Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Dalton Transactions

An international journal of inorganic chemistry
www.rsc.org/dalton

ROYAL SOCIETY OF CHEMISTRY

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Dalton Transactions

ARTICLE TYPE

Nanostructured manganese oxide/carbon nanotubes, graphene and graphene oxide as water-oxidizing composites in artificial photosynthesis†

Mohammad Mahdi Najafpour,[*a,b] **Fahime Rahimi,**[a] **Maryam Fathollahzadeh,**[a] **Behzad Haghighi,**[a,b]
5 **Małgorzata Hołyńska,**[c] **Tatsuya Tomo**[d,e] **and Suleyman I. Allakhverdiev**[f,g]

Herein, we report on nano-sized Mn oxide/carbon nanotube, graphene and graphene oxide as water-oxidizing compounds in artificial photosynthesis. The composites are synthesized by different and simple
10 procedures and characterized by some methods. The water-oxidizing activities of these composites are also considered in the presence of cerium(IV) ammonium nitrate. Some composited are efficient Mn-based catalysts with TOF (mmolO$_2$/molMn.s) ~ 2.6.

The finding of an efficient, cheap and environmentally friendly
15 water-oxidizing compound is highly desirable for artificial photosynthetic systems because water oxidation is a bottleneck for water splitting into H$_2$ and O$_2$.[1] H$_2$ production by water splitting is currently much discussed as a promising route for the conversion of sustainable, but intermittent energies.[2]
20 Among different compounds, Mn compounds are very interesting because they are not only cheap and environmentally friendly but also efficiently used by Nature for water oxidation.[3] The water-oxidizing centre (WOC) of Photosystem II (PSII) in plants, algae and cyanobacteria is a
25 Mn$_4$CaO$_5$ cluster catalyzing the light-induced water oxidation (Fig. 1).[4a,b] The WOC may be considered as a nano-sized Mn oxide in a protein matrix.[4c]
T. S. Glikman and I. S. Shcheglova (1968) were the first scientists that indicated Mn oxides can catalyze water
30 oxidation in the presence of cerium(IV) ammonium nitrate (Ce(IV)) as an oxidant.[7a] M. Morita in 1977 showed that electrochemical water oxidation is possible with the aid of Mn dioxide.[7b] A. Harriman in 1988 showed that cobalt, iridium, and ruthenium oxides are efficient catalysts for water
35 oxidation.[8] Among Mn oxides, Mn(III) oxide is an efficient catalyst.[7b,8] A. Harriman's group also reported on water-oxidizing activity of colloidal Mn oxide prepared by gamma radiolysis of aqueous solutions of Mn(ClO$_4$)$_2$ saturated with N$_2$O.[8] Since these pioneering studies, many groups have
40 evaluated different Mn oxides as water-oxidizing catalysts.[6,9]
Nanostructured Mn oxide clusters supported on mesoporous silica were reported by F. Jiao and H. Frei as efficient catalysts for water oxidation in aqueous solution under mild conditions.[10] Layered Mn oxides were reported as efficient
45 catalysts for water oxidation. A layered Mn oxide activated by

gold nanoparticles also showed promising activity towards water oxidation.[11] In 2012, a highly active MnO$_x$/glassy carbon catalyst for water oxidation and oxygen reduction by atomic layer deposition was reported.[12] In 2013, G. C. Dismukes'
50 group prepared very pure β-MnO$_2$, R-MnO$_2$, α-MnO$_2$, δ-MnO$_2$, λ-MnO$_2$, LiMn$_2$O$_4$, Mn$_2$O$_3$, and Mn$_3$O$_4$ compounds.[13] They reported that Mn$_2$O$_3$ and Mn$_3$O$_4$ are among most active Mn oxides for water oxidation.[13] They hypothesized that the Mn(III)-O bonds in edge sharing octahedra at the surface are
55 more reactive catalytically due to Jahn-Teller effect/weakening of these bonds. Recently, our group found that many Mn oxides in the presence of Ce(IV) or in electrochemical water oxidation, convert to a layered Mn oxide after a few hours.[14,15] A self-healing for Mn oxides under high potentials also
60 reported.[16] In recent years, Mn oxides were proposed as the *true catalysts* in many Mn-based water oxidation reactions in the presence of chemical[17] and electrochemical oxidants.[18] Interestingly, a few groups reported that treatment of Mn oxide with organic compounds does increase the efficiency of Mn
65 oxides toward water oxidation.[19]
Carbon nanotubes (CNT), graphene (G) and graphene oxide (GO) have been combined with a variety of inorganic compounds, including oxides, nitrides, carbides, chalcogenides, and ceramics to form a more useful material.
70 Applications of these nano compounds include environmental chemistry, catalysis, energy conversion, and electrochemistry.[20] Combination of these compounds with nanocarriers improves their response time, efficiency, and sensitivity. P. Strasser and M. Behrens reported on incipient
75 wetness impregnation and a novel deposition symproportionation precipitation for the preparation of

MnO$_x$/CNT electrocatalysts for efficient water splitting.[21] The MnO$_x$/CNT sample obtained by conventional impregnation was identified as a promising catalytic anode material for water electrolysis at neutral pH showing a high activity and stability.[21] Here, we prepared different nanostructured Mn oxides/CNT, G or GO by different reactions, and considered the water-oxidizing activities of these composites in the presence of Ce(IV).

Experimental
Material and methods

All reagents and solvents were purchased from the commercial sources and were used without a further purification. We used multi-wall nanotubes (outer diameter: 10-20 nm, length: ~ 30 µm, purity > 0.95). TEM and SEM were carried out with a Philips CM120 and LEO 1430VP microscopes, respectively. Mn atomic absorption spectroscopy (AAS) was performed on an Atomic Absorption Spectrometer Varian Spectr AA 110. Prior to the analysis, the composites were added to 1 mL of concentrated nitric acid and H$_2$O$_2$, 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. Cyclic voltammetry was performed using an Autolab potentiostat-galvanostat model PGSTAT30 (Utrecht, The Netherlands). In this case, a conventional three electrode set-up was used in which a Pt electrode or Pt electrode modified with the catalyst, a Ag|AgCl|KCl$_{sat}$ electrode and a platinum rod served as the working, reference and auxiliary electrodes, respectively.

Synthesis

Mn-Ca oxide: The compound was synthesized by a previously reported method.[15]

CNT-1: Mn(NO$_3$)$_2$·4H$_2$O (100 mg) was dissolved in 10 mL water. To this solution, 100 mg CNT was added and the mixture was sonicated for half an hour under argon. The mixture was left for two days. Then, a KMnO$_4$ solution (50 mg KMnO$_4$, 0.5 g KOH) in 5 mL water was added to the solid. The solid was left at room temperature in dark for one day and then it was dried at 100 ^{o}C.

CNT-2: Mn(NO$_3$)$_2$·4H$_2$O (100 mg) was dissolved in 10 mL water. To this solution CNT (20 mg) was added and the mixture was sonicated for 10 minutes. The obtained solid was separated, washed by water, and dried at 90 ^{o}C.

CNT-3: Mn(OAc)$_2$·4H$_2$O (100 mg) was dissolved in 25 mL water contains 365 mg KOH. Then, 30 mg CNT was added to the mixture and sonicated for 15 minutes. The mixture was left for one day. In the next step, the solid was separated, washed with water and dried at 90 ^{o}C.

CNT-4: Mn-Ca oxide and CNT were added to 15 mL water and the mixture was sonicated. Then, the mixture was dried at 80 ^{o}C for one day. The obtained solid was separated, washed and dried. The amounts of Mn-Ca oxide and CNT were: (30 mg:70 mg), (50 mg:50 mg) and (70 mg:30 mg).

CNT-5: 100 mg CNT was added to 10 ml water and sonicated. Subsequently, 30 mg KMnO$_4$ in 30 ml water was added and stirred for 4 days. The obtained solid was separated, washed carefully to remove KMnO$_4$ and dried at 60 ^{o}C.

