Near-infrared–driven decomposition of metal precursors yields amorphous electrocatalytic films

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Amorphous metal-based films lacking long-range atomic order have found utility in applications ranging from electronics to heterogeneous catalysis. Notwithstanding, there is a limited set of fabrication methods available for making amorphous films, particularly in the absence of a conducting substrate. We introduce herein a scalable preparative method for accessing oxidized and reduced phases of amorphous films that involves the efficient decomposition of molecular precursors, including simple metal salts, by exposure to near-infrared (NIR) radiation. The NIR–driven decomposition process provides sufficient localized heating to trigger the liberation of the ligand from solution-deposited precursors on substrates, but insufficient thermal energy to form crystalline phases. This method provides access to state-of-the-art electrocatalyst films, as demonstrated herein for the electrolysis of water, and extends the scope of usable substrates to include nonconducting and temperature-sensitive platforms.

INTRODUCTION

Amorphous metal-based films are pervasive in a myriad of applications [for example, transistors (1, 2) and flexible electronics (3)], including schemes that involve the electrocatalytic oxidation of water into clean hydrogen fuels. Indeed, there is a growing body of evidence showing that amorphous films mediate the oxygen evolution reaction (OER; Eq. 1) (4–8) and hydrogen evolution reaction (HER; Eq. 2) (9, 10) more efficiently than do crystalline phases of the same compositions. These findings are particularly important in the context of efficiently storing electricity produced from intermittent and variable renewable energy sources (for example, sunlight and wind) as high-density fuels (for example, hydrogen) (11, 12).

$$2\text{H}_2\text{O}(l) \rightarrow 4\text{e}^- + 4\text{H}^+_\text{(aq)} + \text{O}_2(g)$$

(1)

$$2\text{H}^+_\text{(aq)} + 2\text{e}^- \rightarrow \text{H}_2(g)$$

(2)

Most amorphous metal oxide films reported in the literature are formed by electrodeposition (4–7), sputtering (13), thermal decomposition (3, 14), or ultraviolet (UV) light–driven decomposition (8) of metal precursors. Although films prepared by these methods can demonstrate state-of-the-art electrocatalytic OER activities (15–20), the syntheses are not necessarily amenable to scalable manufacture because of sensitivities to metal work functions, reaction media, or prohibitively expensive precursors. Consequently, accessing specific compositions of amorphous metal oxides for commercial applications is not trivial, particularly when complex metal compositions are desired (3, 8). Moreover, the isolation of amorphous metals is substantially more challenging because single-element metallic films typically require sophisticated protocols (21).

We report here a previously untested method for generating amorphous metal-based films, in the reduced and oxidized phases, that relies merely on the exposure of transition metal salts [for example, MClₙ and M(NO₃)ₓ₋ₙ] to near-infrared (NIR) radiation under inert and aerobic environments, respectively (Fig. 1). This method is distinctive from the UV–driven photochemical decomposition of metal complexes (8) in that it is ultimately a thermally driven process and therefore does not require photoactive precursors. Notwithstanding, this NIR–driven decomposition (NIRDD) process furnishes amorphous metal oxide films that display properties commensurate with films prepared by more complex methods and precursors, yet is amenable to curing techniques widely used in large-scale manufacturing processes, including roll-to-roll processing (22, 23). We therefore contend that NIRDD represents a significant advance toward a solar fuel economy, which will invariably require electrocatalysts to efficiently mediate small-molecule transformations. Moreover, NIRDD provides access to reduced phases of amorphous films using moderate experimental conditions. We demonstrate the broad use of this fabrication technique herein by examining the formation of amorphous oxide films containing metals of relevance to the OER reaction [for example, iron (7, 8), iridium (18, 24), manganese (6, 25), nickel (7, 8, 26), and copper (27, 28)]. We also provide evidence that NIRDD, which works despite substrate temperatures not reaching 200°C (fig. S1), can also be extended to substrates that are nonconducting and sensitive to temperature and UV radiation by documenting amorphous metal oxide film formation interfaced with Nafion.

