Multiple exciton generation in single-walled carbon nanobutes

Satoru Konabe[1,2] and Susumu Okada[1,2]

[1] Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan
Phone: +81-29-853-5600 (Ex.8233) E-mail: konabe@comas.frsc.tsukuba.ac.jp
[2] Japan Science and Technology Agency, CREST, 7 Gobancho, Chiyoda, Tokyo 102-0076, Japan

1. Introduction

Multiple electron-hole or exciton generation certainly advance the efficiency of photovoltaic devices, because the single photon create two or more electron-hole pairs or executions. It has been demonstrated that such multiple generation has been realized in the system with low-dimension and nanometer scale, such as semiconductor nanocrystal and carbon nanotubes. During the process, the Coulomb interaction plays decisive role to induce energy transfer, which overcomes the dissipation process associating with phonons [1]. This process is called as the multiple exciton generation (MEG).

While various theories have been proposed regarding the efficiency and the threshold energy, the mechanism of MEG in semiconducting nanocrystals is still controversial [2,3,4]. In addition to semiconducting nanocrystals, single-walled carbon nanotube (SWNT) is possible prototype to examine the MEG since their quasi-one-dimensional structure gives rise to a substantial Coulomb interaction.

In this study, we, thus, theoretically determine the fundamental process of MEG in SWNTs [5]. We show that MEG occurs in SWNTs by the direct photogeneration of multiple excitons. In addition, we also demonstrate that the high efficiency of MEG is due to the strong Coulomb interaction between excitons and to a singularity in the density of states of multiple-exciton states. This study provides a specific criterion for distinguishing the microscopic mechanisms of MEG in SWNTs.

2. Theory

We consider direct photoinduced generation of multiple excitons. Of the various possible multiple exciton states, we consider only two-exciton final states. By considering the excited states of a single exciton as superposed states, a single photon can generate two excitons due to resonant coupling between the superposed states and the multiple-exciton states induced by the Coulomb interaction. The direct generation of two excitons by a single photon is forbidden by the selection rule, as shown in Fig. 1.
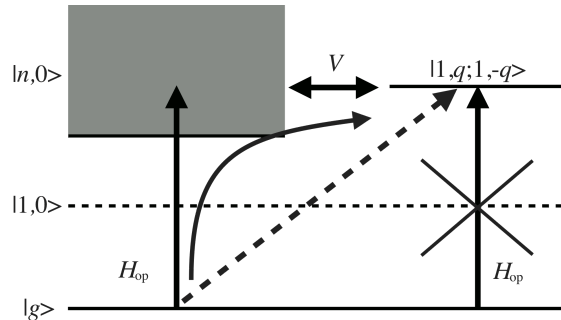

Fig.1 Schematic diagram depicting the MEG process.

The MEG rates are calculated using the following expression of the Fermi golden rule:

$$\Gamma_{\mathrm{MEG}}(\omega) = \frac{2\pi}{\hbar} \sum_q \left| \sum_n \frac{\langle g|\mathcal{H}_{\mathrm{op}}|n,0\rangle \langle n,0|V|1,q;1,-q\rangle}{E_q^1 + E_{-q}^1 - E_0^n + i\gamma} \right|^2 \\ \times \delta(\hbar\omega - E_q^1 - E_{-q}^1) \tag{1}$$

where $|n,q\rangle$ is the nth exciton state with momentum q and E_q^n is the corresponding exciton energy. The two-exciton state is denoted by $|1,q;1,-q\rangle$. Resonant coupling between the excited states of the single exciton and the multiexciton state is characterized by the following perturbation process (see Fig. 1). First, the excited states of a single exciton with zero momentum $|n,0\rangle$ are generated by the exciton–photon interaction, which is denoted by H_{op}. These excited states then act as intermediate states and resonate with the final states, the two-exciton state with a total momentum $|1, q; 1, -q\rangle$, of zero through the Coulomb interaction V. Finally, a single photon generates two excitons as the final state (i.e., the two-exciton state). We phenomenologically consider the dephasing processes for the intermediate states by accounting for the dephasing rate γ in the denominator of Eq. (1).
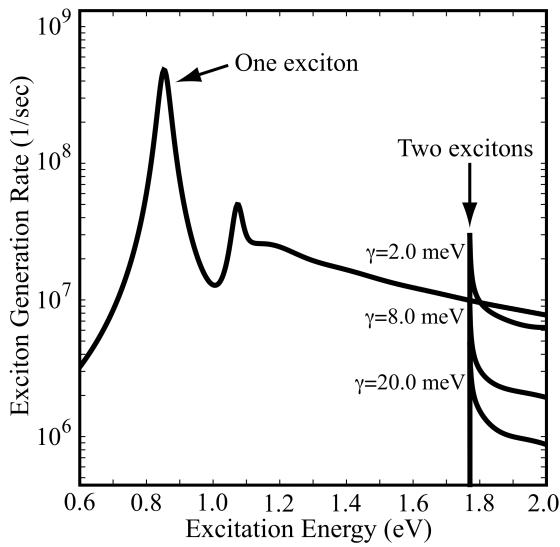
Fig.2 Generation rates for one and two excitons.

