

Nanolayered manganese oxide/C₆₀ composite: a good water-oxidizing catalyst for artificial photosynthetic systems†

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For the first time, we considered Mn oxide/C₆₀ 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 the nanolayered Mn oxide/C₆₀ composites show promising activity toward water oxidation.

Introduction

In recent years, because of environmental problems and energy crises, water oxidation^{1,2} or reduction,³ CO₂ reduction/storage⁴ and O₂ reduction⁵ have attracted significant interest.

Large scale H₂ production by water splitting is a promising route for the conversion of sustainable but intermittent energy.⁶ However, water oxidation is a bottleneck for water splitting into H₂ and O₂. Hence, finding 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 in nature for water oxidation.⁷ Among the different Mn compounds, Mn oxides are promising for application in artificial photosynthetic systems.⁸

The water-oxidizing center (WOC) of Photosystem II (PSII) in plants, algae and cyanobacteria is a Mn₄CaO₅ cluster catalyzing light-induced water oxidation,⁹ and the WOC may be considered to be 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} In 1977, Morita demonstrated electrochemical water oxidation by MnO₂.^{11b} In 1988, Harriman and coworkers in their 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)₃³⁺ as a chemical oxidant.¹² They also reported factors in water oxidation by oxides such as calcination temperature and effects of different supports.¹² Since these pioneering studies, other groups have evaluated different Mn oxides under 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)₃³⁺.¹⁴ Among the different Mn oxides, layered Mn oxides were reported to be efficient catalysts for water oxidation. Gold particles on these layered Mn oxides improve their activity toward water oxidation.¹⁵ Atomic layer deposition was also reported to achieve highly active MnO_x/glassy carbon catalyst toward water oxidation.¹⁶

Very pure β-MnO₂, R-MnO₂, α-MnO₂, δ-MnO₂, λ-MnO₂, LiMn₂O₄, Mn₂O₃, and Mn₃O₄ compounds were reported by Dismukes.¹⁷ They found that Mn₂O₃ and Mn₃O₄ 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 the active sites for water oxidation.¹⁷ Recently, Najafpour and coworkers 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 of Mn oxides was also reported.¹⁹ In the self-healing reaction, decomposition products from Mn oxide in water oxidation reaction can react or combine to reproduce Mn oxide.¹⁹

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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 several factors, such as surface, oxidation state of Mn oxide, dispersion, calcination temperature and crystallinity, are important in water-oxidizing activity.^{22,23}

Here, for the first time, we report that nanolayered Mn oxide/C₆₀ composites are good water-oxidizing catalysts. Because C₆₀ 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

C₆₀ (purity 99.5%) was purchased from SES company. All the reagents and solvents were purchased from commercial sources and were used without further purification. TEM and SEM were carried out using Philips CM120 and LEO 1430VP microscopes, respectively. Powder X-ray diffraction patterns were recorded on a Bruker D8 ADVANCE diffractometer (CuK_α radiation). Mn atomic absorption spectroscopy (AAS) was performed on an atomic absorption spectrometer Varian Spectra AA 110. Prior to analysis, the compounds were added to 1 mL of concentrated nitric acid and H₂O₂, left at room temperature for at least 1 h to ensure that the oxides were completely dissolved. These solutions were then diluted to 25.0 mL and analysed by AAS.

Synthesis

Four methods were used to synthesize Mn oxide/C₆₀ composites:

1: Solution 1: C₆₀ (200 mg) in water (5 mL) was sonicated and added to 2 mL water containing Mn(OAc)₂·4H₂O (122 mg), and then stirred for 5 minutes.

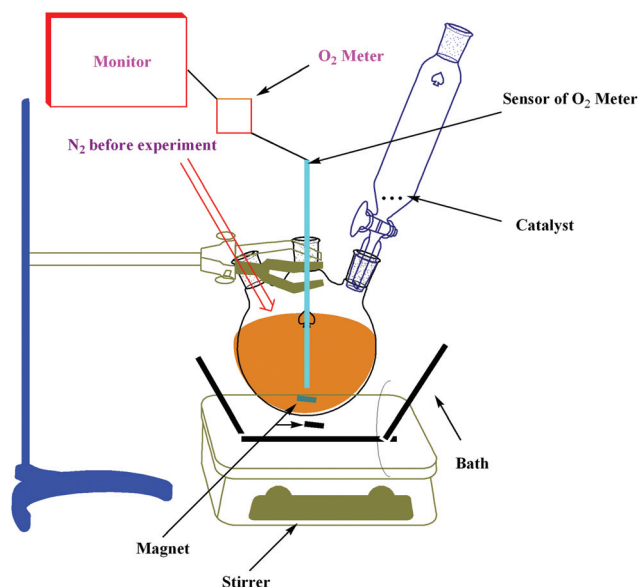
Solution 2: KOH (40 mg) and KMnO₄ (40 mg) were added to 8 mL water.

