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

Dalton Transactions

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Carbon for engineering of a water-oxidizing catalyst†

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5 Herein we report that the reaction of $KMnO_4$ with cobalt nanoparticles coated with multiple graphene layers forms a promising catalyst toward water oxidation. The compound was characterized by scanning electron microscopy, energy-dispersive spectroscopy, high resolution transmission electron microscopy, X-ray diffraction, electronic spectroscopy, Fourier transform infrared spectroscopy, and atomic absorption spectroscopy. In addition to the Mn oxide-based characteristics of catalyst, it is a conductive,
10 self-healing, recycling, high dispersible, magnetically separable, environmentally friendly, and nano-sized catalyst for water oxidation. The turnover frequency for the catalyst toward water oxidation is 0.1 and 0.05 (mmol O_2/mol Mn.s) in the presence of cerium(IV) ammonium nitrate and photo-produced $Ru(bpy)_3^{3+}$.

Introduction

15 An important goal in artificial photosynthesis is using solar energy to split water.[1] In water splitting, the finding of an efficient, cheap and environmentally friendly water-oxidizing compound is highly desirable because water oxidation is a
20 bottleneck for water splitting into H_2 and O_2.[2,3] Many compounds were reported as water-oxidizing catalysts. Cobalt compounds including nanostructured Co_3O_4 and Co_3O_4-based hybrids, Co_2O_3 nanoparticles (NPs), cobalt phosphate material, Co/Fe oxide composites, Co complexes, Co(III) hangman β-octafluoro
25 corroles, $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, $NiCo_2O_4$ aerogels, and other cobalt oxides have been extensively studied as efficient catalysts toward water oxidation.[3] Among other compounds, Mn oxides[4] are very promising and interesting because they are not only cheap and environmentally friendly, but also efficiently used by
30 Nature[5] for the same reaction. In other words, a Mn oxido cluster is efficiently used by Nature to water oxidation.[5]

Oxygen evolution by MnO_2 in the presence of cerium(IV) ammonium nitrate (Ce(IV)) as an oxidant was reported by Glikman and Shcheglova in 1968.[6] Then, Shilov's group
35 extended the experiments to other Mn oxide and oxidants.[7] Electrochemical water oxidation by Mn oxides and the important role of Mn(III) was reported by Morita's group in 1977.[8] Harriman's group in 1988 showed that Mn(III) oxide is an efficient catalyst in the presence of Ce(IV).[9] Harriman's group
40 also reported on water-oxidizing activity of nano-sized Mn oxide.[9]

Layered Mn oxides with different cations between layers were reported as efficient catalysts for water oxidation among Mn-based catalysts.[10-14] However, the role of ions between layers is a
45 puzzle in the field.[10-15] Jiao and Frei reported nanostructured Mn oxide clusters supported on mesoporous silica as efficient catalysts for water oxidation in an aqueous solution under mild conditions and in the presence of $Ru(bpy)_3^{2+}$.[16] They proposed that the roles of support are proton transfer and stabilizer of Mn
50 oxide.[16] Gorlin and Jaramillo's groups reported a very active nanostructured Mn(III) oxide for both oxygen reduction and water oxidation, with similar activity to Pt, Ru and Ir.[17]

In 2011, Boppana and Jiao showed that the crystal structure and morphology of the MnO_2 catalyst have no significant effect on its
55 photocatalytic activity, while the activity could be greatly improved by increasing the surface area.[18]

In 2013, 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 were synthesized and water-oxidizing activities of them were studied.[19] Mn_2O_3 and Mn_3O_4 are
60 among the most active Mn oxides for water oxidation.[19] However, it was reported that Mn oxide phases in the presence of Ce(IV) or in electrochemical water oxidation are converted to a layered Mn oxide with no long-range order.[20,21] Such Mn oxides in nanoscale phase may be formed immediately after the reaction
65 by Ce(IV). The finding is important because it shows that the new phase, which is different from origin phase is true catalyst toward water oxidation in the condition.

Suib's group systematically studied the water oxidation and oxygen reduction processes by α, β, δ-MnO_2 and amorphous Mn
70 oxide in alkaline media.[22] These results showed that the water-oxidation reaction is strongly dependent on the structure of the catalyst, and follows an order of α-MnO_2 > amorphous > β-MnO_2 > δ-MnO_2.[22]

The electro water-oxidation of Mn oxide nanorods modified Pt,
75 Au and glassy carbon (GC) electrodes shows a significant enhancement of the electrocatalytic activity of the Pt, Au and GC electrodes towards the water oxidation upon the electrodeposition of Mn oxide nanoparticles (nano-MnO_x).[23,24]