G-1: Mn(NO$_3$)$_2$·4H$_2$O (100 mg) was dissolved in 10 mL water. To this solution, G (100 mg) was added and the mixture was sonicated for 15 minutes. Then, the mixture was heated for one day at 100 ^{o}C. The obtained solid was separated, washed and dried.

G-2: Mn-Ca oxide and G were added to 15 mL water and the mixture was sonicated. Then, the mixture was dried at 80 ^{o}C for one day. The amounts of Mn-Ca oxide and G were: (30 mg:70 mg), (50 mg:50 mg) and (70 mg:30 mg). The obtained solid was separated, washed and dried.

G-3: The composite was synthesized by a procedure similar to CNT-5 using G instead of CNT.

GO-1: Mn-Ca oxide and GO were added to 15 mL water and the mixture was sonicated. Then, the mixture was dried at 80 ^{o}C for one day. The used amounts of Mn-Ca oxide and GO were: (30 mg:70 mg).

GO-2: Mn(NO$_3$)$_2$·4H$_2$O (1.25 g) was dissolved to 10 mL water. To this solution GO (100 mg) was added and the mixture was stirred for 15 minutes. The solution was heated for 48 hours at 100 ^{o}C. Then, the solid was washed with water and dried at 100 ^{o}C.

GO-3: The composite was synthesized by a procedure similar to CNT-5 using GO instead of CNT.

Water Oxidation

Water oxidation experiments in the presence of Ce(IV) were performed using an HQ40d portable dissolved oxygen-meter connected to an oxygen monitor with digital readout at 25 ^{o}C. 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 a 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. Electrochemical water oxidation was performed with the use of a setup shown in Scheme S1.

Fabrication of a modified electrode

The Pt electrode was mechanically polished with 1, 0.3 and 0.05 μm alumina and washed ultrasonically with ethanol and distilled water. Then, 30 μL of 1 mg/ml composite suspension was dripped on the Pt electrode surface and dried at room temperature. Eventually, 5μL of 0.5 wt % Nafion solution was deposited onto the centre of the modified electrode. A three-electrode system was applied for investigation of electrochemical properties of modified electrodes by cyclic voltammetry in 25 ml of 0.1 M (pH 6.3) lithium perchlorate solution.

Results and discussion

The Mn oxide/CNT, G or GO were synthesized by different methods and under different conditions. In one of the procedures, we used Mn-Ca oxide that is known to be amorphous and as an efficient water-oxidizing catalyst (CNT-4, G-2 and GO-1) (Fig. 3).[9]

CNT-1 was prepared by the reaction of Mn^{2+} and MnO_4^- ions in the presence of CNT. SEM images show that the composite (Fig. 2c) is a very good mixing of the Mn oxide and CNT. The images show lumps of Mn oxide and CNT. The turnover frequency (TOF, mmol O_2/mol Mn per second) for the composite (0.56) is very similar as for the Mn oxide. The number for high concentrations of Ce(IV), 0.44 and 0.66 M, is nearly constant.

CNT-2 is based on decomposition of $Mn(NO_3)_2$ that produces Mn(III) oxides.[22a] The TOF for the composite is 0.4.

CNT-3 is based on formation of Mn_3O_4.[22b] As Mn_3O_4 oxide is not efficient water-oxidizing composite, the Mn_3O_4-CNT is also not efficient catalyst toward water oxidation as well (TOF ~ 0.24).

For CNT-4, we used a simple method that shows advantages of both Mn oxides, such as efficient water-oxidizing activity, and of nanocarbons. In other words, in the procedure, we can synthesize an efficient catalyst and then mix it with CNT, G and GO. The TEM image of Mn oxide/CNT shows that the mixing in the composite (CNT-4) is good (Fig. 3). The water-oxidizing activity per mol of Mn per second does not depend on the ratio of Mn oxide:CNT and the TOF is ~ 0.5 ([Ce(IV)] = 0.22 M). The TOF for Mn-Ca oxide under these conditions is 0.5-0.6. For CNT-5, G-3 and GO-3, in the reaction of G, GO or CNT suspension and $KMnO_4$ are stirred at room temperature, a slow redox reaction between the nanostructured carbon and $KMnO_4$ could take place and can be described as:[23a]

$$4MnO_4^- \text{ (aq)} + 3C(s) + H_2O(l) \rightarrow 4MnO_2(s) + CO_3^{2-}(aq) + 2HCO_3^-(aq) \quad \text{(Eq. 1)}$$
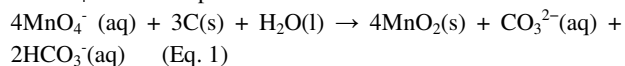
The slow redox reaction usually leads to the precipitation of MnO_2 on the surface of the nanostructured carbon. Such strategy forms a more efficient catalyst toward water oxidation. The TOF for CNT-5 is very promising and more efficient than CNT-4. The TOF in the presence of Ce(IV) (0.11 M) is high among Mn oxides. A low amount of Mn oxide on the surface of CNT is promising in water oxidation. HRTEM of CNT-5 shows only a few short-range orders among layers (Fig. 3 and

Fig. S1, ESI†). The effects of different parameters are very similar as in case of the pure Mn oxides (Table 1).[6,9] Water oxidation by the composite is influenced by their temperatures of calcination. The best catalysts for water oxidation were the ones prepared at ~200-300 °C.

In higher temperatures, a high amount of crystallized Mn oxide with a low surface area is formed indicating that all these factors could be substantial in reducing of the water-oxidizing activity of the Mn oxides.[24] On the other hand, temperature has effect on oxygen evolution reaction.[24] The rate of oxygen evolution increases with increase in temperature in the range of 10-35 °C with activation energies ~ 45-60 kJ/mol similar as for Mn oxides.[9] However, in high temperatures (35-40 °C) decomposition of the catalyst to MnO_4^- ions occurs. Thus, the increase in water oxidation rate is not clear at 35-40 °C (Table 1).

To study of the effect of the amount of the catalyst, reactions were done with different amounts of oxides keeping all other factors constant (Table 1). The increase in the rate of oxygen evolution with the increase of oxide concentration is linear, and thus, TOF is very similar. In contrast to pure Mn oxides,[24] for CNT-5, the rate of oxygen evolution does not linearly increase with increase in the concentration of Ce(IV). We related[24] the effect to decomposition of particles of the catalyst to MnO_4^- at high concentrations of Ce(IV). In other words, in high temperatures both high rate of oxygen evolution and decomposition of catalyst can occur, and thus, we observed similar TOFs even at high concentrations of Ce(IV).

TEM images of CNT and layered Mn oxide are shown in Fig. 3. These images for CNT clearly show nanotubes with diameters ranging from about 10-20 nm and lengths up to 100 μm. The images for the layered Mn oxides clearly show a layered structure. SEM image show Composites that obtain by mixing nanocarbon structures and Mn oxide show particles with 40-70 nm diameters.

Table 1 The effects of different parameters for the composites in water oxidation.

Composite	Temperature (°C) of Calcination	Temperature (°C) of O_2 evolution	[Ce(IV)]	Catalyst (mg)	TOF
CNT, G or GO	100	25	0.11-0.66	5	trace
Mn oxide without CNT/G/GO	60	25	0.11-0.66	5	0.4-0.6
CNT-1	100	25	0.11	5	0.56
CNT-2	90	25	0.11	5	0.4
CNT-3	90	25	0.11	5	0.24
CNT-4	80	25	0.22	7	0.5
CNT-5	60	25	0.11	5	2.22
CNT-5	150	25	0.11	5	~3.0
CNT-5	250	25	0.11	5	~3.0
CNT-5	350	25	0.11	5	0.20
CNT-5	60	10	0.11	5	0.44
CNT-5	60	25	0.11	5	2.22
CNT-5	60	35	0.11	5	2.66
CNT-5	60	25	0.11	5	2.22
CNT-5	60	25	0.11	10	1.97
CNT-5	60	25	0.11	15	1.97
CNT-5	60	25	0.11	5	2.22
CNT-5	60	25	0.22	5	2.35
CNT-5	60	25	0.33	5	2.40

CNT-5	60	25	0.44	5	2.45
G-1	100	25	0.22	2	0.4
G-2	80	25	0.22	7	0.47
G-3	60	25	0.11	5	<0.1
GO-1	80	25	0.22	7	0.4
GO-2	100	25	0.22	4	<0.1
GO-3	60	25	0.11	5	1.73

To answer to the question that why do some composite show low activity toward water oxidation, we focus on the phase of Mn oxide in each composite. The intensity of patterns at $2\theta =$ 25.6 and 43.48° correspond to the MWCNT walls. In CNT-1 and CNT-4, only peaks related to layered Mn oxide are observed. CNT-2 shows no special Mn oxide but cystaline phase of Mn_3O_4 are clear in CNT-3. CNT-5 contains layered Mn oxides with poor patterns in XRD.

