Optics and Spectroscopy, 2023, Vol. 131, No. 12

02

Spectral Measurement of a Single Semiconductor Nanoplatelets Cluster in Radio-frequency Trap

© V.V. Rybin, S.S. Rudyi, D.I. Klimenko, A.V. Ivanov, D.P. Shcherbinin

ITMO University,
197101 St. Petersburg, Russia

e-mail: vadi.rybin@gmail.com

Received July 25, 2023
Revised December 6, 2023
Accepted December 7, 2023

In this work, we study the optical response of microclusters of CdSe nanoplates localized in an radio-frequency trap. The luminescence spectra of the stock solution of nanoplates, its microclusters on a glass substrate, and in an radio-frequency trap are compared. The redshift and broadening of the exciton luminescence band, as well as the formation of additional luminescence bands in the long-wavelength region of the spectrum as a result of the aggregation of nanoplates, is shown. The spectra of microclusters localized in an radio-frequency trap are characterized by a greater redshift and broadening of the main band, as well as an increase in the relative contribution of long-wavelength luminescence bands to the spectral response. The possible mechanisms leading to the modification of the luminescence spectra of nanoplate microclusters are discussed.

Keywords: photoluminescence, nanoplatelets, radio-frequency traps

DOI: 10.61011/EOS.2023.12.58174.5426-23

1. Introduction

Spectral optical analysis methods are actively used to study the internal energy structure, chemical composition, and surface morphology of various nanoparticles and materials based on them. Techniques for measuring absorption and transmission spectra, luminescence and luminescence excitation spectra, time-resolved spectroscopy techniques, and pump-probe spectroscopy are now widely known. All these techniques involve the study of nanoparticles in a colloidal solution or on a substrate. In this case, measurement data provide information about the whole system, including the properties of the environment and the influence of the environment on the properties of the sample. In addition, it is almost impossible to exclude interactions of individual particles of the sample with each other. Interpretation of such measurements often requires a number of assumptions, which in turn affects the accuracy and validity of the study results. It is a complex and non-trivial task to exclude the influence of the external environment on the studied parameters and conduct single-particle studies.

One approach to isolate a single object in space is electrodynamic trapping of charged particles. A single charged object ranging in size from several nanometers to hundreds of micrometers can be captured by interacting with the alternating electric field of a radio frequency trap. The basic principles of electrodynamic trapping of charged particles are described in detail in [1–3]. Radiofrequency traps allow one to isolate the object of study in space (in a buffer gas or vacuum) with the possibility of precise control of its position. In the optical spectrum recorded from a trapped levitating particle, effects due to the interaction of this particle with the medium and other particles will be minimized.

Several scattered experimental works on techniques for measuring the optical properties of individual micro- and nanoparticles levitating in radiofrequency traps have been published to date. The optical spectra of quantum dots and their clusters localized in the field of radio frequency traps [4,5] have been studied. The sizes of single trapped aerosol particles were determined by interference methods and techniques based on Mie scattering theory [6,7]. Although the first attempts at optical studies of levitating particles in RF traps have already been made, the spectroscopy of single particles in RF traps remains new and poorly understood.

Furthermore, the potential for investigating single objects in an RF trap is not limited to spectral optical techniques alone. Radiofrequency traps allow a wide class of methods to be used to determine the physical characteristics of a trapped particle, such as size, mass, charge, and density [8–10]. A combination of spectral-optical and mass spectroscopic approaches will enable the development of a new class of measurement techniques for comprehensive analysis of single particles.

In the present work, we demonstrate a new approach in spectral optical research based on the examination of single particles localized in a radio-frequency trap. Luminescence spectra of single microclusters of semiconductor nanoplatelets localized in the field of a quadrupole radiofrequency trap under atmospheric pressure conditions are investigated. Comparative studies of the luminescence spectra of nanoplatelets and their microclusters in colloidal

