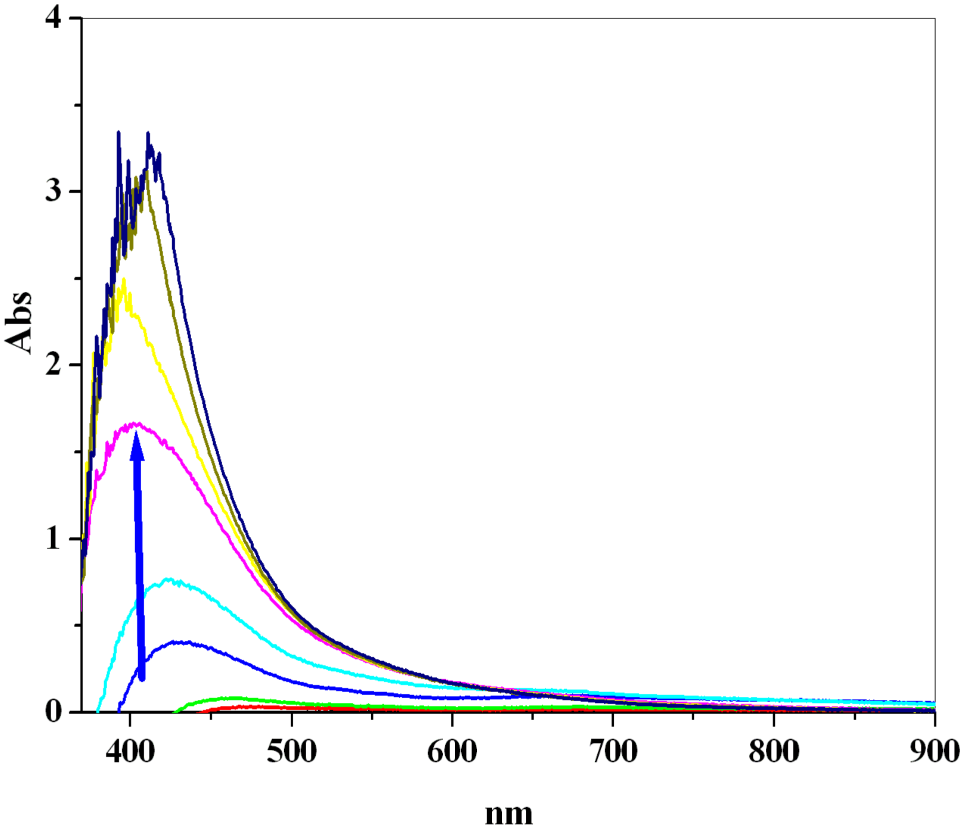


Fig. S1. The reactor set-up for oxygen evolution experiment in the presence of Ce(IV).


4
3
2
1
0
Abs
400
500
600
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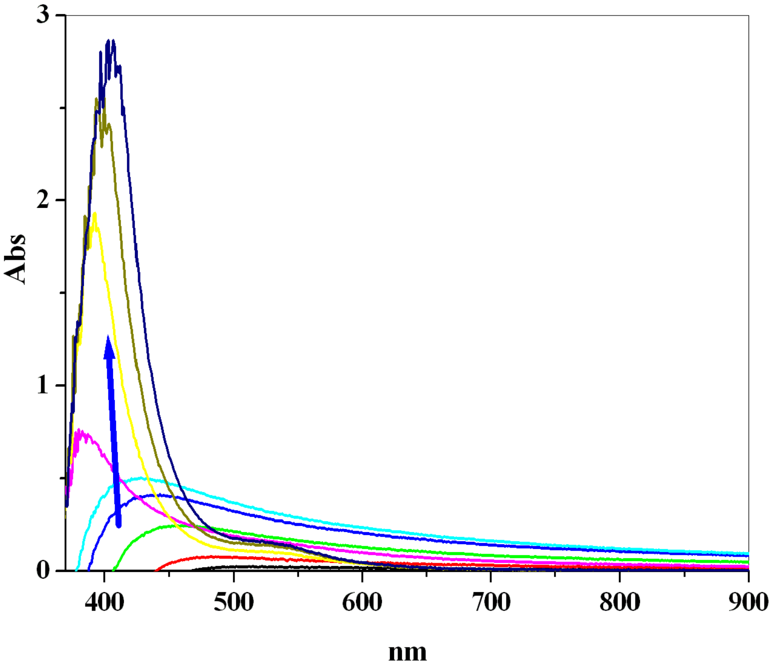
nm