In G-1, α-Mn_2O_3 and ε-MnO_2 are observed. In G-2, layered Mn oxide are detectable. In contrast to GO-3 or CNT-5, G-3 shows high amounts of Mn_3O_4. In GO-3, layered Mn oxide is detectable but in GO-1 no special phase is observed. Thus, the reactions of Mn oxides with these carbon nanosreuctures are different and different phases from Mn oxides are formed. Composites with layered or amorphous structures show efficient catalytic activity toward water oxidation.
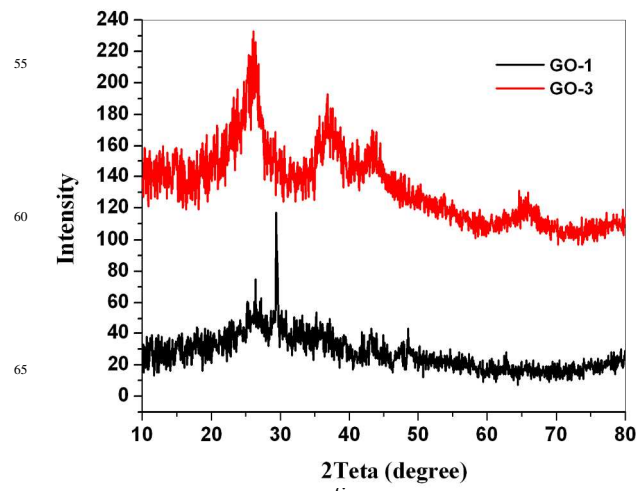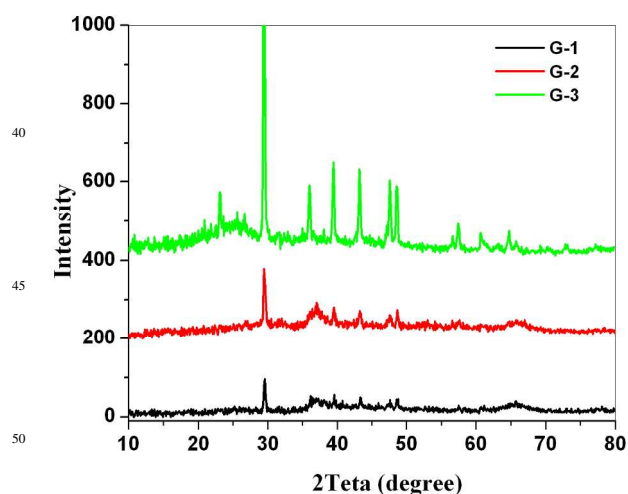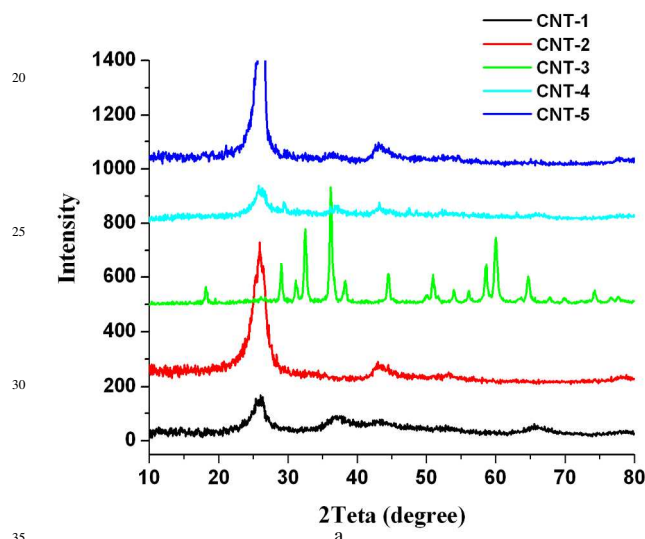

Fig. 1   XRD patterns for CNT (a), G (b) and GO (c) -Mn oxide composites. For details see ESI.

Similar to other Mn oxides, FTIR spectra of Mn oxide/carbon nanostructured show a broad band at ~ 3200-3500 cm⁻¹ related to antisymmetric and symmetric O-H stretchings. At ~ 1630 cm⁻¹ a peak related to H-O-H bending is observed. The intensities of these peaks reduced in higher temperature. The absorption bands characteristic for a MnO_6 core in the region ~ 400-600 cm⁻¹ assigned to stretching vibrations of Mn-O bonds in Mn oxide was also observed in the FTIR spectra of these composites (Fig. S2, ESI†).[11] CNT shows weak peaks at 600, 1041, 1384, 1631 and 3437 cm⁻¹. The peaks for G are at 827, 1424, 1630 and 3434 cm⁻¹. GO indicates peaks at 880, 1062, 1432, 1630 and 3435 cm⁻¹. Peaks in 1630 and 3430 cm⁻¹ are related to water molecules.
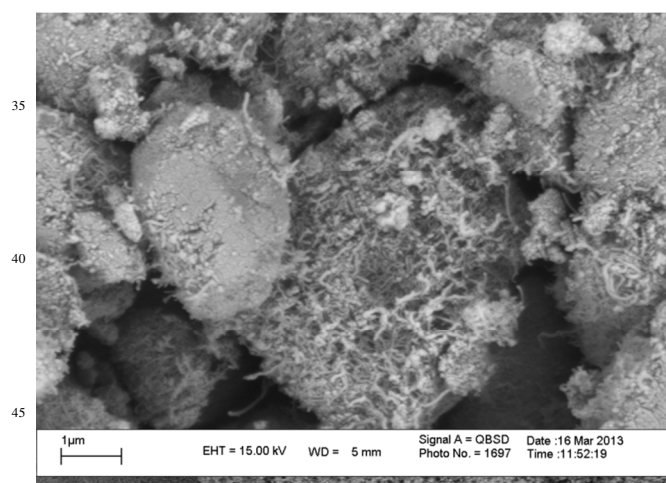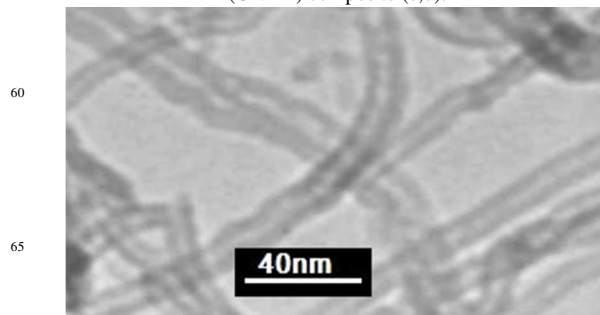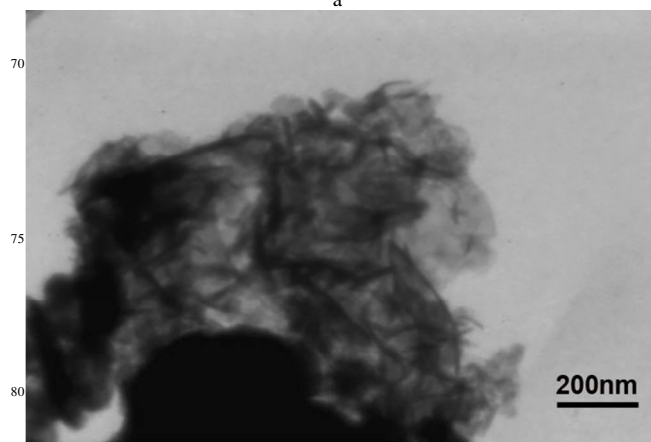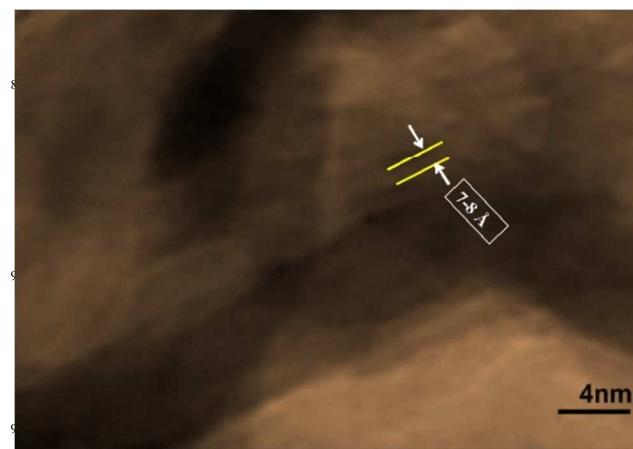
b

