The physics of plasmon-driven energy conversion

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INTRODUCTION

Nanostructures of metals[1] and degenerately doped semiconductors[2] host large numbers of free charge carriers in a nanoscale volume. At such high densities, Coulomb repulsion dominates,[3] as a result of which the free carrier gas exhibits density oscillations when perturbed by electromagnetic radiation resonant with the natural frequency of oscillation. This collective mode of excitation, known as a localized surface plasmon resonance (LSPR) or plasmon, constitutes a strong light–matter interaction. For decades, this resonant interaction has been used for confining and manipulating light on the nanoscale.[4] The intense electromagnetic fields achieved by extreme light confinement have been employed to amplify spectroscopic processes, such as linear absorption and surface-enhanced Raman scattering (SERS).[5,6]

In recent years, however, there has been growing appreciation that photonic energy confined in the form of an LSPR can be converted into other forms, including heat, chemical energy, and mechanical motion[7] when the plasmonic antenna is electronically coupled with a transduction element, e.g., a reactive molecule. Interest in these phenomena has surged hand-in-hand with the resurgence in the search for alternative forms of energy storage and generation that are clean and renewable. Plasmonic nanostructures—especially those comprised of Au, Ag, and Cu—have naturally found a central role in energy research due to their ability to strongly absorb and harvest solar radiation, an abundant source of clean energy. Some prime examples of plasmon-driven energy conversion include the use of Ag nanoparticles to enhance the light absorption of photovoltaic cells,[8] visible-light sensitization of solar cells and titania (TiO_2) photocatalysts by plasmonic nanoparticles,[9] and the generation of hot electrons in a plasmon-excited nanostructure followed by their transfer to a semiconductor or a charge collection device.[10,11] However, the most pivotal has been the discovery that the photoexcitation of a plasmonic nanostructure induces adsorbates on the nanostructure surface to undergo chemical reactions. Seminal examples of such plasmon-driven chemistry include bond scission,[12,13] but this domain has rapidly expanded to include multielectron redox reactions,[14] nanoparticle growth,[15,16] electrochemical transformations,[17,18] and thermodynamically uphill fuel synthesis reactions,[19] thereby providing a large repertoire for the conversion of light energy to chemical energy and solar-powered chemical manufacturing. Plasmon-driven chemistry is being leveraged to catalyze reactions that otherwise proceed at a low thermal rate and to induce excited-state reactions that otherwise are unfavorable in the dark.

These exciting advances pave the way for achieving the central aspiration of chemical physics: using plasmonic excitations for controllably depositing energy in a specific electronic or vibrational mode of a molecule so that a desired chemical step can be directed with scalpel-like precision. To achieve such control, which would naturally lead to high conversion efficiency and selectivity, we must first develop a comprehensive picture of the full cascade of processes starting from the point of photon absorption and encompassing multiple timescales, ranging from femtoseconds to seconds, and spatial scales, ranging from nanometers to micrometers. Many of the elementary processes remain shrouded in mystery. Uncovering them will require the creative application of state-of-the-art, time- and state-resolved spectroscopic probing complemented by multi-physics models that integrate electrodynamics, quantum mechanics, and molecular dynamics. Another challenge in this area is that plasmon-driven energy conversion is invariably accompanied by the thermal dissipation of the deposited energy due to the fast carrier relaxation.[20] The effect of photothermal heating can obscure[21,22] the role of photoexcited carriers and local electric fields and must therefore be carefully parsed out and controlled. Alongside these efforts, we must continue to discover new implementations of plasmon-driven energy conversion and chemistry and advance the atomically precise synthesis of hybrids of plasmonic nanostructures with other functional elements.[23] This will ensure that we continue to expand the paradigm and fill existing gaps in our physical intuition and models. In addition to being an important frontier in chemical physics, the investigation of plasmon-driven energy conversion presents a ripe opportunity for the chemical physics community to partner with researchers in materials science, photonics, chemical engineering, and condensed matter theory.

This special issue highlights recent theoretical and experimental efforts that are providing new physical insights or capabilities and ultimately paving the way for plasmon-driven renewable power generation and green manufacturing.

SUMMARY OF AREAS COVERED

To aid readers in exploring the issue, we have summarized the contributions by dividing them into four categories that also represent exciting thrusts in the area of plasmon-driven energy conversion:

The first category is the development of hybrid nanostructures that improve hot carrier generation and enable plasmon-induced photochemistry and optoelectronic devices over a wider spectral window. Manoukian et al.[24] report that Cu–Pd alloy films exhibit composition-tunable generation of hot carriers under near-infrared (NIR) illumination. Karaballi et al.[25] find that Cr_2N nanoparticles synthesized by a solid-state nitridation reaction support pronounced ultraviolet (UV)-region LSPRs that would be of use for photocatalytic biodegradation and water disinfection. Yalavarthi et al.[26] used Ni–Au nanopillars modified by a Pd co-catalyst for photo-enhancing the electrooxidation of formic acid. Comparing faceted polyhedral and spherical Pd nanoparticles, the authors find a drastic difference in activity, which is attributed to differences in electromagnetic field confinement and hot-carrier generation for the two shapes. Kim et al.[27] report that a MnO_2 co-catalyst influences plasmon-enhanced photocatalytic oxidation of ethane; in particular, the location of the MnO_2 nanoparticle influences the photocatalytic activity. Yoshiiri et al.[28] find that the photocatalytic activities of commercial TiO_2 are altered and enhanced by the loading of Ag nanoparticles. The Ag nanoparticles function as sensitizers in the visible region and as electron traps in the UV region.

