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Development of optically transparent water oxidation catalysts using manganese pyrophosphate compounds

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ABSTRACT

One challenge in artificial photosynthetic systems is the development of active oxygen evolution catalysts composed of abundant elements. The oxygen evolution activities of manganese pyrophosphate compounds were examined in electrochemical and photochemical experiments. Electrocatalysis using calcium–manganese pyrophosphate exhibited good catalytic ability under neutral pH and an oxygen evolution reaction was driven with a small overpotential ($\eta < 100$ mV). UV–vis diffuse reflectance measurements revealed that manganese pyrophosphates exhibit weak absorption in the visible light region while commonly used oxygen evolution catalysts exhibit intense absorption. Therefore, the efficient light absorption of a photocatalyst was retained even after surface modification with a manganese pyrophosphate, and photochemical oxygen evolution was achieved by using magnesium ferrite modified with manganese pyrophosphate nanoparticles under the illumination of visible light at wavelength of over 420 nm.

1. Introduction

Splitting water into hydrogen (H_2) and oxygen (O_2) using sunlight is a clean and sustainable proposition for addressing energy and environmental problems because solar energy and water are plentiful and hydrogen is a clean fuel [1–5]. To realize solar water splitting, one of the most challenging issues has long been the development of highly active water oxidation catalysts, as the O_2 evolution reaction that proceeds through the four-electron oxidation of two water molecules usually requires a significant additional voltage (overpotential) [6–9]. Therefore, extensive research efforts have been devoted to developing O_2 evolution catalysts and a variety of metal oxides based primarily on iridium [10,11], ruthenium [12,13], and first row transition metals such as cobalt [14–17], iron [18], and manganese [19–30] have been developed.

Manganese (Mn)-containing compounds are attracting considerable interest owing to the fact that only Mn has been utilized for the natural water oxidation catalyst, the oxygen evolving center (OEC) of photosystem II (PSII) [31–33]. In almost all photosynthetic organisms, $CaMn_4O_5$, the μ-oxo-bridged tetrameric Mn cluster, acts as an OEC. This Mn_4 cluster can catalyze water oxidation to molecular O_2 with a low overpotential (160–300 mV) and high turnover frequency (maximum 10^3 s^{-1}) under mild pH conditions [34,35]. Therefore, the Mn cluster within photosynthetic organisms has triggered extensive research efforts to develop an active O_2 evolution catalyst composed of abundant, non-toxic, and low-cost Mn. To date, there have been notable developments of Mn-containing water oxidation catalysts including simple [19–27] and mixed-metal oxides [28–30] and complexes [36–39] simultaneously with the clarification of the reaction mechanisms [40–43]. In contrast, few studies have been reported concerning the O_2-evolving activity of polyanion compounds [44,45]. Polyanion compounds are a class of materials in which tetrahedral polyanion units $(XO_4)^{n-}$ and their derivatives $(X_mO_{3m+1})^{n-}$ (X = P, Si, S, As, etc.) combine with MO_x (M = transition metal) polyhedra. They can be considered to be attractive materials for catalytic application owing to their variable redox and structural properties, which can be systematically tuned according to the combination of polyanion units and transition metals [46,47]. An immense variety of derivatives have already been developed for the anode materials of lithium ion batteries [48,49]. Also, in polyanion compounds, because the strongly covalent X–O bonds in polyanion units make the neighboring transition-metal ions strongly ionic, the electronic interaction between metal ions and polyanions is weak [50–52]. As a result, polyanion compounds generally have a wide band gap and exhibit weak absorption in the visible light region. For the construction of

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efficient solar energy conversion systems, the weak light absorption of a multielectron transfer catalyst is preferable because if the catalyst absorbs light intensively, most of incident photons would be interrupted by the surface-associated multielectron transfer catalyst without reaching the interior photocatalysts or photoelectrodes.

Herein, we examined the capability of manganese pyrophosphates which are a type of polyanion compound, to function as an O_2 evolution catalyst under neutral pH conditions. They were found to initiate O_2 evolution at a potential near the thermodynamic reversible potential of the four-electron oxidation of H_2O. Additionally, when they were attached on the surface of magnesium ferrite, they were found to drive O_2 evolution under the irradiation of visible light.

2. Experimental

2.1. Sample preparation

Calcium-manganese pyrophosphate ($CaMnP_2O_7$) was synthesized by a solid state reaction [53]. Briefly, stoichiometric amounts of calcium carbonate ($CaCO_3$, Kanto Chemical, 99.5%), manganese dioxide (MnO_2, Kojundo Chemical Lab., 99.99%), and phosphorus oxide (P_2O_5, Wako, 98.0%) were mixed and milled thoroughly, then calcined in air at 1323 K for 48 h to obtain a pale yellow powder. Dimanganese pyrophosphate ($Mn_2P_2O_7$) was prepared using phosphoric acid (H_3PO_4, Wako Chemical), manganese nitrate ($Mn(NO_3)_2$, Wako Chemical, 98.0%), and nitric acid (HNO_3, Kanto Chemical) in accordance with a previously reported method [54].

