Photochemical Water Oxidation in a Buffered Tris(2,2′-bipyridyl)ruthenium–Persulfate System Using Iron(III)-Modified Potassium Manganese Oxides as Catalysts

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Supporting Information

ABSTRACT: Study of manganese oxides for electrocatalytic and photocatalytic oxidation of water is an active area of research. The starting material in this study is a high-surface-area disordered birnessite-like material with K⁺ in the interlayers (KMnOₓ). Upon ion-exchange with Fe³⁺, the disordered layer structure collapses (Fe(IE)MnOₓ), and the surface area is slightly increased. Structural analysis of the Fe(IE)MnOₓ included examination of its morphology, crystal structure, vibrational spectra, and manganese oxidation states. Using the Ru(bpy)₃²⁺−persulfate system, the dissolved and headspace oxygen upon visible light photolysis with highly dispersed Fe(IE)MnOₓ was measured. The photocatalytic activity for O₂ evolution of the Fe(IE)MnOₓ was three times better than KMnOₓ, with the highest rate being 9.3 mmolO₂ molMn⁻¹ s⁻¹. The improvement of the photocatalytic activity was proposed to arise from the increased disorder and interaction of Fe³⁺ with the MnO₆ octahedra. As a benchmark, colloidal IrO₂ was a better photocatalyst by a factor of ~75 over Fe(IE)MnOₓ.

INTRODUCTION

Photocatalytic water splitting with solar energy to produce hydrogen and oxygen is of current interest. In this process, the water oxidation couple is more challenging because of unfavorable thermodynamics and kinetics. Rare metal oxides, including IrO₂ and RuO₂, are very good catalysts for water oxidation, as demonstrated with the tris(2,2′-bipyridyl)-ruthenium–persulfate system, but they are not practical for large-scale use because of their limited occurrence in nature. Considerable research has, therefore, focused on the first-row transition metals, including Mn, Co, Ni, and Fe, because of their high natural abundance. The oxides and hydroxides of these metals exhibit both electrocatalytic and photocatalytic activity. Other well-studied water oxidation systems include photoelectrochemical organic species, inorganic oxides with appropriate band gaps, and polymeric photocatalysts.

Stemming from the presence of the manganese oxide cluster for water oxidation in photosystem II of natural photosynthesis, considerable research has focused on manganese oxides. Different crystalline polymorphs of manganese oxides exhibit photocatalytic activity. Structural aspects such as elongated, flexible, and weaker MnO₆−O bonds (Jahn–Teller distortion) found in edge-sharing MnO₆ octahedra in manganese oxides are correlated with catalytic properties. Amorphous manganese oxides are also water-oxidizing catalysts, and the importance of a disordered structure in promoting oxygen mobility was noted. The disorder exposes more Mn-active sites and cationic vacancies containing unsaturated oxygens, promoting catalysis. Birnessites, layered like manganese oxide, contain ion-exchangeable hydrated cations within the interlayers. Various synthetic strategies are reported for incorporation of elements into birnessites, including ion-exchange, doping, and coating with metals. Copper was introduced into a birnessite structure by in situ method and via ion-exchange. The presence of Cu⁺ alters the electrical properties of birnessite, lowering the charge transfer resistance and promoting the catalysis. Intercalating Ni²⁺ and Co²⁺ into the birnessite interlayer also enhances electrochemical catalytic activity of birnessite as compared to cations doped into octahedral sites of the lattice. Cobalt-intercalated birnessite has been investigated as a cathode electrode material for lithium-ion batteries.

In this study, we start with a very disordered birnessite structure with K⁺ in the interlayers and ion-exchange Fe³⁺ into this material. We examine how the ion-exchange process alters the structure of KMnOₓ as well as the photocatalytic water...
oxidation activity of the ion-exchanged samples. Structural analysis involves examining the morphology, crystal structure, surface spectroscopy, and Raman spectroscopy. Photocatalytic activity was examined by measuring dissolved and headspace oxygen produced in the presence of Ru(bpy)_3^2+ and S_2O_8^2-. These iron-based modifications of KMnOx have not been examined for photocatalytic water splitting.