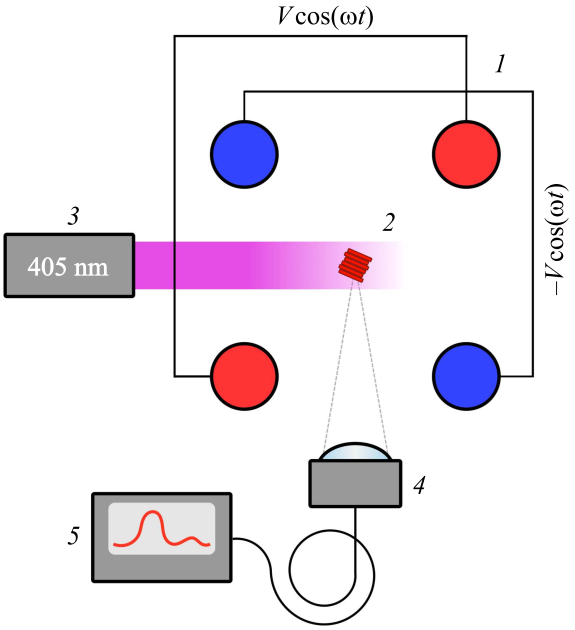

Figure 1. Schematic diagram of the experimental setup, top view. *1* — Vertically-aligned radiofrequency trap, *2* — single cluster of CdSe nanoplatelets, *3* — 405 nm laser, *4* — long-focus lens with fiber output, and *5* — portable spectrometer.

solution, on a substrate, and in a radiofrequency trap are carried out. An interpretation of the results obtained is given.

2. Methods and materials

The approach proposed in this paper consists in trapping a single particle in a radio-frequency trap, subsequent excitation, and recording of its photoluminescence. The schematic diagram of the experimental setup is shown in Fig. 1. A vertically-aligned quadrupole radiofrequency trap with a single end-cap electrode [5] was used to localize the object under investigation. Such an RF trap consists of four cylindrical rod electrodes providing radial confinement and one end-cap electrode compensating for the gravity of a charged particle. Alternating voltage of the order of $V = 2.5\,\mathrm{kV}$ at frequency $\omega = 50\,\mathrm{Hz}$ was applied to the rod electrodes in pairs in counter-phase. A high DC voltage up to 300 V was applied to the end-cap electrode. This configuration of the electrodynamic trap allows one to fix the object of study on the vertical axis and adjust its axial position smoothly (Fig. 1). The photoluminescence excitation and recording system consists of a UV laser with a wavelength of 405 nm, a long-focus lens with fiber output, and a portable spectrometer (R-Aero). The luminescence signal was collected at an angle of 90° to excitation radiation. The excitation radiation and lens were focused to a single point on the axis of the electrodynamic trap at a height of the order of 5 mm above the end-cap electrode.

A pre-synthesized colloidal solution of cadmium selenide nanoplatelets with a thickness of 5 monolayers was studied. The synthesis procedure is described in [11]. The work investigates nanoplatelet microclusters obtained by drying the precipitate of a colloidal nanoparticle solution after centrifugation with the addition of a precipitant (isopropanol). Absorption spectra of the colloidal solution of nanoparticles in chloroform were measured using a SF-56 (LOMO) spectrophotometer, and luminescence spectra of the same solution were measured using a FP-8200 (Jasco) spectrofluorimeter. Luminescence spectra of nanoplatelets in colloidal solution and on a glass substrate after deposition were recorded for comparative analysis. The spectrum of microclusters on the substrate was recorded using an excitation and recording scheme similar to that described in the method for measuring luminescence spectra in a radiofrequency trap.

3. Results and discussion

Figure 2 shows the absorption and luminescence spectra of solutions of semiconductor nanoplatelets in chloroform (green and blue curves, respectively). Among all colloidal semiconductor nanoparticles, cadmium selenide nanoplatelets are of particular interest because of the narrow luminescence peak due to the lack of inhomogeneous broadening of the spectral band [12,13]. The spectral position of the luminescence band is determined by the number of atomic layers in the studied platelets and is controlled well during the synthesis process. The studied nanoplatelets have 5 atomic layers, which determine the position of the exciton band in the optical density (515 nm) and luminescence (516 nm) spectra. The width of the luminescence band of nanoplatelets in solution is characterized by = 9 nm.

Spectral optical measurements of microclusters deposited on a glass substrate were performed to investigate the evolution of spectra of nanoplatelets during the preparation of their microclusters. In Fig. 2, the yellow curve indicates a typical luminescence spectrum of a microcluster on a substrate. A red shift of 5 nm (luminescence peak at 521 nm) and broadening of the luminescence band maximum by 5 nm (FWHM = 14 nm) relative to the band maximum in solution are observed. In addition, the spectrum of deposited nanoplatelets is characterized by the emergence of additional luminescence bands in the long-wavelength region of the spectrum. The red curve in Fig. 2 depicts a typical luminescence spectrum of a nanoplatelet microcluster in a radiofrequency trap. The loading of nanoplatelet microclusters into the radiofrequency trap leads to an even larger (8 nm, the luminescence peak is at 524 nm) red shift and broadening of the main luminescence band (FWHM = 19 nm), as well as an increase in the relative contribution of additional long-wavelength luminescence bands.

