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Optical Nanospectroscopy

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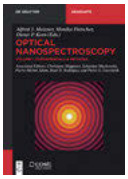

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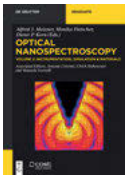

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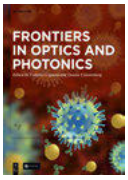

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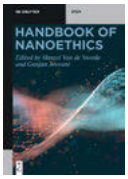

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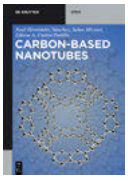

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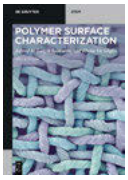

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Optical Nanospectroscopy

Applications

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Editorial for the textbook Optical Nanospectroscopy

Welcome to the three-volume textbook "Optical Nanospectroscopy". This book offers a comprehensive overview over the emerging research field of nanospectroscopy, reviewing the theoretical basis of optics and spectroscopy, relevant experimental and numerical techniques, and a snapshot of state-of-the-art applications of nanospectroscopy, as well as novel developments.

Optical spectroscopy is the study of the interaction between electromagnetic radiation and matter, to reveal its optical and electronic properties and chemical structure. Nanospectroscopy can be both the spectroscopy of very small objects down to single molecules or atoms or spectroscopy performed with very high spatial resolution from regions much smaller than the wavelength of the radiation. Nanospectroscopy is a rather young and interdisciplinary field of science that developed over the past 20 years, based on new theoretical insight into the field of light–matter interaction and stimulated by new powerful experimental capabilities leading to seminal breakthroughs in single-molecule spectroscopy, near-field optical microscopy, and nano-optics.

The motivation to advance the field originates from the need to resolve increasingly smaller structures with ever finer details on the nanometer length scale, which has been made possible by the tremendous recent advances in nanoscience and associated technologies. Imaging small complex structures with a spatial resolution of a few nanometers or even better and revealing their chemical structure or their local optical, electronic, and chemical properties is of supreme importance in microelectronics, material science, engineering, nanotechnology, chemistry, life science, and medicine.

This book is based upon work from the COST Action MP1302 Nanospectroscopy, supported by COST (European Cooperation in Science and Technology, www.cost.eu). COST is a funding agency for research and innovation networks. Its Actions help connect research initiatives across Europe and enable scientists to grow their ideas by sharing them with their peers, boosting their research, their careers, and innovation.

The COST Action Nanospectroscopy took place from 2013 to 2017. With the support of COST a network of experts in optical nanospectroscopy from all across Europe and beyond was established. More than 230 principal investigators plus their group members from 35 countries combined forces in discussing the state-of-the-art and working collectively to forge the future of optical nanospectroscopy. The interdisciplinary groups contributed complementary expertise in nanostructure synthesis or nanofabrication, microscopic and spectroscopic techniques, data analysis, and numerical simulations and theoretical modeling, as well as commercial instrumentation and end-user applications of nanospectroscopy. This network therefore offered a unique pool of expertise to draw from for the contents of this book. Many participants, both leaders in the field and early-stage researchers, contributed their specific expert knowledge to the three volumes. At the same time the editorial team took care that the first two

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volumes follow the coherent outline of a textbook rather than forming a collection of articles. For this purpose, the current state of the field of optical nanospectroscopy was carefully mapped in a meta-review, and a table of contents covering the relevant information was drafted to be filled by the contributors [1].

Since nanospectroscopy is a fast-developing research field with contributions from many interdisciplinary research areas having far-reaching consequences for the future of nanoscience and technology, it is imperative that a new generation of scientists and interested individuals is trained in the topic, taking into account relevant aspects from physics and chemistry as well as its potential impact on biology, medicine, engineering, consumer products, safety and security, or even cultural heritage studies. The three volumes of this book therefore aim at readers with a basic science training, e. g., students of the natural sciences at the Bachelor or Master level, or interested readers that are entering this field and desire or need to learn more about this fascinating topic with its ever-increasing range of applications and fundamental discoveries.

In the first volume the fundamentals of optical nanospectroscopy are treated. The outline starts from the basics of light–matter interaction, continues with an overview of optical spectroscopies in general, and ends with specific techniques in nanospectroscopy that either offer nanoscale resolution or are addressed to nano-objects. In the second volume, theoretical and experimental methods essential for nanospectroscopy are covered. The necessary instrumentation is explained, insights into simulation tools for modeling nanospectroscopic processes are given, and a wide variety of nanomaterials that are typically being investigated by nanospectroscopy are introduced. Finally, in the third volume individual authors highlight current examples how optical nanospectroscopy is and may be exploited in modern photonics, sensing, e. g., in environmental monitoring, the life sciences, medicine, or diverse nuanced applications in material, chemical, and biological sciences.

The making of this book was a major milestone of the COST Action Nanospectroscopy coordinated by the undersigned and would not have been possible without the time, support, and dedication of many contributors. We would like to express our gratitude and thanks to all people involved: The international textbook team Pierre-Michel Adam, Antonio Cricenti, Volker Deckert, Johannes Gierschner, Pietro Gucciardi, Christiane Höppener, Ulrich Hohenester, Mile Ivanda, Florian Kulzer, Teresa I. Madeira, Jana Nieder, Raul Rodriguez, Ludovic Roussille, Manuela Scarselli, Evgeniya Sheremet, Dietrich Zahn, and Dai Zhang, all the authors and contributors of the book, the members of the COST Action Nanospectroscopy, and especially of the Working Group 4, for fruitful discussions, the COST Association for supporting the Action, Gabriele Thomas for editing support, Konrad Kieling for encouragement, as well as the editorial team at De Gruyter, especially Nadine Schedensack, for valuable assistance throughout the whole process of creating this book. We hope you enjoy reading about the art of optical nanospectroscopy.

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Tübingen, November 2022

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cost EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY

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Editorial for Volume 3: Applications

The third volume "Applications" is the final volume of the three-part book "Optical Nanospectroscopy". While the first two volumes are clearly structured in the style of a textbook and designed to address students and interested individuals entering the field, the third volume has a different character in that it illustrates individual modern applications of nanospectroscopy in a collection of articles. The chapters represent the work and perspectives of the respective authors and are curated to cover a wide range of relevant topics.