We reported that Au nanoparticles deposited on layered Mn oxide
80 enhances water-oxidizing activities of these catalysts in the presence of Ce(IV).[25] However, such effects were not observed

for Ag nanoparticles.[25] Jaramillo's group found that adding Au to MnO_x significantly enhances the water-oxidizing activity of this composite related the effect to the redox properties of both MnO_x and Au when the two materials are present in one composite catalyst.[26] Recently, Suib and He's groups showed that doping MnO_x/gold nanoparticles can result in a strong enhancement of water oxidation up to 8.2 times in the photochemical and 6 times in the electrochemical system, compared with the activity of pure α-MnO_2.[27a] Although, the true role of Au or Pt on water-oxidizing activity of Mn oxides is a challengeable issue.[27b-c]

Nanocarbon structures are interesting properties to be used as a support for metal oxides. Mn oxide/carbon nanotubes, graphene, graphene oxide,[28,29,30] C_{60}[31a] and nanodiamond[31b] were shown as promising composites for water oxidation. Herein, we reported a conductive, self-healing, recycling, high dispersible, magnetically separable, environmentally friendly, and nano-sized catalyst for water oxidation in the presence of Ce(IV).

Experimental

Characterization

All reagents and solvents were purchased from the commercial sources and were used without a further purification. TurboBeads™ Amine was purchased from Sigma-Aldrich.

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$_\alpha$ 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

The compound was synthesized by a very simple and green method. The cobalt nanoparticles coated with multiple graphene contains Ph-CH_2-NH_2 groups (TurboBeads™ Amine from Sigma-Aldrich) (100 mg) was added to 20 mL water containing 15 mg $KMnO_4$. The mixture was stirred for one day at room temperature. Then, the solid was separated and washed to remove $KMnO_4$. Finally, the solid was dried at 60 °C. Amount of Mn in the **MnT** in this condition is 4.3 wt% (by AAS).

Water oxidation

The procedure for water oxidation experiments was used as reported previously (Scheme S1, ESI†).

Results and discussion

Different compounds contain Fe, Co, Ni, Fe_3O_4 and $CuFe_2O_4$ could be used to synthesize magnetically separable catalysts.[32] A strategy is covering these magnetic particles by different inert compounds. Some coating materials such as silica,[33,34] transition-metal oxides,[35,36] gold,[37] and carbon[38] have been used. Carbon is more promising because gold is expensive, and covalent bonds on silica and other metal oxides are not kinetically and thermodynamically stable.[32] To design a promising catalyst for artificial photosynthetic systems both stability and efficiency of

catalyst are important. The cobalt nanoparticles coated with multiple graphene contains Ph-CH_2-NH_2 groups (from Sigma-Aldrich, TurboBeads™ Amine, **T**) was reacted by MnO_4^- to obtain catalyst (**MnT**) (eq. **1** and **Fig. 1**):

$$4MnO_4^- + 3C \text{ or Ph-CH}_2\text{-NH}_2 \text{ groups} + H_2O \rightarrow 4MnO_2 + CO_3^{2-} + 2HCO_3^- \text{ (eq. 1)}$$
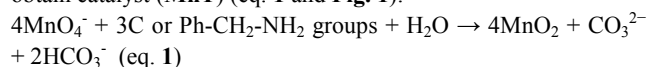
T combines the magnetic properties and the possible functionalization of the surface. The decreasing of the concentration of MnO_4^- is observed by electronic spectroscopy when **T** is added to the solution.
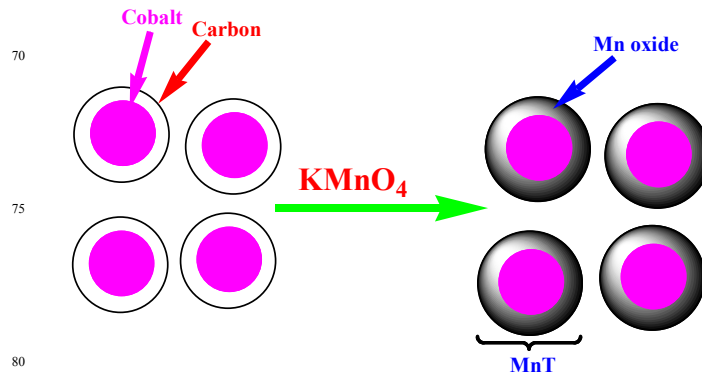

Fig. 1 The reaction of a solution of MnO_4^- and **T** produces a conductive, self-healing, recycling, high dispersible, magnetically separable, environmentally friendly, and nano-sized catalyst for water oxidation.

