Nanostructured Nonlinear Optical Materials

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Studies of Clusters, Quantum Dots and Nanoparticles

By

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To my parents, wife, son and daughter

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PREFACE

The great attention associated with nanoscience developments in different directions is related to the potential applications of small-sized objects in different areas of science. Among those areas, the nonlinear optics and morphology studies of such objects attracted the efforts of numerous research groups. The significance and timeliness of these topics are the applications in the formation of the efficient sources of coherent extreme ultraviolet radiation, as well as the potential use of non-spherical nanostructured species in optics and optoelectronics.

There are not many books on this topic field and certainly none with the detailed level of research comprising different topics of these studies. My previous book on those topics (R. A. Ganeev, "Nanostructured Nonlinear Optical Materials: Formation and Characterization," Elsevier, 2018) served as an introduction in the field of the optical nonlinearities of nanostructures. The present book ("Nanostructured Nonlinear Optical Materials: Studies of Clusters, Quantum Dots and Nanoparticles") comprises further consideration of novel approaches developed in this area during the last three years. This book can be considered as a continuation of the above publication, which comprises main topics and most recent advances in the optical and nonlinear optical science of different nanostructures. The major difference in the case of the proposed book with respect to previous publications is related to the broader consideration of different aspects of light-nanostructure interactions. Particularly, it contains the collection of most recent studies of the non-spherical nanoparticles and quantum dots, as well as their applications for the analysis of the lower- and higher-order nonlinear optical processes. The necessity in this collection of various studies is related to the compilation of various nanomaterials studies disseminated in different journals. The collection of these studies in a single book helps the reader to learn about the most recent achievements in the morphological, optical, and nonlinear optical features of different nano-species possessing advanced properties. The book describes the advantages achieved during the last few years in the studies of different nanomaterials for nonlinear optical applications involving laser-nanostructure interactions. This book helps to provide an insight into the complex field of nonlinearities in nanostructures. It would certainly help the audience be able to quickly become involved in this field and could also help as a reference book for certain topics.

This book, apart from the above-mentioned advantages, has the following attractive features:

i. Highly topical: focuses on the novel applications of laser-plasma physics such as the development of ultrashort-wavelength coherent light sources based on nanoparticles applications
ii. Balanced coverage: the consideration starting from the smallest species consequently moves towards the largest nanoparticles
iii. Detailed description of methods and approaches: this book details the experimental aspects of nanostructures formation, morphology characterization, optical and nonlinear optical application of nanostructures in liquids, and plasmas.
iv. Interdisciplinary: useful for physicists, material scientists, and engineers interested in the nanomaterials used in plasma physics, laser technology, and spectroscopy.

This book is aimed to support researchers and other readers in their development of useful nanostructures-based optoelectronic devices, as well as in the advanced studies of nanoparticles for the formation of new sources of radiation in different short-wavelength spectral ranges. The researchers involved in the development of new methods in optics and nonlinear optics will be benefited by finding the most recent novelties in this field. The undergraduate students can find interesting information about recent findings of plasma harmonic research. Additionally, the usefulness of the book could be proven by potential applications of the new knowledge developed during the recent times for ultrafast pulses generation using the proposed schemes of plasma-light interaction. Thus the audience may also include those researchers involved in the state-of-art developments of attophysics.

The primary groups of readers comprise researchers in the fields of nanomaterial science and nonlinear optics. The book would be interesting for both academics and professionals in the applied fields, as well as for the high education students and postdocs, who are aimed at further development of their career in the fields of laser-matter interaction. Additionally, any professionals interested in material science could be also benefited from updating their knowledge of new methods of material studies using high-order nonlinear spectroscopy. The potential collective users could be the numerous universities and scientific institutes where the nonlinear optical studies have the connection with plasma physics, ultrashort pulses generation, coherent processes analysis, and laser-matter interactions.

The results presented in this book comprise studies during the last few years. All these amendments of the nanoscience studies could not be realized without the fruitful collaboration of different groups involved in similar research activities. I would like to thank H. Kuroda, T. Ozaki, P. D. Gupta, P. A. Naik, J. P. Marangos, J. W. G. Tisch, M. Castillejo, H. Zacharias, G. S. Boltaev, V. V. Kim, O. V. Ovchinnikov, A. I. Zvyagin, N. V. Kamanina, C. Guo, K. Zhang, Y. Fu, W. Yu, and A. S. Alnaser for the long-lasting collaboration.

The inspirers of this activity are my wife Lydia, son Timur and daughter Dina, who help me overcome various obstacles of life.