The second category is the enhancement of electrochemical redox transformations on plasmon-excited nanoparticle-based electrodes. Qiu et al.[29] report the electrochemical oxidation of 4-(hydroxymethyl)benzoic acid on a Au nanoparticle-decorated electrode promoted by plasmonic excitation. Joshi and Wilson[30] report that electrochemical water reduction reaction in acetonitrile has a drastically boosted rate on a plasmon-excited electrode comprised of Au nanoparticles; the authors also find that solvent polarity plays an important role in plasmonic modulation of electrochemical activity. Ramasamy and Ha[31] report that the removal of organic surfactant ligands from the surfaces of gold nanorods by oxygen plasma treatment promotes electrical contact between the gold nanorods and an underlying electrode and activates the Au nanorods for plasmon-assisted electrochemistry.

In the third category, we have mechanistic studies of plasmon-assisted light-to-chemical energy conversion. Schürmann et al.[32] investigate plasmon-induced carbon–halogen bond cleavage in halogenated benzenes. The authors find similar reaction rates for different halogen substituents (F, Cl, and Br), which points to a two-step charge generation and transfer mechanism. Chen and Wang[33] investigate the plasmon-induced dimerization of aniline molecules tethered to the surfaces of plasmonic nanostructures via thiolates and ethynyl groups. The authors demonstrate that the conformational flexibility of the metal–adsorbate linkage is conducive to a fast coupling reaction. This shows that apart from plasmonic characteristics of the nanoparticles, metal–adsorbate interactions constitute an important factor governing the kinetics of plasmon-induced chemistry. Kim et al.[34] employ a Pt–Ag–TiO_2 antenna–reactor structure to study plasmon-assisted photoelectrochemical water splitting and find that hot electrons and holes generated by plasmonic excitation of the Ag nanoislands are responsible for enhancing both oxygen evolution and hydrogen evolution half-reactions.

The fourth category involves the nanophotonic modulation of plasmon-enhanced processes. Lee and Yu[35] employ a dielectric photonic crystal structure to strongly confine light to Ag nanoparticles and find dramatically boosted hot-carrier extraction efficiencies. Sun et al.[36] investigate the photoluminescence emission decay of single quantum dots located near plasmonic Au nanoparticles and find faster decay when the excitation wavelength is spectrally overlapped with the LSPR. The authors attribute this effect to the excitation-wavelength dependence of the plasmonic near-field enhancement. Imada et al.,[37] using scanning tunneling microscopy, find that the luminescence of a single molecule placed in a plasmonic nanocavity does not follow Kasha's rule. Such an anomaly is attributed to Purcell enhancement of emission from the vibrationally excited states in the first singlet and second singlet excited states. Ma et al.,[38] employing time-dependent density-functional theory, find that plasmon-induced transfer of charge carriers from a

Ag nanocluster to a TiO_2 slab is influenced by the orientation of incident light polarization with respect to the Ag–TiO_2 interface.

These contributions present state-of-the-art research that strengthens the foundation of plasmon-driven energy conversion and motivates new ideas in this exciting field.

CONCLUSIONS

Plasmon-driven energy conversion has drawn immense attention from laboratories around the world due to its promise to enable the conversion of electromagnetic radiation, particularly in the solar range, into desired forms of chemical energy. The excellent contributions in this special issue articles collectively constitute an advance in the fundamental understanding and control of energy conversion processes induced by plasmon excitation.

ACKNOWLEDGMENTS

We thank all the authors for contributing high-quality manuscripts and making this special issue a great success. We also appreciate the work of all the dedicated referees for their time and effort and the excellent editorial team and staff of the Journal of Chemical Physics, including associate editor Dr. Lasse Jensen, for curating the collection. P.K.J. acknowledges the support of the National Science Foundation through Grant No. CHE-2304910. W.D.W acknowledges the support from National Science Foundation under Grant CHE-1808539 and the University of Florida Research Foundation. Z.H.K. acknowledges the support of the National Research Foundation (NRF) of Korea funded by Korean government through Grant No. 2021R1A2C3012659.

AUTHOR DECLARATIONS

Conflict of Interest. The authors have no conflicts to disclose.

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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