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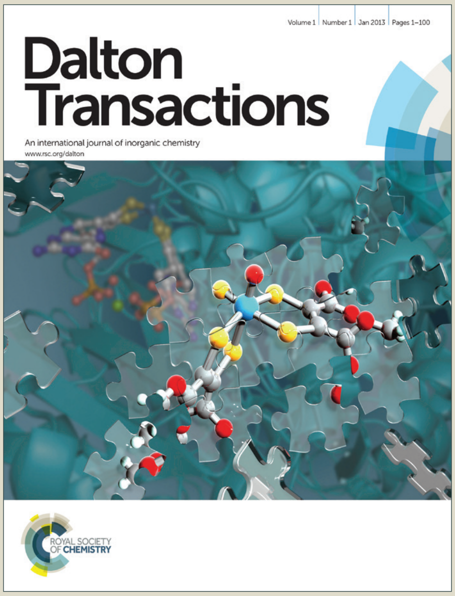

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Nanolayered manganese oxide/C_{60} composite: A good water-oxidizing catalyst for artificial photosynthetic systems†

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For the first time, we considered Mn oxide/C_{60} composites as water-oxidizing catalysts. The composites were synthesized by easy and simple procedures, and characterized by some methods. The water-oxidizing activities of these composites were also measured in the presence of cerium(IV) ammonium nitrate. We found that nanolayered Mn oxide/C_{60} composites show promising activity toward water oxidation.

Introduction

In recent years, regarding environmental issues and energy crisis, water oxidation[1,2] or reduction,[3] CO_2 reduction/storage[4] and O_2 reduction[5] have initiated a great interest.

High scale H_2 production by water splitting is a promising route for the conversion of sustainable but intermittent energies.[6] However, water oxidation is bottleneck for water splitting into H_2 and O_2 and thus, the finding of an efficient, cheap and environmentally friendly water-oxidizing compound is highly desirable for artificial photosynthetic systems.[6] Mn compounds are very interesting because they are not only cheap and environmentally friendly but also are efficiently used by Nature for water oxidation.[7] Among different Mn compounds, Mn oxides are promising to use in artificial photosynthetic systems.[8]

The water-oxidizing center (WOC) of Photosystem II (PSII) in plants, algae and cyanobacteria is a Mn_4CaO_5 cluster catalyzing light-induced water oxidation[9] and the WOC may be considered as a nano-sized Mn oxide in a protein matrix with high proton and electron conductivity.[10] Since 1968, different Mn oxides were reported as water-oxidizing catalysts.

Glikman, Shcheglova and Shilov found that Mn oxides are catalysts toward water oxidation in the presence of cerium(IV) ammonium nitrate (Ce(IV)) as an oxidant.[11a] Then, Morita in 1977 showed electrochemical water oxidation by MnO_2.[11b] Harriman's group in 1988 in his extended studies showed that cobalt, iridium, manganese(III) and ruthenium oxides are efficient catalysts for water oxidation in the presence of Ce(IV) or $Ru(bpy)_3^{3+}$ as chemical oxidant.[12] The group also reported factors in water oxidation by the oxides such as calcination temperature and effects of different support.[12] Since these pioneering studies, other groups have evaluated different Mn oxides in different conditions as water-oxidizing catalysts.[13]

Jiao and Frei reported nanostructured Mn oxide clusters supported on mesoporous silica in the presence of $Ru(bpy)_3^{3+}$.[14] Among different Mn oxides, layered Mn oxides were reported as efficient catalysts for water oxidation. Gold particles on these layered Mn oxides improve their activity towards water oxidation.[15] The atomic layer deposition was also reported to obtain a highly active MnO_x/glassy carbon catalyst toward water oxidation.[16]

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 Dismukes.[17] They found that Mn_2O_3 and Mn_3O_4 are among the most active Mn oxides for water oxidation. The Mn(III)-O bonds in edge sharing octahedra at the surface are proposed as active sites for water oxidation.[17]

