PAPER

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A single step electrodeposition of α -Fe₂O₃ films under hydrothermal conditions without post-annealing requirement is described. Primary attention is paid to understand the effects of synthesis conditions, such as temperature, precursor concentration, pH, and time on the structure and morphology of the films. Moreover, the photoelectrochemical properties of hematite films grown by hydrothermal-electrochemical deposition (HED) are also discussed. It is discovered that HED enables the production of crystalline α -Fe₂O₃ phase without thermal annealing as opposed to electrodepositions reported at ambient temperature. Photoelectrochemical studies demonstrated that better performance can be obtained with the films prepared at higher pH. A net photocurrent density of 23.6 $\mu\text{A cm}^{-2}$ is obtained in 0.1 M NaOH under 1 sun conditions at 1.23 V vs. NHE with the film prepared from a bath containing 0.05 M FeCl₂ and 0.2 M NaCH₃COO via hydrothermal-electrodeposition with a photocurrent onset potential of 0.96 V vs. NHE.

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Introduction

There is a strong motivation to prepare ferric oxide nanoparticles of various sizes due to their novel properties and potential applications in medicine, catalysts, magnetic recording media, pigments, anticorrosive agents, gas sensors and electrochemical capacitors.¹ Further, ferric oxide (α -Fe₂O₃, hematite) has become a very desirable material to construct photoelectrochemical cells due its bandgap ($E_g = \sim 2.2$ eV), which allows the utilization of a considerable portion of solar energy and its stability in harsh chemical environments.² Non-toxicity, low cost and relative abundance of hematite on earth also add to its charm. Despite these exiting features, hematite suffers from poor conductivity, short photogenerated carrier life-time and a short hole diffusion length.³ It has been demonstrated that poor charge-transport properties can be improved with nanostructured morphology that provides higher surface area.⁴

Several methodologies were employed to grow hematite nano-crystals including high-temperature-based techniques such as pulsed layer deposition, catalyst-assisted chemical vapour deposition and thermal oxidation.⁵ Techniques that require lower temperatures like solution-based approaches, chemical precipitation, sol-gel, forced hydrolysis and hydrothermal synthesis were also applied.^{1,6} Electrochemical

synthesis is a simpler and cheaper alternative to produce semiconductor nanostructures. It is an efficient and environmentally friendly method in which thin films on various substrates of any shape and size can be produced at relatively lower temperatures from aqueous media. Furthermore, by controlling the deposition parameters like temperature, applied potential, precursor concentration, and growth rate; film thickness, composition and morphology of the films can be modified,^{7–9} which are important factors for the optimization of hole diffusion length or recombination rate in hematite structures.² In spite of its advantages, electrochemical synthesis requires strict control over the applied potential and pH since the Pourbaix diagram of Fe–water system reveals the possibility to obtain several different iron oxide phases.¹⁰ It has been reported that magnetite (Fe₃O₄), goethite (α -FeOOH) and lepidocrocite (γ -FeOOH) can be obtained by increasing the potential from -0.4 V to 1.0 V vs. Ag(AgCl) from aqueous solutions containing FeSO₄(NH₄)₂SO₄·6H₂O and CH₃COOK (pH = 6) at 90 °C.⁹ Both cathodic or anodic electrodepositions of α -Fe₂O₃ from aqueous solutions involve the deposition of an iron oxyhydroxide phase followed by heat treatment to produce a hematite phase.^{11–14}

The hydrothermal approach also offers some advantages such as control over particle size and shape, homogeneity of the products and well-crystallized particles.¹⁵ However, similar to electrodeposition, most cases of hydrothermal hematite synthesis involve the formation of β -FeOOH precursor, which is further dehydrated into α -Fe₂O₃ through calcinations or annealing.¹ Jia and Gao reported the direct synthesis of single-crystalline α -Fe₂O₃ submicron-cubes via the hydrothermal method at 180 °C in the presence of a surfactant with relatively

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long reaction times (16–36 h).¹⁶ Hence, in this study, we combined the benefits of hydrothermal synthesis with electrochemical deposition to obtain α -Fe₂O₃ films directly. It is demonstrated that the single-step synthesis of crystalline hematite nanostructures is possible with hydrothermal-electrochemical deposition (HED), owing to the high growth rate facilitated by high temperature.

