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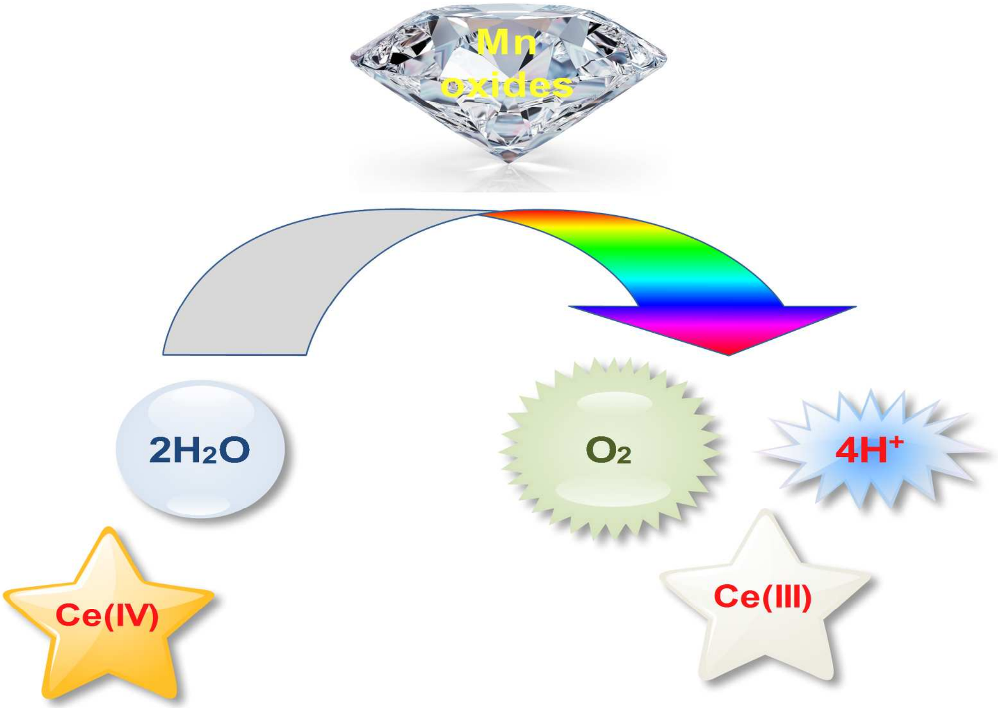

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Mn oxide/nanodiamond composite: A new water-oxidizing catalyst for water oxidation†

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Here, we reported nano-sized Mn oxide/nanodiamond composites as water-oxidizing compounds. The composites were synthesized by easy and simple procedures by the reaction of Mn(II) and MnO_4^- in the presence of ND (**1**), the reaction of MnO_4^- and ND in different temperatures (**2** and **4**) and simple mixing Mn-Ca oxide and ND (**3**). The compounds were characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction spectrometry, Fourier transform infrared spectroscopy and atomic absorption spectroscopy. The water-oxidizing activities of these compounds were also considered in the presence of cerium(IV) ammonium nitrate. A Mn oxide/nanodiamond from the reaction of MnO_4^- and ND shows turnover frequency ~ 1 (mmol O_2/mol Mn.s). However, other Mn oxide/nanodiamond composites show lower activity toward water oxidation.

Introduction

Water oxidation is known as a source for "cheap electrons".[1] In future, the reaction may provide electrons for not only proton reduction but also for other reduction-reactions which are equally important in artificial photosynthesis. Thus, water oxidation and a *super anode* for the reaction is important subject in science.[2]

The water-oxidizing complex of photosystem II (PSII)[3] is a very efficient, and the only system to catalyze water oxidation in *Nature*. The water-oxidizing complex (WOC) is a Mn_4O_5Ca cluster housed in a protein environment in PSII that controls reaction coordinates, proton movement and water access.[4] In 2011, Shen and his co-workers have reported the crystal structure of the Mn-Ca cluster at an atomic resolution.[4] In this structure metal ions, one Ca and four Mn ions, are bridged by five oxygen atoms. Four water molecules were found also in this structure that two of them are suggested as the substrates for water oxidation.[4]

Many compounds were reported as water-oxidizing catalysts but the use of them for global scale water oxidation is problematic owing to concerns about low earth abundance, toxicity, and high cost. Mn is considered for water oxidation because it is not only earth abundance, environmentally friendly, and low cost but also it is efficiently used by *Nature* as water-oxidizing catalyst for biological water oxidation.[5] However, a few Mn complexes have been discovered so far that are able to act as a homogeneous or heterogeneous catalyst[6] for the oxidation of water, but Mn oxides have been reported as heterogeneous catalysts for water oxidation by Glikman and Shcheglova,[7] Shilov,[8] Morita,[9] Harriman[10] and other groups.[11] Interestingly, Mn oxides are also proposed as true catalysts for water oxidation in many Mn-based water-oxidation reactions.[12,13] Recently, layered Mn oxides have been studied as one of the most efficient Mn-based catalysts for water oxidation.[14] However, the efficiency of these oxides is much low as compared with water-oxidizing complex in *Nature*.