For photochemical experiments, a magnesium ferrite ($MgFe_2O_4$) powder modified with $Mn_2P_2O_7$ nanoparticles was prepared. The $MgFe_2O_4$ powder was prepared by calcinating a mixture of magnesium oxide (MgO, Kanto Chemical, 99.99%) and hematite (α-Fe_2O_3, Kojundo Chemical Lab., 99.9%) at 1373 K for 12 h. $Mn_2P_2O_7$ nanoparticles were synthesized by adding 50 mL of 5 mM manganese chloride ($MnCl_2$, Wako Chemical, 99.0%) dropwise into 100 mL of 5 mM tetrasodium pyrophosphate ($Na_4P_2O_7$, Wako Chemical, 99.0%) while stirring. The synthesized white powder was recovered by filtration, washed, dried, and ground with $MgFe_2O_4$ powder. The molar ratio of $Mn_2P_2O_7$ to $MgFe_2O_4$ was 0.05. After calcination at 773 K for 1 h, $Mn_2P_2O_7$ modified $MgFe_2O_4$ was obtained.

2.2. Characterization

The crystal structures of the prepared powders were determined by X-ray diffraction (XRD, PW-1700, Panalytical). The optical spectra were measured in diffuse reflectance (DR) mode using a UV–visible (UV–vis) spectrometer (V-650, JASCO) and barium sulfate ($BaSO_4$) as a reflectance standard. Fourier transform infrared spectroscopy (FT-IR) spectra of samples were recorded with an IR Prestige-21 (Shimadzu) in transmission mode. A scanning electron microscope (SEM; S-4500, Hitachi) was used to observe the morphology of the prepared photocatalysts. Transmission electron microscopy (TEM) inspection of the powder samples was conducted using a Tecnai Osiris instrument (FEI Co.) which was operated at 200 kV and equipped with an energy-dispersive X-ray (EDX) spectrometer. Elemental analysis was conducted by inductively coupled plasma atomic emission spectroscopy (ICP-AES, PS3500DD, Hitachi).

2.3. Electrochemical measurements

Electrochemical water oxidation was performed on a commercial potentiostat and potential programmer (HZ-5000, Hokuto Denko) using a carbon paste electrode modified with 15 wt% of the manganese pyrophosphate catalyst as a working electrode (7.1 mm^2), a silver/silver chloride reference electrode (Ag/AgCl/KCl (sat.)) and a platinum (Pt) wire as a counter electrode. A carbon paste electrode was prepared by thoroughly mixing 9 mg of catalyst and 51 mg of a mixture of graphite powder and paraffin oil

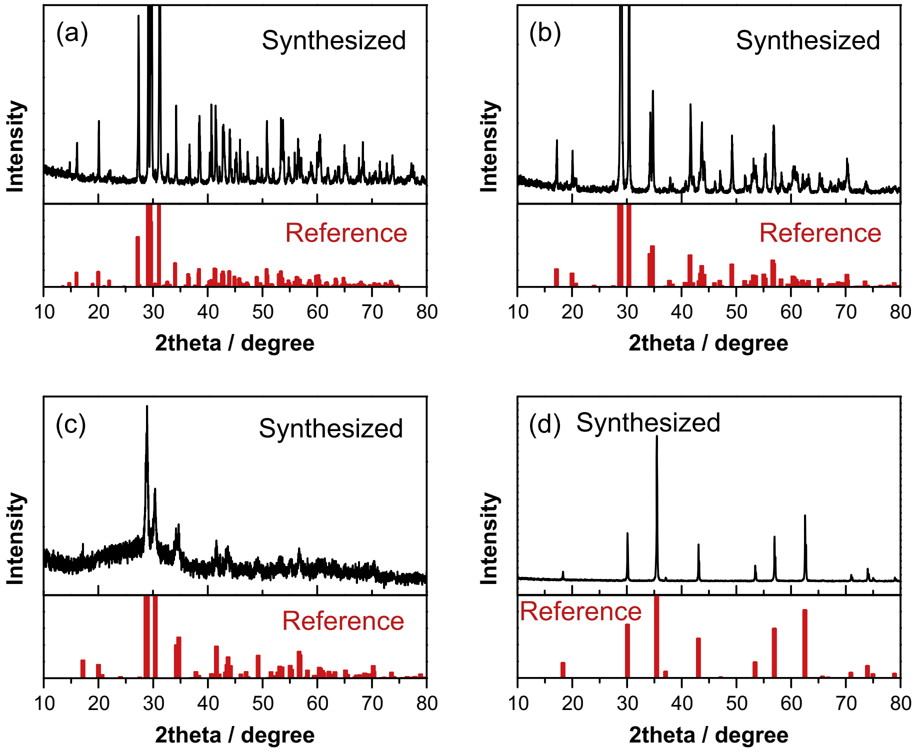

Fig. 1. XRD patterns of (a) $CaMnP_2O_7$, (b) $Mn_2P_2O_7$, and (c) $Mn_2P_2O_7$ nanoparticles, and (d) $Mn_2P_2O_7$-modified $MgFe_2O_4$.