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

2: C₆₀ (200 mg) in water (10 mL) was sonicated and added to 10 mL water containing 20 mg KMnO₄. The mixture was dried at 90 °C and then washed with 20 mL water.

3: C₆₀ (100 mg) in water (5 mL) was sonicated and added to 5 mL sonicated water containing 100 mg Mn–Ca oxide.¹⁵ The mixture was stirred at 60 °C until a dry solid was obtained.

4: C₆₀ (250 mg) in water (10 mL) was sonicated and added to 10 mL water containing 50 mg KMnO₄. The mixture was stirred for one day at 25 °C, and the solid was separated and washed to remove KMnO₄. Finally, the solid was dried at 60 °C.



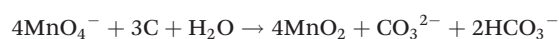
Scheme 1 Set up for water-oxidation experiments.

Water oxidation

Evolution of oxygen from aqueous solutions in the presence of Ce(IV) was investigated using an HQ40d portable dissolved oxygen-meter connected to an oxygen monitor with a digital readout. The reactor was maintained at 25.0 °C 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 an air-tight reactor. After ensuring a constant baseline reading, water in the reactor was replaced with the Ce(IV) solution. Without the catalyst, Ce(IV) was stable under these conditions and oxygen evolution was not observed. After the 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 the linear fits of data by an initial rate. Water oxidation was performed using a set up shown in Scheme 1.

Results and discussion

1–4 were synthesized using simple methods. 1 was prepared by the reaction of Mn(II) and MnO₄[−] ions in the presence of C₆₀. Such procedure with other nanocarbons show a very good mixing of the Mn oxide and C₆₀. 2 and 4 were synthesized by the reactions of MnO₄[−] and C₆₀:



In this procedure, C₆₀ serves as a sacrificial reductant and converts MnO₄[−] to Mn oxide. However, the reaction of 2 and 4 occurs at 25 and 90 °C, respectively.

To synthesize 3, layered Mn–Ca oxide and C₆₀ were simply mixed. Simple van der Waals interactions are usually sufficient