Layered Mn oxides, Mn oxide clusters supported on mesoporous silica in the presence of $Ru(bpy)_3^{3+}$,[15] gold particles on layered Mn oxide,[16] MnO_x/glassy carbon,[17] and very pure β-MnO_2, R-MnO_2, α-MnO_2, δ-MnO_2, λ-MnO_2, $LiMn_2O_4$, Mn_2O_3, and Mn_3O_4 compounds were reported by different groups.[18] Many Mn oxides in the presence of cerium(IV) ammonium nitrate (Ce(IV)) or in electrochemical water oxidation are converted to layered Mn oxides after a few hours.[19,20,21] Self-healing for Mn oxides were also reported.[22] In the self-healing reaction, decomposition products from Mn oxide in the water oxidation reaction can react or combine to remake Mn oxide.[22]

Recently, Dau's group by a specific electrodepostion protocol synthesized a Mn oxide that oxidizes water at neutral pH.[23]

Carbon is an interesting element that can form various original structures such as C_{60}, carbon nanotubes (CNT), graphene (G), graphene oxide (GO) and nanodiamond (ND). The compounds show exceptional structural and chemical properties.[24]

Mn oxide/CNT was shown as promising composites for water oxidation.[25] Many factors such as surface, oxidation state of Mn oxide, dispersion, calcination temperature and crystalinty are important in water-oxidizing activity.[11] It is known that compared to other allotropic forms of carbon such as C_{60} and CNT, ND constituted by sp^3 carbons are remarkable inert.[26a] Recently, optical and biological applications of ND were considered.[26b] ND was also used as electrode material in electrochemical applications.[26a] On the other hand, ND supported metal oxides or other metal compounds exhibit excellent catalytic activity for different reactions. In these reactions, ND acts as an excellent support material for catalysts.[26b]

Regarding these interesting properties of ND, we considered Mn oxide/ND composite as an effective water-oxidizing catalyst.

Experimental

Material and methods

All reagents and solvents were purchased from the commercial sources and were used without a further purification. Nanopowder diamond (ND), <10 nm particle size (TEM), ≥ 97% trace metals basis was purchased from Sigma-Aldrich company. 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 diffractometer (CuK_α radiation). Mn atomic absorption spectroscopy (AAS) was performed on an Atomic Absorption Spectrometer Varian Spectr AA 110. 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 analyzed by AAS.

Synthesis

We used four methods to synthesize the composites:

1:

Solution 1: ND (200 mg) in water (5 mL) was sonicated and added to 2 mL water contains $Mn(OAc)_2.4H_2O$ (122 mg), and stirred for 5 minutes.

Solution 2: KOH (40 mg) and $KMnO_4$ (40 mg) was added in 8 ml water.

Solution 2 was added to solution 1, and the mixture was stirred for one hour. Then, it was dried at 90 °C and the solid was washed by water.

2: ND (200 mg) in water (10 mL) was sonicated and added to 10 mL water contain 20 mg $KMnO_4$. The mixture was dried at 90 °C and then the solid was washed by water.

3: ND (100 mg) in water (5 mL) was sonicated and added to 5 mL sonicated water contain 100 mg Mn-Ca oxide.[16] The mixture was stirred at 60 °C to dry and obtain a powder.

4: ND (250 mg) in water (10 mL) was sonicated and added to 10 mL water contain 50 mg $KMnO_4$. The mixture was stirred for one day at 25 °C, and the solid was separated and washed to remove $KMnO_4$. The solid was dried at 60 °C.

Water Oxidation

Oxygen evolution from aqueous solutions in the presence of Ce(IV) was investigated 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 experiment, the instrument readout was calibrated against air-saturated distilled water stirred continuously with a magnetic stirrer in the air-tight reactor. After ensuring a constant baseline reading, water in the reactor was replaced with Ce(IV) solution. Without the catalyst, Ce(IV) was stable under these conditions and oxygen evolution was not observed. After deaeration of the Ce(IV) solution with argon, Mn oxides as several small particles were added, and oxygen evolution was recorded with the oxygen meter under stirring (Scheme S1). The formation of oxygen was followed and the oxygen formation rates per Mn site were obtained from linear fits of the data by the initial rate.