Experimental

Iron(II) chloride hexahydrate (FeCl₂·6H₂O, 99% purity) was purchased from Sigma-Aldrich. Sodium acetate (NaCH₃COO, NaAc) was obtained from Merck. Indium tin oxide (ITO) ($\Omega < 5.0 \times 10^{-4}$ ohm cm) ($R_s < 100$ ohm sq⁻¹) was purchased from Teknoma Ltd, Izmir, Turkey, and fluorine-doped tin oxide (FTO) was obtained from Solaronix SA. Double-distilled high purity water was used from Milli-Q water (Millipore) system. The depositions were performed in a hydrothermal glass reactor (100 ml, Büchi Glas Uster, picoclave) at a constant potential at 130 °C. The reference electrode was Ag/AgCl saturated with KCl (Corr Instruments, S/N P11092), whereas a Pt wire served as the counter electrode. Both acidic and neutral plating solutions were used for the anodic depositions at 1.2 V (vs. Ag/AgCl (sat'd)).¹³ The acidic plating solution contained 0.02 M FeCl₂ (pH ~ 3.8) and neutral plating solution consisted of 0.02 M FeCl₂ and 0.08 M NaCH₃COO (pH ~ 6.2–6.8). The films were annealed at 520 °C for 30 minutes. The reaction parameters are summarized in Table 1. The crystal structure and crystallinity of the thin films were analyzed by Bruker D8 Advance with DaVinci X-ray diffractometer (XRD). ZEISS Ultraplus Field Emission Scanning Electron Microscope (FE-SEM) was used to study the surface morphology of the samples.

Raman scattering experiments were carried out using a Renishaw Raman Microscope system at room temperature. Before conducting any measurements, the instrument was calibrated using an internal Si sample, which was measured at a Raman shift of 520 cm⁻¹. A 633 nm laser beam was focused on the samples. Phase transformations from FeO to Fe₃O₄, from Fe₃O₄ directly to α -Fe₂O₃ (martitization)¹⁷ and from Fe₃O₄ first to γ -Fe₂O₃ then to α -Fe₂O₃¹⁸ are reported for iron oxide films during Raman scattering at high laser powers. Hence, sacrificial films were first excited at different laser powers to determine a threshold power, so that no phase transformations take place and high enough power for reasonable signal to noise ratio is achieved. At 0.12 mW, the signal intensity was very low and a laser power of 1.2 mW was determined to be a safe limit with no

change in the observed spectra and high intensity signals. The spectra were taken over a range of wavenumbers from 200 cm⁻¹ to 1500 cm⁻¹. The acquisition time was 10 s to 30 s.

The diffuse reflectance spectra of the investigated samples were performed using a Shimadzu UV-vis-NIR 3600 spectrophotometer using integrating sphere attachments. Photoelectrochemical analyses were performed with Bio-Logic VSP model potentiostat/galvanostat system. The current-voltage (*I*-*V*) characteristics of the electrodes were measured under amplitude modulated-light illumination with a 300 W xenon arc lamp (Oriel, Stratford, CT) with the 3 electrode cell system in an aqueous solution of 0.1 M NaOH. An AM 1.5 air filter was used to mimic solar radiation with a power of 100 mW cm⁻².

Results and discussion

We have investigated the effect of electrodeposition under hydrothermal conditions from both acidic and neutral deposition solutions on the structure and phase of iron oxide films. The hematite thin films deposited using the hydrothermal-electrochemical deposition range in colour from brown to deep red. It was observed that the films tend to adhere on the FTO surface more strongly than ITO-coated glass. Hence, FTO was chosen as the substrate for the rest of the study. Increased precursor concentration and high pH enhance the adherence of iron oxide on the substrates. Fig. 1 shows the FE-SEM images of pristine and annealed films deposited at 130 °C and ~2 bar. FE-SEM study showed that the pristine film prepared from an aqueous bath containing 0.02 M FeCl₂ (pH = 3.8) with anodic electrodeposition, H1, is composed of monodisperse almost-spherical particles of around 300–400 nm, which preserved their size and morphology after annealing (Fig. 1a and b). By increasing the concentration of Fe²⁺ from 0.02 to 0.05 M, H3, the spherical shape develops into a polyhedra shape and high polydispersity in size (80–150 nm) is observed (Fig. 1e). Although particles with smaller sizes (~50 nm) do exist, mostly larger aggregates of varying sizes are present after annealing (Fig. 1f). Nano-iron oxide particles prepared from a neutral deposition bath, H2, exhibit higher polydispersity than its counterpart that are prepared from an acidic deposition bath and distortion from spherical morphology (Fig. 1c). Nano-particles with diameters of 50–100 nm are observed to form large, spherical aggregates of the order of micrometers. The size and morphology are preserved after annealing (Fig. 1d). When Fe²⁺ concentration was increased from 0.02 to 0.05 M (and corresponding [NaCH₃COO]), H4, spherical nanoparticles with diameters of ~50 nm and well-faceted polyhedra with a broad range of particle sizes form together (Fig. 1g). After annealing, an increase in the average diameter of the spherical nanoparticles to around 100 nm and the formation of micrometer sized aggregates are observed (Fig. 1h). In addition, polyhedral particles seem to have disappeared.

