Light-Directed Growth of Semiconductor Nanomaterials by Photoelectrodeposition

Chu Qin
Washington University in St. Louis

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Light-Directed Growth of Semiconductor Nanomaterials by Photoelectrodeposition
by
Chu Qin

A dissertation presented to
The Graduate School
of Washington University
in partial fulfillment of the
requirements for the degree
of Doctor of Philosophy

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Chu Qin

Washington University in St. Louis

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ABSTRACT OF THE DISSERTATION

Light-Directed Growth of Semiconductor Nanomaterials by Photoelectrodeposition

by

Chu Qin

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Professor Sophia Hayes, Chair

In this work, the chemical and physical properties of semiconductor microcrystals and metastable polymorphs were transformed through photoexcitation during electrochemical synthesis. Interfacial charge transfer using photogenerated carriers were used to successfully control the growth of metal oxide semiconductors and change their morphology, composition improve their catalytic activity. The main material systems studied in this thesis are electrodeposited copper oxide (Cu$_2$O) and manganese oxide (MnO$_x$) semiconductor films. Illumination can direct the shape transformation of Cu$_2$O crystals at the nanoscale by facet-selective charge transfer. During photoelectrodeposition on Cu$_2$O microcrystals with well-developed facets, light mediates the deposition of copper metal selectively on the {100} facets while the crystal interior is etched at {111} facets to form a shell structure. This process reveals that the combination of an applied electrochemical bias and illumination can control the facet-dependence of photochemical reactions on the surface of Cu$_2$O. Illumination can also enhance the catalytic activity of MnO$_x$ films through transforming their composition and morphology during growth. MnO$_x$ films synthesized under illumination display a significantly higher activity for the oxygen evolution reaction (OER), better stability, and a lower onset potential compared to MnO$_x$ films synthesized in the dark. Structural and electrochemical characterization reveal that MnO$_x$
films formed under illumination undergo a phase change to develop structural features that increase their stability and activity for the OER. This thesis provides insights into the spatial separation of photo-induced charge carriers on the surface of semiconductors during photoelectrochemical synthesis. Photoelectrodeposition has been shown as a novel method to control redox reactions at preferred surfaces of the nanomaterials. It can tailor the morphology and control the oxidation states of transition metal ions in metal oxide semiconductors and enhance desirable properties including catalytic activity. Thus, photoelectrochemical synthesis helps us design functional materials at the nanoscale.
Chapter 1: Introduction

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1.1 Shape Control of Structures during Electrodeposition

Electrodeposition is a highly scalable, additive growth method capable of plating uniform films over large areas (up to square meters) in a continuous fashion.\(^1\) Electrochemical and photoelectrochemical devices typically incorporate metallic or semiconducting films or particles as their main component. The incorporation of nanoscale materials in electrochemical devices possess high surface areas that can enhance their catalytic performance during chemical catalysis. Nanostructured semiconductors also lead to more efficient charge extraction in electrochemical and photoelectrochemical devices because of shorter diffusion lengths need to reach the semiconductor/liquid interface. As the surface morphology and nanoscale features can change the optical properties and catalytic activities of semiconductors significantly, methods to control the nanoscale morphology of semiconductors are desirable. The nanoscale morphology of particles can be controlled via different growth methods. Electrodeposition is a good way to grow semiconductors and metal films under mild conditions. The growth can be controlled by applying different electrochemical conditions and by using different growing baths and surfactants. Atoms are deposited to certain regions through interfacial charge transfer and the crystals grow into
different shapes. Shape control by electrodeposition is critical in tuning the surface structure of the nanomaterials to enhance desired properties.\textsuperscript{2-4}

There are several ways to control morphology of materials grown by electrodeposition, including preferential adsorption, the use of templates, and through mass-transport-limited growth.\textsuperscript{5} Through the combination of these methods, various crystal shapes can be created.\textsuperscript{2} Shape control by the preferential adsorption of facet-selective binding agents is a common way to control the growth of both colloidal particles and electrodeposited structures.\textsuperscript{2} Preferential adsorption occurs when using a growth medium containing a surfactant that can preferentially adsorb on specific crystallographic planes or step edges of the crystal. Different crystal facets have different arrangements of atoms and charge densities. Thus, the binding strength of the surfactants to different surfaces varies. Preferential adsorption can be used to tune the shape of the crystal if relative growth rates along two or more crystallographic axes can be controlled.

When the material is electrodeposited at or near equilibrium, surfactants can bind to a specific surface and lower its surface energy. The surfaces with the lowest energy will dominate as the crystals grow under equilibrium. In this growth regime, the crystals are thermodynamically stable, and the overall surface free energy is minimized. When the material is electrodeposited away from equilibrium, surfactant molecules preferentially adsorbed on a surface will block access of adatoms to be deposited on that surface. Thus, growth occurs on other surfaces that do not have bound surfactants and leads to a high-energy, non-equilibrium shape.\textsuperscript{6} Electrodeposition using surfactants can change the overall surface energy of the crystal and affect the growth rate in an anisotropic way.
Chapter 2 discusses the photo-induced transformation of cuprous oxide (Cu$_2$O) microcrystals that already have well-developed facets. In previous reports, Cu$_2$O microcrystals have been successfully grown in a variety of shapes and morphologies by tuning the reaction conditions like potential, pH, temperature, and deposition time.\textsuperscript{2, 7} Shape-controlled Cu$_2$O microcrystals can be grown by electrodeposition or by colloidal synthesis. This work mainly focuses on electrodeposition of Cu$_2$O microcrystals. The $\{111\}$ facets of Cu$_2$O possess higher surface energies than $\{100\}$ facets. When electrodeposited without any surfactants, Cu$_2$O microcrystals will grow into a cubic shape with $\{100\}$ facets in order to minimize surface energy. The shape control of the crystal can be achieved by adding sodium dodecyl sulfate (SDS) as a surfactant.\textsuperscript{2} SDS selectively adsorbs to $\{111\}$ planes and lower their surface energy. So, Cu$_2$O crystals are grown into octahedral shapes as SDS decreases the growth rate along the $\langle111\rangle$ directions. The shape of Cu$_2$O crystals can also be controlled by other additives. For example, NO$_3$\textsuperscript{-} ions can stabilize the $\{100\}$ facets, while SO$_4^{2-}$ ions can stabilize the $\{111\}$ facets of Cu$_2$O crystals.\textsuperscript{8} When Cu$_2$O microcrystals are grown in a solution containing NH$_4^+$ ions, $\{110\}$ and $\{111\}$ facets develop simultaneously.\textsuperscript{8} In Chapter 2, Cl$^-$ ions are used to synthesize Cu$_2$O microcrystals with a cuboctahedral shape with a mixture of $\{100\}$ and $\{111\}$ facets. Octahedral Cu$_2$O microcrystals can be transformed into a cubic shape if Cl$^-$ ions are added to the growing bath, as Cl$^-$ ions stabilize $\{100\}$ facets. By controlling the reaction time and the amount of SDS and Cl$^-$ ions, different ratios of $\{100\}$ and $\{111\}$ facets in the crystals can be achieved, including the cuboctahedral shape, where the amount of two facets are nearly equal.\textsuperscript{8}

Crystals with simple facets can be electrodeposited under or near equilibrium. To grow crystals with more complicated shapes, the electrodeposition process needs to be conducted away from equilibrium. Several methods can be used to grow crystals with high-energy, non-equilibrium
shapes, including applying high overpotentials and mass-transport limited growth. These methods can lead to the branched growth of the crystals. The advantage of electrodeposition is that it can be paused anytime, so the electrochemical conditions can be changed, and the electrode can be moved to another growth bath containing different surfactants. So, growing crystals with more complicated shapes can be achieved by growing crystals with simple facets first, then moving the electrode to another medium and applying an overpotential or a different electrochemical program. The branched growth of metal oxides can also be controlled by varying temperature during electrodeposition. A change in temperature of the reaction system will significantly affect the reaction by changing surfactant adsorption/desorption, the complexing stability, the growth rate, and hence the shape and size distribution. As a change in temperature leads to changes in many parameters at once, it is not an ideal way to control growth in general, but has been used to control the growth dendritic zinc crystals.

Although shape control by electrodeposition is commonly used, it still has several limitations. First, electrodeposition consumes electrical energy. From an energy-saving perspective, it is desirable to use sunlight light to direct the growth of semiconductors with the freely available energy of photons. Also, obtaining desired shapes by electrodeposition is complicated. The desired shape must be designed beforehand as the synthesis route contains a series of different surfactants and electrochemical methods. Photoelectrodeposition, however, is able to deposit materials that are simultaneously responsive to light. So, the growth to desired shapes is more self-directed and it can enhance light absorption of semiconductor nanomaterials to improve certain properties.
1.2 Fundamentals of Semiconductors

The fundamental properties of semiconductors and light-matter interactions in semiconductors will be discussed first to help understand light-directed growth. Many inorganic materials are responsive to external stimuli like illumination, temperature, pH, etc., and their chemical transformation can be controlled by tuning these parameters. The broad purpose is to utilize solar energy to control the shape and morphology of semiconductor nanoparticles, and thus develop semiconductor materials that can harvest sunlight more efficiently.

The photovoltaic properties of semiconductors have attracted intensive research interests in science and engineering for decades. The photovoltaic effect was first experimentally demonstrated by French physicist Edmond Becquerel in 1839, and it refers to the process in which photons of incident light excite electrons in a semiconductor into a higher state of energy and generate electron-hole pairs. The opposite types of charge carriers are the separated and extracted to an external circuit, and photocurrent is generated. Since the development of the solar cell industry in the 1970s, semiconductor electrodes with higher conversion efficiency and lower cost are being pursued. Scientists have been working on simplification of photovoltaic panel manufacturing process, reduction in the materials usage and cost, and improvement of cell and module efficiency to create better photovoltaic systems.

An energy gap, or band gap, is an energy range in which no electron states can exist in a defect-free semiconductor. The size of the band gap in a semiconductor is directly related to its optical properties because the band gap determines which part of the solar spectrum a photovoltaic cell can absorb photons. It is crucial to choose a material with just the right size of band gap, and it would be desirable if the band gap falls into the visible light region and absorbs light most efficiently there. If the band gap is too large, then most of the incident solar irradiation cannot be
absorbed as the photons do not possess sufficient energy. If the band gap is too small, a great amount of energy will be wasted as only energy equal to the band gap will be converted, and the solar cell cannot produce a high enough electrical potential.\textsuperscript{11}

Controlling the nanoscale morphology of semiconductors can change the efficiency of photovoltaic devices. For example, thin film solar cells could have lower efficiencies due to a higher density of defects.\textsuperscript{12} On the other hand, the travel distance for charge carriers to reach front or back contact is shorter in thin films so the purity of the semiconductors does not need to be as high to efficiently extract charges. TiO\textsubscript{2} nanotubes have outstanding photovoltaic performance because of the high surface areas and more efficient charge transfers of the nanotube arrays.\textsuperscript{12} As we are trying to convert as much solar energy as much as possible, attention should be paid to all steps in the conversion of photon energy, including photon absorption, generation of charge carriers, their transport, separation, and charge-carrier extraction.

In this work, the discussion will be focused on how the morphology of a semiconductor affects its absorption. For solid-state photovoltaics, the number of photons absorbed determines the concentration of mobile charge carriers. Surface morphology is important in controlling the absorption strength of a semiconductor. In the initial step of photon absorption, there is a trade-off between the absorption coefficient of the semiconductor and the minority-carrier diffusion length. The minority-carrier diffusion length is the average distance the minority carrier can move from the point of generation to recombination.\textsuperscript{13} We tend to design thinner solar cell devices as it consumes less material and is lighter in weight. It can also minimize bulk recombination of charge carriers if the thickness is smaller than the diffusion length of minority carriers.\textsuperscript{13} On the other hand, the Beer-Lambert law relates the attenuation of light to the path length of the beam through the material and its absorption strength. The Beer-Lambert law states the minimum thickness to
obtain reasonable light absorption for a given material system. So, it is critical to synthesize semiconductors with nanostructures that can enhance light absorption. To solve this conflict many resolutions have been proposed, including designing wavelength-scale photonic substrates, plasmonic materials and semiconductor quantum dots.\textsuperscript{14-18} Historically, people have made subwavelength textured surfaces to trap light in a thin film.\textsuperscript{19, 20} Nowadays nanowire arrays have been a trending structure in solar cells. Vertically aligned nanowires provide a long optical path length and short distance for carriers to travel in a photoelectrochemical cell.\textsuperscript{21, 22} A radial contact can be difficult to achieve in a solid-state device, but can be easily made in a photoelectrochemical cell where there is a semiconductor/liquid junction. So, they can absorb enough light, and charge carriers can travel their way out in the radial direction before recombination. When a beam of light interacts with a surface, the beam will lose energy due to two processes: absorption and incoherent scattering. As nanowires can change the scattering and absorption coefficient of the surface, they are able to increase light absorption. However, there are still some limitations of nanowire devices. For example, the synthesis of nanowires is not yet scalable to be manufactured in a high yield.

### 1.3 Light-Directed Growth of Semiconductors

Researchers have used light-directed growth to synthesize materials and to enhance certain desirable properties. However, sometimes the synthesized structures of light-directed growth cannot be predicted and is worth more research effort. The light-directed growth of semiconductors is mediated by combining electrodeposition with the photovoltaic effect. The nanoscale structure of a material sculpts the way it interacts with light.\textsuperscript{1} As described above for solid-state photovoltaics, well-designed structures, like textured nanoscale surfaces or nanowire arrays, can
enhance light absorption and improve efficiency of charge collection. The same principles can be applied to the electrodeposition of structured semiconductors. Electronic excitation in semiconductors can lead to interfacial charge transfer that can change the growth rate of materials. As the film is nonuniform at nanoscale, the distribution of light absorption is also nonuniform due to different local morphologies of the growing film. During photoelectrochemical growth, photogenerated charge carriers can be used to grow or etch materials on the surface through interfacial charge transfer. For example, during photoelectrodeposition of chalcogenides, charge transfer leads to deposition of the films onto the substrate, and Se-Te particles will be added preferentially in regions that have stronger photon absorption. In this case, the structure is driven towards morphological features that can amplify its optical response and this is one of the goals of light-directed growth.

Light-directed growth of electrodeposited semiconductor films has previously been used to synthesize nanostructures with high surface areas. For example, light-directed growth has been previously observed in chalcogenide semiconductors. Anisotropic and ordered nanoscale lamellar morphologies of Se–Te films were synthesized by photoelectrodeposition. The orientation and periodicity of Se–Te films can be controlled by the polarization, incident angle and wavelength of the incident light.

This thesis focuses on applying light-directed growth to metal oxide semiconductors, including Cu₂O and MnOₓ. Light-directed growth has not previously been applied to control the morphology of electrodeposited metal oxides. Light is used to direct crystal growth by enhancing the electrochemical potential through the combination of an external bias and interactions between the growing semiconductor film and the incident illumination.
1.4 Dissertation Overview

This thesis focuses on how light can direct the growth of metal oxide films during electrodeposition and examines the influence of illumination on the morphology and catalytic activities of electrodeposited films. Photogenerated electrons and holes created by absorption of incident photons make the growth semiconductors responsive to light. Light-directed growth of metal oxides during electrodeposition has not been explored extensively. So, it is critical to study the transformation in morphology, composition, and catalytic performance of metal oxides during this process.