RESULTS

Synthesis Strategy. The synthesis strategy for KMnOx has been reported in the literature and involves mixing an aqueous solution of manganese(II)acetate and potassium permanganate to form birnessite.21 The reaction proceeds as follows:

$$3\text{Mn}^{2+} (aq) + 2\text{KMnO}_4 (aq) + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 (s) + 4\text{H}^+ (aq) + 2\text{K}^+ (aq)$$

This is a complicated multistep electron transfer reaction involving several intermediate oxidation states of manganese, in particular Mn^{3+}.30,31 Though most of the Mn^{3+} is oxidized to Mn^{4+}, some remains and is incorporated into birnessite.32 This is an autocatalytic reaction, with initial formation of birnessite follows:

$$5\text{MnO}_2 (s) + 2\text{K}^+ (aq) + 2\text{H}^+ (aq) + 2\text{O}_2 (g) \rightarrow 5\text{KMnO}_4 (s)$$

The Mn 3s splitting for KMnOx is −5.15 eV, and from the interpretation of the Mn 2p3/2 region,32,39 and are used as structural characterization. KMnOx. Elemental analysis for Mn in KMnOx was carried out with atomic absorption spectroscopy (AAS) and found to be 48% Mn (by weight) and is reported in Table 1. The electron micrograph of KMnOx shown in Figure 1a indicates aggregates of ~100 nm particles.

Table 1. Elemental Composition (wt % of Mn and Fe Determined by AAS) and BET Surface Area of KMnOx, Fe(IE)MnOx_N, and Ga(IE)MnOx (Experimental Condition Defines the Preparation Conditions)

| samples          | experimental condition | Mn (wt %) | Fe (wt %) | BET surface area (m^2/g) |
|------------------|------------------------|-----------|-----------|--------------------------|
| KMnOx            | Mn(II)acetate/KMnO4    | 48.0      |           | 212                      |
| Fe(IE)MnOx_5     | 5 mM Fe(III)           | 46.0      | 3.2       | 287                      |
| Fe(IE)MnOx_50    | 50 mM Fe(III)          | 33.0      | 8.9       | 260                      |
| Fe(IE)MnOx_200   | 200 mM Fe(III)         | 34.0      | 10.4      | 220                      |
| Fe(IE)MnOx_400   | 400 mM Fe(III)         | 33.0      | 10.2      | 256                      |
| Ga(IE)MnOx_400   | 400 mM Ga(III)         | 28.0      |           | 204                      |
AOS of Mn to be +3.4 for KMnOx. For O 1s, an example of the calculation is provided in the Supporting Information section (Table S1) and calculates a value of +3.5. The bulk AOS was determined by a chemical titration method, which involves reaction of oxalic acid with the sample and then back-titration by KMnO4,46 which determined AOS of +3.2. The AOS from the three methods averages to +3.4. The XPS-based methods provided AOS of $3.72^{−3.75}$ for a birnessite-type compound on granular activated carbon.33

Fe(IE)MnOx. Fe(IE)MnOx_5, Fe(IE)MnOx_50, Fe(IE)-MnOx_200, and Fe(IE)MnOx_400 contain Mn (wt %) of 46.0, 33.0, 34.0, and 33.0 and Fe (wt %) of 3.2, 8.9, 10.4, and 10.2, respectively (Table 1). The electron micrographs of these samples shown in Figure 2 are similar to KMnOx (Figure 1a), consisting of aggregates of primary particles ($\sim$100 nm), and readily dispersed in aqueous solution by sonication. The surface areas of Fe(IE)MnOx_5, Fe(IE)MnOx_50, Fe(IE)-MnOx_200, and Fe(IE)MnOx_400 were 287, 260, 220, and 256 m²/g, respectively.

Powder diffraction of the Fe(IE)MnOx shown in Figure 3 consists of broad peaks at $\sim$37° (100) and $\sim$66° (110). The basal peaks at $\sim$12° and $\sim$24° present in KMnOx were absent in all samples, indicative of a structure in which there is random stratification of the layers and possibly stacking of only a few layers. Such XRD patterns have been reported in the literature.47−49 For example, the XRD pattern similar to Figure 3 with the absence of basal reflections was observed in the early stages of birnessite formation before the sheets had an opportunity to stack up along the c axis.47 In another study, with increasing Al3+ and Fe3+ introduced during the synthesis of birnessite, the basal reflections disappeared.48 Also, manganese oxide nanoparticles synthesized on polystyrene spheres only showed the $h\bar{l}$ peaks and assigned to ultrathin stacks of very few lamellae.49

The Raman spectra and the curve deconvolution for Fe(IE)MnOx samples are shown in Figure 4. The major