Recently, Najafpour's group showed that different Mn oxide phases in the presence of Ce(IV) or in electrochemical water oxidation convert to a layered Mn oxide after a few hours.[18] Self-healing for Mn oxides were also reported.[19] In the self-healing reaction, decomposition products from Mn oxide in the water oxidation reaction can react or combine to remake Mn oxide.[19]

Mn oxide/carbon nanotubes (CNT), graphene (G) and graphene oxide (GO) were shown as promising composites for water oxidation.[20,21]

Recently, it was found that many factors such as surface, oxidation state of Mn oxide, dispersion, calcination temperature and crystalinty are important in water-oxidizing activity.[22,23]

Here we, for the first time, reported that nanolayered Mn oxide/C_{60} composites are good water-oxidizing catalysts. As C_{60} and Mn oxides exhibit exceptional and interesting structural and chemical properties, such composites are important in the scientific community.[24,25]

Experimental

Material and methods

C_{60} (purity 99.5%) was purchased from SES company. All reagents and solvents were purchased from the commercial sources and were used without a further purification. 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 analysed by AAS.

Synthesis

Four methods were used to synthesize Mn oxide/C_{60} composites:

1:

Solution 1: C_{60} (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) were added in 8 ml water.

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

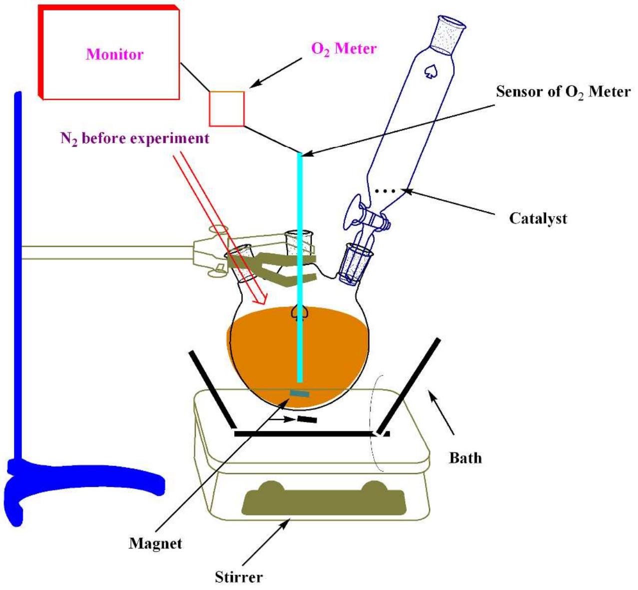
2: C_{60} (200 mg) in water (10 mL) was sonicated and added to 10 mL water contains 20 mg $KMnO_4$. The mixture was dried at 90 °C and then was washed by 20 mL water.

3: C_{60} (100 mg) in water (5 mL) was sonicated and added to 5 mL sonicated water contains 100 mg Mn-Ca oxide.[15] The mixture was stirred at 60 °C to dry and obtain a solid.

4: C_{60} (250 mg) in water (10 mL) was sonicated and added to 10 mL water contains 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 run, 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 1). 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. Water oxidation was performed by a set up shown in Scheme 1.



Scheme 1 Set up for water-oxidation experiments.

Results and discussion

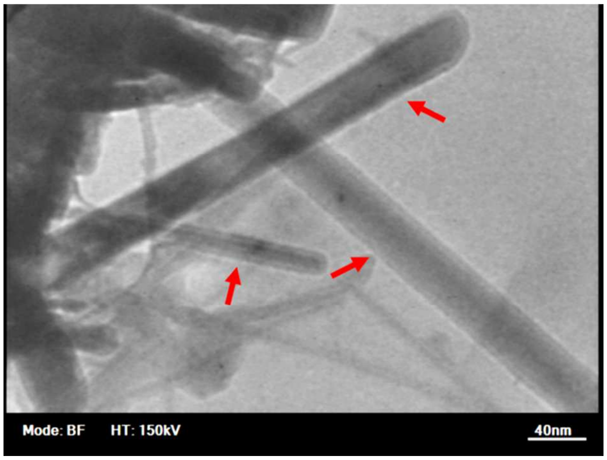
1-**4** were synthesized by simple methods. **1** was prepared by the reaction of Mn(II) and MnO_4^- ions in the presence of C_{60}. Such procedure with other nanocarbons show a very good mixing of the Mn oxide and C_{60}. **2** and **4** were synthesized by the reactions of MnO_4^- and C_{60}:

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

In this procedure, C_{60} serves as a sacrificial reductant and converts MnO_4^- to Mn oxide. However, the reaction of **2** and **4** occurs at 25 and 90 °C, respectively.

To synthesize of **3**, layered Mn-Ca oxide with C_{60} were simply mixed. Simple van der Waals interactions are usually sufficient to provide a strong enough adhesion between C_{60} and Mn oxides. We expected that **3** shows efficient water-oxidizing activity.

In IR spectra of **1**-**4**, 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). The absorption bands characteristic for a MnO_6 core in the region ~ 600 cm^{-1} assigned to stretching vibrations of Mn-O bonds in Mn oxide was also observed in the FTIR spectra of **1** and **3**. However, peaks related to MnO_6 core were not observed for **2** and **4** because of low amounts of Mn oxide in the composite. 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 and Fig. S2.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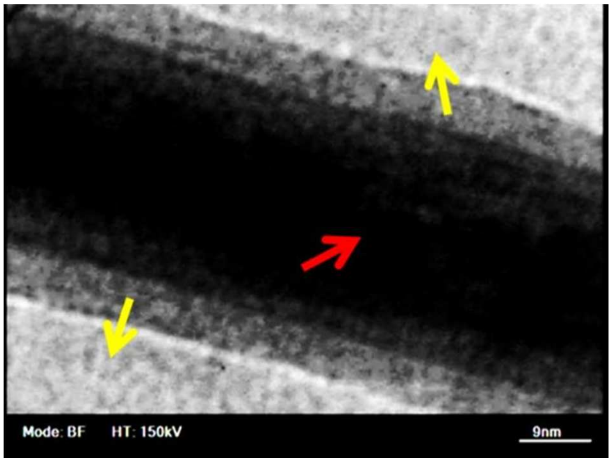
