



Enhancing photocatalytic oxygen evolution activity of cobalt-based spinel nanoparticles



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ABSTRACT

Photocatalytic water oxidation is one of the critical reactions for solar fuel production from abundant sources. Among all the metal oxides, Co₃O₄ spinel exhibits a high activity as an oxygen evolution catalyst. In this paper, we demonstrate that the photocatalytic oxygen evolution activity of Co₃O₄ spinel can be further enhanced by substituting cobalt with manganese in the spinel structure. Using a facile hydrothermal approach, we have successfully synthesized pure, Mn-substituted, and Ni-substituted Co₃O₄ nanoparticles with a typical particle size of 5–7 nm. The morphologies and crystal structures of the as-synthesized nanoparticle catalysts have been carefully examined using various structural characterization techniques, including PXRD, TEM, gas adsorption, and XAS. The photocatalytic activities of as-made nanoparticles have been investigated using a well-studied visible light driven [Ru(bpy)₃]²⁺-persulfate system. In both Clark electrode and reactor/GC systems, Mn-substituted Co₃O₄ nanoparticles exhibited the highest TOF among all the three catalysts. The data presented in this paper suggest that the photocatalytic water oxidation activity of Co₃O₄ spinel catalyst could be further enhanced by Mn^{3,1+} substitution at the octahedral sites.

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1. Introduction

The future of green and sustainable energy depends on the capability to store energy in a cheap and efficient way, because the energy generation from renewable and sustainable sources (e.g. solar panels, biomass, wind, and wave energy) is intermittent [1–5]. Liquid fuel is an ideal medium for energy storage, because it is easy to store and use in the current infrastructure [5]. In the past decades, many approaches have been proposed to produce fuels from water and carbon dioxide using sunlight as the energy source [6–10]. A range of methods, including solar thermal, photoelectrochemical, and photochemical approaches, have been proposed to produce solar fuel efficiently and economically [3,4,11–13]. Regardless of which approach is used, catalytic oxygen evolution from water is the critical reaction, because it provides electrons and protons for solar fuel production through either hydrogen evolution and/or proton-assisted CO₂ reduction to hydrocarbons [5,14–19]. In order to produce solar fuel on a terawatt scale, photon-assisted water oxidation is the only way to generate a sufficient source of protons and electrons. Compared to the reduction half reaction, visible light assisted oxygen evolution from water has slow kinetics and requires large overpotentials. Therefore, an efficient oxygen

evolution catalyst is essential to enhance the reaction rate and/or lower the overpotential for complete solar fuel production.

Many efforts toward this goal have recently been made with catalysts made of abundant first-row transition metals [20–27]. Among all the catalysts, cobalt-based materials exhibited high activities for the water oxidation reaction through photocatalytic approaches [23,25,28–34]. In 2009, we reported the first example of Co₃O₄ nanoclusters supported in mesoporous silica SBA-15, which exhibited a high activity in visible-light-driven water oxidation reaction [30]. Following that work, a few other nanostructured cobalt based oxides have been reported to be efficient oxygen evolution catalysts. For example, Dismukes and his co-workers demonstrated that Li₂Co₂O₄ with a spinel structure is a highly efficient water oxidation catalyst [32]. A turnover frequency (TOF) of $1 \times 10^{-3} \text{ s}^{-1}$ per cobalt was observed, which is similar to the TOF of Co₃O₄ nanoclusters supported in mesoporous silica. Another report by Wang et al. described a successful synthesis of Co₃O₄ nanoparticles with tunable particle size and showed that Co₃O₄ nanoparticles are much more active than other cobalt catalysts in photochemical and electrochemical water oxidation [35]. Although these works suggest that cobalt oxide with a spinel structure shows a unique property in photocatalytic water oxidation, the origin of the high oxygen evolution activity in the Co₃O₄ spinel remains unknown. A better understanding of the spinel oxygen evolution catalyst is crucial for us in order to rationally design more efficient water oxidation catalysts.

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We recently synthesized a series of mesoporous metal-substituted Co_3O_4 catalysts using a hard-templating method and investigated their photocatalytic properties for water oxidation [36,37]. The results show that both Ni- and Mn-substituted Co_3O_4 (denoted as Ni- Co_3O_4 and Mn- Co_3O_4 , respectively) exhibited lower activities than that of pure Co_3O_4 spinel. The origin of the decrease in oxygen evolution activity has been explored by X-ray absorption spectroscopy (XAS) analysis. We found that Ni/Mn dopants preferentially occupied octahedral sites and have an average oxidation state much higher than 3+. Because of their high oxidation states, Ni and Mn cations bind too strongly to oxygen (compared to Co^{3+}), leading to poor activities in oxygen evolution [37]. We suspect that by reducing the oxidation state of Ni/Mn to 3+ it is possible to obtain oxygen evolution catalysts with higher activities than pure Co_3O_4 . In this paper, we synthesized Co_3O_4 , Mn- Co_3O_4 , and Ni- Co_3O_4 nanoparticles using a hydrothermal approach and found that $\text{Mn}^{3.1+}$ substitution could further enhance photocatalytic oxygen evolution activity of Co_3O_4 .