In this reaction, graphene serves as a sacrificial reductant and reduces MnO_4^- to Mn oxide. In diffuse reflectance infrared Fourier transform spectroscopy spectra of the catalyst (**MnT**), a broad band at ~ 3200-3500 cm^{-1} is related to antisymmetric and symmetric O-H stretchings (**Fig. 2**). The absorption bands characteristic for organic groups (Ph-CH_2-NH_2) are in the region ~ 1280-1400 cm^{-1}. However, peaks related to MnO_6 core were not observed because of low amounts of Mn oxide (Mn% ~ 4%), amorphous and very small particles.[28-31]
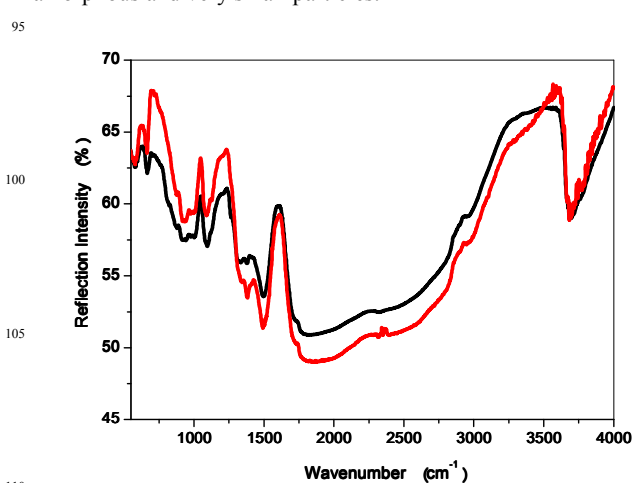

Fig. 2 The diffuse reflectance infrared Fourier transform spectroscopy spectra of **T** (black) and **MnT** (red).

To characterize the morphology of **MnT**, they were studied by scanning electron microscopy (SEM) and High-resolution transmission electron microscopy (HRTEM) (**Fig. 3**, and Fig. S1-S4). HRTEM images show small particles on the graphene layer, and make the carbon layer darker (**Fig. 3 a,b**). SEM images show

MnT consists of nanoparticles in diameter less than 50 nm (**Fig. 3c,d**).
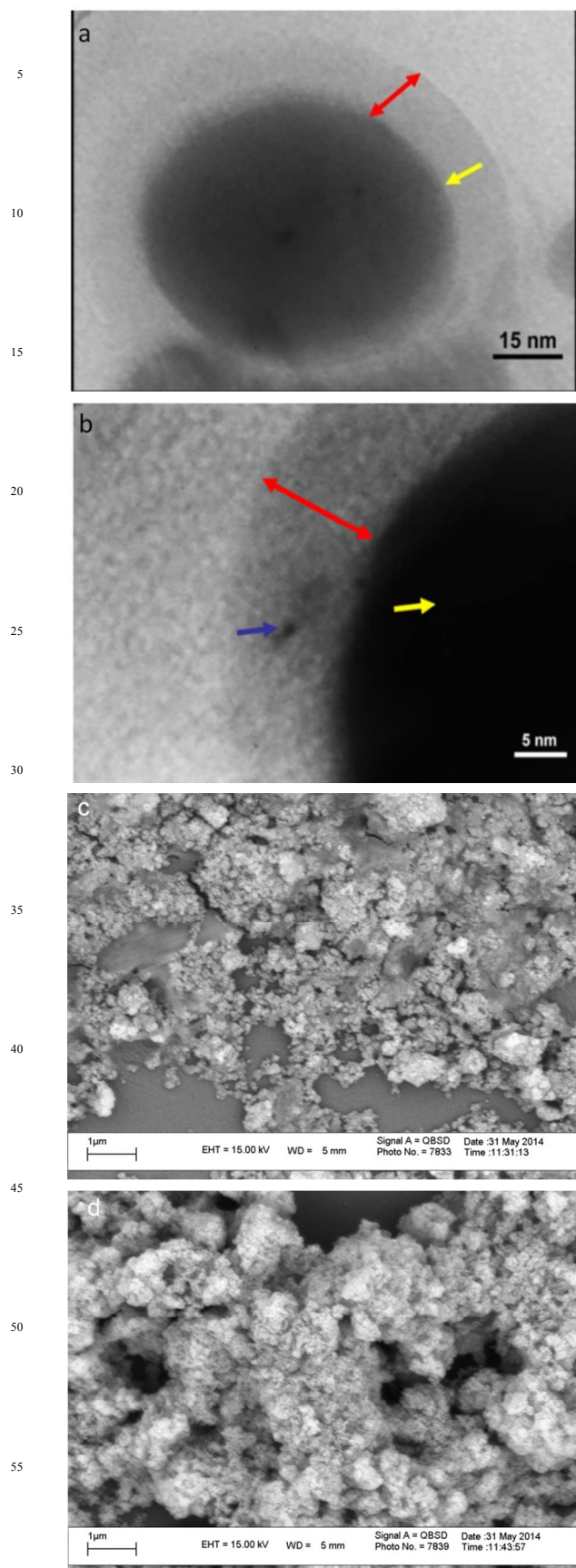
Fig. 3 TEM images for **T** (a), **MnT** (b) and SEM from **T** (c) and **MnT** (d). Red, yellow and blue arrows show graphene, cobalt and Mn oxide.

