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ARTICLE

Gold nanorods or nanoparticles deposited on layered manganese oxide: New findings†

Mohammad Mahdi Najafpour,*[ab] Seyedeh Maedeh Hosseini,[a] Małgorzata Hołyńska,[c] Tatsuya Tomo,[d] and Suleyman I. Allakhverdiev[efg]

Herein we consider the role of gold nanorods, with diameter ~10 nm or nanoparticles (size <100 nm), deposited on nanolayered Mn oxide toward water oxidation. The catalysts were synthesized by simple methods and characterized by scanning electron microscopy, energy dispersive spectrometry, high resolution transmission electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, and atomic absorption spectroscopy. In the next step, the water-oxidizing activities of these composites were studied in the presence of cerium(IV) ammonium nitrate as a non-oxo transfer oxidant. A comparison with other previously reported Mn oxides and important factors influencing the water-oxidizing activities of Mn oxides are also discussed. Our results show that gold has no significant effect on the water-oxidizing activity of the Mn oxide phase at least in the presence of Ce(IV).

Introduction

Employing sustainable energies, water splitting into hydrogen and oxygen on an industrial scale is an important key strategy for energy storage.[1] In the next step, hydrogen can either be used directly as a fuel, converted to liquid fuels, or used to produce electricity in fuel cells. However, water oxidation is a bottleneck for the industrial-scale water splitting.[1]

Efficient catalysts for water oxidation in form of metal complexes were reported,[2] but many of them are expensive and (or) toxic. Mn oxides are highly attractive as catalysts for water oxidation because they are low-cost, stable, and environmentally friendly.[3] They can be used as bulk, supported and colloidal forms and synthesized by simple methods.[3]

Nature also uses an Mn oxido cluster (known as the water-oxidizing complex (WOC) or oxygen-evolving complex (OEC)) to oxidize water (**Fig. 1**).[4,5] In the biological site, there are many residues of amino acids where only a few of them are directly coordinated to the Mn and Ca ions.[5] The roles for these residues are the regulation of charges and electrochemistry of the Mn-Ca part, electron and proton transfer, providing water molecules at appropriate metal sites, and enhancing the stability of these inorganic cores. In artificial photosynthesis, the residues of amino acids can be replaced by completely different groups, but the same role can be achieved.[4,5] These compounds are usually more stable than residues of amino acids.[4,5]
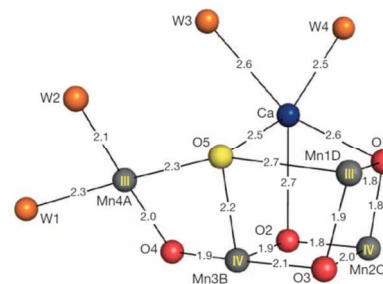

Fig. 1 The structure of the water-oxidizing complex (WOC) in PS II. Reprinted with permission from ref. 5. Copyright (2015) by Macmillan Publishers Ltd.

Since 1968, many research groups have reported on many Mn oxides as water-oxidizing catalysts using many strategies.[3]

Among different strategies, a few groups reported the effect of platinum and gold on the water-oxidizing activity of Mn oxides and showed that low amounts of platinum or gold could cause a significant enhancement of the water-oxidizng activity of MnO_x. Thus, a scalable catalyst production is possible under these conditions:[6-11]

Ohsaka's group reported on the electro water-oxidizing activity of platinum and gold electrodes modified with Mn oxide nanorods in 0.5 M KOH solution and reported a significant effect of platinum and gold electrodes on the water oxidation process upon the electrodeposition of Mn oxide nanoparticles (nano-MnO_x).[6,7] The highest shift in the onset potential of the

water oxidation was observed in 0.5 M KOH whereas the optimum loading (surface coverage) was about ca. 52%.[6,7]

The group proposed that the role of platinum or gold on water-oxidizing activity of Mn oxide may be related to a redox mediation.[6,7]

It was also reported that gold nanoparticles increase the water-oxidizing activities of Mn oxides in the presence of cerium(IV) ammonium nitrate (Ce(IV)).[8] Such effects were not observed for silver nanoparticles.[8] In the case of silver, the authors reported a decrease in water-oxidation reaction catalysis as compared to Mn oxides, most probably because of the lower numbers of Mn ions on the surface of the compounds.[8]