RESULTS AND DISCUSSION

The formation of amorphous metal oxide films upon exposure of metal salts to NIR radiation was confirmed by placing FeCl₃ spin-cast on FTO, FeCl₃/FTO, under a 175-W NIR lamp for 120 min in an aerobic environment. The color change from yellow to light brown upon irradiation supported the formation of iron oxide (UV–vis spectra are provided in fig. S2), whereas the absence of reflections in the powder x-ray diffraction (XRD) patterns indicated the amorphous nature of the material (figs. S3 and S4). (A signature Bragg reflection of hematite is apparent at 2θ = 35.5° only after annealing the same film in air for 1 hour at 600°C.) The electrochemical behavior of this amorphous film, a-FeOₓ, in aqueous media was also consistent with previous accounts of amorphous iron oxide (Fig. 2 and Table 1). These films demonstrated oxidative stability at a current density of 10 mA/cm² over a 2-hour period (fig. S5). An extensive electrochemical analysis indicated that a-FeOₓ could be readily produced from other iron compounds [for example,

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Fe(NO₃)₃ and Fe(eh)₃; eh = 2-ethylhexanoate] (fig. S6) and that the NIRDD method translated effectively to other metals: Films of a-IrOₓ, a-NiOₓ, and a-MnOₓ were also formed when the corresponding metal compounds were subjected to NIR radiation (figs. S7 and S8). The electrocatalytic properties of a-IrOₓ in 1 M H₂SO₄ (fig. S8) are consonant with literature values, as are those for a-NiOₓ and a-MnOₓ in alkaline conditions (Table 1).

The discovery that NIRDD could drive a-MOₓ formation was not expected given the low absorptivities of the films at λ > 600 nm (fig. S2). We therefore contend that the efficacy of the process is due to localized heating of the film rather than a photochemical effect. This assessment is validated by the observations that: (i) substrates do not exceed 200°C under our experimental conditions (fig. S1); (ii) bulk samples of FeCl₃ do not decompose to a mass corresponding to Fe₂O₃ until >300°C (figs. S9 and S10); (iii) samples of precursors on FTO exposed to 1 hour of constant irradiation yielded complete decomposition, whereas six successive 10-min segments of exposure separated by 5-min periods in the dark did not; and (iv) films of precursors on FTO did not show the same rates of decomposition when placed in an oven set at 200°C (fig. S11). The temporal resolution of the NIRDD process was evaluated by tracking the formation of a-FeOₓ during the NIR irradiation of Fe(eh)₃, which contains reporter ligands that can be tracked by Fourier transform IR (FTIR) spectroscopy (17, 29), and indicated complete ligand loss within 1 hour in both air and N₂ (Fig. 3). The absorption spectra (fig. S2), lack of powder XRD reflections (figs. S3 and S4), and electrochemical data (Table 1) collectively support the assignment of the as-prepared films as a-FeOₓ. Films of a-MOₓ (M = Ir, Ni, Mn) derived from Ir(acac)₃ (acac = acetylacetonate), Ni(eh)₂, or Mn(eh)₂, were each formed quantitatively within 4 hours of irradiation (fig. S12).

The formation of a-FeOₓ from FeCl₃ signaled that oxygen was derived from the aerobic environment, thus raising the possibility that reduced forms of the films could be accessed merely by carrying out NIRDD in an inert atmosphere. This hypothesis was tested by irradiating a film of FeCl₃ on FTO under nitrogen, which yielded a light gray film, denoted a-Fe, that did not produce any Bragg reflections (figs. S3 and S4). Moreover, the electrochemistry of a-Fe on FTO in 0.1 M KOH(aq) contained a lower average iron valency than that of a-FeOₓ. Films of a-MOₓ (M = Ir, Ni, Mn) derived from Ir(acac)₃ (acac = acetylacetonate), Ni(eh)₂, or Mn(eh)₂, were each formed quantitatively within 4 hours of irradiation (fig. S12).

