Efficient Noble Metal-Free (Electro)Catalysis of Water and Alcohol Oxidations by Zinc–Cobalt Layered Double Hydroxide

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S *Supporting Information*

ABSTRACT: Replacing rare and expensive noble metal catalysts with inexpensive and earth-abundant ones for various renewable energy-related chemical processes as well as for production of high value chemicals is one of the major goals of sustainable chemistry. Herein we show that a bimetallic Zn–Co layered double hydroxide (Zn–Co–LDH) can serve as an efficient electrocatalyst and catalyst for water and alcohol oxidation, respectively. In the electrochemical water oxidation, the material exhibits a lower overpotential, by ~100 mV, than monometallic Co-based solid-state materials (e.g., $Co(OH)_2$ and Co_3O_4)-catalytic systems that were recently reported to be effective for this reaction. Moreover, the material's turnover frequency (TOF) per Co atoms is >10 times as high as those of the latter at the same applied potentials. The Zn–Co–LDH also catalyzes oxidation of alcohols to the corresponding aldehydes or ketones at relatively low temperature, with moderate to high conversion and excellent selectivity.

Figure 1. (A) OEC active site of PS II (PS II-OEC site). (B,C) Structural models for synthetic WOCs possessing a M_4O_4 cubane-type topology (B) and an edge-shared octahedral topology (C).

The search for sustainable chemical processes has never been more important than it is today in light of current dwindling nonrenewable energy resources such as petroleum and, more importantly, their unabated negative environmental impacts. This is happening also at a time when we continue to rely on noble metal catalysts to carry out a range of chemical processes that are important to our daily life, e.g., the chemical reactions we use for conversion of fossil fuels into transportation fuels and other value-added chemical products.[1] Despite their high efficiency, the widespread use of noble metals as catalysts is limited by their high cost and scarcity in nature. Thus, it is highly desirable to find suitable alternatives to noble metal catalysts that are composed of inexpensive and earth-abundant elements and possess good catalytic activity and selectivity for renewable energy applications, synthesis of various valuable chemical products, and so on.

As we search for or develop such catalysts, it is vital to take lessons from "mother nature" where earth-abundant and non-noble metal-based catalysts are ubiquitous and/or known to effectively catalyze a number of biological processes for millions of years. Among such processes in which non-noble metals play important catalytic roles, oxidation is unarguably one of the most notable and important ones. This includes the biocatalytic

oxidation of water into molecular oxygen in Photosystem II (PS II), which is carried out with the help of a Mn_4O_4Ca cubane-type cluster (Figure 1A) serving as the oxygen evolving catalytic (OEC) site.[2] This reaction is what makes photosynthesis possible, thereby allowing many biological systems to produce the chemical energy they require from water and carbon dioxide in presence of sunlight.

Inspired by PS II, researchers have been exploring synthetic approaches for making catalytic systems for energy conversion processes, and their efforts have already led to numerous promising synthetic water-oxidation catalysts (WOCs) for transformation of light/electrical energy into chemical energy/bonds (e.g., water splitting).[3] While noble-metal based oxide materials such as IrO_2 and RuO_2 have been found to be effective WOCs over the past few years,[4] the development of non-noble metal (e.g., Mn and Co) based WOCs is more appealing due to the high natural abundance of the metals in the latter. Of particular interest are those that can mimic the active site of PS II, such as M_4O_4 cubanes (M = Mn or Co,[5a,b] Figure 1B) and polyoxometallate (POM-)stabilized Co-oxide clusters.[5c] Thanks to some of the recent research works in this area, there are now a number of examples of such noble-metal free WOCs possessing a M_4O_4 topology, analogous to the active site of PS II (e.g., Co_3O_4,[6] λ-MnO_2,[7] and $Li_2Co_2O_4$[8]). Interestingly, some noble metal-free oxides without a M_4O_4 topology, but with catalytic activity toward water oxidation, have also been reported (e.g., Co-based perovskites,[9] Co-aluminophosphate,[10] α-Mn_2O_3,[11] $CaMn_2O_4 \cdot xH_2O$,[12] $Mn_3O_4/CoSe_2$,[13] Co–Mn–Ga spinel oxide,[14] and MnO_2[15]).