Once nanospectroscopic methods have been thoroughly mastered, they can be profitably employed to deliver new insights into fundamental complex physical, biological, or chemical processes and material properties. Likewise they can be exploited to target a cornucopia of everyday questions of high societal relevance. Nanospectroscopy shows exciting promise and vast possibilities in such varied fields as sensing, quantum information, food safety and authentication, cultural heritage, or optoelectronic devices. With spectroscopic technologies increasingly moving from the research stage to the marketplace, impressive progress has been made in application areas from early-stage cancer detection to trace detection in liquids. Moving from conventional optical spectroscopy to nanospectroscopy has a great potential to overcome analytical problems and disadvantages by boosting limits of detection, multiplexing approaches, and spatial resolution to the single-nanometer scale. While many nanospectroscopic techniques are still mostly used by specialists and limited to laboratory use, real-world applications are growing and conquering new realms. The objective of the present volume is thus to highlight such directions and review the state-of-the-art in relevant fields.

The structure of the volume is grouped into different application areas: after a general introduction (Chapter 1), it takes a closer look at nanospectroscopy for new photonic technologies (Part 2), sensing (Part 3), life sciences (Part 4), and analytical and material science (Part 5). For each area examples are selected that show how the field can profit from nanospectroscopy and how existing knowledge, devices, or materials in these areas can be advanced by applying nanospectroscopic techniques. We thus get to travel to such diverse pastures as quantum systems, photovoltaics, radiation detectors, sensing of explosives, cancer cell detection, food science, or dating of historic art. In this fast-moving field, the given insights can only ever offer brief snapshots of the status quo. In a sense, they can be viewed as the tips of an iceberg of applications that are still going to emerge.

Each chapter was written by experts in the respective area. The authors have accepted the challenge to guide readers by not only describing the state-of-the-art, but also offering perspectives and directions for future developments for those entering the field. We are indebted to the contributors for their dedication, knowledge, and time. The contributors originate from countries all across Europe and beyond and range from early-stage researchers to senior experts. Sincere thanks go to Christophe

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This volume can be seen as one of many possible compilations of exciting emerging applications of optical nanospectroscopy. We are looking forward to the compilations that will be enabled by the ongoing development of the coming decades.

November 2022
Volume 3 Editors

Evgeniya Sheremet
Norman McMillan
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Part 1: **Introduction**

Spectroscopy is the study of the interaction between electromagnetic radiation and matter, to reveal optical and electronic properties and the chemical structure. Nanospectroscopy can be both the spectroscopy of very small objects down to single molecules or atoms or spectroscopy performed with very high spatial resolution from regions much smaller than the wavelength of the radiation. Optical nanospectroscopy uses ultraviolet (UV), visible, and near-infrared (NIR) light sources for obtaining nanoscale information via the interaction of light and matter. The impressive recent progress in multiexcitation, superresolution, and near-field optical techniques offers unique possibilities of probing nature at the nanoscale – far below the diffraction limit – with extremely high spatial, temporal, and spectral resolution and chemical sensitivity. These techniques can be applied to metallic, semiconducting, or molecular systems that can be prepared using bottom-up or top-down strategies, as well as biomolecules and living cells.

Impressive progress has been made to date in various nanospectroscopy application areas with a strong impact on society, from early-stage cancer disease diagnostics to trace detection in gases and liquids. Optical nanospectroscopy offers great prospects of overcoming analytical problems and disadvantages of other analytical techniques, and is progressively becoming a powerful alternative to conventional methods used, e. g., for the evaluation of food quality, authentication, and safety. Application of optical nanospectroscopy in the food and agricultural sector helps in detecting contaminants, for smart packaging, and in food forensics. Furthermore, nanospectroscopic tools show considerable potential for advancing the development of high-sensitivity sensors, standards for the quantitative comparison of instruments and techniques, or single-photon sources and detectors. In biomedicine they are used for cellular imaging and quantitation of viruses, amongst others. Nanospectroscopy approaches allow for extending methods that mostly exist in the laboratory to real-life applications (taking into account portability, nontrivial environments, mobile phone applications, databases of chemically specific spectra, data evaluation, ease-of-use, etc.), e. g., for point-of-care medical home applications. In the field of cultural heritage, methods of optical nanospectroscopy are used for analysis and characterization of new nanomaterials for the restoration, preservation, and conservation of artworks and for the minimally invasive study of historical artifacts for dating and determining provenance. Optical nanospectroscopic sensing approaches can be used for the detection of potentially hazardous compounds such as pollutants, toxins, drugs, and explosives with chemical specificity in gaseous, liquid, or solid phases. Nanospectroscopy tools are likewise applied in material sciences, to learn more about the synthesis of novel (nano)materials and for characterization of nanobiophotonic materials. Additionally, they promote advances in optical communication and energy conversion and storage.

The main limitation of optical nanospectroscopic techniques is that they are still mostly used by specialists and are not sufficiently known by potential end-users. The knowledge of appropriate methodology needs to be simplified and reachable for the

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end-users. The instrumentation up to now is often highly specialized, expensive, sensitive to changes, and neither sufficiently standardized nor portable, while also being not specifically adapted to the respective needs, i. e., by supplying specific evaluation routines or databases for nonexpert users in the different application fields.

This volume emerged from the need to compile a collection of specific milestones and insights that optical nanospectroscopy is already providing in various areas of research. The status quo is recorded as a snapshot at a given point in time, and remaining challenges are discussed. The selection of the areas and methods is not arbitrary: It is based on the systematic analysis of a vast number of publications via their keywords in order to map out where the key advances are taking place, as outlined in the publication "Novel advanced scoping meta-review methodology for defining a graduate level textbook in an emerging subject area" [1]. The bar chart in Figure 1 illustrates that the number of publications on optical nanospectroscopy over the last decade is both significant and covering a wide area of application fields.