A study by Subbaraman et al. using Pt(111) and Au(111) single crystal surfaces demonstrated that the water-oxidizing activity of four first row transition metal oxides did not vary with the nature of the metal support but was linearly dependent on the coverage of the support by the metal oxide.[9]

A catalytic Mn oxides-based system that contains gold and nanoparticulate MnO_x was also reported by the Jaramillo's group. They found that adding gold to MnO_x significantly enhances the water-oxidizing activity of this composite.[10] The effect was related to the redox properties of both MnO_x and gold when the two materials are present in one composite catalyst.[10]

The Suib and He's group showed that doping MnO_x/gold nanoparticles can result in a strong enhancement of the water oxidation process by MnO_x.[11] The groups proposed the increase in the amount of Mn(III) ions as the important factor for water oxidation. They indicated that gold nanoparticles improve the catalytic activity up to 8.2 times in the photochemical and 6 times in the electrochemical system, compared with the activity of pure α-MnO_2.[11]

Herein, we study the deposited gold nanorods with diameter ~10 nm or nanoparticles (size <100 nm) in different amounts on layered Mn oxide and report their catalytic activities toward water oxidation in the presence of Ce(IV).

Experimental

Materials

All reagents and solvents were purchased from Aldrich and Merck and used without further purification. Gold nanorods (30 µg/mL, diameter ~ 10 nm, absorption/780 nm) (Fig. S1, ESI†) and gold nanoparticles (<100 nm) were purchased from the Sigma-Aldrich company.

Synthesis of composites containing gold nanorods on the layered Mn phase (A-A2)

Gold as dispersed nanorods (30 µg/mL, diameter ~10 nm, absorption/780 nm) was added to dispersed layered Mn–Ca oxide[14] (20 mg) in water and the solution was heated at 90 °C to evaporate water. The amounts of gold in different catalysts are shown in **Table 1**.

The solid was calcined at different temperatures for 10 h.

Nanoparticles deposited on the layered Mn oxide phase (A3-A13)

The catalyst was synthesized by a simple and green method. Gold nanoparticles (diameter <100 nm) were added to dispersed layered Mn–Ca oxide (20 mg) in water (1 mL) and the solution was heated at 80 °C to evaporate water. The solid was calcined at different temperatures for 10 h. The amounts of gold in different catalysts are shown in **Table 1**.

Characterization

SEM images were taken with a REM JEOL JSM-7500F device. For HRTEM and TEM, samples were placed on copper grids covered with carbon film and examined with a 300 keV Transmission electron microscope JEM-3010 UHR (JEOL Ltd., Japan), equipped with a retractable high-resolution slow scan CCD-Camera (Gatan Inc., USA) with GOS phosphorous scintillator and lanthanum hexaboride cathode as the electron source.

The X-ray powder patterns were recorded with a Bruker, D8 ADVANCE (Germany) diffractometer (CuK$_\alpha$ radiation). Atomic absorption spectroscopy (AAS) was performed on an Atomic Absorption Spectrometer Varian Spectr AA 110 to determine the content of Mn. Prior to each analysis, the analyzed oxide (2 mg) was added to concentrated nitric acid and H_2O_2, left at room temperature to ensure that the oxides were completely dissolved. The solutions were then diluted to 50 or 100 mL and analyzed by AAS. EDX analyses/mapping were carried out with the scanning electron microscope CamScan 4DV (CamScan UK). The infrared spectra were obtained on a FT-IR Bruker Vector spectrometer with a pressed KBr pellet. The amounts of gold used to synthesize the investigated composites were directly used to determine the % of the gold content.

Water oxidation

The procedure for water oxidation experiments was used as reported previously (Fig. S2, ESI†).[14]

Results and discussion

Synthesis and characterisation of the composite materials

We synthesized composites with different amounts of gold with diameter ~ 10 nm or nanoparticles (<100 nm) (**Scheme 1**). In the procedure, we added the prepared nano-sized gold to Mn oxides. We used no $HAuCl_4$[9] and reductants in the presence of Mn oxide because such procedure may cause the changes in the efficiency of layered Mn oxide toward water oxidation.