Table 2. Relevant Parameters from XPS Data

| samples                  | Mn 2p\textsubscript{3/2} BE (eV) | Mn 2p\textsubscript{1/2} BE (eV) | Mn AOS (3s) | Mn AOS (O 1s) |
|--------------------------|---------------------------------|---------------------------------|-------------|---------------|
| KMnOx                    | 642.09                          | 653.81                          | +3.4        | +3.5          |
| Fe(IE)MnOx\_5            | 641.88                          | 653.61                          | +3.3        | +3.4          |
| Fe(IE)MnOx\_50           | 642.15                          | 653.79                          | +3.3        | +3.4          |
| Fe(IE)MnOx\_200          | 642.17                          | 653.78                          | +3.3        | +3.4          |
| Fe(IE)MnOx\_400          | 641.95                          | 653.76                          | +3.4        | +3.4          |
| Ga(IE)MnOx\_400          | 642.41                          | 654.15                          | +3.5        | +3.4          |

Figure 1. (a) SEM micrograph of KMnOx, (b) XRD pattern of KMnOx (stick spectrum is the standard pattern for natural birnessite from the MINDAT database), (c) Raman spectrum of KMnOx (excitation line—$\sim$785 nm), and (d) Mn 2p XPS spectrum of KMnOx [Mn 2p\textsubscript{3/2} peak at 642 eV with shoulders at $\sim$640 and $\sim$643 eV (marked by arrows)].

Figure 2. SEM micrograph of Fe(IE)MnOx\_N samples, with N being (a) 5, (b) 50, (c) 200, and (d) 400.
Raman bands at 287, 506, 573, 640, and 730 cm$^{-1}$ matched with KMnO$_x$, indicating that the MnO$_6$ octahedral structure is being maintained. For samples Fe(IE)MnO$_x$$_{50}$, Fe(IE)-MnO$_x$$_{200}$, and Fe(IE)MnO$_x$$_{400}$, the weak shoulder at $\sim$700 cm$^{-1}$ is observed upon deconvolution and is assigned to ferrihydrite. Typically, ferrihydrite also shows a sharp nitrate Raman band at 1046 cm$^{-1}$, and is not discernible. With the increase in Fe$^{3+}$ content during ion-exchange, the ferrihydrite band remains weak and does not increase in intensity.

XPS data in the K 2p region for the Fe(IE)MnO$_x$ samples are shown in Figure 5. The Fe(IE)MnO$_x$$_{5}$ sample exhibited weak K 2p peaks. In case of other Fe(IE)MnO$_x$ samples, the K$^+$ signal was absent, indicating that K$^+$ is replaced by Fe$^{3+}$ cations. XPS in the Mn 2p region is similar to KMnO$_x$, and suggests that the mixture of Mn$^{3+}$/Mn$^{4+}$ species is remaining unchanged with ion exchange (Figure S3). XPS of the Mn 3s region is shown in Figure S4. The peak because of Fe 3s (94 eV) was observed along with the Mn 3s peak, and the intensity of the Fe peak increased with the increase in the concentration of Fe in the samples. All samples also exhibited peaks at $\sim$710, $\sim$724 eV, and a satellite peak at $\sim$719 eV in the Fe 2p region, indicating the presence of Fe$^{3+}$ cations (Figure S5). From XPS, the ratio of atomic concentration of Fe and Mn (Fe/Mn) was 0.04, 0.15, 0.23, and 0.24 for Fe(IE)MnO$_x$$_{5}$, Fe(IE)-MnO$_x$$_{50}$, Fe(IE)MnO$_x$$_{200}$, and Fe(IE)MnO$_x$$_{400}$, respectively, consistent with the trend of the atomic absorption results shown in Table 1.

The O 1s region XPS spectra are shown in Figure S6, with peaks at $\sim$530 and $\sim$532 eV. Deconvolution of the peaks allows for estimating the adsorbed and bulk oxygen. The ratio of the surface-adsorbed oxygen to the oxygen in Mn–O–Mn is shown in Table S2. Increasing surface-adsorbed oxygen or hydroxyl group (O$_x$) with the introduction in Fe$^{3+}$ is evident from the O 1s XPS (Figure S6 and Table S2). The AOS calculations for Mn in Fe(IE)MnO$_x$ were carried out with Mn 3s and O 1s peaks, and data shown in Table 2, which were in the range of +3.3 to 3.5. The chemical titration method cannot be used for the iron-based compounds.