The anodic deposition of FeOOH films from ferrous sulfate solutions with varying pH was introduced by Cohen and Leibenguth in 1972.¹² The electrodeposited FeOOH films were then converted to hematite phase by annealing. Cohen and Leibenguth used ammonium sulfate/ammonium or boric acid/

Table 1 Deposition parameters for hydrothermal-electrochemical deposition at 130 °C, 1.2 V vs. Ag/AgCl (satd)

Film	[Fe ²⁺]	[NaAc]	Deposition time
H1	0.02 M	—	8 min
H2	0.02 M	0.08 M	8 min
H3	0.05 M	—	8 min
H4	0.05 M	0.2 M	8 min

Fig. 1 FE-SEM images of the films (a) H1 as-deposited, (b) H1 annealed, (c) H2 as-deposited, (d) H2 annealed, (e) H3 as-deposited, (f) H3 annealed, (g) H4 as-deposited, and (h) H4 annealed.

sodium borate to stabilize Fe^{2+} ions in a neutral solution.¹² Spray and Choi modified the neutral deposition bath reported by Cohen and Leibenguth by replacing ammonium sulfate/ammonium or boric acid/sodium borate with NH_4Cl , and they compared the photoelectrochemical properties of the products with that of the films obtained by anodic electrodeposition from the acidic bath.¹³ In this study, NaCH_3COO was chosen for stabilization and electrodeposition was carried out in otherwise identical conditions as the depositions in the acidic solution. The anodic deposition condition used in this study results in the oxidation of Fe^{2+} ions to Fe^{3+} ions (eqn (1)), which is followed by the precipitation of Fe^{3+} ions as amorphous ferric oxyhydroxide due to the limited solubility of Fe^{3+} ions in the plating solution ($[\text{Fe}^{3+}] \approx 1 \times 10^{-7}$ at pH 4.1) (eqn (2));^{9,13}

Hence, it is expected that the as-deposited films contain amorphous ferric oxyhydroxide, which is converted into crystalline $\alpha\text{-Fe}_2\text{O}_3$ upon annealing as reported before.^{12,13} To identify the structure and phases of the obtained films, XRD was employed (Fig. 2). The XRD patterns of the as-synthesized films revealed peaks with the highest intensities at $2\theta = 24^\circ$, 33° , and 35° , which can be indexed to the (012), (104) and (110) reflections of crystalline, rhombohedral $\alpha\text{-Fe}_2\text{O}_3$, hematite structure {JCPDS card no. 86-0550} even before the annealing step without any other phase being detected (Fig. 2). The patterns exhibit an intensity distribution corresponding to the standard polycrystalline hematite structure, where the crystallites are randomly oriented. Moreover, the crystallinity of the films improves with no accompanying compositional changes after annealing (Fig. 2).