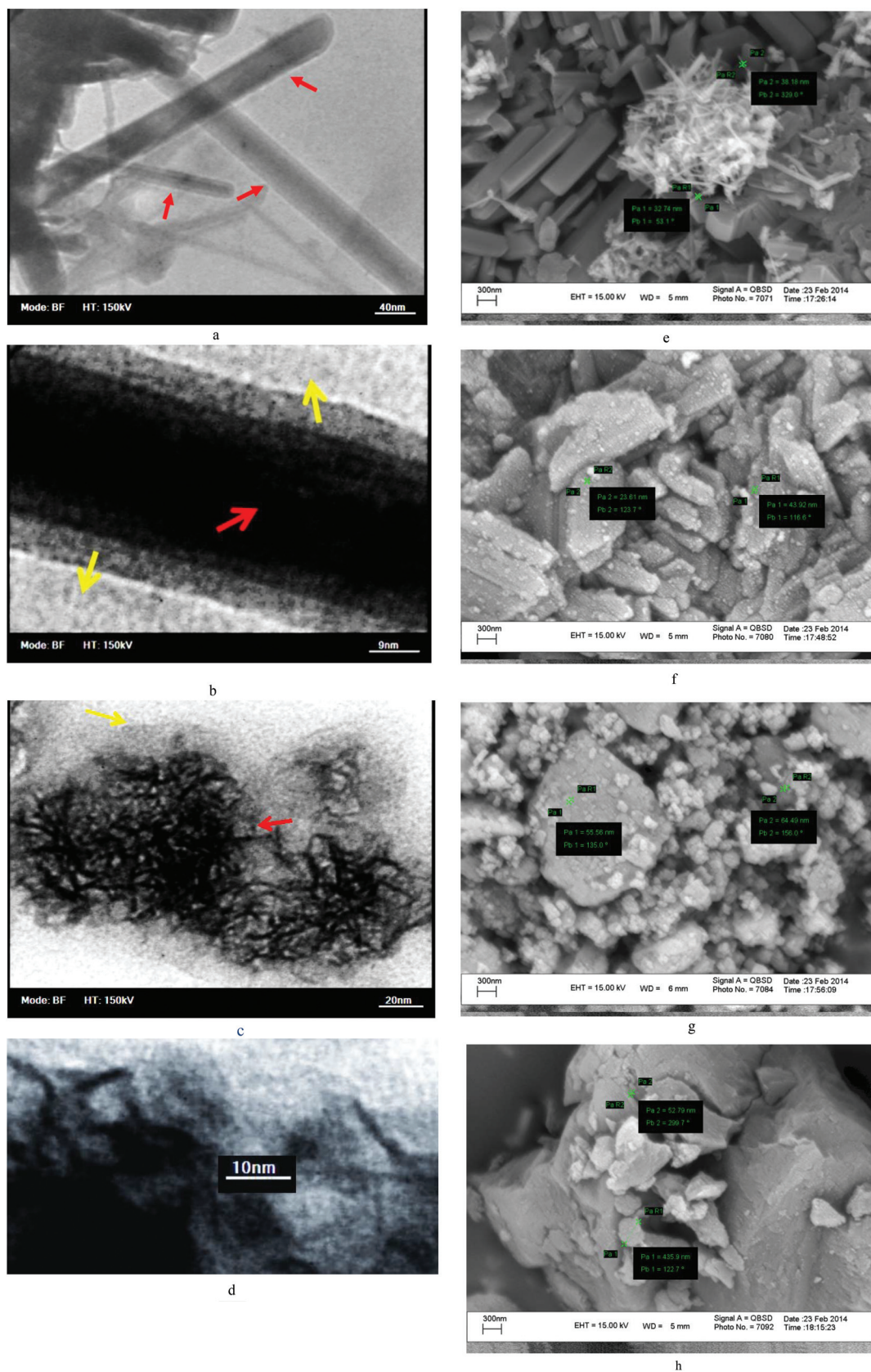


Fig. 1 TEM and HRTEM from **1** (a,b) and **2** (c,d). Red and yellow arrows show Mn_2O_3 and C_{60} phases, respectively. In (d), very small particles (~ 1 nm) and dark area show C_{60} molecules and layered Mn oxides, respectively. Nanolayers of Mn oxides cover these molecules. SEM images of **1**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

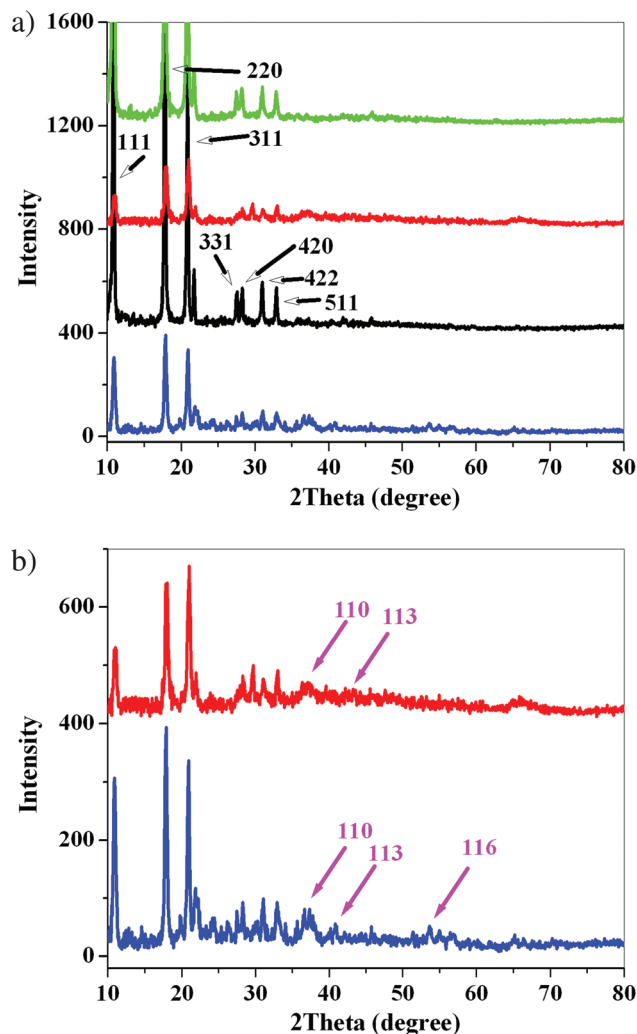


Fig. 2 XRD from 1 (blue), 2 (black), 3 (red) and 4 (green) (a). XRD pattern of 1 (blue) and 3 (red) with the related peaks for Mn_2O_3 (b). Black and magenta arrows show the patterns for C_{60} and Mn_2O_3 , respectively.