The main material systems used in this thesis are electrodeposited Cu$_2$O particles and MnO$_x$ semiconductor films. The main synthetic technique used in this thesis is the electrodeposition of metal oxide crystals and films. Photoelectrodeposition is applied using different light sources such as a broad-spectrum ELH lamp as well as light-emitting diodes (LEDs) of different colors. Different electrochemical conditions (i.e., the applied potential, current, pH, etc.) and varied wavelengths and intensities of light sources are used to control the morphology and composition of the deposited materials. The main material systems used in this thesis are electrodeposited Cu$_2$O particles and MnO$_x$ semiconductor films. The microcrystals and films are characterized by several techniques to provide full details of their structure, composition, and morphology, including scanning electron microscopy for surface morphology, x-ray diffraction for crystal structure, x-ray photoelectron spectroscopy for surface composition, energy-dispersive x-ray spectroscopy for elemental composition, and absorption spectroscopy for band gap energy. The electrochemical properties of the synthesized nanocrystals and films are tested by cyclic voltammetry, linear sweep voltammetry and electrochemical impedance spectroscopy.
This characterization is used to develop a comprehensive mechanism describing the growth of Cu$_2$O microcrystals and MnO$_x$ films under illumination. During photo-induced transformation of Cu$_2$O microcrystals with well-developed facets, the photoexcited charge carriers lead to facet-dependent charge-transfer reactions. Light mediates the growth of copper metal selectively on the \{100\} facets while the crystal interior is etched at \{111\} facets to form a shell structure. For MnO$_2$ films, we propose that illumination can modify the composition and morphology of MnO$_x$ films and incorporate more Mn$^{3+}$ ions into MnO$_2$, which improves their catalytic activity for the water oxidation reaction. This thesis has developed new photoelectrochemical methods to control the morphology and composition of metal oxide semiconductors. Light-directed growth has been used to synthesize novel nanoscale morphologies that cannot be made by traditional synthetic methods and to enhance the electrocatalytic activity of films for industrially important reactions.
Chapter 2: Light-Driven, Facet-Selective Transformation of Cuprous Oxide Microcrystals to Hollow Copper Nanoshells


Abstract

Photoexcitation can be used to control the composition and nanoscale morphology of inorganic materials. Here we report the photoinduced transformation of faceted cuprous oxide (Cu$_2$O) microcrystals to hollow particles consisting of an inner region of cuprous oxide and an outer shell of copper metal. When cuprous oxide microcrystals with mixed {100} and {111} facets are held at a negative bias (−1.0 V vs. Ag/AgCl) in a solution of sodium hydroxide (NaOH), light mediates the growth of copper metal selectively on the {100} facets while the crystal interior is etched at {111} facets. Conformal Cu layers grow to connect at vertices of the cuboctahedral microcrystals and form a hollow shell. This process is only observed in the presence of illumination. Without an applied bias the {100} facets are preferentially etched under illumination in the same NaOH solution. We propose this light-driven, facet-selective transformation arises from the potential-dependent structure and energetics of the semiconductor/electrolyte interface,
which lead to facet-selective extraction of photogenerated electrons from the \{100\} facets when the applied bias is more negative than the flat-band potential of the Cu$_2$O microcrystals. Growth of the Cu shell protects the \{100\} facets while the \{111\} facets are chemically etched in the presence of oxygen and hydroxide.

### 2.1 Introduction

Photochemical and photoelectrochemical reactions use light to drive the formation of chemical products. In semiconductors and plasmonic metals, photon-to-chemical conversion is mediated by the generation of mobile charge carriers that can be extracted from the material to oxidize or reduce surface-adsorbed species. The extraction of photoexcited charges can also be used to grow or transform the material itself. Illumination during growth has produced complex nanoscale morphologies in both semiconductors and metals that are difficult to achieve by other synthetic routes. A prominent example of light-directed growth is the photoinduced conversion of spherical silver nanoparticles to nanorods and nanoprisms. This transformation is initiated by plasmon excitations that decay to generate hot charge carriers. Early reports hypothesized the prism and rod shapes resulted from anisotropic electromagnetic fields produced by plasmon excitation that create preferential regions for growth on the initially spherical Ag seed particles. However, it now appears that the final shape of the Ag nanoparticle is dictated by the specific facets and planar defects (e.g. twin boundaries or stacking faults) present during the early stages of growth.

More recently, illumination has been used to drive the formation of complex, nanoscale patterns during the electrochemical growth of chalcogenide glasses.
interactions (e.g. absorption and scattering) near the surface of the growing film lead to periodic variations in the concentration of photoexcited charge carriers. Because of the low mobility of charge carriers in chalcogenide glasses, only photoexcited electrons near the surface of the films can be used to add material via reduction of ions in solution. In this way, the growth of the film mimics the light-intensity pattern and can be controlled by the wavelength, polarization, and angle of the incident illumination.

In plasmon-mediated growth of Ag nanoparticles, the structure of the Ag seed particles is believed to be dynamic under illumination, making it difficult to correlate the initial structure with the final particle shape. In the photoelectrochemical growth of nanopatterned chalcogenide films, the electrodeposited material is poorly crystalline consisting of nanoscale grains mixed with amorphous material. Thus, the role of surface structure in the resulting morphology during light-directed growth remains underexplored. To expand the range of materials and morphologies that can be grown using light, we decided to study how illumination affects the electrochemical growth of a material system that exhibits highly facet-dependent chemical and physical properties. Cu$_2$O microcrystals serve as a model system for this work as they exhibit facet-dependent growth, catalytic activity, stability, and surface reactivity. In these previous reports, facet effects have been attributed to the relative surface energies of different facets, the passivation of specific facets through selective binding agents, the facet-selective extraction of mobile charge carriers, and the facet-selective adsorption of reactive chemical species.

Previous work has shown that illumination catalyzes the growth of Cu nanowires on Cu$_2$O microcrystals and can be used to prepare n-type Cu$_2$O films that are doped with Cu$^0$. However, neither of these prior examples studied the facet-dependence of these photochemical reactions. In this report, we examined both the oxidative etching of Cu$_2$O and the reductive
deposition of Cu on Cu$_2$O microcrystals that possess a mixture of {100} and {111} facets. Using a combination of illumination and an applied bias, both of these reactions occur selectively on {100} facets, but at different potential windows. We develop a physical mechanism to explain these light-driven transformations, which relies on facet-selective ion adsorption and extraction of photogenerated charge carriers. By controlling these processes, we synthesized a novel nanoscale morphology consisting of a shell of Cu metal deposited selectively on the {100} facets of the initial Cu$_2$O microcrystals. The interior is either hollow or contains Cu$_2$O depending on the growth time.

2.2 Experimental Section

2.2.1 Materials

All chemicals were used as received. Copper nitrate trihydrate (Cu(NO$_3$)$_2$·3H$_2$O, ≥ 99%), copper sulfate pentahydrate (CuSO$_4$·5H$_2$O, ≥ 98%), sodium hydroxide (NaOH, ≥97%), sodium citrate tribasic dihydrate (≥99%), sodium carbonate (Na$_2$CO$_3$, ≥99.95%), sodium dodecyl sulfate (SDS, ≥99%), nitric acid (HNO$_3$, ≥97%), sodium chloride (NaCl, ≥99%), ethylenediamine, and polyvinylpyrrolidone (PVP) with an average molecular weight of 40,000 were purchased from Sigma-Aldrich. Ethanol (200 proof, 100%) was purchased from Fisher Scientific. D-(+)-glucose (≥99%), platinum gauze (Pt, 100 mesh, 99.9% metals basis), and Pt wire (0.5 mm diameter, 99.95% metals basis) were purchased from Alfa Aesar. Chrome-plated tungsten rods and gold pellets (99.999%) for metal evaporation were purchased from Kurt J. Lesker. All aqueous solutions were made using purified water from a GenPure Pro water purification system with at least 17.30 MΩ·cm resistivity.
Preparation of electrodes: The counter electrode consisted of Pt gauze attached to a Pt wire. The Pt wire was soldered to a Sn–Cu wire, and the soldered joint was sealed in a glass tube. For the working electrodes, 100 Å of chromium followed by 500 Å of gold were deposited onto glass slides using an Edwards Auto 306 thermal evaporator with a base pressure below 10^{-7} Torr. Each working electrode was rinsed with purified water and then dried with nitrogen gas before use. A silver/silver chloride (Ag/AgCl) electrode in 3 M NaCl was used as the reference electrode.

2.2.2 Electrodeposition Methods

Electrodeposition of cuprous oxide (Cu₂O) microcrystals: Cu₂O microcrystals were electrodeposited from an aqueous solution of 0.02 M Cu(NO₃)₂ based on a previous report with some modifications. SDS and NaCl were added to the solution in some cases to control the morphology of the microcrystals (see Table S1 in the Supporting Information). Before electrodeposition, the pH of the solution was adjusted to 4.1 through the dropwise addition of 0.1 M HNO₃. If the solution contained SDS, the pH was adjusted before SDS was added because the surfactant prevented a reliable pH reading.

A custom electrochemical cell was used for all electrodeposition experiments. The cell was made from borosilicate glass with openings at the top for the electrodes and a flat window on the side for illumination (used only in the photoinduced transformations described below). The electrochemical cell was partially immersed in a water bath set on a hot plate. A temperature probe was inserted into the electrochemical cell to control the temperature. The electrolyte solution was heated and kept at 60°C during the electrodeposition of all Cu₂O samples.
A BioLogic VSP-300 potentiostat/galvanostat was used to perform all electrochemical and photoelectrochemical experiments. To grow different shapes of Cu$_2$O microcrystals the deposition solution contained 0.17 M SDS and 0.005 M NaCl in some cases (see Table S1 in the Supporting Information). Either a constant current or a pulsed current was used to electrodeposit the microcrystals. A photo scanner was used to scan images of the working electrodes, and their areas were measured using ImageJ software. Table S1 provides the current waveform used for each sample and the total deposition time.

**Synthesis of colloidal Cu$_2$O microcrystals:** The colloidal Cu$_2$O microcrystals shown in Figures S19 and S20 of the Supporting Information were synthesized using a previously reported procedure. First, an aqueous solution was made by mixing 17 mL of water, 1 mL of 0.68 M CuSO$_4$, and 1.2 g of PVP (MW = 40,000) in a round-bottom flask. The solution was stirred using a magnetic stir bar for 15 to 20 min, and then 1 mL of an aqueous solution containing 0.74 M sodium citrate and 1.2 M Na$_2$CO$_3$ solution was added dropwise to the CuSO$_4$ solution. Upon this addition, the solution began to turn dark blue. After 10 min, 1 mL of an aqueous solution containing 1.4 M glucose was added dropwise to the CuSO$_4$ solution. The solution was kept in a water bath at 80°C for 2 h and then cooled to room temperature. The brick-red precipitate was collected by centrifuging the mixture at 8000 rpm for 4 min. The supernatant was removed, and 10 mL of purified water was added to the precipitate. The process of centrifugation, removal of the supernatant, and redispersion in fresh solvent was repeated two more times. For the last two cycles, 10 mL of ethanol was used instead of water. The final dispersion in ethanol was transferred to a glass vial for further use. For the photoinduced transformations described below, the colloidal Cu$_2$O microcrystals were first sonicated to redisperse them into solution. A drop of this suspension was then diluted with 2 mL of ethanol and drop-cast onto a Si (111) substrate.
Photoinduced transformation of Cu$_2$O microcrystals: A broadband, ELH-type light bulb was used as the illumination source for most experiments. The irradiance was measured using a calibrated Si photodiode from ThorLabs (FDS-100 CAL). Before the transformation the photodiode was placed at the same location in the electrochemical cell as the working electrode (facing the optical window of the electrochemical cell), and the current was measured under illumination with the ELH lamp. A typical current reading was 0.02 A, which based on the wavelength-dependent responsivity and active area (3.6×3.6 mm) of the photodiode gives an irradiance of 567 mW/cm$^2$. High-power, light-emitting diodes (LEDs) with peak wavelengths of 455 and 625 nm and full widths at half max of ~30 nm were used in some experiments instead of the ELH lamp (see Table S2 of the Supporting Information). Similar to the electrodeposition of the Cu$_2$O microcrystals, Pt gauze was used as the counter electrode, and Ag/AgCl was used as the reference electrode. The electrodeposited Cu$_2$O microcrystals on Au substrates were used as the working electrode and immersed in a solution of NaOH (typically 5 M). The applied potential used to form the hollow Cu shells was typically –1.0 V vs. Ag/AgCl. The times held at this potential under illumination for different samples are provided in Table S2. Other applied potentials and concentrations of NaOH were used for some samples. The parameters used to prepare different samples are provided in Table S2. In some cases, no bias was applied (labeled as open circuit in Table S2).

2.2.3 Characterization

Cyclic voltammetry (CV) was performed to characterize the potentials for different redox reactions to occur on the Au substrate and Cu$_2$O microcrystals. All CV scans started at open circuit. For each scan, the potential was first swept in the positive direction to +0.2 V vs. Ag/AgCl, then
swept in the negative direction to \(-1.2\) V, and finally swept back to \(+0.2\) V. The scan rate was 20 mV/s, and two consecutive CV scans were performed for each electrode. In some cases, the solution was purged with argon for 30 min. Otherwise, the electrochemical cell was left open to air.

Electrochemical impedance spectroscopy (EIS) was performed to determine the flat-band potential of the as-synthesized Cu$_2$O microcrystals on Au substrates in a solution of 0.1 M NaOH. The frequencies scanned were 5 kHz to 75 kHz. The AC potential oscillation was 10 mV, and the DC potential range was \(-0.2\) V to \(-0.6\) V vs. Ag/AgCl. A circuit consisting of two resistors (R$_1$ and R$_2$), a capacitor (C$_2$), and a restricted diffusion element (M$_2$): \([R_1+C_2/(R_2+M_2)]\) was used to model the electrochemical cell based on fits to Nyquist plots at different applied potentials. Mott-Schottky plots \((1/C_2^2\) vs. the applied potential where C$_2$ is the space-charge capacitance) were extracted from EIS data. The \(x\)-intercepts determined from linear fits to these plots give the flat-band potential, which varied from \(-0.60\) V to \(-0.65\) V vs. Ag/AgCl for different frequencies (see **Table S3 of the Supporting Information**).

Scanning electron microscopy (SEM) images were collected using a JEOL 7001LVF field emission scanning electron microscope operated at an acceleration voltage of 15 kV. After electrodeposition, the working electrode was cut to approximately 1×1 cm pieces, and the conductive top surface of the substrate was connected with copper tape to the SEM sample holder to avoid charge buildup. The SEM was equipped with an Oxford Aztec live x-max energy dispersive x-ray spectroscopy (EDXS) system, and EDXS spectra were collected at an acceleration voltage of 15 kV.

X-ray diffraction (XRD) patterns were collected using a Bruker D8 Advance X-ray Diffractometer (Cu Ka = 0.15418 nm). The step size for the XRD measurements was 0.02° in 20,
and the scan rate was 0.5 s per step. To prepare samples for XRD, the working electrode was cut to approximately 1×1cm pieces and placed onto a zero-background, silicon diffraction plate (MTI Corporation).

X-ray photoelectron spectroscopy (XPS) was performed using a Physical Electronics 5000 VersaProbe II Scanning ESCA (XPS) Microprobe system with a base pressure below $1 \times 10^{-9}$ Torr. XPS data were acquired using the 1486.6 eV line from a monochromated Al Kα source at 150 W with a multichannel detector set to a pass energy of 23.5 eV for the high-resolution scans. The peak fitting was processed using XPSPEAK software with a Shirley background. The kinetic energies of the Auger spectra were calculated by subtracting the binding energies from the x-ray source energy (1486.6 eV). The assignment of peaks in the photoelectron spectra of copper and oxygen and the Auger spectra of copper were based on previous literature.59, 73-75

Absorption spectra of solid samples were acquired by diffuse reflectance using a Cary 5000 spectrometer equipped with a 150-mm integrating sphere. A PMT detector was used for ultraviolet (UV) and visible wavelengths (250 – 800 nm), and a lead sulfide detector was used for near infrared (NIR) wavelengths (800 – 1200 nm). A tungsten halogen lamp was used as the source for visible and NIR wavelengths (350 – 1200 nm), and a deuterium lamp was used for the UV region (250 – 350 nm). The scan rate for each measurement was 600 nm/min, and the step size was 1.0 nm. The absorbance spectrum of a bare Au film was subtracted from the sample spectra of the Cu$_2$O microcrystals electrodeposited on Au. The absorption spectra of solutions of Cu(NO$_3$)$_2$ and NaOH were measured using a Cary 60 spectrometer.