c

d
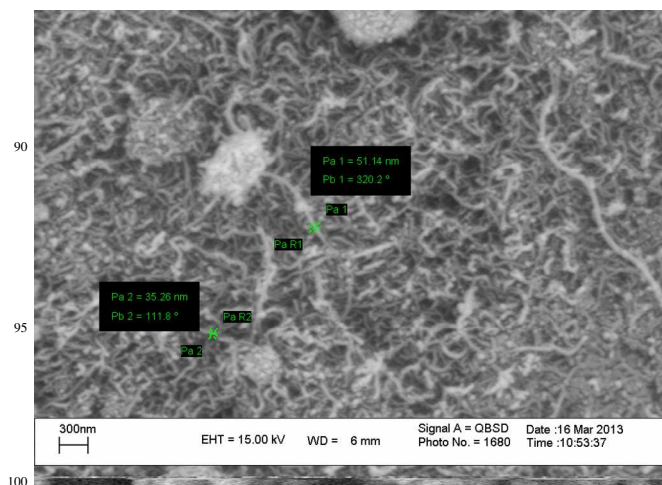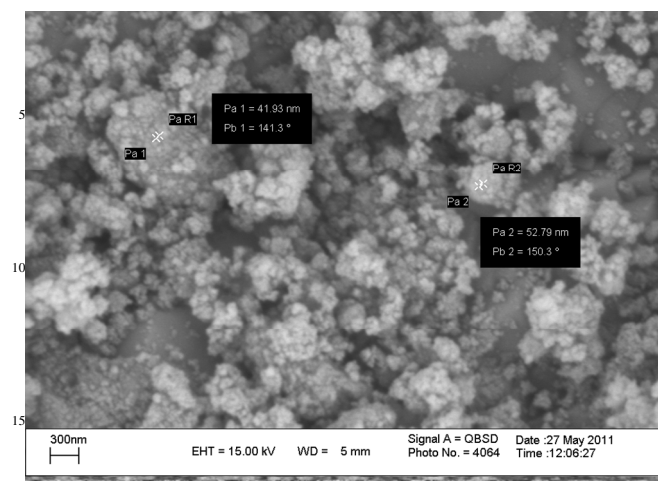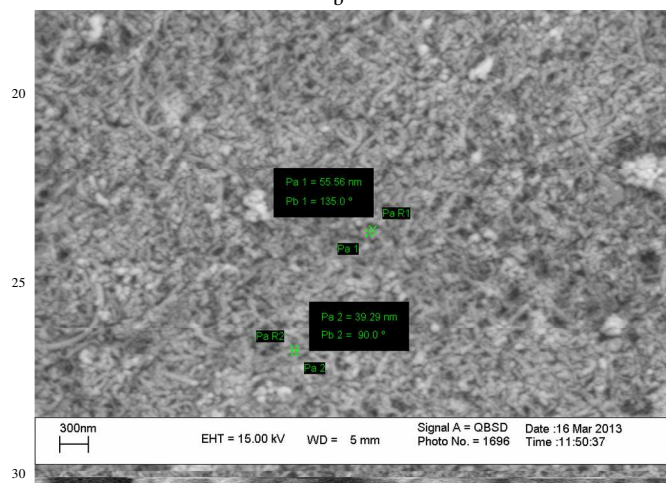
Fig. 2 SEM images of CNT (a), Mn-Ca oxides (b) and Mn oxide-CNT (CNT-1) composite (c,d).

a

b

c

Dalton Transactions Accepted Manuscript
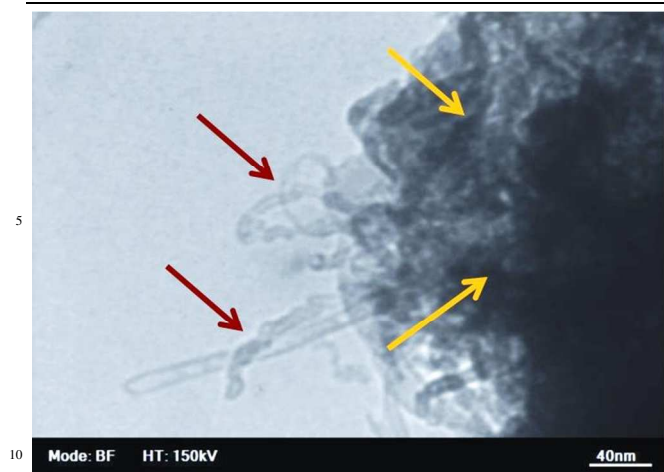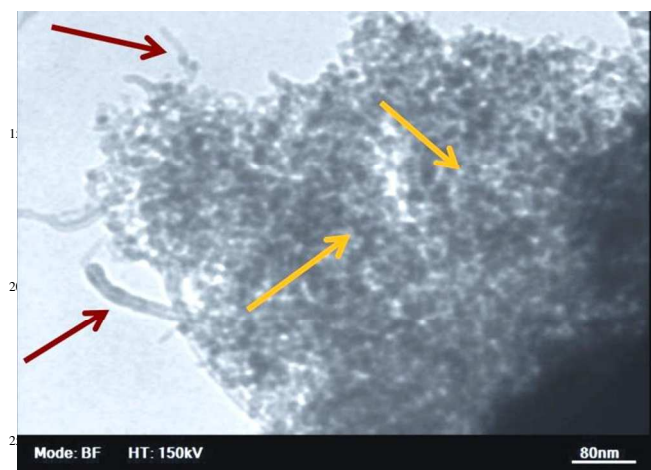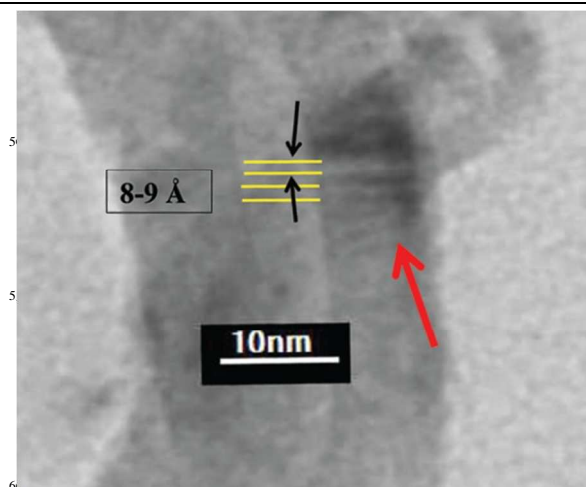
d

e

f

g

Fig. 3 TEM images of CNT (a), Mn-Ca oxides (b,c) and Mn oxide-CNT (CNT-4:Mn-Ca oxide:CNT = 3:7) (d,e). In d and e, orange and red arrows show nanolayered Mn oxide and carbon nanotube, respectively. TEM (f) and HRTEM (g) image for CNT-5. In g, red arrow is related to Mn oxide. The observed patterns are similar to ones in layered Mn oxides.[9]