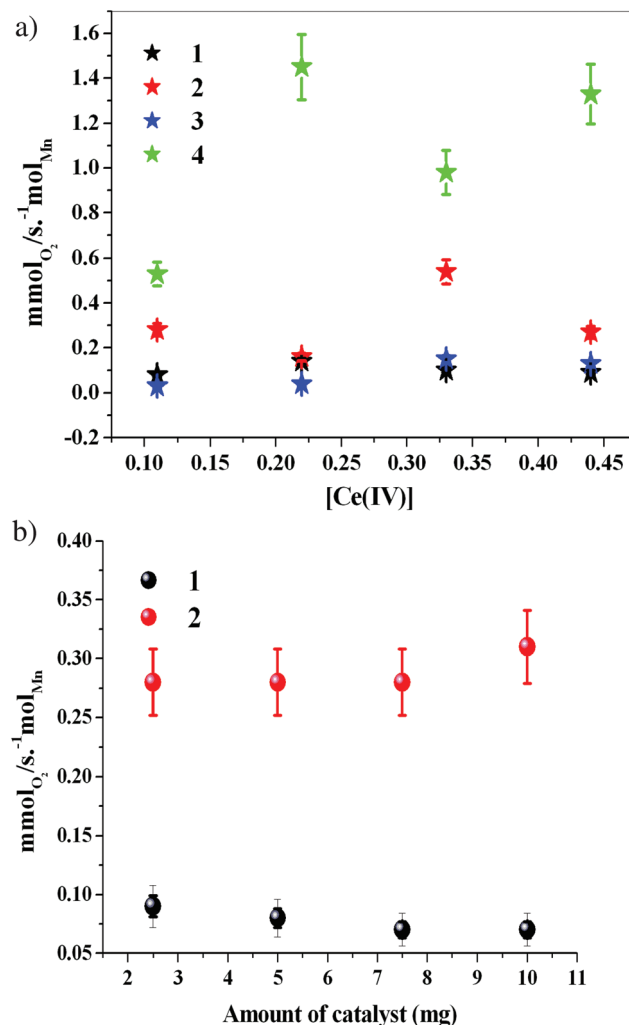


Fig. 3 Oxygen evolution of an aqueous solution of Ce(IV) (40 mL, 0.11–0.44 M) at 25.0 °C in the presence of 1–4 (a). The rates of oxygen evolution in the presence of different amounts of 1 and 2 ($[\text{Ce(IV)}]$: 0.11 M) (b).

to provide a sufficient adhesion between C_{60} and Mn oxides. We expected that 3 shows efficient water-oxidizing activity.

In the IR spectra of 1–4, a broad band at $\sim 3200\text{--}3500\text{ cm}^{-1}$ related to the antisymmetric and symmetric O–H stretching bands and at $\sim 1630\text{ cm}^{-1}$ related to H–O–H bending band were observed (Fig. S1†). The absorption bands characteristic to a MnO_6 core in the region of $\sim 600\text{ cm}^{-1}$ assigned to the stretching vibrations of Mn–O bonds in Mn oxide were 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,† respectively.

Surprisingly, for 1 or 3, TEM and HRTEM images (Fig. 1, Fig. S2, ESI†) showed that in addition to layered Mn oxides, other Mn oxides such as Mn_2O_3 and MnOOH are also present.