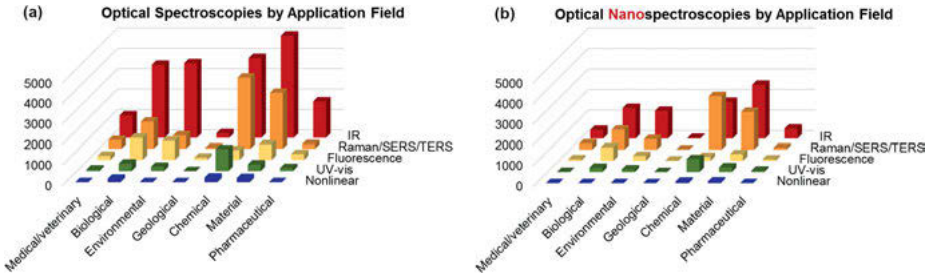

Figure 1: The number of publications from 2008 to 2021 for various optical spectroscopic modalities in various application fields based on a search using the EBSCO Essentials database (South East Technological University) [2] for (a) optical spectroscopy (overall results) and (b) the respective fractions for nano-related optical spectroscopies. For the search, the spectroscopy type was given as a subject heading, and the application area as a search term in the paper abstracts (as a conservative estimate, since the number of papers relevant to a given application is in all probability higher). For the nanosubcategory, "nano*" was added as search term in all fields.

To assist with the research for this volume, the number of publications for each spectroscopic modality has been determined for different application areas. A distinction was made between optical spectroscopic techniques in general and their nanovariants. This study, the result of which is presented in Figure 1, was carried out on the EBSCO Essentials open access database for the period January 2008 to December 2021. The bars give the number of relevant publications per spectroscopic modality for each application market. The full results are shown in Figure 1a, and the respective nanofractions in Figure 1b. The scale is the same for both sample sizes. In this rough overview, it appears that on average about 40 % of the hits refer to nanospectroscopic applications, which is a considerable number given the wide distribution

of optical spectroscopic techniques. The second point worth noting is that activity in nanovolume Raman (i. e., surface-enhanced or tip-enhanced Raman spectroscopy, SERS/TERS) and infrared spectroscopy appear to be much larger than in any other modality. For the case of SERS, this trend is also reflected in the examples given in the chapters of this volume. A third result seems to be that the currently most relevant application areas for optical nanospectroscopy can be found in biological, environmental, chemical, and material sciences, with potential for growth in the medical and pharmaceutical sector. This kind of systematic literature meta-analysis can be helpful to identify new and emerging research fields and follow their development. Such an overview may be strategically insightful for young researchers looking for ways of exploring the potential of research targets they might take on with a view to shaping a research career.

This book was devised as the third volume in the trilogy "Optical Nanospectroscopy" by the same editors. It is thus based on a platform of coherently presented knowledge on the fundamentals and methods of optical nanospectroscopy discussed in Volume 1 and the instrumentation, simulation & materials treated in Volume 2. This fact is reflected in the chapter structure that takes the reader directly to the practical examples of the topic. Each chapter is preceded by a section on "Pre-knowledge" that refers to the relevant basic concepts in the first two volumes. All three volumes have been designed with early-stage researchers and interested readers with a basic science training entering the field in mind, but also to give a wide context of how optical nanospectroscopy methods can impact a variety of areas. In contrast to Volumes 1 and 2, the present volume unites independent chapters by individual authors. While the subject areas were selected following the methodology described above, the contents highlight the viewpoints and the expertise of the respective authors. The chapters also provide a broader context beyond the mere optical methodology. While focusing on optical nanospectroscopy, they likewise introduce additional approaches relevant to the specific application.

The showcased examples are roughly categorized into four application fields: photonic applications, sensing, life sciences, and analytical and material science.

With respect to **photonic technologies**, nanospectroscopy enters into such relevant areas as the investigation of quantum emitters, photovoltaic cells, and radiation imaging detectors.

Chapter 2.1 by Christoph Couteau gives an introduction into the properties of quantum emitters that exhibit an artificial atom-like behavior, in combination with photonic environments such as cavities, photonic crystals, optical fibers, quantum photonic circuits, or plasmonic nanoantennas. Nanospectroscopic methods can be employed to probe the signal from quantum emitters that are forming indispensable building blocks for quantum technologies. In Chapter 2.2 by Andreas Kaltzoglou, Athanassios Kontos, and Polycarpos Falaras, the beneficial role of nanospectroscopy in advancing different types of next-generation photovoltaics, such as multijunction,

organic, dye-sensitized, quantum dot, or perovskite solar cells, is illustrated. Nanostructured interfaces are developed in order to continuously improve photovoltaic conversion efficiencies. Nanospectroscopy allows for the investigation of the optoelectronic and vibrational properties of the nanocomponents at such interfaces. In Chapter 2.3, Rosa Maria Montereali, Francesca Bonfigli, Enrico Nichelatti, Massimo Piccinini, and Maria Aurora Vincenti take a closer look at the specific challenge of measuring luminescent point defects to create radiation imaging detectors at the nanoscale. The color centers generated by ionizing radiation in lithium fluoride crystals and thin films are exploited for radiation detection and X-ray imaging. The optical properties of the color centers are mapped by nanoscopy, e. g., employing confocal laser scanning microscopy and scanning near-field optical microscopy or absorption and luminescence spectroscopy.

Ultrahigh-sensitivity **optical sensing** is one wide application field in which the advantages of nanostructures come fully into play. We take a closer look at miniaturized resonance shift sensors, investigate the application area of nanosensors for explosives detection, and remain in the liquid phase for lab-on-a-chip platforms and nanotensiography.

Chapter 3.1, by Florian Laible, Anke Horneber, and Monika Fleischer, illustrates the function of localized surface plasmon resonance shift sensors, where optical nanospectroscopy serves as the read-out mechanism to detect the specific binding of analytes from the liquid or gas phase to functionalized nanoantennas. With this technique, sensitivities down to single molecule binding have been demonstrated. One important application area of nanospectroscopy is highlighted in Chapter 3.2 with the detection of explosive chemicals as discussed by Roy Aad, Suzanna Akil, and Safi Jradi. In explosive trace detection, especially the portability of spectroscopic systems in combination with their chemical specificity and the high sensitivity of SERS or fluorescent sensing is of advantage. This is one characteristic example where nanospectroscopy is currently undergoing development from the laboratory to the marketplace. Chapter 3.3 gives an overview of the journey of spectroscopy towards the nanoscale by the example of forensic and agricultural science, as shown by Norman McMillan, Douglas McMillan, Raul Rodriguez, Mark Heaton, Victor Hrymak, Simon Perry, Enisa Omanović-Mikličanin, and Stavros Pissadakis. The chapter considers hardware requirements for micro- and nanovolume spectroscopy and tensiography, including a critical evaluation of the role of data analysis and correlated studies. Techniques both above and below the diffraction limit are evaluated, and a path towards nanoforensics is sketched.

