

CHAPTER 1

Introduction

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If there is a single most important factor that enabled the development of ultrathin oxide layers for advancing photo-, electro-, and thermal catalytic systems for energy, it is the birth of and explosive growth in the field of nanoscience starting in the 1990s. This opened up the capability of synthesizing and manipulating inorganic matter on a length scale of nanometers, which is the scale on which charge transfer, ion transport, and chemical transformations need to be controlled for designing and optimizing catalytic systems for energy conversion applications. The concurrent emergence of an array of new characterization tools, from advanced electron and tunneling microscopies to X-ray spectroscopy and super-resolution optical microscopy, has allowed researchers to characterize nanosized structures at atomic resolution and accelerate the understanding of the fundamental physics and chemistry that underlie nanoscience and nanotechnologies. Breakthroughs over the past two decades in solar cells, batteries, catalysis for the manufacture of chemicals, and sensors, to name just a few, have led to dramatic performance improvements and the implementation of new technological concepts that could not have been contemplated before the advent of the nanoscience revolution.

The special interest in nanoscale components made of metal oxide materials for technological applications should not come as a surprise given the role and impact of thin metal oxide layers that have been part of civilization's

infrastructure and technological advances for millennia. For example, metals such as iron and copper that are ubiquitous in bridges, vehicles, ships, tools, electronics and more are in many cases irreplaceable in their role(s), yet their robustness and durability under use in harsh environmental conditions are often reliant on the presence of thin metal oxide layers that protect the metal from corrosion. A house roof made of copper is a prime example of the enormous practical importance of metal oxide layers in everyday life. Famously, the copper sheets of the Statue of Liberty in New York harbor are only 2.5 mm thick, yet since 1886 have only lost 0.1 mm thickness thanks to protection by copper patina, as illustrated in Figure 1.1a,b.¹ Many metals would not be technologically viable under working conditions were it not for the spontaneous formation of oxide protection layers driven by the high stability of the metal–oxygen chemical bond. In modern societies, nanosized metal oxides find their main importance in the manufacture of everyday chemicals where heterogeneous

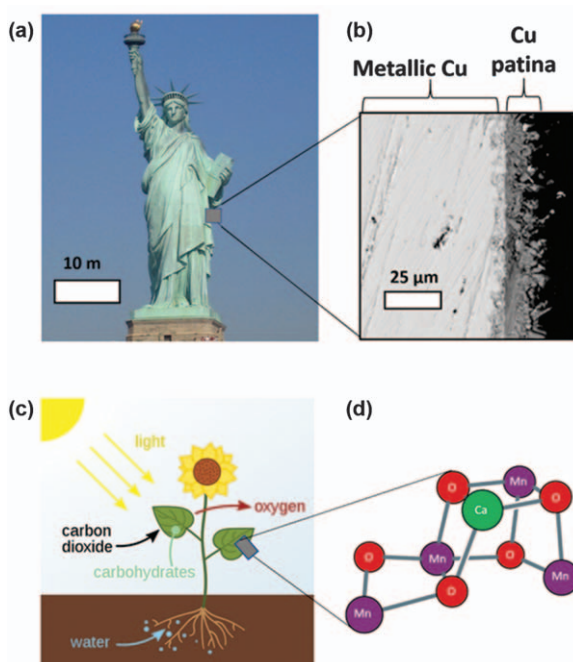


Figure 1.1 (a) Statue of Liberty, New York harbor. Reproduced from https://commons.wikimedia.org/wiki/Statue_of_Liberty#/media/File:Statue-de-la-liberte-new-york.jpg, under the terms of the CC BY-SA 2.0 license, <https://creativecommons.org/licenses/by-sa/2.0/deed.en>. (b) Cu patina preventing further oxidation. Reproduced from ref. 1 with permission from Springer Nature, Copyright 2012. (c) Plant photosynthesis. Reproduced from https://commons.wikimedia.org/wiki/File:Photosynthesis_en.svg, under the terms of the CC BY-SA 4.0 license, <https://creativecommons.org/licenses/by-sa/4.0/deed.en>. (d) Mn_4CaO_5 catalyst for water oxidation in photosystem II. Reproduced from ref. 2 with permission from Springer Nature, Copyright 2018.