Results and discussion

We used different methods to synthesize these Mn oxide/ND composites. In these procedures, we try to synthesize nanolayered Mn oxides that are known as efficient water-oxidizing catalyst.

1-**4** were synthesized by simple methods. The reaction of Mn(II) and MnO_4^- ions in the presence of ND forms **1**. **2** and **4** were synthesized by the reactions of MnO_4^- and ND:[26c]

$4MnO_4^- + 3C + H_2O \rightarrow 4MnO_2 + CO_3^{2-} + 2HCO_3^-$

However, we used different temperatures for the synthesis of **2** and **4**, respectively.

As discussed by Eder from the *University of Cambridge*,[27] in some cases simple van der Waals interactions are sufficient to provide a strong enough adhesion for inorganics/nanocarbon.[27] For **3**, we simply mixed layered Mn-Ca oxide with ND.

In IR spectrum of ND, 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. S1). Bands at 1110-1600 cm^{-1} are related to the C-H, C=O, C=C, and C-O stretching and bending deformation modes of the hydroxyl, carboxylic acid, and the anhydride, carbonyl, CH, and C=C surface functional groups.[28]

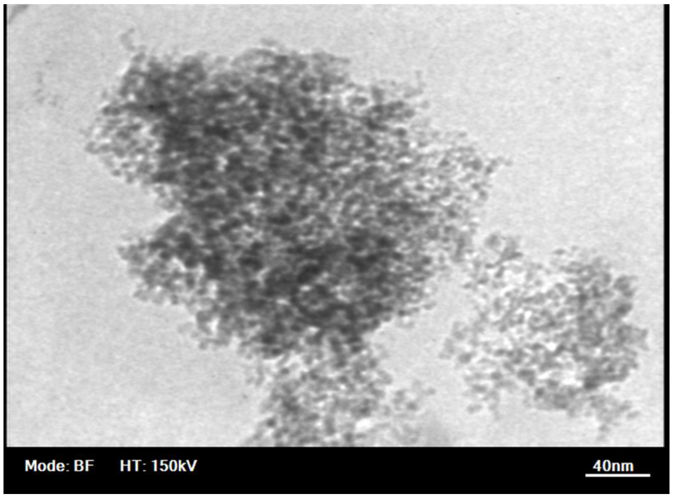
In **1**-**4**, the absorption bands characteristic for a MnO_6 core in the region ~ 500-600 cm^{-1} assigned to stretching vibrations of Mn-O bonds in Mn oxide was also observed in the FTIR spectra of **1**-**4**. To characterize the morphology of the prepared oxides, they were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM and TEM images are shown in Fig. 1, Fig. S2 and Fig. S3. SEM images for **1** show aggregated particles with diameters of 30-40 nm. The images indicates that a mixing occurs for ND and Mn oxide**.** TEM and HRTEM for **1** also show an appreciated good mixing for ND and Mn oxides. These images show diameters of ND particles are ~ 10 nm.

SEM images for **2** show aggregated ND**.** TEM and HRTEM images show covered ND particles by Mn oxide as black materials.

SEM images for **3** in addition to ND particles show bigger aggregated particles (~ 50-70 nm) related to Mn-Ca oxides. TEM and HRTEM images in addition to ND particles (~ 10 nm) show layered Mn oxide.

SEM images for **4**, similar to **2**, show aggregated ND with diameters of around 30-40 nm. TEM and HRTEM images show covered ND particles by Mn oxide as black materials. These images show that diameter of each ND particle is ~ 10 nm.