In addition to the strides made in the synthesis of bioinspired WOCs, the *in situ* formation of a class of cobalt-based WOCs (e.g., CoO_x/PO_4) from Co(II) ions in buffer solutions during
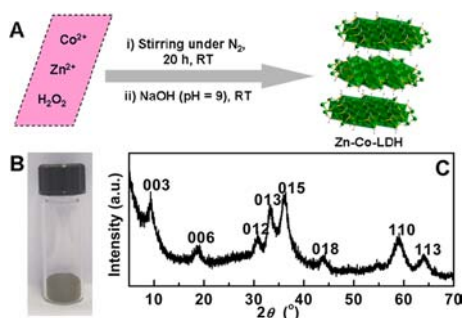
Figure 2. (A) Schematic illustration of the synthesis and structure of Zn−Co−LDH. The interlayer anions and H_2O molecules are not shown for clarity. (B) Digital image and (C) XRD pattern of Zn-Co−LDH.

Figure 3. (A) LSV curves in 0.1 M KOH solution with no catalyst (blank GCE) and with ZnO, Zn−OH, Co_3O_4, Co−OH, and Zn−Co−LDH as the electrocatalyst. (B) A current−time curve obtained for water oxidation reaction in the presence of Zn−Co−LDH at 0.83 V vs NHE. (C) LSV curves obtained with as-prepared Zn−Co−LDH, before recycling, (olive curve) and 10 h after use under the current−time measurement shown in Figure 3B (black curve). (D) A plot of TOFs with respect to Co atoms of Co_3O_4, Co−OH, and Zn−Co−LDH at different overpotentials vs applied potential (green: LDH, pink: Co−OH, blue: Co_3O_4). The sample loading on the GCE was 0.28 mg/cm^2 in all the cases.

electrochemical water oxidation was recently reported.[3b,16] Although the resulting materials were shown to have efficient electrocatalytic activity for water oxidation, their chemical structures remained controversial. Whereas some researchers proposed that these materials possessed a disordered network of interconnected Co-oxo cubanes (Figure 1B),[17] others claimed that the materials were composed of stacked sheets of edge-shared octahedra as shown in Figure 1C, with a structure similar to those of layered double hydroxides (LDHs).[16c,18] These ongoing debates on the structures of these materials, coupled with their good catalytic activity toward water oxidation, prompted us to explore the potential electrocatalytic activity of neat LDH materials themselves for water oxidation.

LDHs are a class of layered materials with positively charged layers and charge-balancing anions located in the interlayer region, and they are represented by the formula $[M^{z+}_{1−x}M^{3+}_x(OH)_2]^{q+}(X^{n−})_{q/n}\cdot yH_2O$, where Z = 2 is the most common, although LDHs with Z = 1 are also known.[19,20] Although LDHs with a few different types of compositions were applied for *photocatalytic* water oxidation in the presence of sacrificial metal ions,[20a,b] under these conditions the sacrificial metal ions undergo concomitant reduction, forming metal deposits on the LDHs, thereby compromising the LDHs' catalytic activity and reusability. Moreover, despite LDHs have been used as support material for noble metal-based oxidation catalysts,[20c] they have never been shown to catalyze oxidations on their own.

Herein we report that a Zn− and Co−based LDH, dubbed Zn−Co−LDH, shows efficient electrocatalytic activity toward water oxidation and selective catalytic activity toward alcohol oxidations. To the best of our knowledge, this is the first time that a pure LDH material (without a secondary phase, e.g., a metal hydroxide) or a Zn-based LDH material is shown to have *electrocatalytic* activity for water oxidation and *intrinsic catalytic activity* for selective alcohol oxidations. Notably also, the material exhibited these catalytic activities without any sacrificial agent and noble metal, respectively.

