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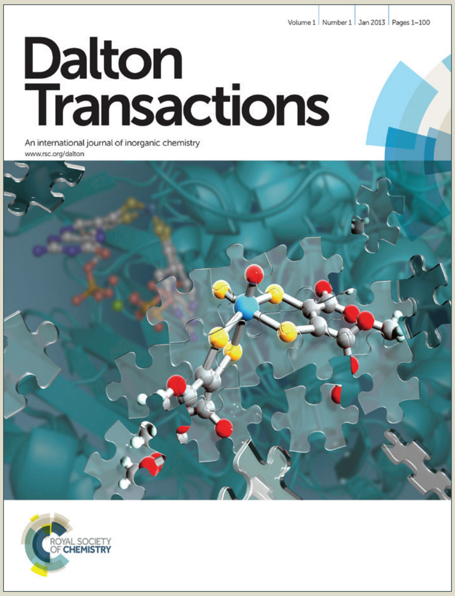

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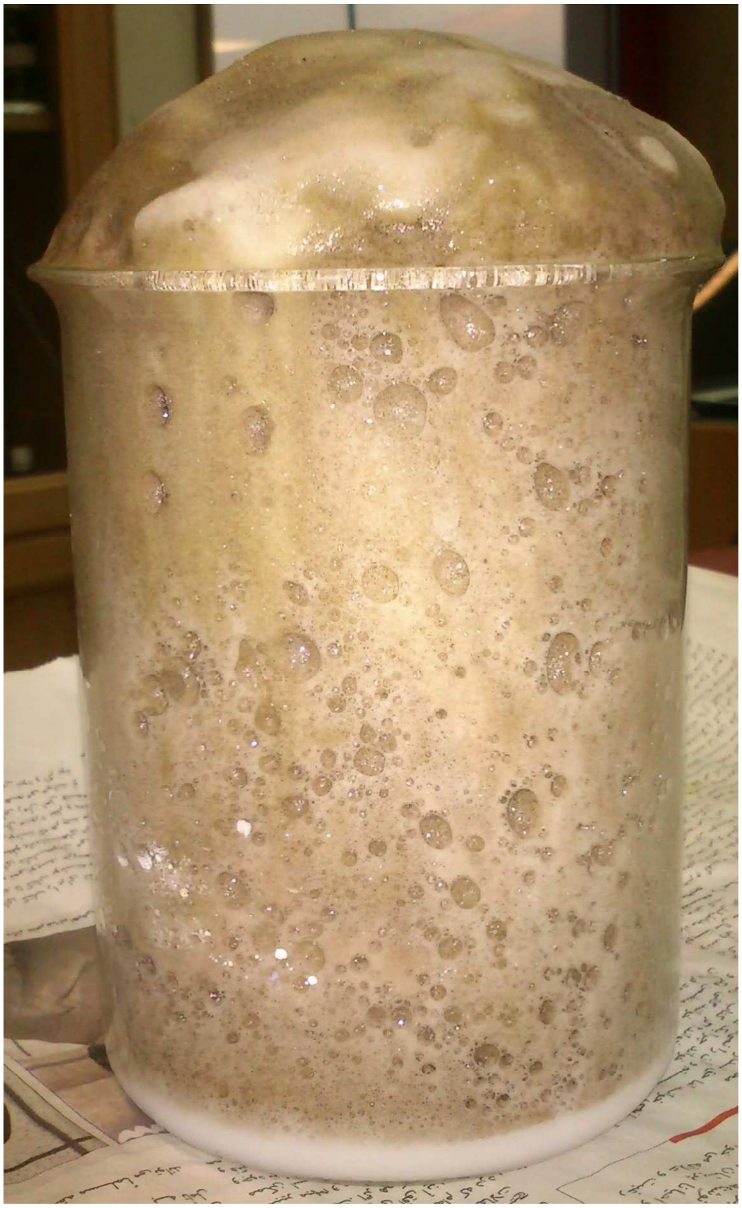
Compound	Oxidant	TOF mmol O_2/mol Mn	References
Nano scale Mn oxide within NaY zeolite	Ce(IV)	2.62	43
Layered Mn-Ca oxide	Ce(IV)	0.8-2.2	27, 42
Layered Mn-Al, Zn, K, Cd and Mg oxide	Ce(IV)	2.2	24, 44
Layered Ni(II) oxide	Ce(IV)	0.4-0.6	45
$CaMn_2O_4.H_2O$	Ce(IV)	0.54	20
Amorphous Mn Oxides	$Ru(bpy)_3^{3+}$	0.06	46
	Ce(IV)	0.52	
Nanolayered Mn oxide	Ce(IV)	0.45	This work
$CaMn_2O_4.4H_2O$	Ce(IV)	0.32	20
Mn oxide nanoclusters	$Ru(bpy)_3^{3+}$	0.28	47
β-MnO(OH)	CAN	0.24	48
Mn oxide-coated montmorillonite	Ce(IV)	0.22	49
Layered Mn-Cu(II)	Ce(IV)	0.2-0.35	45
Mn_3O_4	CAN	0.01-0.17	48
Octahedral Molecular Sieves	$Ru(bpy)_3^{3+}$	0.11	46
	Ce(IV)	0.05	
MnO_2 (colloid)	Ce(IV)	0.09	50
α-MnO_2 nanowires	$Ru(bpy)_3^{3+}$	0.059	51
$CaMn_3O_6$	Ce(IV)	0.046	52
$CaMn_4O_8$	Ce(IV)	0.035	53
α-MnO_2 nanotubes	$Ru(bpy)_3^{3+}$	0.035	51
Mn_2O_3	Ce(IV)	0.027	20
β-MnO_2 nanowires	$Ru(bpy)_3^{3+}$	0.02	51
$Ca_2Mn_3O_8$	Ce(IV)	0.016	53
$CaMnO_3$	Ce(IV)	0.012	53
Nano-sized λ-MnO_2	$Ru(bpy)_3^{3+}$	0.03	54
Bulk α-MnO_2	$Ru(bpy)_3^{3+}$	0.01	51
Mn Complexes	Ce(IV)	0.01-0.6	55-56
PSII	Sunlight	$100\text{-}400 \times 10^3$	57,58



