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On the size dependence and spatial range for the plasmon effect in photovoltaic efficiency enhancement

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ABSTRACT

The plasmonic photovoltaic effect of mediation by surface plasmons in the harvesting of solar light energy in metallically surface-nanomodified photodiodes or solar cells is described in the microscopic manner. The experimentally observed increase in the efficiency of the photo-effect due to plasmons is explained by the competition between two opposing effects: that of the field concentration in plasmon oscillations and that of the admittance of indirect inter-band transitions in a semiconductor substrate induced by dipole coupling to plasmons at the nanoscale without translational invariance. The former effect favors larger metallic nanocomponents, whereas the latter effect prefers smaller nanocomponents. Both factors are quantitatively addressed within the quantum Fermi golden rule scheme, which allows for the size analysis of the plasmon effect and for its optimization. Experimental verification of the theoretical predictions is presented, including the demonstration of the proximity and size effect in double-layer photo-active substrate. The experiment reveals that the plasmon effect is still present if metallic nanoparticles are separated from substrate by the distance of order of 1 μm.

1. Introduction

Considerable interest in the so-called plasmonic photovoltaic (PV) effect has rapidly emerged within the past few years as a result of the experimental demonstration of a significant increase in the efficiency of the photo-effect when it is mediated by surface plasmons in metallic nanoparticles deposited on the photoactive surface of the photodiode or semiconductor solar cell [1–8]. The planar density of the metallic nano-coverage of the solar-cell surface that causes such an effect resides at a small scale, approximately 10^{8-10} 1/cm^2, thus allowing these techniques to be relatively inexpensive, even though the most suitable materials are nanoparticles of noble metals (Au or Ag). Moreover, the deposition of such sparse and irregular coatings is readily achievable using various simple and low-cost methods. These findings are of high prospective importance for the development of a new generation of solar cells with enhanced efficiency, especially for the improvement via the metallic nano-modification of the surfaces of thin-film cells or even organic cells, which may soon exist alongside silicon solar systems [7,9–14,4,15–17]. The feasibility of plasmonic improvement is strongly supported by the successful utilization of metallic nanocomponents to achieve an order-of-magnitude increase in the sensitivity of Raman spectrometers that employ nanometallic concentrators [18,19]. A similar improvement of STM microscopy by the utilization of surface plasmons was also proposed [20]. Moreover, another phenomenon that is worthy of consideration is the plasmon-assisted transport in metallic nanostructures, in which hybridized collective modes of surface plasmons and photons result in plasmon-polaritons [21,22] with properties that are highly attractive for applications in nanophotonics and microelectronics [21,23] with sub-diffraction arrangements of light-plasmon circuits. In such circuits, light signals can be converted into plasmon-polaritons with the same energy but with a wavelength of one or two orders of magnitude lower [22,24–26]. These direction of research meets also with rapidly developing field of metamaterials.

Plasmon excitations in metallic particles have been widely investigated since they were initially described by Mie [27] in 1908 within the framework of the classical electrodynamics theory. Originated by this paper the so-called Mie theory of surface plasmons in metallic nanoparticles was then developed based on Maxwell electrodynamics for the scattering and absorption of light by finite metallic systems using a phenomenologically modeled

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dielectric function of the metal [28]. Finite metallic systems were also subjected to a very thorough quantum analysis, including the application of the shell model and numerical quasi-exact studies in a framework known as the LDA (Local Density Approximation) and its time-dependent version (TDLDA) to metal clusters, although with relatively small numbers of electrons (up to approximately 300). The numerical LDA and TDLDA methods are strongly limited by computational constraints, which enhance sharply with an increasing number of electrons [29–33]. For larger clusters, the random phase approximation (RPA) approach proves to be effective [33,29,30]. As a rule, in this treatment, the so-called *jellium* model was utilized. This model enabled the neglect of ion dynamics because in metals, ions are much more inertial in comparison with electron fluids because of the much greater mass of ions compared with the electron mass [29,31,33]. In all these studies, attention was focused on the collective electron–liquid fluctuations called plasmons. In bulk metals, the plasmon energy is $\hbar\omega_p = \sqrt{\frac{e^2 n}{\varepsilon_0 m}} \simeq 10$ eV, which is larger than the Fermi energy. This fact indicates that plasmons are not excitations near the Fermi surface and that they weakly interact with Landau quasiparticles because of the large energy incommensurability. The origin of such high-energy plasmon excitation is Coulombic interactions between electrons and with the jellium, which was elegantly illustrated in the Pines-Bohm RPA theory of plasmons [34–36]. To repeat this approach in the case of finite metallic nanoparticle is a challenging issue because of the effectiveness of the related formulation without invoking extended numerical modeling.

In finite nanometer-scale metallic systems, a new opportunity for plasmon oscillations arises that was not possible in the bulk case. These new types of oscillations are called surface plasmons and correspond to a translational movement of the electron liquid with respect to the jellium, resulting in imbalanced charge fluctuations only at the surfaces of the finite nanoparticles. When the oscillations have an inhomogeneous compressional character along the system radius, they are referred to as volume plasmons in the finite system, in close analogy to plasmons in the bulk case.