The Zn−Co−LDH was synthesized *via* a simple coprecipitation reaction at rt (see Supporting Information, SI, for details).[21,22] As shown in Figure 2A, Zn^{2+} and Co^{2+} ions (from $ZnSO_4\cdot7H_2O$ and $CoSO_4\cdot7H_2O$, respectively) and H_2O_2 (as an oxidant) were used for the synthesis. After mixing Zn^{2+} and Co^{2+} ions and H_2O_2, the pH of the solution was increased to ∼9.0 with aqueous NaOH solution. This finally led to the formation of a violet precipitate (Figure 2B), which is, Zn−Co−LDH. The yield of the as-obtained Zn−Co−LDH was ∼100% based on the amount of metals used. The violet color was indicative of the presence of a large density of Co^{3+} ions in the material. Further
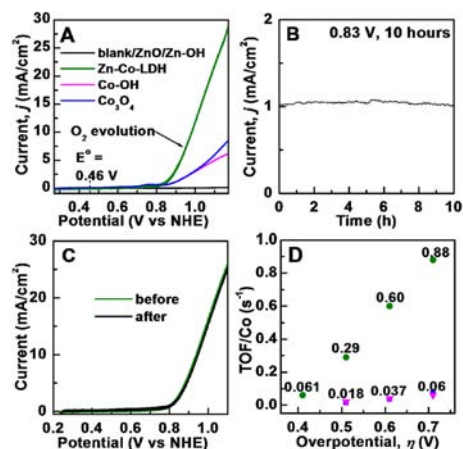
investigation using iodometric redox titration revealed that the ratio of Co^{3+} to Co^{2+} in the material was ∼1:1. ICP-MS showed that the Co to Zn ratio in the material was ∼1:1. The material was characterized further by XRD (Figure 2C) and FT-IR spectroscopy (Figure S1), which confirmed that the Zn−Co−LDH possessed a brucite-type layered structure,[22] with sulfate ions and water molecules located within its interlayer regions. Two more materials were synthesized by using only Co^{2+} or Zn^{2+} ions under otherwise similar synthetic conditions. The resulting monometallic materials were denoted here as Co−OH and Zn−OH, respectively. In addition, Co_3O_4 and ZnO were also synthesized by calcination of Co−OH and Zn−OH, respectively. These four materials were used for control experiments (see below and SI for details).

The catalytic activity of Zn−Co−LDH toward water oxidation was measured using a typical three-electrode system in 0.1 M (pH = 13.0) KOH solution, in which a glassy carbon electrode (GCE) modified with the samples was used as the working electrode (see SI for details). For comparison purposes, the catalytic activities of Co−OH, Zn−OH, Co_3O_4, and ZnO were also measured under the same conditions while keeping the same weight of samples on the GCE (0.28 mg/cm^2) in each case. It is worth noting here that Co_3O_4 was particularly included as a reference material for evaluating the catalytic performance of Zn−Co−LDH since it was previously shown to be an excellent WOC in basic media.[6]

Figure 3A shows linear sweep voltammetry (LSV) curves of all the samples. As expected, the catalytic activities of Zn−OH and ZnO were almost similar to that of the blank GCE (having no sample), and in all of these cases no current was produced even when the potential was increased to 1.2 V vs NHE. This indicates that these two monometallic Zn-based samples possess no catalytic activity toward water oxidation or Zn in these materials does not serve as catalytic active site for this reaction. In contrast to the monometallic Zn-based materials, all of the Co-containing materials gave current associated with O_2 evolution from the

water oxidation reaction at relatively low potentials. The formation of O_2 in these reactions was further confirmed by gas chromatography. For Zn−Co−LDH, the onset potential for O_2 evolution was *ca.* 0.8 V (*i.e.*, an overpotential (η) = 0.34 V), which is lower (and hence better) than those of Co_3O_4 and Co−OH, whose onset potentials and overpotentials were found to be ≈ 0.9 V and $\eta ≈ 0.44$ V, respectively. This means, the catalytic activity toward water oxidation of the Co-containing materials increased in the order Co−OH ≈ Co_3O_4 ≪ Zn−Co−LDH. For example, at 1.0 V, the current densities (a measure of catalytic activity) of Co−OH, Co_3O_4, and Zn−Co−LDH were 2.88, 2.90, and 11.6 mA/cm^2, respectively. Hence, the activity of Zn−Co−LDH can be said to be ∼4 times higher than those of Co_3O_4 and Co−OH.