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Nanolayered Mn oxides have been prepared by a very simple, cheap and high-yield method using soap, KOH, $MnCl_2$ and H_2O_2.

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ARTICLE

A very simple and high-yield method to synthesize nanolayered Mn oxide†

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Nanolayered Mn oxides have been prepared by a very simple, cheap and high-yield method using soap, KOH, $MnCl_2$ and H_2O_2. Scanning electron microscopy, transmission electron microscopy, dynamic light scattering, thermogravimetric analysis, Fourier transform infrared spectroscopy, and X-ray diffraction spectrometry have been used to characterize the phase and the morphology of the nanolayered Mn oxide. The nanolayered Mn oxide shows good catalytic activity toward water oxidation in the presence of cerium(IV) ammonium nitrate.

Introduction

Mn oxides are attractive materials because of their physical and chemical properties. They are low-cost and environmentally friendly that were used as efficient catalysts for oxidation of organic,[1] and inorganic compounds such as carbon monoxide,[2] ammonia[3] and water.[4-15] They have also potential applications for high energy density lithium batteries.[16-18] They were used as bulk, supported, nano-sized nanostructures with large surface area, and colloidal forms. The structures of these compounds are polynuclear and could favor the occurrence of multi-electron and complicated reactions.

The simple, low-cost, environmentally friendly and high-yield methods to synthesis of nanoscale Mn oxides, which could exhibit the unique physiochemical properties as compared with the bulk compound is necessary to use the compounds in industrial application. Many methods for the synthesis of Mn oxide nanoparticles were reported. Among them, solvothermal,[19] oxidation/reduction,[20] decomposition,[21] surfactant-mediated[22,23] and oxidation-reduction[24] are popular. As the nanolayered Mn oxide is low-cost and environmentally friendly, the method could be good candidate to synthesize efficient catalysts in artificial photosynthetic systems. In Nature water oxidation performs by a Mn-Ca cluster housed in a protein matrix.[25] The structure can be considered as nano-sized Mn oxido cluster in an organic matrix.[14,26,27] Thus, Mn oxides as water-oxidizing catalysts are very interesting. They are cheap, environmentally friendly, and used by Nature to oxidize water.[28] They are even proposed as the product of decomposition of Mn complexes in the presence of (electro)chemical oxidants in water-oxidation reaction.[5,29,30,31] Thus, they are true catalysts in water-oxidation reaction by many Mn complexes.[5,29,30,31] In water oxidation reactions, cerium(IV) ammonium nitrate (Ce(IV)) is an usual oxidant.[32] It is a non-oxo transfer and a strong one-electron oxidant.[32] Membrane-inlet mass spectrometry (MIMS) showed oxygen evolution from catalysts in the presence of Ce(IV) is a true water-oxidation reaction and both oxygen atoms of the O_2 originate from the water.[33] Glikman and Shcheglova from Russia reported for the first time that MnO_2 is a water-oxidizing catalyst in the presence of cerium(IV).[34] Electrochemical water oxidation by MnO_2 was reported by Morita in 1977.