**Supporting Information Available:** Supporting Tables providing the conditions used to prepare different samples of the Cu$_2$O microcrystals and hollow Cu nanoshells, cyclic voltammetry of the Au substrates and Cu$_2$O microcrystals, current traces during the transformation of Cu$_2$O
microcrystals in the dark and under illumination, SEM images of Cu₂O microcrystals transformed in the dark at higher current densities, absorption spectrum of Cu₂O microcrystals, SEM images of Cu₂O microcrystals transformed under different light intensities and wavelengths, additional XRD patterns and XPS of Cu₂O microcrystals transformed under different potentials and illumination conditions, cyclic voltammetry and absorption spectrum of the NaOH solution used to transform the Cu₂O microcrystals, SEM images of Cu₂O microcrystals transformed with Cu(NO₃)₂ added to the electrolyte solution, SEM images and XRD pattern of Cu₂O microcrystals transformed using lower concentrations of NaOH, SEM images of Cu₂O microcrystals transformed using solutions purged with Ar and O₂, SEM images of Cu₂O microcrystals etched in NaOH in the dark, SEM images of Cu₂O microcrystals transformed without an applied bias, photocurrent traces for Cu₂O microcrystals at different applied potentials, Mott–Schottky plots at different frequencies, Supporting Table of flat-band potentials measured at different frequencies.

2.3 Results and Discussion

2.3.1 Results

Arrays of Cu₂O microcrystals on conductive substrates were prepared by electrodeposition under controlled current conditions following modifications to previously reported procedures.⁴,⁵¹ Both the waveform of the deposition current vs. time and the addition of facet-selective binding agents (sodium dodecyl sulfate and chloride ions) were used to tune the ratio of {100} to {111} facets. The conditions used to grow Cu₂O microcrystals of different morphologies are provided in detail in the Experimental Section. A scanning electron microscopy (SEM) image of cuboctahedral microcrystals with mixed {100} and {111} facets is shown in Figure 2.1a. The
facets can be distinguished by their symmetry as \{111\} facets with 3-fold rotational symmetry appear as triangles or as triangles with truncated corners. The \{100\} facets with 4-fold rotational symmetry appear as squares or squares with truncated corners.

![Figure 2.1](image)

**Figure 2.1** Electrochemical transformation of Cu$_2$O microcrystals under illumination and in the dark. a) SEM image of the initial Cu$_2$O microcrystals electrodeposited on a Au substrate. b) Cu$_2$O microcrystals after 5 min of illumination with an ELH lamp while the electrode was held at a constant potential of $E = -1.0$ V vs. silver/silver chloride (Ag/AgCl) in 5 M NaOH. The inset shows a magnified image of a single hollow microcrystal with the 100 and etched 111 facets labeled. c) Cu$_2$O microcrystals after 5 min of being held at the same potential in 5 M NaOH in the dark.

An x-ray diffraction (XRD) pattern of the initial Cu$_2$O microcrystals electrodeposited on a Au substrate is shown in **Figure 2.2** (blue trace). The strongest reflection at 38° in 2θ belongs to the Au substrate as the deposited microcrystals are relatively sparse on the substrate. However, the peaks at 29° and 36° in 2θ match the \{110\} and \{111\} reflections for the cubic phase of Cu$_2$O (see **Figure S9** for a XRD pattern of the Cu$_2$O microcrystals over a wider 2θ range). The \{200\} reflection for Cu$_2$O at 42° is likely absent due to the preferential alignment of \{111\} planes parallel to the substrate. SEM images of Cu$_2$O microcrystals with predominantly \{100\} facets and predominantly \{111\} facets are shown in **Figure 2.5a** and **2.5c**, respectively.
Figure 2.2 X-ray diffraction patterns of the initial Cu$_2$O microcrystals electrodeposited on a Au substrate (blue trace, top), Cu$_2$O microcrystals after 5 min while the electrode was held at a constant potential of E = −1.0 V vs. Ag/AgCl in 5 M NaOH in the dark (black trace, middle), and Cu$_2$O microcrystals after 5 min of illumination with an ELH lamp while the electrode was held at the same potential in 5 M NaOH (red trace, bottom). The lines at the bottom are the reflections for standard XRD powder patterns of Cu$_2$O (purple lines, PDF file #04-007-9767), Cu (orange line, PDF file #00-004-0836), and Au (green lines, PDF file #00-004-0784).

Cyclic voltammetry (CV) of the microcrystals shows a cathodic peak at −0.41 vs. silver/silver chloride (Ag/AgCl) corresponding to the reduction of Cu$_2$O to Cu metal (Figures S2, S3). The reduction of adsorbed hydroxide ions occurs on the exposed regions of the Au substrate at −0.71 V vs. Ag/AgCl (Figure S1).

Previous reports have shown that changes in the local pH and potential can induce either oxidation or reduction of Cu$_2$O. We found that these chemical transformations are significantly altered in the presence of illumination. Figure 2.1 shows SEM images of the Cu$_2$O
microcrystals grown on Au after the substrates were held at a potential of $E = -1.0 \, \text{V vs. Ag/AgCl}$ in a solution of 5 M NaOH both under illumination (Figure 2.1b) and in the dark (Figure 2.1c). An ELH-style halogen lamp was used as the light source, and the typical irradiance at the electrode was between 300 and 655 mW/cm$^2$. Under illumination, hollow structures are formed in which a shell has grown selectively on the $\{100\}$ facets while the interiors of the microcrystals have been etched at $\{111\}$ facets. As shown in Figure 2.1c, the hollow nanoshells are not formed in the dark. Illuminating the electrode increases the current when it is held at $-1.0 \, \text{V vs. Ag/AgCl}$ (Figure S4). However, simply increasing the current density in the dark (through either applying a more negative potential or under constant current conditions) did not lead to the nanoshell formation (Figure S5). The threshold irradiance to observe the formation of the hollow nanoshells was 50 mW/cm$^2$ using an ELH lamp (Figure S7). At lower light intensities, etching of the microcrystals in the NaOH solution outcompetes growth of the shells resulting in broken particles (Figure S7).

While a broadband ELH lamp was used for most experiments, we also used narrow-band (full width at half max of $\sim 30$ nm) light-emitting diodes (LEDs) with wavelengths of 455 and 625 nm. Based on its band gap energy of 2.1 eV, Cu$_2$O strongly absorbs blue light (see Figure S6 for an absorption spectrum of the Cu$_2$O microcrystals). Correspondingly, illumination with the 455-nm LED produced the same hollow nanoshells as when the ELH lamp was used (Figure S8a). However, as Cu$_2$O does not significantly absorb red light, the 625-nm LED produced structures similar to those formed in the dark (Figure S8b).

The combination of an applied potential and exposure to the NaOH solution led to compositional changes in the Cu$_2$O microcrystals both under illumination and in the dark. We monitored these changes using XRD and x-ray photoelectron spectroscopy (XPS). XRD showed that after applying a bias of $-1.0 \, \text{V vs. Ag/AgCl}$ for 5 minutes while the microcrystals were
immersed in 5 M NaOH (both in the dark and under illumination), a reflection at 43° in 2θ corresponding to Cu metal appeared in the diffraction patterns while the peaks at 29° and 36° belonging to Cu₂O disappeared (Figure 2.2). Figure S9 provides XRD patterns over a wider 2θ range. The presence of Cu metal on the surface of the microcrystals was also verified by x-ray photoelectron spectroscopy in the Auger region for Cu LMM electrons (Figure 2.3b and Figure S11). Before and after the transformation, the samples possessed a peak with a kinetic energy of 916.8 eV indicative of Cu⁺. After the transformation in both the light and dark, a new peak appeared at 918.5 eV corresponding to metallic Cu⁰. ⁷³,⁷⁴

**Figure 2.3** a) XPS showing the binding energy regions for Cu 2p₃/₂ electrons. b) Auger spectra in the region for Cu LMM electrons. In both panels, the blue trace (top) shows the initial Cu₂O microcrystals electrodeposited on a Au substrate, the black trace (middle) shows the Cu₂O microcrystals after 5 min while
the electrode was held at a constant potential of \( E = -1.0 \text{ V} \) vs. Ag/AgCl in 5 M NaOH in the dark, and the red trace (bottom) shows Cu\(_2\)O microcrystals after 5 min of illumination with an ELH lamp while the electrode was held at the same potential in 5 M NaOH. Dashed lines show deconvolution of the peaks as described in the text. The vertical lines indicate the expected energies for Cu in the 0, +1, and +2 oxidation states based on previous assignments.\(^{53-54}\) Peaks at 913 eV and 921 eV in the Auger spectra have been observed previously for Cu\(_2\)O, but have not been assigned to a particular oxidation state.\(^{53}\)

Based on SEM images, etching still occurs even when the microcrystals are held at a negative bias. As described further below, the combination of OH\(^-\) ions and dissolved O\(_2\) in the electrolyte solution leads to oxidation of Cu\(_2\)O microcrystals similar to previous reports.\(^{62}\) The presence of Cu\(^{2+}\) cannot be easily identified in the Auger region as it appears at 917.8 eV in between the Cu\(^+\) and Cu\(^0\) peaks. On the other hand, photoelectron spectra in the binding energy region for Cu 2p\(_{3/2}\) electrons can identify the presence of Cu\(^{2+}\), but cannot distinguish between Cu\(^+\) and Cu\(^0\).\(^{73, 74}\) A broad peak with a binding energy of approximately 933.4 eV in the Cu 2p\(_{3/2}\) photoelectron spectra corresponding to Cu\(^{2+}\) was observed for all three samples. This peak was the strongest after transformation of the microcrystals in the dark (Figure 2.3a). The contribution from Cu\(^{2+}\) also increased when the microcrystals were immersed in 5 M NaOH in the dark without an applied bias (Figure S10). XPS in the binding energy region for O 1s electrons show contributions from both oxygen in the Cu\(_2\)O microcrystals as well as surface-adsorbed oxygen species both before and after the applied bias (Figure S12).

Figure 2.4 shows the evolution of the microcrystals under illumination as a function of time while the substrate was held at \( E = -1.0 \text{ V} \) vs. Ag/AgCl in 5 M NaOH. In the first minute of the reaction Cu nanoparticles grow on the \{100\} facets of the Cu\(_2\)O microcrystals (Figure 2.4a). At longer deposition times the Cu nanoparticles grow and merge into polycrystalline layers covering the \{100\} facets. The Cu layers formed on different \{100\} facets connect at the vertices of each
cuboctahedral microcrystal (*Figure 2.4b*). After 2.5 minutes the Cu$_2$O surfaces exposed at {111} facets have begun to etch in the NaOH solution (*Figure 2.4c*). The Cu shell is resistant to etching while the interiors of the Cu$_2$O microcrystals are hollowed out through further etching at the {111} facets (*Figure 2.4d*).

**Figure 2.4** SEM images of Cu$_2$O microcrystals on Au substrates after a) 1 min, b) 2 min, c) 2.5 min, and d) 5 min, respectively of illumination with an ELH lamp while the electrode was held at a potential of E = −1.0 V vs. Ag/AgCl in 5 M NaOH.

The Cu$_2$O microcrystals are oxidatively etched by the combination of OH$^-$ ions and O$_2$ in the electrolyte solution. CV scans of the used NaOH solution showed the presence of Cu$^{2+}$ in solution after the transformation as a resulting of this etching (*Figure S13*). However, adding Cu(NO$_3$)$_2$ intentionally to the deposition solution did not alter the formation of the Cu nanoshells (*Figure S14*). When the NaOH concentration was lowered to either 2.5 or 1 M, etching of the {111} facets was slower, leading to thicker Cu shells and Cu$_2$O remaining in the interior of the particles for longer times (*Figures S15, S16*). The preparation of the NaOH solution and the transformation of
the microcrystals were both typically performed in air. Some hollow nanoshells were still observed under illumination at \(-1.0\) V vs. Ag/AgCl when the NaOH solution was purged with argon (Figure S17). However, both the nanoshell formation and etching of the \{111\} facets were less uniform indicating that dissolved O\(_2\) is involved in the transformation.

Selective deposition of Cu on \{100\} facets and etching of the \{111\} facets occurs even when the ratio of these two surfaces is changed. Figure 2.5 shows SEM images of truncated cubic Cu\(_2\)O microcrystals with predominantly \{100\} facets (Figure 2.5a), cuboctahedral microcrystals with mixed \{100\} and \{111\} facets (Figure 2.5b), and octahedral microcrystals with predominantly \{111\} facets (Figure 2.5c). After the cubic microcrystals were held at \(-1.0\) V vs. Ag/AgCl for 5 min under illumination, Cu shells have covered the majority of the surface of the microcrystals. However, the truncated corners corresponding to \{111\} facets have been etched. Under the same conditions, octahedral microcrystals are converted into hollow frames where Cu has grown on the edges and corners of the original microcrystals.

**Figure 2.5** Facet-dependence of the photoinduced transformation of Cu\(_2\)O microcrystals. a-c) SEM images of the initial Cu\(_2\)O microcrystals with a) truncated cubic, b) cuboctahedral, and c) octahedral morphologies.

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d-f) Hollow Cu microcrystals grown from Cu$_2$O microcrystals with d) truncated cubic, e) cuboctahedral and f) octahedral morphologies after 5 min of illumination with an ELH lamp while the electrode was held at a constant potential of $E = -1.0$ V vs. Ag/AgCl in 5 M NaOH.

The hollow nanoshell morphology for particles shown in Figures 2.1, 2.4, and 2.5 is only formed when the applied potential is sufficiently negative. In the absence of an applied potential and at more positive potentials, the {100} facets are selectively etched under illumination. Figure S20 in the Supporting Information shows selective etching of {100} facets for both electrodeposited and colloidally synthesized Cu$_2$O microcrystals when illuminated in 5 M NaOH in the absence of an applied bias for 3 and 10 minutes, respectively. Without either light or an applied bias (i.e. just immersing the microcrystals in 5 M NaOH), etching of the {100} facets was still observed at longer times (20 minutes), although the etching was not as uniform (Figure S19). Figure 2.6 shows SEM images of Cu$_2$O microcrystals after being held for 5 minutes at a series of different potentials under illumination with an ELH lamp in a solution of 5 M NaOH. At a potential of $E = -0.4$ V vs. Ag/AgCl, the {100} facets were selectively etched while no obvious deposition of Cu was observed (Figure 2.6a). At an applied potential of $E = -0.5$ V vs. Ag/AgCl, the {100} facets were still etched and large Cu particles were deposited non-selectively on the microcrystals (Figure 2.6b). Figure 2.6c shows that as the applied potential was made more negative ($E = -0.8$ V vs. Ag/AgCl), a Cu shell formed selectively on the {100} facets of the microcrystals. However, the Cu coating formed at $-0.8$ V was not as uniform as when a potential of $E = -1.0$ V vs. Ag/AgCl was used (Figure 2.6d).
The currents both in the dark and under illumination are shown at different applied potential in Figure 2.7. Spikes in the current were observed when the illumination was turned on and off, which have been previously observed for Cu$_2$O microcrystal photoelectrodes\textsuperscript{77} as well as for TiO$_2$-based, dye-sensitized photoelectrochemical cells.\textsuperscript{80-82} Mallouk and coworkers attributed the current spikes to the redistribution of charge carriers among trap states with different energies, while the slower change in current was assigned to surface processes.\textsuperscript{82} As we are primarily interested in surface processes (i.e., surface reduction of copper ions and oxidation of Cu$_2$O), we focus on the changes in current following the initial spikes. Furthermore, regions of the Au electrode are still exposed after growth of the Cu$_2$O microcrystals, and the reduction of OH$^-$ and O$_2$ on the Au substrate leads to a small cathodic background current (see Figure S1). However, as this background current does not change under illumination, we ascribe the changes in current
when the electrode is illuminated to result from photoexcitation of the Cu$_2$O semiconductor microcrystals.

