



Calcium manganese oxide catalysts for water oxidation: Unravelling the influence of various synthesis strategies



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ABSTRACT

Three different mixed oxide catalysts primarily consisting of calcium and manganese oxides targeting artificial photosynthesis were synthesized and studied. According to the results, their catalytic activity for water oxidation was enhanced by the presence of mixed valence states of Mnⁿ⁺ ions ($3.0 \leq n < 4.0$), while the specific surface area had negligible effect.

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1. Introduction

The growing demand for energy and environmental problems that the world is currently facing leads us to develop alternative and renewable energy sources to replace fossil fuels and nuclear energy [1]. Hydrogen is considered as a potentially emissions-free alternative fuel. One promising and attractive strategy is to develop materials that mimic the natural photosynthesis. Artificial photosynthesis is a process inspired by nature that allows obtaining hydrogen and oxygen from water with help of sunlight [2,3]. The decomposition of water into hydrogen and oxygen is a challenging process requiring a standard potential of 1.23 V versus normal hydrogen electrode. In natural photosynthesis, oxidation of water takes place at the oxygen evolving complex of Photosystem II, which is comprised of an inorganic manganese based cluster surrounded and functionally important protein ligands. The structure (Mn₄O₅Ca) is responsible for the transfer of four electrons and four protons as well as for the O—O bonding, which readily oxidizes water into O₂ [4–6]. In the view of mimicking this cluster, many research groups have invested considerable efforts to

create a synthetic inorganic water oxidation catalyst similar to that of the CaMn-oxide cluster in Photosystem II [7].

A material that has potential as an applicable solution should be efficient, recyclable, cost-effective and abundant. Over the years, several candidate water oxidation catalysts have been developed that are based on noble metals such as ruthenium [8,9] and iridium [10] but also compounds of transition metals such as manganese [11,12] and cobalt [13] have been considered. Particular attention was paid to manganese oxides as oxidation catalysts because it is earth-abundant and environmentally friendly. Recently, Kurz et al. showed that an addition of calcium into the manganese compound structure can improve the materials catalytic activity for water oxidation [14]. As a continuation, another study was recently published demonstrating the preparation of calcium manganese oxides from cyanamide precursors [15].

However, in our approach, a different strategy was chosen. To our knowledge, the utilization of nano-casting and benzyl alcohol routes for the synthesis of calcium and manganese oxide based catalysts has never been reported. In this study, we present three different methods for the synthesis of catalysts employing (1) a direct soft template (ST), (2) a hard silica-based template (HT) and (3) a benzyl alcohol (BA) route leading to three merely different catalysts denoted as STCM, HTCM and BACM, respectively. Although the synthesis methods suffered from possible shortcomings, the investigation of the electrochemical performance showed highly efficient catalysts for water oxidation.

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2. Experimental

2.1. Materials

Ammonium fluoride (Alfa Aesar; $\geq 96\%$), pluronic[®] P-123 (Aldrich; Mn $^{1/4}$ 5800 in poly(ethylene glycol), 30%), *n*-decane (Alfa Aesar; $\geq 99\%$), sodium hydroxide (NaOH, EKA Chemicals AB; 98%), tetraethyl orthosilicate (TEOS, Aldrich) hydrochloric acid (HCl, AnalaR Normapur; 37%), calcium nitrate tetrahydrate (Ca (NO₃)₂·4H₂O, Scharlau), manganese (II) chloride tetrahydrate (MnCl₂·4H₂O, MERCK; $\geq 98\%$), manganese (II) acetylacetonate (Mn (Acac)₂; Aldrich), ammonium fluoride tetrahydrate (NH₄F·4H₂O), *n*-butanol (Aldrich, $\geq 99\%$), tetraethyl orthosilicate (Alfa Aesar; $\geq 99\%$), benzyl Alcohol (BnOH, Aldrich; ACS reagent, $\geq 99.0\%$), ethyl alcohol (EtOH, Solveco; 99.9%). All solvents were used without distillation or purification.