[35] Shilov extended water oxidation by Mn oxides in the presence of chemical oxidants.[36] Harriman's group in 1988 extensively studies many metal oxides as water-oxidizing catalysts in the presence of chemical oxidants.[37] Among of these metal oxides, Mn(III) oxide was reported as an efficient catalyst toward water oxidation.[35,37] Efficient water oxidation by nanostructured Mn_2O_3 clusters supported on mesoporous silica in the presence of $Ru(bpy)_3^{3+}$ was reported by Frei and Jiao.[6,8] The proposed roles for the silica support are providing high surface area for Mn oxides, protecting the Mn ions from deactivation by surface restructuring and helping in proton transfer.[6,8] Layered A-Mn oxides (A: inert-redox ions) without long-range order were reported as efficient catalysts for water oxidation.[28] Such compounds show considerable thermodynamic stability. Gold particles on these layered Mn oxides were reported to improve activity of Mn oxide toward water oxidation both chemically and electrochemically.[38,39]

Recently, our group showed that many phases from Mn oxide in the presence of Ce(IV) or in electrochemical water oxidation convert to a layered Mn oxide after a few hours.[11,40]

Spiccia group showed that Mn oxide derived from a Mn complex decomposition have one order of Mn higher water-oxidation catalytic activity per Mn compared to many unsupported solid-state Mn oxide.[41] The group recently using TEM and electron scattering simulations results showed that the structure exhibit high degree of layer mis-registration, and Mn vacancies, compared to other Mn oxides. Thus, they proposed that water oxidation in the compounds is related to the differences in the degree of disorder.[41]

Many of these methods to prepare efficient water-oxidizing Mn oxides are expensive and thus a simple, high-yield and green method are promising in this regard. Herein we report a very simple and high-yield to synthesize nanolayered Mn oxide. In the next step, we used the oxide as water-oxidizing catalyst.

Experimental

Material and methods

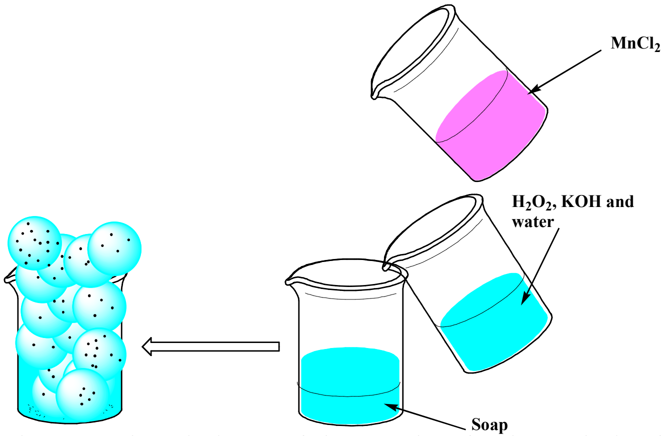
All reagents and solvents were purchased from the commercial sources and were used without a further purification. Soap was purchased from Tage company. As reported by the company, the product was synthesized by sulfonic acid, sodium lauryl sulfate, diethanolamine, cocamide diethanolamine, sodium hydroxide, carbamid, methylene phosphonic acid, dye, sodium chloride and water. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were carried out with Philips CM120 and LEO 1430VP, respectively. The X-ray powder patterns were recorded with a X'Pert Pro MPD from PANalytical company (CuK$_\alpha$ radiation). MIR spectra of KBr pellets of compounds were recorded on a Bruker vector 22 in the range between 400 and 4000 cm^{-1}. Mn atomic absorption spectroscopy (AAS) was performed on an Atomic Absorption Spectrometer Varian Spectr AA 110. Dynamic light scattering (DLS) result was obtained by a Nano ZS (red badge) ZEN 3600 from Malvern company. Prior to the analysis, the compounds 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 analysed by AAS. The thermogravimetric analysis (TG) was performed by using a NETZSCH STA 409 PC/PG instrument with a heating rate of 10 °C min^{-1} in oxygen flow.