a

b
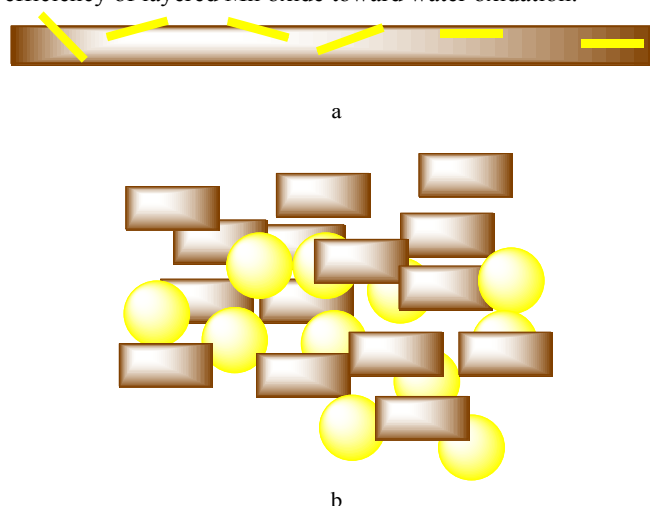
Scheme 1 The schematic image of gold nanorods deposited on layered Mn oxide (a) and nanoparticles, <100 nm, deposited on layered Mn oxide (b) composites.