We also synthesized a very similar composite to CNT-1 but with a very low amount of Mn oxide (> 0.3%). SEM-EDX images of the material are shown in Fig. 4. The composite shows a very low water-oxidizing activity (< 0.1) most probably because of decomposition of small Mn oxides to MnO_4^-.[24]
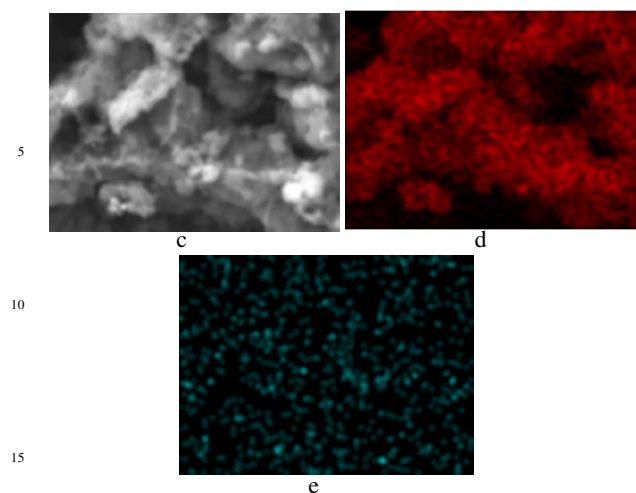

a

c

d

e
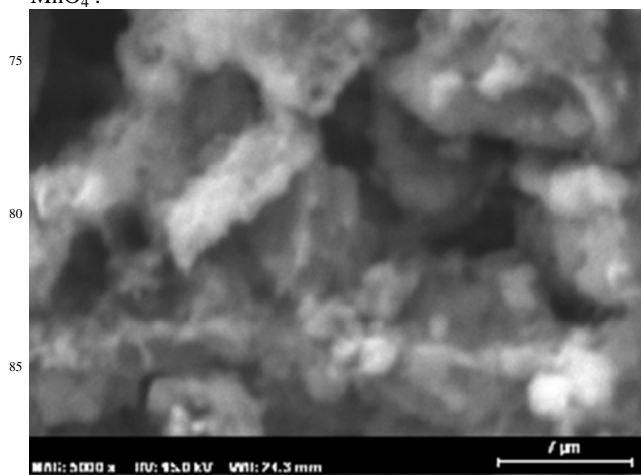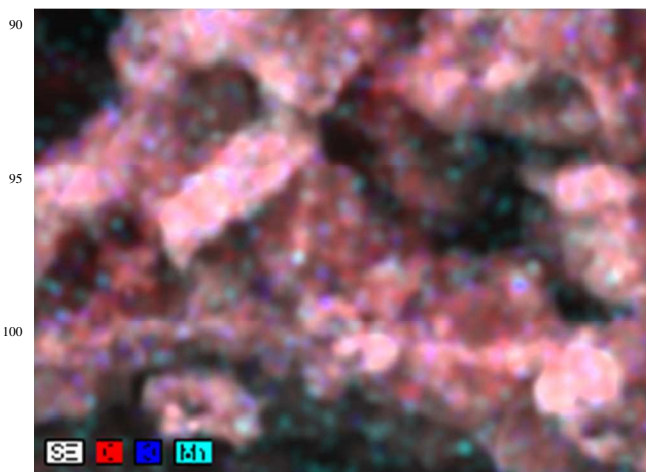
Fig. 4 SEM (a, c), SEM-EDX for low amounts (Mn: > 0.3%) of Mn
oxide on hydroxylated CNT, prepared by a method similar to the
20 synthesis of CNT-1 (C: red; O: blue and Mn: green) (b), the dispersion
of C (d) and Mn (e) in the image of c.

G-1 was synthesized in decomposition of $Mn(NO_3)_2$ that
produces Mn(III) oxides. The TOF in water oxidation process
25 catalysed by the composite is 0.4. SEM images show very
small nanoparticles on the layered structure of G (Fig. 5). TEM
images also show such particles among the layers of G (Fig. 6).
G-2 was synthesized with a simple method by mixing of Mn
oxide and G. The TOF for G-1 and G-2 are very similar.
30 GO-1 was synthesized by a mixing method as shown for CNT-
4 and G-2. TOF in this case is 0.4; very similar as in the case
of CNT-4 and G-2. The decomposition method for GO-2
produced a non-efficient catalyst displaying a low TOF (<0.1).
GO-3 and G-3 were synthesized by a method similar for CNT-
35 5, but G-3 is not a good water-oxidizing composite. GO-3 is a
good catalyst toward water oxidation with the TOF ~ 1.73.
Heating, similar to other Mn oxides, improves water oxidation,
but also decomposes the nanocarbon structure.[9] The TOF for
these Mn oxide/nanocarbons are among the best Mn based
40 catalyst toward water oxidation (Table 2). In addition to the
efficiency, these nanocarbons can improve other properties
such as electron transfer in these composites.

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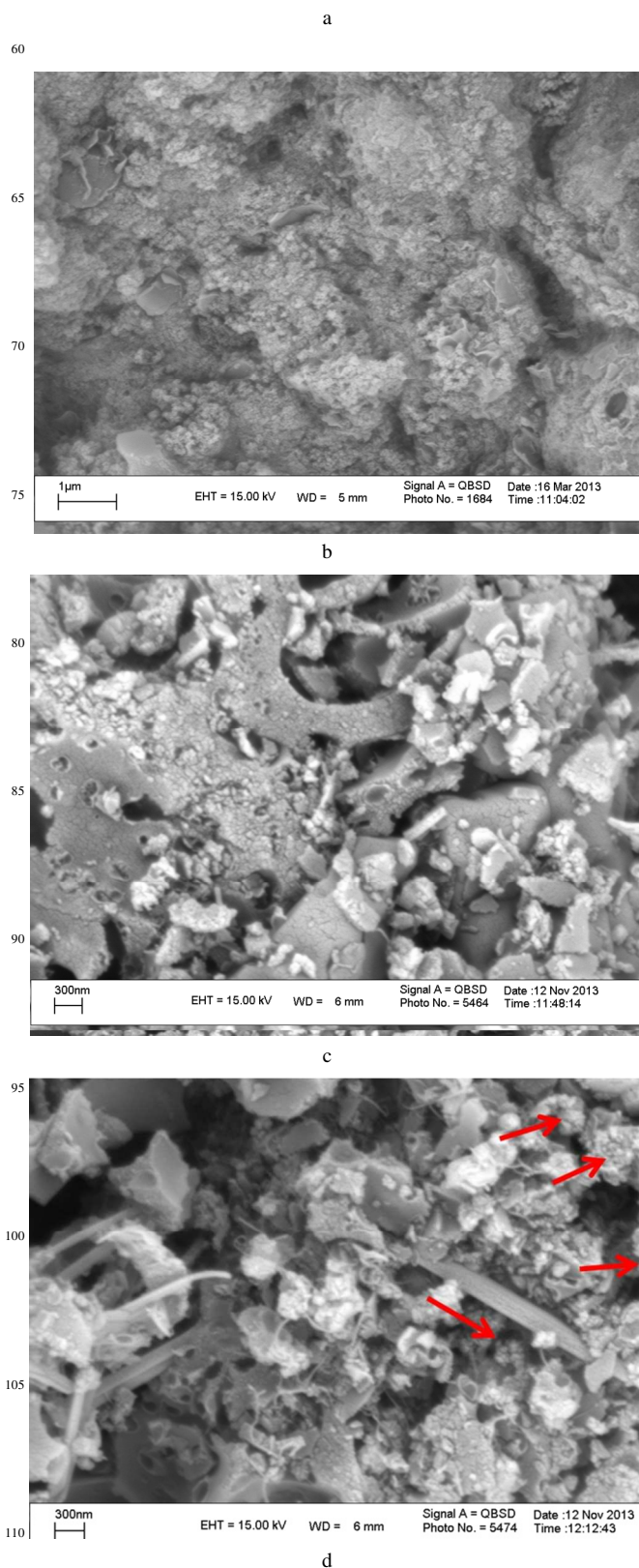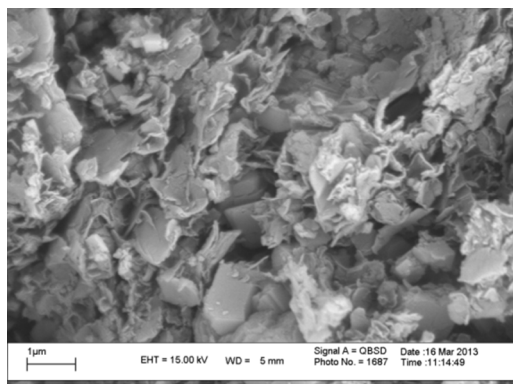45 for water oxidation in the presence of non-oxygen transfer oxidant.
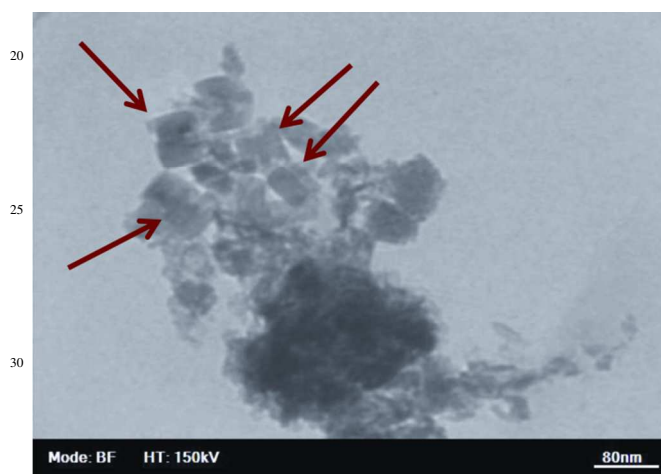

