22.1 Introduction

Over the past two decades, there have been extensive studies on the optical properties of semiconductor nanomaterials from the fundamental physics viewpoint and from the interest in the application to functional devices, because they exhibit unique size-dependent quantum properties [1–11]. In this chapter, we discuss optical properties of semiconductor nanomaterials of zero-dimensional (0D) nanoparticle quantum dots and one-dimensional (1D) carbon nanotubes. In optical studies of nanoparticle quantum dots and carbon nanotubes, we would like to point out two important reports opening new active fields: the discovery of room-temperature-visible luminescence from porous silicon in 1990 [12] and the discovery of efficient luminescence from isolated carbon nanotubes in 2002 [13]. These observations of efficient luminescence clearly show that nanoparticles and carbon nanotubes are high-quality crystalline semiconductors. Many different fabrication methods have been developed to obtain stable and efficient luminescence from nanoparticles and carbon nanotubes, e.g., core/shell nanoparticles, suspended isolated nanotubes, and so on [14–20]. These nanomaterials become new materials for optoelectronic devices such as wavelength-tunable light-emitting diodes and lasers, quantum light sources, and solar cell applications.

When semiconductor nanoparticle sizes are comparable to or smaller than the exciton Bohr radius in bulk crystals, the excited state energies and optical properties are very sensitive to their sizes [1,21,22]. Usually, nanoparticle samples are an inhomogeneous system in the sense that they have a distribution of size and shape, and variations of surface structures and surrounding environments [2]. A large nanoparticle has small band-gap energy and a small nanoparticle has large band-gap energy. Furthermore, the nanoparticles have large surface-to-volume ratios, and then the optical properties of nanoparticles are also sensitive to surrounding environments. The exciton band-gap energy of semiconducting carbon nanotubes is also sensitive to the nanotube diameter and the chiral index. Then, we need to study the intrinsic optical processes in nanoparticle quantum dots and carbon nanotubes hidden by sample inhomogeneity using sophisticated optical spectroscopy.

If the laser light excites all nanoparticles or all nanotubes in the sample, the sample shows broad luminescence, reflecting size or diameter distributions. This “global” photoluminescence (PL) or nonresonantly excited luminescence contains contributions from all nanoparticles or all nanotubes in the sample, and the PL spectrum is inhomogeneously broadened, as shown in Figure 22.1a. These sample inhomogeneities are the origin of nonexponential PL decay. In inhomogeneously broadened systems, resonant excitation spectroscopy is a powerful method to obtain intrinsic information from broadened optical spectra. Under resonant excitation at energies within the global PL band, we can observe fine structures in PL spectra at low temperatures, as shown in Figure 22.1b. Resonant excitation at energies within the luminescence band results in a single zero-phonon PL line or a well-resolved phonon progression in PL spectra at low temperatures. In this case, we suppress the inhomogeneous broadening of the luminescence by selectively exciting a narrow subset of nanoparticles. Resonant excitation results in fluorescence line narrowing (FLN) in nanoparticle samples [23–27]. The resonantly excited PL spectra are sensitive to the nature of the band-edge structure and the surface structure [27–29]. Moreover, luminescence hole-burning (LHB) spectroscopy is another resonant excitation spectroscopy. In the LHB experiments, the sample is excited by intense laser at the energy within the PL band [30–32]. After prolonged laser irradiation (burning laser excitation), a spectral hole is formed near the burning laser energy in the luminescence
22.2 Carbon Nanotubes

A single-walled carbon nanotube (SWNT) with about 1 nm diameter and a length greater than several hundred nanometers is a prototype of 1D structures. The recent discovery of efficient PL from semiconducting SWNTs [13,38] has stimulated considerable efforts in understanding optical properties of SWNTs. The semiconducting SWNTs are 1D direct-gap band structures [8]. Because of the extremely strong electron–hole interactions (excitonic effects) in 1D materials, unique optical properties of SWNTs are determined by the dynamics of 1D excitons [8,39]. In addition, the electronic structure and the PL energy of SWNTs strongly depend on the diameter and the chiral index [38]. The SWNT samples are also inhomogeneous systems, similar to the nanoparticle samples, because many different species of nanotubes exist in the sample. The inhomogeneous broadening and the spectral overlapping of PL spectra cause the complicated PL dynamics of SWNTs. Single nanotube spectroscopy reveals the intrinsic excitonic properties of SWNTs [40–46], such as exciton energy, bright and dark exciton structures, exciton–phonon interaction, and so on.