For composites with enough gold, the metal lines are clearly observed in XRD patterns (lines 111, 200, 220 and 311, **Fig. 2**). However, the patterns for layered Mn oxide are not detectable.
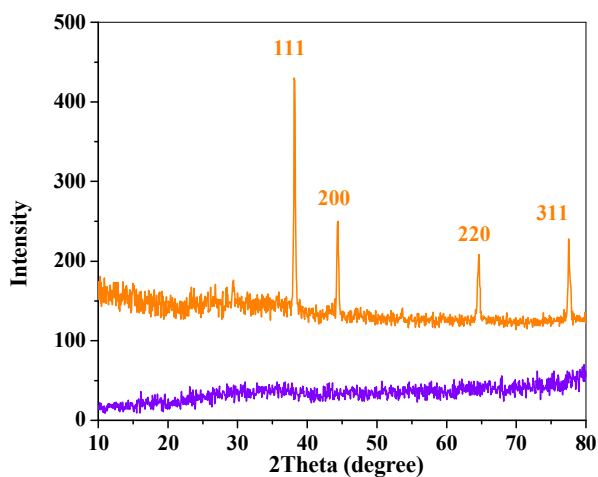
Fig. 2 XRD patterns for Ca-Mn oxide (violet) and gold nanoparticles deposited on the Ca-Mn oxide phase (orange). The 111, 200, 220 and 311 lines are attributed to gold nanoparticles.
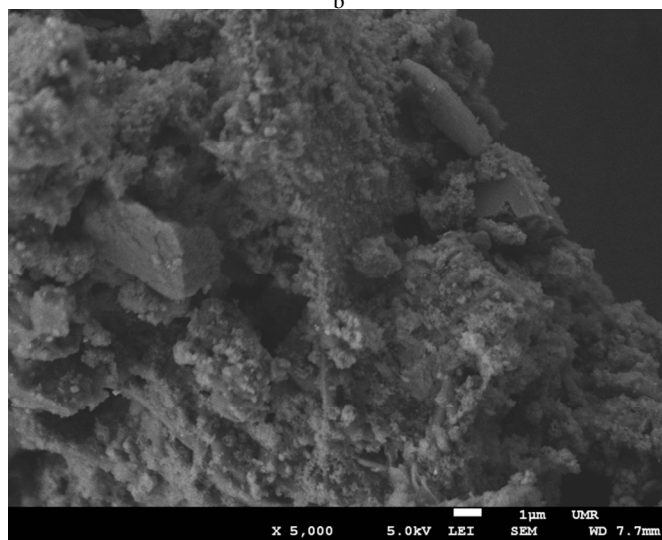
In SEM images for gold nanorods deposited on Ca-Mn oxide, only amorphous particles of Mn oxide with diameter of less than 60-70 nm (**Fig. 3**) are observed. Gold nanorods could not be detected on SEM images.
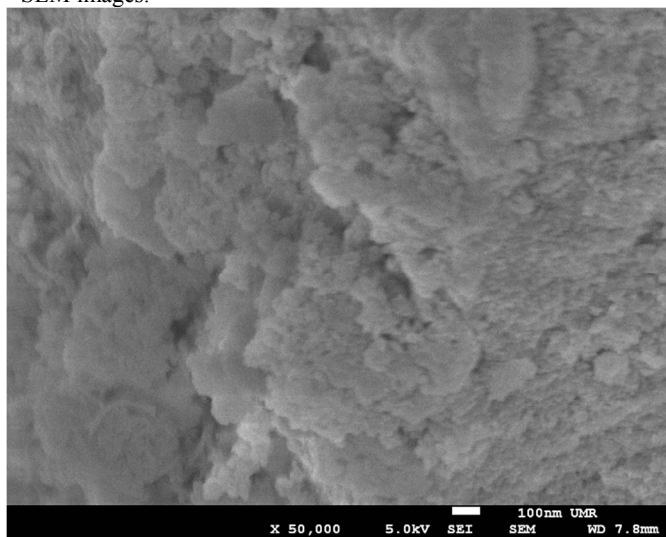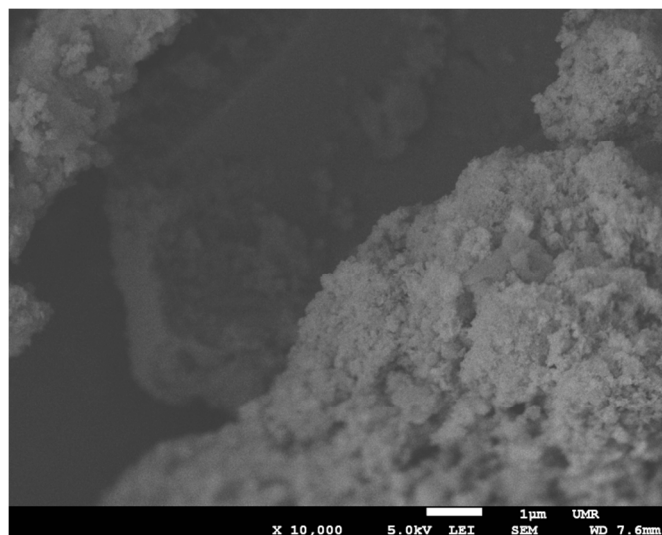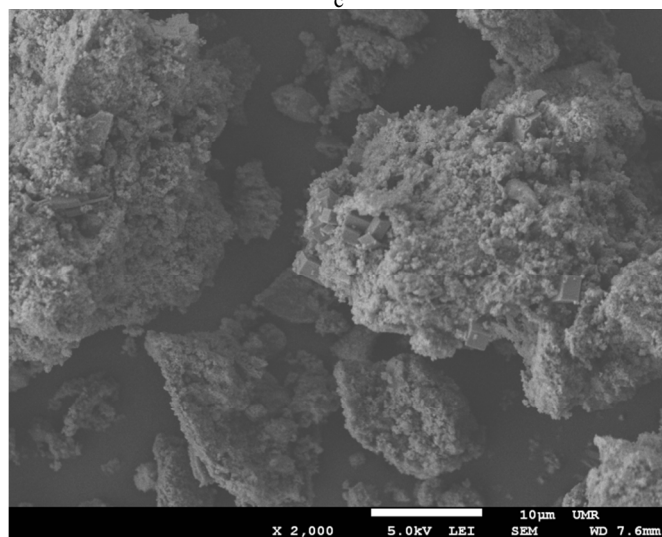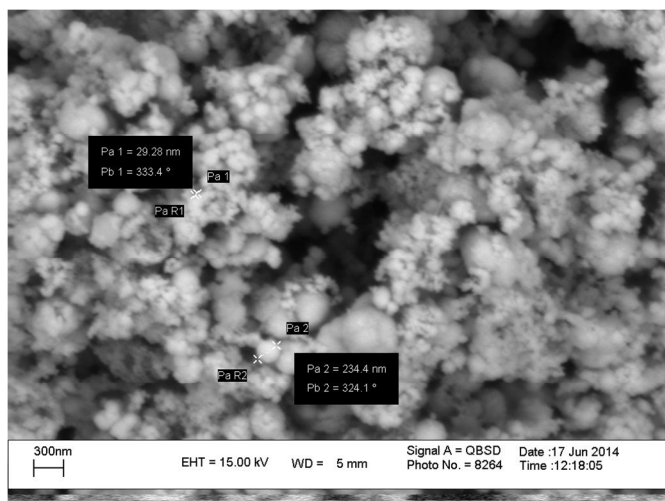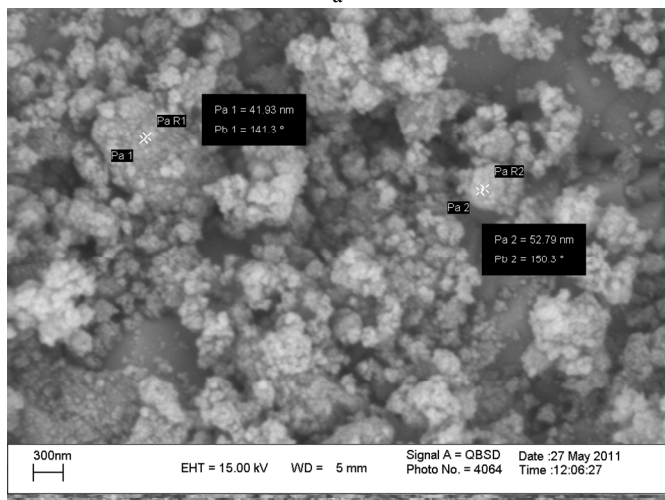