a

b

c

d

Fig. 5 SEM images of G (a), G-2 (b), GO (c) and GO-1 (d).

a

b

Fig. 6 TEM images of G-1 (a,b). The arrows indicate the particles of Mn oxide.

The results reported here show that the synthesis of Mn oxide-nanocarbon composites with efficient water-oxidizing activity and using a simple method is possible. As discussed by Dominik Eder from the *University of Cambridge*,[24] in the cases of inorganics/CNT, simple van der Waals interactions are sufficient to provide a strong enough adhesion.[25] In contrast to the effect of nano-sized gold particles on water-oxidizing activity of Mn oxides,[11] the nanocarbons show no special effect as we did not observe any changes for CNT-1 or CNT-4. However, a dispersion Mn oxide on CNT as we observed for CNT-5 does improve water-oxidizing activity of Mn oxides.

Thermogravimetric measurements for the Mn oxide-carbon nanostructures are shown in Fig. 7.[21] Temperatures below the drying temperature of 110 ^{o}C are related to the emission of weakly-bonded re-absorbed water molecules.[21] In higher temperatures, removing of the hydroxyl groups is observed. The emission of water molecules, located between layers is observed at 200-300 ^{o}C. At higher temperature (500 ^{o}C), other Mn oxides-phases are formed. G, GO and CNT are stable until 400, 360 and 560 ^{o}C.[21] CNT-4 is more stable than CNT-1.
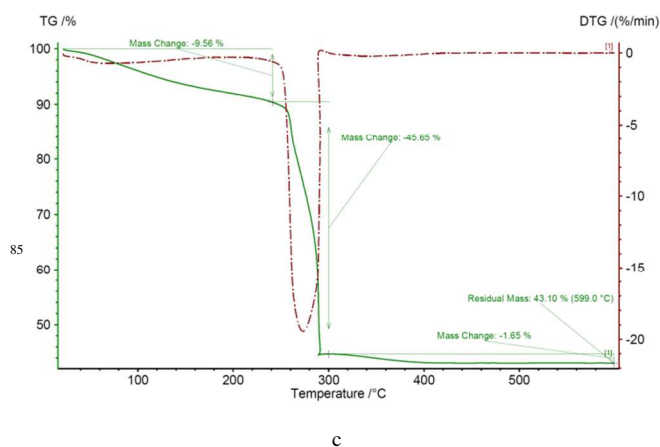
Most probably Mn oxides strongly attached to CNT assist to shift decomposition of CNT at lower temperatures.[21] Attaching Mn oxide to G or GO shows a similar effect (Fig. S3, ESI†).
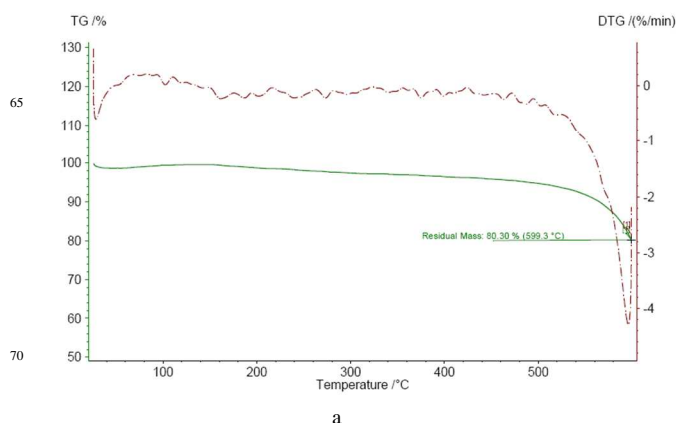
a
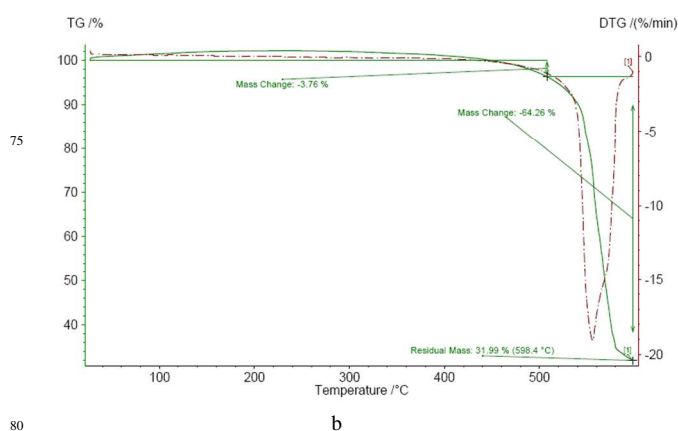
b

c

Fig. 7 DTG and TG diagrams for nanostructured carbon - Mn oxide composites. CNT (a), CNT-4 (Mn oxide:CNT 30:70) (b) and CNT-1 (c).

Cyclic voltammograms (CVs) of the Mn oxide/G, GO and CNT materials on Pt electrode show that the nanocarbon structures have a very low effect on the electrochemical behavior of Mn oxides (Fig. 8). However, a peak related to Mn(III)/Mn(IV) oxidation is observed in layered Mn oxides that is not clear in these composites, most probably, because of

low concentration of Mn oxides in these composites (Fig. 8).
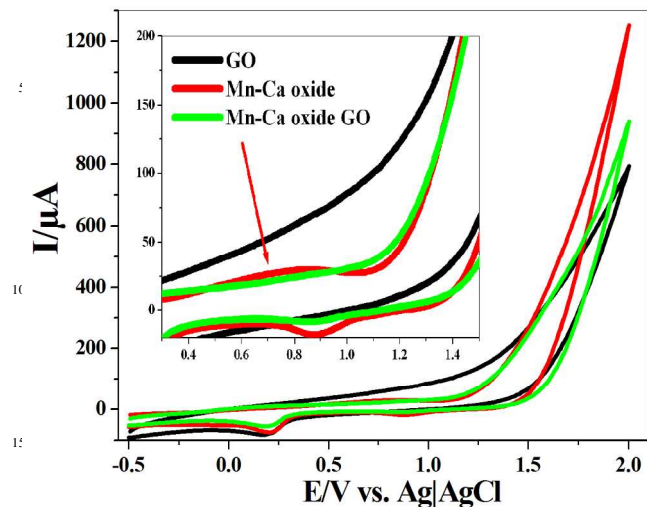
a
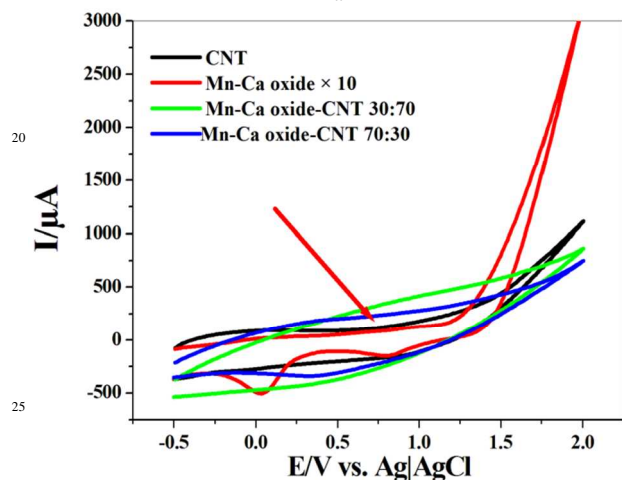
b

c

d

Fig. 8 Cyclovoltamograms of a GO-1 (a), CNT-1 (b) and G-1 (c). Results obtained by linear sweep voltammetry (LSV) of Mn oxide/GO are shown in (d). For all composites, the second cycles are shown. Red 55 arrows show the Mn(III) to Mn(IV) oxidation process.