(a)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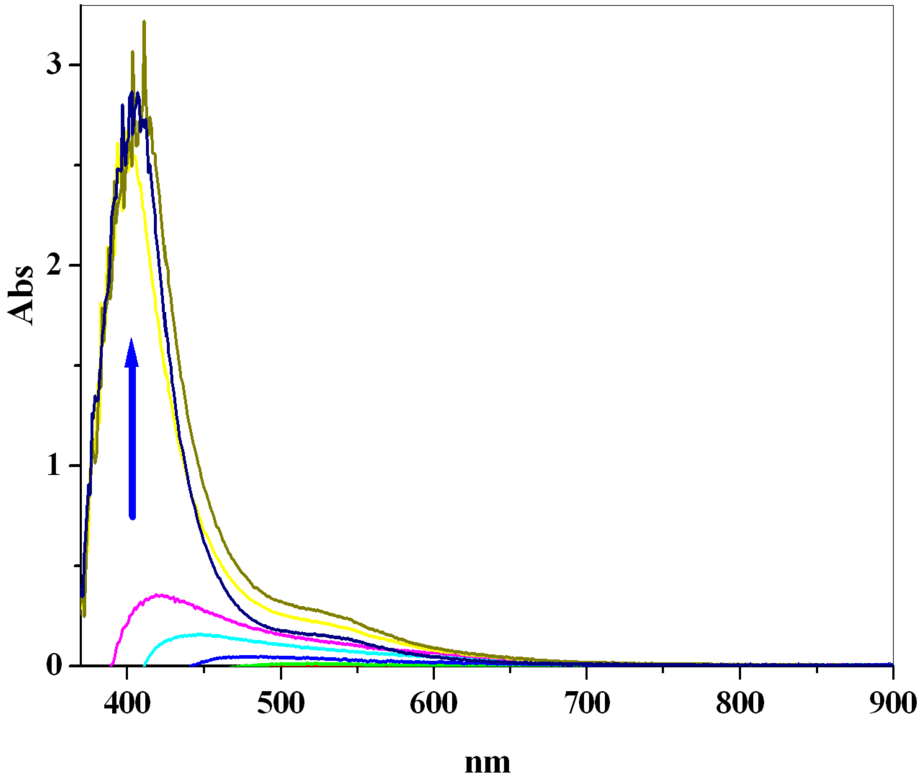
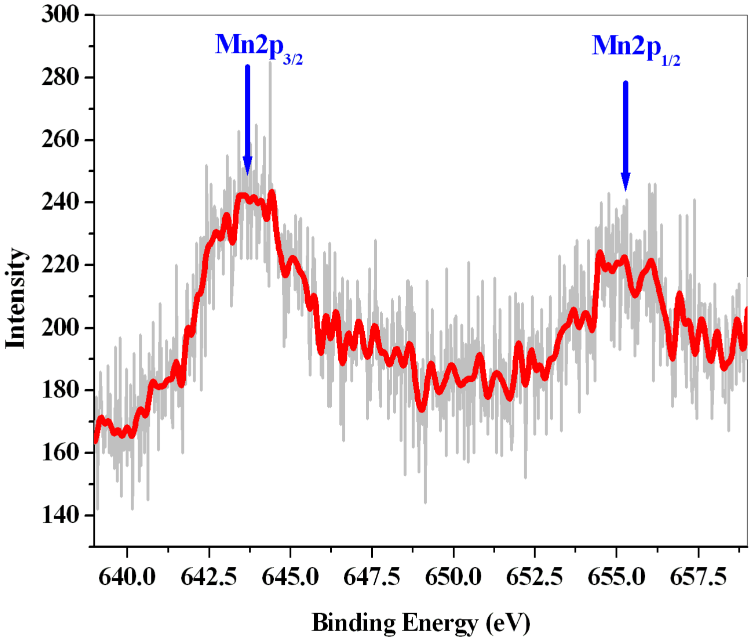
(b)



(c)

Fig. S2The UV-Vis spectra of titration of complex complex 2a (a), complex 3 (b) and complex 10 (c) (0.25 M) with Ce(IV) (Ce(IV) used as a reference solution (7.7 mM)). For a 4 (red), 2 (green), 2 (blue), 10 (cyan), 10 (magenta), 20 (yellow), 25 (olive) and 25 (navy) µL Ce(IV) (0.27 M) was added to complexes (3.5 mL, 1mM). For b 2 (black), 4 (red), 2 (green), 2 (blue), 10 (cyan), 10 (magenta), 20 (yellow), 25 (olive) and 25 (navy) µL Ce(IV) (0.27 M) was added to complexes (3.5 mL, 1mM). For c 2 (green), 2 (blue), 10 (cyan), 10 (magenta), 20 (yellow), 25 (olive) and 25 (navy) µL Ce(IV) (0.27 M) was added to complexes (3.5 mL, 1mM).