Evidence for the oxidized and reduced forms of the films formed under aerobic and nitrogen environments, respectively, is further supported by the different absorption (fig. S2) and x-ray photoelectron spectroscopy (XPS; figs. S13 and S14) data. The XPS data for a-FeOₓ.

### Table 1. Benchmarked OER activities of a-MOₓ films.

| Sample* | Onset η (V versus RHE) | Tafel slope (mV dec⁻¹) | η₁₀ mA/cm² (V)¹ |
|---------|------------------------|-----------------------|-----------------|
| a-FeOₓ  | 0.33                   | 38                    | 0.24           |
| a-NiOₓ  | 0.21                   | 62                    | 0.36           |
| a-Fe₃Ni₃Oₓ | 0.19                  | 34                    | 0.33           |
| a-MnOₓ  | 0.22                   | —                     | 0.43           |
| a-IrOₓ  | 0.10                   | 45                    | 0.26           |

*Oₓ is broadly defined as oxo/oxyl/hydroxyl. †Overpotential required to reach 10 mA/cm². Unless otherwise indicated, without correcting for mass transport. ‡Overpotential required to reach 1 mA/cm². §Corresponds to FeNiOₓ. ¶Recorded at pH 0; all other data in table recorded at pH 13.
contain a signature iron(III) satellite signal at 719 eV that is not observed for a-Fe, and an iron 2p3/2 envelope that could be accurately modeled using peak parameters corresponding to Fe2O3 (30). The 2p3/2 envelope of a-Fe was fit to a combination of iron(III), iron(II), and iron(0), where the zero valency was implicated by the low-energy shoulder. Although these results confirm that a-Fe exists in a more reduced form, the high susceptibility of the films to areal oxidation prevented confirmation that elemental iron was being formed in exclusivity during the NIRD process. We therefore analyzed surrogate films of a-CuOx and a-Cu prepared by applying the NIRD process to Cu(eh)2 on FTO under air and nitrogen, respectively, in view of elemental copper oxidizing less readily to Cu2O and, in turn, CuO (under FTO under air and nitrogen, respectively, in view of elemental copper oxidizing less readily to Cu2O and, in turn, CuO (31). XPS data recorded on these samples did indeed yield different spectroscopic signatures (Fig. 4 and fig. S15): The copper 2p3/2 envelope for a-CuOx showed a mixture of CuO and Cu(OH)2, whereas the same envelope for a-Cu shows a single peak corresponding to zero- or mono-valent copper sites. The Cu LMM peak indicated the presence of CuO (fig. S15), possibly due to aerial oxidation. Visible inspection of the samples prepared by NIRD in an inert atmosphere indicated a color consistent with elemental copper (fig. S16), with XRD measurements ruling out formation of crystalline domains (fig. S17), lending credence to the samples existing in a reduced form, and potentially metallic phase, when prepared under nitrogen.

Mixed-metal oxides are known to exhibit superior electrocatalytic behavior in basic media, which prompted us to synthesize the binary solid, a-Fe2Ni3Ox, by subjecting a mixture of iron precursors (for example, Fe(eh)3, FeCl3, or Fe(NO3)3·xH2O) and nickel precursors [Ni(eh)2, NiCl2, or Ni(NO3)2·xH2O] (mol Fe/mol Ni 2:3) spin-cast on FTO to the NIRD process (fig. S18). The resultant films were amorphous according to powder XRD measurements (fig. S19), and the energy-dispersive x-ray spectrometry (EDX) measurements recorded on different regions of the films confirmed uniform metal distributions across the substrates (table S1). The electrochemical behavior, including OER catalytic activity, also matches films of similar compositions prepared by other methods (fig. S20A and Table 1), including the absence of an oxidative peak at Et = 1.45 V that is present in pure phases of NiO2 (7).