Fig. 3 SEM images for A (a), A0 (b), A2 (c) A calcined at 300° (d).

In SEM and EDX-Mapping images for gold nanoparticles deposited on Ca-Mn oxide, both gold nanoparticles with spherical morphology (diameter <100 nm) and amorphous particles with diameter of less than 60-70 nm being Mn oxide are observed (**Fig. 4**, Fig. S3 and Fig. S4, ESI†).

a

b

c

d

e

f

g
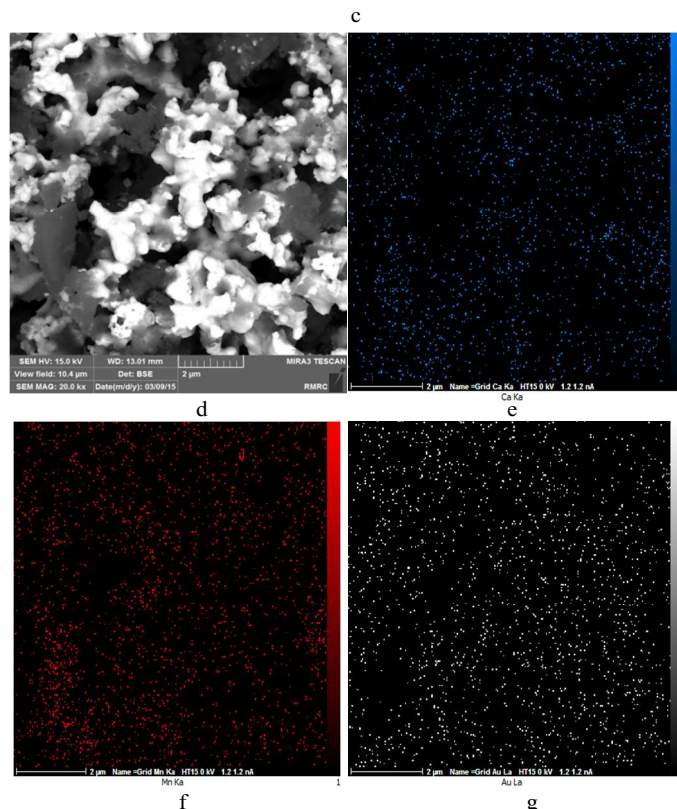
Fig. 4 SEM images from gold nanoparticles (a), Mn-Ca oxide (b) and gold nanoparticles/Mn-Ca oxide composites (c). SEM (d) and EDX mapping (e: Ca, f: Mn, g: Au) for A10.