Conclusions

Regarding the presented results we concluded that:

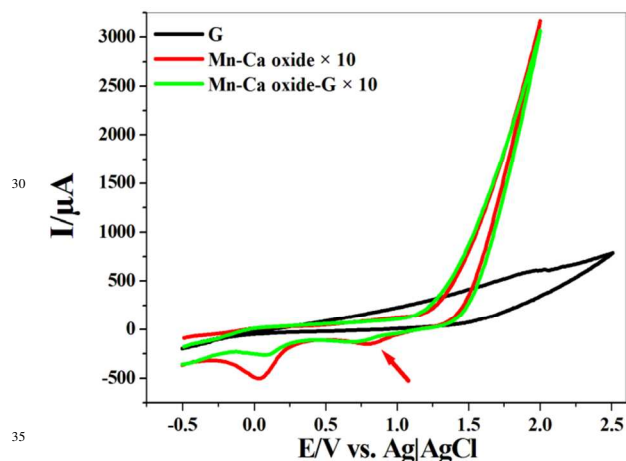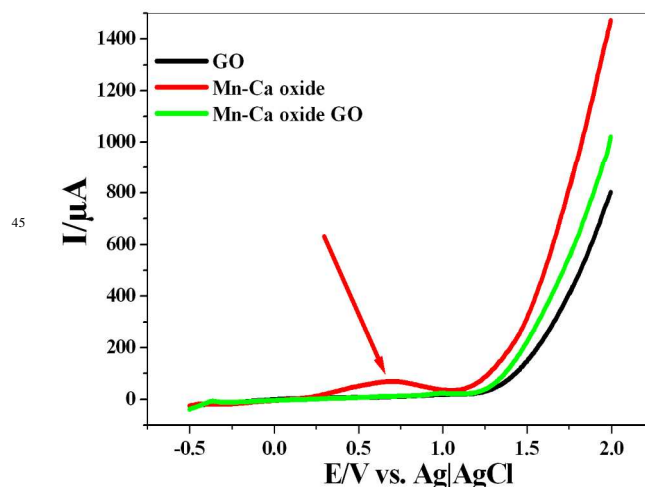- Synthesis of nano-sized Mn oxide/CNT, G and GO as efficient water-oxidizing composites by very 60 simple methods, such as mixing, is possible. The presented methods are promising because in the first step efficient catalysts are produced and in the next step yields composites with a nanocarbon component. The simple van der Waals interactions 65 are sufficient to provide strong enough adhesion between Mn oxides and CNT.
- The water-oxidizing activities of Mn oxide/CNT, G or GO depends on Mn oxides, and nanocarbon structures do not decrease the activity of Mn oxides 70 toward water oxidation. On the other hand, the nanocarbons may improve other properties of the Mn oxides. For example, MnO_x materials suffer from low conductivity. These nanocarbons can improve electron transfer in the composites.
- Similar to other Mn oxide-based water-oxidation 75 reactions by amorphous or layered Mn oxides show the highest water- oxidizing activity when combined with the carbon.
- The reaction of MnO_4^- with nanocarbons is a promising procedure to synthesize of water-oxidizing 80 composites. In this case, a composite with the TOF ($mmolO_2/molMn.s$) ~ 2.6 can be obtained. Composites with other phases such as Mn_3O_4 shows little water-oxidizing activity.
- Low amount of Mn oxide on GO and CNT is 85 promising toward water oxidation with a TOF more than 2. Dispersion of Mn oxide on the nanocarbon component may be a useful method in artificial photosynthetic systems.

Notes and references

aDepartment of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran

bCenter of Climate Change and Global Warming, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran

cFachbereich Chemie and Wissenschaftliches Zentrum für Materialwissenschaften (WZMW), Philipps-Universität Marburg, Hans-Meerwein-Straße, D-35032 Marburg, Germany

dDepartment of Biology, Faculty of Science, Tokyo University of Science, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162-8601, Japan

ePRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan

fControlled Photobiosynthesis Laboratory, Institute of Plant Physiology, Russian Academy of Sciences, Botanicheskaya Street 35, Moscow 127276, Russia

gInstitute of Basic Biological Problems, Russian Academy of Sciences, Pushchino, Moscow Region 142290, Russia

*Corresponding author; Phone: (+98) 241 415 3201; E-mail: mmnajafpour@iasbs.ac.ir

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

1 O. M. Bockris, Energy-the solar hydrogen alternative, Wiley & Sons, New York (1977).

2 M. W. Kanan and D. G. Nocera, *Science*, 2008, **321**, 1072.

3 K. Sauer, J. Yano and V. K. Yachandra, *Coord. Chem. Rev.*, 2008, **252**, 318; A. Zouni, H. T. Witt, J. Kern, P. Fromme, N. Krauss, W. Saenger and P. Orth, *Nature*, 2001, **409**, 739; K. N. Ferreira, T. M. Iverson, K. Maghlaoui, J. Barber and S. Iwata, *Science*, 2004, **303**, 1831; B. Loll, J. Kern, W. Saenger, A. Zouni and J. Biesiadka, *Nature*, 2005, **438**, 1040; J. Yano, J. Kern, K. Sauer, M. J. Latimer, Y. Pushkar, J. Biesiadka, B. Loll, W. Saenger, J. Messinger and A. Zouni, *Science*, 2006, **314**, 821.

4 a) Y. Umena, K. Kawakami, J. R. Shen and N. Kamiya, *Nature*, 2011, **473**, 55. b) Y. Umena, N. Kamiya and J. R. Shen, *J. Photochem. Photobiol. B*, 2011, **104**, 9. c) M. M. Najafpour, A. Nemati Moghaddam,Y. N. Yang, E. Aro, R. Carpentier, J. J. Eaton-Rye, C. Lee and S. I. Allakhverdiev, *Photosynth. Res.*, 2012, **114**, 1.

5 M. M. Najafpour and S. I. Allakhverdiev, *Int. J. Hydrogen Energy*, 2012, **37**, 8753; A. Singh, L. Spiccia, *Coord. Chem. Rev.,* 2013, **257**, 2607; W. Ruttinger and G. C. Dismukes, *Chem. Rev.*, 1997, **97**, 1; M. Yagi and M. Kaneko, *Chem. Rev.*, 2001, **101**, 21; H. J. M. Hou, *J. Integr. Plant. Biol.*, 2010, **52**, 704; H. J. M. Hou, *Materials*, 2011, **4**, 1693; K. Beckmann, H. Uchtenhagen, G. Berggren, M. F. Anderlund, A. Thapper, J. Messinger, S. Styring and P. Kurz, *Energy Environ. Sci.*, 2008, **1**, 668; W. He, K.Zhao and H. J. M. Hou, NanoPhotoBioSciences, 2013, **1**, 63; L. Chou, R. Liu, W. He, N. Geh, Y. Lin, E. Y. F. Hou, D. Wang, and H. J. M. Hou, *Int. J. Hydrogen Energy*, 2012, **37**, 8889.

