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Edited by
Pedro H.C. Camargo and Emiliano Cortés

# Plasmonic Catalysis

From Fundamentals to Applications

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## From Fundamentals to Applications

*Edited by*

***Pedro H.C. Camargo***

***Emiliano Cortés***

WILEY-VCH

**Editors**

***Prof. Pedro H.C. Camargo***

University of Helsinki

Department of Chemistry

A.I. Virtasen aukio 1

PO Box 55

00014 Helsinki

Finland

***Prof. Emiliano Cortés***

University of Munich (LMU)

Faculty of Physics

Nanoinstitute Munich

Königinstr. 10

80539 Munich

Germany

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# Prologue

*Naomi J. Halas[1] and Peter Nordlander[2]*
*[1]Department of Chemistry, Laboratory for Nanophotonics, Department of Electrical and Computer Engineering, and Department of Physics and Astronomy, Rice University, Houston, Texas 77005, United States*
*[2]Laboratory for Nanophotonics, Department of Electrical and Computer Engineering, and Department of Physics and Astronomy, Rice University, Houston, Texas 77005, United States*

Humans have long been fascinated by the chemical reactions of nature: from plant growth to the putrefaction of waste, we have marveled, explored and hoped to mimic nature’s processes in the hopes of achieving similar chemical transformations. Many of the chemical mysteries that fascinated ancient humans were frequently reactions facilitated by enzymes, nature’s catalysts, which had been highly optimized, some for many millions of years, accelerating reaction rates with tremendous specificity. But the energy sources of nature’s chemical reactions were not initially obvious. So when first alchemists, then chemists, began to attempt chemical transformations, the only energy sources they could rely upon were those they could control: fire, for raising temperatures, and eventually, pressure, with the advent of strong materials in which to contain and confine chemical reactions.

Chemistry became a vast and mature science in the last two centuries, opening entire new fields ranging from organic chemistry, allowing us to synthesize the molecules of nature in our own ways, to physical chemistry, advancing our understanding of the phases of matter, the elements, and eventually, the atom and quantum mechanics. But the energy toolkit of the chemist – the way energy was applied to scale reaction barriers – remained largely unchanged. With the dawn of our understanding of electricity came electrochemistry. While electrical current could now be harnessed to drive chemical reactions, our understanding of electromagnetism had not progressed far enough at that point for us to understand how to use light to directly deliver energy into a chemical reaction. Einstein’s insight, followed by the advent of modern, controllable light sources, brought us new ways to deposit energy into chemical reactions. Still, the ultralow efficiencies that haunted the first chemists largely remained. The catalysts developed for conventional energy sources brought advances, but still proved to be so limited that the chemical industry became the single largest consumer of energy on the entire planet.

Our modern understanding of how to deliver light energy efficiently to chemical reactions, to lower reaction barriers and direct chemical outcomes, is still in its infancy. But advances made possible by the nanoscience revolution of the past twenty years, in particular in nanophotonics, brought us the concept of nanoscale, optical frequency “antennas,” capable of capturing light from the far field and localizing it in confined volumes whose dimensions are compatible with chemical processes. Ironically, it was Faraday, one of the fathers of electrochemistry, who also advanced the first nanoscale antennas, in the form of gold colloid that he synthesized. Noble metal nanoparticles, each with their characteristic plasmon resonances, form the foundation of localized light delivery that is the central theme of this book. Shape modification to control the photon energy that can be coupled into nanoparticles provides an important “tuning knob” to control localized energy delivery even further, in new ways.