Fig. 5 shows TEM and HRTEM images of gold/Mn oxide composites. For gold nanorods deposited on the Ca-Mn oxide phase, only Mn oxide with low crystalinity could be observed. Such low amounts of gold could not be observed in both XRD and EDX experiments.
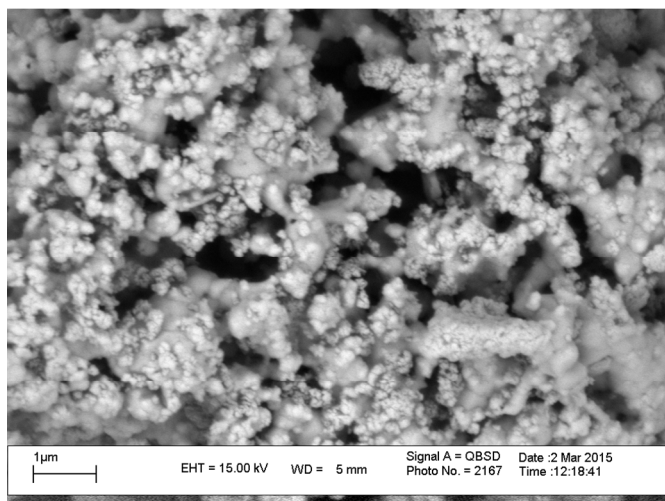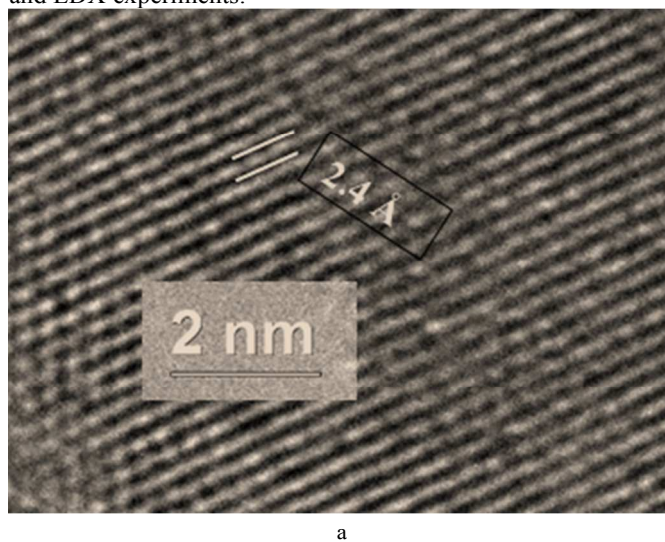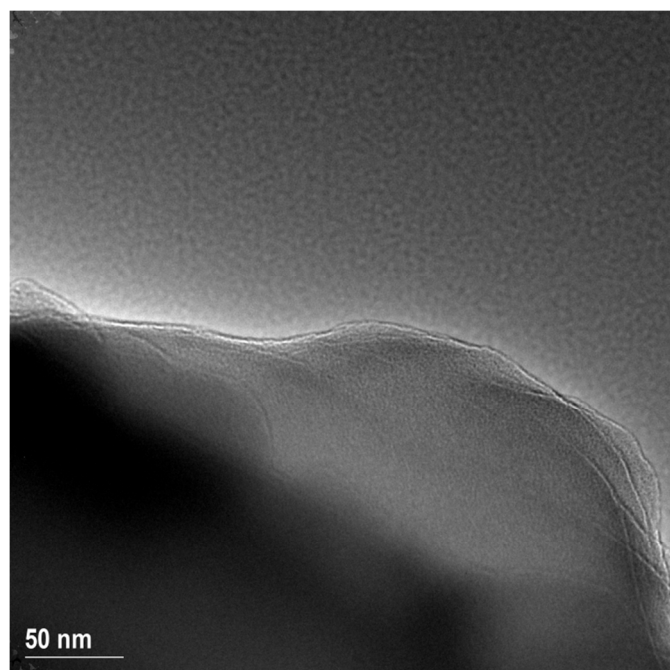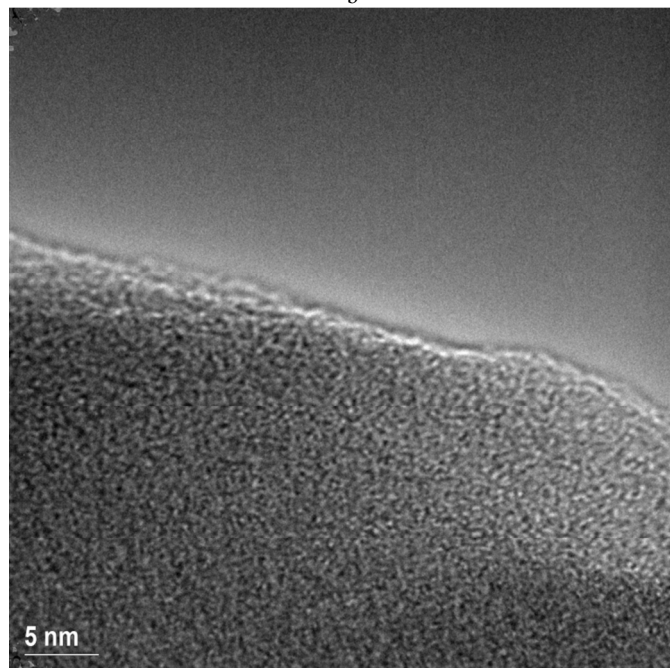
a