The section on sensing already provided a first glimpse into the potential of optical nanospectroscopy for learning more about biological processes at the nanoscale. This approach is further pursued in the section on nanospectroscopy in the **life sciences**. Especially SERS as a label-free, chemically specific technique offers new ways of biomolecular and cancer detection and can more generally be employed to probe the chemical environment in cell cultures.

Chapter 4.1 is a joint contribution by Antonino Foti, Barbara Fazio, Cristiano D'Andrea, Maria Grazia Donato, Valentina Villari, Onofrio Maragò, Ramzi Maalej, Sameh Kessentini, and Pietro Gucciardi. The authors take an in-depth look at SERS for the detection of dyes, chemicals, and biomolecules at ultralow concentrations. SERS enhancement is closely connected to the optical properties of nanoantennas, which are introduced together with optical forces between such particles. In Chapter 4.2 Gamze Yesilay, Ertug Avci, Mine Altunbek, Sevda Mert, and Mustafa Culha point out that label-free cancer detection methods can avoid possible false results found in label-based methods. SERS is a promising technique that can reduce analysis times, but further improvements of the reproducibility and reliability of the detection are required. Examples of protein, cellular, and tissue analysis with respect to cancer diagnostics are showcased. Chapter 4.3, by Janina Kneipp and Daniela Drescher, picks up on the relevance of SERS for bioapplications and its ability to probe complex biological environments, e. g., in cells and tissues. Here, SERS relies on the uptake of metal nanoparticles together with reporter molecules as SERS probes, which needs to be monitored by complementary techniques. A perspective towards in vivo subsurface molecular imaging even up to the study of larger animals is given.

Finally, in **analytical and material sciences**, optical nanospectroscopy can be applied to a multitude of complex systems to elucidate their optical, electronic, and mechanical properties at the nanoscale. Exemplarily, we illustrate its use in such varied areas as food science and agriculture, cultural heritage studies, cyanine dyes, and carbon-based materials.

Chapter 5.1, written by Enisa Omanović-Miklićanin, deals with the questions of food authentication, safety, and quality by introducing common analytical methods in general and nanospectroscopic methods and nanosensors in particular. Considering the legal frameworks and consumer expectations, optical sensors and vibrational spectroscopy methods are shown to be most promising for rapid food analysis and cost-effective monitoring. Chapter 5.2 by Elena Shabunya-Klyachkovskaya gives a detailed account of optical spectroscopic approaches for identifying dyes in cultural heritage for the purpose of pinpointing their origin, age, and authenticity. An important challenge is maintaining the integrity of the artwork, which leads to the development of specialized sample preparation techniques that are included in the chapter. The success of the approach is showcased by some impressive case studies. A more fundamental application in material science is shown in Chapter 5.3 by Vesna Vodnik, Bojana Laban, and Dragana Vasić-Anićijević. Here cyanine dyes in J-aggregates on noble metal nanoparticles are studied in a highly correlative approach that joins multiple microscopic and spectroscopic techniques. The self-organized dyes form relevant artificial light-harvesting systems that can be employed in various detection techniques and inorganic–organic hybrid systems for bioimaging, sensing, and optoelectronics. Finally, Chapter 5.4, by Gagik Shmavonyan, Tran Tuan Hoang, Dmitriy Cheshev, Andrey Averkiev, and Evgeniya Sheremet, takes us on a journey through the preparation and properties of carbon nanomaterials, graphene, and other 2D and hybrid atomic

materials. Due to the strong Raman signature of carbon materials, a plethora of information beyond their mere identification can be gained by investigating such samples with high-resolution nanospectroscopic techniques, informing us about their chemical state, internal stress/strain, and configuration at the nanoscale. The many perspectives for carbon- and 2D material-based consumer products are outlined.

As demonstrated in the selected examples in this volume, optical nanospectroscopy is an emerging field of research and technology that is beginning to translate from requiring large lab equipment to showing that it may indeed take root in manifold areas throughout society. Commercialization of new nanospectroscopic techniques for sensing and analysis is being established and progressing. Instrumentation such as near-field optical microscopes, TERS platforms, surface plasmon resonance detectors, or superresolution imaging setups have been commercially available for some time now. Likewise, a broad range of custom-designed colloidal nanoparticles, nanocrystals, semiconductor quantum dots, and fluorescent markers can be purchased on the market. SERS substrates, fluorescence- and SERS-based measurement devices, and localized surface plasmon resonance sensors are being established. Still, further development and integration of operational devices will be required. Here the role of sensor miniaturization, multiplexed performance, portability, reproducibility, performance speed, and ease of use ("turnkey" instrumentation for nonexpert users) needs to be pushed further to make them attractive for additional application areas in everyday life. In addition, connecting to big data platforms will be key for more powerful chemical or medical diagnostics, not just for patients but for environmental, industrial, and consumer applications. Since these are still early days in the rapidly advancing field of optical nanospectroscopy, the current chapters can only give a snapshot of the fast-developing applications and may soon be overtaken by new developments. By showing some possible directions, we strive to give an incentive for scholars to join the effort to further advance this exciting field.

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Part 2: **New photonic technologies**

The International Year of Light and Light-Based Technologies hosted by the United Nations in 2015 highlighted the leading role of photonic technologies in the twenty-first century. Photonics is the science and technology of generating, controlling, and detecting photons, the particles of light. It was postulated that the twenty-first century will depend as much on photonics as the twentieth century depended on electronics, with huge societal and economic impact [1]. Areas such as the energy, the building and the mobility sector, communication technologies, medical diagnostics, all the way to arts and culture underlined the truly global relevance of photonics [2]. Future disruptive technologies such as quantum sensing and computing rely heavily on complex optical arrangements or photonic integrated circuits [3, 4]. The human eye as a sophisticated optical instrument enables us to navigate the world, but is limited in the size scales it can resolve. Here researchers for centuries have dedicated their efforts to developing ever more sensitive, high-resolution, and even chemically specific microscopic and spectroscopic techniques to investigate the world around us and drive further innovation. Since photonic technologies are already based on light, they are closely related to optical spectroscopic techniques. Ongoing miniaturization of on-chip devices strengthens the need to extend the spectroscopic resolution for investigation of the relevant components to the nanoscale [5]. Strain fields in advanced semiconductor structures e. g. become accessible via localized Raman spectroscopy [6, 7], facilitating sophisticated band-structure engineering. Molecular-scale fluorescence spectroscopy enables deciphering relevant processes in photosynthesis [8], etc. In the present volume, exemplary applications of optical nanospectroscopy in the emerging field of nanoemitters for quantum technologies, the continuously evolving field of photovoltaics that keeps gaining in relevance, and devices for improved photonic technologies by the example of radiation imaging detectors are highlighted.

