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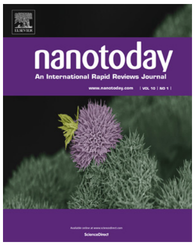

REVIEW

Plasmon resonances for solar energy harvesting: A mechanistic outlook

Jeremy G. Smith, Jacob A. Faucheaux, Prashant K. Jain*

Department of Chemistry and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

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Summary In the last 10 years, there has been extensive research by the nanoscience and catalysis communities on the potential use of plasmonic nanoparticles for both solar-to-electrical energy and solar-to-chemical fuel conversions. Herein, we present a critical review of the quickly expanding field of plasmon resonance-enhanced light energy harvesting. A wide range of enhancement phenomena have been observed: from enhanced light trapping in silicon solar cells loaded with plasmonic nanoparticles to plasmonically assisted hot carrier generation for photoelectrolysis, all of which are discussed in this review. We examine seminal findings, present various physical mechanisms potentially responsible for plasmonic enhancement, and also clear up some common fallacies about such enhancement phenomena. In addition, the review covers wide-open research opportunities for furthering deeper mechanistic understanding of plasmonic effects, engineering hybrid nanosystems optimized for efficient light-to-energy conversion, and translating promising effects to technologically relevant objectives. Plasmonically assisted solar energy conversion is a field rife with questions and opportunities for chemists and materials engineers alike.

Introduction

Light energy conversion technologies are central to realizing the promise of solar energy as a cleaner, abundant, renewable replacement for fossil fuels. Alongside solar-to-electrical energy conversion technologies (photovoltaics), solar-to-chemical fuel conversion (photocatalysis), has also received attention due to the need for addressing the intermittency of solar radiation. Chemical fuel, e.g., hydrogen, generated photocatalytically can be stored in the form of chemical bonds until the demand for electrical power arises. For both technologies, there is still an open need for improving the energy conversion efficiency in order for solar energy harvesting to become economically competitive with alternative sources such as wind energy and natural gas. Even modest gains of two-to-four-fold in efficiency are thought

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* Corresponding author. Tel.: +1 2173333417.
E-mail address: jain@illinois.edu (P.K. Jain).

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to be valuable. The scientific community is contributing to this objective through advances in materials and by devising better control of physical processes involved in light energy conversion.

Plasmon resonances represent a strong form of light-matter interaction, therefore it is natural to see them being utilized for the capture of light and its conversion into chemical or electrical energy. Early demonstrations of the utility of plasmons for solar energy harvesting were modeled after dye-sensitization experiments, where a plasmonic nanoparticle served as a visible light absorber to sensitize titania (TiO_2), which by itself lacks visible absorption [1,2]. Considering the short lifetime of excited charge carriers in a metal, unlike those in a dye, the sensitization effect ought to have been small at best. Nevertheless, measurable enhancements in visible-light photocurrent or photoactivity were seen in Au nanoparticle/TiO_2 heterostructures in a range of studies [1,2]. This resulted in an explosion of research on the use of plasmonic nanoparticles as visible-light sensitizers in hybrid metal/semiconducting oxide systems for enhancing photocatalytic and photovoltaic processes. More recently, there has been interest in harvesting plasmon resonances of noble metal nanoparticles themselves, without a semiconductor, for activating reactions, performing thermodynamically uphill reactions, and producing photocurrent or electromotive force. On another front, the use of roughened silver as a backside electrode in silicon photovoltaics catapulted the exploration of the use of plasmonic nanoparticles for light trapping and enhancing light absorption in silicon solar cells [3].

While there have been a wide range of demonstrations, questions remain as to which of these examples truly result from plasmonic excitation [4—7]. Placing a metal in close contact with a semiconductor, oxide, or reactive adsorbate opens up the possibility of metal-induced chemistry (doping of the semiconductor, generation and ionization of oxygen vacancies, formation of metal-induced gap states, and enhanced adsorption of molecules) or metal photochemistry of non-plasmonic origin (development of new charge transfer bands or generation of hot electrons via inter-band excitation of the metal). Additionally photothermal heating resulting from phonon—phonon decay of the plasmonic excitation is also expected to be responsible for some of the observed enhancement [8—10]. Such plasmonic photothermal heating can contribute to the observed photoactivity due to its ability to effectively concentrate heat energy within the reactive zone at the surface of the nanoparticle, often in interfacial contact with a semiconductor or adsorbed molecules [11,12]. This effect is expected to lead to an increased free carrier concentration in the semiconductor or enhanced surface reactivity, which would otherwise not be achievable with equilibrium heating. These latter processes can shroud truly plasmonic effects by giving rise to enhancement in photocurrent or photoactivity.

Review of the work in the field shows that the terms 'plasmonic catalysis' and 'plasmonic photocatalysis' are used loosely. In most cases, the terms simply mean enhanced visible-light activity resulting from the presence of plasmonic nanoparticles, whether or not an optoelectronic effect of the plasmon resonance is involved. It is however critical to make such distinctions; after all, understanding of the physical origin of enhanced activity is necessary for the rational design of materials optimized for visible-light harvesting. For the purpose of this review, we classify purely plasmonic effects in photocatalysis as those involving one of the following:

i) The generation of a hot carrier distribution in the metal from decay of the plasmon resonance, which can then be collected in the form of a photocurrent via transfer of the hot carriers to a semiconductor or surface adsorbates. Thus a plasmon oscillation is converted into an energetic charge separated state at a metal/semiconductor or metal/adsorbate interface, which can be thought of as an AC → DC rectification process (Fig. 1).
ii) The enhanced absorption of visible light within the semiconductor due to plasmonic near-fields, where an interplay of both effects may also be operative in some systems.

We review specific principles behind each of these phenomena, proof-of-concept demonstrations, and applications.

Physical principles of plasmon resonances

A description of the physics of plasmon resonances is necessary for understanding plasmon enhanced photocatalytic and photovoltaic effects. We first outline the steady-state optical properties resulting from the plasmon resonance (Fig. 2).

A plasmon resonance arises from the collective response of free carriers to the electromagnetic field of light. Waves of collective electron oscillations confined to the surface of the nanoparticle are produced in response to light excitation. A formal treatment of the phenomenon requires a full multipolar expansion; however, when the size of the particle is much smaller than the wavelength of light, the electron oscillation can be accurately described by the dipolar term [9,10,13]. Under the assumption that the field is constant across the nanoparticle (i.e., the quasi-static limit), the dipolar polarizability α is given by:

$$\alpha(\omega) = (1+\kappa)\varepsilon_0 V \frac{[\varepsilon(\omega) - \varepsilon_m]}{[\varepsilon(\omega) + \kappa\varepsilon_m]} \tag{1}$$

where V is the volume of the particle, $\varepsilon(\omega)$ is the complex dielectric function of the particle, ε_m is the medium dielectric constant, ε_0 is the permittivity of free space, and κ is a shape factor [13]. While κ has a value of 2 for spheres, surfaces with high curvature or sharp features can have much larger values for κ [14]. From Eq. (1), the polarizability is seen to be maximized at the frequency which matches the resonance condition:

$$Re(\varepsilon) = -\kappa\varepsilon_m \tag{2}$$

Thus, plasmonic nanoparticles are highly polarizable at their resonance frequency, as a result of which they exhibit both high absorption and scattering cross-sections at this frequency. Resonant frequencies for spherical nanoparticles of gold, silver, and copper are in the visible region, making them attractive for visible-light harvesting. The most attractive aspect is that the absorption cross-sections are orders of magnitude larger than those of typical visi-