processes play a dominant role, whether as robust catalysts or as supports. Zeolites, which are microporous aluminosilicates featuring oxide nanowalls, play a huge role as acid catalysts in the preparation of transportation fuel from petroleum resources, or as supports for nanoparticle or organometallic catalysts for the manufacture of specialty chemicals. The role of metal oxide nanolayers in renewable energy technologies is currently nowhere more prominent than in advanced solar cells, and the multitude of physical properties of metal oxides and their diverse chemistry are what drives their expanding use in emerging technologies. Beyond imparting chemical stability, many classes of metal oxide materials possess tunable electronic and/or optical properties that can be manipulated by varying the identity of the metal(s), the metal-to-oxygen stoichiometry, structural phases and morphologies, and dopant species. As a prime example, the electronic conductivity of a number of metal oxides can be varied from metal-like to insulator-like through the selection and control of the concentrations of various dopant elements. Similar control knobs can be used to tailor the optical properties of oxides to vary from completely transparent to completely opaque across the visible spectrum, while the ability to tune the structural characteristics of oxides, such as their microporosity, can give them built-in molecular sieving capabilities that can be leveraged to enable selective transport of molecules and ions while blocking others to control reactant and intermediate concentrations at active sites in catalytic, electrocatalytic, and photocatalytic systems.

Humans are not the only species on Earth to have taken advantage of the unique and tunable properties of metal oxides, as evidenced by their use in Nature. The most prominent nanoscale metal oxide component in the living world is the Mn_4CaO_5 cluster catalyst for oxygen evolution from water, whose function in photosystem II is essential for life of Earth (Figure 1.1c,d).² While biological function relies overwhelmingly on the assembly and control of soft matter components, Nature's design features at the nanoscale for accomplishing unparalleled selectivity and specificity of highly complex processes of charge, ion, and molecule transport and of chemical transformations are a great source of principles and inspiration for guiding new or improved engineered function. Ultrathin oxide layers have emerged as particularly useful components for engineering systems and devices that strive to implement this level of control and efficiency using the methods and tools of nanoscience.

Thanks to advances in nanofabrication and characterization over the past 20–30 years, ultrathin oxide layers with tunable properties have enabled new approaches and methods for enhancing the activity and selectivity of catalytic materials to be developed, dramatically improving the durability of semiconductor light absorbers, photocatalysts, and heterogeneous thermal catalysts and facilitating integration of functional components at the nanoscale. As a result, the use of ultrathin layers has been rapidly expanding in the areas of solar, catalytic, and (photo)electrocatalytic energy conversion technologies. However, much of the emerging knowledge in this area is scattered across the literature of disparate fields of specialization, making it difficult to gain familiarity and take advantage of these developments for

new applications. This motivated the overall purpose of this book, which is to describe in a single place the fundamentals and emerging applications that may accelerate the use and benefits of ultrathin oxide layer materials.