Synthesis

The compounds were prepared by a simple method. Soap, H_2O_2, KOH, and $MnCl_2$ solutions were mixed (for details see Table 1) in the same time to produce these nanolayered Mn oxides (Fig. S1, ESI). The compounds were washed carefully by water and calcined at different temperatures. Yield is more than 95% based on $MnCl_2$.

Table 1 The amounts of different compounds to synthesize nanolayered Mn oxides.

Compound	H_2O_2 (mL)/KOH (mg) in 3.0 mL water	Soap (mL)	$MnCl_2$ (mg) in 5.0 mL water
1	10/400	10	1250
2	10/400	10	500
3	2/400	2	250
4	10/400	10	250
5	2/400	2	100
6	2/400	2	50
7	10/400	10	25
8	2/400	2	5
9	10/400	10	100
10	10/400	10	100
11	10/400	-	500



Scheme 1 Schematic image of the procedure for the synthesis of nanolayered Mn oxides.

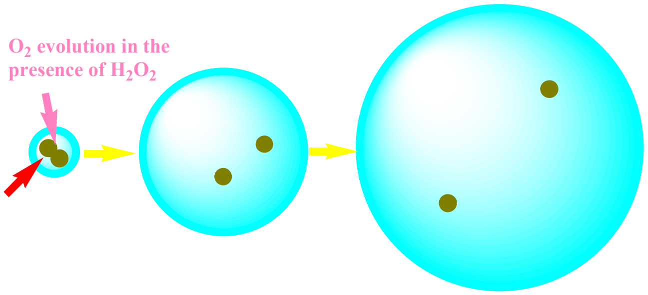
Water oxidation

Water oxidation experiments were performed by previously reported method (Scheme S1, ESI).[24]

Results and discussion

Synthesis

After mixing H_2O_2, KOH, and $MnCl_2$ solutions, immediately, nanolayered Mn oxide forms, which reacts with H_2O_2 to evolve O_2. In the next step, big bubbles from soap in the presence of O_2 were formed. Two factors are important in this procedure. The first, soap molecules around particles inhibits agglomeration of Mn oxide (Fig. S1, ESI). The second, the growth of bubbles increase the distance among particles, and again, inhibits agglomeration.

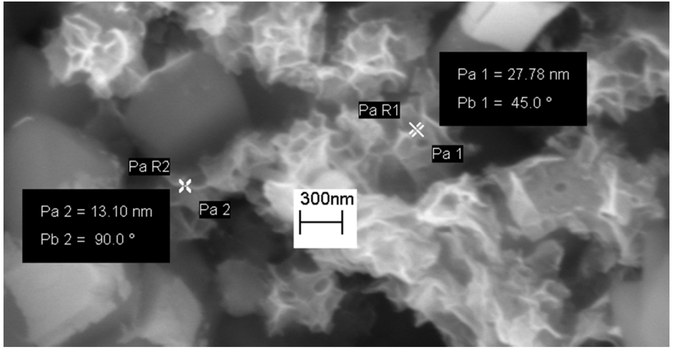


Scheme 2 A proposed mechanism to synthesize Mn oxide.