Rashid A. Ganeev
Riga, Latvia
March 2022

INTRODUCTION

The small-sized objects for a long period attracted great attention associated with nanoscience developments in different directions. Numerous journal articles and tens of books appear yearly to maintain the science of nanomaterials at the highest state of development. Each of the new books comprises some particular aspects since it is hard to imagine how the whole area of this enormously broadened field of science can be compiled in a single publication. These monographs or collections of chapters restrict the topics of nanoscience subjects. In the present book, we also follow those principles and describe a few groups of studies, which for a long time attracted the attention of this author.

There is a classical book relevant to the nonlinear optical processes in gaseous media [1]. Another book [2] is related to the spectroscopic details of nonlinear optical studies. Separate chapters of the book [3] were also related to the above-described processes. Some details of plasma properties relevant to those at which the resonance processes play an important role are discussed in [4]. Other related titles relevant to some topics considered in the present book include [5-7]. However, neither of them covers a broad area of the optical nonlinearities of different nanostructures.

There are not many books on this topic field and certainly none with this detailed level of research. The only book that covers some of these parts is [8]. However, ten years from the publication of this book, many new approaches emerged, which are discussed in the present book. Some low-order nonlinear optical studies of nanoparticles are collected in [9].

Finally, the previous book of this author [10] served as an introduction in the field of nanostructures, as well as the optical and nonlinear optical research involving nanomaterials. The present book comprises further consideration of novel approaches developed in this area during the last three years. This book can be considered as a continuation of the above publication and contains main topics and most recent advances in the optical and nonlinear optical science of different nanostructures. The major difference in the case of this book with respect to previous publications is related to the broader consideration of different aspects of light-nanostructure interactions. Particularly, it comprises the collection of most recent studies of the non-spherical nanoparticles (NP) and quantum dots, as well as their applications for the analysis of the lower- and higher-order nonlinear optical processes.

This book contains the analysis of recent studies of the morphological, optical, and nonlinear optical properties of nanostructured materials. It compiles studies of large molecules, thin films, clusters, quantum dots (QDs), and NPs reported during the last three years. The book is structured by dividing the text into nine chapters, each containing the characterization of dyes, fullerenes, and perovskites, morphology and optical properties of elliptical, triangular, and cube-like nanoparticles, analysis of the nonlinearities of oxidized nanostructures, studies of third-harmonic generation in nanoparticles, and analysis of the high-order harmonics produced in nanostructures, like clusters and quantum dots.

The important topics include the studies of small-sized nanoparticles (quantum dots) as the sources of coherent extreme ultraviolet radiation, analysis of their low-order nonlinear optical properties, formation and characterization of non-spherical nanoparticles (i.e. triangles, ellipsoids, and square-like species) during laser ablation of different materials in liquids. Other important topics include the comparison of the optical and nonlinear optical responses of various nanostructured species. Below we briefly describe the structure and basic principles of the collection in this book the reported studies of nonlinear optical properties of nanostructured materials. The detailed references to the topics of those studies will be presented in the corresponding chapters. Here we just underline the basic principles of our analysis of different materials and processes under consideration.

Dyes. The high-frequency Kerr effect, two-photon absorption (2PA), saturated absorption (SA), multi-photon absorption, and reverse saturated absorption (RSA) are the main nonlinear optical processes during the propagation of ultra-short laser pulses through large-sized molecules like dyes. Variations of the nonlinear optical characteristics of dyes depend on such factors as the intensity of probe pulse, solvents, temperature, etc. The irreversible changes in dyes lead to variations of their nonlinear optical parameters, such as saturation intensities, nonlinear absorption coefficients, etc. To analyze the complex behaviour of the dyes one has to measure the nonlinear optical parameters, such as the 2PA, SA, RSA, and in some cases the nonlinear refraction using various laser sources. The latter process (high-frequency Kerr effect induced nonlinear refraction) rarely plays a decisive role compared to other nonlinear optical processes, while the SA was frequently realized in many dyes. The dynamics of singlet-singlet ($S_1 \rightarrow S_0$) relaxation of dye solutions is determined by the features of dye and solvent. The population of dye molecules to higher singlet states S_n ($n > 2$) opens decay channels mainly to the S_1 state, S_0 state, triplet states, and molecular decomposition. Frequently, as a consequence, the bleaching of dyes is observed due to SA of the intermediate state.