Dynamic light scattering (DLS) shows the diameter 100-300 nm for the particles (**Fig. 4**). Finding larger particle in DLS compared with particles in SEM or TEM images indicates agglomeration in solution.
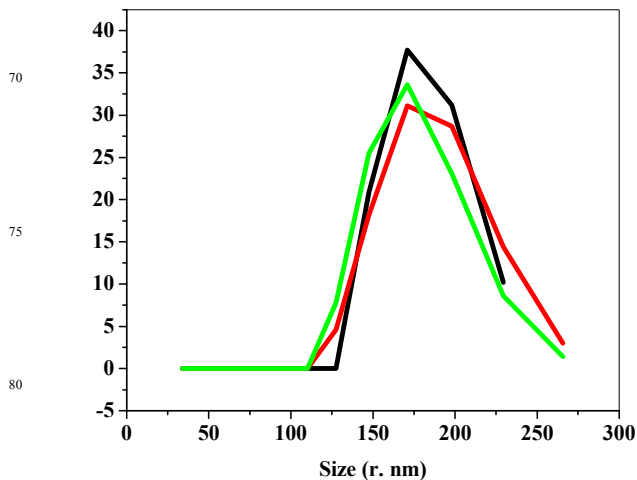

Fig. 4 DLS results for **MnT** by intensity (black) volume (red), and number (green).

X-ray Diffraction (XRD) patterns show no clear peaks for Mn oxides (**Fig. 5**).[28-31] It is not surprising because the synthetic method forms Mn oxides without long-range order. In addition to it, the amounts of Mn oxide is low on the surface of **MnT**.
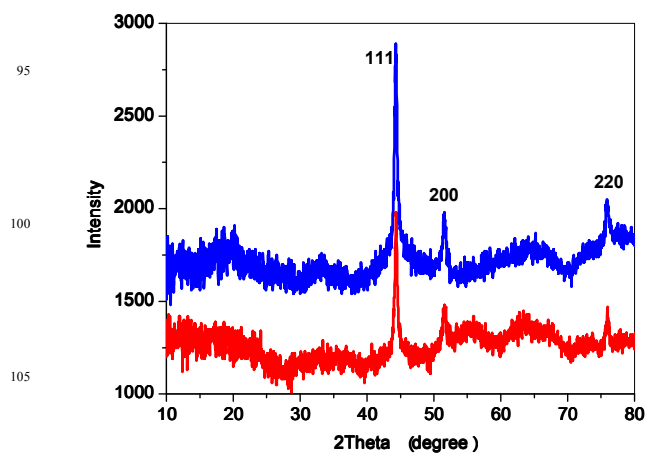

Fig. 5 XRD patterns for **T** (blue) and **MnT** (red). The peaks are related to metallic cobalt.

EDX-mapping shows a good dispersion of Mn oxide on the surface of **MnT** (**Fig. 6**).
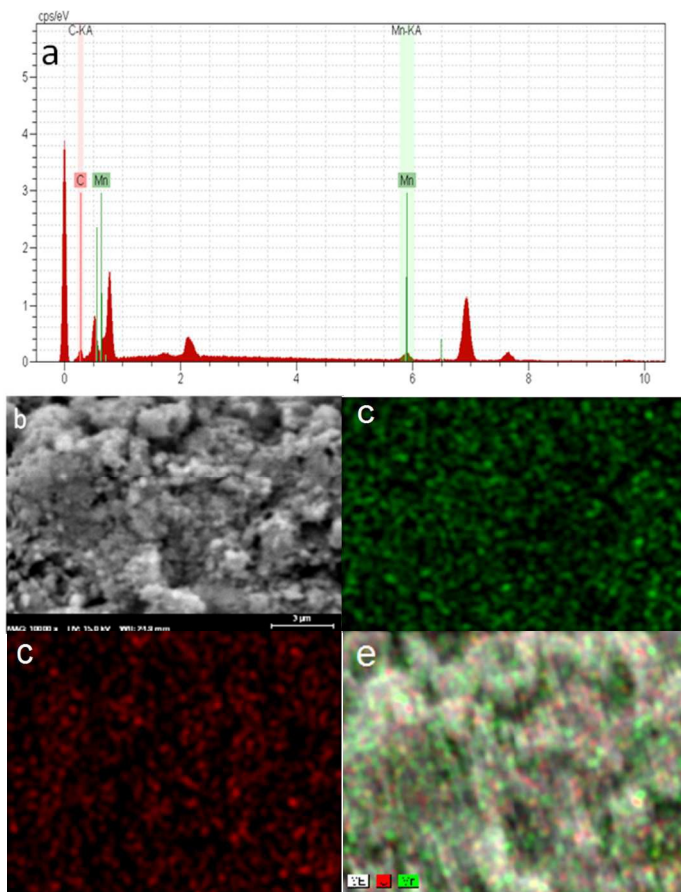
Fig. 6 EDX (a), SEM (b), and EDX-mapping (c-e) for **MnT**. Mn and carbon are shown in green and red, respectively. The scale bar is 3 μm.