(a)

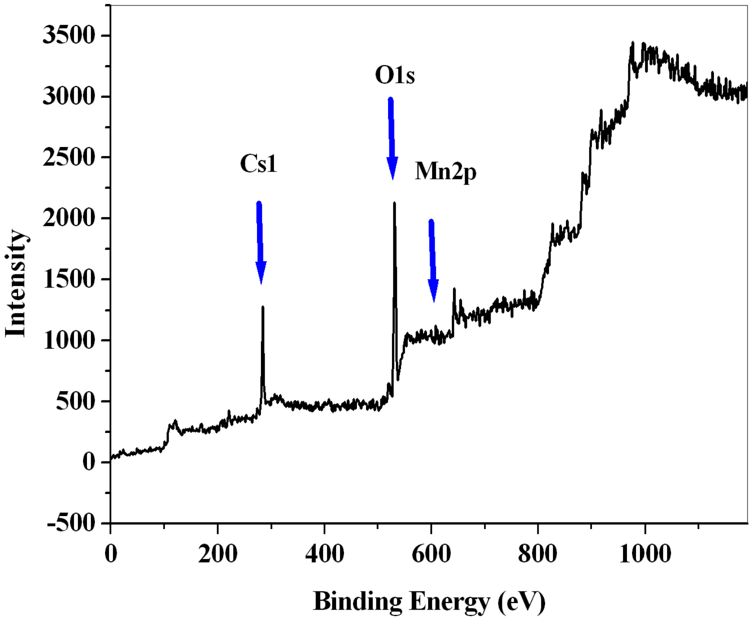
