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Multiexciton Generation and Recombination in Semiconductor Nanomaterials

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1. Introduction

The optical and electronic properties of semiconductor nanomaterials such as nanocrystals (NCs) and carbon nanotubes (CNTs) have been studied extensively over the past two decades, both from their fundamental physics interest and their potential applicability in photonic devices. NPs and CNTs serve as building blocks for tailored materials with fascinating multifunctional properties beyond those of bulk crystals and isolated NPs and CNTs [1]. Recently, high-quality NCs and CNTs provide an excellent new stage for experimental studies of many-body effects on optical processes for electrons and excitons in nanoscale materials [2].

Because of strong Coulomb interactions between confined electrons, semiconductor nanomaterials show unique optical phenomena such as quantized Auger recombination and multiexciton generation (or carrier multiplication) [3]. Since the first proposal in 2002 [4] and the first experimental demonstration in 2004 [5], there has been an explosive growth of scientific interest in the role of multiexciton generation in photovoltaic phenomena. Multiexciton generation is expected to become a new way for exceeding the Shockley-Queisser limit for single band-gap solar cells [6,7]. Multiexciton generation is regarded as an inverse Auger process. Auger recombination is the dominant nonradiative recombination process in NCs [8]. Thus, deep understanding of three-body Auger recombination in semiconductors is very important for developing new photonics devices. In this paper, we discuss the mechanism of Auger recombination and multiexciton generation in NCs and CNTs. We also discuss ways to utilize multiexciton states for enhancing the conversion efficiency of solar cells.

2. Multiexciton recombination

In semiconductor bulk crystals, photoluminescence (PL) spectrum and dynamics depend on the excitation laser intensity. The PL decay dynamics are determined by the temporal change in the carrier density. The band-to-band recombination rate of electrons and holes is expressed as a power series in the photogenerated carrier density. The rate equation includes the nonradiative single-carrier trapping rate, the two-body radiative recombination rate, and the three-body nonradiative Auger recombination rate [9,10].

At high carrier densities, the PL lifetime and the PL intensity are determined by three-body Auger recombination. In light-emitting diodes and lasers, the efficiency decreases with an increase of forward current. At high currents, Auger recombination dominates the carrier density, thereby determining the device performance. For example, InGaN-based LEDs show a significant efficiency droop at high injected carrier densities. It is believed that Auger recombination is the dominant mechanism for efficiency droop of LEDs.

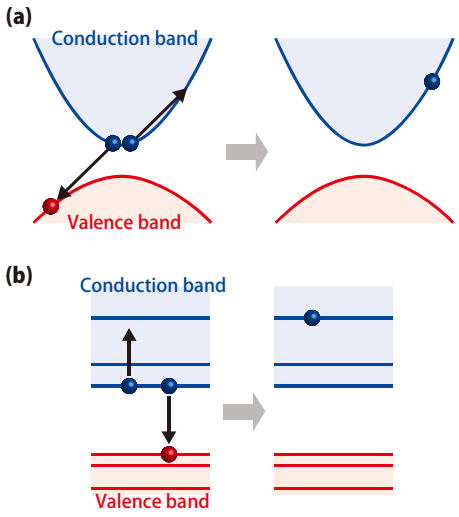

Fig. 1. Auger recombination in (a) bulk crystals and (b) nanocrystals.

In bulk crystals, the *k*-conservation rule dictates the Auger recombination rate, because the third electrons need to gain both the energy and momentum of the recombined electron and hole pairs [Fig. 1(a)]. Then, the Auger rate depends exponentially on the band-gap energy and temperature. In nanomaterials, the Auger rate is enhanced. In one-dimensional CNTs, the Auger lifetime is about 1 ps [11-13]. Rapid Auger recombination between excitons causes the saturation of PL intensity. The rapid Auger process determines the PL dynamics of CNTs. The mechanism of fast exciton decay dynamics is under discussion. In zero-dimensional NCs, the breakdown of the *k*-conservation rule leads to the enhancement of the Auger rates, compared to bulk crystals [Fig. 1(b)]. The Auger rate of the NC depends on its size, shape, and composition [14,15]. Control of the Auger rate is very important to extract charge carriers from NCs for photovoltaic applications.

3. Multiexciton generation

In Auger recombination, the electron–hole recombination energy is transferred to another electron or hole. The numbers of electrons and holes decrease, and hot electrons or holes are produced. In multiexciton generation process, the excess energy of a hot electron is used to generate a new electron-hole pair [Fig. 2(a) and (b)]. Multiexciton generation by a single photon is an inverse Auger process.

In bulk crystals, multiexciton generation usually occurs in the blue and ultraviolet spectral region. Then, the spectral overlap between the carrier gain and the sun light is very poor. Then, multiexciton processes are not notable for practical devices, although multiexciton generation has been studied over 50 years [16]. However, extremely high multiexciton generation efficiencies have been initially reported in PbSe and PbS NCs [5]. Multiexciton generation has also been observed in CNTs [13]. It is anticipated that the multiexciton generation process plays an essential role in next-generation photovoltaics based on nanomaterials. In bulk crystals, multiexciton generation occurs through impact ionization [17]. In NCs, many papers reported high multiexciton generation efficiencies and low multiexciton generation thresholds. The importance of enhanced Coulomb interactions between carriers on multiexciton generation has been discussed. For model materials, PbSe and PbS, the low threshold for multiexciton generation was observed, although they have large dielectric constants and then screening of Coulomb interactions between carriers occurs effectively. Thus, several models have been proposed for efficient multiexciton generation in NCs. A favored model is the impact ionization one [18,19]. However, the detailed mechanism of multiexciton generation by a single photon in NCs remains unclear.

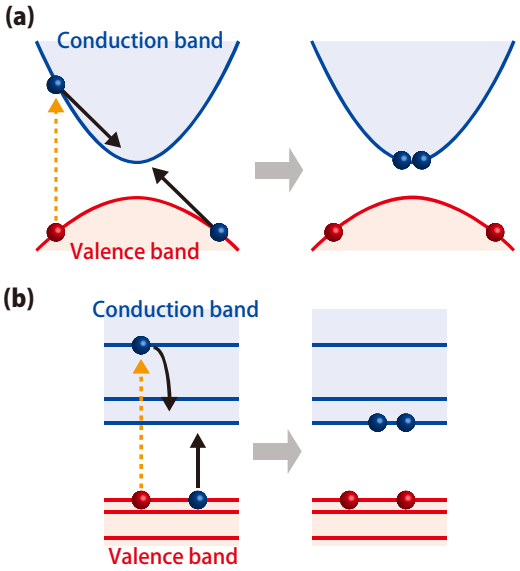

Fig.2. Multiexciton generation in (a) bulk crystals and (b) nanocrystals.

Multiexciton generation competes with cooling process of hot electrons through electron-phonon interactions and Auger recombination. We discuss that heterostructured NCs have some advantages for enhancing the multiexciton generation efficiency. We also discuss the rapid charge separation process in NCs with staggered alignment of band edge structures for photovoltaic applications [20].

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