The obtained results suggest that a red shift of the luminescence band accompanied by its broadening is observed

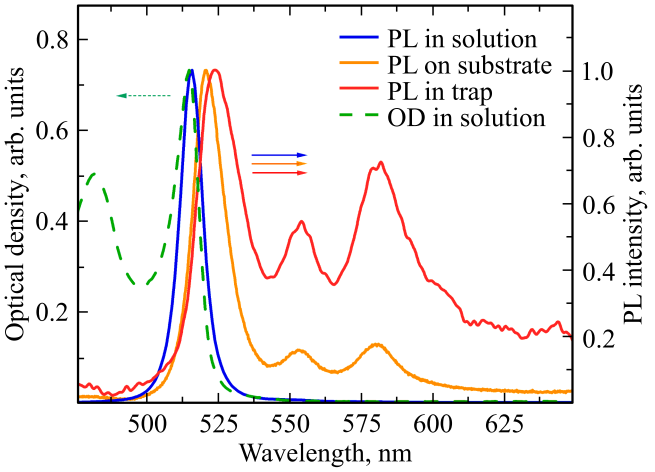

Figure 2. Optical density spectra (green curve) with the exciton band peak at 515 nm and luminescence spectra (blue curve) with the exciton band peak at 516 nm, FWHM = 9 nm, of a colloidal solution of nanoplatelets; luminescence spectrum (yellow curve) with the exciton band peak at 521 nm, FWHM = 14 nm, of a nanoplatelet microcluster on the substrate; and luminescence spectrum (red curve) with the exciton band peak at 524 nm, FWHM = 19 nm, of a nanoplatelet microcluster in the radio-frequency trap

during the formation of nanoplatelet microclusters and their loading into the radiofrequency trap. In addition, new features of the spectrum in the long-wave region appear.

Deposition of a colloidal solution of nanoplatelets leads to self-organization of nanoparticles into ordered clusters ranging in size from several tens to several hundreds of nanometers [14,15]. The red shift of the luminescence peak may appear due to mechanical stresses in individual nanoplatelets during cluster formation and drying [16,17]. The large surface area of nanoplatelets increases the probability of both mechanical stresses and surface defects. The red shift and broadening of the luminescence band can also be caused by a change in the dielectric permittivity of the surrounding medium and the ligand layer during cluster drying [15].

The emergence of additional long-wavelength luminescence bands in the spectrum of deposited nanoplatelet microclusters can be explained by radiative relaxation of a charge carrier through a defect state in the band gap associated with uncoordinated surface atoms [16,17]. In ordered clusters, due to a small Stokes shift, large overlap of absorption spectra, and large Förster radius, an exciton can migrate along the cluster [14]. Exciton migration in the cluster increases the probabilities of its trapping in defect surface states of a certain nanoplatelet in the cluster, which leads to a decrease in the luminescence quantum yield of the main exciton transition. As a consequence, the contribution of long-wavelength bands of defect luminescence relative to the exciton band increases.

The localization of a single nanoplatelet microcluster in a radiofrequency trap is only possible in the presence of uncompensated electric charge on the cluster surface. In the case of microparticles and the RF trap configuration described above, the uncompensated charge of the localized object can reach 10^5 elementary charges [8,10]. The increase in red shift and additional broadening of the exciton luminescence band of a cluster of nanoplatelets localized in a radio-frequency trap can then be explained by the mechanism of the quantum-confined Stark effect, as it was described for quantum dots in [18]. In addition, the quantum-confined Stark effect leads to spatial separation of an electron-hole pair and, as a consequence, to a decrease in the overlap integral of wave functions of an electron and a hole and a decrease in the quantum yield of luminescence of the main exciton transition [18].

It is also worth noting that the electric intensity created by the confinement field of the trap is of the order of 5 kV/cm, which is not sufficient for manifestation of the quantum-confined Stark effect in nanoparticles.