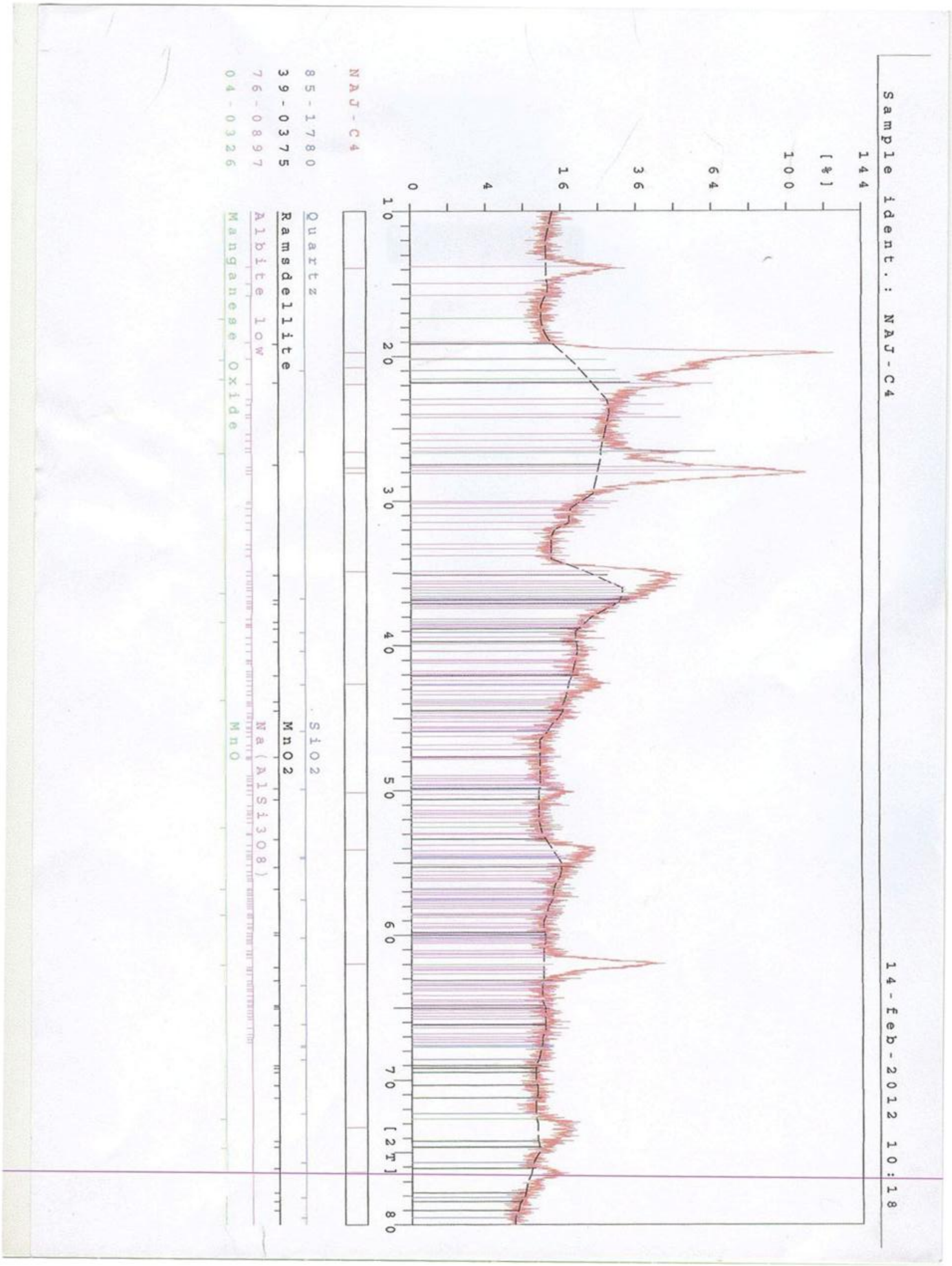
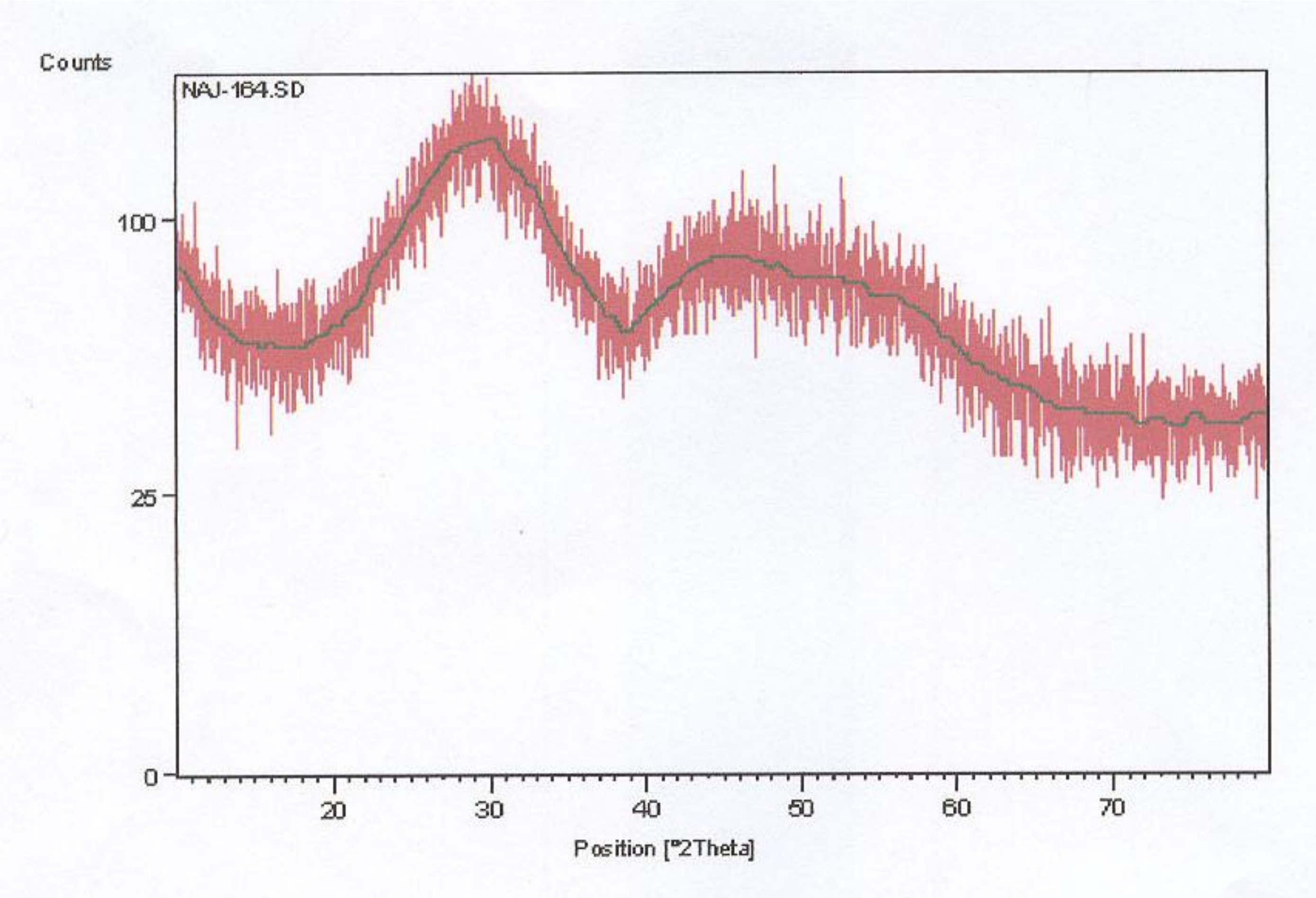