To further evaluate the purity of the hematite phase, Raman spectroscopy was used. Hematite belongs to the D_{3d}^6 space group and seven transitions are expected in the Raman

spectrum.^{17,19,20} Two A_{1g} modes at 225 and 498 cm^{-1} and five E_g modes at 247 , 293 , 299 , 412 and 613 cm^{-1} are expected. The Raman spectrum of the as-synthesized films at 130°C exhibit major peaks at 226 , 247 , 296 , 411 , and 615 cm^{-1} with 226 and 296 cm^{-1} being the strongest; all these peaks correspond well to $\alpha\text{-Fe}_2\text{O}_3$ peaks (Fig. 3). In addition to these peaks, the modes around $\sim 660\text{ cm}^{-1}$ and $\sim 1320\text{ cm}^{-1}$ were present in all the hematite Raman spectra obtained in the whole study. The 660 cm^{-1} mode is present in several published hematite spectra, and it is either assigned to magnetite/wüstite (FeO) impurity or considered as the characteristics of hematite and assigned to a disorder phase.^{21–23} There is no evidence of any other iron oxide phase in the XRD diagrams (Fig. 2). The lack of evidence for the presence of impurity phase suggests that the 660 cm^{-1} peak is related to the hematite phase, which has been ascribed to the disorder in the crystal lattice and the breaking of symmetry

Fig. 2 XRD profiles of the hematite films electrodeposited at 130°C , ~ 2 bar. The following symbols represent the reflections associated with ■ ITO (JCPDS card no. 89-4597) and * SnO_2 (JCPDS card no. 41-1445).

Fig. 3 Raman spectra of the hematite films electrodeposited at 130 °C, ~2 bar.

upon crystallization.²¹ The mode around 1320 cm⁻¹ has been suggested to be an overtone of the peak at 660 cm⁻¹.²¹ It was also ascribed to two-magnon scattering including magnon-magnon interactions of antiferromagnetic hematite.¹⁷ Further, there are additional peaks around 820 and 1050–1100 cm⁻¹. They are reported to exist in the xx polarized hematite spectra.¹⁹ Hence, Raman spectroscopy data (Fig. 3) together with XRD (Fig. 2) demonstrate that the hematite phase forms directly with hydrothermal-electrochemical deposition at 130 °C. This behaviour is contradictory to the expected amorphous ferric oxyhydroxide (γ -FeOOH, as stated above)^{12,13} or goethite²⁴ formation with anodic electrodeposition under ambient conditions and moderate temperatures. An example Raman spectrum for one of the annealed films is also provided in Fig. 3.

Cohen and coworkers carried out the anodic deposition from ferrous sulfate solutions in a neutral medium (pH varying between 6.6 and 8) and studied reaction kinetics.¹² They have shown that the deposition rate increases with both pH and [Fe²⁺]. Leibenguth and Cohen discussed that the deposition proceeds through the diffusion and oxidation of ferrous hydroxyl complex and the formation of FeOOH instead of Fe₂O₃ depends on how fast the ions are transferred to the anode. They proposed that FeOOH forms rather than Fe₂O₃ owing to the fact that OH⁻ ions migrate easier than Fe²⁺ ions because of their smaller positive charge. The fact that the α -Fe₂O₃ phase is obtained directly from both acidic and neutral HED suggests that the temperature effect rather than OH⁻ ion concentration has a major role. Fig. 4 shows the charge vs. time plot for depositions with varying parameters such as temperature, pH and initial [Fe²⁺]. (Electrodeposition at 75 °C was also carried out under identical conditions.) It can be seen that the deposition rate increases with concentration (H1 ([Fe²⁺] = 0.02 M) and H3 ([Fe²⁺] = 0.05 M) at pH 3.8); (H2 ([Fe²⁺] = 0.02 M) H4 ([Fe²⁺] = 0.05 M) at pH ~6.4) and pH (when H1 is compared with H2 and H3 is compared with H4), which is in accordance with what is reported by Leibenguth and Cohen. Moreover, the deposition rate increases much more effectively when the

Fig. 4 Effect of initial [Fe²⁺], pH, and temperature on the electrodeposition rate.

temperature is increased from 75 °C to 130 °C, while all the other parameters are kept constant (Fig. 4). The growth of hematite can be explained by the following reaction:

with the following equilibrium potential at 25 °C calculated by using the tabulated thermodynamic values for chemical species and Nernst equation:

$$E = 0.728 - 0.177\text{pH} - 0.0592 \log[\text{Fe}^{2+}] \quad (4)$$

which results in the thermodynamic potentials of -0.734 V for [Fe²⁺] = 0.02 M and -0.75 V for [Fe²⁺] = 0.05 M at 130 °C, pH = 6.4, and -0.112 V for [Fe²⁺] = 0.02 M and -0.128 V for [Fe²⁺] = 0.05 M at 130 °C, pH = 3.8. Considering the fact that high overpotential is applied during deposition, the formation of hematite phase directly at high temperatures might be explained by higher reaction kinetics.

