

Short communication

Oxygen vacancy induced enhancement of photochemical water oxidation on calcium manganese oxide catalyst

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ABSTRACT

The oxygen-deficient $\text{Ca}_2\text{Mn}_2\text{O}_5$ perovskite nanoparticles exhibit remarkably higher catalytic activity compared to CaMnO_3 and MnO_2 nanoparticles for photochemical water oxidation. The fraction of surface adsorbed hydroxyl groups on these catalysts has been suggested to be the dominant factors affecting water oxidation activity compared to the other parameters such as oxidation states of manganese and crystal structure.

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1. Introduction

The photo(electro)chemical splitting water into hydrogen and oxygen has attracted tremendous attention in recent years because of its great potential in solar energy conversion and storage applications [1]. In respect to hydrogen evolution reaction, a two-electron-transfer process, oxygen evolution reaction is more complex, which involves four-electron-transfer process. Currently, owing to the slow four-electron transfer rate and the high activation energy barrier for O–O bond formation, the oxygen evolution is the main obstacle limiting the efficiency of overall water splitting [2]. Searching environmentally-friendly and efficient oxygen evolution catalysts (OECs) is an urgent and challenging task among the solar water splitting community.

In nature, a Mn_4CaO_5 cluster as the oxygen evolving complex in photosystem II (PS II), has been identified as the catalytic site for the four-electron involved water oxidation [3]. Inspired by the natural photosynthesis process in PS II, synthetic manganese-containing compounds are thought to be very promising candidates as functional water oxidation catalysts to mimic the role of Mn_4CaO_5 cluster in water oxidation [4].

Various nanostructured solid manganese oxides (MnO_x) including MnO_2 , Mn_2O_3 , Mn_3O_4 , MnO_x , MnO , $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, $\text{CaMn}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ and amorphous Ca_xMnO_y have been synthesized and tested as OECs in either electrochemical or photochemical systems [5–12].

Recently, oxygen deficient $\text{CaMnO}_{3-\delta}$ compounds have been reported as electrocatalysts for oxygen evolution/reduction reactions [13,14]. The results suggest that the oxygen-deficient $\text{CaMnO}_{3-\delta}$ compounds are promising and inexpensive bifunctional catalytic materials for reversible oxygen reduction and evolution reactions. Therefore, it is highly desirable to further investigate the oxygen-deficient $\text{CaMnO}_{3-\delta}$ as the OECs in a photochemical system for potential application in solar water splitting. In this work, we have synthesized CaMnO_3 and $\text{Ca}_2\text{Mn}_2\text{O}_5$ perovskite nanoparticles and evaluated their photocatalytic performance in water oxidation with $\alpha\text{-MnO}_2$ nanorods as a reference sample.

2. Experimental

2.1. Catalysts preparation

The synthesis of CaMnO_3 was done by a sol-gel method with citric acid as complexing agent and detailed procedure was shown in

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supporting information. The as-prepared CaMnO_3 powder was reduced under $\text{Ar}-5\% \text{H}_2$ at 400°C for 3.0 h in a tube furnace to get single phase $\text{Ca}_2\text{Mn}_2\text{O}_5$ powder. Nanostructured $\delta\text{-MnO}_2$ was prepared according to the literature [15].

2.2. Characterization of catalysts

The reflective XRD pattern was recorded on a PANalytical X-ray diffractometer with graphite-monochromatized $\text{Cu } K_\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), employing a scan rate of $1.5^\circ \cdot \text{min}^{-1}$ in the 2θ range of 10° to 100° . The microstructures of samples were inspected by scanning electron microscopy (SEM) on a JEOL 6700F scanning electron microscope. X-ray photoelectron spectroscopy (XPS) was performed using an X-ray photoelectron spectrometer (a monochromated Al KR x-ray source, thermos Escalab 250). The BET surface area of the samples were determined based on the N_2 adsorption isotherms at 77 K with a Coulter Omnisorp 100 CX apparatus.