Characterization

IR spectra of these compounds show a broad band at ~ 3200-3500 cm^{-1} related to antisymmetric and symmetric O-H stretchings and at ~ 1630 cm^{-1} related to H-O-H bending are observed (Fig. S2, ESI). The absorption bands characteristic for a MnO_6 core in the region ~ 520 cm^{-1} assigned to stretching vibrations of Mn-O bonds was also observed in the compounds. Although high temperatures (> 250 ^{o}C) decompose organic compounds, but weak peaks related to organic compounds in soap (1047-1117 cm^{-1}) are present in the compounds until 350 ^{o}C (Fig. S2, ESI).

SEM images show nanolayered structures with thickness 10-30 nm in the compound (Fig. 1a,b). SEM images show that more agglomerization occurs if soap is not used in the procedure (Fig. 1c). TEM and HRTEM images show clearly layers in this compound (Fig. 1d,e, for more SEM and TEM images see Fig. S3 and S4 images in ESI). In the support of layered structure, XRD data for these prepared compounds at room temperature was of poor resolution, but the peaks at 2θ ~ 12, 25, 38 and 65^{o} found in most layered Mn oxides were observed in XRD patterns of these compounds (Fig. 2f). DLS results show that agglomeration occurs for the compounds in solution. These results show that three peaks, 40, 80 and 140 nm, are observed (Fig. 2g).



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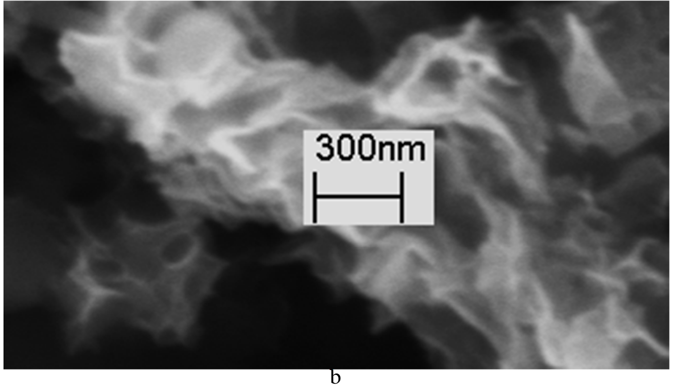

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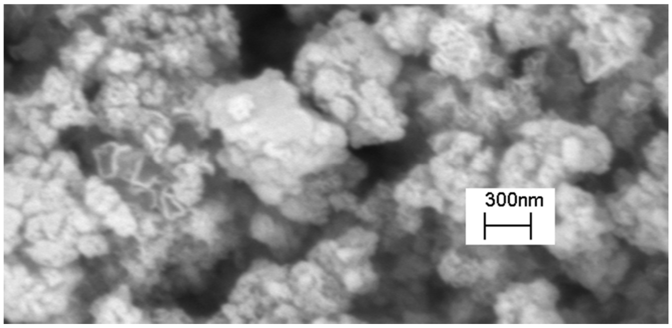

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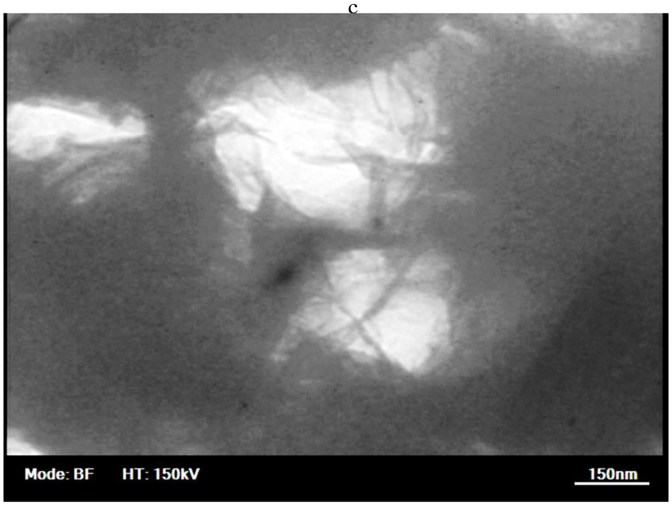