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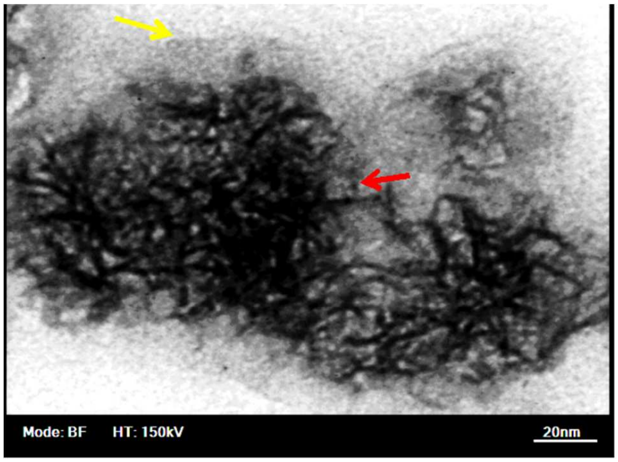
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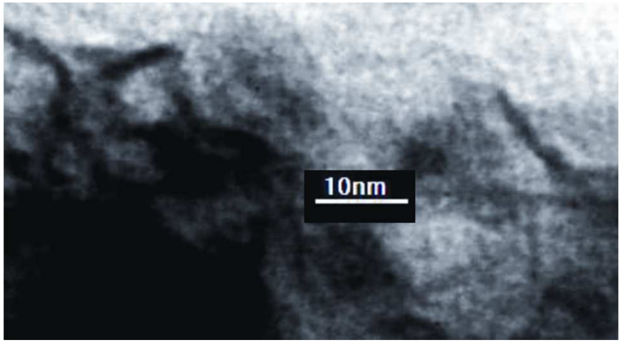
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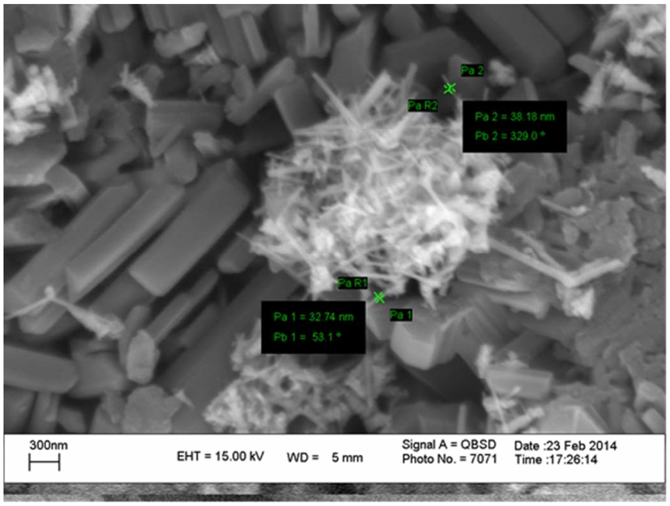
d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Pa R2
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Pb 2 = 329.0 °
Pa R1
Pa 1
Pa 1 = 32.74 nm
Pb 1 = 53.1 °
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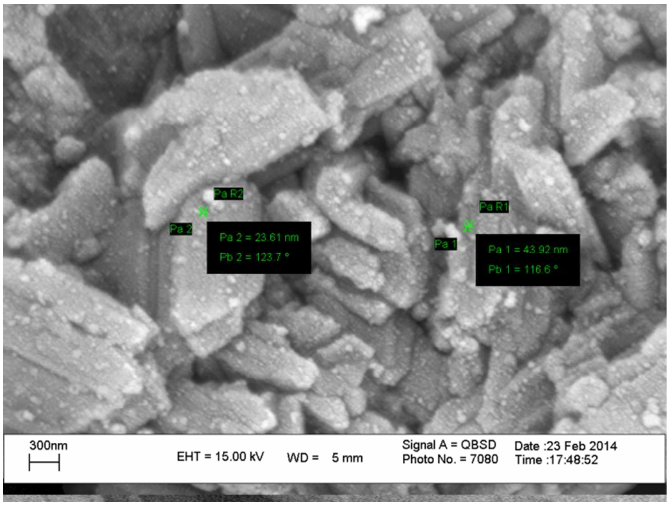
e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Pa R1
Pa 1
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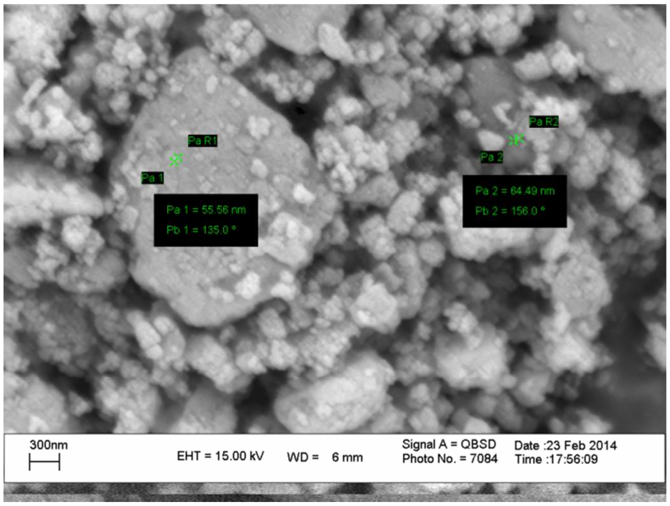
f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Pa R2
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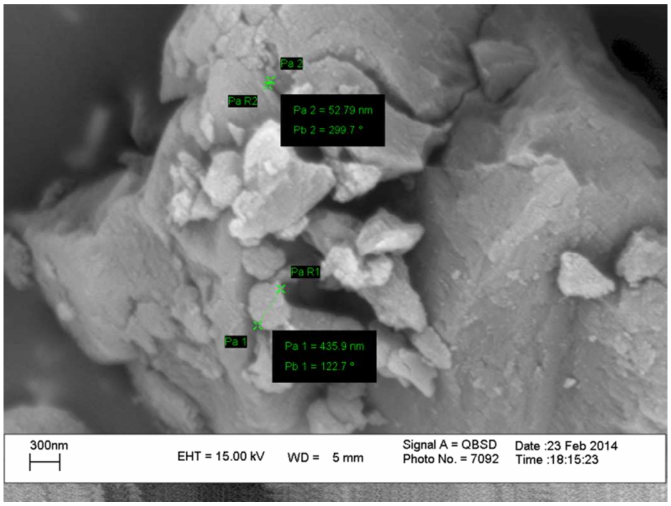
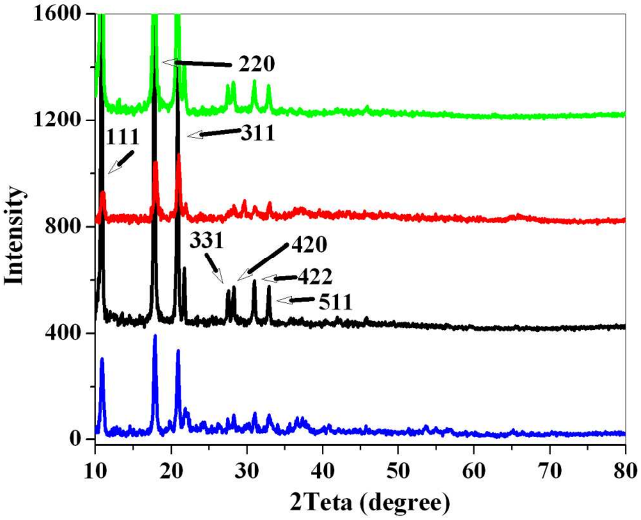
g