b

c

Fig. 5 HRTEM images for a gold nanoparticle (a) and A1 (b,c). The spacing of 0.24 nm for the high-contrast region probably corresponds to the (111) planes of gold.

In FTIR spectra of gold nanoparticles deposited on Ca-Mn oxide a broad band at ~ 3450 cm^{-1} is observed that is related to asymmetric and symmetric O-H stretchings. On the other hand, the band at ~ 1633 cm^{-1} in FTIR spectra of these compounds is related to H-O-H bending from water (Fig. S5-S10, ESI†). In addition to these peaks, Ca-Mn oxide shows a band at 526 cm^{-1} related to the MnO_6 cores in the Mn oxide phase (Fig. S5-S10, ESI†).[14] Gold nanoparticles show no sharp peaks in the FTIR spectrum.

Water oxidation

In the previous studies,[8,11] gold nanoparticles deposited on layered Mn oxide phase were reported. Such materials show higher activities toward water oxidation compared with gold nanoparticles or nanolayered Mn oxide. Herein we used commercial gold nanoparticles to synthesize well-defined composites.

We used Ce(IV) as usual oxidant for the water-oxidation reaction. This oxidant is a non-oxo transfer agent, soluble in water, stable, strong and usually a one-electron oxidant.[2,3,12]

We introduced two modifications compared with the previous studies:[8,11] firstly we eliminated the effect of reductants on Mn oxide using commercial gold and secondly the oxygen evolution rate in O_2 (mg/L·s) per gram of Mn oxide was calculated.

At higher calcination temperatures, Mn ions may not be carefully detected by AAS. Gold nanoparticles without Mn oxide show no water-oxidizing activity in the presence of Ce(IV), (Fig. S11, ESI†), but Mn oxide/gold nanoparticles composite is a good catalyst toward water oxidation. However, as shown in **Table 1**, gold even at different ratios has a low effect on the efficiency of Mn oxides but calcination temperatures[15] have an important effect on water oxidation as previously reported.

Table 1 The rate of water oxidation catalyzed by the gold/Ca-Mn based catalysts for water oxidation in the presence of Ce(IV) (0.11 M) at 25 °C.

Composite	Au% (W)	Mn% (W)	Ca% (W)	Calcination temperature (°C)	O_2 (mg/L·s) per gram Mn oxide × 10^3
A	0.15±1	50±1	4±1	300±10	1.6 ±0.1
A0	0.45±1	50±1	4±1	300±10	1.4±0.1
A1	0.70±1	50±1	4±1	300±10	1.0±0.1
A2	0.75±1	50±1	4±1	300±10	1.7±0.1
A3	1.60±1	49±1	4±1	300±10	1.0±0.1
A4	5.40±1	48±1	4±1	300±10	1.0±0.1
A5	16.60±1	42±1	4±1	200±10	1.1±0.1
A6	29.00±1	30±1	2±1	200±10	1.1±0.1
A7	50.00±1	25±1	2±1	200±10	1.3±0.1
A8	16.60±1	42±1	4±1	300±10	0.9±0.1
A9	29.00±1	30±1	2±1	300±10	1.0±0.1
A10	50.00±1	25±1	2±1	300±10	1.1±0.1
A8	16.60±1	42±1	4±1	400±10	1.1±0.1
A9	29.00±1	35±1	2±1	400±10	1.0±0.1
A10	50.00±1	25±1	2±1	400±10	1.6±0.1
A11	0	50±1	4±1	200±10	0.9±0.1
A12	0	50±1	4±1	300±10	1.5±0.1
A13	0	50±1	4±1	400±10	1.6±0.1

A maximum turnover frequency of 0.4 (mmol O_2/mol Mn·s) is observed under these conditions. On the other hand, compared with the water-oxidizing activities of Mn oxides without gold in the presence of Ce(IV) (**Table 2**), gold has no significant effect on the water-oxidizing activity of Mn oxide.