TEM images show some ND particles are covered by Mn oxide in **2** and **4**. Such ND particles are darker than usual ND. TEM images for **1** and **3** shows both Mn oxide and ND in the structures.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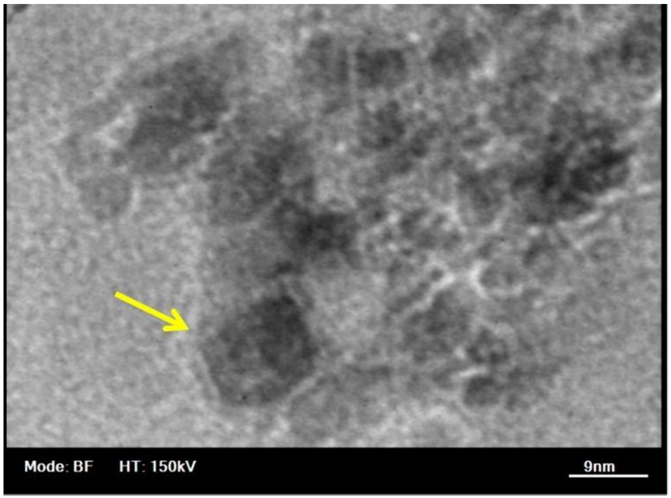
a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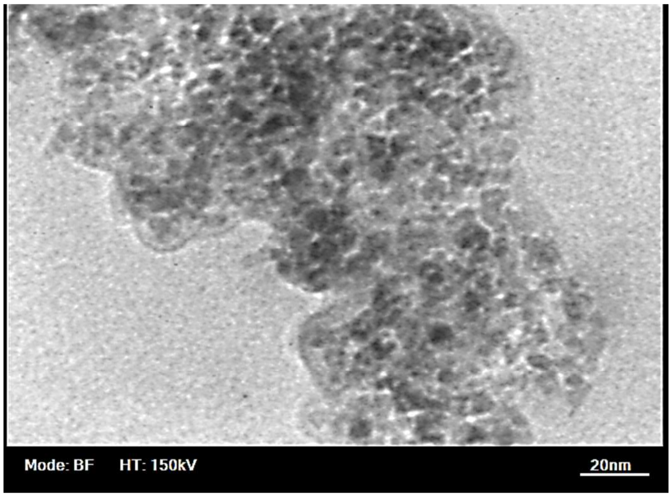
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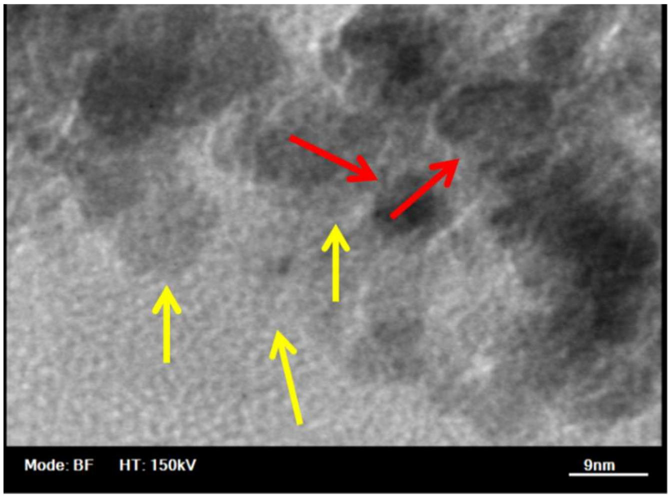
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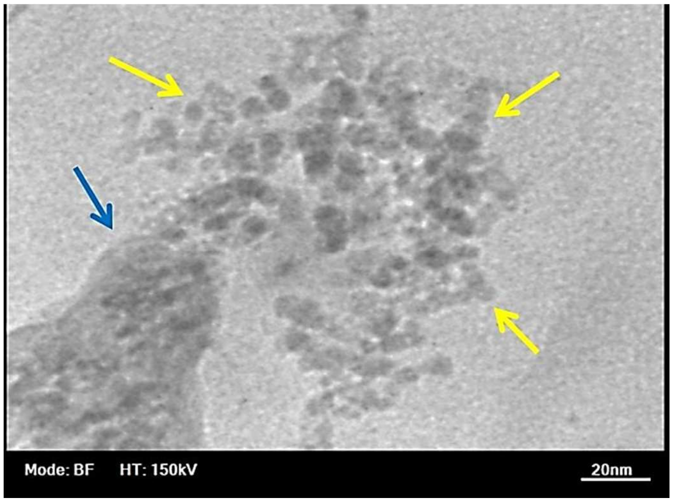
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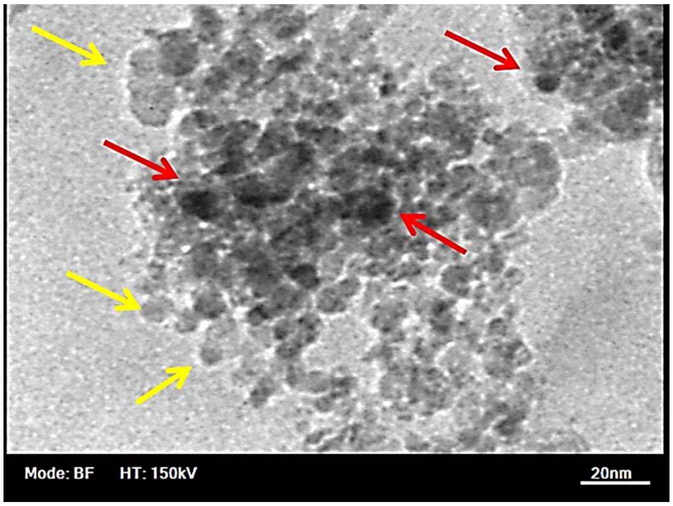
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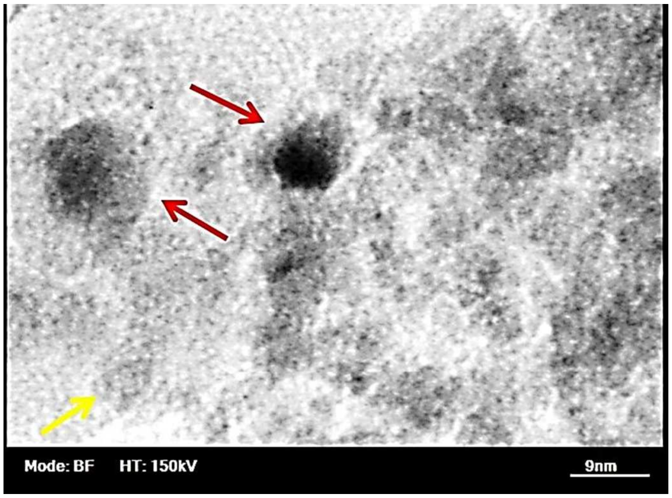