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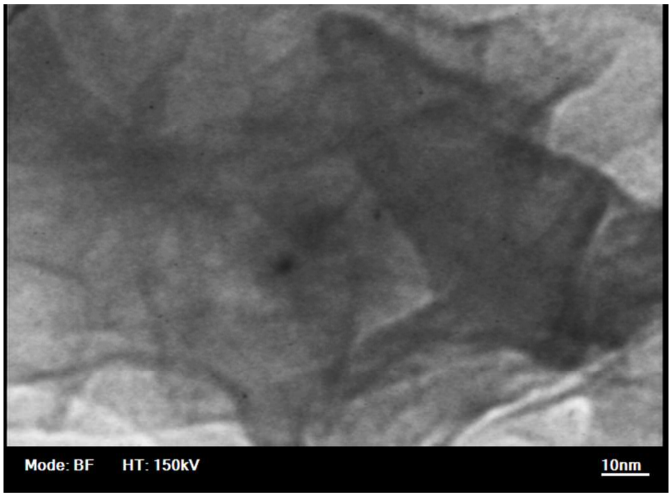

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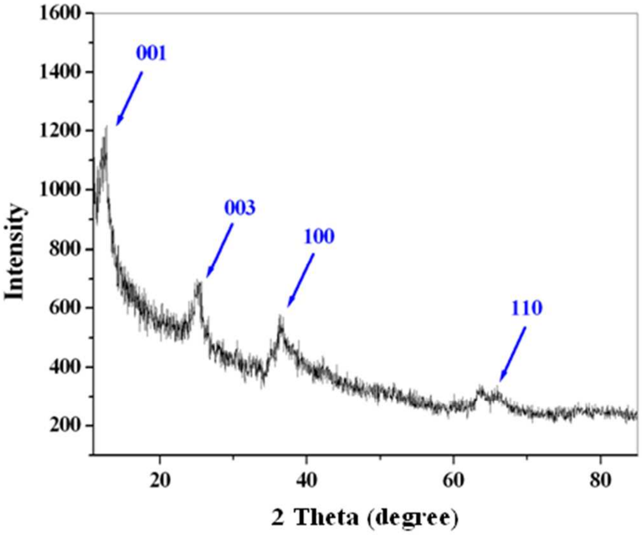

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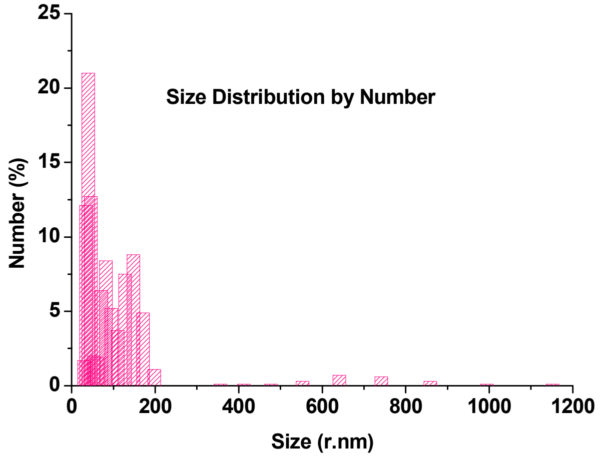
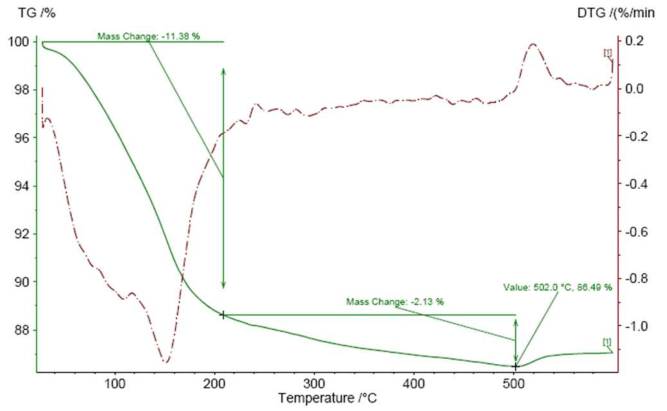


g

Fig. 1 SEM images from **6** (a,b) and **11** (c). TEM images from **6** (d,e), XRD pattern (f) and DLS (g) result from **6**.