Although amounts of Mn oxides on the surface of **T** were low, it could be considered by X-ray photoelectron spectroscopy (XPS). The Mn $2p_{3/2}$ binding energy of the coating was consistent with that of Mn(III,IV) oxide (**Fig. 7**).
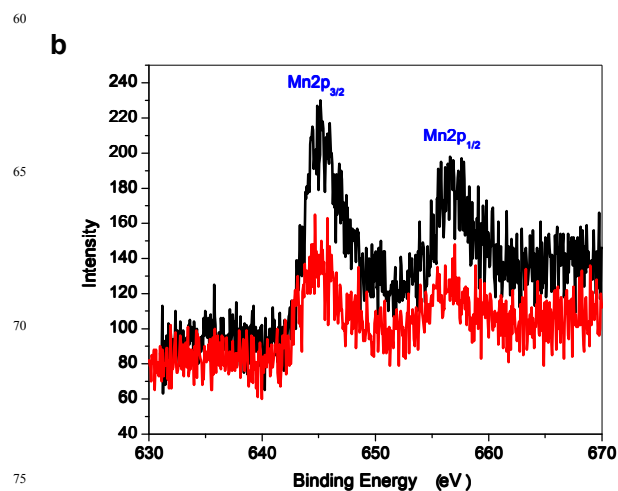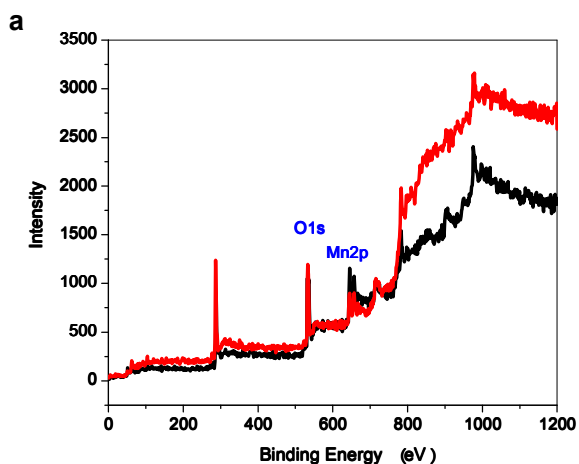

Fig. 7 XPS for nano-sized Mn oxide on **T** before (red) and after reaction by Ce(IV) (72 hours, 0.5 M) (a,b). The related peaks for Mn and O are shown by blue.

Water oxidation

After synthesis and characterization of catalyst, we studied the water-oxidation activity of the compounds. There are three methods to study of water oxidation of a compound. Photochemical,[39] electrochemical,[40] and water oxidation in the presence of chemical oxidant.[41] Ce(IV) and photoproduced Ru(bpy)$_3$$^{3+}$ are non-oxo transfer, soluble in water, strong and one-electron oxidants, which are used extensively in water oxidation.[41] The oxidants oxidize water-oxidizing catalyst, and in the next step, the oxidized catalyst can oxidize water molecules. We selected these oxidants to test water-oxidizing activity of **MnT**. It has been shown that in the oxygen evolution by Mn oxide in the presence of Ce(IV), both oxygen atoms originate from water molecules, and thus, the reaction is a true water oxidation.[41b] **MnT** is only stable at low concentrations of Ce(IV) (< 0.044 M), at higher concentrations the decomposition reaction were observed. In low concentration of Ce(IV) (< 0.044 M), the compound in the presence of Ce(IV) can be magnetically separated and reused at least for three times without any decreasing in activity (**Fig. 8**). Turnover frequency for **MnT** was 0.1 (mmol O_2/mol Mn. s) in 0.022 M Ce(IV), which shows the compound in the low concentration of Ce(IV) is a good catalyst toward water oxidation (**Table 1**). **T** in this condition shows no water-oxidizing activity. Even after 72 hours in 0.022 M Ce(IV), high amount of the compound can be separated by magnet.
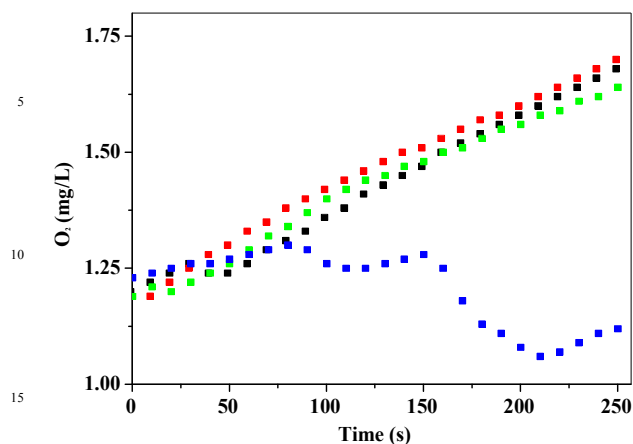
Fig. 8 Oxygen evolution of an aqueous solution of Ce(IV) (40 mL, 0.022 M) at 25.0 °C in the presence of 10 mg **MnT** after magnetically separating and reusing for three times. The first, second and third results are shown in black, red and green, respectively. Blue shows water oxidation for **T** in the same condition.