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Christophe Couteau

2.1 Application review of quantum emitters in nanospectroscopy

2.1.1 Key messages

- Quantum systems are governed by quantum physics, which is a discipline with special importance for nanospectroscopy. Quantum emitters can be of different types but are all modeled using "artificial atom" behavior.
- Quantum systems are unique systems with quantum mechanical properties. These are usually found at the nanoscale and as such require tools developed for nanospectroscopy.
- Quantum optics experiments and tools are necessary to characterize quantum systems and in particular to ensure that we observe single-photon sources (SPSs), indistinguishable photons, or entangled photons.
- Nanospectroscopic theory is required for characterizing quantum systems that can be used as single quantum emitters for quantum technology applications or to better understand some biophotonics or sensing effects. Quantum systems are important to understand and to extract ensemble measurements for control of photovoltaic or lighting applications.

2.1.2 Pre-knowledge

In order to facilitate the understanding of this chapter, readers may gain pre-knowledge from previous parts and chapters, in particular from Volume 1 "Optical Nanospectroscopy: Fundamentals & Methods", especially the parts elucidating atomic descriptions of light–matter interactions such as the Hertz dipole, the concept of the photon, Rabi oscillations, and Bloch equations, as the notion of optical radiating dipoles and single photons will be very present in many of the cases seen. By the same token, the theory on optical properties of solid-state band structure, excitons, and plasmons will be assumed to be known for the discussions here about plasmons and excitons. This chapter is about applications to nanospectroscopy and is consequently quite experimentally oriented, thus some basic experimental techniques are necessary and the reader is referred to Volume 1, Section 2 and the chapters on photoluminescence, single-photon spectroscopy (time correlation), and single-molecule spectroscopy (confocal). This study will mainly focus on four types of quantum emitters: molecules, quantum dots (QDs), nanocrystals (NCs) (semiconductor ones mainly, leaving aside works on perovskites [1, 2]), and color centers in diamond (although there are other defects in other materials such as silicon carbide [3] or 2D materials [4]) as they were the first systems to be used for the main observations discussed in this chapter, and as such the reader might want to refer to Volume 2, Section 6 on nanostructures used in nanospectroscopy, nanoparticles, QDs, NCs, and optical antennas (top-down).

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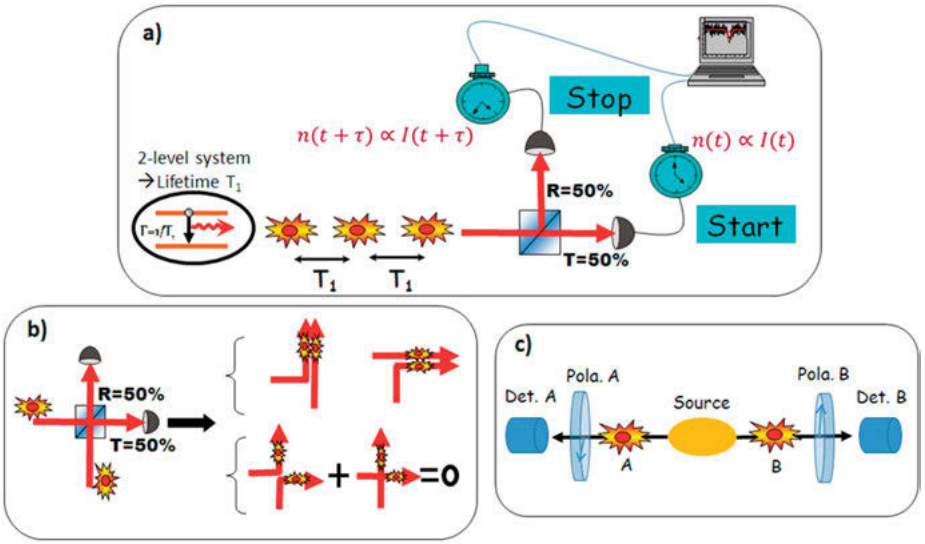

Figure 2.1.1: (a) Scheme of a typical experimental setup to measure whether an emitter emits a single photon. (b) Quantum two-photon interference effect. (c) Scheme of two entangled particles.

The discussion on quantum systems is restricted to some particular quantum states of light, namely the notion of single photons (Fig. 2.1.1a), indistinguishable photons (Fig. 2.1.1b), and entangled photons (Fig. 2.1.1c). Consequently, there will be a quick overview of these concepts. Figure 2.1.1a presents a typical experimental setup to measure whether an emitter emits a single photon. For that, we measure the so-called photon antibunching effect, which simply says that if an emitter emits one photon at a time (say like a two-level system with a certain lifetime T_1), when this single photon impinges on a 50/50 beamsplitter, then there should be no coincidental detection events from the two detectors at the same time. In Figure 2.1.1a, one detector is the "start-event" detector and the other one the "stop-event" detector. A measurement of the autocorrelation function of the signal at t with the signal itself at $t + \tau$ is then taken:

$$g^{(2)}(\tau) = \frac{\langle n(t)n(t+\tau)\rangle}{\langle n(t)\rangle^2}, \tag{2.1.1}$$

taking the time average of the number n of photons recorded at time t and at time $t + \tau$ later. This is equivalent to recording the light intensity, as the light intensity I is directly proportional to the number of photons n according to:

$$I = \frac{\mathcal{P}}{S} = \frac{\mathcal{E}}{S \cdot t} = \frac{n \cdot h\nu}{S \cdot t}, \tag{2.1.2}$$

with $\mathcal{P}$ being the light power, S the light beam surface, h the Planck constant, ν the frequency of light, and $\mathcal{E}$ the photon energy. For a single photon though, we can show that $g^{(2)}(0) = 0$. In other words, for zero delay between the start event and the stop event, there cannot be any double event (coincident event) in the case of a true single photon. Indeed, a single photon has to "choose" between being reflected ($R = 50\,\%$ at the beamsplitter) or being transmitted ($T = 50\,\%$ at the beamsplitter), but it cannot be both reflected *and* transmitted, and as such, a dip in the double count rate is expected to

occur, reflecting the condition $g^{(2)}(0) = 0$. This type of experiment in Figure 2.1.1a is called a Hanbury Brown and Twiss experiment for historical reasons.