Following this introductory chapter, the book covers two main areas of focus and ends with a forward-looking closing chapter. In the first focus area, which contains Chapters 2–5, recent breakthroughs in improving the stability and efficiency of semiconductor light absorbers in photovoltaic (PV) cells for electricity generation and photoelectrochemical (PEC) cells for solar fuel generation are described. In *Chapter 2*, Davis, Garland, and Strandwitz lay out recent advances in synthesis techniques for metal oxide nanolayers for PV and PEC devices, and introduce the basic physical and chemical processes by which these coatings enhance the performance of the light absorber. These include electronic passivation of semiconductor surfaces for enhancing the productive use of separated charges, chemical protection that improves durability, and the introduction of selective electrical contacts. Although the main focus of this chapter is on crystalline Si, the techniques are equally effective for III–V semiconductors where they have led to dramatic stability increases, even allowing the revival of materials with highly favorable electronic properties that previously were found unsuitable for applications owing to a lack of chemical stability. In *Chapter 3*, Palmstrom and Reese explain in depth the full range of diverse functional roles of ultrathin oxide layers for PV technologies, often with more than one role being played by a single metal oxide layer. Examples focus on thin-film PV technologies and range from next-generation materials to commercially established PV devices. Among the ultrathin coatings, blocking layers permit directional control of charge flow by functioning as a tunneling barrier, or serving as part of an energy cascade. Next, the mechanisms by which oxide blocking layers impose directionality on visible light-driven electron transfer and how they can be leveraged to optimize performance are investigated by ultrafast THz and transient optical absorption spectroscopy in *Chapter 4* by Swierk. For the systems discussed in this chapter, the light harvesting is accomplished by dye molecules attached to the oxide layer. Through the use of advanced electrochemical and spectroscopic methods, Swierk describes how ultrathin oxide blocking layers incorporated into dye-sensitized solar cells or photoelectrochemical cells for water splitting can lead to substantial improvements in the performance of these devices. In *Chapter 5*, Wang and Cronin discuss the recent burst of efforts in the exploration and understanding of the remarkable effects of TiO₂ nanolayers on the photoelectrochemical performance of III–V semiconductor-based systems. Ultrathin titania layers inserted between semiconductor light absorber and metal catalyst films or nanoparticles, including those with plasmonic properties, are shown to enhance photoelectrocatalytic H₂O splitting or CO₂ reduction efficiency, dramatically in some cases, by selecting the appropriate structural phase and thickness of the titania layers, by the generation of defects, through the influence of built-in electric fields at the TiO₂/III–V semiconductor interface, or by plasmonic effects. Elucidation of the underlying

mechanisms using advanced microscopy, spatially resolved electron spectroscopy, and photoelectrochemical methods reveals the atomic and electronic structural factors responsible for the substantial improvements in stability, charge separation and transport efficiency, and lowering of overpotentials for reactant activation.

While Chapters 2–5 are primarily focused on the solid-state physics associated with the use of oxide layers deposited on semiconductor light absorbers, Chapters 6–11 place greater emphasis on applications in which ultrathin oxides are also intimately involved with electrocatalytic or catalytic processes. As a bridge between these two areas of emphasis, the topic of *Chapter 6* is the study of oxide-based co-catalyst layers that are deposited directly on photoelectrodes where their function extends beyond those discussed in Chapters 2–5 to also directly participate in electrocatalytic reactions. Transient optical spectroscopy has recently revealed that the mechanistic roles of such ultrathin co-catalyst layers in many photoanode materials such as Fe_2O_3 , BiVO_4 , TiO_2 , and Si is highly complex. Motivated by the need to pin down the precise roles of co-catalyst layers and how they depend on the details of the photoanode/co-catalyst interfacial properties and experimental conditions, Qiu, Nellist, and Boettcher present results from recent studies using dual working electrode and potential-sensing electrochemical–atomic force microscopy techniques of several photoanode–co-catalyst assemblies.

Ultrathin oxide layers have similarly resulted in big leaps in the performance of heterogeneous catalysts and photocatalysts. Here, additional properties of oxide nanolayers beyond optimization of photoinduced charge transport and chemical protection discussed in the earlier chapters come into play, namely the ability to design microporous structures for controlling catalytic activity and/or selectivity by providing selective access of reactant species to active sites located at buried interfaces between the oxide overlayer and underlying catalyst. In the next five chapters, the relevant physicochemical phenomena and models for species transport through oxide layers are introduced, and synthetic methods and applications in heterogeneous thermal catalysis, electrocatalysis, photocatalysis, and ultrathin separation membranes for artificial photosynthesis are described. To provide guidance for designing oxide overlayers for electrocatalysts, *Chapter 7* by Esposito, Guilimondi, Vos, and Koper presents the principles of species transport through metal oxide nanolayers and reaction kinetics at the buried interface that govern the operation of electrocatalysts encapsulated by semipermeable oxide nanolayers, in addition to a brief overview of experimental methods for the quantitative performance assessment of oxide-encapsulated electrocatalysts. The design principles introduced in this chapter provide guidance for the design of nanoscale oxide overlayers to optimize catalytic activity and product selectivity. The practical importance of improved chemical stability and prolonged activity of heterogeneous catalysts imparted by ultrathin metal oxide coatings cannot be overstated in light of the dominant role of heterogeneous catalysis in the manufacture of