h

Fig. 1 TEM and HRTEM from **1** (a,b) and **2** (c,d). Red and yellow arrows show Mn_2O_3 and C_{60} phases. In d, very small particles (~ 1 nm) and dark area show C_{60} molecules and layered Mn oxides, respectively. Nanolayers of Mn oxides cover these molecules. SEM images of **1** (e), **2** (f), **3** (g) and **4** (h).

Surprising for **1** or **3**, TEM and HRTEM images (Fig. 1, Fig. S2 ESI†) show that in addition to layered Mn oxides, other Mn oxides such as Mn_2O_3 and MnOOH are also present. In **1**, rod morphology (diameter: 20-40 nm) related to Mn_2O_3 and MnOOH are observed. Thus, most probably in **1** and **3**, Mn_2O_3 or MnOOH instead of layered Mn oxides are formed. However, in **2** and **4**, layered structures are observed in both TEM and HRTEM images. SEM images (Fig. 1 and Fig. S3 ESI†) for **1** show rod morphology related to Mn_2O_3 and MnOOH (diameter 20-40 nm). In **2**, small nano-structure Mn oxides (~ 20 nm) are observed that cover the surface of C_{60}. In **3**, mixing Mn-Ca oxides (50-60 nm) and C_{60} are observed. In **4**, SEM images show no clear images from Mn oxide phase most probably because of very small particles prepared in the mild condition. In XRD of **1** and **3**, patterns related to C_{60} and crystalline phase of Mn oxides such as Mn_2O_3 or MnOOH are observed (Fig. 2). In **1** and **3**, patterns for C_{60} are not as sharp as related patterns for **2** and **4** most probably because oxidation of C_{60}. However, only very low amounts of Mn_2O_3 or MnOOH are detected in **2** and **4**.