![Figure 2.7 Current vs. time traces for Cu$_2$O microcrystals while the illumination from an ELH lamp was switched on and off at applied potentials of a) E = −0.3 V, b) E = −0.5 V and c) E = −0.8 V, and d) E = −1.0 V vs. Ag/AgCl in 5M NaOH. The dashed red and blue lines show examples of when the lamp was turned on and off, respectively.](image)

The open-circuit potential for the initial Cu$_2$O microcrystals in 5 M NaOH is −0.37 V vs. Ag/AgCl. At potentials more positive than open circuit (e.g. E = −0.3 V vs. Ag/AgCl), the current is anodic (oxidative) in the dark, and the steady-state anodic current (i.e. following the initial spike)
is enhanced under illumination (Figure 2.7a). At potentials more negative than the open-circuit potential, the dark current is negative due to reduction of Cu2O to Cu (Figure S2). Just as Figure 2.6b shows photoetching of {100} facets along with non-selective deposition of Cu at E = −0.5 V vs. Ag/AgCl, the current trace at this potential (Figure 2.7b) shows a slightly cathodic (reductive) current in the dark that becomes anodic under illumination. Similar changes in the current were observed at E = −0.4 V vs. Ag/AgCl. Choi and coworkers also reported similar changes in current for electrodeposited Cu2O microcrystals where the current was cathodic in the dark and became anodic under illumination over this potential range. At more negative potentials of E = −0.8 and −1.0 V vs. Ag/AgCl, the current is cathodic in the dark, and the steady-state current becomes more negative under illumination (Figure 2.7c, d). Figure S21 provides the changes in current under illumination at applied potentials of −0.55 V, −0.60 V, −0.65V, and −0.70 V vs. Ag/AgCl. The crossover between when illumination makes the current more positive and when illumination makes the current more negative occurs between −0.60 and −0.65 V vs. Ag/AgCl.

2.3.2 Discussion

Compositional changes in Cu2O microcrystals. The following half-reactions control the oxidation and reduction of Cu2O:

\[
\begin{align*}
\text{Cu}_2\text{O} + \text{H}_2\text{O} + 2e^- & \rightleftharpoons 2\text{Cu} + 2\text{OH}^- \quad (1) \\
2\text{CuO} + \text{H}_2\text{O} + 2e^- & \rightleftharpoons \text{Cu}_2\text{O} + 2\text{OH}^- \quad (2)
\end{align*}
\]

The potentials for both of these reactions are pH dependent. For the 5 M NaOH solution used in these experiments (pH = 14.7), the electrode potentials for these half reactions are −0.6 V vs. Ag/AgCl for reaction 1 and −0.4 V vs. Ag/AgCl for reaction 2. Based on the Pourbaix diagram for Cu, CuO will dissolve in 5 M NaOH (pH = 14.7) via the following reaction:
Based on XPS, both surface oxidation and reduction of the Cu$_2$O microcrystals occur when the microcrystals are immersed in 5 M NaOH (Figures 2.3, S10, and S11). As shown in Figure 2.7, these processes are both enhanced under illumination, but at different potential windows. At more positive potentials, illumination produces an anodic current, while illumination enhances the cathodic current at more negative potentials. The absorption of photons with energies above the band gap of Cu$_2$O creates photoexcited electron-hole pairs. Photogenerated electrons in the conduction band can reduce Cu$_2$O either directly via reaction (1) or through the redeposition of copper ions that have dissolved in the NaOH solution. Two observations suggest the direct reduction of Cu$_2$O occurs at the surface of the microcrystals: 1) Cu deposition was not found on the exposed regions of the Au substrate as measured by energy dispersive spectroscopy. 2) As noted above, adding Cu(NO$_3$)$_2$ to the deposition solution does not alter the formation of the hollow Cu nanoshells (Figure S14). Photogenerated holes in the valence band can oxidize Cu$_2$O via reaction (2) leading to the dissolution of [Cu(OH)$_4$]$^{2-}$ ions via reaction (3). As described in the next section, the initial electrochemical potential of the Cu$_2$O microcrystals in combination with the applied potential controls whether electrons or holes are driven to the semiconductor/liquid interface. Even though the measured current is cathodic at potentials of −0.8 and −1.0 V vs. Ag/AgCl (Figure 2.7c, d), etching of the {111} facets still occurs as shown in Figure 2.6c, d. In these cases, oxygen can serve as the oxidant to etch the microcrystals via the following reactions:

\[
\text{CuO} + \text{H}_2\text{O} + 2\text{OH}^- \rightarrow [\text{Cu(OH)}_4]^{2-} \quad (3)
\]

\[
\text{Cu}_2\text{O} + \frac{1}{2} \text{O}_2 + 3\text{H}_2\text{O} + 2\text{OH}^- \rightarrow 4\text{Cu(OH)}_2 \quad (4)
\]

\[
\text{Cu(OH)}_2 + 2\text{OH}^- \rightarrow [\text{Cu(OH)}_4]^{2-} \quad (5)
\]
Correspondingly, we observed slower etching of the \{111\} facets at –1.0 V vs. Ag/AgCl when the concentration of NaOH was decreased to 2.5 or 1 M (Figures S15 and S16).

**Energetics of the semiconductor/liquid interface.** Figure 2.8a shows the alignment of the electronic band edge potentials for Cu$_2$O with the electrode potentials for reactions 1 and 2 that control the reduction and oxidation of Cu$_2$O (the energies of the conduction and valence band edges are divided by the charge of an electron to convert them to potentials). This alignment is based on a previous report by Kelly and coworkers for electrodeposited Cu$_2$O films.\textsuperscript{84} As has been previously demonstrated for metal oxide semiconductors, we also assume that both the conduction and valence band levels of Cu$_2$O move 59 mV per pH unit.\textsuperscript{85, 86} Thus, the relative differences between the electrode potentials in reactions 1 and 2 and the band edge positions of Cu$_2$O do not change with pH. We performed electrochemical impedance spectroscopy (EIS) to measure the flat-band potential of the semiconductor microcrystals and determine the initial position of the Fermi level for Cu$_2$O before contact with the solution. Mott-Schottky plots ($1/C^2$ vs. applied potential where $C$ is the space-charge capacitance measured from EIS) at different frequencies are provided in Figure S22. The x-intercepts for these plots give the flat-band potential, which has a value between –0.60 and –0.65 V vs. Ag/AgCl for frequencies ranging from 5 to 75 kHz. The average value of –0.63 V vs. Ag/AgCl indicates that our Cu$_2$O microcrystals are slightly n-type with the Fermi level closer to the conduction band edge (Figure 2.8a). While Cu$_2$O is often p-type due to the presence of native copper ion vacancies, dendritic Cu$_2$O films electrodeposited under similar conditions to our samples were also found to be n-type with a flat-band potential of –0.78 V vs. Ag/AgCl.\textsuperscript{77} Our measured value of the flat-band potential also agrees with the photocurrent measurements shown in Figure S21 where there is a crossover between illumination
making the current more positive and it making the current more negative in between –0.60 and –
0.65 V vs. Ag/AgCl.

**Figure 2.8** Energy level diagrams showing band bending at the semiconductor/liquid interface at different
applied potentials. (a) Alignment of the conduction and valence bands of Cu$_2$O with the electrode potentials
that control the oxidation and reduction of Cu$_2$O. (b) Equilibration of the Fermi level of Cu$_2$O with either
redox couple leads to upward band bending of the conduction and valence bands at the semiconductor/liquid
interface such that photogenerated holes in the valence band of Cu$_2$O will migrate to the surface. (c) A
negative bias will reduce the degree of band bending and (d) lead to downward band bending at a bias
greater than the flat-band potential such that photogenerated electrons in the conduction band will migrate
to the surface. (e) Summary of the dark current ($i_d$) and photocurrent ($i_{ph}$) contributions at different potential
windows. $V_{oc}$ = the open-circuit potential, and $V_{fb}$ = the flat-band potential. All potential values are
referenced to Ag/AgCl.
As the initial Fermi level position for Cu$_2$O is more negative (i.e. closer to the vacuum level) than the electrode potential for either redox couple, upwards bending of the conduction and valence bands occurs at open circuit (Figure 2.8b). Thus, in the absence of an applied potential photogenerated hole carriers will be driven to the semiconductor/liquid interface leading to oxidative etching of the microcrystals as observed in Figure S18 and S20. As the applied potential is made more negative, the degree of band bending will decrease (Figure 2.8c). Under these conditions, the dark current will be cathodic as observed in Figure 2.7b. However, under illumination photogenerated holes will still be driven to the semiconductor/liquid interface leading to an anodic photocurrent contribution (i.e. oxidation of Cu$^+$) as seen in Figure 2.7b and enhanced etching of the microcrystals as observed in Figure 2.6a, b. Once the applied potential is more negative than the flat band potential, the band bending in Cu$_2$O reverses such that holes are depleted at the semiconductor/liquid interface. Thus, at more negative potentials (E = –0.8 and –1.0 V vs. Ag/AgCl), electrons are driven to the surface leading to the observed cathodic current that is enhanced under illumination (Figure 2.7c, d). Correspondingly, at these potentials the reduction of copper ions leads to formation of the Cu shell as observed in Figure 2.6c, d, while etching at {111} facets occurs via reactions 4 and 5 (using O$_2$ as the oxidant rather than photogenerated holes). Once Cu metal has grown on the {111} facets, further extraction of photogenerated charges will be controlled by the energetics of the Cu$_2$O/Cu interface. Based on the work function of polycrystalline Cu near 4.5 eV vs. vacuum (giving a potential of ~0.2 V vs. Ag/AgCl), photogenerated electrons will still be driven to the surface of the microcrystals over the potential range in which we observe growth of the Cu nanoshells.

Figure 2.8e summarizes the expected currents in the dark and under illumination at different potential windows based on the model described above. This model matches the observed
photocurrents shown in Figures 2.7 and S21. At a bias that is more positive than the open-circuit potential the dark current is anodic. At a bias that is in between the open-circuit and flat-band potentials, the dark current is cathodic corresponding to reduction of the Cu$_2$O microcrystals. However, under illumination the combination of photogenerated holes and surface-adsorbed hydroxide ions leads to oxidative etching of the {100} facets via reactions 2 and 3. At potentials more negative than the flat-band potential, illumination drives electrons to the surface to reduce Cu$^+$ ions at {100} facets according to reaction 1. Changes in the surface area of the Cu$_2$O microcrystals during the transformation as well as dopant density (as Cu$^0$ is an n-type dopant in Cu$_2$O) will also affect the resulting current density. However, it is difficult to disentangle the relative contributions of these simultaneous changes as both the dopant density and electrochemical surface area appear in the denominator of the Mott-Schottky equation used to determine the flat-band potential.

**Facet-selectivity of photoelectrochemical reactions on Cu$_2$O.** The schematic in Figure 2.8 does not include the effect of surface structure on the degree of band bending at the semiconductor/liquid interface. Different structures for {100} and {111} facets interfaced with vacuum have been determined using density functional theory. Generally, the {100} surface is terminated with coordinatively unsaturated oxygen while the {111} surface contains both coordinatively unsaturated Cu and O atoms. These different surface terminations affect the electric dipole at the semiconductor/liquid interface and lead to different degrees of band bending.

We attribute the light-driven growth of a Cu shell on the {100} facets at more negative potentials (Figure 2.7c, d) to the selective extraction of photogenerated electrons from these surfaces. Facet-selective extraction of photogenerated charge carriers has been observed in other
semiconductor microcrystals including BiVO$_4$ and TiO$_2$. While there is some debate in the current literature,$^{55,56}$ several reports have used DFT calculations to show that the potential of the valence band for the {100} surface of Cu$_2$O is more positive (further from the vacuum level) compared to the {111} surface creating a potential barrier for photogenerated holes.$^{57,58}$ This hole-blocking layer will lead to selective extraction of photogenerated electrons from {100} facets. As discussed further below, both experiment and theory indicate that O$_2$ and OH$^-$ bind more strongly to the {100} facets of Cu$_2$O. However, once the Cu layer has formed on the {100} facets they are protected from chemical etching, while the exposed {111} facets under these conditions are slowly etched via reactions 4 and 5.

Oxidative photoetching of the Cu$_2$O {100} facets via reactions 2 and 3 as observed in Figure 2.6 at applied potentials more positive than the flat-band potential requires both photogenerated holes at the surface and the adsorption of hydroxide anions. Note that these surface reactions do not involve O$_2$ like the oxidative etching of {111} facets observed at more negative potentials via reactions 4 and 5. Thus, while the exclusion of O$_2$ by purging the solution with Ar did inhibit growth of the hollow nanoshells at −1.0 V vs. Ag/AgCl (Figure S17), it did not have a noticeable effect on the selective photoetching of {100} facets in the absence of an applied potential (Figures S18). The light-driven etching of {100} facets at more positive potentials (Figure 2.6a, b) could arise from the selective extraction of photogenerated holes from the {100} facets. This mechanism would require a potential-dependent change in the relative positions of the electronic energy levels for the {100} and {111} facets such that holes are selectively extracted from {100} facets at more positive potentials, while electrons are selectively extracted from {100} facets at more negative potentials. The applied potential would control restructuring of the {100} and {111} facets and change the relative degree of band bending at the semiconductor/liquid interface. Restructuring
of copper and copper oxide surfaces under an applied potential has been observed by scanning tunneling microscopy.\textsuperscript{93-95} This mechanism could explain debate in the literature as to whether \{100\} facets provide a potential barrier for electrons or holes.\textsuperscript{55-58} The potential-dependent surface structure of the \{100\} and \{111\} facets would determine which carrier is preferentially extracted from which facet.

While we cannot rule out the mechanism above, we propose the facet-selective etching of \{100\} facets is due to selective adsorption of hydroxide ions on the \{100\} facets. The adsorption of OH\(^-\) is needed in the oxidative dissolution of Cu\(_2\)O to [Cu(OH)\(_4\)]\(^2-\). Both x-ray photoelectron spectroscopy as well as DFT calculations on single crystal Cu\(_2\)O surfaces indicate that H\(_2\)O and OH\(^-\) as well as other oxygen-containing species including O\(_2\), CO\(_2\), and glucose bind more strongly to the Cu\(_2\)O \{100\} surface than the \{111\} surface.\textsuperscript{59, 69, 96-100} Structures similar to those observed in Figures 2.6 and S20 (with the \{100\} facets etched) have been observed through oxidative etching in the dark.\textsuperscript{53, 65, 101} We also observed slow etching of the \{100\} facets when the microcrystals were immersed in NaOH in the dark (see Figure S19), but the process was significantly slower compared to when the microcrystals were illuminated.