On the other hand, if one looks at two-photon interferences, in the case where the two photons are twins, i. e., indistinguishable, then when one photon arrives at one port of a 50/50 beamsplitter and the other photon arrives at the other port, a two-photon coalescence effect occurs. This effect was first observed in 1987 and is known as the Hong–Ou–Mandel effect [5]. It relates to the fact that photons are bosons and as such, if they are truly indistinguishable in polarization, energy, and momentum, they consequently tend to bunch together. Figure 2.1.1b illustrates this effect, where we can see that the cases where the two photons come out from different ports actually interfere destructively, and the cases where the photons come out together are left. This is a pure quantum effect that can only be understood using the quantum theory of light [6], and it is very important for quantum computation applications where quantum states with high coherence/high indistinguishability are needed.

The third quantum state envisaged for our quantum systems are the so-called Einstein–Podolsky–Rosen (EPR) pairs of particles [7], which will be photons in our case. Another name is entanglement, where two particles (say two photons A and B like in Figure 2.1.1c) are entangled in polarization where the quantum state of the two particles $|\psi\rangle_{AB}$ cannot simply be written as the product of the quantum states $|\psi\rangle_A$ and $|\psi\rangle_B$ of the two photons:

$$|\psi\rangle_{AB} \neq |\psi\rangle_A|\psi\rangle_B. \tag{2.1.3}$$

If the entanglement is polarization-based it means that when A is a vertically polarized photon $|V\rangle_A$, then B has to be horizontally polarized (for instance) $|H\rangle_B$, but the inverse is also true at the same time, and a possible entangled state could be written:

$$|\psi\rangle_{AB} = \frac{1}{\sqrt{2}}\left(|V\rangle_A|H\rangle_B + |H\rangle_A|V\rangle_B\right) \neq |\psi\rangle_A|\psi\rangle_B. \tag{2.1.4}$$

We note the use of the Dirac notation with bra and ket, standard in quantum mechanics. The EPR state is at the heart of Bell's theorem stating that there is no physical theory with local hidden variables that can reproduce all the predictions of quantum mechanics [8]. This type of entangled state, also purely quantum, is very important for quantum cryptography and communications as well as for quantum simulation.

As a broad definition, we will say that a quantum system is a physical system capable of producing one of these three aforementioned types of quantum states of light.

2.1.3 Importance of the application

For the first time in 2011, IBM implemented optical fibers on an electronic chip board (the IBM Power P775 system) demonstrating the power of a future computer using electronics AND photonics. So far, the overheads are massive by introducing optical fibers, and a new generation of integration on the chip level will be necessary for electro-optical elements. The future for photonic integrated circuits (PICs) shows great promise as light is already in use for carrying information, but it would be even more promising if it could also realize information processing and computation in a chip. These technological advances should ensure the future of a market in photonics and integrated optics for computation purposes.

In the meantime, recent developments in quantum optics and nanophotonics have resulted in better control of quantum systems [9, 10], and quantum technologies are now seen to be within reach of real applications. Harnessing light and especially "quantum light" will be the future of information and communication technologies. This chapter focuses on quantum systems, i. e., light emitters that do provide quantum states of light (mainly as SPSs) coupled to photonic devices. The focus will be primarily on near-UV to near-IR photons for optical fibers as well as satellite and free-space communications. As such, the easiest quantum emitter is any two-level system such as a single atom in an optical trap or a single electron trapped by electrodes in a 2D electron gas. To fit within the broad range of nanospectroscopy, we will focus on nanoemitters that have been recently coupled to photonic (such as photonic crystals – PhCs) and plasmonic (such as metallic nanoparticles) structures.

There are several potential applications for sensing or light harvesting but the one which perhaps holds the most hope is to go towards a future quantum computer/simulator. For that, one needs so-called nodes of stationary quantum bits (qubits) where computation is carried out (usually obtained from solid-state quantum systems) and so-called flying qubits (photons) in order to communicate between computing nodes in a complex network. Despite many improvements, efficient interfacing between the two types of qubits remains a challenging goal, and a complete control of light–matter interaction is still lacking. Photons are the natural choice for flying qubits where solid-state nanoemitters such as nitrogen-vacancy (NV) color centers in diamond [11, 12], QDs [13, 14], NCs [15], and single molecules [16] seem to be promising candidates compared to atomic systems, usually requiring complex and not always scalable setups. These are the four systems that will be considered in what follows in this chapter. Engineering a versatile platform in order to achieve efficient interfacing between quantum emitters and photons is thus an important area of research involving the nanospectroscopy of quantum systems. The emission from emitters and, in general, the matching from the nano- to the microworld is a key objective for nanophotonics.

A second key element is being able to miniaturize optical devices in the same way as electronic devices which have now attained tens of nanometers. The advantage of scaling down optical devices and in particular to go towards quantum optical circuits is to be able to add more functionalities for future quantum technologies or for the "Internet of Things" revolution that is predicted. There is, however, a major limitation with respect to downsizing optical devices that is well known, and it is called the diffraction limit roughly on the order of $\lambda/2$, thus a few hundred nanometers for our range of wavelengths. For current and future PIC devices, one needs to scale things down to what is already in place with microelectronic components, i. e., to the order of a few tens of nanometers. In this chapter, we will describe some of the strategies used to beat this limit and thus to go towards nanoscale photonic devices. This chapter is comprised mostly of two parts, the "conventional" dielectric approach, with optical cavities such as micropillars, PhCs, or optical fibers, and the metallic approach to make use of plasmonic confinement to subwavelength levels. There is however a

third way, which is the hybrid metallo-dielectric photonic systems currently being envisaged.