Thin NP-contained films. Thin-film materials have gained great attention due to their various potential applications. Particularly, the unique properties of low-dimensional materials necessitated analysis of the optical and nonlinear optical features of thin films, which could be useful in various fields of optoelectronics and laser physics. The availability of laser sources with ultra-short pulse duration allowed a considerable increase in the laser intensities used in those experiments, therewith presenting the opportunity to investigate thin materials close to their optical breakdown intensities (10^{12}-10^{13} W cm^{-2}). Particularly, the results of nonlinear refraction studies of C_{60} thin (100 nm) films have shown that their large third-order susceptibility causes strong self-focusing with a nonlinear refractive index (γ) exceeding 2×10^{-9} cm^2 W^{-1}. Notice that fullerenes dissolved in toluene at a similar concentration showed two orders of magnitude less nonlinear susceptibility. Chalcogenide films also demonstrate considerable values of optical nonlinearities. Studies of the nonlinear absorption coefficients (β) of $As_{20}S_{80}$ (3×10^{-6} cm W^{-1} at the wavelength $\lambda = 532$ nm) and $3As_2S_3/As_2Se_3$ (10^{-7} cm W^{-1} at $\lambda = 1064$ nm) have shown that some thin (200 nm) chalcogenide films possess large third-order nonlinear susceptibility. Even in the case of thick media containing thin layers of active elements, such as nanoparticles, these layers have demonstrated enhanced nonlinear absorption and refraction. In particular, thin (60 nm) layers of copper nanoparticles implanted in silica glass caused strong nonlinear absorption (~10^{-6} cm W^{-1}). Furthermore, the nonlinear refraction of CdS thin films at $\lambda = 532$ nm was measured to be -5.2×10^{-11} cm^2 W^{-1}, while the measured value of the nonlinear refractive index of bulk CdS in this spectral region was reported to be -6×10^{-13} cm^2 W^{-1}, i.e. two orders of magnitude smaller than former structure. A considerable increase in the nonlinearity of thin films in those and other studies makes their nonlinear optical features close to those of nanoparticles.

The quantum confinement effect allows distinguishing the parameters of nanoparticles with regard to the bulk materials. A further search of prospective materials in nanoparticle form, their preparation, and application of quantum confinement are of considerable importance. Meantime, the unique properties of low-dimensional materials have ignited numerous studies of their characteristics. The investigations of these films have shown their prospects as optical limiters. One can investigate thin (of the order of a hundred nanometres) films. Particularly, gold nanocomposites have tremendous applications in various fields due to the influence of their surface plasmon resonance (SPR) on optical properties. In the past decade, researchers have demonstrated the potential applications of gold NPs using different lasers.

During the last decade, there has been an interest in the nonlinear optical features of chalcogenide thin films. Significant efforts have been made in the syntheses of metal chalcogenide nanocrystals (NCs) due to their attractive size-tuneable optical properties and possible applications in various technological fields including light-emitting diodes, photovoltaic devices, and fluorescent biological labels. Several other sulphide precursors were subsequently reported, but elemental sulphur has been the most widely used as a less air-sensitive precursor in the syntheses of metal sulphide NCs. Decreasing the size of such materials allow to tune their physical properties and observe new phenomena. Taking this into account, newly synthesized semiconductor nanoparticles should be studied under different conditions to understand the nonlinear optical mechanisms and use their attractive properties for practical applications. Further analysis of linear and nonlinear optical features of the thin films comprising metal sulphide NCs is important for their possible use in various fields of optoelectronics and laser physics. To verify the generalized effective-medium theories for linear and nonlinear optical properties of metal sulphide NPs and QDs one has to analyze the linear and nonlinear susceptibilities of the constituent materials. Ag_2S QDs are non-cadmium and non-lead fluorescent nanomaterials developed in recent years, and Ag_2S QDs are known for displaying large optical nonlinearities. Ag_2S QD thin films can have even higher nonlinearities.

Perovskites. Due to its unique crystal and electronic structure, the large molecular ABX_3 materials have excellent photoelectric properties, which can be applied to a series of research optoelectronic devices such as solar cells, light-emitting diodes, lasers, field-effect transistors, and photodetectors. The perovskite materials appeared as polycrystalline thin films, nanowires, nanosheets, nanorods, quantum dots, and single crystals. In the above morphology, the perovskite crystal has more excellent electron transport properties due to its own fewer defects and grain boundaries, which reveals that the application of such material would be a promising way to improve the performance of devices such as solar cells and detectors. Moreover, many studies have shown that the quantum yield of perovskite material can reach 70-90%, indicating that it also has good luminescent properties.