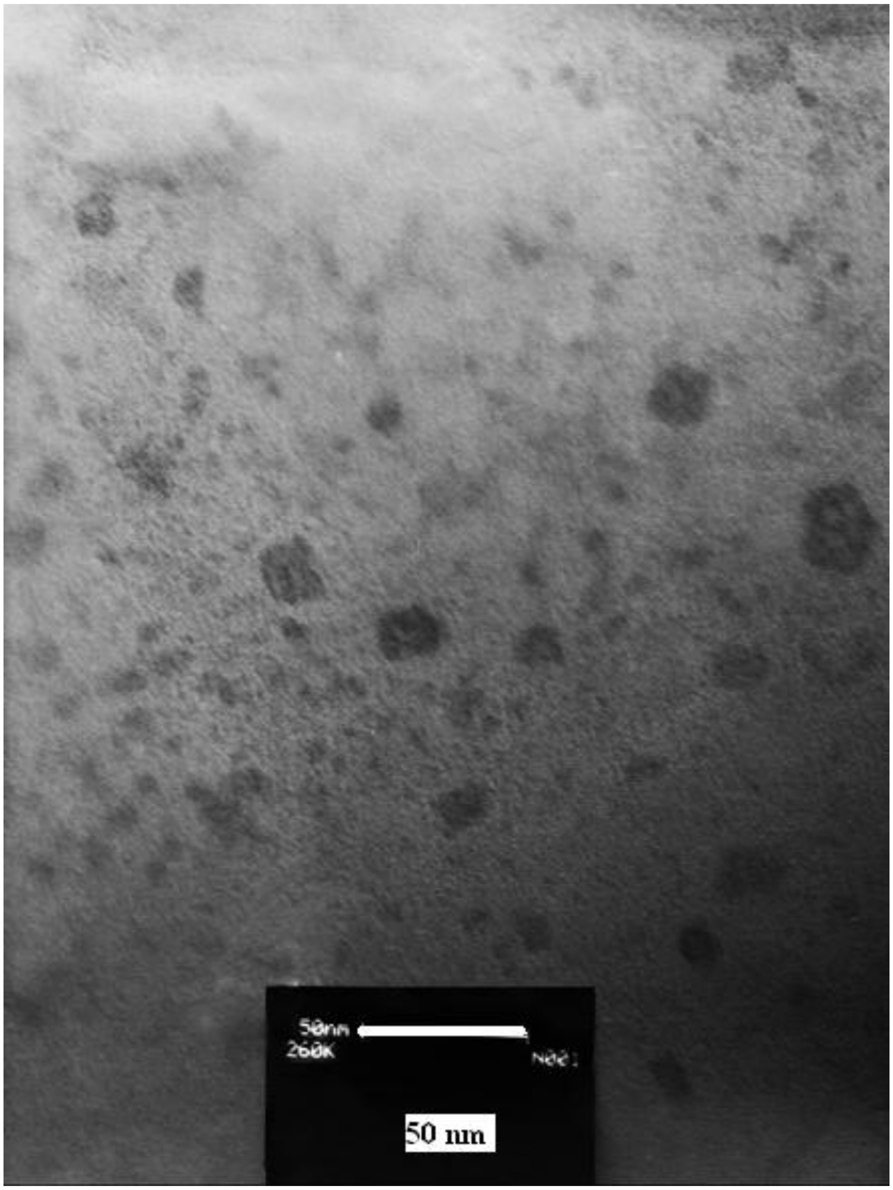
Fig. S5 XPS spectrum of the separated brown colloid formed in the reaction of high amount of complex 7 as solid and Ce(IV).