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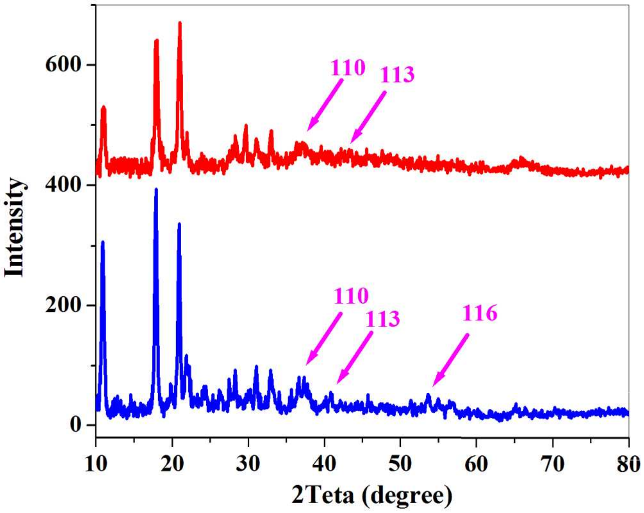
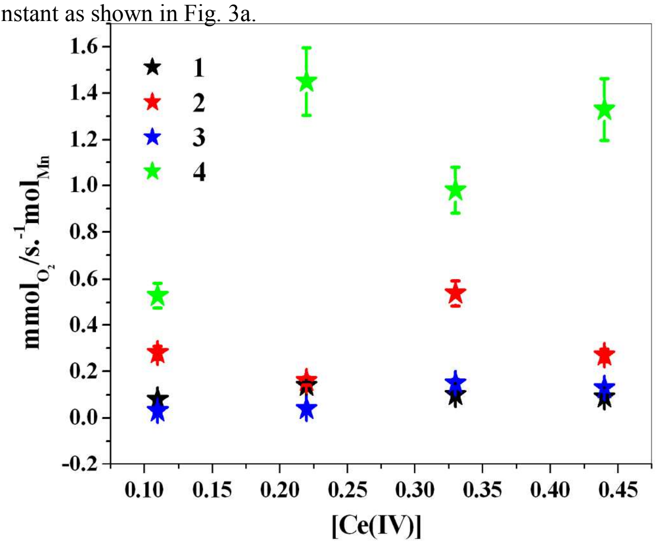


b

Fig. 2 XRD from **1** (blue), **2** (black), **3** (red) and **4** (green) (a). XRD for **1** (blue) and **3** (red) with related peaks for Mn_2O_3. The black and magenta arrows show patterns for C_{60} and Mn_2O_3, respectively.

In the next step, we considered water oxidation activity of these compounds in the presence of Ce(IV). To study of the effect of concentration of Ce(IV) on water oxidation, reactions were done with different concentrations of Ce(IV) keeping all other factors constant as shown in Fig. 3a.



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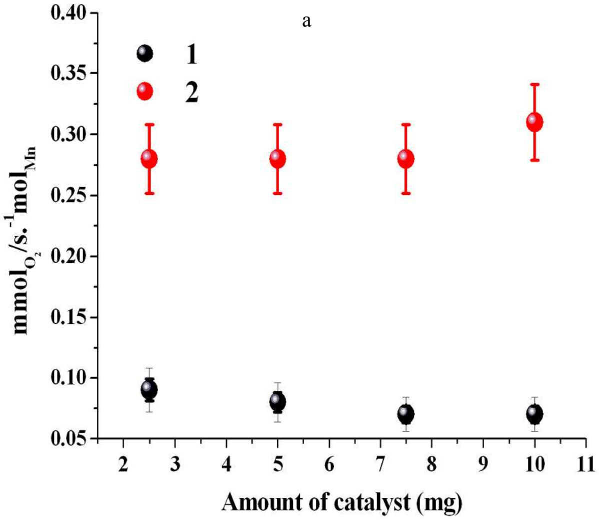