2.3. Photochemical water oxidation experiments

Photochemical water oxidation experiments were performed in a 0.65 L home-made quartz reactor equipped with a water jacket for cooling. A typical water oxidation experiment was carried out using $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (100 μM) as a photosensitizer, $\text{Na}_2\text{S}_2\text{O}_8$ (10 mM) as sacrificial electron acceptor in 100 mL borate buffer solution (pH 9) along with the catalyst (25 mg). The reactants were purged with Ar for 1 h to remove all dissolved oxygen from the aqueous solution. The quartz reactor was then illuminated using a 250 W iron-doped halide UV-vis lamp with an ultraviolet cutoff filter ($>420 \text{ nm}$). The evolved oxygen gas in the headspace of reactor under irradiation was then examined intermittently using an online gas chromatograph (Agilent 3000 Micro Gas Chromatograph).

3. Results and discussion

3.1. Characterization of catalysts

Pure CaMnO_3 was prepared via a sol-gel process and single phase $\text{Ca}_2\text{Mn}_2\text{O}_5$ was obtained through the reductive calcination of as-prepared CaMnO_3 under $5\% \text{H}_2/\text{Ar}$ atmosphere according to the literature [14]. $\alpha\text{-MnO}_2$ nanorods were prepared by thermal treatment of layered $\delta\text{-MnO}_2$ at 600°C for 3 h [15]. Fig. 1 displays the powder XRD patterns and their structures of the different manganese oxide samples. The CaMnO_3 sample exhibits typical orthorhombic ($Pnma$) phase structure (JCPDS No. 76-1132), whereas the peaks of CaMnO_3 are splitted at around 2θ of 34° , 48° and 60° after reduction, which can be indexed to a different structure ($Pbam$) of $\text{Ca}_2\text{Mn}_2\text{O}_5$ (JCPDS No. 76-1133). In addition, the intensities of CaMnO_3 peaks were slightly reduced after reduction due to the crystal distortion and oxygen vacancy formation. The peaks of MnO_2 can be assigned to $\alpha\text{-MnO}_2$ (JCPDS 44-0141) with a tetragonal phase. The intensities and widths of the diffraction peaks of $\alpha\text{-MnO}_2$ are slightly lower and broader than that of CaMnO_3 because of the relative lower temperature synthesis. The reason that we chose $\alpha\text{-MnO}_2$ nanorods as a reference is that nanostructured $\alpha\text{-MnO}_2$ nanotubes and nanowires have been early reported as the efficient OECs [5, 6]. For CaMnO_3 , each Mn atom is coordinated by six oxygen atoms with forming MnO_6 octahedra structure. In contrast, all the MnO_6 octahedra are transformed into MnO_5 square pyramids in $\text{Ca}_2\text{Mn}_2\text{O}_5$ due to the loss of oxygen atoms. However, the framework of the perovskite structure is maintained for the $\text{Ca}_2\text{Mn}_2\text{O}_5$. The microstructures of the manganese oxides observed by SEM were shown in Fig. S1. The calcium manganese oxide samples are porous, with an average primary particle size about 50–300 nm. The $\alpha\text{-MnO}_2$ nanorods displayed uniform morphologies with diameters of approximately 50 nm and length of 300 nm. Furthermore, the BET surface areas of CaMnO_3 , $\text{Ca}_2\text{Mn}_2\text{O}_5$