6 M. M. Najafpour, *Chem. Commun.*, 2011, **47**, 11724; M. M. Najafpour, *J. Photochem. Photobiol. B*, 2011, **104**, 111; M. M. Najafpour, D. Jafarian Sedigh, C. K. King'ondu and S. L. Suib, *RSC Adv.*, 2012, **2**, 11253; F. Zhou, A. Izgorodin, R. K. Hocking, V. Armel, L. Spiccia and D. R. MacFarlane, *ChemSusChem*, 2013, **6**, 643; A. Schöler, I. Zaharieva, S. Zimmermann, M. Wiechen, A. Manke, P. Kurz, C. Plieth and H. Dau, *Eur. J. Inorg. Chem.*, 2014, **4**, 680; I. Zaharieva, P. Chernev, M. Risch, K. Klingan, M. Kohlhoff, A. Fischer and H. Dau, *Energ. Environ. Sci.*, 2012, **5**, 7081; A. Indra, P. W. Menezes, I. Zaharieva, E. Baktash, J. Pfrommer, M. Schwarze, H. Dau, M. Driess, *Angew. Chem. Int. Ed.*, 2013, **52**, 13206.

7 a) T. S. Glikman and I. S. Shcheglova, Kinetika i Kataliz. 1968, **9**, 461. b) M. Morita, C. Iwakura and H. Tamura, *Electrochim. Acta*, 1977, **22**, 325.

8 A. Harriman, I. J. Pickering, J. M. Thomas and P. A. Christensen, *J. Chem. Soc., Faraday Trans.* 1, 1988, **84**, 2795.

9 M. M. Najafpour, F. Rahimi, E. Aro, C. Lee, and S. I. Allakhverdiev, *J. R. Soc. Interface*, 2012, **9**, 2383.

10 F. Jiao and H. Frei, *Chem. Commun.*, 2010, **46**, 2920.

11 M. M. Najafpour, F. Rahimi, D. J. Sedigh, R. Carpentier, J. J. Eaton-Rye, J.-R. Shen and S. I. Allakhverdiev, *Photosyn. Res.*, 2013, **117**, 423.

12 K. L. Pickrahn, S. W. Park, Y. Gorlin, H. B. R. Lee, T. F. Jaramillo and S. F. Bent, *Adv. Energ. Mat.*, 2012, **2**, 1269.

13 D. M. Robinson, Y. B. Go, M. Mui, G. Gardner, Z. Zhang, D. Mastrogiovanni, E. Garfunkel, J. Li, M. Greenblatt and G. C. Dismukes, *J. Am. Chem. Soc.*, 2013, **135**, 3494.

14 M. M. Najafpour and D. Jafarian Sedigh, *Dalton Trans.*, 2013, **42**, 12173.

15 M. M. Najafpour, B. Haghighi, D. Jafarian Sedigh and M. Zarei Ghobadi, *Dalton Trans.*, 2013, **42**, 16683.

16 M. M. Najafpour, M. Kompany-Zareh, A. Zahraei, D. J. Sedigh, H. Jaccard, M. Khoshkam, R. D. Britt and W. H. Casey, *Dalton Trans.*, 2013, **42**, 14603.

17 M. M. Najafpour and A. Nemati Moghaddam, *Dalton Trans.,* 2012, **41**, 10292; M. M. Najafpour, A. Nemati Moghaddam, H. Dau and I. Zaharieva, *Submitted manuscript*.

18 R. K. Hocking, R. Brimblecombe, L.-Y. Chang, A. Singh, M. H. Cheah, C. Glover, W. H. Casey and L. Spiccia, *Nature Chem.*, 2011, **3**, 461.

19 T. Takashima, K. Hashimoto and R. Nakamura, *J. Am. Chem. Soc.*, 2012, **134**, 18153; M. M. Najafpour, B. Haghighi, M. Zarei and D. J. Sedigh, *Chem. Commun.*, 2013, **49**, 8824; A. Singh, R. K. Hocking, S. L. Y. Chang, B. M. George, M. Fehr, L. Klaus, A. Schnegg and L. Spiccia, *Chem. Mater.*, 2013, **25**, 1098; Y. Y. Kim, D. Williams, F. C. Meldrum and D. Walsh, *Small*, 2013, **9**, 61; M. M. Najafpour, M. Amouzadeh Tabrizi, B. Haghighi and Govindjee, *Dalton Trans.*, 2012, **41**, 3906.

20 P. M. Ajayan and O. Z. Zhou, in Carbon Nanotubes, Springer, 2001, pp. 391-425.

21 K. Mette, A. Bergmann, J. P. Tessonnier, M. Havecker, L. Yao, T. Ressler, R. Schlögl, P. Strasser and M. Behrens, *ChemCatChem*, 2012, **4**, 851.

22 a) M. M. Najafpour, F. Rahimi, M. Amini, S. Nayeri and M. Bagherzadeh, *Dalton Trans.,* 2012, **41**, 11026; b) I. K. Gopalakrishnan, N. Bagkar, R. Ganguly, S. K. Kulshreshtha, *J. Crys. Growth.*, 2005, **280**, 436.

23 H. Xia, Y. Wang, J. Lin and L. Lu, *Nanoscale Res. Lett.*, 2012, **7**, 33.

24 M. M. Najafpour, M. Abbasi Isaloo, M. Abasia and M. Hołyńska, *New J. Chem.*, 2014, **38**, 852.

25 D. Eder, *Chem. Rev.*, 2010, **110** (3), 1348.

26 M. M. Najafpour and M. Abbasi Isaloo, *RSC Advances*, 2014, **4**, 6375.

27 C. E. Frey, M. Wiechen and P. Kurz, *Dalton Trans.*, 2014, **43**, 4370.

28 M. M. Najafpour, B. Pashaei, *Dalton Trans.*, **41**, 2012, 10156.

29 M. M. Najafpour, S. Nayeri and B. Pashaei, *Dalton Trans.*, **40**, 2011, 9374.

30 M. M. Najafpour, B. Pashaei and S. Nayeri, *Dalton Trans.*, 2012, **41**, 7134.

31 M. M. Najafpour, D. Jafarian Sedigh, B. Pashaeia and S. Nayeri, *New J. Chem.*, 2013, **37**, 2448.

32 M. M. Najafpour, T. Ehrenberg, M. Wiechen and P. Kurz, *Angew. Chem., Int. Ed.*, 2010, **49**, 2233.

33 A. Iyer, J. Del-Pilar, C. Kithongo King'ondu, E. Kissel, H. Fabian Garces, H. Huang, A. M. El-Sawy, P. K. Dutta and S. L. Suib, *J. Phys. Chem.* C, 2012, **116**, 6474.

34 Y. Okuno, O. Yonemitsu and Y. Chiba, *Chem. Lett.*, 1983, 815.

5 35 M. M. Najafpour and A. N. Moghaddam, *New J. Chem.*, 2012, **36**, 2514.

36 M. M. Najafpour, *Dalton Trans.*, 2011, **40**, 3805.

37 V. B. R. Boppana and F. Jiao, *Chem. Commun.*, 2011, **47**, 8973.

38 M. M. Najafpour, *Dalton Trans.*, 2011, **40**, 3793.

10 39 M. M. Najafpour, S. Nayeri and B. Pashaei, *Dalton Trans.*, 2012, **41**, 4799.

40 D. M. Robinson, Y. B. Go, M. Greenblatt and G. C. Dismukes, *J. Am. Chem. Soc.,* 2010, **132**, 11467.

41 C. W. Cady, R. H. Crabtree and G. W. Brudvig, *Coord. Chem.*
15 *Rev.*, 2008, **252**, 444.

42 R. Ramaraj, A. Kira and M. Kaneko, *Angew. Chem.,* 1986, **98**, 824.

43 G. C. Dismukes, R. Brimblecombe, G. A. N. Felton, R. S. Pryadun, J. E. Sheats, L. Spiccia, G. F. Swiegers, *Acc.*
20 *Chem. Res.*, 2009, **42**, 1935.

44 G. Ananyev and G. C. Dismukes, *Photosynth. Res.*, 2005, **84**, 355.

25