Intrigued by the potential to access amorphous metal alloys, we set out to prepare the binary film a-Fe2Ni3 in the same manner as a-Fe2Ni3Ox but under nitrogen. The electrocatalytic behavior of the films indicated a more reduced phase compared to that of a-Fe2Ni3Ox (fig. S20B). The film contained a uniform distribution of metals within the solid (table S1). Although the film was found not to be a state-of-the-art HER electrocatalyst, it is superior to pure phases of a-Fe and a-Ni, thus highlighting that metal cooperativity with other metal combinations may unearth superior catalysts in future studies (7, 17, 32).

Finally, we tested the viability of this synthetic method for situations where the substrate is nonconductive or sensitive to high temperatures (for example, interfacial layers in solar cells and carbon-based substrates). Proof-of-principle experiments of relevance to electrolysis were designed where an 180-μm-thick film of Nafion was coated with Ir(acac)3 and subjected to the NIRD process. The exclusive formation of amorphous IrO2, interfaced with the Nafion was found within 120 min of irradiation, with no damage to the membrane according to electrochemical and FTIR data (figs. S21 and S22). These results show that NIRD may have the potential to efficiently coat three-dimensional substrates which may prove to be particularly important in contemporary electrolyzers.

Fig. 3. FTIR spectra for thin films of Fe(eh)3. (A and B) FTIR spectra for thin films of Fe(eh)3 on FTO upon exposure to NIR radiation for (A) 0 min (black) and 4, 16, 32, and 64 min (blue) in air, and (B) 0 min (black) and 60 min (blue) under nitrogen. Arrows indicate trends in the intensities of the C-H and C-O vibrational modes of 2-ethylhexanoate (8). a.u., arbitrary units.

Fig. 4. XPS spectra of the copper 2p3/2 region. (A and B) Fitting of the copper 2p3/2 region of XPS recorded on thin films of Cu(eh)2 on FTO after being subjected to the NIRD process under (A) air and (B) nitrogen, respectively. Sums of the fitting components are indicated (red traces). Fitting of the data used center-of-gravity peaks for (A) Cu(O) (green) and Cu(OH)2 (orange), and (B) Cu(I)/Cu(O) (green). Signature copper(II) satellite peaks present in (A), but not in (B), confirm a more reduced form of the film when prepared under nitrogen. The computed baselines are indicated in blue.
CONCLUSIONS

Amorphous metal-based films can be prepared by exposing metal salts (for example, FeCl₃) to NIR radiation. This NIRDD process also appears to provide facile access to more reduced phases of the films by avoiding the presence of oxygen during the irradiation process. This method presents the opportunity to prepare films on various substrates, and offers the ability to manufacture state-of-the-art electrocatalysts and other thin-film applications using infrastructure related to those used in curing processes currently used in industry (22, 23). Moreover, the NIRDD method provides strikingly easy access to complex metal compositions in the amorphous phase, and offers a much broader substrate scope than is available to other widely used methods.

MATERIALS AND METHODS

Materials

Iron(III) 2-ethylhexanoate [Fe(eh)₃, 50% (w/w) in mineral spirits], iridium(III) acetylacetonate [Ir(acac)₃], nickel(II) 2-ethylhexanoate (Ni(eh)₂, 78% (w/w) in 2-ethylhexanoic acid), manganese(III) 2-ethylhexanoate [Mn(eh)₃, 40% (w/w) in 2-ethylhexanoic acid], and copper(II) 2-ethylhexanoate [Cu(eh)₂] were purchased from Strem Chemicals. Nafion N117 proton exchange membranes (177.8 μm thick) were purchased from Ion Power; ferric chloride (98%) anhydrous (FeCl₃) was purchased from Aldrich; iron(III) nitrate nonahydrate [Fe(NO₃)₃ ⋅ 9H₂O], manganese(III) nitrate hexahydrate [Mn(NO₃)₃ ⋅ 6H₂O], nickel nitrate hexahydrate [Ni(NO₃)₂ ⋅ 6H₂O], and nickel chloride hexahydrate (NiCl₂ ⋅ 6H₂O) were purchased from Fischer Scientific. All reagents were used without further purification.