2.2. Preparation of STCM (soft template calcium manganese)

The synthesis method applied has been earlier described by Dahal et al. [16] and was adapted to this study. A solution containing ethyl alcohol (30 mL), water (30 mL) and NaOH (1.2 g)

was introduced to 2.45 g of Pluronic[®] P-123 in a 250 mL balloon closed by a tape and subjected to stirring at room temperature until complete dissolution. The measured pH of the solution was 13.6. After adding 0.028 g (0.81 mmol) of NH₄F, the pH fell to 13.2. In order to bring the pH to 12.7, approximately 25 mL of 1.07 M HCl was added in the solution under continuous stirring whereupon the stirring was commenced for additional 30 min. As the next step, 15 mL of *n*-decane was carefully incorporated under stirring and after 30 min stirring, a precursor solution containing both Ca and Mn precursors (470 mg, 2 mmol of Ca(NO₃)₂·4H₂O and 550 mg, 2.8 mmol of MnCl₂·4H₂O dissolved into 6 mL of EtOH) were added to the mixture and stirred for additional 2 h. Finally, the mixture was kept at 35 °C for 20 h and then transferred into a 200 mL Naglene bottle and stored for 48 h, at 82 °C in an oven set at 85 °C. The obtained suspension was centrifuged and dried at 85 °C overnight. Consequently, the obtained brown powder was calcined at 500 °C for 4 h (ramping 1 °C/min).

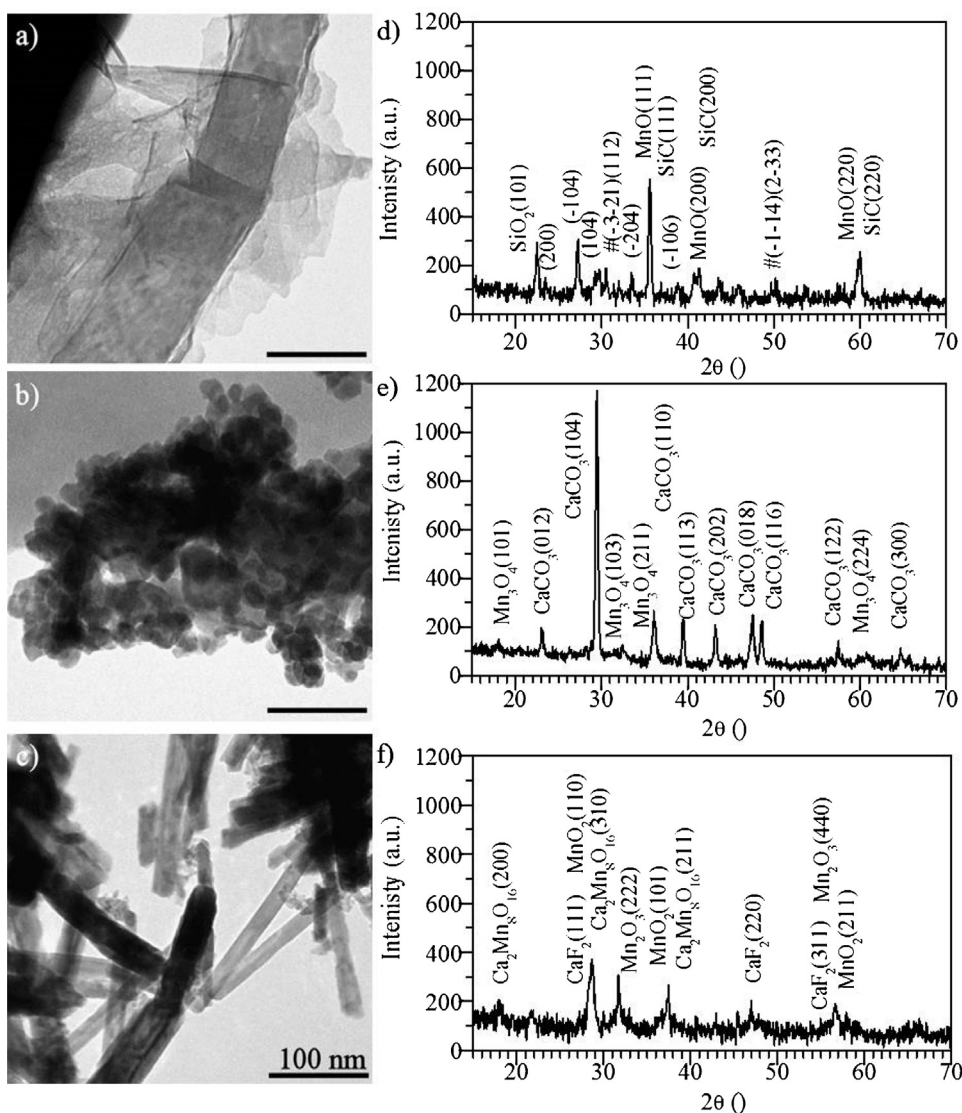


Fig. 1. TEM images and XRD patterns of the catalysts. a) TEM image of HTCM, b) TEM image of BACM, c) TEM image of STCM, d) XRD pattern of HTCM, e) XRD pattern of BACM and f) XRD pattern of STCM materials. Note: symbols in panel a) denote • Ca(Mn²⁺, Ca) Si₂O₆ and # Ca_{0.813}Mn_{0.187}SiO₃.

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