Hematite nanoparticles are useful for various applications such as the anode of photoelectrochemical cells for water splitting, detection electrode for gas sensors, the positive electrode for Li-ion batteries and the photodegradation of dyes may be promising.^{25–27} We have evaluated the optical and photoelectrochemical performances of the films post-annealing at 520 °C, except H1 as it did not adhere onto the substrate very effectively. The optical absorbance spectra of the films (Fig. 5a) exhibit two broad absorption bands centered at around 345 nm and 514 nm. These bands are slightly blue shifted from the reported absorption bands of hematite, which are normally observed at around 400 and 530 nm.^{28–30} The degree of change of the peak positions is reported to depend on the shape and size of the particles.²⁷ Hence, the shift can be attributed to the size quantization of the hematite nanoparticles. The band at lower wavelengths can be attributed to ⁶A₁ → ⁴E and the ⁶A₁ → ⁴E ligand field transitions of Fe³⁺.^{27,28} The low energy band is ascribed to the ⁶A₁ → ⁴T₂ ligand field transition of Fe³⁺.^{27,29} In addition, two charge-transfer transitions accompany

Fig. 5 (a) UV-visible light absorption spectra of hematite films electrodeposited at 130°C , ~ 2 bar; (b) the photocurrent responses of the hematite films at 1.1 V vs. NHE under amplitude modulated illumination; (c) the photocurrent responses of H4 with varying deposition times at 1.1 V vs. NHE under amplitude modulated illumination; (d) photocurrent-voltage ($J-V$) curves of H4_8 min under dark and illumination at 100 mW cm^{-2} (AM 1.5 air filter).

these processes: a direct transition corresponding to the ligand-metal transfer ($\text{O}_2 \rightarrow \text{Fe}^{3+}$) at higher energy and an indirect transition at higher wavelength from the metal-metal transfer.^{27,31}

The PEC performances of annealed $\alpha\text{-Fe}_2\text{O}_3$ electrodes were measured under amplitude modulated 1 sun illumination at 1.1 V vs. NHE in 1 M NaOH (Fig. 5b) at a lower potential than theoretical water oxidation potential (eqn (3); $E^\circ(\text{O}_2/\text{H}_2\text{O}) = 1.23 \text{ V vs. NHE}$ at pH 13.5). The anodic nature of the photocurrent produced suggests n-type behavior for all the films and the responses are quite stable with no sign of photocorrosion. The net photocurrent densities of the films are 11.3, 11.4, and $23.6 \mu\text{A cm}^{-2}$, respectively, for H2, H3 and H4. The photoresponse of the film prepared from a highly concentrated neutral bath (H4) is almost twice that of the responses of the other films. In addition, the photocurrent switching (ON/OFF) response of H4 is faster than both H2 and H3. Even though, H2 consists of smaller sized particles (Fig. 1), which provide higher surface

area, and therefore, beneficial to decrease the recombination losses,¹³ H4 generates higher photocurrent than H2.

The difference in the photoresponses of H2 and H4 can be attributable at least, in part, to higher Fe_2O_3 loading on H4. As discussed above, the deposition rate increases with increasing $[\text{Fe}^{2+}]$. Hence, a higher amount of hematite should be deposited from a more concentrated deposition bath at a given time, which would result in increased number of generated electron-hole pairs that can contribute to the photocurrent generation for H4. On the other hand, a similar deposition rate for H3 and H4 (Fig. 4) suggests similar Fe_2O_3 loading for these films. In addition, as evident in Fig. 5a, H3 displays higher photon absorption. Therefore, H3 was expected to generate higher photocurrent. However, H3 is composed of 300–400 nm sized polyhedra, whereas spherical nanoparticles of around 100 nm are observed for H4. A smaller particle size, and hence, higher surface area of H4 allows more holes to reach the hematite/electrolyte interface, which reduces the recombination losses¹³ and results in higher photocurrent generation.

Fig. 6 FE-SEM images of (a) H4_4 min and (b) H4_16 min and cross-sectional FE-SEM images of (c) H4_4 min, (d) H4_8 min and (e) H4_16 min.