3. Result

Figure 2 shows the conversion rates calculated from Eq. (1). The spectral profile for one-exciton generation has the usual structure of the linear absorption spectrum with peaks for the lowest exciton state E_{11} and higher states and a continuum for excitons above the band gap. In contrast, two-exciton generation increases abruptly at the threshold energy, which corresponds to twice the lowest exciton energy (i.e., $2E_{11}$). The threshold energy is solely determined by energy conservation expressed by the Dirac delta function in Eq. (1). Further increasing the excitation energy rapidly reduces the rate. The nature of the spectrum for two-exciton generation can be explained by considering the density of states of the two-exciton state. Due to the quasi-one-dimensional structure of SWNTs, the density of states for excitons possesses van Hove singularities. Thus, the spike at the threshold originates from the van Hove singularity in the density of states for excitons.

We estimate the conversion efficiency of MEG to investigate whether the process can be used to improve photovoltaic devices. The efficiency is evaluated using the following formula:

$$\eta(\omega) = 1 + \frac{\Gamma_{\text{MEG}}(\omega)}{\Gamma_{\text{s}}(\omega) + \Gamma_{\text{MEG}}(\omega)} \quad (2)$$

where $\Gamma_{\text{MEG}}(\omega)$ is defined by Eq.(1) and $\Gamma_{\text{s}}(\omega)$ is the generation rate for a single exciton, respectively. Figure 3 shows the calculated conversion efficiencies for dephasing factors of $\gamma = 2.0, 8.0, 20.0$ meV. The efficiency reaches 175 % for $\gamma = 2.0$ meV, which is close to the maximum efficiency (200%) for two-exciton generation. This remarkably high efficiency is ascribed to both the van Hove singularity in the density of states of the final states and the strong resonance between the intermediate and final states mediated by the Coulomb interaction, which exceeds the
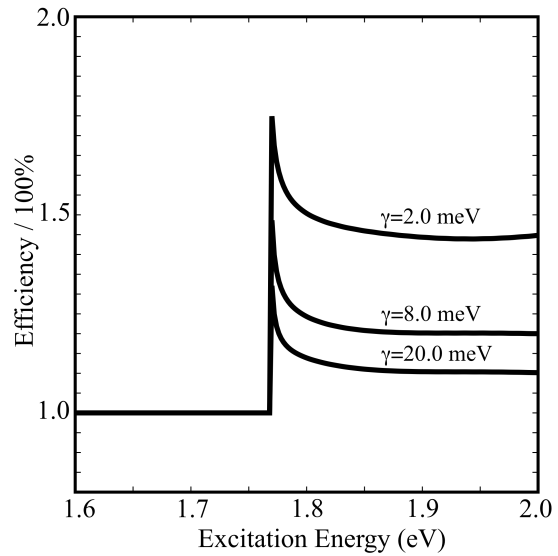

Fig.3 Conversion efficiency for photogeneration of two excitons plotted for dephasing rates of 2.0, 8.0, and 20.0 meV.

dephasing process represented by γ. The MEG efficiency is largest at the threshold energy corresponding to the van Hove singularity, as is the MEG rate (see Fig. 2).

4. Conclusion

We have studied MEG in SWNTs. Our calculation has demonstrated that it is possible to generate two excitons by a single photon due to resonant coupling between the optically active one-exciton state and two-exciton states. This resonance is ascribed to the unique characteristics of SWNTs that originate from their quasi-one-dimensional structures, resulting in a strong Coulomb interaction between excitons competing with phonon dephasing and the van Hove singularity in the density of states of the two-exciton states. The present study clarifies the microscopic process of MEG in SWNTs. MEG raises the possibility of designing high-efficiency photovoltaic devices with low energy consumptions by using SWNTs as constituent units.

References

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