b

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

In this condition, no oxygen evolution was observed by C_{60} (Fig. S4). The TOFs for different amounts of each catalyst are the same. It means that the rate of oxygen evolution increases linearly with amount of catalyst. The increasing in the concentration of Ce(IV) has complicated effects on the water oxidation because of both oxygen evolution and catalyst decomposition reactions.[26] Among these compounds, **4** shows promising water oxidation at 0.22 M of Ce(IV) (TOF = 1.5). The TOF is among the best Mn based catalyst toward water oxidation (Table 1). In the higher concentration of Ce(IV) (> 0.2 M), TOF decreases. We relate this decreasing to decomposition of catalyst. Similar to previously reported results, nanolayered Mn oxides are efficient catalysts toward water oxidation. As we discussed before, the mixing of nanolayered Mn oxide and C_{60} to synthesize **1** and **3** changes the structures of C_{60} and Mn oxides. In this case, Mn_2O_3 and MnOOH are produced that both of them are not efficient catalyst for water oxidation. Between **2** and **4**, **4** is the better catalyst most probably because higher temperature used in preparation of **2** converts a few amounts of layered Mn oxide to other phases.

Comparing with other Mn oxides (Table 1), **4** is among efficient catalysts toward water oxidation. In this condition, C_{60} may improve other properties of the Mn oxides. For example, MnO_x materials suffer from low conductivity. C_{60} can improve electron transfer in the composites.

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 nano-sized Mn oxide/C_{60} composites as efficient water-oxidizing catalysts by very simple methods are possible. Although, C_{60} oxidation occurs in some cases but C_{60} can be a support for Mn oxides. The simple van der Waals interactions between C_{60} and Mn oxides are sufficient to provide strong enough adhesion. Nanolayered Mn oxides show good water-oxidizing activity when combined with C_{60}. The reaction of MnO_4^- with C_{60} is a promising procedure to synthesize of water-oxidizing composites but the reaction should be performed in ambient temperature to inhibit C_{60} oxidation. In this case, low amount of Mn oxide on C_{60} is promising toward water oxidation. Similar to other nanocarbons, it shows that dispersion of Mn oxide on the nanocarbon component may be a useful method in artificial photosynthetic systems. In other words, fragile structure, low surface area and sublimation temperature of C_{60} limit[25] it to be used as a support for heterogeneous catalysis but using new strategies may cause the application C_{60} as a support for heterogeneous catalysts. The results clearly show that in the cases that nanolayered Mn oxide remains intact, efficient water oxidation is observed by nanolayered Mn/C_{60} composite.

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Notes and references

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

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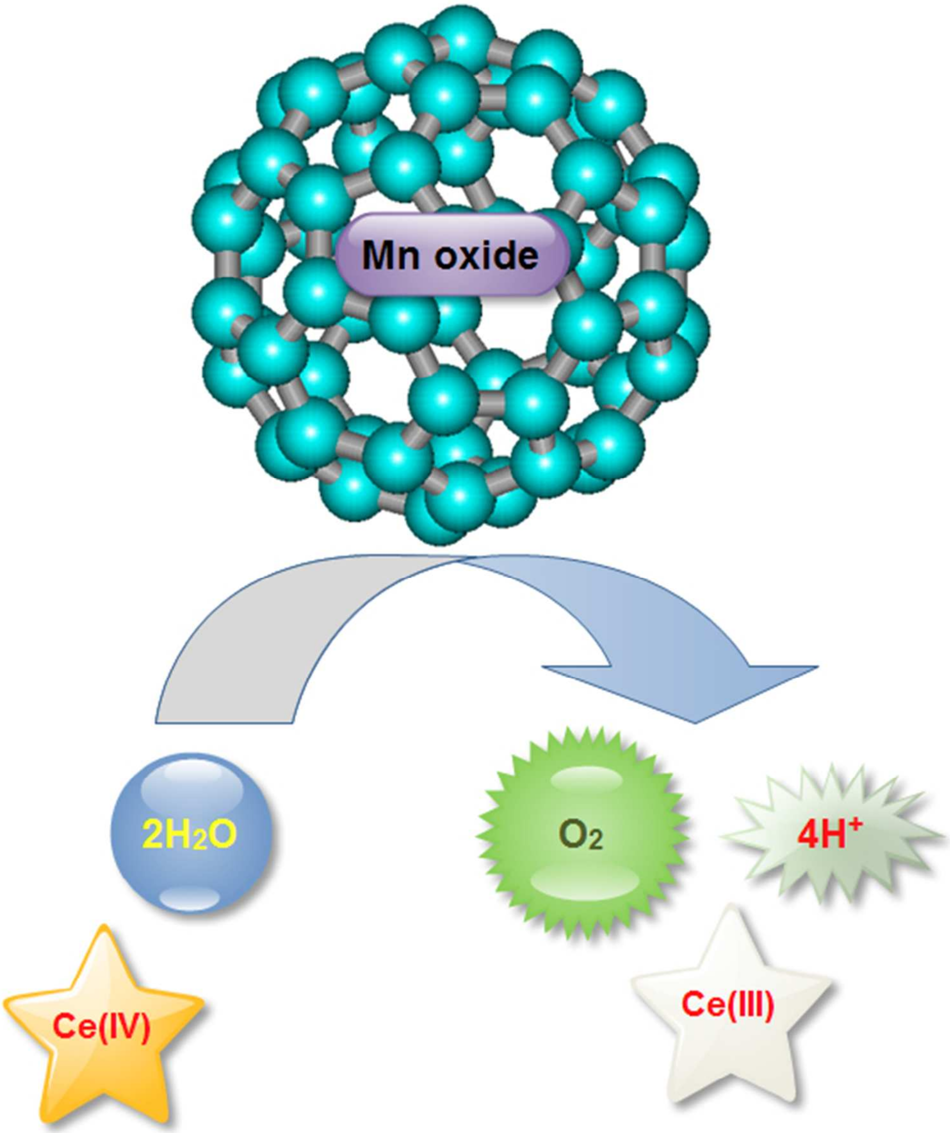
We reported that nanolayered Mn oxide/C_{60} composites show promising activity toward water oxidation.