In recent years, organo-lead halide perovskites, such as methylamino lead halide perovskites ($MAPbX_3$, MA=$CH_3NH_3^+$, X=Cl^-, Br^-, or I^-) have attracted widespread attention due to their attractive optical and low-temperature solution processibility. $MAPbBr_3$ and $MAPbI_3$ used for high-efficiency solar cells or optoelectronic devices have been widely studied due to their narrow band gap and wide adsorption range located at visible or even near IR range. Compared to those two materials, $MAPbCl_3$ was rarely studied due to its wide band gap and specific adsorption properties. Most research on $MAPbCl_3$ was mainly focused on the growth of single crystals, the structural characterization, and phase transitions with the change of the environment. Meanwhile, the single-crystal $MAPbCl_3$ demonstrates its attractiveness due to its intrinsic structural features. Until recently, the study of perovskite materials by Raman method mainly focused on its structure properties or phase transitions, and Raman spectroscopy only plays a role in the structural characterization of the perovskite materials. However, Raman technique is a very significant method in the interfacial charge transfer property studies and the intensive exploration of the correlation between the interfacial optical or photo-electronic and Raman properties of the perovskite materials must be crucial for applying perovskite materials in photo-electronic devices.

Optical nonlinearities of NPs. The study of optical limiting with metallic nanoparticles has attracted a considerable amount of attention because of the increasing demand for protection against laser threats to sensors and human eyes. One major approach to be through the use of optical limiters. Metal NPs and QDs have attracted much attention due to their high surface-to-volume ratio and small particle effect. These nanocomposites have special nonlinear optical behaviour as compared to the bulk materials. For instance, optical nonlinearities and optical limiting (OL) effects of the nanocomposites of the metals can be significantly enhanced by increasing the number density and low size of metal particles. These particles display a drastic optical extinction due to nonlinear scattering. Among metal nanoparticle limiters, gold and silver nanoparticles have received special attention because they both show a broad SPR absorption band in the visible region, which is substantially different from the absorption of the corresponding bulk metals in this region. One can anticipate that variations of the sizes of NPs can significantly enhance OL. OL behaviour of silver nanoparticles with different sizes and shapes was investigated and compared to the optical limiting performance of conventional carbon black suspension. It was found that the optical limiting effect is strongly particle size-dependent and the best performance is achieved with the smaller particles.

The majority of studies have been based on the formation of various NPs by focusing the laser pulses on the metal targets immersed in liquids.

Due to the resonance effect arising from the SPR of some NPs their size and shape can be controlled by laser irradiation in various solvents. Advantages of this method are the high purity of the NPs, variety of materials, and the in-situ dispersion of NPs in different liquids tolerating safe and stable control of the colloids. Also, the solvent molecules surrounding NPs can protect them in some cases from aggregation due to their viscosity and other properties. One can anticipate the crucial influence of the wavelength and pulse duration of laser radiation on the size and shape of produced NPs.

Different mechanisms are responsible for the nonlinear optical properties of small-sized species, which include saturable absorption, two-photon absorption, optical limiting, and optical Kerr nonlinearities. SA has a profound influence on the overall nonlinear optical response at sufficiently high power of employed laser pulse. Another phenomenon called reverse saturable absorption may counteract the absorption saturation processes. RSA occurs as a result of large absorption by the nonlinear absorber at high laser energy via excited-state absorption because of the depletion of the ground state with the increase of the incident laser energies. The performance of small-sized nonlinear materials is limited by the accompanying linear absorption at low input energy. In this case, the incident photons may be further absorbed by excited states when their population gets large enough in an excited state. These processes not only depend on the intensity of the incident photon but also on the frequency of the incident photon, which plays an important role in their nonlinear optical properties depending on the resonant or nonresonant transitions. Apart from nonlinear optical properties of nanomaterials, many-body interactions in condensed matter and molecular systems have been of great concern because the properties like electrical, thermal conduction, superconductivity to Raman scattering, polaron formation are highly affected by an ultrafast process such as electron-phonon interactions. There has been a great advancement to understand the role of electron-phonon interaction on the properties of low-dimensional systems. A vast literature is presented on electron-phonon interaction in NPs. The interaction of NPs with short laser pulses undergoes various ultrafast processes such as electron-electron coupling, electron-phonon coupling, and phonon-phonon coupling. Thus many studies have focused on the dissipation of the acoustic vibration in noble NPs based on the size, shape, and surrounding mediums.

The performance of materials at the nanoscale is totally different from their macroscopic behaviour. Many factors, such as laser pulse duration and fluence, type of surrounding media, the temperature of the liquid, and characteristics of irradiated targets, influence the properties of NPs. It was shown that the morphology and size of synthesized particles can cause variations of different macroscopic properties of NP-containing substrates and suspensions. Besides that, the formation mechanism of Al NPs should be investigated under different regimes of the bulk target ablation.