**Photocatalytic Activity.** Control experiments were carried out for blank samples (without catalyst) for photocatalytic water oxidation. As reported in the literature, there was a small amount of dissolved oxygen formation ($<0.3 \mu$mol) within the first 50 s with only Ru(bpy)$_3^{2+}$ and S$_2$O$_8^{2-}$ in the borate buffer system (Figure S7). However, there was no photocatalytic activity in the absence of Ru(bpy)$_3^{2+}$ and S$_2$O$_8^{2-}$. In addition, as the Fe(IE)MnO$_x$ is colored, we repeated the photolysis experiment with only Fe(IE)MnO$_x$ and persulfate, and no oxygen evolution was observed (shown in Figure S8.)

The catalyst amounts used in the photolysis of all samples were different as they were adjusted to the same Mn content of 1 mg. Thus, catalytic activity because of Mn can be compared between samples without any normalizing. The amount of dissolved oxygen as a function of photolysis time was measured with a fluorescence probe, similar to numerous studies reported in the literature. These experiments usually last a few minutes, and a saturated level of dissolved oxygen is reached. Headspace oxygen measurements are discussed later. Figure 6a compares the photocatalytic ability of KMnO$_x$ with...
Fe(IE)MnOx. The turnover frequency (TOF) and the total amount of dissolved oxygen are shown in Table 3.

*KMnOx*. The catalytic activity of KMnOx was $3.2 \pm 0.1 \text{ mmol}_O_2 \text{ mol}_Mn^{-1} \text{ s}^{-1}$ (experiment repeated three times with different sample aliquots of KMnOx).

*Fe(IE)MnOx*. For *Fe(IE)MnOx*$_5$, *Fe(IE)MnOx*$_{50}$, *Fe(IE)MnOx*$_{200}$, and *Fe(IE)MnOx*$_{400}$, oxygen evolution rates were $7.7 \pm 0.2$, $8.1 \pm 0.6$, $8.8 \pm 0.8$, and $9.3 \pm 0.7 \text{ mmol}_O_2 \text{ mol}_Mn^{-1} \text{ s}^{-1}$ [experiments repeated three times with different sample aliquots of Fe(IE)MnOx]. With the increase in concentration of Fe(III), the catalytic activity of Fe(IE)-MnOx keeps increasing.

Raman spectra suggested the presence of ferrihydrite in the samples. To evaluate the impact of ferrihydrite on the catalytic activity, photocatalytic water oxidation was carried out with ferrihydrite (5 mg of Fe in the sample). The catalytic activity for ferrihydrite was poor compared to the catalysts shown in Figure 6, with 2.5 μmol of total dissolved oxygen and a rate of 0.7 mmol$_O_2$ mol$_Fe^{-1} \text{ s}^{-1}$ (Figure S9). Besides the low catalytic activity of ferrihydrite, the amount of ferrihydrite in Fe(IE)-MnOx is small, and, thus, ferrihydrite is not contributing to the increased rate of oxygen evolution for Fe(IE)MnOx. Moreover, as the catalyst used in the photolysis was adjusted to the same amount as Mn (1 mg of Mn, based on the elemental analysis) in all samples, the presence of ferrihydrite should not influence the rate calculated based on the Mn.

As *Fe(IE)MnOx*$_{400}$ was the most active catalyst, reusability tests were carried out with this sample. The photolysis with *Fe(IE)MnOx*$_{400}$ was carried out for three cycles (1st, 2nd, and 3rd runs) without washing between cycles (so as not to lose catalyst). The *Fe(IE)MnOx*$_{400}$ catalyst showed repeatable performance with a TOF of $12.0 \pm 0.5$ mmol$_O_2$ mol$_Mn^{-1} \text{ s}^{-1}$ as shown in Figure 6b. After the catalysis experiments, Fe 2p and Ru 3p XPS spectra were examined for the recovered Fe(IE)MnOx$_{400}$. The ratio of Fe/Mn atomic concentration in the recovered sample was 0.22, and close to the starting Fe/Mn ratio (0.24) for this particular Fe(IE)-MnOx$_{400}$ sample (Figure S10), indicating no leaching of Fe$^{3+}$. There was no Ru found in the used catalyst, as seen from the Ru 3p XPS data (Figure S11), indicating that the decomposition of the Ru photosensitizer and deposition on the MnOx is not occurring.

