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Article

In situ doping brushite on zinc manganese oxide toward enhanced water oxidation performance: Mimicry of an oxygen-evolving complex

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ABSTRACT

We report *in situ* doping of brushite on zinc manganese oxide (ZMO), fabricated by calcining a Mn(II) oxalate-impregnated metal-organic framework. The doping process was conducted in combination with the photocatalytic water oxidation reaction which was catalyzed by ZMO in neutral phosphate-buffered aqueous solution containing $[Ru(bpy)_3]^{2+}$-$Na_2S_2O_8$ and calcium(II) triflate salt, exhibiting greatly enhanced water oxidation performance with optimized turnover frequency of 0.18 $mmol_{O2}$ mol_{Mn}^{-1} s^{-1}. Different analytical techniques indicated that photodeposited calcium-phosphate (CaP) acted as a co-catalyst to promote the O_2 evolution activity of ZMO. This system involved the use of manganese oxide and calcium ion, and the operation was conducted under ambient temperature and neutral conditions, thus, it efficiently mimicked the oxygen-evolving complex in photosystem II.

1. Introduction

Producing renewable and clean energy is regarded as an effective strategy for meeting the energy needs of present and future generations [1]. Sunlight is the only source that provides sustainable and carbon-neutral energy to reduce the stress from the shortage of fossil fuels and environmental crises caused by the use of fossil fuels [2]. Consequently, researchers have long been focusing on the conversion and utilization of solar energy. One of the most promising strategies in pursuit of such ideal energy is water splitting to produce H_2 by either photo-induced routes or electronic techniques [3–10]. However, a key challenge limiting the improvement of overall water splitting efficiency is the complicated and sluggish water oxidation reaction that involves the $4H^+/4e^-$ oxidation of two water molecules to dioxygen. Meanwhile, an efficient catalyst must tolerate the harsh conditions for water oxidation (*i.e.*, sufficient power), under which most functionalized moieties lose their activities for sustained water splitting [11]. In natural photosynthesis, sunlight is converted and stored via an oxygen-evolving complex (OEC) in photosystem II (PS II), which contains a Mn_4CaO_5 cluster surrounded by protein matrixes [12,13]. Inspired by nature's wisdom, numerous efforts have been devoted to developing an efficient artificial photosynthe-

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sis system [14–19], especially where manganese oxide and calcium ions are involved. Mn chemistry exhibits multiple oxidation states and is capable of the Kok cycle of the natural PS II system. Ca^{2+} is widely recognized as a weak Lewis acid promoting the proton-coupled electron transfer (PCET) process between proteins and Mn-Ca cluster, and/or as the binding site for water molecular substitution [20]. In biomimetic studies, plenty of chemists have endeavored to develop calcium manganese oxide ($CaMnO_x$)-based systems, giving solid evidence for improved catalytic activity through the incorporation of Ca^{2+} in Mn oxides [20]. Li et al. [21] fabricated nanostructured non-crystalline $CaMnO_x$ showing enhanced activity in water oxidation reactions for both chemical and photocatalytic systems. This work demonstrated that the disordered structure of $CaMnO_x$ and a modest valence state of Mn were important factors for achieving high water oxidation activity. Several reports have provided similar insights into the relevance of highly crystalline structures of Mn oxides and their lower efficiencies in water oxidation compared to those of amorphous phases. Kurz and coworkers [22] synthesized layered Mn oxides containing a series of alkaline earth cations, e.g., K, Ca, Sr, and Mg. That with Ca incorporated reached the highest catalytic activity. Thapper's work studied the influence of phosphate ion on the construction of Mn oxide structures and valence state of Mn [23]. Considering the Angström-scale Mn_4CaO_5 cluster in OEC [24], the preparation of different phases of Ca-Mn oxides with ultra-small size and their use in photocatalytic water oxidation under neutral conditions would be of great interest.