Progress in the RPA formulation of plasmons in metallic nanospheres [37] has enabled descriptions of both volume and surface plasmons in spheres with radii ranging between approximately 5 nm and 100 nm for Au, Ag or Cu particles. In this size range, the quasiclassical RPA approach proves to be sufficiently accurate. For smaller clusters, more precise quantum models are needed, especially for radii of 1–2 nm, for which the pronounced surface effects are of primary importance. One such effect is the so-called spill-out of the electron liquid beyond the jellium rim. Spill-out occurs on the scale of the Thomas-Fermi length [34] and gradually loses its significance as the sphere radius increases. Similarly, the other major quantum phenomenon, the so-called Landau damping of plasmons as a result of coupling to high-energy particle–hole excitations [38] is of lesser significance as the radius increases. All these quantum phenomena, although of primary importance in small metallic clusters, are negligible for a radius of $a > 5$ nm. In smaller clusters, the spill-out effect is considered to be the cause of the red-shift of the dipole surface oscillation frequency (Mie frequency) as a result of the reduction in the electron density caused by the spill-out of the electron liquid. For ultra-small clusters, this property has been confirmed experimentally in K, Au and Ag [30]. In larger metallic nanospheres, a strong red-shift of the plasmon resonance is also observed but is apparently caused by another mechanism because for $a > 5$ nm, all surface-induced effects are negligible. The most important factor in larger metallic nanospheres has been identified to be the rapid enhancement of irradiation losses of plasmon oscillations in the radius range $a \in (5, 100)$ nm, whereas irradiation was rather insignificant in small metallic clusters. The damping of the plasmons causes the red-shift of the resonance, and this satisfactorily explains observations of the plasmonic frequency shift in large metallic nanospheres [39].

The identification of the major driving factor of plasmon attenuation in the radiation phenomena of large nanospheres clarified why such metallic particles are so effective in light energy transfer when they are deposited on the photo-active surfaces of solar cells [2,5,3,40–43]. Metallic nanospheres (or nanoparticles of other shapes [44]) can act as light converters because of their capability for high absorption and irradiation of energy, which originates from a mutual mirror relationship between the two directions of quantum transitions [45].

The incident photon energy that is absorbed in surface plasmon oscillations in metallic nanoparticles can then be transferred to the semiconductor substrate in a very efficient manner, highly exceeding the efficiency of the ordinary photo-effect. We identify the origin of this efficiency enhancement in two competing factors. The first is the local enhancement of the electric field of the surface plasmon oscillations in the nanosphere as a result of collecting the energy of many photons, which results in an increase in the plasmon oscillation amplitude. This effect is proportional to a^3 (a is the nanosphere radius) and reflects the fact that all electrons participate in the oscillations even though charge fluctuations occur only on the surface, which is not screened by the jellium. The second factor is the allowance of the indirect inter-band electron transitions in the semiconductor substrate, which are permitted in the system with broken translational symmetry. This occurs for dipole interactions of the surface plasmon oscillations in the local nanoscale system. The momentum conservation rule does not, in this case, select vertical transitions as the only possible transitions, as in the ordinary photo-effect in semiconductors. It is well-known that in the ordinary photo-effect, the momentum (or quasimomentum) of an electron undergoing a photon-induced transition between the valence and conduction bands does not change because of the extremely low momentum of photons that is required for consistency in energy with the forbidden gap in the semiconductor (because of the high velocity of light). This results in so-called vertical optical transitions, significantly reducing the efficiency of the photo-effect. In the case of interactions with plasmon dipoles in the local nanosphere vicinity, all indirect intraband excitations are permitted, which enhances the energetic efficiency of this channel. It is clear that this factor prefers smaller radii of the nanospheres, for which the breaking of the translation invariance is more important, whereas the effect weakens with increasing radius. This phenomenon has not yet been described in detail, and the microscopic quantum analysis of this effect together with other competing mechanisms is the primary objective of the present paper. The concept described above was originally formulated in a previous report [37] and was recently utilized in another publication [46]. This idea was also discussed in an earlier paper [12].

The present paper is organized as follows. In the next section, a short review of the model constructed previously to describe plasmon oscillations in large metallic nanospheres will be presented in the framework of the RPA approach [37], in analogy to the Pines–Bohm RPA theory of plasmons in a bulk metal [34,35]. The most important advantage of this approach [37,39] resides in its fully analytical formulation, which enables its straightforward and controllable application to a description of plasmon damping – the problem is beyond the capability of even large numerical simulations. In the next paragraph, we will present a thorough analysis of the so-called Lorentz friction for plasmons, which is essential to the radiative properties of surface plasmons in metallic nanoparticles, which determine their usefulness as energy transmitters. The next section of the paper will address the calculation of the inter-band electron transitions in a semiconductor substrate induced by plasmon oscillations. The fully analytical calculus will then allow for an analysis of the size dependence of the plasmon effect. A comparison with experimental observations will be