For single nanotube spectroscopy, we synthesized spatially isolated carbon nanotubes on Si substrates using an alcohol catalytic chemical vapor deposition method [45,46]. In our experiments, the Si or SiO$_2$ substrates were patterned with parallel grooves, typically 500 nm wide and 500 nm deep using an electron-beam lithography technique. The isolated SWNTs grow from one side toward the opposite side of the groove. We used these SWNT samples without matrix and surfactant around the nanotubes to reduce the local environmental fluctuation effect. We show a typical PL spectrum of a single carbon nanotube suspended on the groove [assigned chiral index: (7,6)] at about 40 K in Figure 22.2a [46]. Very broad PL bands are observed in the ensemble-averaged spectrum of micelle-wrapped SWNTs dispersed in gelatin. The PL spectral shape of a single carbon nanotube.

![Figure 22.1](image1)

**FIGURE 22.1** Luminescence spectra of semiconductor nanoparticles: (a) global luminescence spectrum, (b) resonantly excited luminescence spectrum, (c) LHB spectrum, and (d) single nanoparticle luminescence spectrum.

![Figure 22.2](image2)

**FIGURE 22.2** (a) PL spectrum of a typical suspended single SWNT [assigned chiral index (7,6)] in comparison with the ensemble-averaged spectrum of micelle-wrapped SWNTs dispersed in gelatin. (b) Polar plot of the PL intensity of a typical single SWNT versus the polarized direction of the excitation laser. The PL data (circle) were fitted using $\cos^2\theta$ (solid line). (Reprinted from Matsunaga, R. et al., *Phys. Rev. Lett.*, 101, 147404, 2008. With permission.)
nanotube is given by a Lorentzian function, and its linewidth of a few meV reflects homogeneous broadening. Figure 22.2b shows a polar plot of the PL intensity of a typical single carbon nanotube versus the polarization direction of the excitation laser light [46]. Since a 1D dipole moment exists, strong optical absorption occurs when the polarization of the excitation light parallels the nanotube axis. This PL anisotropy is useful for determining the direction of the observed nanotube axis for single nanotube spectroscopy and modulation spectroscopy.

The sharp luminescence spectra provide detailed information on the exciton fine structures. We studied the PL fine structure of single SWNTs under magnetic fields at low temperatures. A single sharp PL spectrum arising from bright exciton recombination is observed at zero magnetic field, as shown in Figure 22.2a. When the magnetic field is parallel to the nanotube axis, a new peak appears below the bright exciton peak. Figure 22.3a shows PL spectra of a single carbon nanotube under magnetic fields [46]. These PL spectra are fit well by two Lorentzian functions. With the magnetic field, the lower energy peak shows a redshift and the lower-energy peak intensity increases. We cannot observe these changes when the magnetic field is perpendicular to a single nanotube axis, as shown in Figure 22.3b [46]. The splitting of the PL peak occurs due to the magnetic flux parallel to the nanotube axis. These splitting and magnetic field dependence can be explained by the Aharonov–Bohm splitting of excitons based on the Ajiki and Ando model [8,47]. The singlet exciton states split into the bonding and antibonding exciton states, and this due to the short-range Coulomb interaction. The bonding state is odd parity (bright) and the antibonding is even (dark). The energy difference between the bright and dark exciton states also depends on the diameter of SWNTs. These experimental observations are consistent with the theoretical calculation. The dark exciton state exists about several meV below the bright exciton state. Studies of 1D dark excitons influencing optical responses of carbon nanotubes [48–52] are very important for optical device applications.

The diameter dependence of the exciton energy in single carbon nanotubes is also revealed by single nanotube spectroscopy. At room temperature, the experimentally obtained PL spectra can be approximately reproduced by single Lorentzian functions. The observed PL peaks correspond to the zero-phonon lines of free excitons, and the spectral linewidth of the PL spectra is determined by the homogeneous broadening. We obtained PL spectra from many different isolated SWNTs with a variety of chiral indices. Figure 22.4a shows a distribution of the PL peak energies for the single SWNTs, indicated by diamonds [45]. In Figure 22.4b, we show some of the PL spectra from isolated SWNTs with various emission energies [45]. Only a single sharp peak can be seen in each spectrum. The PL linewidth clearly becomes broader as the diameter decreases. This shows that the exciton–phonon interaction is stronger in smaller diameter tubes.