Non-spherical NPs. The oxide of copper, cupric oxide (CuO), and cuprous oxide (Cu_2O) are typical representatives of such species. Compared to macro-targets, the properties of ellipsoidal micro/nano-sized CuO/Cu_2O are quite different due to the increase of surface/volume ratio and the influence of the quantum size effect. As a semiconductor material, CuO is environmentally friendly, low-cost, and has numerous applications in the field of photovoltaics because of its high absorption of the solar spectrum and high carrier concentration. In addition, applications based on CuO/Cu_2O micro/nanoparticles and micro/nanostructures, electrochemical materials, and super-capacitors have received a great amount of attention, also. Triangles of Al NPs have a role in propellants and pyrotechnics because they can provide additional heat release during exothermic oxidation. The optical character of Al spherical and triangle NPs also contributes to their application for solar cells, optoelectronic devices, metal-enhanced fluorescence devices, and broad-band wire-grid polarisers. The interest in the study of the optical and structural properties of non-spherical ZnO nanostructures is due to the low cost, nontoxicity, and stability of the ZnO nanomaterials. The second- and third-order nonlinear optical properties of ZnO NPs have been applied in biomarkers and optical imaging. The noncentrosymmetric structures of ZnO NPs can exhibit relatively strong second harmonic generation (SHG). The SHG in nanocrystallites can be used in laser spectroscopy, frequency converters, and LEDs, as well as in bioimaging, and chemical sensing. Additionally, the enhancement of the third-order nonlinearity of ZnO nanorods with regard to the bulk and thin films was observed. Laser ablation is useful for the preparation of non-spherical nanoparticles from bulk metal or semiconductor targets. Particularly, the influence of surrounding liquid media and the ablating conditions resulted in the fabrication of Cu nanoparticles (NPs) in acetone and CuO NPs in chloroform, which demonstrated the urchin-like shapes.

Quantum dots. The quantum dots of semiconducting materials took attention due to their potential applications as biomarkers and sensors in medicine, as well as in the processes of photosynthesis. The optical properties of II-IV semiconductor nanoparticles (i.e. nanosized crystallites, QDs), as well as the quantum confinement effect, were observed in semiconductor QDs. The propagation of laser radiation through the materials containing Ag_2S QDs induces various nonlinear optical processes, which could be useful in photonics. It has been reported that the visible light being transmitted through such structures becomes limited particularly due to RSA caused by two-photon optical transitions that involve excitation of the energy levels of Ag_2S photoluminescence centres. The presence of thermal lens in the case of long probe pulses significantly complicated the whole pattern of nonlinear optical properties of these species, while short laser pulses caused the two-photon absorption. Note that the sole role of RSA in the observed nonlinear absorption still remains disputable since the direct 2PA could also be properly matched with the probe pulse wavelength and band gap of Ag_2S QDs. Particularly, in the case of some other QD sulphides, such as ZnS nanocrystallites, the observed nonlinear absorption has resulted from 2PA. Femtosecond pump-probe studies show the two-photon absorption above 630 nm and slow-decaying excited state absorption below 600 nm. In experiments, open-aperture z-scans demonstrate strong 2PA at the wavelength of $\lambda = 532$ nm, with a nonlinear absorption coefficient of ZnS QDs in the range of 10 to 100 cm GW^{-1}. Transient absorption and open-aperture z-scan data have shown both RSA and strong 2PA in the case of Ag_2S nanocrystallites as well. In the nanosecond timescale, a large enhancement of 2PA was observed with the growth of Ag_2S nanoparticles concentration. Similarly to ZnS, it was suggested that for $\lambda > 670$ nm one can expect a larger influence of 2PA, while for $\lambda < 670$ nm the RSA could play the dominant role in nonlinear absorption.

One of the perspective semiconductor-based materials for these tasks is the silver sulphide, which initially was applied as a photosensitizer in photography. Silver sulphide QDs primarily attractive due to their potential application in different photovoltaic devices, photoconductors, and electrochemical storage cells. These QDs belong to the class of nanocrystallites with a lattice distance of ~0.3 nm. The colloidal Ag_2S QDs dispersed in gelatine are characterized by the formation of crystal nuclei with the size of ~2.0 nm and a shell of gelatine and its complexes with various components, such as dyes. Silver is not a toxic metal unlike many other heavy metals hence Ag_2S QDs are suitable for applications in the biomedical field. The use of Ag_2S QDs would for instance enable one to image and treat cancerous cells simultaneously. This should drastically reduce the time and number of invasive procedures. Note that the sole role of RSA in the observed nonlinear absorption still remains disputable since the direct two-photon absorption (2PA) could also be properly matched with the probe pulse wavelength and band gap of some QDs. Particularly, in the case of some other QD sulphides, such as ZnS nanocrystallites, the observed nonlinear absorption has resulted from 2PA. It can be assumed that for λ > 860 nm one can expect a larger influence of three-photon absorption (3PA) in ZnS QDs, while for λ < 860 nm the RSA could play the role in nonlinear absorption, while the consideration of the role of 2PA could be also reasonable.