In 1, a rod-like morphology (diameter: 20–40 nm) related to Mn_2O_3 and MnOOH was observed. Thus, most probably in 1 and 3, Mn_2O_3 or MnOOH were formed instead of layered Mn oxides. However, in 2 and 4, layered structures are observed in both TEM and HRTEM images. The SEM images (Fig. 1 and Fig. S3, ESI†) for 1 show a rod-like morphology related to Mn_2O_3 and MnOOH (diameter 20–40 nm). In 2, small nano-structure Mn oxides ($\sim 20\text{ nm}$) that cover the surface of C_{60} were observed. In 3, mixing Mn–Ca oxides (50–60 nm) and C_{60} were observed. In 4, SEM produced no clear images from Mn oxide phase most probably because of very small particles prepared under mild conditions. In XRD of 1 and 3, the patterns related to C_{60} and crystalline phase of Mn oxides, such as Mn_2O_3 or MnOOH , were observed (Fig. 2). In 1 and 3, the patterns for C_{60} were not as sharp as the related patterns for 2 and 4 probably because of the oxidation of C_{60} . However, only very low amounts of Mn_2O_3 or MnOOH were detected in 2 and 4.

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

Compound	Oxidant	TOF mmol O ₂ mol ⁻¹ 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 ₂ O ₄ ·H ₂ O	Ce(IV)	0.54	32
Amorphous Mn oxides	Ru(bpy) ₃ ³⁺	0.06	33
	Ce(IV)	0.52	
CaMn ₂ O ₄ ·4H ₂ O	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 ₂ O ₃	Ce(IV)	0.15	36
Octahedral molecular sieves	Ru(bpy) ₃ ³⁺	0.11	33
	Ce(IV)	0.05	
MnO ₂ (colloid)	Ce(IV)	0.09	37
α-MnO ₂ nanowires	Ru(bpy) ₃ ³⁺	0.059	38
CaMn ₃ O ₆	Ce(IV)	0.046	39
CaMn ₄ O ₈	Ce(IV)	0.035	40
α-MnO ₂ nanotubes	Ru(bpy) ₃ ³⁺	0.035	38
Mn ₂ O ₃	Ce(IV)	0.027	32
β-MnO ₂ nanowires	Ru(bpy) ₃ ³⁺	0.02	38
Ca ₂ Mn ₃ O 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

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

Under this condition, no oxygen evolution was observed by C₆₀ (Fig. S4†). The TOFs for different amounts of each catalyst were the same, which means that the rate of oxygen evolution increases linearly with an increasing amount of catalyst. The increase in the concentration of Ce(IV) has complicated effects on 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). This TOF is among the best for an Mn-based catalyst toward water oxidation (Table 1). TOF decreases at higher concentrations of Ce(IV) (>0.2 M). We relate this decrease to the decomposition of the catalyst. Similar to previously reported results, nanolayered Mn oxides are efficient catalysts toward water oxidation. As discussed before, the mixing of nanolayered Mn oxide and C₆₀ to synthesize **1** and **3** changes the structures of C₆₀ and Mn oxides. In this case, Mn₂O₃ and MnOOH are produced, in which both are not efficient catalysts for water oxidation. Between **2** and **4**, **4** is the better catalyst probably because the higher temperature used in the preparation of **2** converts small amounts of layered Mn oxide to other phases.

Comparing with other Mn oxides (Table 1), **4** is an efficient catalyst toward water oxidation. Under this condition, C₆₀ may improve the other properties of Mn oxides. For example, MnO_x

materials suffer from low conductivity. C₆₀ can improve electron transfer in the composites.

Conclusions

We conclude that the synthesis of nano-sized Mn oxide/C₆₀ composites as efficient water-oxidizing catalysts by very simple methods is possible. Although C₆₀ oxidation occurs in some cases, C₆₀ can be a support for Mn oxides. The simple van der Waals interactions between C₆₀ and Mn oxides are sufficient to provide strong adhesion. Nanolayered Mn oxides show good water-oxidizing activity when combined with C₆₀. The reaction of MnO₄[−] with C₆₀ is a promising procedure to synthesize water-oxidizing composites but this reaction should be performed at ambient temperature to inhibit C₆₀ oxidation. In this case, low amount of Mn oxide on C₆₀ is promising toward water oxidation. Similar to other nanocarbons, it shows that a dispersion of Mn oxide on a nanocarbon component may be a useful method in artificial photosynthetic systems. In other words, the fragile structure, low surface area and sublimation temperature of C₆₀ limits²⁵ its use as a support for heterogeneous catalysis but new strategies may allow the application C₆₀ as a support for heterogeneous catalysts. The results clearly show that in cases when nanolayered Mn oxide remains intact, efficient water oxidation by nanolayered Mn/C₆₀ composites is observed.

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