156x188mm (96 x 96 DPI)

Compound	Oxidant	TOF mmol O_2/mol Mn	References
Optimistic Ca-Mn oxide	Ce(IV)	3.0	27
Nano scale Mn oxide within NaY zeolite	Ce(IV)	2.62	28
Layered Mn-calcium oxide	Ce(IV)	2.2	29
Layered Mn-Al, Zn, K, Cd and Mg oxide	Ce(IV)	0.8-2.2	30,31
Nanolayered Mn oxide/C_{60}	Ce(IV)	1.5	This work
$CaMn_2O_4.H_2O$	Ce(IV)	0.54	32
Amorphous Mn Oxides	$Ru(bpy)_3^{3+}$ Ce(IV)	0.06 0.52	33
$CaMn_2O_4.4H_2O$	Ce(IV)	0.32	32
Mn oxide nanoclusters	$Ru(bpy)_3^{3+}$	0.28	34
Mn oxide-coated montmorillonite	Ce(IV)	0.22	35
Nano-sized α-Mn_2O_3	Ce(IV)	0.15	36
Octahedral Molecular Sieves	$Ru(bpy)_3^{3+}$ Ce(IV)	0.11 0.05	33
MnO_2 (colloid)	Ce(IV)	0.09	37
α-MnO_2 nanowires	$Ru(bpy)_3^{3+}$	0.059	38
$CaMn_3O_6$	Ce(IV)	0.046	39
$CaMn_4O_8$	Ce(IV)	0.035	40
α-MnO_2 nanotubes	$Ru(bpy)_3^{3+}$	0.035	38
Mn_2O_3	Ce(IV)	0.027	32
β-MnO_2 nanowires	$Ru(bpy)_3^{3+}$	0.02	38
$Ca_2Mn_3O_8$	Ce(IV)	0.016	40
$CaMnO_3$	Ce(IV)	0.012	40
Nano-sized λ-MnO_2	$Ru(bpy)_3^{3+}$	0.03	41
Bulk α-MnO_2	$Ru(bpy)_3^{3+}$	0.01	38
Mn Complexes	Ce(IV)	0.01-0.6	42-43
PSII	Sunlight	100-400 × 10^3	44,45