Our modern knowledge of condensed matter physics opened the door to understanding the specific processes that illuminated noble metal nanoparticles could deliver to chemical reactions. The collective electronic, or plasmon, resonance, a coherent oscillation of its delocalized electrons, is responsible for an extremely strong coupling between incident light waves and the nanoparticles. The quanta of light energy deposited into a metal nanoparticle can be dissipated in several important, and ultimately useful, ways. The coherent oscillation can be damped by coupling to phonons, resulting in highly efficient photothermal heating at the nanoparticle surface and in its direct surroundings. The plasmon can also decay in two ways by emitting a photon: direct radiative decay, i.e., scattering, an efficient process particularly for large nanoparticles; and the radiative recombination of hot carriers, also known as plasmon-induced photoluminescence, an indirect and relatively rare process, but one that can provide important information regarding the actual electron temperature within the nanoparticle. But perhaps most importantly, plasmons can decay by the excitation of an energetic “hot” electron-hole pair within the nanoparticle. The nonequilibrium carriers excited by this process can transfer from the surface of the metal nanoparticle, to, or from, the molecular orbitals of an adsorbate molecule on the metal nanoparticle’s surface. The transfer of an electron to an otherwise unoccupied orbital of an adsorbate molecule, creating a transient negative ion state, can substantially lower the barrier to molecular dissociation. Hot carriers can also transfer their energy to adsorbed molecules through Auger-like shake-up processes, leaving the molecule in an excited state. Thus we see how optically excited “plasmonic” nanoparticles can, in relatively simple processes, photocatalyze a chemical reaction that would normally require high temperatures to achieve the same molecular rearrangement. What is required, however, is the energy of the plasmon excitation exceeds that of the energy of the unoccupied molecular orbital with respect to the Fermi energy of the metal. It is a substantial challenge for theoretical chemists to calculate these energy offsets with high accuracy: it is the key to using this process for many more plasmon-mediated chemical reactions, and a current critical challenge for this field. This effect is also further complicated by the electronic structure of the metal itself: for example, metals with prominent occupied d-bands, such as gold can produce both hot and warm electrons, and cold and warm holes, for a substantial range of excitation energies. The energy required for a straightforward charge transfer process to an adsorbate orbital may dictate a preference for certain noble metal nanoparticles over others.

While noble metal nanoparticle “antennas” possess several properties that can efficiently drive chemical reactions with light excitation, they also have a fundamental limitation: low chemical affinities for most adsorbate molecules of interest for chemical reactions. So judiciously incorporating more reactive materials, in the form of individual atomic reactive sites, multi-atomic reactive regions, or entire layers of new materials with greater chemical affinities, plasmon-induced chemistry can be substantially extended to more types of chemical reactions and processes. In these more complex, “antenna-reactor” constructs, one can also observe other important electronic processes: specifically, the desorption of adsorbates from surfaces due to the hot electrons excited by plasmon decay. Electronic desorption processes were discovered and studied decades ago on bulk metal surfaces, but with metal nanoparticles, where plasmons can readily be excited by direct illumination, these processes become almost universal. The plasmon-induced desorption of adsorbates from binding sites can eliminate the irreversible binding, known as “poisoning” of reactive sites, an extremely common problem for conventional thermocatalysts. This process can also be used to modify reactive chemical outcomes, removing reactive adsorbates abruptly before a reaction can proceed further offers a new way to control the product of a chemical reaction. Thermocatalysts have no similar ability for active chemical control.

This book embodies an entirely new, twenty-first century path forward for the control of chemical processes. The low reaction temperatures and record efficiencies that have been observed thus far in plasmonic photochemistry truly tantalize us. The incredible boost in the efficiencies of visible light sources, such as LEDs, have made photons extraordinarily inexpensive. Is this the new path forward for chemistry? Will this direction transition into a new, light-based chemical industry where low-temperature, low-pressure light-induced photocatalytic reactions ultimately make the massive chemical plants of the twentieth century obsolete? If that is the case, what does the next generation of chemists and chemical engineers need to learn about light-particle interactions to master this new type of light-based chemical reactivity? Will sunlight, a free source of photons energetic enough to drive these reactions, be used to directly drive these types of chemistries instead of using photovoltaics as intermediaries? Perhaps photosynthesis, the object of our millennia-old fascination, will finally be realistically copied – along with the low temperatures and high efficiencies characteristic of nature’s processes – with precisely designed and engineered nanoantennas and nanoreactors. We eagerly look forward to many exciting advances in this field, for years to come.