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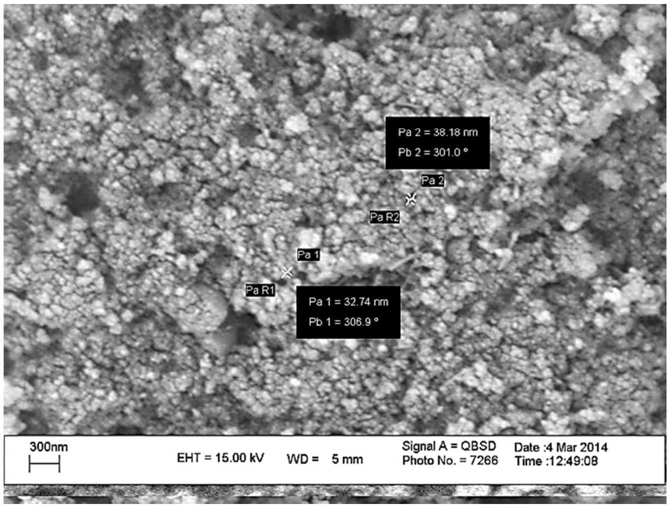

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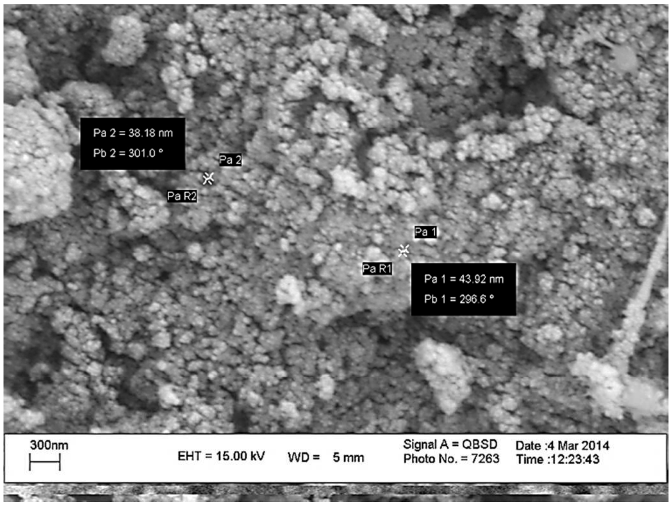

