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FERMI THEORY ON DIMENSION EFFECTS IN MULTIPLE EXCITON GENERATION

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Abstract*. The article has expanded the application of the statistical Fermi method to describe the MEG effect in particles of different dimensions.*

Keywords: *MEG, Quantum dots, nanorods, dimension effect.*

One of the remarkable nanoeffects occurring in semiconducting nanostructures is the multiple exciton generation [1-8], a generation of multiple excitons upon absorption of a single photon. This effect is potentially promising to increase the efficiency of solar energy conversion, particularly in photovoltaics and photocatalysis. The Shockley-Queisser (SQ) detailed balance analysis limits the power conversion efficiency to 33% for a single light-absorbing layer. However, the generation of multiple excitons upon the absorption of a single photon could potentially increase the power conversion efficiency to above 40% [3,7].

The first experimental observation of MEG was reported in different quantum dots, including PbSe [1], PbS [2,6], PbTe [10], Si [5], CdSe [4], InAs [11,10]. Many theoretical investigations [11-17] followed the experiments to explain the MEG effect. The quantum yields (QYs) measured initially by different research groups in identical materials were contradictory [8,18,19],

Usually, the QYs measurements [20] can be plotted versus $h\nu/E_g$, where $h\nu$ is the photon energy, E_g is the bandgap energy, and the efficiency of an electron-hole pair multiplication (η_{exc}) is then obtained from the following relationship between the QY and $h\nu/E_g$ for $h\nu > h\nu_{th}$.

$$QY = \left(\frac{h\nu}{E_g} - 1\right)\eta_{exc}. \qquad (1)$$

The dimension of nanostructures was chosen as one of the factors to boost further the MEG performance in PbS and PbSe nanomaterials. It was shown that at similar threshold photon energy, quantum rods exhibited 2-fold reduction of the energy of an electron-hole pair creation over QDs attributed to increased Coulombic coupling in the quasi-1D structure [21] at the optimal aspect ratio of 6-7 [21]. At those optimal aspect ratios, the average energy of an electron-hole pair creation in PbSe nanorods was ~ $2.5E_g$, while in PbSe QDs it was equal to $4.3E_g$. It was supposed that decreasing of the quantum efficiency at larger aspect ratios is likely due to the restored 1D translational momentum conservation which impose additional restrictions on the MEG process [21].

Dimension effect in Fermi statistical theory. The statistical theory was originally developed by E. Fermi [22] to describe the process of generation of multiple particles at nucleon-nucleon collisions. According to this approach [22,17], the statistical weight of n particle generation in the effective volume Ω, taking into account the conservation of energy is written as

$$S(n) = \frac{(f_e f_h)^{3n/4} m_o^{3n/2} \Omega^n}{2^{3n/2} \pi^{3n/2} \hbar^{3n}} \frac{T^{\frac{3n}{2}-1}}{\left(\frac{3n}{2}-1\right)!} \quad (2)$$

Here, $m_e = f_e m_0$; $m_h = f_h m_0$ are the effective masses of an electron and a hole, respectively; m_0 is the free electron mass; T is the kinetic energy of the generated particles. The latter can be defined through the energy of a photon $(h\nu)$ and the energy of an electron-hole pair creation (ε_{e-h}), according to the expression

$$T = h\nu - \frac{n}{2} \varepsilon_{e-h}. \quad (3)$$

In our earlier work [16,17], we supposed the ultimate case of kinetic energy when the energy of an electron-hole pair creation is equal to the bandgap energy (E_g). As a result, higher values of quantum yield of MEG were obtained [16,17] close to the earliest experimental results [15,19]. In general, from Eqn. 2, it can be seen that three quantities (the coefficient of effective masses, the effective volume and the kinetic energy of the particles) are varied depending upon the materials, size and shape of nanostuctures, in which multiplication takes place.

From Eqn. 2, the dimension effect on MEG observed in experiments [21] can be explained due to different values of effective volume of nanorods and kinetic energy of the generated particles. The effective volume of quantum dots is taken as $(\Omega = (3/4)\pi R^3)$, while for nanorods, it is defined as $\left(\Omega = \pi R^2 L_{eff}\right)$, in which L_{eff} is the effective length of the nanorod, which for PbSe can be taken at optimal aspect ratios of 6-7 [21]. As it was mentioned above [21], the energy of creation an electron-hole pair in nanorods is smaller than that in quantum dots, so in the nanorods, the kinetic energy of the particles will be greater. Thus, the higher efficiency of MEG in PbSe nanorods established from the experiments [21] over quantum dots at the same bandgap energy can be explained due to the higher effective volume and kinetic energy of the particles in the nanorods. Estimations of the quantum yields for PbSe nanostructures can be easily made using the following formula for the average multiplicity

$$\bar{n} = \frac{\sum_n nS(n)}{\sum_n S(n)}, \quad (4)$$

and taking into account the average energy of an electron-hole pair creation equal to $2.5E_g$ for nanorods and $4.3E_g$ for QDs [21].

Thus, the Fermi statistical model can be used to explain the higher efficiency of MEG in nanorods over quantum dots established in experiments. Higher effective volume in which multiplications take place, and smaller energy of an electron-hole pair creation can results in higher quantum yields of MEG in nanorods compared to that in quantum dots. The model allows to estimate the MEG performance in PbSe 0D and 1D nanostructures.

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