Houston, TX, USA
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*Naomi J. Halas*
*Peter Nordlander*

# Introduction

*Pedro H.C. Camargo*[1] *and Emiliano Cortés*[2]
[1]*Department of Chemistry, University of Helsinki, Helsinki, Finland*
[2]*Faculty of Physics, Nanoinstitute Munich, University of Munich (LMU), Munich, Germany*

Catalysis is central to move toward a more sustainable future and enable our society to transition to a circular economy. For this reason, the possibility of harvesting sunlight to drive, accelerate, and control chemical reactions via photocatalysis has fascinated scientists for years. The unique optical properties of metal nanoparticles in the visible and near-infrared ranges turn them into ideal candidates for sunlight-activated catalysts. In fact, is has been recently established that the excitation of the localized surface plasmon resonance (LSPR) in these systems can be employed to drive and accelerate a variety of chemical reactions. This has led to the rise of plasmonic catalysis as a new frontier in catalysis, photocatalysis, and photoelectrocatalysis.

Plasmonic catalysis is the acceleration of a chemical reaction due to a plasmon excitation. To understand this simple definition is necessary to incorporate concepts from various research fields such as heterogeneous catalysis, nano-optics, physical chemistry, and material science. This book emerged as a necessity for unifying concepts, ideas, techniques, and advances in the rapidly growing field of plasmonic catalysis. To the best of our knowledge, this is the first book dedicated to this emerging area of research, covering its most important concepts and recent developments. To do so, a big, diverse, and heterogeneous group of world leaders in the field prepared exciting contributions for this book. The book comprises 10 chapters encompassing topics such as theoretical considerations of using plasmons for catalysis, optical and catalytic properties in plasmonic nanoparticles and hybrid systems, their synthesis, the fundamentals and mechanisms by which plasmonic excitation leads to the acceleration of reaction rates, examples and discussion of plasmonic catalysis applied to important chemical transformations, plasmonic catalysts based on earth-abundant materials, plasmonic electrocatalysis, and plasmonic metal–semiconductor heterostructures. Here is a quick overview of the main aspects covered in each chapter.

The book starts by describing in **Chapter 1** the theoretical framework of plasmon excitation and decay in the context of plasmonic catalysis. Energy conversion from photons to molecules and transfer from the plasmonic catalyst to the environment are the fundamental processes that take place in a plasmon-catalyzed chemical reaction. The chapter provides a detailed theoretical analysis of plasmon excitation, decay mechanisms, energy transfer, and carrier injection across different interfaces, near-field and scattering enhancements, and photoheating. Toward the end of the chapter and in order to exemplify these theoretical concepts, the chapter overviews a series of applications and experiments where these phenomena can be spotted. As such, this chapter sets the ground to understand the physics behind the uses of plasmons for chemistry.

We move next to the characterization and properties of plasmonic catalytic systems in **Chapter 2**. From conventional heterogeneous catalysis methods to plasmonic techniques, this chapter tackles the integration of conventional methods as well as new methods able to unravel the optical, electronic, and chemical properties of these systems. Different approaches can be followed in order to study chemical reactions mediated by plasmons either at the ensemble level or at the nanoscale, as well as to disentangle the role of light, heat, and carriers in the underlying mechanism. This chapter groups techniques with different temporal, spatial, and chemical resolution in order to gain deeper insight of the behavior of plasmonic catalysts under light illumination.

It has been recognized that the optical properties arising from the LSPR excitation are strongly dependent on several physical and chemical parameters that define the plasmonic nanoparticles. These include size, shape, composition, and structure (solid or hollow interiors) of the nanoparticles. Because these properties are related to the performances in plasmonic catalysis, the synthesis of plasmonic nanoparticles where these parameters can be tightly controlled has gained increased attention. In fact, this is important not only to optimize performances, but also to unravel–structure performance relationships that may aid on the rational design of plasmonic catalysts with desired performances for a reaction of interest. In this context, **Chapter 3** discusses the fundamentals and important examples on the controlled synthesis of metal nanoparticles that are relevant for plasmonic catalysis. The chapter begins by focusing on several methods for the controllable synthesis of Ag, Au, Cu, and Al nanoparticles. The chapter pays particular attention on shape control, in which morphologies such as quasispheres, nanocubes, nanowires, among others, are described. Then, different assemblies having these nanoparticles are presented. These colloidal assemblies are important as they often outperform their individual counterparts due to the formation of electromagnetic hot spots, which can enhance plasmonic catalytic activities. The chapter then moves to bimetallic nanoparticles. This is attractive because nanoparticles having a plasmonic and a catalytic metal