Third harmonic generation. There are several reports on the use of THG as a characterization scheme for generated mono- and nanoparticles in plasma. This was achieved by changing the arrival time of the excitation pulses relative to the heating pulses. Measurements based on the time delay of the third harmonic radiation showed the presence of large aggregates formed by laser ablation, which can also be further analyzed when they are deposited on nearby substrates. The plasma created during laser ablation contains electrons, atoms and molecules, ions, neutrals, clusters, quantum dots, and NPs. Ni plasma formation in the air can serve, particularly, as a nonlinear medium for harmonic generation in the plasma containing NPs. The formation of NPs during plasma formation in ablation plume has been shown to significantly influence the efficiency of high-order harmonic generation. At the same time, Ni NPs can be applied to study the low-order harmonic generation in cuboids structures. Increasing the pulse energy (i.e. the number of photons in the pulse) to 10 mJ allows the generation of harmonics with pulse energy up to several tens of µJ at a laser repetition rate of 10 Hz. Alternatively, using a large number of photons per second (i.e., a high pulse repetition rate) at low pulse energy can also lead to an increase in the number of coherent photons in the UV range. In particular, 100 kHz class lasers produce ~100 W of the average power of femtosecond pulses, which in turn can be converted to a third harmonic with an average power of 0.1 W.

High-order harmonic generation in NP-contained media. Nanostructured and ion-implanted semiconductor targets paved a path to produce strong high-order harmonics as compared to un-patterned samples. The dynamics of plasma formation, in that case, can be considered as follows. The material directly surrounding the NPs is a polymer (epoxy glue), which has a considerably lower ablation threshold than the metallic materials. The NPs absorb the laser pulse energy and pass the thermal energy to the surrounding media. Therefore, the NPs-carrying polymer begins to ablate at relatively low intensities, resulting in the lower laser fluence required for the preparation of the appropriate nonlinear medium for the high-order harmonic generation (HHG). This feature allowed for easier creation of the optimum plasma conditions, which resulted in better HHG conversion efficiency, particularly, from the Au NPs-containing plume compared to the plasma from the bulk target.

The application of different pumps of plasmas allows exploring various new schemes of high-order harmonic generation using ultrashort laser pulses. Particularly, the application of mid-infrared femtosecond pulses for HHG in laser-induced plasmas (LIP) using a two-colour pump allows further filling of the extreme ultraviolet range with odd and even harmonics. In the case of HHG in gases, this approach has been demonstrated in numerous studies using 800-nm-class lasers. Another approach, which considers harmonic generation as a method of nonlinear spectroscopy, has recently been emerged in the case of HHG in narrow and extended LIPs. Further developments of plasma HHG using this approach could be related to the search of single harmonic enhancement and application of nanoparticle-containing plasmas.

Among different methods of harmonic enhancement, one can admit the formation of the quasi-phase-matching (QPM) conditions between the driving and generating waves during HHG in NP- and QD-contained plasmas. This mechanism has been originally demonstrated in the visible range using solid materials. Application of this concept in the case of the shorter-wavelength region requires the conditions when the absorption of generating harmonic waves becomes insignificant with regard to the enhancement of this radiation at the conditions when the transfer of energy from driving to harmonic waves occurs at similar phase velocities.

Generation of harmonics using quantum dots. Quantum dots play an important role in different technological fields. One interesting application is the formation of QD-containing media for frequency conversion of ultrashort laser pulses from the IR towards the extreme ultraviolet range. Previous studies on HHG after ablation of small-sized nanoparticle-containing targets have revealed the advantages of such species for frequency conversion in the XUV range. A larger cross-section of recombination and the possibility of recombination of an accelerated electron with the parent particle through either recombination with the same or a neighbouring atom, or with the multi-atomic particle as a whole, were considered as the most probable reasons for the growth of HHG yield in such plasmas. One explanation was based on the disintegration of larger species into small clusters, which probably could reach the interaction area at the short delays employed. However, no sufficient confirmation of this assumption has been provided. Taking into account the anticipated velocities of atoms, molecules, and ions ($\sim 1\times10^4$ m s^{-1}), QDs ($\sim 1\times10^3$ m s^{-1}) and nanoparticles [$(1\text{-}5)\times10^1$ m s^{-1}] of the same material one can expect their arrival in the region of the femtosecond laser beam propagation a few tens of nanosecond, a few hundreds of nanosecond, and a few tens of microsecond from the beginning of ablation, respectively. Small-sized aggregates subject to intense laser pulses produce a strong low-order nonlinear optical response (e.g., nonlinear refraction and nonlinear absorption), as well as the emission of coherent extreme ultraviolet radiation through the harmonic generation. Previous studies of the HHG from such objects were limited to the clusters of Ar and Xe being formed in high-pressure gas jets due to rapid cooling by adiabatic expansion, as well as to the relatively large nanoparticles ablated from the bulk surfaces.