The lowest exciton has fine structures (bright and dark excitons), and the fine structures will determine optical responses and cause unique phenomena. At low temperatures, we observe an interesting phenomenon, spectral diffusion. A few ten percents

FIGURE 22.3 (a) Normalized magneto-PL spectra of a single (9,4) carbon nanotube at 20 K in the Voigt geometry. The split PL spectra are fit by two Lorentzian functions. (b) The normalized magneto-PL spectra of a single (9,5) carbon nanotube at 20 K in the Faraday geometry. The PL spectra are fit by a Lorentzian function. (Reprinted from Matsunaga, R. et al., Phys. Rev. Lett., 101, 147404, 2008. With permission.)

FIGURE 22.4 (a) PL peak energy distribution of obtained PL spectra from about 180 different isolated SWNTs. (b) PL spectra for several species of single SWNTs at room temperature. SWNTs with higher PL emission energy tend to have a larger spectral linewidth. (Reprinted from Inoue, T. et al., Phys. Rev. B, 73, 233401, 2006. With permission.)
of the nanotubes show spectral diffusion. We consider that spectral diffusion is related to the exciton fine structure, bright and dark excitons. The PL fluctuation due to spectral diffusion is clearly observed at low temperatures. Spectral fluctuation occurs very slowly, the order of several seconds. Figure 22.5a shows a typical temporal evolution of the PL spectrum of SWNT showing spectral fluctuations at 40 K [53]. During spectral diffusion, the PL spectra clearly show two peaks. The lower energy is fitted by Gaussian and the higher energy is Lorentzian. From spectral fitting, we can determine the peak positions and linewidth of both peaks of the PL spectra. Temporal changes in two PL peak energies and linewidths of the lower energy PL band are shown in Figure 22.5b [53]. The higher energy peak is almost constant, but the lower energy peak fluctuates. We find a good correlation between the PL peak energy and the PL linewidth of the lower energy band. When the PL peak shows a low energy, the linewidth becomes wider. To clarify the origin of the spectral diffusion in the lower energy peak, the PL linewidth of the lower energy peaks is plotted as a function of the emission energy. We obtain the square root dependence of the linewidth on the emission energy [53]. This dependence suggests the quantum-confined Stark effect [54]. The spectral diffusion can be explained by the fluctuation of local electric field. The Stark effect causes a redshift in the exciton energy. A small, fast, local electric field fluctuation results from surface charge oscillations. These observations show that the energy splitting between the bright and the dark exciton states is estimated to be about a few meV [53]. This conclusion is well consistent with the magneto-optic results as mentioned before. Detailed understanding of fine structures of the lowest excitons is important for the optoelectronic applications of carbon nanotubes.

### 22.3 Nanoparticle Quantum Dots

Similar spectral diffusion and PL blinking phenomena are also observed in nanoparticle quantum dots. PL blinking phenomenon is quite enhanced in 0D nanoparticles rather than 1D carbon nanotubes. PL blinking in single nanoparticles is caused by a random switching between light-emitting "on" and non-light-emitting "off" states under continuous-wave (cw) laser excitation. Since the first blinking observation in nanoparticles [35], the mechanism of nanoparticles PL blinking has been extensively discussed [55–70]. Ionization of nanoparticles due to nonradiative Auger recombination plays an essential role in PL blinking of single nanoparticles [55]. It is well accepted in this field that PL blinking originates from the photoionization and neutralization of nanocrystals under cw light illumination. In CdSe nanocrystals, for example, the non-light-emitting off-time state is due to positively charged nanoparticles, and the light-emitting on-time state is due to the neutral nanoparticle [55,70]. Spectral fluctuations during on-time suggest that both electrons and holes trapped on the nanoparticle surface cause transient and local electric field fluctuations in the light-emitting neutral nanoparticle. In neutral nanoparticles, excitons recombine radiatively. In ionized (or charged) nanoparticles, the photogenerated excitons and excess holes recombine nonradiatively through fast three-body Auger recombination. The PL blinking means that a nanoparticle repeats the neutralization and ionization under cw laser excitation.