Figure 3B depicts the current−time curve of the Zn−Co−LDH-catalyzed water oxidation reaction over 10 h at 0.83 V at pH=13. The result revealed that Zn−Co−LDH retained its catalytic activity over this time. This was further confirmed by LSV, which showed that the Zn−Co−LDH afforded almost a similar LSV curve after 10 h reaction time as before (Figure 3C). Overall, these results indicate that Zn−Co−LDH has excellent stability as electrocatalyst in water oxidation at pH 13.0. Moreover, the total turnover number (TON) (calculated with respect to the total moles of cobalt in Zn−Co−LDH) after 10 h was found to be >1250, suggesting that the O_2 evolution was a result of the catalytic process, rather than a simple stoichiometric chemical reaction.

To further assess the catalytic activities of the three cobalt-containing materials, their turnover frequencies (TOFs) at different overpotentials were calculated and plotted as a function of overpotential (Figure 3D). TOFs were calculated based on the assumption that all the Co ions present in the material were catalytically active (this method was also used previously[16a]). The as-obtained TOFs might be a gross underestimation of the real TOFs of active sites though, because not every Co in the material may be catalytically accessible or active. Nevertheless, Zn−Co−LDH exhibits a linear increase in TOF with over-potential, affording much higher TOFs than both Co_3O_4 and Co−OH. For instance, at an overpotential of 0.71 V, the TOF of Zn−Co−LDH (0.88 s^{-1}) is more than 10 times as high as those of Co_3O_4 (0.07 s^{-1}) and Co−OH (0.06 s^{-1}). Also noteworthy, the TOF of Zn−Co−LDH is ∼6.1×10^{-2} s^{-1} at an overpotential of 0.41 V whereas the TOF of the previously reported amorphous Co-based WOC (CoO_x/PO_4), whose structure was suggested to be LDH, is only 2×10^{-3} s^{-1} at the same overpotential.[3b,16a]
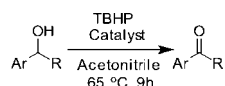
The above results also clearly suggest that Co is mainly responsible for the Zn−Co−LDH's catalytic activity toward water oxidation, with Zn rendering structural support and/or providing cooperative effects. Thus, the mechanism by which Zn−Co−LDH catalyzes the water oxidation reaction can be expected to be similar to those proposed for other analogous Co-based WOCs, such as Co_3O_4 and CoO_x/PO_4. In the latter cases, mechanistic studies suggested that the water oxidation reaction involve proton-coupled electron transfer (PCET) processes, in which the key step is the proton-coupled one-electron conversion of Co^{III}−OH to Co^{IV}−O, prior to O_2 evolution.[5c,6,16a,c] Despite the strong resemblance among the catalytic sites (and possibly their mechanisms too) of these materials, Zn−Co−LDH exhibits the highest electrocatalytic activity toward water oxidation. Moreover, the trend in the catalytic activity of the materials does not correlate with the materials' surface areas, as the BET surface area of Zn−Co−LDH is 8.2 m^2/

g and that of Co_3O_4 is 23.4 m^2/g (as obtained by N_2 adsorption/desorption measurements). Therefore, the most plausible explanation that can support the observed trends in catalytic activity should be the inherent structural differences between the two types of materials. In contrast to Co_3O_4, which possesses a dense structure, Zn−Co−LDH has a layered and relatively open structure. This may, result in more accessible electrocatalytically active Co sites, fast diffusion of reactants/products, and even rapid PCET in Zn−Co−LDH, ultimately rendering it enhanced electrocatalytic activity toward water oxidation. The rapid electron transfer (ET) and faster water oxidation reaction kinetics in the presence of Zn−Co−LDH were confirmed by electrochemical impedance measurements (Figure S2), which showed a much lower Faradaic impedance for Zn−Co−LDH than Co_3O_4. In addition, the bimetallic Zn−Co−LDH material gave a reduced overpotential for water oxidation, by ∼100 mV, compared with monometallic Co-based materials. This suggests that, despite playing no role as an active catalytic site, the redox-inactive Zn^{2+} ions in Zn−Co−LDH might still play some roles by assisting the reacting species in accessing the highly oxidized Co ions in the material, thereby allowing to undergo the catalytic reactions more efficiently. This argument is also based on recent reports of an analogous catalyst, $[Mn_3CaO_4]^{6+}$, in which redox-inactive Ca^{2+} ions were suggested to enhance the catalytic activity of the material by facilitating the formation of higher oxidation Mn sites in it.[22] Similarly, the redox inactive Ca^{2+} or Sc^{3+} ions were suggested to provide stability and improved ET pathways to high-valent Fe-oxo species during catalysis.[23]