### 2.4 Conclusion

Hollow Cu nanoshells and Cu\(_2\)O/Cu core/shell heterostructures have been synthesized through the transformation of faceted Cu\(_2\)O microcrystals using illumination and an applied bias. Light mediates the deposition of copper metal on the \{100\} facets due to selective extraction of photogenerated electrons from these surfaces. This process only occurs when the applied potential is sufficiently negative to produce downwards band bending at the semiconductor/liquid interface.
The formation of the hollow structures can be controlled by tuning the reaction time, intensity and wavelength of the incident light, and the electrolyte concentration. While the focus of this work was the growth mechanism of these novel structures, hollow metal nanoshells have applications in electrocatalysis\textsuperscript{102, 103} and in chemical sensing via surface-enhanced Raman scattering.\textsuperscript{104, 105}
Chapter 3: Photoelectrochemical Deposition of Manganese Oxide as an Oxygen Evolution Catalyst

Abstract

Photoexcitation can be used to control the composition and nanoscale morphology of inorganic materials during electrodeposition. Here we report the photoelectrochemical synthesis of manganese oxide (MnO$_x$) as a catalyst for the oxygen evolution reaction (OER) with remarkable OER performance. MnO$_x$ films synthesized by multipotential deposition under illumination with a 405-nm light-emitting diode (LED) exhibit significantly higher OER current density, better stability, and a lower onset potential compared to films synthesized by the same method in the dark. The illuminated films have a Tafel slope of 64.1 mV/decade in alkaline solution (pH 13). Electrochemical characterization including cyclic voltammetry, Tafel plots, and electrochemical impedance spectroscopy show that the composition and nanoscale structure of illuminated MnO$_x$ films remain stable during OER, while films synthesized in the dark lose 90% of their initial activity for OER within one hour due to morphological, compositional, and structural changes. Results show that the loss of activity for dark samples mainly arises from increased resistance and a decreased electrochemical surface area after water oxidation. We propose that the enhanced catalytic activity for OER observed for illuminated MnO$_x$ films arises from light-induced morphological and compositional changes. The MnO$_x$ films contain a mixture of Mn ions in both the +3 and +4 oxidation states and possess a disordered structure which has character of both the $\delta$-MnO$_2$ (birnessite) phase and the $\alpha$-Mn$_3$O$_4$ (hausmannite) phases. The as-synthesized,
illuminated samples contain a higher concentration of Mn$^{3+}$, which is critical for improving OER activity. The structure of the dark samples after OER resembles mainly $\delta$-MnO$_2$ (birnessite) in character, while the illuminated samples after OER retain a considerable degree of $\alpha$-Mn$_3$O$_4$ (hausmannite) character. This work provides a new method to synthesize MnO$_x$ catalysts for OER with high stability and activity under illumination.

3.1 Introduction

Electrochemical water oxidation, also known as the oxygen evolution reaction (OER), has attracted much attention in the field of energy conversion, as it plays a critical role in the production of hydrogen fuel via water splitting. Developing OER catalysts with higher activity and better stability is important for the renewable energy industry. The OER activity for several state-of-the-art electrocatalysts as measured by the overpotential at 10 mA/cm$^2$ current (relevant metric for solar fuels) and Tafel slopes in alkaline solution are provided in Table 1. Oxides that are based on metals like Ir and Ru are considered the best OER electrocatalysts, so far, despite their high cost.\textsuperscript{106} Ru and Ir possess excellent OER activity with a 30-40 mV/decade Tafel slope showing the increase in overpotential needed to increase the current density by a factor of 10. First-row transition metal oxides are more affordable choices, like the oxides of Fe, Ni, Co and Mn. Among them, manganese is one of the most abundant metals on earth, and electrodeposited manganese oxides have shown to be promising catalysts for OER with excellent activities.\textsuperscript{107-110} The stoichiometry, crystal structure, and morphology of the manganese oxide catalyst has been shown to largely affect its activity for OER. For example, previous studies have shown that different phases of manganese oxide possess very different OER activities.\textsuperscript{106} At a current density of 0.1 mA/cm$^2$,
electrodeposited porous Mn₂O₃ films have an overpotential of 170 mV, while electrodeposited porous Mn₃O₄ films have an overpotential of 290 mV. In Table 1, the OER activities for state-of-the-art metals, iridium oxides and different stoichiometries of MnOₓ are listed.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Overpotential (mV) at 10 mA cm⁻²</th>
<th>Tafel slope (mV dec⁻¹)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru and Ir</td>
<td>-</td>
<td>30-40</td>
<td>¹¹³</td>
</tr>
<tr>
<td>IrO₂</td>
<td>338</td>
<td>47</td>
<td>¹¹⁴</td>
</tr>
<tr>
<td>α-MnO₂ nanorods</td>
<td>450</td>
<td>73</td>
<td>¹¹⁵</td>
</tr>
<tr>
<td>Porous α-Mn₂O₃</td>
<td>370</td>
<td>50</td>
<td>¹¹²</td>
</tr>
</tbody>
</table>

*The α-MnO₂ nanorods prepared by hydrothermal synthesis have an overpotential of 450 mV and a Tafel slope of 73 mV/decade. The porous α-Mn₂O₃ film prepared by electrodeposition has a better OER activity with an overpotential of 370 mV and a Tafel slope of 50 mV/decade but is only stable for about 2 hours.

Electrodeposited Mn-based catalysts have promising activity for OER, but they are typically stable for less than 1 to 2 hours. More stable MnOₓ films need to be developed before they can be incorporated into electrochemical devices for water splitting. In this work, we focus on improving the activity of Mn³⁺-incorporated manganese oxide films synthesized by photoelectrodeposition to increase both the activity and stability of the catalysts. As the films possess Mn ions in a mixed oxidation state, they will be referred to as MnOₓ in the following discussion. Previous literature has reported that the introduction of Mn³⁺ ions into MnO₂ can greatly enhance its catalytic activity. The introduction of Mn³⁺ can be achieved by several methods during the synthesis of manganese oxide, which include thermal methods like calcination, and electrochemical methods like cathodization and multipotential deposition. Electrodeposited manganese oxide films prepared through multipotential deposition where positive and negative pulses are alternately applied have demonstrated higher oxygen evolution reaction (OER) activity compared to films deposited using
a constant potential or a constant current.\textsuperscript{116, 120} Multipotential deposition has been shown to produce MnO\textsubscript{x} films with a higher Mn\textsuperscript{3+} ratio than films synthesized by other electrochemical methods.\textsuperscript{116} Multipotential deposition can also lead to changes in the Mn–O bonding environment. During the electrochemical oxidation of Mn\textsuperscript{2+} to Mn\textsuperscript{4+} to deposit MnO\textsubscript{2} using a pulsed potential, Mn\textsuperscript{3+} ions can be formed by the comproportionation between Mn\textsuperscript{2+} and Mn\textsuperscript{4+} ions and incorporated into the lattice. It is important to keep Mn\textsuperscript{3+} ions stable during OER as the MnO\textsubscript{x} structure is oxidized under positive potentials. For MnO\textsubscript{x} films synthesized by electrodeposition, Mn ions in tetrahedral sites can be kinetically trapped by structural constraints and forced to remain as Mn\textsuperscript{3+}, while all octahedrally coordinated Mn\textsuperscript{3+} ions are fully oxidized to Mn\textsuperscript{4+}.\textsuperscript{116, 117} The suppression of the disproportionation of Mn\textsuperscript{3+} ions has been confirmed as a key step in maintaining the Mn\textsuperscript{3+} oxidation state, and the presence of Mn\textsuperscript{3+} is critical in enabling reductive elimination of oxygen, thus making Mn\textsuperscript{3+} stable and active during OER.\textsuperscript{116, 120-122}

However, the activity and stability of these manganese oxide films are still limited compared to top performing OER catalysts like Ir and Ru, especially when running OER for hours at high current densities (10 mA/cm\textsuperscript{2}). In this chapter, we introduce a method to photoelectrodeposit manganese oxide films under the illumination of a light-emitting diode (LED). Photogenerated charge carriers can induce interfacial charge-transfer during the electrochemical synthesis of semiconductors.\textsuperscript{1} While illumination has been previously utilized to induce structural and compositional transformations during electrodeposition (as described in Chapters 1 and 2), here we show that photoelectrodeposition can produce nanostructured electrocatalysts exhibiting higher activity and stability. We have successfully improved the performance of the manganese oxide films through morphological, compositional, and structural changes induced by light-matter interactions during growth. We observed that films prepared under illumination possess
significantly improved stability, and they can maintain high activity for 18 hours while performing OER at a high current density (10 mA/cm²). We investigated the mechanism of how light interacts with the metal oxide during growth and changes the structure of MnOₓ films during photoelectrodeposition.

A variety of characterization methods were used to compare the electrochemical and structural properties of electrodeposited manganese oxide films and determine how illumination during growth changed their structure and OER activity. Films synthesized in the dark and under illumination were investigated both before and after water oxidation. Cyclic voltammetry (CV) showed that MnOₓ films synthesized under illumination have a higher current density for oxygen evolution than MnOₓ films synthesized in the dark. Illuminated samples also had a lower onset potential for OER compared to dark samples. Stability tests by constant-current electrolysis showed that when operating at the same current density, illuminated samples can maintain a stable and lower potential for a longer time. Oxygen evolution tests showed that illuminated samples produced a larger amount of oxygen compared to dark samples over the same time period. For electrochemical measurements, Tafel plots (i.e., potential vs. log of current density) showed that the Tafel slope of illuminated samples are smaller than dark samples, indicating that light samples require a smaller increase in overpotential to increase the current density for same magnitude compared to dark samples. Electrochemical impedance spectroscopy (EIS) provides insights into the impedance changes of samples after water oxidation. EIS showed that the dark samples became more resistive after OER and lost their activity, their resistance increased from 54.19 Ω to 160.6 Ω, while the illuminated samples only increased from 63.13 Ω to 69.88 Ω after OER. SEM images indicate that the illuminated and dark samples possess different surface morphologies after OER. Furthermore, dark samples showed a sharp decrease in surface area after OER, which was further
confirmed by electrochemical surface area (ECSA) measurements. X-ray photoelectron spectroscopy and Raman spectroscopy indicate that the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio was higher for illuminated samples than for dark samples.

Based on these results, MnO$_x$ films synthesized under illumination demonstrated better OER catalytic performance than MnO$_x$ films synthesized in the dark. The light samples have higher OER activity, are more stable, and can maintain the high activity for a longer time. EIS, XPS and SEM indicate that the films synthesized under illumination and in the dark have different structures, composition, and morphologies. The growth mechanisms of the two types of films are discussed in detail below.

### 3.2 Experimental Section

#### 3.2.1 Materials

All chemicals were used as received. Manganese chloride (MnCl$_2$·4H$_2$O, ≥99%), manganese (IV) oxide (MnO$_2$, ≥99%), manganese (II, III) oxide (Mn$_3$O$_4$, ≥97%), manganese (III) oxide (Mn$_2$O$_3$, ≥99%), manganese (II) oxide (MnO, ≥99%), sodium hydroxide (NaOH, ≥97%), potassium hydroxide (KOH, ≥85%), and potassium nitrate (KNO$_3$, ≥99%) were purchased from Millipore Sigma. Platinum gauze (Pt, 100 mesh, 99.9% metals basis) and Pt wire (0.5 mm diameter, 99.95% metals basis) were purchased from Alfa Aesar. All aqueous solutions were made using purified water from a GenPure Pro water purification system with at least 17.30 MΩ·cm resistivity.
3.2.2 Electrochemical Synthesis

**Preparation of electrodes:** The counter electrode consisted of Pt gauze attached to a Pt wire. The Pt wire was soldered to a Sn–Cu wire, and the soldered joint was sealed in a glass tube. A silver/silver chloride (Ag/AgCl) electrode in 3 M NaCl was used as the reference electrode. Glass slides coated with fluorine-doped tin oxide (FTO) from MSE Pro with a resistivity of 15 Ω/sq were cut into smaller pieces to use as working electrodes with a typical surface area of 1×2 cm. The FTO electrode was connected to the potentiostat with a copper clip. Each working electrode was rinsed with purified water and then dried with nitrogen gas before use.

**Electrodeposition of MnOₓ films:** The MnOₓ catalyst films were electrodeposited from an aqueous solution containing 0.5 mM MnCl₂ and 0.9 M KNO₃ based on a previous report with modifications. The pH of the solution was adjusted to 8 using a diluted KOH solution before use. The MnOₓ films were prepared by a multipotential deposition method, where the electrode was initially held at +0.9 V vs. Ag/AgCl or 3 s, followed by −0.6 V vs. Ag/AgCl for 2 s; this cycle was repeated for either 40 mins or 1 h. The electrodeposition was performed either in the dark or under illumination with a high-power, light-emitting diode (LED) with a peak wavelength of 405 nm and a full width at half maximum of ~30 nm. The irradiance was measured using a calibrated Si photodiode from ThorLabs (FDS-100 CAL). A custom electrochemical cell was used for all electrodeposition experiments. The cell was made from borosilicate glass with openings at the top for the electrodes and a flat window on the side for illumination. A BioLogic VSP-300 potentiostat/galvanostat operated using EC-Lab software (V11.33) was used to perform all electrochemical experiments and tests. A photo scanner was used to scan images of the working electrodes, and their surface areas were measured using ImageJ software.
3.2.3 Characterization

Electrochemical characterization

*Cyclic voltammetry (CV):* CV was performed to characterize the onset potential and current density for oxygen evolution that occurs using the MnO\textsubscript{x} films as the working electrode. All CV scans started at open circuit. For each scan, the potential was first swept in the positive direction to +1.2 V vs. Ag/AgCl, then swept in the negative direction to 0 V vs. Ag/AgCl. The scan rate was 20 mV/s, and two consecutive CV scans were performed for each electrode to observe the change in current density.

*Stability of electrodes:* The ability of the MnO\textsubscript{x} films to sustain stable activity for the oxygen evolution reaction was evaluated by constant-current electrolysis. The MnO\textsubscript{x} films prepared by multipotential deposition were tested at a current density (j) of 10 mA/cm\textsuperscript{2} in a solution containing 0.1 M KOH and 0.9 M KNO\textsubscript{3} as a supporting electrolyte. The solutions were stirred at \(\sim 600\) rpm throughout the experiment using a magnetic stir plate and stir bar. The potential was measured every 0.5 s and recorded over 10 h of continuous electrolysis, and the stability was analyzed by tracking the change of potential over time. A CV scan was taken after the stability test.

*Oxygen evolution test:* An aqueous solution containing 0.1 M KOH was purged with argon for 30 min before the oxygen evolution test was performed in an electrochemical cell sealed with parafilm. The MnO\textsubscript{x} films were biased at a potential of +1.4 V vs. Ag/AgCl for 1h, and the dissolved oxygen concentration was tested every 10 min using a YSI ProODO optical dissolved oxygen meter with the probe inserted in the electrochemical cell.

*Electrochemical impedance spectroscopy (EIS):* Electrochemical impedance spectroscopy (EIS) was performed to determine the impedance and capacitance of the MnO\textsubscript{2} catalysts before and after OER. Mott-Schottky plots (\(1/C^2\) vs. the applied potential where C is the space-charge
capacitance) and Nyquist plots were extracted from EIS data and were fit using EC-Lab software (V11.33). Impedance measurements were conducted in a solution containing 0.1 M KOH and 0.9 M KNO₃. For Mott-Schottky plots, the AC potential oscillation was 10 mV, and the DC potential range was from +1.0 V to 0.2 V vs. Ag/AgCl. The frequencies scanned ranged from 10 kHz to 1 kHz, but only the data at 10 kHz is shown in the figures below. No iR compensation was applied during these measurements. For Nyquist plots, the frequencies scanned were 3 MHz to 30 Hz, the AC potential oscillation was 10 mV, and the DC potential range was +0.1 V to +0.4 V vs. Ag/AgCl. Only the data at a potential of +0.2 V is shown in the figures below. A modified Randles circuit was used to model the electrochemical cell based on the fitting of Nyquist plots at different applied potentials. The circuit model consists of two resistors (R₁ and R₂), a capacitor (C₂), and a Warburg impedance (W₂): \[ R_1 + C_2/(R_2 + W_2) \].