Table 3. Photocatalytic Rate of KMnOx and Fe(IE)MnOx$_N$ and Ga(IE)MnOx Samples (All Samples Used in These Catalytic Experiments Contained 1 mg Mn, Done by Adjusting the Weight Based on the Mn Elemental Analysis)

| samples          | TOF (mmol$_O_2$ mol$_Mn^{-1}$ s$^{-1}$) | dissolved oxygen (μmol) |
|------------------|--------------------------------------|-------------------------|
| KMnOx            | 3.2 ± 0.1                            | 8.0                     |
| Fe(IE)MnOx$_5$   | 7.7 ± 0.2                            | 13.0                    |
| Fe(IE)MnOx$_{50}$| 8.1 ± 0.6                            | 18.0                    |
| Fe(IE)MnOx$_{200}$| 8.8 ± 0.8                           | 18.0                    |
| Fe(IE)MnOx$_{400}$| 9.3 ± 0.7                           | 20.0                    |
| Ga(IE)MnOx$_{400}$| 4.0                                  | 9.5                     |
| ferrihydrite     | 0.7                                  | 2.5                     |

For ferrihydrite was poor compared to the catalysts shown in Figure 6, with 2.5 μmol of total dissolved oxygen and a rate of 0.7 mmol$_O_2$ mol$_Fe^{-1} \text{ s}^{-1}$ (Figure S9). Besides the low catalytic activity of ferrihydrite, the amount of ferrihydrite in Fe(IE)-MnOx is small, and, thus, ferrihydrite is not contributing to the increased rate of oxygen evolution for Fe(IE)MnOx. Moreover, as the catalyst used in the photolysis was adjusted to the same amount as Mn (1 mg of Mn, based on the elemental analysis) in all samples, the presence of ferrihydrite should not influence the rate calculated based on the Mn.
chains which are stacked together, with charge-balancing K+ m2/g for Fe(IE)MnOx_400. The Raman spectra (Figure 4) surface area of KMnOx was 212 m2/g and increased to 256 increased slightly with iron incorporation, for example, the They all were aggregates of changes in morphology of Fe(IE)MnOx samples (Figure 2).

XPS indicates that K+ is missing in Fe(IE)MnOx_400, with the ionic radii are proposed to be located above and below the packing of the layers of KMnOx. Transition metals with small ionic radii are proposed to be located above and below the MnO6 octahedral vacancy in a layer separate from the water layer, where the larger K+ is expected to be located.54,55 These transitions in the XRD. The difference between Fe(IE)MnOx and KMnOx is the increased disorder in the structure. In the ion-exchanging process, Fe3+ replaces K+ cations and brings about disorder in packing of the layers of KMnOx. Transition metals with small ionic radii are proposed to be located above and below the MnO6 octahedral vacancy in a layer separate from the water layer, where the larger K+ is expected to be located.29

Manganese oxides with defects and distorted structure lead to structural flexibility and expose weak Mn3+-O bonds at the edge-sharing MnO6 octahedra, which can be involved in accumulation of the holes, proton release during catalytic cycle, and weak Jahn–Teller distorted Mn3+–O (because of the population of antibonding orbital) bonds.23 These weak and flexible Mn3+-O bonds are favorable for water oxidation because of suitable Mn–O–Mn motifs for O–O bond formation. Longer Mn–O–Mn bridges (mono μ-oxo bridges) in the manganese oxides are active sites for water oxidation, which are mainly found in the disordered structure.54,55 These sites contain unsaturated oxygen and hydroxyl groups, which can be involved in accumulation of the holes, proton release upon hole capture, and proton-coupled electron transfer necessary for water oxidation.20,22,24

The difference in the electric fields because of the higher charge to radius ratio of Fe3+ in Fe(IE)MnOx can induce disorder. This electrostatic-driven disorder could be playing a role in the better catalytic activity of Fe(IE)MnOx samples. To verify this hypothesis, Ga3+, which has similar size to Fe3+ (sizes of Ga3+ and Fe3+ are 0.61 and 0.64 nm, respectively), was ion-exchanged into KMnOx and the photocatalytic activity was examined. Gallium exchange also led to a significant loss of the basal reflections in the XRD. The amount of oxygen possible is controlled by the amount of S3O42−, which was 1600 μmol; thus, the total possible oxygen is ~800 μmol and dissolved oxygen at saturation is ~92 μmol (considering 25 °C and 1 bar pressure). The saturation of the level of dissolved oxygen well before the stoichiometric amounts of O2 are formed is typical of all studies using Ru(bpy)32+ and S3O42−.23,25,52