Sample ident.: NAJ-C4
14-feb-2012 10:18
144
[%]
100
64
36
16
4
0
10
20
30
40
50
60
70
[2T]
80
NAJ-C4
85-1780 Quartz SiO2
39-0375 Ramsdellite MnO2
76-0897 Albite low Na(AlSi3O8)
04-0326 Manganese Oxide MnO



(b)

Fig. S6 XRD patterns of the obtained from 4- clay hybrid that shows the compound contains SiO_2 (blue), $Na(AlSi_3O_8)$ (pink), MnO (green), and Ramsdellite-MnO_2 (black) (a) and the separated brown colloid formed in the reaction of high amount of solid manganese complexes and Ce(IV) that shows the compound is amorphous (b).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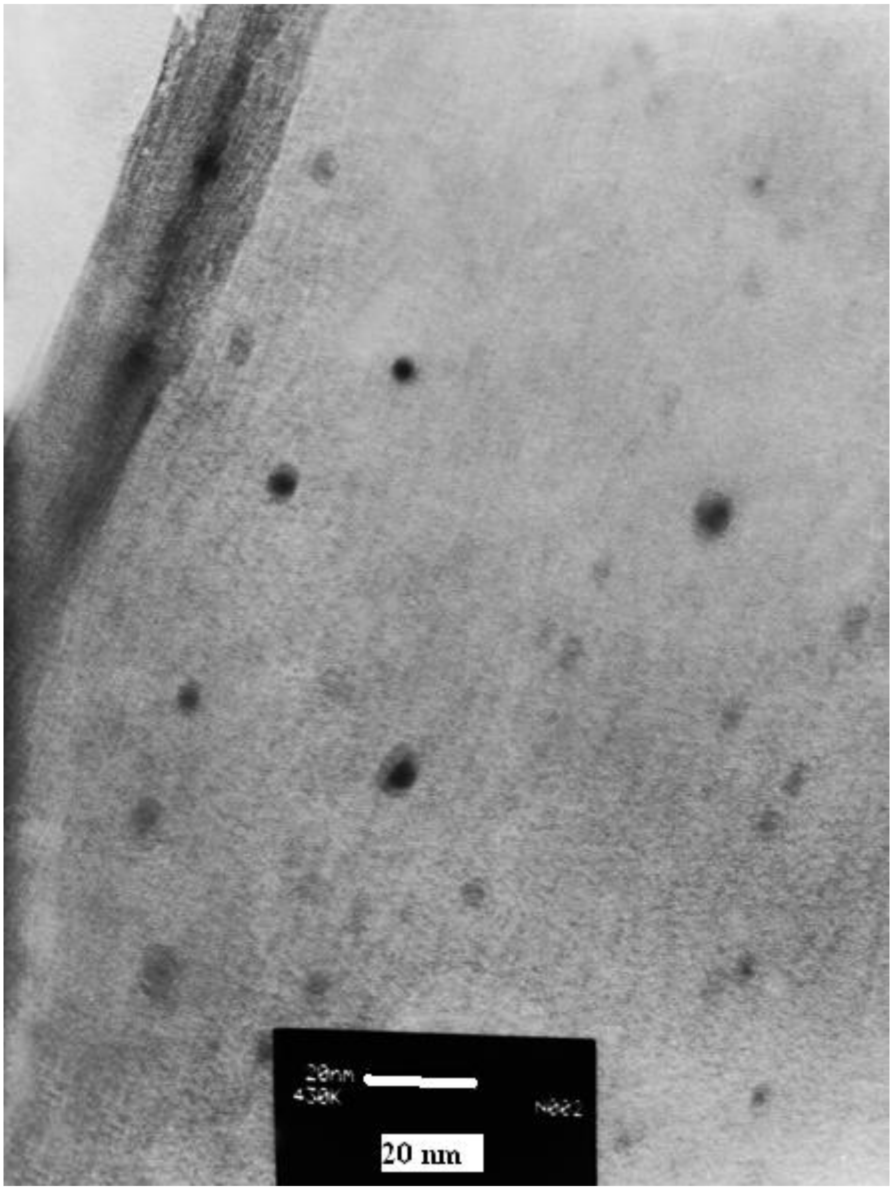
260K
50 nm