*Tafel plots:* The OER activity of MnOₓ films was evaluated by measuring the steady-state current density (j) as a function of applied potential (E) during oxygen evolution in an aqueous solution containing potassium phosphate buffer at pH 7 with 0.9 M KNO₃ as a supporting electrolyte. The solutions were stirred at ~600 rpm with a Teflon stir bar to minimize mass-transport limitations during data collection. The highest potential was held for 200 s to minimize any pseudocapacitance, and a series of discrete monotonically decreasing potentials ranging from +1.05 V to +0.95 V vs. Ag/AgCl were applied to the electrode for 30 s each to allow the current to reach a steady-state value. All potentials were automatically iR compensated for the solution and substrate (i.e., FTO) resistance. The current density–potential data were plotted in the form of the applied potential E versus log j to present Tafel plots; plots using E will result in the same Tafel slope as those using the overpotential (η). Control studies with bare FTO show that it is a poor catalyst for OER and exhibits high Tafel slopes (over 500 mV/decade). Its current density for OER
is at least two orders of magnitude lower than that of MnO$_x$ catalyst films, and thus it serves as a
good substrate for comparing the activity of MnO$_x$ films prepared by different methods.

*Electrochemical surface area (ECSA):* The electrochemical surface area of different samples was
calculated from the electrochemical capacitance determined by CV at different scan rates over a
potential window where there is no Faradaic current in the bath that contains 0.1 M KOH and 0.9
M KNO$_3$. The potential window used was ±0.05 V with respect to the open-circuit potential of the
film. CV measurements were conducted by sweeping the potential in this region at 8 different scan
rates: 5, 25, 50, 75, 100, 125, 150, 175 mV/s. The working electrode was held at each vertex
potential for 10 s before beginning the next sweep.

**Structural characterization**

*Scanning electron microscopy (SEM):* SEM images were collected by using a ThermoFisher
Quattro S environmental scanning electron microscope operated at an acceleration voltage of 10
kV. After electrodeposition or OER, the working electrode was cut into an approximately 1×1 cm
piece, and the conductive top surface of the substrate was connected with copper tape to the SEM
sample holder to avoid charge buildup.

*X-ray photoelectron spectroscopy (XPS):* XPS was performed by using a Physical Electronics
5000 VersaProbe II Scanning ESCA Microprobe system with a base pressure below $1 \times 10^{-9}$ Torr.
XPS data were acquired using the 1486.6 eV line from a monochromated Al K$_\alpha$ source at 150 W
with a multichannel detector set to a pass energy of 23.5 eV for the high-resolution scans. High-
resolution spectra in the binding regions for Mn 2p, Mn 3s, Mn 3p, C 1s, and K 2p electrons were
measured for the MnO$_x$ films before and after OER. Four standard powders: manganese (IV) oxide,
manganese (III) oxide, manganese (II, III) oxide, and manganese (II) oxide were used as references
for the peak positions of Mn in different oxidation states. To monitor changes in the Mn oxidation state of the MnOₙ films, we measured the position of Mn 2p₁/₂ peaks as well as the position of the Mn 3p peaks, which have been previously shown to increase in binding energy with increasing Mn oxidation state in the powder standards.₁²³,₁²⁴

*Raman spectroscopy:* To characterize the structure of the MnOₓ films, Raman spectroscopy was carried out using an InVia Raman Microscope (Renishaw, UK). The excitation source was a 514-nm laser (~4 mW), and a grating of 1800 lines/mm was used. A 20× Leica objective and a reduced power of 50% were utilized. The integration time for each measurement was 10 s, and the step size was 1.2 cm⁻¹.

### 3.3 Results and Discussion

The catalyst loading on substrate is important in determining the catalytic activity for OER; films that are too thin are not durable enough. Thus, the electrochemical conditions and number of pulses during the potential cycle were varied to obtain an optimized film thickness. We found that films synthesized under illumination deposited between 40 min to 1 h exhibited the best activity and stability. CV scans of the as-synthesized, dark and illuminated MnOₓ films are shown in Figure 3.1a. The CV scans were carried out in the dark in a solution of 0.1 M KOH and 0.9 M KNO₃. The initial current densities for OER of the dark and illuminated samples are similar at 1.2 V vs. Ag/AgCl. The as-synthesized, illuminated sample reached a current density of 9.9 mA/cm² at 1.2 V vs. Ag/AgCl, and the second cycle of CV scan retained the same high activity. The current density of as-synthesized, dark sample was 8.8 mA/cm² at 1.2 V vs. Ag/AgCl during the first scan, but in the second cycle of CV scan it dropped to 7.8 mA/cm² at 1.2 V vs. Ag/AgCl. Figure 3.1b
shows CV scans of dark and illuminated samples after 1 h of OER at a current density of 10 mA/cm². While the current density of illuminated sample persisted at 9.9 mA/cm² at 1.2 V vs. Ag/AgCl, the current density of dark sample decreased significantly to 0.8 mA/cm². The dark film lost almost all OER activity, indicating poor stability even after one hour of water oxidation. The onset potential of OER for the illuminated sample was 0.61 V vs. Ag/AgCl before OER, which was lower compared to the onset potential of 0.69 V for the dark sample. The onset potential for illuminated sample was still 0.61 V after OER. However, the onset potential for dark sample after OER was difficult to measure because it was too close to background current density produced by the FTO substrate. CV scans were also performed for films after OER at current densities of 3 mA/cm² or 5 mA/cm². At these lower current densities, dark films took a longer time to lose all their activity for OER.

Figure 3.9 CV scans of MnOₓ films in 0.1 M KOH synthesized in the dark (black traces) and under illumination (red traces). (a) initial activity of the films for OER. (b) activity after 1 hour of OER at a current density of 10 mA/cm².
Figure 3.2 shows the stability of the electrodes during OER as measured by constant-current electrolysis in 0.1 M KOH. The MnO\textsubscript{x} films synthesized under illumination and in the dark were tested at a constant current of 10 mA/cm\textsuperscript{2} in the dark. The stability of each electrode was evaluated based on the change in the potential needed to maintain a constant current. The half reaction for water oxidation in alkaline solutions is:

\[ 4OH^- \leftrightarrow 2H_2O(l) + O_2(g) + 4e^- \]

The standard electrode potential at 1 atm and 25 °C for OER is 0.404 V vs. NHE when all products have unit activity. In this work, the potential is referenced to the Ag/AgCl half-cell, which can be converted to NHE scale by the following relation: \( E_{NHE} = E_{Ag/AgCl} + 0.197 \text{V} \). A stable film would be able to maintain the high current density at a lower overpotential (i.e., less positive potential). It is shown in Figure 3.2 that over the 40-min test period, the illuminated sample operated at a relatively stable potential window near 1.4 V. Due to structural changes that will be discussed in more detail below, the operating potential of the illuminated sample even decreased to 1.2 V by the end of the 40-min test. However, for the dark sample, the potential required to maintain 10 mA/cm\textsuperscript{2} continuously increased over the 40-min test period and eventually reached a high value of 2.4 V. In a control experiment, a bare FTO substrate showed a similar potential (~2.5 V) to the dark sample after OER, indicating a near complete loss of the OER activity.
Figure 3.10 Applied potential vs. time for a MnO₅ film synthesized in the dark (black trace) and a film synthesized under illumination (red trace) during constant-current electrolysis at a current density of 10 mA/cm² to test the stability of the catalyst. A lower potential indicates a better stability in OER, while an increase in potential indicates that the catalyst is not stable.

Figure 3.3 shows the Tafel plots of MnO₅ films synthesized in the dark and under illumination before and after OER. A Tafel slope reveals how much the applied potential needs to be increased to increase the current density by a factor ten. A low value of the Tafel slope for an ideal electrocatalyst means the overpotential needed to run the reaction is small. When the electrode reaction is not-limited by mass transport, the Tafel slope reflects the kinetics of OER. In an alkaline medium, a Tafel slope of ~ 60 mV/decade for oxygen evolution indicates that there is an inverse first-order dependence on proton concentration based on previous work. A one-electron, one-proton, proton-coupled electron transfer (PCET) pathway is dominant under alkaline conditions. The PCET step is rapid and in quasi-equilibrium and is followed by a rate-determining chemical step, which has been proposed to correspond to the release of O₂ from the electrode surface. All electrodes were scanned from 1.05 V to 0.95 V vs. Ag/AgCl under stirring at 500 rpm to
minimize mass-transport limitations. The as-synthesized, illuminated sample had a Tafel slope of 64.1 mV/decade, while the as-synthesized, dark sample had a slope of 72.7 mV/decade, which shows that the illuminated sample displays slightly better overpotential for OER than the dark sample. The $R^2$ values of the linear fits were larger than 0.995. Next, both electrodes were used to perform OER at a constant current of 5 mA/cm$^2$ for 40 min. The slope for the illuminated sample after OER was 71.4 mV/decade, while the slope for dark sample after OER was 138.6 mV/decade. These results show that illuminated sample was able to maintain a relatively high activity during oxygen evolution as there was only a 7.3 mV/decade increase in its Tafel slope. However, the Tafel slope of dark sample increased significantly after OER by 65.9 mV/decade, which indicates that it was not stable during oxygen evolution.
Figure 3.11 Tafel plots of films synthesized under a 405-nm LED before (red triangles) and after (orange circles) OER, and films synthesized in the dark before (blue triangles) and after (light-blue squares) OER. The slopes for samples grown under illumination were 64.1 mV/decade before OER and 71.4 mV/decade after OER. The slopes for the dark samples were 72.7 mV/decade before OER and 138.6 mV/decade after OER. The lines connecting the symbols represent linear fits of the raw data used to calculate the Tafel slopes.

Figure 3.4 shows measurements of the dissolved oxygen concentration over time during OER for MnO$_x$ samples synthesized in the dark and under illumination. The dissolved oxygen concentration was measured with an optical oxygen meter in a sealed electrochemical cell purged with argon. A reading was taken every 10 minutes. After one hour of OER operated at 1.4 V vs. Ag/AgCl, the dissolved oxygen was 4.8 mg/L for the dark sample and 11.2 mg/L for the illuminated sample. A FTO substrate operated at the same potential was used as a blank, and the background dissolved oxygen concentration was 2.2 mg/L. We did not calculate a Faradaic efficiency for OER because a single compartment cell was used in this test in which oxygen reduction can occur at the counter electrode. However, based on these results, the amount of O$_2$
produced by the illuminated sample over 1 h was 9.0 mg/L which was over 3 times as much as the amount produced by dark sample (2.6 mg/L). OER at other applied potentials was carried out, and generally, the MnO\textsubscript{x} films synthesized under illumination produced a much higher amount of oxygen over 1 h of OER compared to films synthesized in the dark.

![Graph showing dissolved oxygen concentration vs. time during OER.](image)

**Figure 3.12** The dissolved concentration of oxygen vs. time during OER measured by an oxygen meter in a sealed cell. The red line represents the amount of oxygen produced by a MnO\textsubscript{x} film synthesized under illumination during 1 h of OER. The blue line represents the amount of oxygen produced by a MnO\textsubscript{x} film synthesized in the dark during 1 h of OER. The black line represents the amount of oxygen produced by a FTO substrate during 1 h of OER, and it serves as a blank sample. The amount of oxygen produced by each sample was calculated by subtracting the amount of oxygen produced by FTO substrate. The black triangles indicate the points when measurements were made.

**Figure 3.5** shows SEM images of the MnO\textsubscript{x} films. The as-synthesized, illuminated and dark sample both have platelet-like morphologies. The darker background under the catalyst is the FTO substrate. After OER, the illuminated sample maintained the platelet-like morphology, while individual platelets became less distinct in the dark sample. As the electrochemical activity of the
illuminated sample was stable while the dark sample dramatically decreased in activity, these observations indicate that the platelet-like morphology is good for OER. The electrochemical activity is closely related to the surface area of the electrode. Based on the SEM images, the platelet-like morphology provides a higher surface area, which was quantified by measuring the electrochemically active surface area (ECSA) as shown in Figure 3.6.

**Figure 3.13** SEM images of (a) as-synthesized MnO$_x$ film grown by multipotential deposition under a 405-nm LED; (b) film synthesized under a 405-nm LED after 1 h of OER; (c) as-synthesized film formed by multipotential deposition in the dark; (d) film synthesized in the dark after 1 h of OER. The scale bar of 1 µm applies to all images.

The electrochemical double-layer capacitance was calculated from CV scans shown in Figure 3.6 that were performed at different scan rates over a 0.1-V potential window centered around the
open-circuit potential, which was obtained from a CV scan before the test. The non-Faradaic current in this potential range was considered to be from double-layer charging. The relationship between the double-layer charging current, $i_c$, and double-layer capacitance, $C_{DL}$, is shown in equation 1:

$$i_c = \nu C_{DL}$$  \hspace{1cm} (1)

where $\nu$ is the potential scan rate. Thus, plotting the double-layer current at the open-circuit potential versus the scan rate will give a straight line, and the double-layer capacitance can be calculated from the slope. **Figure 3.6 a, c, e, g** show CV scans at different scan rates within the non-Faradaic region measured using the dark sample before OER, the dark sample after OER, the illuminated sample before OER, and the illuminated sample after OER, respectively. The positive current values at the open-circuit potential were used to make the plots shown in **Figure 3.6 b, d, f, h**, and the double-layer capacitance for each film was calculated from a linear fit of the data. The electrochemical surface area (ECSA) can be calculated from double-layer capacitance according to equation 2:

$$ECSA = C_{DL}C_s$$  \hspace{1cm} (2)

where $C_s$ is the specific capacitance of the sample. It refers to the capacitance per unit area of an atomically smooth planar surface of the material under identical electrolyte conditions. Since the ECSA is proportional to $C_{DL}$, and the specific capacitance for photoelectrodeposited MnO$_x$ films has not been reported yet, we used $C_{DL}$ to compare differences in the electrochemical surface area of different films. The $C_{DL}$ was 1.58 mF/cm$^2$ for dark sample before OER and 0.25 mF/cm$^2$ for dark sample after OER; there was clearly a large decrease. The $C_{DL}$ was 2.83 mF/cm$^2$ for illuminated sample before OER and 1.99 mF/cm$^2$ for illuminated sample after OER. These results indicate that the initial ECSA of dark sample was smaller than that of illuminated sample. The
difference in ECSA helps explain why the initial OER current density and Tafel slope of illuminated sample were higher than that of dark sample. These results also indicate that the ECSA of dark sample decreased drastically after OER and explain the loss of OER activity from a morphological perspective.
Figure 3.14 CV scans used to measure the electrochemical surface area (ECSA) of the MnOx films. (a, b) CV scans and linear $i_c$ - $ν$ fitting of dark sample before OER; (c, d) CV scans and linear $i_c$ - $ν$ fitting of dark sample after OER; (e, f) CV scans and linear $i_c$ - $ν$ fitting of illuminated sample before OER; (g, h) CV scans and linear $i_c$ - $ν$ fitting of illuminated sample after OER. The double-layer capacitance values
obtained from the slopes of the linear fits are labeled next to each fit along with the R² value for each linear fit.

Electrochemical impedance spectroscopy (EIS) enabled us to correlate changes in the resistivity of the MnOₓ films with changes in their electrochemical surface area. EIS was carried out in an aqueous solution containing 0.1 M KOH and 0.9 M KNO₃ in the dark at different potentials. Two types of plots were derived from the EIS data – Mott–Schottky plots and Nyquist plots. The Mott–Schottky equation relates the capacitance (C) of a semiconductor electrode to its carrier concentration (N_d) and its flat-band potential (V_FB), as shown in equation 3:

\[
\frac{1}{C^2} = \left( \frac{2}{\varepsilon \varepsilon_0 A^2 N_d} \right) \left[ V - V_{FB} - \frac{k_B T}{e} \right]
\]  

(3)

where \( \varepsilon_0 \) is the permittivity of vacuum, \( \varepsilon \) is the relative permittivity of the semiconductor, \( A \) is the electrochemical surface area, \( V \) is the applied potential, \( k_B \) is Boltzmann’s constant, and \( T \) is temperature. Either the electrochemical surface area or the carrier concentration can be determined from the slope of Mott-Schottky plot if the other value is known. As discussed in Chapter 2, the flat-band potential, \( V_{FB} \), can be determined from the intercept with the x-axis.
Figure 15.7 Mott-Schottky plots of MnO$_x$ films synthesized under a 405-nm LED before (red triangles) and after (orange circles) OER, and films synthesized in the dark before (blue triangles) and after (light-blue squares) OER. The lines represent linear fits of the raw data used to calculate the Mott-Schottky slopes.