In addition to electrocatalysis, we also investigated the catalytic properties of Zn−Co−LDH toward conventional chemical oxidation reactions. The study was primarily intended to explore the structural advantages of Zn−Co−LDH in simple catalytic oxidation reactions. As a model system, chemical oxidation of benzyl alcohols was used. Besides its simplicity and importance in fine chemical industries, the reaction was chosen because there is a considerable literature for comparing our results with.[24] All the reactions were carried out at 65 °C in acetonitrile as solvent with 1 mmol of substrate (See SI for detailed procedure). When the monometallic Zn-based materials (Zn−OH and ZnO) were used as catalyst, in the presence of TBHP, similar conversions to the uncatalyzed reaction were obtained. This, indicates that Zn^{2+} is again unable to catalyze simple oxidation reactions on its own. Yet, Zn−Co−LDH along with TBHP catalyzed the reactions, with a rate directly dependent on TBHP's concentration (Figures S3, S4). Similarly, under the same reaction conditions, Co−OH and Co_3O_4 catalyzed the oxidation reactions of benzyl alcohols, but with lower catalytic activity than Zn−Co−LDH. The relative catalytic activities of Co−OH and Co_3O_4 toward benzyl alcohol oxidation remained similar to their relative electrocatalytic activities toward water oxidation though. The catalytic performance of the physical mixture of Zn−OH and Co−OH (or ZnO and Co_3O_4) followed the reactivity trend obtained for their respective pure Co-based systems. All these results suggest the importance of the bimetallic LDH skeleton in catalysis and support our hypothesis that Zn^{2+}, in spite of being relatively inactive in the catalytic process, offers unique synergistic effect in the catalytic system (possibly by assisting the interactions between the reactants and the catalyst), yielding improved catalytic activity.

The recyclability of the Zn−Co−LDH catalyst was assessed in the catalytic reactions of benzyl alcohols (Figure S5). The result indicated that the catalyst did not show any obvious loss of catalytic activity and selectivity after 3 cycles. The microstructure

Table 1. Zn−Co−LDH Catalyzed Oxidation of Benzylic Alcohol(s) with TBHP as Oxidant[a]

Entry	-Ar	-R	Cat.	Conv. (%)[b]	Sel. (%)[b]
1	(phenyl)	-H	Zn-Co-LDH	72	90
2	(O₂N-C₆H₄-)	"	"	~100	90
3	(MeO-C₆H₄-)	"	"	60	100
4[c]	(phenyl)	-Me	"	~100	~100

[a]1 mmol of substrate, ~5 equiv of TBHP, and 2.5 mol % of the catalyst (based on Co) were used. [b]Based on GC. [c]6 h.

of the catalyst also remained intact after 3 cycles of reactions, as evident from its XRD pattern (Figure S6). In addition, leaching tests showed no detectable leached metallic species in the reaction mixture (Figure S7).

The substrate scope of Zn−Co−LDH with different benzylic alcohols was also explored (Table 1). Among different benzylic alcohols, the one with electron-withdrawing −NO₂ group at the *para* position showed the highest reactivity (entry 2), followed by the unsubstituted benzyl alcohol and the one with the electron donating methoxy group at the para position (entries 1 and 3 respectively). Additionally Zn−Co−LDH catalyzed the oxidation of a secondary alcohol at a faster rate than benzyl alcohol; e.g., while the yield was ~100% in 6 h for the former (entry 4), the yield was only 72% in the same time period for the latter.

In summary, Zn−Co layered double hydroxide is shown to have efficient catalytic activities toward water/alcohol oxidations. Although the Zn species in the material shows no catalytic activity for the oxidation reactions, its presence is clearly shown to play an essential role in the Zn−Co−LDH's efficient catalytic activity. The results presented herein can be anticipated to give a fresh impetus to the rational design of other bi- or multimetallic materials with earth-abundant elements for catalysis and electrocatalysis applications.

ASSOCIATED CONTENT

ⓈSupporting Information

Experimental details and supporting results. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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