Water oxidation experiment under the photochemical condition in the presence of $^3[Ru(bpy)_3]^{2+}/S_2O_8^{2-}$ shows oxygen evolution with TOF ~ 0.05 (mmol O_2/mol Mn·s) (**Fig. 9**) (for details see ESI†).
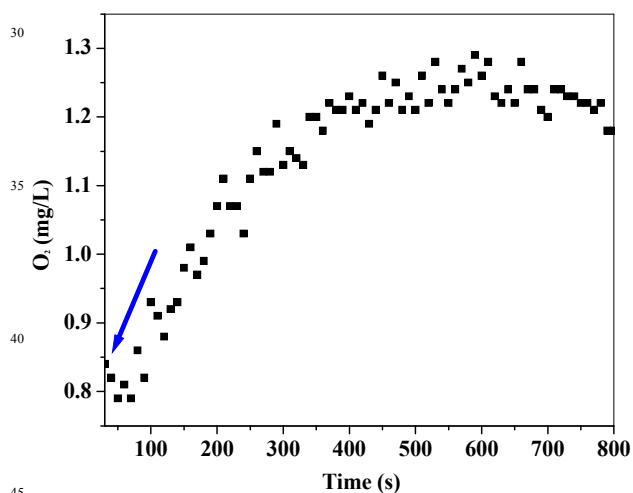
Fig. 9 The water oxidation of **MnT** in the presence of Ru(bpy)₃Cl₃/K₂S₂O₈ and blue LED (for details see ESI†) at 30 °C. The blue arrow shows start point for photochemical reaction in the presence of light.

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 oxidants. Reprinted with permission from ref. 29. Copyright (2014) by RSC publications.

Compound	Oxidant	TOF mmol O_2/mol Mn.s
Nano scale Mn oxide within NaY zeolite	Ce(IV) > 0.22 M	2.62
Layered Mn-Ca oxide	Ce(IV) > 0.22 M	2.2
Layered Mn-Al, Zn, K, Cd and Mg oxide	Ce(IV) > 0.22 M	0.8-2.2
Layered Ni(II) oxide	Ce(IV) > 0.22 M	0.4-0.6
CaMn₂O₄.H₂O	Ce(IV)	0.54
Amorphous Mn Oxides	Ru(bpy)₃³⁺ Ce(IV) > 0.22 M	0.06 0.52
Nanolayered Mn oxide	Ce(IV) > 0.22 M	0.45
CaMn₂O₄.4H₂O	Ce(IV) > 0.22 M	0.32
Mn oxide nanoclusters	Ru(bpy)₃³⁺	0.28
β-MnO(OH)	Ce(IV) > 0.22 M	0.24
Mn oxide-coated montmorillonite (low surface)	Ce(IV) > 0.22 M	0.22
Layered Mn-Cu(II)	Ce(IV) > 0.22 M	0.2-0.35
Mn₃O₄	Ce(IV) > 0.22 M	0.01-0.17
Octahedral Molecular Sieves	Ru(bpy)₃³⁺ Ce(IV) > 0.22 M	0.11 0.05
MnT	Ce(IV) (0.022 M)	0.1
MnO₂ (colloid)	Ce(IV)	0.09
α-MnO₂ nanowires	Ru(bpy)₃³⁺	0.059
CaMn₃O₆	Ce(IV) > 0.22 M	0.046
CaMn₄O₈	Ce(IV) > 0.22 M	0.035
α-MnO₂ nanotubes	Ru(bpy)₃³⁺	0.035
Mn₂O₃	Ce(IV) > 0.22 M	0.027
β-MnO₂ nanowires	Ru(bpy)₃³⁺	0.02
Ca₂Mn₃O₈	Ce(IV) > 0.22 M	0.016
CaMnO₃	Ce(IV) > 0.22 M	0.012
Nano-sized λ-MnO₂	Ru(bpy)₃³⁺	0.03
Bulk α-MnO₂	Ru(bpy)₃³⁺	0.01
Mn Complexes	Ce(IV) > 0.22 M	0.01-0.6
PSII	Sunlight	100-400 × 10³