4. Conclusion

Electrodynamic trapping of charged particles allows for controlled confinement of individual micro- and nanoparticles isolated in space. The approach of electrodynamic trapping of single particles can be used to investigate their spectral characteristics, excluding the influence of the environment. At the same time, localization of particles in the electrical field of electrodynamic traps implies the presence of uncompensated charge on the surface of the investigated samples, which can lead to modification of spectral properties. In the present work, the evolution of luminescence spectra of microclusters of CdSe nanoplatelets with a thickness of 5 monolayers was investigated. Luminescence spectra of the stock solution of nanoplatelets and luminescence spectra of their microclusters measured on a glass substrate and upon loading into a radiofrequency trap were compared. It was shown that the aggregation of nanoplatelets leads to a red shift of the exciton luminescence band and its broadening. This aggregation results in the formation of defect luminescence bands in the long-wavelength region of the spectrum. When microclusters are loaded into the RF trap, an additional red shift and broadening of the main luminescence band is observed, as well as an increase in the relative contribution of defect luminescence to the spectral response. The shift and broadening of the exciton luminescence band and the emergence of defect long-wavelength luminescence were discussed in terms of the change in the dielectric permittivity of the environment, the emergence of mechanical stresses and defects on the surface of nanoparticles during their drying, and the presence of an uncompensated electric charge on the particle surface during localization in the radiofrequency trap. The application of electrodynamic traps for the localization of micro- and nanoparticles can be a promising direction for the development of single-particle spectroscopy techniques.

Acknowledgment

The study was supported by the Russian Science Foundation, grant No. 22-42-05002. The authors express their gratitude to the center for collective use " Nanotechnology" of the ITMO University.

Declaration of interest

The authors declare that they have no conflict of interest.

References

[1] W. Paul. Reviews of modern physics, **62**(3), 531 (1990).

[2] E.A. Vinitsky, E.D. Black, K.G. Libbrecht. American Journal of Physics, **83**(4), 313 (2015).

[3] V. Rybin, S. Rudyi, Y. Rozhdestvensky. International Journal of Non-Linear Mechanics, **147**, 104227 (2022).

[4] C.R. Howder, B.A. Long, D.M. Bell, K.H. Furakawa, R.C. Johnson, Z. Fang, S.L. Anderson. ACS nano, **8**(12), 12534 (2014).

[5] V.V. Rybin, D.P. Shcherbinin, S.S. Rudyi, A.A. Babaev, I.G. Spiridonov, Y.V. Rozhdestvensky, A.V. Ivanov. In *SPIE Future Sensing Technologies 2023*, 12327, 339–342, (SPIE, 2023).

[6] I. Shopa, M. Kolwas, I. Kamińska, G. Derkachov, K. Nyandey, T. Jakubczyk, T. Wojciechowski, A. Derkachova, D. Jakubczyk. Journal of Quantitative Spectroscopy and Radiative Transfer, 108439 (2022).

[7] R.K. Kohli, J.F. Davies. Analytical Chemistry, **93**(36), 12472 (2021).

[8] C. Xiong, H. Liu, C. Liu, J. Xue, L. Zhan, Z. Nie. Analytical chemistry, **91**(21), 13508 (2019).

[9] G. Hars, Z. Tass. Journal of applied physics, **77**(9), 4245 (1995).

[10] V. Rybin, D. Shcherbinin, M. Semynin, A. Gavenchuk, V. Zakharov, A. Ivanov, Y. Rozhdestvensky, S. Rudyi. Powder Technology, 118717 (2023).

[11] T. Galle, M. Samadi Khoshkhoo, B. Martin-Garcia, C. Meerbach, V. Sayevich, A. Koitzsch, V. Lesnyak, A. Eychmuller. Chemistry of Materials, **31**(10), 3803 (2019).

[12] T.K. Kormilina, S.A. Cherevkov, A.V. Fedorov, A.V. Baranov. Small, **13**(41), 1702300 (2017).

[13] S. Cherevkov, A. Fedorov, M. Artemyev, A. Prudnikau, A. Baranov. Physical Review B, **88**(4), 041303 (2013).

[14] B. Abécassis, M.D. Tessier, P. Davidson, B. Dubertret. Nano letters, **14**(2), 710 (2014).

[15] A. Antanovich, A. Prudnikau, A. Matsukovich, A. Achtstein, M. Artemyev. The Journal of Physical Chemistry C, **120**(10), 5764 (2016).

[16] B.M. Saidzhonov, V.B. Zaytsev, R.B. Vasiliev. Journal of Luminescence, **237**, 118175 (2021).

[17] B.M. Saidzhonov, V.B. Zaytsev, M.V. Berekchiian, R.B. Vasiliev. Journal of Luminescence, **222**, 117134 (2020).

[18] S.A. Empedocles, M.G. Bawendi. Science, **278**(5346), 2114 (1997).

Translated by D.Safin