The main difference between Fe(IE)MnOx and KMnOx is the increased disorder in the structure. In the ion-exchanging process, Fe3+ replaces K+ cations and brings about disorder in packing of the layers of KMnOx. Transition metals with small ionic radii are proposed to be located above and below the MnO6 octahedral vacancy in a layer separate from the water layer, where the larger K+ is expected to be located.29

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catalytic activity of the Ga-exchanged sample (Ga³⁺ concentration used for ion-exchange, 400 mM) was 4.0 mmol O₂ mol⁻¹ Mn⁻¹ s⁻¹ (9.5 μmol of dissolved O₂) improved over KMnO₅, but not as high as Fe(IE)MnOₓ. The structural and catalytic characteristics of the Ga-exchanged sample are shown in Figures S12–S15. Thus, Fe³⁺ within the interlayers is inducing other effects. One possibility is the formation of oxo bridges between the manganese in the basal plane and iron in the interlayers, a motif found in ribonucleotide reductase and involved in oxygen activation chemistry.⁵⁶

Intercalation of Ni²⁺ and Co²⁺ into birnessites via ion-exchange leads to more effective electrochemical water oxidation over materials made by substituting cations in the lattice of octahedral sheets.²⁷,²⁸ A hypothesis was proposed that both Co²⁺ and Ni²⁺ can promote interlayer water ordering that is facilitating the electron transfer process necessary for the catalysis. With intercalated Cu cations, binding to neighbor oxygen atoms and elongation of the Mn−O bond have been proposed.³⁴

**Comparison with Literature.** Even with the same polymorph of manganese oxides, different water oxidation measurement systems can demonstrate different catalytic activities.³⁵ The manganese oxides reported in the literature with measurement of dissolved oxygen are listed in Table 4. These measurements of dissolved oxygen are typically carried out in the time frame of minutes.

It is difficult to compare different studies even if they are using similar Ru-based photocatalysis because of experimental parameters, such as differences in light intensity and surface area of the catalysts. We synthesized Mn₂O₃ following a previous experimental procedure;²³ the XRD is shown in Figure S16 and a TOF of 1.02 mmol O₂ mol⁻¹ Mn⁻¹ s⁻¹ was found, compared to the literature report of 0.37 mmol O₂ mol⁻¹ Mn⁻¹ s⁻¹. This shows that despite the same catalyst system, the performance of manganese oxides between different studies in the literature will differ (the light intensity in ref 23 was lower than in the present experiments). Fe(IE)MnOₓ₄₀₀ exhibited the most active, stable, and robust water oxidation activity with a TOF of 9.3 ± 0.7 mmol O₂ mol⁻¹ Mn⁻¹ s⁻¹, and has the best results so far compared to the literature (Table 4).

Another way to standardize the catalytic activity is to compare with colloidal IrO₂ as the benchmark.⁵ Colloidal IrO₂ (6.2 × 10⁻⁴ M) was compared with the best performing Fe(IE)MnO₅₄₀₀, with a TOF of dissolved oxygen of 7.3 × 10⁻⁴ mmol O₂ mol⁻¹ Ir⁻¹ s⁻¹. The catalytic activity of IrO₂ and the performance of colloidal IrO₂ were better by a factor of 79 as shown in Figure 7a.

Analysis of oxygen in the headspace was also carried out to evaluate catalytic activity. These measurements typically last tens of minutes until the photosensitizer Ru(bpy)₃Cl₂ decomposes. The results of headspace oxygen with Fe(IE)-MnOₓ₄₀₀ as measured by gas chromatography (GC) is shown in Figure 7b. The TOF of oxygen evolution was 0.71 mmol O₂ mol⁻¹ Mn⁻¹ s⁻¹. Under the same condition, for 0.5 mL of colloidal IrO₂ (6.2 × 10⁻⁴ M), the TOF of oxygen evolution of colloidal IrO₂ was 5.23 mmol O₂ mol⁻¹ Ir⁻¹ s⁻¹. The performance of colloidal IrO₂ was better by a factor of ~74 in GC measurement as well, similar to dissolved oxygen measurement (the cost difference between these two oxides is 3400).