Interestingly, this compound shows self-healing in the presence of Ce(IV). There are a few proposed mechanisms for self-healing of Mn oxides in the water-oxidation condition.[11,42-46] In the presence of Ce(IV), our group reported a self-healing reaction that remakes Mn oxide from MnO_4^-.[44-47]

In the reaction of these Mn oxides with Ce(IV), MnO_4^- is the

decomposition product of catalyst. The MnO_4^- concentration changes with time and, interestingly, in all experiments the MnO_4^- ions were consumed in the end of the reaction, suggesting the operation of a self-healing mechanism (**Scheme 1**).[46] A solution of MnO_4^- ions in the presence of Mn oxide showed a linear reduction in concentration, providing that a reaction between MnO_4^- and Mn oxide occurs.[46] On the other hand, the MnO_4^- ions formation in the reaction of Mn(II) nitrate (0.5 mM) and Ce(IV) (0.2-2 M) (**Scheme 1**). The amount of the MnO_4^- ions in the absence of Mn oxide showed no change during 100 hours of the experiment indicating that Mn oxide is necessary for the reduction of MnO_4^-.[46]
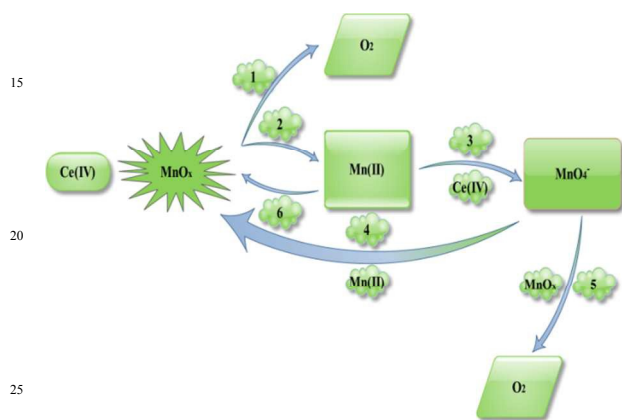
Scheme 1 Self-healing in water oxidation catalysed by Mn oxides in the presence of Ce(IV). 1: Oxygen evolution was detected with an oxygen meter. The origin of oxygen is water. 2: Mn(II) was detected by EPR (see text). 3: the MnO_4^- ions formation could be detected by UV-Vis in the reaction of Mn(II) and Ce(IV). 4: It is known that in the reaction of Mn(II) and MnO_4^- at different pH values, Mn oxide is formed. 5: The MnO_4^- ions in the presence of Mn oxide oxidize water. In this reaction, the MnO_4^- ions are reduces to Mn oxide. 6: Mn(II) in the presence of Ce(IV) forms Mn oxide. In a typical experiment, the reaction of $MnSO_4$ in the presence of Ce(IV) (1.0 M) forms MnO_2 that can be detected by XRD. Images and captions are taken ref. 46a. Reprinted with permission from ref. 46a. Copyright (2013) by Royal Society of Chemistry.