In addition, metal-organic frameworks (MOFs) represent a class of coordination polymers with inherent features like ultrahigh porosity, enormous internal surface area, and flexibility [25–28]. Calcinating MOFs in atmosphere could afford neat metal oxides or metal oxides embedded in carbon matrices derived from organic units, owing to the periodical assembly of metal nodes and organic linkers in the frameworks. The resulting metal oxides may inherit some advantages from the pristine MOF such as enlarged surface area or ordered structures and thus exhibit excellent performances in various applications including catalysis, adsorption, as well as energy-related areas [29,30]. To the best of our knowledge, the use of MOF-templated transition metal oxides, especially Mn oxides, as photocatalysts for light-driven water oxidation has seldom been studied. Moreover, calcium-phosphate (CaP) including brushite is a class of inorganic minerals and normally non-toxic to living beings and the environment [31–34]. Their effects on water splitting reactions have not been studied before.

Herein, we report the design and synthesis of a MOF-templated Zn-Mn oxide (ZMO)-catalyzed water oxidation system to verify the role of calcium ion. The catalytic performances of photochemical water oxidation in phosphate-buffered neutral aqueous solution containing $[Ru(bpy)_3]^{2+}$ and $S_2O_8^{2-}$ were found to be 10-fold higher when the reaction was carried out in the presence of Ca^{2+} in comparison with those in the absence of Ca^{2+}. CaP was deposited *in situ* on ZMO during the photocatalytic reaction and played a key role in boosting the water oxidation reaction. Control experiments with prolonged irradiation time demonstrated increased CaP contents in the resulting materials, which essentially influenced the catalytic activity. The ZMO material doped CaP *in situ* and its use in light-driven water oxidation involved the use of earth-abundant elements, ambient temperature, and neutral conditions, and thus could be regarded as an efficient functional model for OEC.

2. Experimental

2.1. General

Commercially available chemicals and reagents involved in this study were purchased from Shanghai Aladdin Reagent Co. Ltd and Macklin Biochemical Co. Ltd, China, and used without further purification unless otherwise indicated. $Ru(bpy)_3(PF_6)_2$ (bpy = 2,2'-bipyridine) was purchased as chloride salt and metathesized in water by precipitation with excess NH_4PF_6. The orange solid obtained was further recrystallized with ether from a minimum volume of acetone solution.

2.2. Synthesis

ZIF-8 was prepared according to the literature with a few modifications [35]. Typically, $Zn(NO_3)_2\cdot 6H_2O$ (22.6 mmol, 6.7 g) was dissolved in 160 mL methanol. Another 160 mL methanolic solution containing 2-methylimidazole (180.3 mmol, 14.8 g) was added to the above solution with vigorous stirring. The mixture solution was kept stirring for 24 h. All operations were performed at room temperature. The product was separated by centrifugation and thoroughly washed twice with methanol , and finally dried at 50 °C overnight in a drying oven. The obtained ZIF-8 powders were further activated at 100 °C under vacuum for 10 h prior to use.

Zinc-manganese oxides (ZMOs) were synthesized by a conventional impregnation method followed by MOF-templated calcination. In a typical synthesis of ZMO, manganese(II) oxalate dehydrate (0.5 g) was dissolved in 20 mL ethanol. ZIF-8 powder (0.5 g) was added to the above solution. After stirring at room temperature for 2 h, the product was separated by centrifugation and washed thoroughly with ethanol and water. The resulting powders were dried in an oven at 80 °C overnight. After that, two-stage calcination was performed to obtain ZMO. The dry powders were first annealed at 400 °C for 8 h in nitrogen at a heating rate of 2 °C min^{-1} and cooled to room temperature. Then, the thermolysis temperature was elevated to 600 °C with the same heating program and maintained for 3 h in air flow. After cooling to ambient temperature, the produced powders were collected, dispersed in NH_4Cl-$NH_3\cdot H_2O$ (5–2.5 mol L^{-1}) aqueous solution to remove excess ZnO, and washed with water. The final product was obtained after drying overnight in an oven at 80 °C. In addition, a series of ZMOs were prepared using the same procedure, changing only the time of the second calcination stage from 2 to 5 h or the amount of Mn oxalate from 0.1 to 0.7 g to obtain ZMOs with varied Zn/Mn ratios.

Mn_2O_3-syn was synthesized according to the literature [36].