Concluding the introduction to this book the author would like to underline a few features of this collection, which can be useful in different fields of science. The academic audience of this book is likely works in the field of nanostructures and optical nonlinearities. This is a very broad field, with many researchers have published journal articles on this subject. The novelty in laser-nanoplasma interaction shown in this book would attract various groups of researchers, particularly those involved in applications of lasers and the development of short-wavelength coherent sources.

This book is organized as follows. In Chapter 1, we analyze the saturated and two-photon absorption of various classes of large molecules like heterocyclic dyes, as well as nanostructured dye suspensions. Nonlinear absorption of thiazine, xanthene, and carbocyanine dyes, peculiarities of the nonlinear optical absorption of methylene blue and thionine in different solvents, nonlinear optical characterization of colloidal solutions containing dyes and Ag_2S quantum dot associates, and nonlinear optical absorption in mixtures of dye molecules and ZnS nanoparticles among the topics of a few sections. Nonlinearities of thin films containing complex and nanostructured materials comprise the content of Chapter 2. Among the subjects under consideration, the strong nonlinear absorption in perovskite films, the nonlinear optical studies of gold nanoparticle films, and the low- and high-order nonlinear optical properties of Ag_2S quantum dot thin films. Chapter 3 formulates the principles of characterization of the nonlinear optical properties of perovskites. We discuss the charge transfer effects on resonance-enhanced Raman scattering for molecules adsorbed on single crystalline perovskite, femtosecond laser-induced micro- and nano-structures with significantly enhanced fluorescence on $MAPbBr_3$ single crystal surface, and provide the comparative analysis of optical limiting effects in metal nanoparticles and perovskite nanocrystals. Laser-synthesized nanoparticles formation and characterization is the main subject described in Chapter 4. We will consider the strong third-order optical nonlinearities of Ag nanoparticles synthesized by laser ablation of bulk silver in water and air, laser ablation-induced synthesis and nonlinear optical characterization of titanium and cobalt nanoparticles synthesized by laser ablation of bulk materials, the effect of nanoparticle sizes on the saturable absorption and reverse saturable absorption in silver nanostructures, and discuss the mechanism of laser-assisted generation of aluminium nanoparticles, their wettability and nonlinearity properties.

Chapter 5 describes the morphological and optical characteristics of nanoparticles. Among the topics considered here are the structural variations during the aging of the particles synthesized by laser ablation of copper in water, pulse duration and wavelength effects of laser ablation on the oxidation, hydrolysis, and aging of aluminium nanoparticles in water, formation, aging, and self-assembly of regular nanostructures from laser ablation of indium and zinc in water, and effect of different hardness and a melting point of the metallic surfaces on structural and optical properties of synthesized nanoparticles. In Chapter 6, we focus on the size- and shape-dependent properties of nanoparticles. Among them are the size-dependent off-resonant nonlinear optical properties of gold nanoparticles and demonstration of efficient optical limiting, nonlinear optical characterization of copper oxide nanoellipsoids, and low-order nonlinear optical studies of ZnO nanocrystals, nanoparticles, and nanorods. Third harmonic generation in nanoparticle-contained media is considered in Chapter 7. We analyze the reports on the ablated nickel nanoparticles and third harmonic generation and optical nonlinearities in those species, as well as third and fifth harmonics generation in air and nanoparticle-containing plasmas using 150 kHz fibre laser. Chapter 8 collects the most recent studies of the high-order harmonics generation in nanoparticles. Among them are the high-order harmonic generation in Ag, Sn, fullerene, and graphene nanoparticle-containing plasmas using two-color mid-infrared pulses, high-order harmonic generation in Au nanoparticle-contained plasmas, and effects of laser-plasma formation on quasi-phase-matching of high-order harmonics from nanoparticles and atoms. High-order harmonics generation in the smallest structures (clusters and quantum dots) is discussed in Chapter 9. Those studies include the analysis of the role of carbon clusters in high-order harmonic generation in graphite plasmas, effective high-order harmonic generation from metal sulphide quantum dots, and high-order harmonic generation using quasi-phase-matching and two-colour pump in the plasmas containing molecular and alloyed metal sulphide quantum dots. Finally, a summary of discussed issues presents the whole pattern of the studied areas.