20nm
430K
N002
20 nm

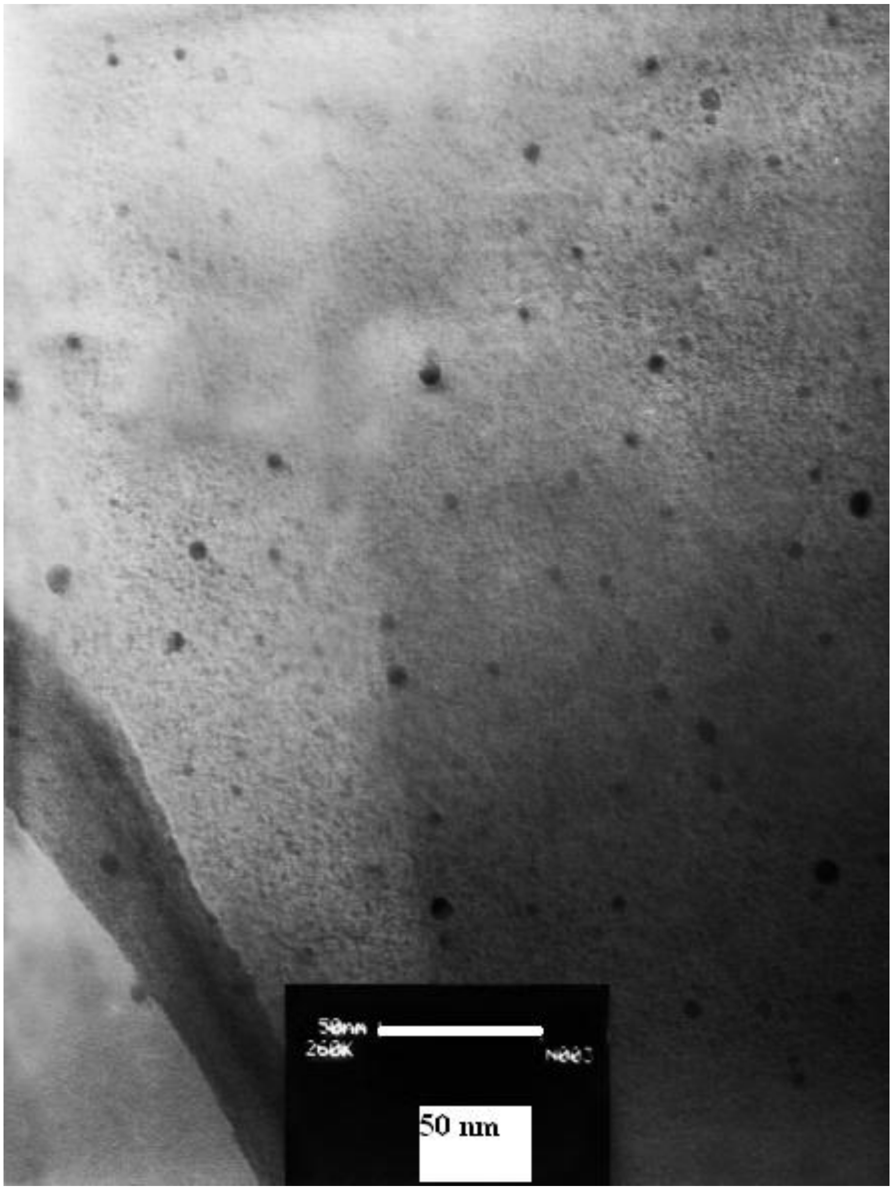
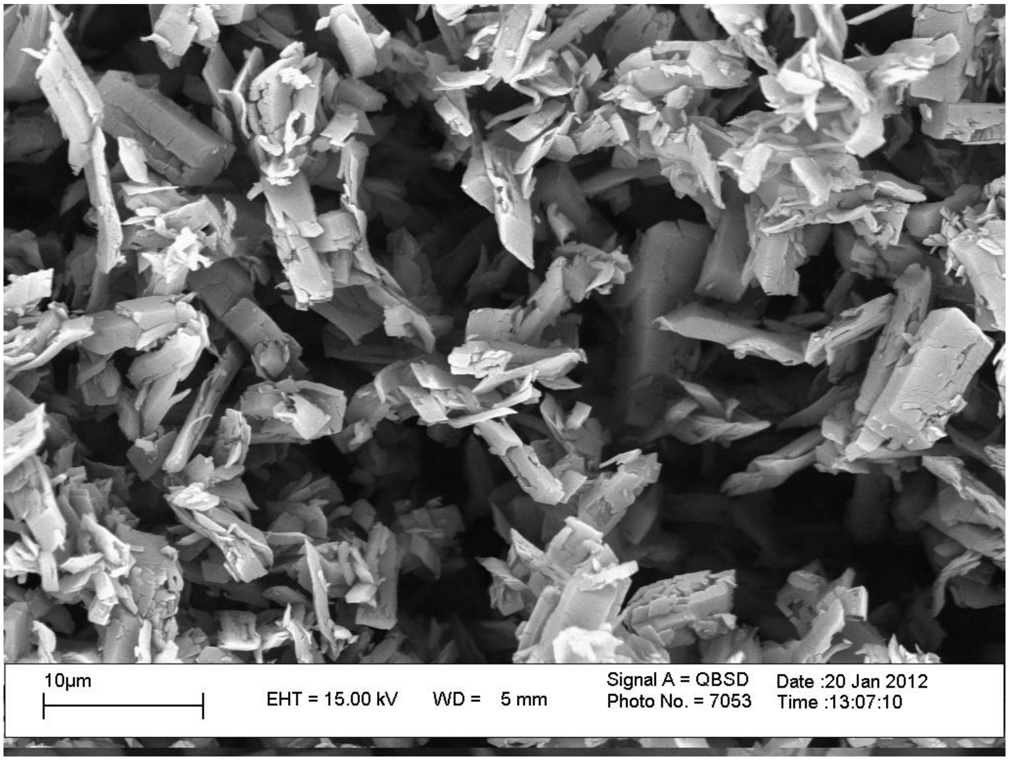
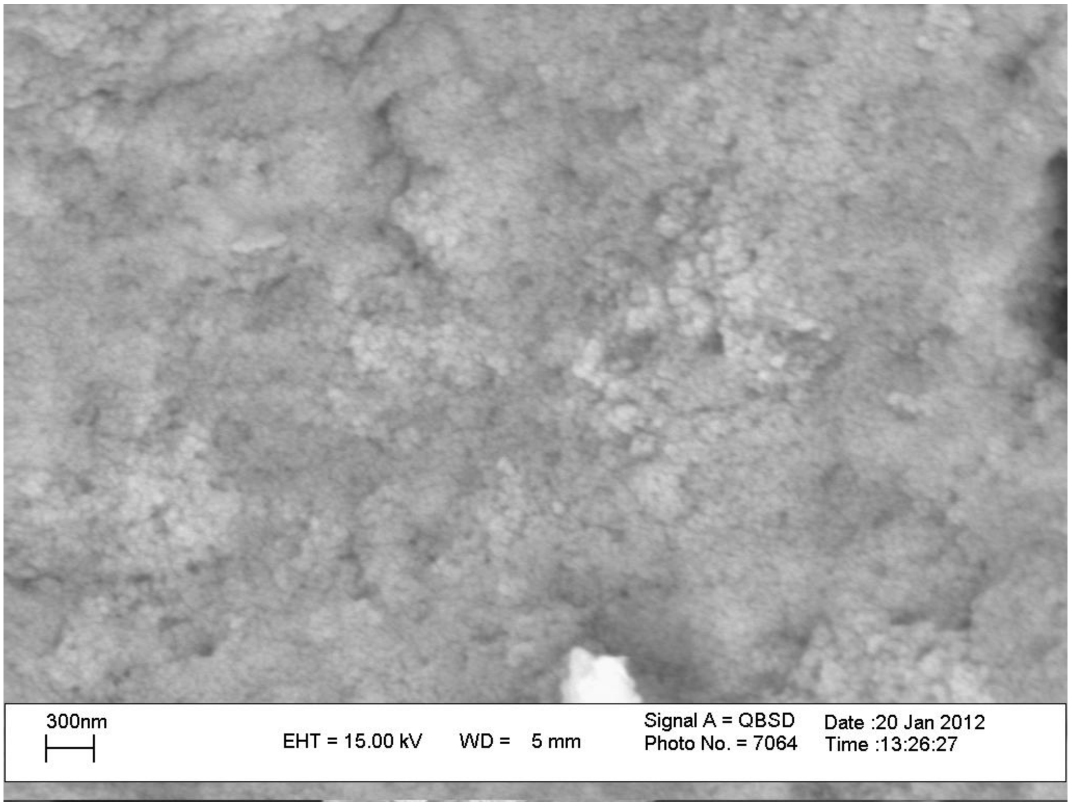