2.1.4 State-of-the-art

2.1.4.1 Light–matter interaction

In the 1940s, people working with radars knew that it was possible to control directionality, amplitude, and range of radio waves using antennas, amplifiers, and filters for instance. As it was simply put by Edward Purcell in an article published in 1946 in *Physical Review* (actually more a long footnote than an article), "*... for a system coupled to a resonant electrical circuit, ...the spontaneous emission probability is ... increased, and the relaxation time reduced by a factor of* $F_p = 3Q(\frac{\lambda}{n})^3/(4\pi^2 V)$, *where V is the volume of the resonator*" and where Q is the quality factor of the resonator [17]. In our case, we are dealing with optical cavities and those are our "electrical circuits" and "resonators." This Purcell effect was first observed in the optical domain in the late 1960s by K. H. Drexhage, where thin films of controlled nanothicknesses filled with europium ions were spaced nearby a metallic mirror [18]. The lifetime of these ions was recorded as a function of the spacing; and the lifetime was modified, thus spontaneous emission was observed. This was the first demonstration of the Purcell effect in the visible range.

2.1.4.2 Cavity quantum electrodynamics and strong coupling

Following Drexhage's experiment, some tremendously significant observations were made using atoms (as is usually the case) in the early 1980s by the Haroche group in Paris and the Kleppner group at MIT [19, 20]. In both cases, the experiment consisted in measuring the lifetime of some energy transitions from atoms going through a resonant cavity and observing how it would change. In fact, in these two occurrences, one observation was enhancement [19] and the other one was inhibition of the spontaneous emission rate [20]. The birth of quantum electrodynamics (QED) came from these experiments. Not so long after, similar first results arrived from molecules in cavities [21–25]. A short while after these pioneering experiments, work was done in solid-state systems with observation of strong coupling between excitons and light in a quantum well. These new "particles" called polaritons (hybrid photon-emitter quantum states) were first observed in 1992 in an article published by Weisbuch et al., where an anticrossing in the spectrum was observed, typical of a strong coupling regime, and the characteristic photon-exciton mode splitting was determined for a 7.6 nm thick quantum well [26].

At this stage, we should specify what we mean by the strong coupling regime. When one observes the Purcell effect such as Drexhage did in 1970, one can see this effect as the modification of the spontaneous emission rate from the environment of the emitter (a mirror or a metallic nanoantenna as we shall see later on) and as such, one can talk about being in the weak coupling regime of the light–matter interaction. But if the conditions are right, i. e., if the emitter is placed in a cavity with very low losses, then the strong coupling regime can be reached where an emitter decays spontaneously, emitting its photon into the cavity. But in the case of the strong coupling regime, the emitter in the cavity has a high probability of re-absorbing the very same photon and so on and so forth. We then end up with a coherent exchange of photons between the emitter and the cavity mode, some kind of "quantum ping pong game" effect characteristic of the energy exchange between two strongly coupled resonators. The conditions for strong coupling and the quantum state of the emitter/photon are thus given by

$$g \gg \gamma, \kappa \quad |\psi\rangle_{\mathrm{QED}} = \frac{1}{\sqrt{2}}(|e\rangle_{\mathrm{at}}|0\rangle_{\mathrm{ph}} \pm |g\rangle_{\mathrm{at}}|1\rangle_{\mathrm{ph}}), \tag{2.1.5}$$

where g is the emitter-photon coupling constant, κ is related to the incoherent leaky modes of the cavity, and γ is the incoherent spontaneous emission rate of the emitter into the noncavity modes. We assume the atom in the cavity has two levels, a ground state $|g\rangle_{\mathrm{at}}$ and an excited state $|e\rangle_{\mathrm{at}}$. This QED quantum state $|\psi\rangle_{\mathrm{QED}}$ is simply the superposition state of the atom in the excited state and no photon in the cavity $(|e\rangle_{\mathrm{at}}|0\rangle_{\mathrm{ph}})$ and the atom in the ground state with one photon in the cavity $(|g\rangle_{\mathrm{at}}|1\rangle_{\mathrm{ph}})$. Figure 2.1.2 illustrates these parameters, where an emitter with a transition frequency ω_{A} is tuned to the energy ω_{C} of a cavity mode. A "standard" cavity with two mirrors is represented in Figure 2.1.2, but we will see in particular with metallic nanoantennas that this geometry is not the only one. Examples of the Purcell effect in single-molecule spectroscopy can be found, e. g., in [24, 25].

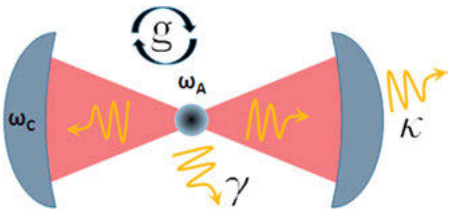

Figure 2.1.2: Two-level system with a frequency ω_A and radiative decay rate γ coupled to a cavity with frequency ω_c and loss decay rate κ, g being the coupling constant between photon and emitter.

2.1.4.3 Purcell effect and single-photon sources

Polaritons in a quantum well are a good example of a particular nanocavity as described in [26], and thus after this proof-of-concept that effects in atomic physics can be translated into solid-state systems, it was then natural to think of inserting true 0D emitters with 3D confinement such as QDs into photonic structures. These "artificial atoms" were behaving very much like a two-level system, and a configuration like in Figure 2.1.2 could thus be envisaged. This idea originated from the France-Telecom research laboratory in Bagneux in France in the mid-1990s, where a layer of QDs was grown deterministically between two distributed Bragg reflectors (DBRs) forming a Fabry–Pérot cavity. Once the DBRs and the QDs were grown, the as-grown sample surface would be etched down to form micropillars/microcavities like in Figure 2.1.3a [27, 28]. With this, the first observation of the Purcell effect by a factor of 5 was obtained followed by the first observation that a single QD could provide single photons [29] (and in fact single NCs were also proven to provide single photons by the same group in the same year [30]). At the time, there were many leaky modes (see spectrum from Figure 2.1.3a) due to the fact that many QDs were grown at once, and the cavity constructed afterwards would select/filter a certain QD that happened to be at the right place and in resonance with the cavity. Nevertheless, having these two very important conditions of being at the right place and with the right resonance simultaneously was very unlikely but was the only known way of succeeding. Indeed, if one recalls the full condition for the Purcell effect F_p to occur, this expresses the ratio of the change of decay rate between the dipole/emitter in free-space γ_0 and in the modified environment γ, and it is given by

$$F_p = \frac{\gamma}{\gamma_0} = \frac{\pi^3 c^3}{\omega_0^2} \rho_u(\boldsymbol{r}_0, \omega_0), \tag{2.1.6}$$

where ω_0 is the frequency associated with the two-level system of the electrical dipole, c is the speed of light, and $\rho_u(\boldsymbol{r}_0, \omega_0)$ is the partial local density of states (LDOS) for a dipole oscillating in a direction $\boldsymbol{u}$ related to a dipole moment $\boldsymbol{p}$. This LDOS can be obtained by the Green's formalism, it can be analytically described using Fermi's golden rule in some simple cases, or it can be obtained also using a numerical solution of Maxwell's equations, for example here using the FDTD method.