Figure 3.7 shows Mott-Schottky plots (i.e., $1/C^2$ versus the applied potential, V vs. Ag/AgCl) measured at a 10-kHz frequency for both the as-synthesized MnO$_x$ films and MnO$_x$ films after 1 hour of OER. The positive slopes of the Mott-Schottky plots in all four samples indicates n-type conductivity of the MnO$_x$ thin films with the Fermi level closer to the conduction band edge.$^{107}$ The slope of the plot for the MnO$_x$ film grown under illumination was similar before and after OER. On the other hand, the slope of the dark sample after OER was much greater compared to the dark sample before OER and both illuminated samples. Since the surface area is a factor in the slope of the Mott-Schottky plot, the high slope for dark samples after OER indicates that the surface area decreased significantly. The change in the slope of Mott-Schottky plot agrees with the SEM images (Figure 3.5) and ECSA (Figure 3.6) results that the surface area for dark samples decreased during the OER.
**Figure 16.8** Nyquist plots of films synthesized under a 405-nm LED before (red) and after (orange) OER, and films synthesized in the dark before (blue) and after (light blue) OER.

[Image 101x537 to 511x720]

**Figure 17.9** Equivalent circuit model used to fit Nyquist plots. This model applies to all electrodeposited MnO$_x$ films discussed in this chapter. $R_1$ represents the solution resistance, $C_2$ represents double-layer capacitance, $R_2$ represents charge-transfer resistance, and $W_2$ represents a Warburg impedance.

The Mott-Schottky analysis described above indicates that the carrier concentration of the dark sample decreased significantly after OER. It was also found that the resistance of a “dead” dark film after OER could reach several MΩ in resistance on its surface as tested by multimeter. Nyquist plots shown in **Figure 3.8** were used to quantify the change in resistance of the MnO$_x$ films after OER. Under kinetic control, the radius of the semicircle indicates the charge-transfer resistance. The Nyquist plots were extracted from EIS measurements and fit using EC-Lab.
software (V11.33). The x-axis shows the real part of the frequency response while the y-axis shows the imaginary component of the frequency as the variable. Figure 3.9 shows the equivalent circuit model used to fit the Nyquist plots, which applies to all samples shown in Figure 3.8. The resistor, $R_2$ in the circuit model represents charge-transfer resistance, which is approximately the resistance of the electrode. So, the value of $R_2$ can be used to evaluate the change in surface-resistance of the MnO$_x$ films. Based on the fitting of impedance data using this circuit model, the charge-transfer resistance is 63.13 Ω for the illuminated sample before OER, 69.88 Ω for illuminated sample after OER, 54.19 Ω for dark sample before OER, and 160.6 Ω for dark sample after OER. The resistance of dark sample increased significantly after OER, which agrees with the Mott–Schottky plots shown in Figure 3.7 and was further confirmed by four-point resistance measurements. Both samples tend to have an increasing resistance as OER proceeds, but the resistance of the dark film increased dramatically and was much higher than the resistance of illuminated film after OER.

The structure and composition of the MnO$_x$ films were further explored by Raman spectroscopy. Raman spectra of dark and illuminated samples before and after water oxidation were measured on films electrodeposited on FTO substrates. Raman spectra of MnO$_2$, Mn$_2$O$_3$, Mn$_3$O$_4$, and MnO standards were also measured for comparison by placing the corresponding powder on a FTO substrate. A peak at 1092 cm$^{-1}$ (not shown) was assigned to the FTO substrate for all samples. As shown in Figure 3.10, the as-synthesized, illuminated sample possessed two main peaks at 602 and 657 cm$^{-1}$. After OER, the illuminated sample exhibited two extra peaks at 574 cm$^{-1}$ and 634 cm$^{-1}$. The peak at 634 cm$^{-1}$ partially overlaps with the original peak at 657 cm$^{-1}$. The as-synthesized, dark sample had one main peak at 657 cm$^{-1}$ along with a broad shoulder at lower wavenumbers. After OER, the peak at 657 cm$^{-1}$ for the dark sample became less intense, while a new peak appeared at 634 cm$^{-1}$ and the intensity to lower wavenumbers increased.
In Figure 3.10, the main Raman peak at 657 cm\(^{-1}\) observed for both of the as-synthesized samples is indicative of hausmannite \(\alpha\)-Mn\(_3\)O\(_4\) and corresponds to different vibrational modes of [MnO\(_6\)] octahedra. Hausmannite also has a shoulder peak that is shifted to 602 cm\(^{-1}\) in electrodeposited films (observed here in the as-synthesized, illuminated sample), and its character originates from the vibration of Mn–O bonds. The relative intensity of the shoulder peak is closely related to the average oxidation state of Mn cations.\(^{125}\) These peaks decreased in their relative intensity after OER. It has been previously reported that Raman peaks at 574 cm\(^{-1}\) and 634 cm\(^{-1}\) are indicative of electrodeposited \(\delta\)-MnO\(_2\) (birnessite) with an in-plane, Mn–O stretching vibration at 574 cm\(^{-1}\) and an out-of-plane stretching vibration at 651 cm\(^{-1}\) that shifts to 634 cm\(^{-1}\) during electrodeposition.\(^{116} \text{,}^{126} \text{,}^{127}\) As OER proceeded, the intensity of the patterns at both of these wavelengths increased indicating that the films became more like \(\delta\)-MnO\(_2\) in character. Combined with the analysis of XPS described below, these results indicate that Mn\(^{3+}\) ions were oxidized to Mn\(^{4+}\) under the strong anodic potential. Thus, the content of the hausmannite phase decreased and that of the birnessite phase in the films increased during water oxidation. However, even though OER increased the fraction of \(\delta\)-MnO\(_2\) in the illuminated sample, the two peaks belonging to hausmannite still existed after OER, indicating that Mn\(^{3+}\) ions the in illuminated sample were not fully oxidized to Mn\(^{4+}\).
Figure 18.10 Raman spectra of MnOₓ films. Red trace: as-synthesized, illuminated sample; Orange trace: illuminated sample after OER; Blue trace: as-synthesized, dark sample; Light blue trace: dark sample after OER.

To further support the structural analysis obtained through Raman spectroscopy, we also performed XPS of the MnOₓ films before and after water oxidation as shown in Figure 3.11. The peak positions of the MnOₓ films were corrected based on the C 1s peak when analyzing XPS data. The positions of the 2pₓ/2 peaks after correction based on C 1s peak in Figure 3.11a are: 653.8 eV for as-synthesized, illuminated sample, 653.9 eV for illuminated sample after OER, 654.4 eV for as-synthesized, dark sample, and 654.4 eV for dark sample after OER. The 2pₓ/2 peak positions for standard powders of MnO₂ and Mn₂O₃ are located at 654.0 eV and 653.6 eV, respectively. Thus, a higher binding energy for the 2pₓ/2 peak indicates that the sample contains a higher fraction of Mn⁴⁺ ions. The 2pₓ/2 peaks for the dark samples before and after OER are located at a higher
binding energy by 0.4 eV compared to standard position of the MnO\(_2\) sample. On the other hand, the peak positions of the illuminated samples before and after OER were located in between those of the MnO\(_2\) and Mn\(_2\)O\(_3\) standard samples. Thus, the relative binding energies of the Mn 2p\(_{1/2}\) peaks indicated that illuminated samples possessed a higher fraction of Mn\(^{3+}\) compared to dark samples. The 3p peak positions shown in Figure 3.11b are 49.6 eV for the as-synthesized, illuminated sample, 49.7 eV for illuminated sample after OER, 49.9 eV for as-synthesized, dark sample, and 50.0 eV for dark sample after OER, respectively. The standard 3p peaks for MnO\(_2\) and Mn\(_2\)O\(_3\) are located at 49.6 and 49.0 eV, respectively. Thus, a higher binding energy value suggests a higher amount of Mn\(^{4+}\). Similar to the 2p\(_{1/2}\) peaks, the lower binding energies of the 3p peaks in the illuminated samples before and after OER suggest they contain a higher fraction of Mn\(^{3+}\) in the films. Together, the XPS and Raman results show that the as-synthesized, illuminated sample has a higher fraction of Mn\(^{3+}\) and hausmannite \(\alpha\)-Mn\(_3\)O\(_4\) character than the dark sample. After water oxidation both films have increased amount of Mn\(^{4+}\) and birnessite character, but the fraction of Mn\(^{3+}\) is still higher in the illuminated film than the dark film. Consistent with the stability tests, a higher fraction of hausmannite character was retained in the illuminated sample after OER, but the content of hausmannite in the dark sample was lower based on the change of the main Raman peak at 657 cm\(^{-1}\).
**Figure 19.11** XPS of MnO\textsubscript{x} films. (a) Binding energy region for Mn 2p\textsubscript{1/2} electrons. (b) Binding energy region for Mn 3p electrons. Red traces: as-synthesized, illuminated sample. Orange traces: illuminated sample after OER. Blue traces: as-synthesized, dark sample. Light blue traces: dark sample after OER.

Based on previous literature\textsuperscript{126-129} during the electrodeposition of MnO\textsubscript{x} films a comproportionation reaction can occur between Mn\textsuperscript{4+} and Mn\textsuperscript{2+} ions in the presence of OH\textsuperscript{-} ions. The multipotential process used to deposit the films oxidizes Mn\textsuperscript{2+} ions to Mn\textsuperscript{4+} during the positive pulse. The OH\textsuperscript{-} ions formed by reduction of NO\textsubscript{3}\textsuperscript{-} during the negative pulse are necessary to induce the comproportionation reaction and form Mn\textsuperscript{3+}. In this way, multipotential deposition introduces Mn\textsuperscript{3+} ions into the growing film, and the initial δ-MnO\textsubscript{2} (birnessite) structure undergoes a phase change to form α-Mn\textsubscript{3}O\textsubscript{4} (hausmannite). The subsequent anodic pulse during deposition brings the film back to a disordered δ-MnO\textsubscript{2} phase, which can also occur during OER. This disordered phase containing both Mn\textsuperscript{3+} and Mn\textsuperscript{4+} ions has previously been shown to possess high activity for OER.\textsuperscript{116, 120}
Hausmannite $\alpha$-Mn$_3$O$_4$ has the spinel structure with a tetragonal distortion along the c-axis due to the Jahn-Teller effect in the octahedrally coordinated Mn$^{3+}$ ions. The Mn$^{3+}$ ions occupy octahedral sites while Mn$^{2+}$ ions occupy tetrahedral sites. Hausmannite and bixbyite, Mn$_2$O$_3$, (both containing a significant fraction of Mn$^{3+}$ ions) have been reported to be the most active polymorphs of manganese oxides for water oxidation. The Mn$^{2+}$ ions in tetrahedral sites are oxidized to Mn$^{3+}$ during OER, and this is a key step in making hausmannite stable during OER. The presence of Mn$^{3+}$ ions in MnO$_x$ films lowers their overpotential of electrochemical water oxidation. In alkaline solution, the OER reaction proceeds through an one electron, one proton PCET, and terminal oxos bound to Mn$^{3+}$ ions at the surface can couple to release O$_2$. Kinetic trapping of Mn$^{3+}$ ions in tetrahedral sites of the disordered MnO$_x$ film is critical to prevent the disproportionation of Mn$^{3+}$ ions during OER. The stabilized Mn$^{3+}$ ions in the films can keep the MnO$_x$ catalysts running the OER.

The CV scans in Figure 3.1 show that the initial current densities produced by as-synthesized illuminated and dark MnO$_x$ films are similar. However, the illuminated samples can maintain high current densities during OER while the dark samples lose nearly all their activity. The morphology, charge-carrier concentration, and the Mn$^{3+}$ concentration all affect each other and the performance of OER catalysis, and this can help explain why dark samples lose catalytic activity during water oxidation. Mn$^{3+}$ ions in the MnOx films can serve as an electron donor and thus make the MnO$_x$ films n-type. The slope of the Mott–Schottky plot in Figure 3.7 for the dark sample after OER is significantly higher than the other three samples which can arise due to either a decrease in the electrochemical surface area or the donor density. A decrease in surface area in the dark sample after OER is evidenced by the changes in morphology (Figure 3.5) and the double-layer capacitance (Figure 3.6). A decrease in the donor density is evidenced by the change in Nyquist
plot (Figure 3.8) and the increased fraction of birnessite seen by Raman spectroscopy (Figure 3.10). Thus, a decrease in electrochemically active surface area and increase in resistance as Mn$^{3+}$ ions are oxidized to Mn$^{4+}$ work in concert to reduce the activity of the MnO$_x$ films grown in the dark. The MnO$_x$ films grown under illumination retain their high surface area, conductivity, and hausmannite character showing that Mn$^{3+}$ are stabilized in these films leading to sustained activity for OER.

### 3.4 Conclusions

Active and stable MnO$_x$ catalysts have been synthesized for OER. MnO$_x$ films synthesized under illumination with a 405-nm LED show higher activity and stability towards OER than samples synthesized in the dark. The as-synthesized, illuminated and dark samples initially have similar electrochemical performance. However, the activity of MnO$_x$ films synthesized in the dark under the same electrochemical conditions decreased significantly after about 10 mins of OER at 10 mA/cm$^2$. The overpotential and resistance of the dark films increase drastically during OER, while the electrochemical surface area decreases, leading to the loss of catalytic activity. The illuminated MnO$_x$ films maintain high stability during OER at 10 mA/cm$^2$ for about 18 hours with an overpotential of about 350 mV. Based on compositional and structural analysis, the illuminated samples possess a higher amount of hausmannite and Mn$^{3+}$ ions. Due to structural differences, Mn$^{3+}$ ions in the illuminated samples are stabilized against disproportionation during OER. On the other hand, Mn$^{3+}$ ions in the dark samples become oxidized, and the films transform to birnessite MnO$_2$ during OER. The overpotential exhibited by the MnO$_x$ films grown under illumination is
good when compared to other earth-abundant metal oxides. The stability could be further improved by optimizing the combination of illumination and applied potential during growth.
Chapter 4: Conclusions

Learning the mechanism of photogenerated charge transfer is critical in understanding the morphological and compositional changes of inorganic materials during photoelectrodeposition. This thesis has investigated the transformation of cuprous oxide and manganese oxide systems when the films are synthesized under illumination.

Specifically, the light-induced transformation of faceted cuprous oxide (Cu$_2$O) microcrystals was studied, which produces hollow particles consisting of an inner region of cuprous oxide and an outer shell of copper metal. When cuprous oxide microcrystals with mixed {100} and {111} facets are held at a negative bias (−1.0 V vs. Ag/AgCl) in a solution of sodium hydroxide (NaOH), light mediates the growth of copper metal selectively on the {100} facets while the crystal interior is etched at {111} facets. MnO$_x$ films were photoelectrochemically synthesized as a catalyst for the oxygen evolution reaction (OER) with remarkable performance. MnO$_x$ films synthesized by multipotential deposition under illumination from a LED exhibit a significantly higher current density for OER, better stability, and a lower onset potential compared to films synthesized by the same method in the dark. Since Cu$_2$O microcrystals exhibit facet-selective properties, the spatial charge distribution can be largely affected by illumination. Thus, Cu$_2$O particles with well-developed facets undergo a surface-selective transformation. The MnO$_x$ films studied in this work are more disordered. So, while they did not show any facet-selective behavior, the effect of light was shown in the morphological and structural changes. Both systems undergo compositional changes under illumination that can enhance their electrochemical properties.