As an effort to optimize the obtained photoresponse, films were prepared from neutral, concentrated (0.05 M Fe^{2+}) deposition bath with different deposition times (H4_4 min, H4_16 min). The PEC performances were measured under identical conditions.

The photocurrent density increased ~ 40 -fold as the deposition time increased from 4 min ($0.66 \mu\text{A cm}^{-2}$) to 8 min ($23.6 \mu\text{A cm}^{-2}$) (Fig. 5c). Analysis of the FE-SEM images implies that the surface morphologies of the films are very similar with nanometer-sized spherical particles and micrometer-sized aggregates (Fig. 1 and 6). The thickness of the samples was measured by taking cross sectional FE-SEM images. The films deposited for 4 and 8 min resulted in films with average thicknesses of 1.2 and $1.33 \mu\text{m}$, respectively, as calculated from the cross-sectional FE-SEM images (Fig. 6). The increase in the photoresponse from 4 to 8 min can be attributed to an increase in the number of electron-hole pairs due to the presence of additional photoactive oxide in the thicker films. After 16 min of deposition, the generated photocurrent density decreased to around $0.7 \mu\text{A cm}^{-2}$, which is similar to H4_4 min. It is reported that when the thickness of the hematite film reaches beyond $2.6 \mu\text{m}$, the distance that the holes would have to travel to reach the Fe_2O_3 /electrolyte interface is increased, which results in higher recombination probability.³² Increased hole-diffusion length together with reduced photon penetration for a thicker film²⁹ might account for a decrease in the produced photocurrent with H4_16 min.

The photocurrent-voltage (J - V) pattern of H4 measured under identical conditions is shown in Fig. 5d. The onset potential for H4 is calculated by extrapolating the linear portion of the J - V curve to zero current from where the current densities range from 15 to $60 \mu\text{A cm}^{-2}$. The photocurrent onset potential is calculated to be 0.96 V vs. NHE. After onset, the photocurrent shows two separated potential regions.²⁹ In the first region, the photocurrent increases to reach $26.5 \mu\text{A cm}^{-2}$ at 1.23 V vs. NHE and $72.75 \mu\text{A cm}^{-2}$ at 1.6 V vs. NHE. This region corresponds to where the four-electron water oxidation reaction takes place (eqn (5)). The region from 1.6 V to 1.8 V (where the photocurrent density reaches $102 \mu\text{A cm}^{-2}$) is the second region where

the two-electron water oxidation reaction (eqn (6)) also takes place.

The preparation of doped hematite films to enhance the PEC performances by the presented hydrothermal-electrochemical deposition technique and post-surface modifications to reduce the surface recombination probability are currently under study.

Conclusions

Hydrothermal-electrodeposition was successfully employed to produce $\alpha\text{-Fe}_2\text{O}_3$ and the effect of electrodeposition temperature on the structure and phase of iron oxide films was studied. In line with the literature, potentiostatic electrodeposition at ambient temperatures such as 75°C results in the formation of amorphous iron oxide particles, which can be converted to hematite ($\alpha\text{-Fe}_2\text{O}_3$) upon thermal treatment. Combining electrochemistry with the advantages of hydrothermal synthesis allows the growth of crystalline $\alpha\text{-Fe}_2\text{O}_3$ phase directly at a single step on the conducting glass. It is demonstrated that regardless of pH, the growth time and presence of additives (CH_3COO^-), hematite crystals are obtained with anodic HED most probably due to the increased reaction kinetics at high temperature. The thickness of the films can be adjusted with growth time, and the pH is found to be effective on both the reaction kinetics and final particle size. Higher pH and higher precursor concentration favour increased deposition rate in line with the observations of Cohen and Leibenguth and smaller particle size.

Photoelectrochemical studies demonstrated that better performance can be obtained with the films prepared *via* HED than the films electrodeposited at lower temperatures. A net photocurrent density of $23.6 \mu\text{A cm}^{-2}$ is obtained in 0.1 M NaOH under 1 sun conditions at 1.23 V vs. NHE with the film prepared from a bath containing 0.05 M FeCl_2 and 0.1 M NaCH_3COO *via* hydrothermal-electrodeposition with a photocurrent onset potential of 0.96 V vs. NHE.

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