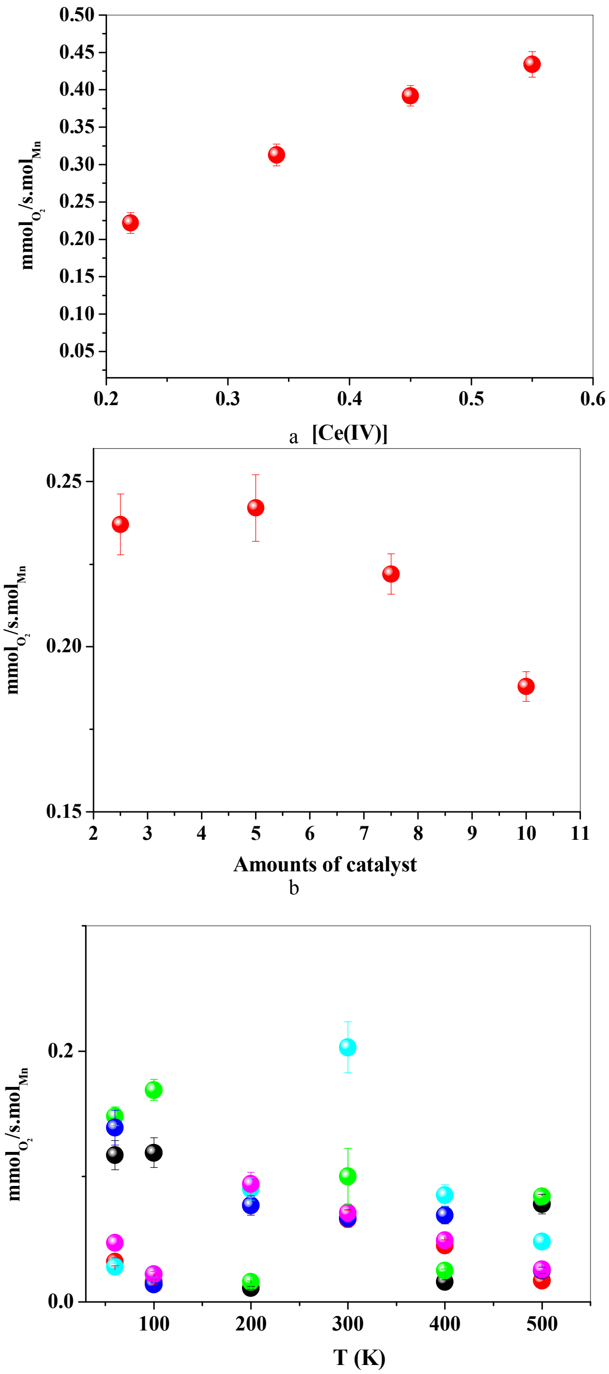
The derivative form of TGA (DTG) indicates two stages for these compounds (Fig. 2). The first stage, which takes place between 60 and 200°C is related to loss of water molecules. The next step occurs between 200 and 500 °C, and is related to decomposition of organic compounds from soap, remove OH groups and phase conversions.



Water oxidation

Herein we used Ce(IV) as an oxidant in our water-oxidation experiments. The calcined nanolayered Mn oxides at 60-500 °C showed different water-oxidizing activity in the presence of Ce(IV). Usually, a maximum of water oxidation was observed at 200-500 °C.[24] The effects of temperature are dehydration, changes in the oxidation state of Mn, and the surfaces of these oxides.[24] Thus, there are not possible to find which factor is more important in this condition. The best turnover frequency (TOF) for the compound is 0.45 mmol O_2/Mn.s

In the next step we studied the effect of concentration of Ce(IV) on water-oxidation reaction. We performed water-oxidation reactions with different concentrations of Ce(IV) keeping all other factors constant as shown in Fig. 3. First, the rate of water oxidation increases with increasing in the concentration of Ce(IV). This increasing of the rate of water oxidation in the less concentration of Ce(IV) is linear in the range of 0.11-0.55 M of Ce(IV). However, in the higher concentrations of Ce(IV), the rate of water oxidation does not increase sharply because of the decomposition of catalysts. In this regard, at higher concentration of Ce(IV), MnO_4^- is detected. With increasing amount catalyst, TOF is constant in the range of 0.2-0.25 (Fig. 3c).