## CONCLUSIONS

Fe³⁺ ion-exchanged into a disordered-birnessite KMnO₅ led to destruction of the stacking of the layers, creating local disorder and randomness in the stacking of layers. The ion-exchanging process introduces Fe³⁺ cations into birnessite without losing its core “MnO₆” structural integrity, as suggested by Raman analysis. The AOS of Mn was unchanged with Fe³⁺ and close to +3.3 to 3.5 in all samples, and the morphology was comparable to KMnO₅, consisting of ~100 nm primary particles. Fe(IE)MnO₅ was found to be significantly more catalytically active as compared to KMnO₅ under similar photolysis conditions. For example, the best Fe(IE)MnO₅ had a TOF of 9.3 ± 0.7 mmol O₂ mol⁻¹ Mn⁻¹ s⁻¹, as compared to 3.2 mmol O₂ mol⁻¹ Mn⁻¹ s⁻¹ for KMnO₅. Fe(IE)MnO₅ was also a robust catalyst and could be recycled. Comparison of Fe(IE)MnO₅ with other manganese oxides reported in the literature indicates that it performed significantly better, though comparisons between studies with different experimental conditions are fraught with issues. The better catalytic activity of Fe(IE)MnO₅ is not solely because of the disordered layers, as Ga³⁺ exchanged KMnO₅, which also disrupted the
stacking order was not as catalytically effective. We propose that the interaction between the Fe$^{3+}$ in the interlayers and the MnO$_x$ in the framework could be playing a role. This study provides new insight into how redox active cations can influence the structure–function role of disordered birnessite.

### EXPERIMENTAL SECTION

**Chemicals.** All chemicals purchased were of analytical grade and used without further purification. Manganese(II)-acetate tetrahydrate (Mn(CH$_3$COO)$_2$·4H$_2$O) and potassium permanganate (KMnO$_4$) were purchased from Sigma-Aldrich. Iron(III)nitrate nonahydrate [Fe(NO$_3$)$_3$·9H$_2$O] was purchased from Mallinkrodt.

**Synthesis.** Synthesis of KMnO$_x$. Mn(CH$_3$COO)$_2$ (60 mM) and KMnO$_4$ (40 mM) were added together in 50 mL deionized water and stirred for 1 h at room temperature. There was an immediate color change and formation of a dark brown precipitate. The brown suspended solution was centrifuged, and the precipitate was collected discarding the supernatant. The precipitate was washed several times and dried in vacuum, and designated as KMnO$_x$.

**Synthesis of Iron(III)-Containing Material (Fe(IE)MnO$_x$).** The as-prepared KMnO$_x$ sample was dispersed in 10 mL of deionized water, and treated with different concentrations of Fe(NO$_3$)$_3$·9H$_2$O for 1 h at room temperature. The concentrations of Fe(NO$_3$)$_3$·9H$_2$O used for iron-exchanging were 5, 50, 200, and 400 mM, and they were designated as Fe(IE)MnO$_x$ 5, Fe(IE)MnO$_x$ 50, Fe(IE)MnO$_x$ 200, and Fe(IE)MnO$_x$ 400, respectively. The samples were washed several times and dried in vacuum at room temperature.

**Characterization.** Powder XRD. Powder XRD patterns were obtained using a Bruker D8 ADVANCE X-ray diffractometer with Cu Ka ($\lambda = 1.5405$ Å) radiation with 0.5 divergence, 0.02 step size, and 1.0 s dwell time.

**Raman Spectroscopy.** Raman spectroscopy was done with a Renishaw–Smith Detection IR-Raman Microprobe, model InVia. A 785 nm-laser line was used for the acquisition of the spectra with laser power of 13 mW (50 s dwell time, 20 scans). Precautions have to be taken during Raman spectra acquisition to preserve sample integrity, including the choice of wavelengths (785 nm preferable to 514.5 nm) and use of a spinning cell.

**X-ray Photoelectron Spectroscopy.** XPS spectra were obtained using a Kratos Axis Ultra X-ray photoelectron spectrometer with Al K$\alpha$ source (12 kV, 10 mA). The region scans were acquired using 20 eV pass energy and the survey scan was obtained using 80 eV. All peaks were calibrated with respect to the C 1s peak position at 284.7 eV.

**Scanning Electron Microscopy.** The morphology of the samples was characterized by FEI Helios Nanolab 600 dual beam focused ion beam/scanning electron microscopes. Electron beams with 5 kV potential and 0.17 nA current were used.

**Surface Area Measurement.** A Nova 2200e Surface Area Analyzer was used to determine the surface area of the samples. Prior to degassing, the samples were stored in a vacuum dryer at room temperature. The samples were degassed under vacuum at room temperature for 24 h. They were degassed at room temperature in order to maintain the structural integrity of the MnO$_x$ samples. Multipoint Brunauer–Emmett–Teller (BET) surface area analysis was carried out employing the N$_2$ adsorption isotherm of the samples.