PL blinking behavior is very sensitive to the local surrounding environments. Figure 22.6 shows the PL intensity time traces of a single CdSe nanoparticle on different substrates: glass, rough, and flat Au surfaces [66]. The samples are excited by cw laser at room temperature. The on-off PL blinking behavior is clearly observed on the glass substrate. The time distribution of the on and off states can be characterized by power law functions [57]. The power law distributions suggest that the PL blinking is caused by a very complicated process. On the metal surfaces, on the other hand, the PL off-time is drastically suppressed. The PL blinking suppression indicates that the very rapid neutralization of ionized nanoparticles occurs through the fast energy transfer. However, the enhancement
and quenching of the PL intensity depend on the roughness of the metal surface. On the rough surface, the PL intensity increases. In this experiment, rough Au surfaces are composed of an assembly of hemispherical particles with lateral sizes of 20–50 nm and peaks and valleys of roughly 15 nm. On the flat surface, however, the PL intensity decreases. The enhancement of the PL intensity depends on the excitation laser wavelength. The enhancement spectrum agrees well with the absorption spectrum for localized plasmon resonance [66].

Even on rough Au surfaces, we can observe both enhancement and quenching phenomena of the PL intensity. PL intensity on a rough Au surface depends on the polarization angle of the excitation laser [71]. Electric field enhancement depends on the polarization direction. The PL intensity of a single nanoparticle on glass does not change with the polarization angle. We obtain the microscopic structure of semiconductor nanoparticles and rough surfaces from the polarization and wavelength dependences. Thus, we conclude that the PL intensity enhancement is related to the electric field enhancement due to localized plasmon excitation. Studying PL blinking behaviors is a way to understand energy transfer processes between nanoparticles and surrounding environments.

Close-packed nanoparticle films or nanoparticle arrays show unique exciton energy transfer and charge carrier transport beyond isolated nanoparticles [72–79]. Many different types of closely packed nanoparticle films, arrayed nanoparticle solids, and nanoparticle suprasolids have been prepared [72–79]. In order to control energy transfer between excitons in semiconductors and plasmons in metals, we fabricate metal-semiconductor hetero nanostructures and their PL spectrum and dynamics. We fabricated two types of semiconductor-metal nanoparticle heterostructures using the Langmuir–Blodgett technique: close-packed CdSe nanoparticle monolayers on Au substrates [80] and mixed CdSe and Au nanoparticle monolayers [81]. In close-packed CdSe nanoparticle monolayers on Au surfaces, the inert polymer thin film was inserted between the nanoparticle monolayer and the Au substrate. The distance between the excitons and plasmons, Δ, is controlled by the polymer thickness. Figure 22.7 summarizes the distance dependence of the PL lifetime and the time-integrated PL intensity [80]. There is a good correlation between the PL decay rate and the PL intensity. PL quenching only occurs when the distance between excitons and plasmons is less than 30 nm. In large distance samples, the PL decay rates in close-packed monolayers are much larger than those in isolated nanoparticles in solutions. The PL lifetime in the CdSe monolayers on the glass is governed by the nonradiative recombination of excitons in nanoparticles and the energy transfer from small to large CdSe nanoparticles, which have lower exciton energies. Furthermore, the PL decay increases with a decrease of the distance between the Au surface and the CdSe nanoparticle monolayer. This can be attributed to energy transfer from nanoparticles to surface plasmons of the Au surfaces. The reduction of both the PL lifetime and the PL intensity simultaneously occurs. PL quenching only occurs in the CdSe nanoparticle monolayer in close proximity to the Au films [80].