2. Experimental

2.1. Synthesis of spinel nanoparticle catalysts

To synthesize Co_3O_4 , Mn- Co_3O_4 , and Ni- Co_3O_4 nanoparticles, a straightforward hydrothermal method was adapted from Dong et al.'s work [38]. In a typical procedure, a Co-containing slurry was obtained by adding 0.50 g of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (2 mmol) into a mixed solvent (2 mL water and 23 mL ethanol) in a 40 mL Teflon liner. A 2.5 mL aqueous solution of ammonia (25wt.%) was added under stirring. The suspension was continuously stirred for 10 min, until a brownish-gray slurry was formed. Then, the liner containing the suspension was carefully sealed in an autoclave and held at 150 °C for 3 h. After the autoclave was cooled down to room temperature in air, the product was collected by washing with DI water via centrifugation–redispersion and drying at 60 °C for 4 h. For M- Co_3O_4 nanoparticles, proper amounts of $\text{M}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (molar ratio = 1:2) were used, maintaining a total amount of 2 mmol salts. The final compositions of metal-substituted Co_3O_4 were determined by ICP-OES analysis.

2.2. Structural characterization

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analysis was carried out in the Soil Lab at the University of Delaware. Powder X-Ray Diffraction (PXRD) analysis was performed with a PANalytical X'Pert X-ray diffractometer using $\text{Cu K}\alpha$ radiation. Transmission electron microscopy (TEM) was carried out with a JEOL JEM-2010F field-emission transmission electron microscope, using an accelerating voltage of 200 kV. Surface area measurements were performed using an isothermal nitrogen adsorption/desorption instrument at 77 K. FT-IR analysis was done by an Alpha-T spectrometer and the OPUS spectroscopic software. X-ray absorption experiments were carried out through the user program at beamline X10c at the National Synchrotron Light Source (NSLS) in Brookhaven National Laboratory (BNL). And the XAS data were analyzed using the free software IFEFFIT package (version 1.2.11, released on August 11, 2008), including Athena and Artemis.

2.3. Photocatalytic oxygen evolution from water

Photocatalytic oxygen evolution activities were measured at room temperature using reactor–gas chromatography (GC) and Clark electrode systems. The Clark electrode system was able to access the activity at shorter time scales (1 min) while the reactor–GC set-up was able to measure activity at much longer

time scales (30 min). A well-studied $[\text{Ru}(\text{bpy})_3]^{2+}$ -persulfate system was used to drive the thermodynamically uphill reaction. In both the Clark electrode and reactor–GC experiments, an aqueous Na_2SiF_6 – NaHCO_3 buffer with a pH value of 5.8 was used to control the pH of the system. In the Clark electrode system, 1.0 mg of catalyst, 2.5 mg of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$, 7.1 mg of $\text{Na}_2\text{S}_2\text{O}_8$, and 21.5 mg of Na_2SO_4 were mixed in 2.2 mL of buffer. The mixture was then purged with nitrogen gas until virtually no oxygen was present. Oxygen concentration was then measured for several minutes to establish a base-line level of oxygen. The Clark electrode system was then exposed to a 300 W Xe research lamp (UV fused silica, 1.3 in collimated, F/1, 1.5 in.) with a 400 nm cut-off filter. During exposure to light, the oxygen concentration was monitored for at least 1 min.

In the reactor GC system, scaled-up amounts of sensitizer, buffer, electrolyte, and electron acceptor were used. This corresponds to 40 mL of aqueous Na_2SiF_6 – NaHCO_3 buffer, 390 mg Na_2SO_4 , 130 mg $\text{Na}_2\text{S}_2\text{O}_8$, and 45 mg $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$. 5 mg of catalyst were used, instead of a scaled up 18 mg, after it was determined that large amounts of catalysts affect the ability of the sensitizer to absorb photons. Several optimization and control experiments were also performed to prove that cobalt catalysts are responsible for the observed oxygen evolution activity. After loading the reactor with proper amounts of reactants, the system was then purged with helium for 10–20 min. Similar to the Clark electrode system, the reactor was then irradiated with a 300 W Xe research lamp with a 400 nm cut-off filter. GC measurements of the headspace after 15 and 30 min of illumination were measured by a Shimadzu GC system (Shimadzu 2014). In order to properly calculate the oxygen produced in the reactor–GC system, oxygen dissolved in the liquid phase of reactor must be accounted for (40 mL of 127 mL reactor). We assume that the concentration of oxygen in the liquid phase is 4 mg/L (i.e. half of the oxygen concentration in water at room temperature).

3. Results and discussion

We first confirmed the compositions of Co_3O_4 , Mn- Co_3O_4 , and Ni- Co_3O_4 nanoparticles using chemical analysis using ICP-OES, and the ratios of Mn/Ni to Co are shown in Table 1. Although the initial ratios of metal precursors are the same ($\text{M}/\text{Co}=0.5$), the amounts of Co that are substituted by Mn/Ni are very different. This difference in atomic ratios might be due to the hydrothermal synthetic conditions. N_2 adsorption–desorption measurements were also performed to obtain the surface areas of as-prepared nanoparticles, and their surface areas were estimated using the Brunauer, Emmett and Teller (BET) method (Table 1). It is evident that all three nanoparticle catalysts have an almost identical surface area, which allows us to decouple the surface area effect in studying water oxidation activities of as-made catalysts.

The morphology of as-made nanoparticles was examined using transmission electron microscopy (TEM). Typical low magnification TEM images are shown in Fig. 1a–c and near-monodispersed spherical particles were clearly observed in all three samples. By examining many particles, an average particle size for each nanoparticle sample was estimated (Table 1). Particle size distributions for all the three samples can be found in the supporting information (Fig. S1). Turning to the atomic structure, three nanoparticle materials were examined by high resolution TEM (HRTEM) first. The HRTEM images (Fig. 1d–f) show clearly lattice fringes in all the as-made catalysts, indicating their highly crystalline nature. The distances between fringes measured from the HRTEM images are consistent with the d -spacings of [1 1 1] and [2 2 0] of a typical Co_3O_4 spinel structure, suggesting that the three as-made nanoparticle samples have a spinel-type crystal structure.

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