**Elemental Analysis.** For elemental analysis, the cold digestion method was adopted to prepare solubilized samples. In a Teflon bottle, 30 mL of mixed HF, HCl, and HNO$_3$ (1:1:1 ratio) was mixed. The MnO$_x$ materials (30–50 mg) were added to the acid solution. After dissolution, 75 mL of 0.86 M boric acid was added to neutralize HF. Deionized water was added to the solution so that the total solution weighs 100 g. Manganese and iron loading in the birnessite was determined using AAS using a Shimadzu AA-7000 atomic absorption spectrophotometer.

**Determination of Average Oxidation State of Mn in KMnO$_x$.** The Mn AOS of KMKO$_x$ was determined with the oxalic acid–permanganate back-titration method. KMnO$_x$ (200 mg) was dissolved in 5 mL of 0.5 M oxalic acid and 10 mL of 1.0 M H$_2$SO$_4$ in order to reduce Mn in KMnO$_x$ into the Mn$^{2+}$ oxidation state. The excess oxalic acid was back-titrated with standardized KMnO$_4$ solution at 75 °C to obtain the AOS of Mn.

**Photocatalytic Water Oxidation.** Dissolved Oxygen Measurement. In a glass reactor, sodium persulfate (0.02 M) (Sigma-Aldrich), sodium sulfate (0.1 M) (Fischer Scientific), tris(2,2’-bipyridyl)ruthenium chloride (6.7 mg) (Sigma-Aldrich), and appropriate amount of powder catalyst (containing 1 mg of Mn) was added to 80 mL of borate buffer (pH 8.5). The solution inside the reactor was sealed and purged with N$_2$ gas for 20–30 min while stirring until the baseline reads 0.00–0.02 ppm O$_2$ reading with a fluorescence probe. After N$_2$ purging, the reactor was illuminated with visible light using a Hg lamp equipped with a dichroic mirror (360 mW/cm$^2$ intensity measured at the sample cell). For the measurement of dissolved oxygen evolution, a YSI instrument fiber optic dissolved oxygen (YSI ProODO) sensor was used. The electrode was calibrated by the two-point calibration method (zero for nitrogen saturated water and 9.5 ppm air-saturated water).

**GC Measurement.** In a glass reactor, sodium persulfate (0.02 M) (Sigma-Aldrich), sodium sulfate (0.1 M) (Fischer Scientific), tris(2,2’-bipyridyl)ruthenium chloride (6.7 mg) (Sigma Aldrich), and appropriate amount of powder catalyst (containing 1 mg of Mn) was added to 40 mL of borate buffer (pH 8.5). The solution inside the reactor was sealed and purged with N$_2$ gas for 20–30 min while stirring. After N$_2$ purging, the reactor was illuminated with visible light using an Hg lamp equipped with a dichroic mirror with 360 mW/cm$^2$ intensity measured at the sample cell. A GC SRI 310 chromatograph equipped with a thermal conductivity detector and a 13X packed molecular sieve column was used for GC detection. The carrier gas used was helium, and the oxygen evolution in the headspace of glass reactor was measured.

### ASSOCIATED CONTENT

*Supporting Information*

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01918.

Raman spectra showing the laser-induced changes of the Fe(IE)MnO$_x$ 5 sample; K 2p, Mn 3s, and O 1s XPS spectra of KMnO$_x$; Mn 2p spectra of Fe(IE)MnO$_x$ N samples; Mn 3s XPS spectra of Fe(IE)MnO$_x$ N samples; Fe 2p XPS spectra of Fe(IE)MnO$_x$ N samples; O 1s XPS spectra of Fe(IE)MnO$_x$ N samples; O 1s peak area and the ratio of the peaks; dissolved oxygen
measurement without using any catalyst; dissolved oxygen measurement without using photosensitizer Ru(bpy)32+: photochemical water oxidation catalytic activity of ferrihydrite; Fe 2p XPS spectra of the initial Fe(II)MnOx sample and the recovered sample of Fe(II)MnOx; Ru 3p XPS spectra of the initial Fe(II)MnOx sample and the recovered sample of Fe(II)MnOx; Mn 3s XPS spectra of the Ga(II)-MnOx sample; Raman spectra of the Ga(II)-MnOx sample; XRD of the Ga(II)MnOx sample; photochemical water oxidation catalystic activity of the Ga(II)MnOx 400 sample; and XRD pattern of Mn2O3 synthesized following ref 23

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Notes
The authors declare no competing financial interest.

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