Close-packed monolayer films composed of CdSe and Au nanoparticles have simple two-dimensional hexagonal lattices [81]. The PL and optical density of the sample films depend on the Au nanoparticle concentration in the film, because of the spectral overlap between the exciton luminescence of CdSe nanoparticles and the plasmon absorption in Au nanoparticle. In the CdSe and Au nanoparticle mixed monolayer samples, the PL decay curves can be reproduced successfully using three exponential decay components. Three kinds of decay channel of excited states exist in the close-packed CdSe and Au nanoparticle monolayer. In mixed monolayer samples, the decay times are classified into three components: 0.2, 1, and 10 ns, as summarized in Figure 22.8a [81]. These decay times are almost independent of
the Au nanoparticle mixing ratio in the film. The 10-ns decay time originates from radiative recombination within CdSe nanoparticles in the films. As the Au nanoparticle fraction increases, the amplitudes of two 1- and 10-ns components decrease. The amplitude of the fast 0.2-ns decay component becomes dominant. These results indicate that the fast PL quenching is caused by the energy transfer to Au nanoparticles for the CdSe nanoparticles in contact with Au nanoparticles. Here, note that the decay component of about 1 ns is a unique characteristic of close-packed mixed nanoparticles solids. Energy transfer between the nearest-neighbor CdSe nanoparticles takes part in the slow PL quenching process of 1 ns in the mixed film. The 1-ns PL quenching process is the stepwise energy transfer from a CdSe nanoparticle to a CdSe nanoparticle to a Au nanoparticle, as illustrated in Figure 22.8b [81]. Therefore, we conclude that the PL dynamics are explained by three kinds of decay channel. The energy relaxation rate in semiconductor nanoparticles is controlled by changing local surrounding environments. These close-packed nanoparticle heterostructures will show unique exciton energy transfer, and charge carrier transport beyond isolated nanoparticles opens new application fields.

### 22.4 Multiexciton Generation

Finally, we discuss unique exciton–exciton interactions in nanoparticles and nanotubes. Nanoparticle quantum dots and carbon nanotubes provide an excellent stage for experimental studies of many-body effects of excitons or electrons on optical processes in semiconductors [82–84]. The reduced dielectric screening and the relaxation of the energy–momentum conservation rule in nanostructures enhance the Coulomb carrier–carrier interactions, leading to multi-carrier processes such as the quantized Auger recombination, multiple exciton generation (MEG), carrier multiplication (CM), and so on [7,85]. The achievement of efficient CM in semiconductors makes it possible to produce highly efficient solar cells with conversion efficiencies that exceed the Shockley–Queisser limit of 32% [86]. Strongly confined electrons and excitons in nanomaterials show unique nonlinear optical properties, compared to semiconductor bulk crystals.

Strong interactions between carriers or between excitons cause fast nonradiative Auger recombination of multiple excitons or carriers [82]. Intense interest in Auger recombination in nanoparticles has been stimulated by investigations and searches for new laser and solar cell materials [87–89]. In laser and solar cell applications, nonradiative Auger recombination dominates both the carrier density and the carrier lifetime, determining the device performance. Moreover, in transient absorption, PL, and terahertz conductivity experiments, fast Auger recombination has also been used as a probe in MEG and CM processes [89–96]. The CM efficiencies of nanoparticles are not clear, and the CM mechanism is under discussion. In SWNTs, for example, strong Coulomb interactions enhance the many-body effects of excitons. The fast Auger recombination of excitons has been observed by means of exciton homogeneous linewidth [97] and pump-probe measurements [98–100]. We studied MEG processes in SWNTs at room temperature by temporal change in the carrier density [101]. The fast-decay component grows at increasing excitation intensity. When the photon energy is three times larger than the band-gap energy, Auger recombination occurs efficiently even in the weak intensity region. In our experiment, CM is estimated to be about 1.3 under 4.65 eV excitation [101]. We pointed out that a possible mechanism of CM in carbon nanotubes is the impact...
ionization. Strong interactions between carriers or between excitons cause unique optical processes in semiconductor nanomaterials. Highly excited semiconductor nanomaterials show new optical functionalities.

### 22.5 Summary

We briefly discussed luminescence properties of carbon nanotubes and nanoparticle quantum dots by means of single molecular spectroscopy and time-resolved optical spectroscopy. These semiconductor nanomaterials show unique luminescence properties such as spectral diffusion and luminescence blinking. Energy transfer between nanomaterials and surrounding environments affects the PL spectra and dynamics of nanomaterials. Although this chapter is written as a review-type survey of our recent studies, we hope that discussions and many references cited are useful for the readers.

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