References to Introduction

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CHAPTER 1

OPTICAL NONLINEARITIES OF LARGE DYE MOLECULES AND NANOSTRUCTURED DYE SUSPENSIONS

Dyes have found their applications in various areas of laser physics. These include frequency conversion of laser radiation in dye vapours, Q-switching and mode-locking in various lasers, the study of bleaching effects under the action of pulses of different duration, analysis of lasing, etc. The lasing using dyes was one of the preferable applications of these media. All these applications assume that the optical and nonlinear optical properties of dyes play an important role during their interaction with laser pulses. The nonlinear absorptive features of dyes find the application in the formation of ultrashort pulses, while the concurrence of various types of these processes may lead to different scenarios during propagation of short or long laser pulses through such media.

Nonlinear optical properties of organic dye vapours were studied for the first time more than forty years ago using benzene vapours (C_6H_6) wherein frequency conversion was carried out [1], as well as in acetylene vapours (C_2H_2) wherein third harmonic generation in ultraviolet range was realized [2]. It was shown that the nonlinear susceptibilities of organic dye molecules with double-conjugated bonds and delocalized π-electrons are comparable with the resonance-enhanced nonlinear susceptibilities of atoms [3,4]. Such molecules with double-conjugated bonds are highly attractive as nonlinear media. The calculations reported earlier have shown that some organic dyes (tetracene, paraterphenyl, pentacene) possess considerable third-order susceptibilities [5].

There is also interest in the studies of the nonlinear refraction and nonlinear absorption in the associates of the dyes of different classes (xanthenes, thiazines, carbocyanines, quinolines) and the metal sulphides quantum dots (QDs) stabilized in gelatin using pulses of different duration. The interest in sulphide-based QDs (ZnS, As_2S_3, CdS, ZnSe, CdSe, Ag_2S, etc.) was due to the high third-order nonlinearities they possess. The dependence of optical absorption in QD-contained solutions demonstrates a considerable departure from the Lambert law. Particularly, in the case of some other QD sulphides, such as ZnS nanocrystallites, the observed nonlinear absorption resulted from 2PA. It can be assumed that for $\lambda >$ 860 nm one can expect a larger influence of three-photon absorption in ZnS QDs, while for $\lambda <$ 860 nm the RSA could play the role in nonlinear absorption, while the consideration of the role of two-photon absorption (2PA) could be also reasonable.

In this chapter, we analyze the studies of different dyes possessing strong nonlinear optical responses. We also discuss the comparative studies of the associates of dyes and quantum dots.

1.1 Nonlinear absorption of thiazine, xanthene, and carbocyanine dyes

There is a group of dyes, which can be analyzed from the point of view of the concurrence of two or more nonlinear absorptive processes, while some of those processes become suppressed. Those dyes belong to different classes [thiazine (thionine), xanthene (erythrosine), and carbocyanine (3,3'-di-(γ-sulphopropyl)-4,4',5,5'-dibenzo-9-ethylthiacarbocyaninebetaine pyridinium salt, DEC)].

Those dyes have different chemical structures and absorption in the near-infrared, visible, and ultraviolet ranges (see Fig. 1.1 showing their absorption spectra in different ranges, the corresponding images of the cells filled with those dyes, and the structural formulas of dyes). Particularly, the structures of thionine existing in different solvents were characterized using spectroscopic methods in Ref. [6]. The wavelengths of the peaks of optical absorption of thionine and erythrosine differ from each other, particularly due to the tendency in formation of the dimers (D) [7], while DEC may form the D- и J-aggregates [8]. There are different conditions for the formation of triplet states in the case of monomers and dimers of these dyes, while the cross-sections of transitions and the lifetimes of excited singlet and triplet states differ from each other.

Meanwhile, no systematic studies of the nonlinear optical properties of those dyes except erythrosine were reported. Erythrosine has a quantum yield of triplet state almost equal to unity and is expected to undergo the following photophysical processes. Absorption of optical energy from the probe pulses produces excited singlet states, which then relax completely into the triplet manifold through the intersystem crossing. The metastable T_1 state has a lifetime ranging from less than 1 ms to several hundred ms depending on the solvent and the dye concentration [9]. Previously, nonlinear optical absorption effects in erythrosine were analyzed using the