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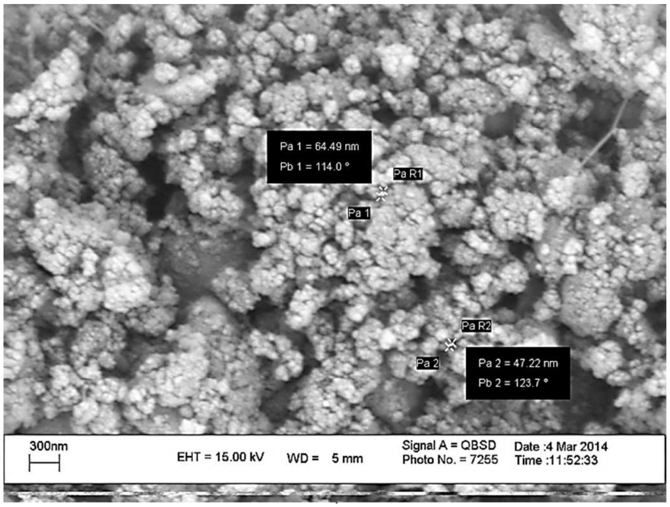

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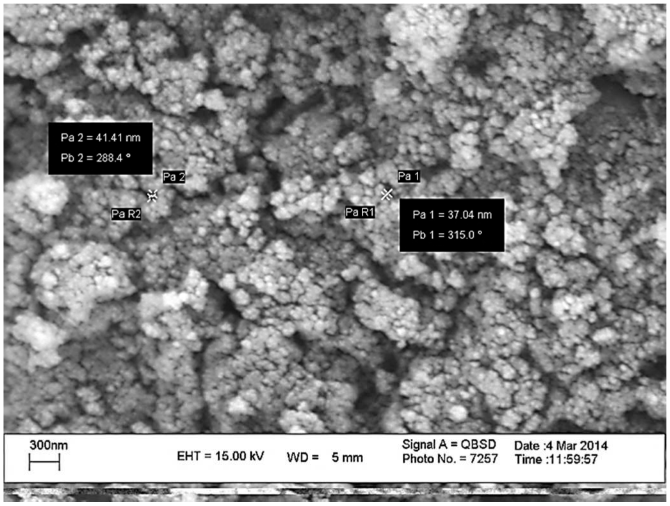
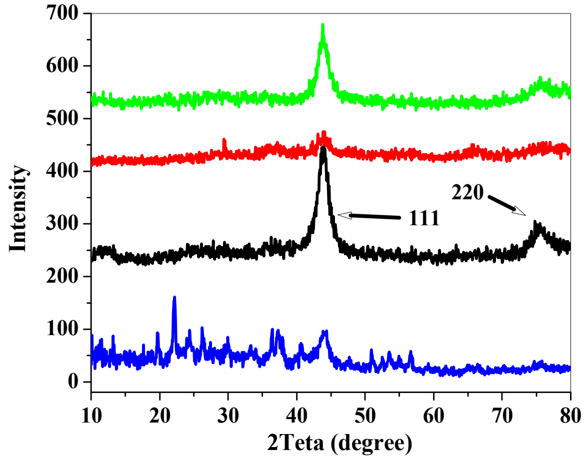


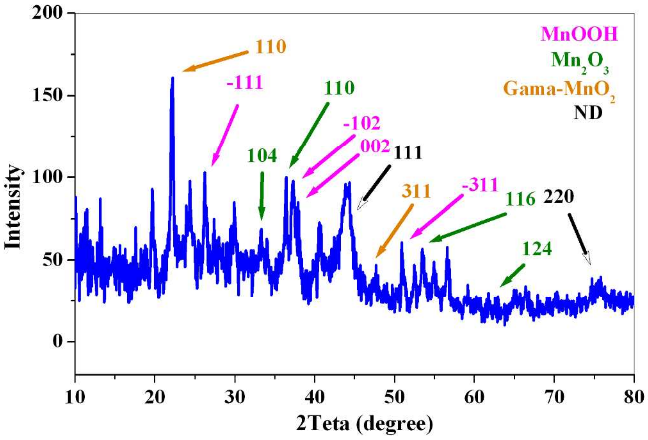
k

Fig. 1 TEM and HRTEM from **1** (a,b), **2** (c,d), **3** (e) and **4** (f,g). Blue, yellow and red arrows show layered Mn oxide, ND and covered ND by amorphous Mn oxide. SEM images of **1** (h), **2** (i), **3** (j) and **4** (k).

In XRD of **1** and **3** (Fig. 2b and Fig. S5-S7), patterns related to ND and crystalline phase of Mn oxides such as Mn_2O_3 or MnO(OH) are observed. In **1** and **3**, patterns for ND are not as sharp as related patterns for **2** and **4** most probably because of oxidation of ND. The peaks for Mn oxides in **2** or **4** are not sharp but can be related to layered Mn oxide without long-range order (Fig. S4 and S6). Such structure can be known as amorphous Mn oxide.