MnO_4^- formation is immediately observed after the reaction of Ce(IV) and **MnT** (**Fig. 10a**). It is important to note that MnO_4^- from the decomposition of **MnT**, after the consumption of Ce(IV) ions, is reduced and healed. In other words, after the Ce(IV) consumption the purple colour of MnO_4^- will be disappeared (**Fig. 10a**). The concentration of a solution of MnO_4^- decreases in the presence of **MnT** (**Fig. 10a**). The experiment shows that MnO_4^-, e.g. from the decomposition of Mn oxides, can be reduced to form catalyst in the presence of **MnT** (**Fig. 10b**). As shown by XPS (**Fig. 7**) after reaction by Ce(IV), again Mn oxide is observed on the surface of catalyst.
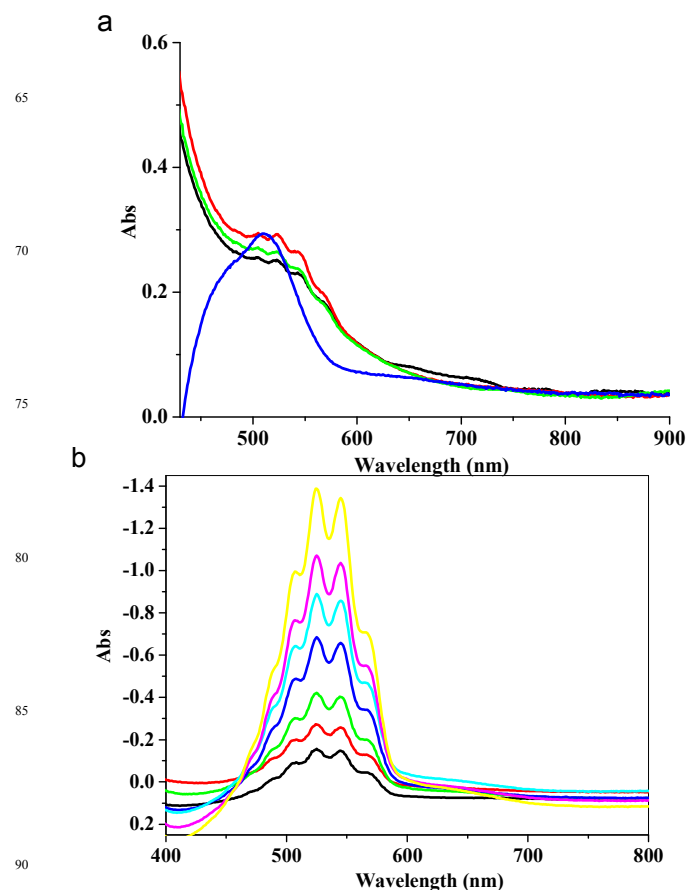
Fig. 10 Electronic spectra of a suspension of **MnT** (25 mg) in the presence of Ce(IV) (3.5 mL, 0.05 M) after 30 s (black), 60 s (red), 300 s (green), and one day (blue). After one day and consumption of Ce(IV) ions, no MnO_4^- was observed (a). The reaction of a solution of MnO_4^- (3 mL, 0.5 mM) and **MnT** (10 mg) after 30 s (black), 60 s (red), 1 h (green), 2 h (blue), 3 h (cyan), 20 h (pink), and one day (yellow) In b, we used a $KMnO_4$ (3 mL, 0.5 mM) as a reference (b).

Conclusions

In conclusion, we reported a very simple strategy to synthesize Mn oxide/graphene/cobalt. Such compounds are promising to be used as a catalyst because there are self-healing, recycling, high dispersible, magnetically separable and environmentally friendly. In addition to it, because Mn oxides suffer from low conductivity, the graphene in the compound may improve electron transfer in the composites. We also propose that such compounds can be attached to electrode by their magnetic properties (e.g. using a magnet in the back of electrode). However, stability of these compounds should be improved.

Acknowledgements

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/b000000x/
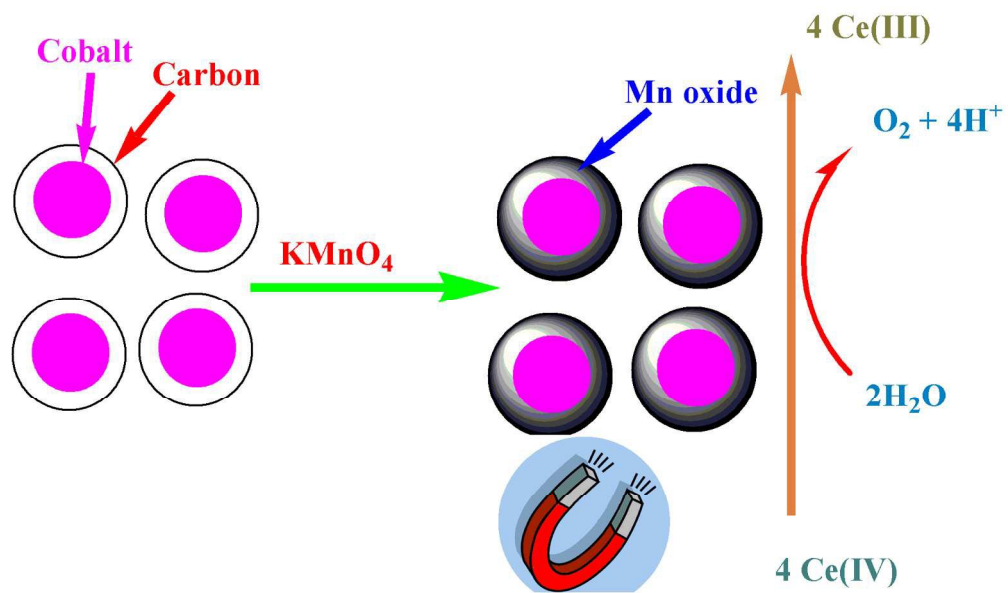
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Herein, we report a conductive, self-healing, recycling, high dispersible, magnetically separable, environmentally friendly, and nano-sized water-oxidizing catalyst. Carbon has significant role for engineering of the water-oxidizing catalyst.

529x310mm (96 x 96 DPI)