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Nanostructured manganese oxide on frozen smoke: A new water-oxidizing composite

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ARTICLE INFO

Article history:
Received 17 September 2015
Received in revised form
22 October 2015
Accepted 1 November 2015
Available online xxx

Keywords:
Artificial photosynthesis
Carbon aerogel
Manganese oxide
Nanotechnology
Oxygen
Self-healing
Water oxidation

ABSTRACT

The water-oxidizing complex or oxygen-evolving complex in plants, algae and cyanobacteria is an Mn_4CaO_5 cluster catalysing light-induced water oxidation. Herein we report that nano-sized Mn oxide/carbon aerogel is an active and low-density catalyst toward water oxidation. The composite was synthesized by a simple, low-cost procedure with different ratio of carbon aerogel to Mn oxide and 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. Then, the water-oxidizing activity of this composite was considered in the presence of cerium(IV) ammonium nitrate. The composites with a high ratio of Mn oxide to carbon aerogel are good Mn-based catalysts with turnover frequencies of ~0.33 (mmol O_2/(mol Mn·s)). In addition to the water-oxidizing activities of these composites under different conditions, their self-healing reaction in the presence of cerium(IV) ammonium nitrate was studied. We also compare the composite with graphene quantum dots/Mn oxide, which is not stable under these conditions. Using hydrogen to store sustainable energies is a promising strategy in the near future and our results show that nano-

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http://dx.doi.org/10.1016/j.ijhydene.2015.11.003

sized Mn oxide/carbon aerogel is a promising catalyst for water-splitting systems toward hydrogen evolution.

Introduction

Nature uses sunlight to oxidize water and to reduce carbon dioxide. Inspired by Nature, artificial photosynthesis can be designed to capture light, oxidize water, and reduce protons or organic compounds to generate useful chemical fuels [1,2]. Hydrogen is a promising chemical to store sustainable energies in near future. Thus, in artificial photosynthetic systems, water oxidation is a key and a bottleneck reaction to generate cheap electrons [1,2]. Such cheap electrons can be used to reduce different compounds such as CO_2 and water. The finding of an efficient, cheap and environmentally friendly water-oxidizing compounds is highly desirable [3–6]. Among different compounds [3–6], Mn oxides are very interesting [7–31] because they are not only cheap and environmentally friendly but also an Mn oxido cluster is efficiently used by Nature for water oxidation [32–39]. In other words, the water-oxidizing complex of Photosystem II is an Mn–Ca oxido cluster catalysing the light-induced water oxidation [32–39].

The water oxidation process catalysed by MnO_2 in the presence of cerium(IV) ammonium nitrate (Ce(IV)) as an oxidant was reported in 1968 [40]. Since 1968, many strategies were used to find an efficient and stable Mn oxide-based water-oxidizing catalyst by many research groups [7–31].

Among different strategies, Mn oxide on carbon nanotubes [41,42], graphene [42], graphene oxide [42], C_{60} [43] or nano-diamonds [44] was introduced as a good catalyst toward water oxidation. In addition to water oxidation, applications of these nano-compounds in environmental chemistry, catalysis, energy conversion, and electrochemistry have been reported [45]. Combination of carbon nanostructures with Mn oxides improves their response time, efficiency, conductivity, and sensitivity. Strasser and Behrens reported on incipient wetness impregnation and a novel preparation method of MnO_x/carbon nanotubes electrocatalysts for efficient water splitting [41]. The MnO_x/carbon nanotubes 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 [41]. The water-oxidizing

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

Composite	$KMnO_4$ (mg)	Mn%	Calcination temperature (°C)	[Ce(IV)]	Catalyst (mg)	TOF (mmol O_2/mol Mn·s)
A	0	0	60	0.11	20	0
A0	0.7	0.3%	60	0.11	20	0
A1	1.3	1.0%	60	0.11	20	0
A2	2.7	1.9%	60	0.11	20	0
A3	4.0	2.6%	60	0.11	20	0
A4	5.4	3.0%	60	0.11	20	0
A5	6.7	3.2%	60	0.11	20	0
A6	8.0	3.8%	60	0.11	20	0
A7	9.3	4.2%	60	0.11	20	0
A8	10.7	4.5%	60	0.11	20	0
A9	13.4	5.58%	60	0.11	20	0.10 ± 0.01
A10	26.8	8.5%	60	0.11	20	0.10 ± 0.01
A11	40.2	10.7%	60	0.11	20	0.10 ± 0.01
A11	40.2		100	0.11	20	0.10 ± 0.01
A11	40.2		200	0.11	20	0.10 ± 0.01
A11	40.2		300	0.11	20	~0
A11	40.2		400	0.11	20	~0
A11	40.2		500	0.11	20	~0
A12	60	14.5%	60	0.11	20	0.10 ± 0.01
A13	200	18.5%	25	0.11	10	0.20 ± 0.01
A14	400	18.7%	25	0.11	10	0.10 ± 0.01
A15	100 + 0.25 mL HNO_3		25	0.11	10	0.15 ± 0.01
A16	100 + 0.5 mL HNO_3		25	0.11	10	0.15 ± 0.01
A16	100 + 0.5 mL HNO_3		25	0.22	10	~0.24 ± 0.01
A16	100 + 0.5 mL HNO_3		25	0.33	10	~0.26 ± 0.01
A17	100 + 0.5 mL HNO_3		25	0.44	10	~0.33 ± 0.01
A18	100 + 100 mg KOH		25	0.22	10	<0.10 ± 0.01
A19	100 + 1.0 g KOH		25	0.11	10	<0.10 ± 0.01
A20	100 + 10 g KOH		25	0.11	10	<0.10 ± 0.01
A21	100	15.0%	25	0.11	20	0.2 ± 0.01