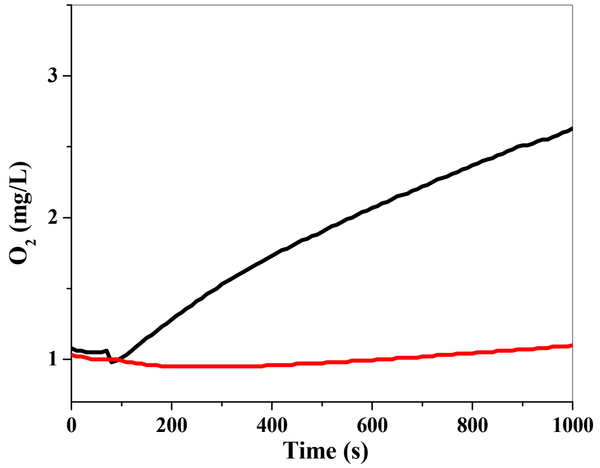
a



b

Fig. 2 XRD patterns from **1** (blue), **2** (black), **3** (red) and **4** (green) (a). XRD for **1** with related peaks for MnO(OH), Gama-MnO_2 and Mn_2O_3.

In the next step, we considered water-oxidation reaction (Fig. 3).



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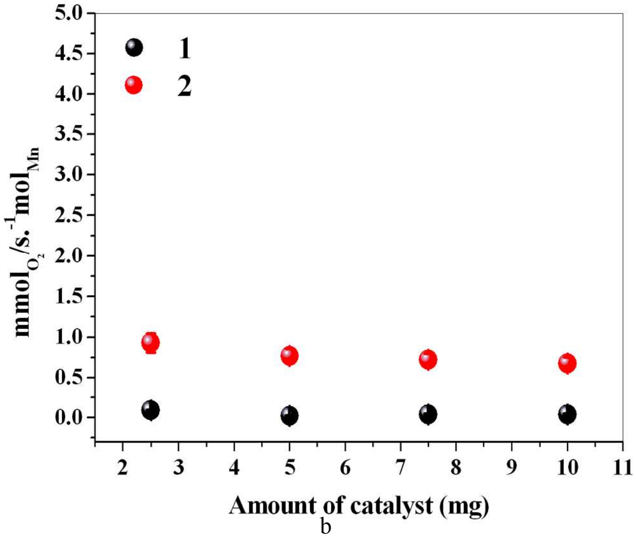

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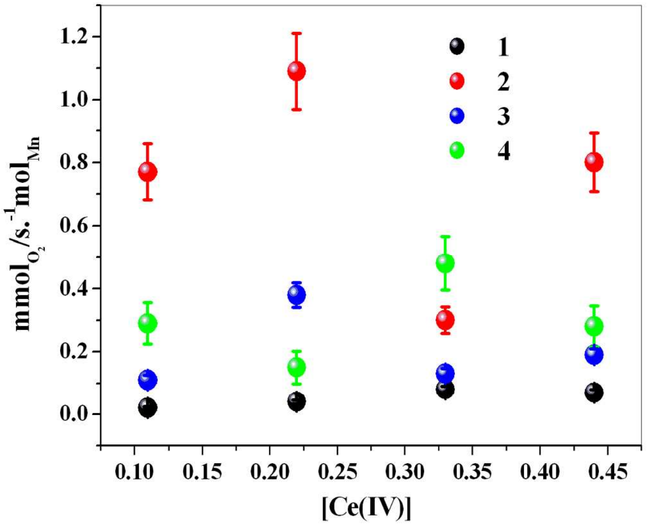

c

Fig. 3 Oxygen evolution by ND (red) and **2** (5 mg) in the presence of Ce(IV) (0.11 M) (a). The rates of oxygen evolution in the presence of different amounts of **1** and **2** ([Ce(IV)]: 0.11 M) (b). Oxygen evolution of an aqueous solution of Ce(IV) (40 mL, 0.11-0.44 M) at 25.0 ºC in the presence of **1-4** (c).