Film syntheses

a-FeOₓ on FTO (or glass). To a 20-ml beaker containing 0.58 g of Fe(eh)₃ (0.60 mmol) was added 1.07 g of hexanes (12.4 mmol). The solutions were then spin-cast onto FTO (or glass) at 3000 rpm for 1 min. The resultant film, Fe(eh)₃/FTO, was subjected to the NIRDD process as described above to form a-FeOₓ.

a-MnOₓ on FTO (or glass). To a 20-ml beaker containing 0.23 g of Fe(eh)₃ (0.24 mmol) and 0.16 g of Ni(eh)₂ (0.36 mmol) was added 1.28 g of hexanes (14.9 mmol). The mixture was spin-cast onto FTO at 3000 rpm for 1 min. The resultant film, Mn(eh)₂/FTO, was then subjected to the NIRDD process to form a-MnOₓ.

a-CuO on FTO (or glass). To a 20-ml beaker containing 0.21 g of Cu(eh)₂ (0.65 mmol) was added 1.62 g of ethanol (35.2 mmol). The solutions were then spin-cast onto FTO at 3000 rpm for 1 min. The resultant film, Cu(eh)₂/FTO, was then subjected to the NIRDD process to form a-CuO.

a-Fe₂Ni₃Oₓ on FTO (or glass). To a 20-ml beaker containing 0.23 g of Fe(eh)₃ (0.24 mmol) and 0.16 g of Ni(eh)₂ (0.36 mmol) was added 1.28 g of hexanes (14.9 mmol). The mixture was spin-cast onto FTO at 3000 rpm for 1 min. The resultant film, FeNi(eh)/FTO, was then subjected to the NIRDD process to form a-Fe₂Ni₃Oₓ.

a-IrOₓ/membrane. Nafion membranes were cut into squares with geometric surface areas of 6.25 cm² and then submerged in a bath of 3% (w/v) H₂O₂ stirring at 800 rpm for ~5 min. The membranes were then left to stand in a bath of stirring 0.5 M H₂SO₄ at 150°C for 60 min. The membranes were dehydrated in a vacuum oven (room temperature, 0.8 atm) for at least 5 hours. Excess acid was removed before dehydration with compressed nitrogen. A solution containing 0.004 g of Ir(acac)₃ (0.009 mmol) in 0.9 ml of chloroform was then spray-coated on the surface of the dehydrated Nafion to form Ir(acac)₃/membrane. The resultant film was then subjected to the NIRDD process to form a-IrOₓ/membrane (~120 min).

Physical methods

Electrochemical measurements were performed on a C-H Instruments Workstation 660D potentiostat. The Ag/AgCl (sat. KCl) reference electrode (E_r) was calibrated regularly against a 1 mM aqueous K₃[Fe(CN)₆]₅ solution. Cyclic voltammograms were acquired at a scan rate of 10 mV s⁻¹ unless otherwise indicated. All potentials were corrected for uncompensated resistance (R_u) and are reported relative to the reversible hydrogen electrode (versus RHE), E_RHE = E + E_ref + 0.059(pH) - iR_u. Tafel plots were acquired through staircase voltammetry (10-mV steps, 50-s intervals for the final 25 s sampled). Chronopotentiometric experiments were held at 10 mA/cm² for 7200 s. For the metal oxide and metal films on FTO, all experiments were carried out using 0.1 M