We successfully used light to conduct shape transformation of cuprous oxide and increase the catalytic activity of MnO$_x$ films. In summary, light-directed growth has been demonstrated a powerful method to control the nanoscale morphology of semiconductors. The extension of light-
directed growth to a broader range of semiconductors will require a better understanding of how different materials respond to light during growth and could be a future research focus. Other semiconductors that are responsive to light or have facet-dependent properties are also worth to be studied, such as ZnO, TiO$_2$, Fe$_2$O$_3$, Al$_2$O$_3$ and BiVO$_4$. The application of single-molecule fluorescence to visualize charge-transfer reactions during light-directed growth may enhance our understanding of these processes.$^1$
Supporting Information

**Table S1.** Electrodeposition parameters used to synthesize different samples of Cu$_2$O microcrystals

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<thead>
<tr>
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**Table S2.** Parameters used for the photoinduced transformation of Cu$_2$O microcrystals
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Figure S1. Cyclic voltammetry (CV) scans of the bare Au substrate used as the working electrode to deposit Cu₂O microcrystals. a) CV scans in a solution of 3 M NaCl before (black trace) and after (red trace) purging the solution with Ar. b) CV scans in a solution of 5 M NaOH before (black trace) and after (red trace) purging the solution with Ar. The peak at –0.24 V vs. Ag/AgCl in the NaCl solution (pH = 8.2) corresponds to the reduction of surface adsorbed OH⁻ to O₂.³³ The peak shifts with pH to –0.71 V vs. Ag/AgCl in the NaOH solution (pH = 14.7).
Figure S2. CV scans of Cu$_2$O microcrystals on a Au substrate in a solution of 5 M NaOH. a) CV scans in the dark. b) CV scans under illumination during the scan with an ELH lamp at an irradiance of 453.0 mW/cm$^2$. The cathodic peak at $-0.41$ V vs. Ag/AgCl corresponds to the reduction of copper oxide to copper metal. The cathodic peak at $-0.69$ V vs. Ag/AgCl may be either due to the reduction of hydroxide ions on the exposed regions of the Au substrate as seen in Figure S1 or the reduction of copper hydroxide on the surface of the Cu$_2$O microcrystals to copper metal. The anodic waves ranging from $-0.37$ to $-0.10$ V vs. Ag/AgCl correspond to the oxidation of Cu to various copper hydroxides and oxides including Cu(OH)$_2$, Cu(OH)$_4^{2-}$, CuO, and Cu$_2$O. Peaks were assigned based on a previous report.$^{76}$
**Figure S3.** CV scan of the Cu$_2$O microcrystals in a 5 M NaOH solution after their transformation to Cu nanoshells by holding the electrode at −1.0 V vs. Ag/AgCl under illumination with an ELH lamp at an irradiance of 501.0 mW/cm$^2$. The CV scans were performed in the dark.
Figure S4. Current density vs. time for the transformation of the Cu$_2$O microcrystals in 5 M NaOH at –1.0 V vs. Ag/AgCl in the dark (black trace) and under illumination (red trace) with an ELH lamp at an irradiance of 492.2 mW/cm$^2$. As indicated by the arrow in the plot, the cathodic current density increased after the lamp was turned on for the red trace.
Figure S5. a) Scanning electron microscopy (SEM) image of Cu₂O microcrystals on a Au substrate after the electrode was held at a potential of E = −1.55 V vs. Ag/AgCl in 5 M NaOH in the dark for 5 minutes. b) SEM image of Cu₂O microcrystals on a Au substrate after 5 minutes of a constant current (−0.88 mA/cm²) in 5 M NaOH in the dark. These conditions were used to test whether increasing the current density in the dark would lead to the hollow nanoshell morphology observed under illumination. However, the hollow nanoshell morphology was not observed in either case.
Figure S6. Absorption spectrum of Cu$_2$O microcrystals electrodeposited on a Au substrate. A spectrum of a bare Au substrate was subtracted from this spectrum. The absorbance increases at wavelengths below 600 nm, which agrees with the band gap energy of Cu$_2$O of 2.1 eV.
Figure S7. SEM images of Cu$_2$O microcrystals on Au substrates while the electrode was held at a potential of $E = -1.0$ V vs. Ag/AgCl in 5 M NaOH for 5 min under different intensities of illumination with an ELH lamp. The irradiances at the electrodes were: a) 2.9 mW/cm$^2$, b) 9.8 mW/cm$^2$, c) 50.2 mW/cm$^2$, and d) 104.5 mW/cm$^2$, e) 215.0 mW/cm$^2$, and f) 396.7 mW/cm$^2$. The hollow shell morphology was not observed at low light intensities. The small spherical particles in between the Cu$_2$O particles seen in panels a), b), and c) are the polycrystalline Au substrate as confirmed by measuring energy dispersive x-ray spectra in different regions of the sample.
Figure S8. SEM images of Cu$_2$O microcrystals on Au substrates while the electrode was held at a potential of $E = -1.0$ V vs. Ag/AgCl in 5 M NaOH for 5 min under illumination using a) a 455-nm LED with an irradiance of 79.4 mW/cm$^2$ and b) a 625-nm LED with an irradiance of 71.1 mW/cm$^2$. The hollow shell morphology was not observed for microcrystals irradiated with 625-nm light, as this wavelength is not significantly absorbed by Cu$_2$O (see Figure S6).
**Figure S9.** X-ray diffraction patterns (XRD) of the initial Cu$_2$O microcrystals electrodeposited on a Au substrate (blue trace) and Cu$_2$O microcrystals after 5 min of illumination with an ELH lamp while the electrode was held at a constant potential of $E = -1.0$ V vs. Ag/AgCl in 5 M NaOH (red trace). This figure shows a wider 2θ scan range than **Figure 2** in the main manuscript. The lines at the bottom are the reflections for standard XRD powder patterns of Cu$_2$O (purple lines, PDF file #04-007-9767), Cu (orange lines, PDF file #00-004-0836), and Au (green lines, PDF file #00-004-0784). The peaks at 29.6°, 36.4°, and 61.4° in the pattern for the initial microcrystals (blue trace) correspond to the (110), (111), and (220) lattice planes of Cu$_2$O. These peaks decrease in intensity after the transformation. The new peak at 43.3° after the transformation (red trace) corresponds to the (111) lattice planes of Cu.
Figure S10. X-ray photoelectron spectra showing the binding energy region for Cu $2p_{3/2}$ electrons. In panel a) the top trace shows the initial Cu$_2$O microcrystals electrodeposited on a Au substrate, the middle trace shows Cu$_2$O microcrystals after 5 min of immersion in 5 M NaOH in the dark without a bias, and the bottom trace shows Cu$_2$O microcrystals after 5 min of being held at $E = -1.0$ V vs. Ag/AgCl in 5 M NaOH in the dark. In panel b) the top trace shows the initial Cu$_2$O microcrystals electrodeposited on a Au substrate (same spectrum as in panel a), the middle trace shows Cu$_2$O microcrystals after 5 mins of immersion in 5 M NaOH under illumination with an ELH lamp without a bias, and the bottom trace shows Cu$_2$O microcrystals after 5 min of illumination with an ELH lamp while the electrode was held at $E = -1.0$ V vs. Ag/AgCl in 5 M NaOH. The red and blue lines show deconvolution of the peaks. Based on previous assignments, the maxima of the blue peaks range from 933.4 to 933.9 eV and correspond to Cu$^{2+}$. The maxima of the red peaks range from 931.9 to 932.4 eV and correspond to a combination of Cu$^+$ and Cu$^0$. The contribution from Cu$^{2+}$ increased after exposure to the NaOH in the dark (both with and without an applied bias).
Figure S11. Auger spectra showing the region for Cu LMM electrons. In panel a) the top trace shows the initial Cu$_2$O microcrystals electrodeposited on a Au substrate, the middle trace shows Cu$_2$O microcrystals after 5 min of immersion in 5 M NaOH in the dark without a bias, and the bottom trace shows Cu$_2$O microcrystals after 5 min of being held at $E = -1.0$ V vs. Ag/AgCl in 5 M NaOH in the dark. In panel b) the top trace shows the initial Cu$_2$O microcrystals electrodeposited on a Au substrate (same spectrum as in panel a), the middle trace shows Cu$_2$O microcrystals after 5 mins of immersion in 5 M NaOH under illumination with an ELH lamp without a bias, and the bottom trace shows Cu$_2$O microcrystals after 5 min of illumination with an ELH lamp while the electrode was held at $E = -1.0$ V vs. Ag/AgCl in 5 M NaOH. The light-green, blue, blue-green, red, and purple lines show deconvolution of the peaks. Based on previous assignments,$^{73,74}$ the maxima of the blue peaks were fixed at 916.8 eV and correspond to Cu$^+$. The maxima of the blue-green peaks were fixed at 917.8 eV and correspond to Cu$^{2+}$. The maxima of the red peaks were fixed at 918.5 eV and correspond to Cu$^0$. The light-green peaks with maxima ranging from 912.6 eV to 913.8 eV and the purple peaks with maxima ranging from 920.9 eV to 921.6 eV have been observed previously in the Auger spectra for Cu$_2$O, but have not been assigned.
to a particular oxidation state of Cu.\textsuperscript{73} For all conditions, the relative amount of surface Cu\textsuperscript{0} increased relative to the initial Cu\textsubscript{2}O microcrystals.

\textbf{Figure S12.} X-ray photoelectron spectra showing the binding energy region for O 1s electrons. The top trace shows the initial Cu\textsubscript{2}O microcrystals electrodeposited on a Au substrate, the middle trace shows the Cu\textsubscript{2}O microcrystals after 5 min of being held at E = −1.0 V vs. Ag/AgCl in 5 M
NaOH in the dark, and the bottom trace shows the Cu$_2$O microcrystals after 5 min of illumination with an ELH lamp while the electrode was held at $E = -1.0$ V vs. Ag/AgCl in 5 M NaOH. The blue-green, blue, and red lines show deconvolution of the peaks. Based on previous assignments,$^{59,75}$ the maxima of the blue-green peaks range from 532.7 to 532.8 eV and correspond to surface-adsorbed oxygen species. The maxima of the blue peaks range from 531.7 to 532.0 eV and correspond to surface hydroxyl groups. The maxima of the red peaks range from 530.2 to 530.5 eV and correspond to lattice oxygen in Cu$_2$O. These spectra show that the relative contributions from surface-adsorbed oxygen species decreased after the application of a bias in both the light and dark.

**Figure S13.** a) CV scan of an aqueous solution containing 0.4 mM Cu(NO$_3$)$_2$ and 5 M NaOH (blue trace) and a CV scan of the 5 M NaOH solution used for the photoinduced transformation of the Cu$_2$O microcrystals (red trace). The working electrode was Au in both cases. The small cathodic wave near $-0.4$ V vs. Ag/AgCl for the red trace indicates the presence of Cu$^{2+}$ in solution due to oxidative etching of the Cu$_2$O microcrystals during their transformation. b) Absorption spectra of a fresh solution of 5 M NaOH (black trace), the solution of 5 M NaOH used for the photoinduced transformation of the Cu$_2$O microcrystals (red trace), and a solution of Cu(NO$_3$)$_2$ (blue trace).
There is a small increase in the absorbance of the NaOH solution after the photoinduced transformation, but the peak belonging to Cu$^{2+}$ is not evident.

**Figure S14.** SEM image of Cu nanoshells grown under illumination using an ELH lamp while the electrode was held at a potential of $E = -1.0$ V vs. Ag/AgCl in a solution that contained 14 M NaOH, 6.2 mM Cu(NO$_3$)$_2$, and 0.1 M ethylenediamine. The images in a) and b) were taken from the same sample at different magnifications.
Figure S15. SEM images of Cu₂O microcrystals on Au substrates after a) 1 min, b) 2 min, and c) 5 min, respectively of illumination with an ELH lamp while the electrode was held at a potential of $E = -1.0 \text{ V vs. Ag/AgCl}$ using a lower NaOH concentration of 2.5 M as the electrolyte. Etching of the \{111\} facets was slower at this lower NaOH concentration leading to thicker Cu shells and Cu₂O remaining in the interior of the particles.
Figure S16. a) SEM image of Cu$_2$O microcrystals electrodeposited on Au after 5 min of illumination with an ELH lamp while the electrode was held at the E = −1.0 V vs. Ag/AgCl in 1 M NaOH. b) X-ray diffraction pattern of a different sample grown under identical conditions. The lines at the bottom are the reflections for standard XRD powder patterns of Cu$_2$O (purple lines, PDF file #04-007-9767), Cu (orange line, PDF file #00-004-0836), and Au (green lines, PDF file #00-004-0784). While the hollow shell morphology was not observed at the lower NaOH concentration (i.e. 1 M instead of 5 M), the XRD pattern appeared similar to the pattern shown in Figure 2 (red trace) of the main manuscript formed under otherwise identical conditions. In both cases peaks corresponding to Cu$_2$O are absent, and a peak at 43° corresponding to Cu is present.
Figure S17. SEM images of Cu$_2$O microcrystals electrodeposited on Au after 5 min of illumination with an ELH lamp while the electrode was held at $E = -1.0$ V vs. Ag/AgCl in a solution of 5 M NaOH that was purged with Ar. The images in a) and b) were taken from the same sample at different magnifications. The exclusion of O$_2$ in the NaOH solution reduces the uniformity of the resulting Cu nanoshells.
**Figure S18.** SEM images of Cu$_2$O microcrystals after immersion in 5 M NaOH under illumination without a bias. a) The NaOH solution was purged with Ar. b) The NaOH solution was purged with O$_2$. Preferential etching of the \{100\} facets was observed in both cases.
Figure S19. SEM images of a) electrodeposited Cu$_2$O microcrystals and b) colloidal Cu$_2$O microcrystals after 20 min of immersion in 5 M NaOH in the dark without an applied bias. Preferential etching of the {100} facets was observed in both cases.
**Figure S20.** SEM images of Cu$_2$O microcrystals before and after immersion in 5 M NaOH under illumination without a bias. a) Initial cuboctahedral Cu$_2$O microcrystals prepared by electrodeposition. b) Initial cuboctahedral Cu$_2$O microcrystals prepared by colloidal synthesis. c) Electrodeposited Cu$_2$O microcrystals after 3 mins of immersion in 5 M NaOH under illumination with an ELH lamp without a bias. d) Colloidal Cu$_2$O microcrystals after 10 mins of immersion in 5 M NaOH under illumination with an ELH lamp without a bias. Preferential etching of the \{100\} facets was observed in both cases.
Figure S21. Current vs. time traces for Cu$_2$O microcrystals while the illumination from an ELH lamp was switched on and off at applied potentials of a) $E = -0.55$ V, b) $E = -0.60$ V and c) $E = -0.65$ V, and d) $E = -0.70$ V vs. Ag/AgCl in 5M NaOH. The dashed red and blue lines show examples of when the lamp was turned on and off, respectively. Illumination makes the current less negative at $-0.55$ V and $-0.60$ V vs. Ag/AgCl. However, illumination makes the current more negative at $-0.65$ V and $-0.70$ V vs. Ag/AgCl.
Figure S22. Mott-Schottky plots (1/C² vs. applied potential where C is the space-charge capacitance) at different frequencies determined from electrochemical impedance spectroscopy. The flat-band potentials were calculated from the x-intercepts of linear fits to the capacitance data obtained at each frequency and are provided in Table S3 below.

Table S3. Flat-band potentials measured at different frequencies based on the linear fits shown in Figure S22.
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References

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