a

b

c

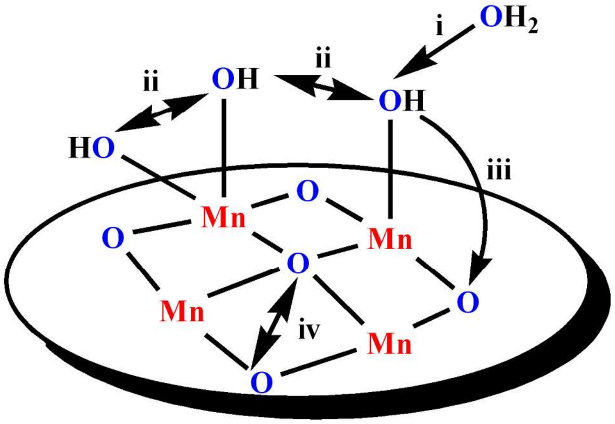
Fig. 3 Water oxidation of an aqueous solution of 0.22-0.55 M Ce(IV) (40 mL) at 25.0 °C in the presence of calcined **9** at 300 °C (a). Water oxidation of an aqueous solution of Ce(IV)(0.11 M, 40 mL) at 25.0 °C in the presence of different amounts (mg) of calcined **9** at 300 °C (b). TOF at 25.0 °C for **1** (magenta), **2** (cyan), **3** (red), **4** (green), **5** (blue) and **6** (black) prepared at different temperatures in the presence of Ce(IV) (0.11 M) (c).

Comparing with other Mn oxides, these oxides show good water oxidizing activity in the presence of Ce(IV). Regarding Table 2, the compounds are more efficient than bulk Mn oxides, crystalline and nano sized β-MnO_2, Nano-sized λ-MnO_2, α-MnO_2, Nano-sized α-Mn_2O_3. In addition to it, these compounds could be synthesized by a low-cost and environmentally friendly procedure.

Table 2 TOFs for water oxidation catalyzed by the various Mn based catalysts for water oxidation in the presence of non-oxygen transfer oxidant.

Mechanism water oxidation by metal oxides is an enigma in inorganic chemistry.[33,59] The water oxidation occur as a four-electron reaction, or in multiple steps with intermediates such as $^{\bullet}OH$, H_2O_2 or $O_2^{\bullet-}$. Comparing the standard reduction potentials for Ce(IV)/Ce(III), it is clear that Ce(IV) cannot oxidize water to $^{\bullet}OH$, H_2O_2 or $O_2^{\bullet-}$. Thus, in Mn oxides multiple Mn sites are involved in charge delocalization and accumulation to a four-electron water-oxidation mechanism.[60]

As shown in Scheme 3, they are four proposed mechanism for water oxidation by these Mn oxides. We found that μ-O groups are too inert to involve in O-O formation. Thus, we proposed patway **i** or **ii** (Scheme 3) for a molecular mechanism for water oxidation.[59] In other words, four Ce(IV) ions oxidize four Mn ions step-by-step such that, after four charge-accumulation steps, a multi-electron oxidation proceeds yielding O_2 from water by pathway i or ii.



Scheme 3 Proposed mechanisms for water oxidation by the layered Mn oxide:[16] Nucleophilic attack of hydroxide on a terminal oxido (i); coupling of terminal oxido ligands (ii), attack of hydroxide on a bridging oxido ligand (iii), coupling of bridging oxido ligands (iv). Image and caption are from ref. 59.

Conclusions

Nano-layered Mn oxide, as a low-cost, easily synthesized and environmentally friendly compound, was synthesized by a simple method, and high-yield in moderated temperature, and characterized by SEM, DLS, XRD, FTIR, AAS and TEM. Comparing with other Mn oxides, these compound act as good catalysts for water oxidation in the presence Ce(IV). These nano-layered Mn oxides as easily synthesized, cheap and environmentally friendly compounds are very promising candidates to be used as water-oxidizing catalysts in artificial photosynthetic systems.

Acknowledgements

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Notes and references

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