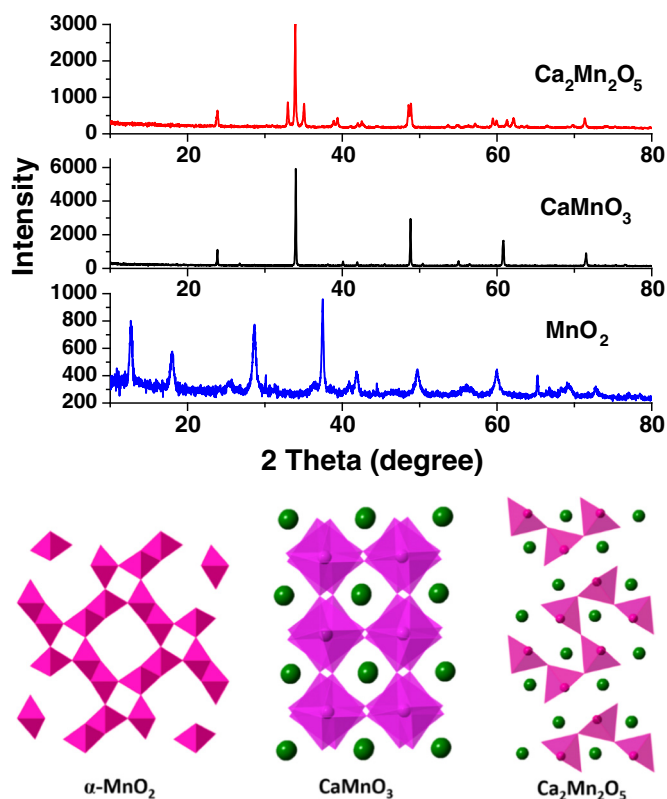


Fig. 1. XRD patterns and illustration of crystal structures of $\alpha\text{-MnO}_2$, CaMnO_3 and $\text{Ca}_2\text{Mn}_2\text{O}_5$ (green spheres indicate calcium cations). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and MnO_2 were determined to be about $5.19 \text{ m}^2/\text{g}$, $5.67 \text{ m}^2/\text{g}$ and $22.67 \text{ m}^2/\text{g}$, respectively.

3.2. Water oxidation tests

A well-established $\text{Ru}(\text{bpy})_3^{2+} - \text{S}_2\text{O}_8^{2-}$ sacrificial water oxidation system was employed to evaluate the photocatalytic performance of manganese oxides [16]. Firstly, experimental conditions for oxygen generation were optimized with varying the concentration of electron acceptor ($\text{Na}_2\text{S}_2\text{O}_8$) and dye sensitizer ($[\text{Ru}(\text{bpy})_3]\text{Cl}_2$) with $\alpha\text{-MnO}_2$ as a model catalyst. As shown in Fig. 2a, the concentration of $\text{S}_2\text{O}_8^{2-}$ varied from 1.0 mM to 50 mM. The highest O_2 yield was obtained with 10 mM $\text{S}_2\text{O}_8^{2-}$ as the electron acceptor. Further increase of the concentration of $\text{S}_2\text{O}_8^{2-}$ reduced the O_2 yield, probably because the generation of $[\text{Ru}(\text{bpy})_3]^{3+}$ oxidant was too fast to efficiently oxidize water on $\alpha\text{-MnO}_2$ catalyst, as the water oxidation reaction catalyzed by $\alpha\text{-MnO}_2$ is the rate-limiting step in the overall process. Alternatively, the strong oxidants would oxidize the organic ligand to decompose the Ru-dye as a competitive reaction [16]. Fig. 2b depicts the effect of concentration of $\text{Ru}(\text{bpy})_3^{2+}$ on the evolution of oxygen. The O_2 yield markedly increased with increasing the concentration from 25 μM to 100 μM . However, further increasing the concentration of $\text{Ru}(\text{bpy})_3^{2+}$ to 200 μM slightly enhanced the O_2 yield. Therefore, the conditions of employing 10 mM $\text{S}_2\text{O}_8^{2-}$ and 100 μM $\text{Ru}(\text{bpy})_3^{2+}$ dye were screened out for performing the water oxidation. Under the optimized conditions, different manganese oxide samples were tested for the O_2 evolution as shown in Fig. 2c. The O_2 yields normalized by Mn atoms on the basis of same quantity of catalyst mass indicated that $\text{Ca}_2\text{Mn}_2\text{O}_5$ is the most active catalyst, whereas CaMnO_3 and MnO_2 samples exhibited similar performance. In addition, the activities of heterogeneous catalysts are strongly affected by surface areas of solid catalysts [17]. Thus, in most cases, the water oxidation activities among different samples are compared after normalization by the surface area. As shown in Fig. 2d, the normalized O_2

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