Fig. S7 TEM image of the centrifuged brown solid resulted from reacting of $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2](ClO_4)_3$ with Ce(IV).


10µm
EHT = 15.00 kV
WD = 5 mm
Signal A = QBSD
Photo No. = 7053
Date :20 Jan 2012
Time :13:07:10

(a)


300nm
EHT = 15.00 kV
WD = 5 mm
Signal A = QBSD
Photo No. = 7064
Date :20 Jan 2012
Time :13:26:27

(b)

Fig. S8 SEM image of complex 7 (a) and the centrifuged brown solid resulted from reacting of complex 7 with Ce(IV) (b).

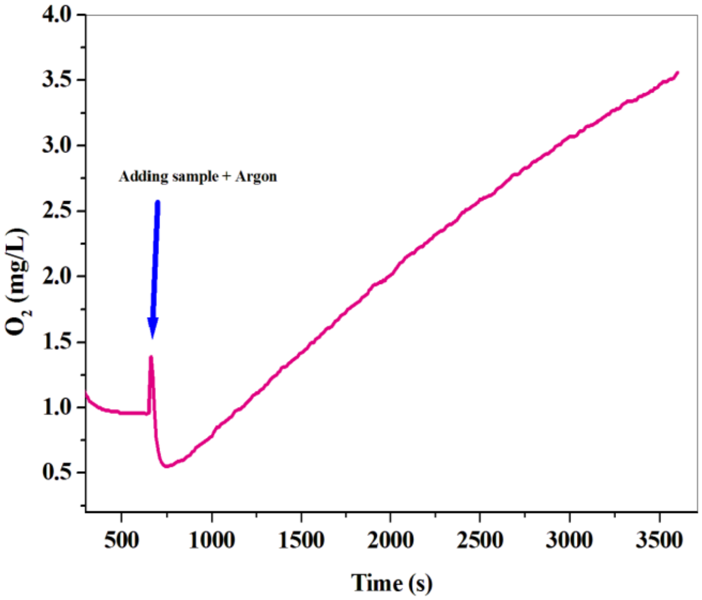


Fig. S9 Oxygen evolution by mixing 5.0 mg manganese oxide on montmorillonite (10% Wt Mn-clay) to Ce(IV) (0.22 M).

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