Ce(IV) is a non-oxo transfer, soluble in water, and stable oxidant, and thus is an usual oxidant in water-oxidation reactions (Parent, A. R.; Crabtree, R. H.; Brudvig, G. W. *Chem. Soc. Rev.* **2013**, *42*, 2247). It oxidizes Mn oxides and in the next step the oxide can oxidizes water.[47] Water oxidation by ND, without Mn oxide, is not observed (Fig. 3a). Turnover frequency (mmol O_2/mol Mn.s) (TOF)'s are the same for different amounts of each catalyst. The effect of concentration of Ce(IV) on water oxidation is shown in Fig. 3c. Both water oxidation and catalyst decomposition (such as MnO_4^- formation for detail see ref. 33) occurs in high concentration of Ce(IV) and, thus, the effect of concentration of Ce(IV) on water oxidation is complicated. Among these compounds, **2** shows promising water oxidation at 0.22 M of Ce(IV) (TOF ~ 1). The TOF is among efficient Mn based catalysts toward water oxidation (Table 1). Regarding XRD results, the reaction of Mn oxide and ND causes decomposition of both Mn oxide and ND. In **1** and **3,** Mn_2O_3 and MnO(OH) are observed that both of them are not good catalyst for water oxidation. However, in **2** such phases are not observed and amorphous Mn oxide is the major phase. On the other hand, TEM and HRTEM images show that in **2** higher dispersion of Mn oxide on ND is observed. These factors may cause higher activity for **2** toward water oxidation. The cause for the relatively low activity of **4** toward water oxidation is unknown but AAS shows that small amount of Mn oxide is placed on ND in **4**.

In this condition, in addition to efficiency of catalysts, ND may improve other properties, such as conductivity, of the Mn oxides.

Table 1 The rate of water oxidation by the various Mn based catalysts for water oxidation in the presence of non-oxygen transfer oxidant chemical oxidant.

Conclusions

We concluded that synthesis of amorphous nano-sized Mn oxide/ND composites as efficient water-oxidizing catalysts by the reaction of MnO_4^- and ND is possible. However, other methods such as mixing Ca-Mn oxide and ND or the reaction of MnO_4^- and Mn(II) in the presence of ND cause reduction of

Mn oxide to Mn_2O_3 and MnO(OH). The simple van der Waals interactions between ND and these Mn oxides are sufficient to provide a strong enough adhesion for inorganics/nanocarbon. Thus, although ND has fragile structure but using new strategies may cause the application it as a support for heterogeneous catalysts. The results clearly show where amorphous Mn oxide remains intact, good water oxidation is observed by amorphous Mn oxide/ND composite (TOF = 1 mmol O_2 per mol Mn per second). Similar results were reported by CNT, GO, G and C60.[48,49]

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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Compound	Oxidant	TOF mmol O_2/mol Mn	References
Optimistic Ca-Mn oxide	Ce(IV)	3.0	29
Nano scale Mn oxide within NaY zeolite	Ce(IV)	2.62	30
Layered Mn-calcium oxide	Ce(IV)	2.2	31
Layered Mn-Al, Zn, K, Cd and Mg oxide	Ce(IV)	0.8-2.2	32,33
Layered Mn/ND	Ce(IV)	~ 1	This work
$CaMn_2O_4.H_2O$	Ce(IV)	0.54	34
Amorphous Mn Oxides	$Ru(bpy)_3^{3+}$	0.06	35
	Ce(IV)	0.52	
$CaMn_2O_4.4H_2O$	Ce(IV)	0.32	34
Mn oxide nanoclusters	$Ru(bpy)_3^{3+}$	0.28	36
Mn oxide-coated montmorillonite	Ce(IV)	0.22	37
Nano-sized α-Mn_2O_3	Ce(IV)	0.15	38
Octahedral Molecular Sieves	$Ru(bpy)_3^{3+}$	0.11	35
	Ce(IV)	0.05	
MnO_2 (colloid)	Ce(IV)	0.09	39
α-MnO_2 nanowires	$Ru(bpy)_3^{3+}$	0.059	40
$CaMn_3O_6$	Ce(IV)	0.046	41
$CaMn_4O_8$	Ce(IV)	0.035	41
α-MnO_2 nanotubes	$Ru(bpy)_3^{3+}$	0.035	40
Mn_2O_3	Ce(IV)	0.027	34
β-MnO_2 nanowires	$Ru(bpy)_3^{3+}$	0.02	40
$Ca_2Mn_3O_8$	Ce(IV)	0.016	42
$CaMnO_3$	Ce(IV)	0.012	42
Nano-sized λ-MnO_2	$Ru(bpy)_3^{3+}$	0.03	43
Bulk α-MnO_2	$Ru(bpy)_3^{3+}$	0.01	40
Mn Complexes	Ce(IV)	0.01-0.6	44
PSII	Sunlight	100-400 × 10^3	45,46