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REVIEW

Photogeneration of hot plasmonic electrons with metal nanocrystals: Quantum description and potential applications

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Summary The paper reviews physical concepts related to the collective dynamics of plasmon excitations in metal nanocrystals with a focus on the photogeneration of energetic carriers. Using quantum linear response theory, we analyze the wave function of a plasmon in nanostructures of different sizes. Energetic carriers are efficiently generated in small nanocrystals due to the non-conservation of momentum of electrons in a confined nanoscale system. On the other hand, large nanocrystals and nanostructures, when driven by light, produce a relatively small number of carriers with large excitation energies. Another important factor is the polarization of the exciting light. Most efficient generation and injection of high-energy carriers can be realized when the optically induced electric current is along the smallest dimension of a nanostructure and also normal to its walls and, for efficient injection, the current should be normal to the collecting barrier. Other important properties and limitations: (1) intra-band transitions are preferable for generation of energetic electrons and dominate the absorption for relatively long wavelengths (approximately >600 nm), (2) inter-band transitions efficiently generate energetic holes and (3) the carrier-generation and absorption spectra can be significantly different.

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The described physical properties of metal nanocrystals are essential for a variety of potential applications utilizing hot plasmonic electrons including optoelectronic signal processing, photodetection, photocatalysis and solar-energy harvesting.

Introduction

Whereas plasmonic properties of metal nanocrystals in terms of optical response have been so intensively investigated [1,2], the internal quantum states of photo-excited electrons inside plasmonic systems are much less known because electrons in nanocrystals oscillate in a nontrivial way, creating a collective excitation, a plasmon. Under optical illumination, the electrons simultaneously form a plasmon excitation and scatter by each other and from the walls and phonons. Experimentally, optically excited electrons in a metal can be registered via a photocurrent in a semiconductor—metal Schottky-barrier photodetector [3] (Fig. 1a) or using surface photochemistry [4,5] (Fig. 1b). It has been recognized recently that plasmonic nanostructures and nano-antennas can be used for hot carrier generation, photocatalysis, and injection. Metal nanocrystals have large absorption cross sections and can efficiently enhance and trap light [6—8]. Plasmonic enhancement of photocurrents and chemical processes can be induced via direct electron transfer from a metal or indirectly via a local amplification of electromagnetic field at functional elements of a device [9]. Several recent papers reported plasmon-enhanced photochemistry [9—22] (when plasmonic nanocrystals are in contact with a liquid) and plasmon-driven photocurrent responses in optoelectronic devices and nanostructures [23—33].

The photo-excited plasmonic electrons look very attractive for applications in photochemistry, solar cells, and photodetectors because metal nanocrystals can absorb light much more efficiently compared to inorganic semiconductors and organic dye molecules. Here are some *advantages* of metal nanocrystals:

- Large absorption cross sections.
- A large number of electrons with appropriate energy levels for electron transfer.
- Efficient tuning of the plasmonic resonances, absorption spectra and local enhancement using the size, shape, orientation and arrangement of nanocrystals [1,2,34—36].

Fig. 2 illustrates gold nanocrystals of various shapes and shows their absorption spectra. We can see that the position of plasmon resonance in absorption can be conveniently tuned with the shape of a nanocrystal. However, there are significant fundamental *limitations* for the use and extraction of plasmonic electrons in photocatalytic and solar conversion applications. These limitations include:

- Fast relaxation and relatively short mean free path of electrons in metals.
- Limited momentum transfer and often a large number of excited electrons with low energies.
- Reflection of electrons from the metal—semiconductor interface.

In this perspective article, we will address physical properties of plasmons in metal nanocrystals, focusing on the microscopic quantum structure of plasmonic oscillations and the non-equilibrium electron distributions in optically driven confined systems. The first sections will describe energy distributions and dynamics of excited electrons in the plasmon waves in the bulk and in confined nanocrystals. The following sections will address model physical systems and devices as well as provide a brief review of experimental work in the field.

Wave functions of plasmons in the bulk and in nanostructures

3D metal

Electrons in metals form a Fermi gas, which is characterized by the Fermi velocity (v_F), Fermi energy (E_F), and bulk plasmon frequency, ($\omega_{p,bulk}$). The non-interacting Fermi-gas model gives the following equations for the above parameters [38,39]

$$E_F = \frac{m_0 v_F^2}{2} = \frac{^2(3\pi^2 n_0)^{2/3}}{2m_0}, \omega_{p,bulk} = \sqrt{\frac{4\pi e^2 n_0}{\varepsilon_0 m_0}},$$

where n_0 is the 3D electron density, m_0 is the electron mass and ε_0 is the background dielectric constant coming from the atomic core electrons. For gold, these numbers are $E_F = 5.5$ eV, $v_F = 1.39 \times 10^8$ cm/s, and $\omega_{p,bulk} = 3.96$ eV [40]. The quantum description of electron gas is based on the density matrix, ρ_{mn} [38]. The elements of the density matrix give us populations of quantum single-particle states in an electron gas driven by optical excitation. The population of a single-particle quantum state in a Fermi gas is simply the corresponding matrix element

$$\rho_{nn}(t) = \left\langle \Psi(t) \right| \hat{c}_n^+ \hat{c}_n \left| \Psi(t) \right\rangle,$$

where $\left|\Psi(t)\right\rangle$ is a non-equilibrium wave function, which may be quite complicated in its exact form, and the operators $\hat{c}_n^+$ and $\hat{c}_n$ are the creation and annihilation operators, respectively. Then, the operator $\hat{c}_n^+ \hat{c}_n$ ''probes'' the many-body wavefunction $\left|\Psi(t)\right\rangle$ and reveals the presence of equilibrium or non-equilibrium electrons in the Fermi sea. In the absence of illumination, the system is in equilibrium and the population is, of course, given by the Fermi distribution function $\rho_{nn} = f_F(E)$, where E is the electron energy. When the electron plasma is illuminated, the non-diagonal elements, like $\rho_{n'n}(t) = \left\langle \Psi(t) \right| \hat{c}_n^+ \hat{c}_{n'} \left| \Psi(t) \right\rangle$, reveal the presence of an excitation, an electron—hole pair, in the Fermi gas (Figs. 3b and 4a). In the election—hole excitation, an electron is promoted from the state $|n\rangle$