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KOH as an electrolyte, unless otherwise noted, in a standard threecompartment electrochemical cell. A Luggin capillary connects the reference and working electrodes, whereas a porous glass frit connects the working electrode to the platinum mesh counter electrode. All experiments involving Nafion were carried out in 0.5 M H2SO4. Membranes were hydrated in 0.2 M H2SO4 before electrochemical experiments. Measurements were performed in a customized three-electrode test cell using the above Ag/AgCl reference electrode. All potentials were corrected for Rct. The membrane electrode assembly was prepared by mechanically pressing a platinum mesh counter electrode (Aldrich), the prepared Nafion membrane, and a Toray carbon paper gas diffusion layer (Ion Power) between two Ti plate electrodes (McMaster-Carr). No aggregation was induced on the test cell besides that from evolved gaseous products. FTIR spectroscopy was recorded on a Bruker alpha spectrometer with a transmission accessory. Thin films were prepared as described above, the disappearance of the vibrations associated with the ligand was followed during photolysis. Powder XRD data were recorded with a Bruker D8 Advance diffractometer using Cu Kα radiation. The test time was 0.6 sunless as indicated. Thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) measurements were collected simultaneously with a PerkinElmer Simultaneous Thermal Analyzer (STA) 6000. These measurements were carried out under both air and N2 at a flow rate of 20 ml min−1. Starting from a temperature of 50°C, the temperature was ramped up (10°C min−1) until 100°C, where it was held for 1 min. It was then ramped at 10°C min−1 until a final temperature of 500°C was reached and held for an additional minute. For constant temperature measurements, the temperature was ramped up (10°C min−1) until 200°C, where it was held for 60 min. UV-v absorption spectroscopy on fresh and on metal oxide films was performed using a PerkinElmer Lambda 35 UV/Vis spectrometer with a solid sample holder accessory. Baseline scans were performed with clean glass. The films examined were prepared from 0.3 M precursor solutions of 1 to 5. XPS measurements were collected on a Leybold MAX200 spectrometer using Al Kα radiation. The pass energy used for the survey scan was 192 eV, whereas for the narrow scan it was 48 eV. Scanning electron microscopy and EDX measurements were carried out on an FEI Helios NanoLab 650 dual beam scanning electron microscope with an EDAX Pegasus system with EDS detector. The magnification was set to x2000, the accelerating voltage was set to 2.0 keV, the current was set to 51 nA, and the working distance was 9 mm.

The temperature of the substrates was tracked with a Fluke 52 thermocouple attached to a multimeter. For the FTO measurements, constant contact of the tip of the detector was maintained throughout the experiment. For the thermocouple measurements, the tip of the detector was dipped in Fe(eh)3 solution. The substrate and thermocouple were placed 2 cm from the lamp. Temperature values were recorded every 5 min.

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**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/1/2/e1400215/DC1

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Fig. S8. Cyclic voltammograms for thin films of a-IrOx, a-NiOx, and a-MnO2.

Fig. S9. TGA and DSC profiles for FeCl3 and Fe(eh)3.

Fig. S10. TGA and DSC profiles for FeO2 and Fe(eh)3.

Fig. S11. FTIR spectra of independent samples of Fe(eh)3/FTO.

Fig. S12. FTIR spectra of thin films of Ir(acac)3/FTO, Ni(eh)2/FTO, and Mn(eh)3/FTO.

Fig. S13. X-ray photoelectron spectra for a-FeO2 and a-Fe on FTO.

Fig. S14. X-ray photoelectron spectra detailing the Fe 2p3/2 region.

Fig. S15. XPS data for a-CuO and a-Cu on FTO.

Fig. S16. Images of solid copper samples.

Fig. S17. Diffractions of a-CuO2 and a-Cu.

Fig. S18. FTIR spectra of Fe5Ni3(eh)3/FTO.

Fig. S19. Diffractions of a-FeNi3O4 and a-Fe2Ni3O4.

Fig. S20. Cyclic voltammograms for thin films of a-Fe2Ni3O4 and a-FeNi3N3.

Fig. S21. Cyclic voltammograms for thin films of a-IrOx/membrane.

Fig. S22. FTIR spectra of Ir(acac)/membrane.

Table S1. Elemental analysis of amorphous metal oxide films determined by EDX.

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