As shown in **Table 2**, dispersed nanolayered Mn oxides on inert-redox supports such as zeolite can significantly increase the water-oxidizing activities of layered Mn oxides. Such effects show that even high turnover frequency such as 2.6 (mmol O_2/mol Mn·s) in the presence of Ce(IV) can be observed when Mn oxide is significantly dispersed in zeolite.

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

Compound	Oxidant	TOF mmol O$_2$/(mol Mn·s)	References
PSII	Sunlight	100-400 × 10^3	28,29
Nano-scale Mn oxide within NaY zeolite	Ce(IV)	2.6	13
Nanolayered Mn-Ca oxide	Ce(IV)	2.2	14
Nanolayered Mn-Al, Zn, K, Cd and Mg oxide	Ce(IV)	2.2	15,16
Gold deposited on layered Mn oxide	Ce(IV)	~ 2	8
Nanolayered Mn-Ni(II) oxide	Ce(IV)	0.6	17
CaMn$_2$O$_4$·H$_2$O	Ce(IV)	0.54	18
Amorphous Mn oxides	Ru(bpy)$_3$$^{3+}$ Ce(IV)	0.06 0.52	19
Gold nanorods or nanoparticles deposited on layered manganese oxide	Ce(IV) (0.11 M)	0.4	This work
Nanolayered manganese oxide	Ce(IV) (0.11 M)	0.4	This work
CaMn$_2$O$_4$·4H$_2$O	Ce(IV)	0.32	18
Mn oxide nanoclusters	Ru(bpy)$_3$$^{3+}$	0.28	20
Mn oxide-coated montmorillonite (low surface)	Ce(IV)	0.22	21
Nanolayered Mn-Cu(II) oxide	Ce(IV)	0.2-0.35	17
Octahedral Molecular Sieves	Ru(bpy)$_3$$^{3+}$ Ce(IV)	0.11 0.05	19
MnO$_2$ (colloid)	Ce(IV)	0.09	22
α-MnO$_2$ nanowires	Ru(bpy)$_3$$^{3+}$	0.059	23
CaMn$_3$O$_6$	Ce(IV)	0.046	24
CaMn$_4$O$_8$	Ce(IV)	0.035	24
α-MnO$_2$ nanotubes	Ru(bpy)$_3$$^{3+}$	0.035	23
Mn$_2$O$_3$	Ce(IV)	0.027	18
β-MnO$_2$ nanowires	Ru(bpy)$_3$$^{3+}$	0.02	23
Ca$_2$Mn$_3$O$_8$	Ce(IV)	0.016	25
CaMnO$_3$	Ce(IV)	0.012	25
Nano-sized λ-MnO$_2$	Ru(bpy)$_3$$^{3+}$	0.03	26
Bulk α-MnO$_2$	Ru(bpy)$_3$$^{3+}$	0.01	23
Mn Complexes	Ce(IV)	0.01-0.6	27

Conclusions

We synthesized gold nanorods, with diameter ~10 nm or nanoparticles (size <100 nm) deposited on layered Mn oxide phase. The composites were characterized by SEM, FTIR, XRD, AAS and TEM. These composites were used as catalysts for water oxidation in the presence of Ce(IV). We found in comparison with layered Mn oxides that gold has no significant effect on the water-oxidizing activity of Mn oxide. Although we showed that gold has lower effect on water-oxidizing than previously reported,[8,11] gold as a stable and conductive compound is a promising additive to Mn oxides.

Acknowledgements

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
eControlledPhotobiosynthesis Laboratory, Institute of Plant Physiology, Russian Academy of Sciences, Botanicheskaya Street 35, Moscow 127276, Russia
fInstitute of Basic Biological Problems, Russian Academy of Sciences, Pushchino, Moscow Region 142290, Russia
gDepartment of Plant Physiology, Faculty of Biology, M. V. Lomonosov Moscow State University, Leninskie Gory 1-12, Moscow 119991, Russia
Corresponding Author:
Phone: (+98) 24 3315 3201. E-mail: mmnajafpour@iasbs.ac.ir;

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