chemicals. In *Chapter 8*, Lu and Elam present a suite of strategies to encapsulate heterogeneous thermal catalysts with emphasis on atomic layer deposition (ALD), with the goals of inhibiting catalyst poisoning, coking, sintering, and other degradation mechanisms in industrially important chemical processes. Central to the discussion are specialized ALD reactor designs and deposition protocols for achieving uniform encapsulation of catalyst nanoparticles on high surface area supports, and methods for deposition on selected areas of the supported nanocatalyst sample that can allow spatial and compositional control of catalyst nanoparticles for enhancing product selectivity. Solution-based chemical processes for ultrathin metal oxide encapsulation of industrial electrocatalysts, with focus on oxygen reduction under acidic conditions, are the topic of *Chapter 9* by Xing. Focus is placed on recent developments in sol-gel and condensed layer deposition methods that afford extraordinary thickness control of oxide nanocoatings for high surface area supported electrocatalysts. The interactions between highly conformal coatings and noble metal catalysts result in a remarkable increase in the longevity of these electrodes and, in some cases, increases in their electrocatalytic activity towards oxygen reduction.

Recent advances in the development of systems comprised of composite materials for solar fuels production have been assisted by an additional unique property of certain ultrathin, pore-free oxide layers, namely the ability to transmit protons while blocking molecules as small as oxygen. Proton permeability of solid oxide barriers that are part of any solar fuel system involving water oxidation is essential because H^+ ions, which are generated upon oxidation of water at anodic sites, need to reach cathodic sites for reduction in order to close the photocatalytic cycle. In *Chapter 10*, Pan, Hisatomi, and Domen present ultrathin dense metal oxide overlayers that are coated on nanoparticle photocatalysts. Within these composite architectures, the oxide overlayers transmit protons but block oxygen transport, thereby preventing the undesirable O_2 reduction reaction from taking place at co-catalyst active sites buried beneath the overlayer. The rich materials chemistry of oxides affords tailored nanolayers of various metals or metal combinations, some in a hydrated state, which permits additional activity-enhancing properties for semiconductor nanoparticle photocatalysts. Specific examples highlighting the ability to control the hydrophilic character and redox selectivity of encapsulated photocatalysts are presented that demonstrate functionality that goes beyond passivation and prevention of photocorrosion. In order to develop ultrathin oxide layers that can serve as membranes separating incompatible redox catalysis environments such as H_2O oxidation and CO_2 reduction, independent optimization of charge transfer, proton transport, and chemical separation properties is required. This task may be achieved by embedding organic molecular wires, which offer precise fine tuning of the charge transport energetics in ultrathin oxide layers. This approach affords independent optimization of charge transfer from proton transport and chemical separation properties. In *Chapter 11* by Jo, Zhang, Katsoukis, and Frei, few nanometer thick silica

layers deposited by ALD are shown to provide high proton conductivity and complete blocking of oxygen and other small molecules, and allow encapsulation of electron- or hole-conducting molecular wires that can be energetically tuned for optimal energy level alignment with light absorbers and catalysts. These ultrathin separation membranes permit the integration of incompatible catalytic environments for the development of complete nanoscale photosynthetic systems, cascade catalysis systems, or nanoscale inorganic/microbial systems (biohybrids), with the short length scale minimizing the major efficiency-degrading processes that are inevitable at the macroscale.

The final *Chapter 12* by Esposito and Frei describes major challenges and opportunities for deepening our understanding of the fundamental physical and chemical processes that occur at the buried interfaces and exposed surfaces of ultrathin oxide layers. With significant continued progress in fundamental research activities that are well aligned with these key challenges and opportunities, we anticipate that the uses and functionalities of ultrathin oxides within modern clean energy technologies will only accelerate in the coming years.

References

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