Since the first experiments in the late 1990s, technology and inventions have advanced significantly so that in situ observation of single QDs in a laser scanning microscope can allow for simultaneous selection of the right QD using a red laser beam and exposure of a photoresist to then build the cavity around it by optical lithography with a green laser beam [33]. This eventually led to the more refined structure presented as a schematic in Figure 2.1.3b where electrical injection is performed and indistinguishable photons come out of this complex structure [31]. In the late 1990s up to the mid 2000s, QD technology was very much a nondeterministic technique where

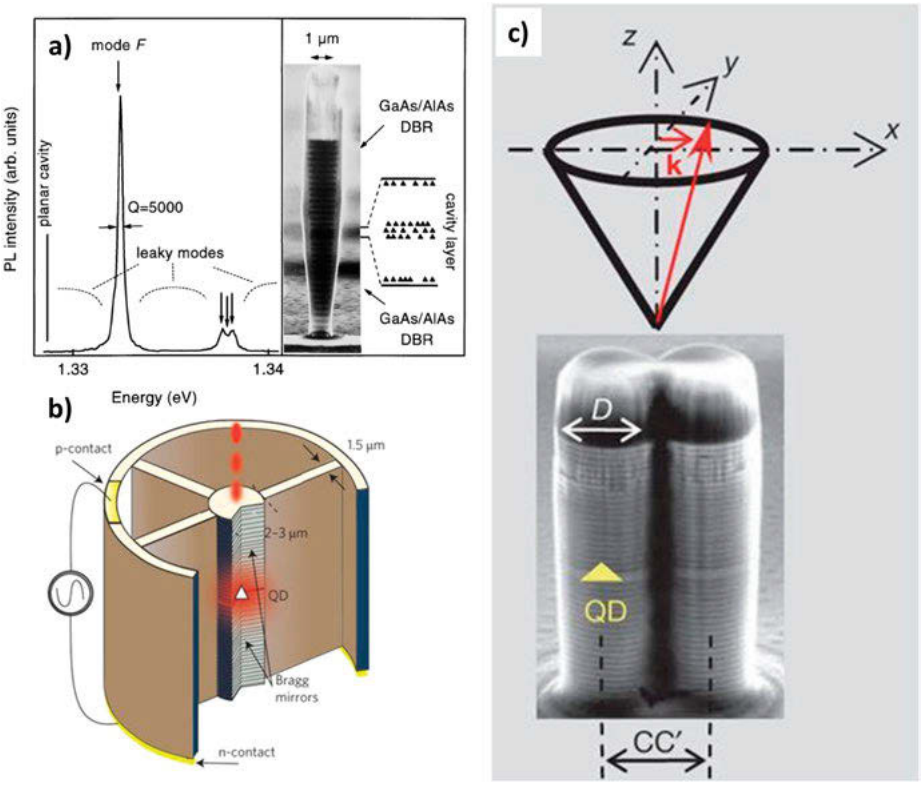

Figure 2.1.3: (a) Spectrum of III-V quantum dots in a micropillar type of Fabry–Pérot cavity (scanning electron microscopy (SEM) picture shown). Reprinted with permission from Ref. [28]. (b) Same type of structure with electrical injection of carriers. Reprinted with permission from Macmillan Publishers Ltd.: Somaschi et al., *Nature Photonics*, vol. 10, 340 (2016) [31]. Copyright 2016. (c) A coupled double cavity for producing entangled states from a single quantum dot. Reprinted with permission from Macmillan Publishers Ltd.: Dousse et al., *Nature*, 466, 217–220 (2010) [32]. Copyright 2010.

one would have to scan through many QDs before finding the right one in terms of brightness, wavelength, and quality of coherence, in order to be able to produce indistinguishable photons [34]. Nowadays, lithographic and growth techniques allow us better control over these parameters. Ideally, the excitonic emission of a QD (and an NC for that matter) should provide indistinguishable (i. e., in the same Fock state), on-demand single photons with an ideal collection efficiency, which is mostly realized by now [31]. Figure 2.1.3c presents the complex arrangement of a QD inserted in a double cavity where each cavity is coupled to one of the first two excitonic transitions of the QD in order to produce an entangled state [32].

All this work is in fact the result of years of single-QD spectroscopy, which proved to be quite complex with the creation of multiexcitons (exciton, biexciton, triexciton, and so on) or charged excitons (two electrons and one hole for instance) and how

to identify them. As a promising feature, when two excitons meet in a QD forming a biexciton, the cascaded recombination (biexciton $X_2 \rightarrow$ exciton $X \rightarrow$ empty QD) should provide a "natural" source of on-demand entangled photons in polarization as predicted by the group of Yamamoto in 2000 [35]. Unfortunately, it is not that simple, as mechanical strain and stress during the growth of QDs tend to deform and elongate the dots and thus break the circular symmetry of a given QD. Figure 2.1.4a presents the ideal cascaded biexcitonic emission where an entangled state such as

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|\sigma^+\rangle_{X_2}|\sigma^-\rangle_X \pm |\sigma^-\rangle_{X_2}|\sigma^+\rangle_X) \tag{2.1.7}$$

is expected to be created. But instead, the polarization states are linear (see Fig. 2.1.4b) with horizontal H and vertical V polarized emission from the X and X_2 lines, and one ends up with a mixed quantum state and not a pure quantum state like in equation (2.1.7). Nevertheless, specific techniques were used in order to tune this fine structure splitting (on the order of $\delta_0 \sim$ few GHz) by spectral filtering (see Fig. 2.1.4c for X_2 and Fig. 2.1.4d for X, in gray zones) for instance, where one selects the "right" photons, the ones with the near-zero δ_0 [36].

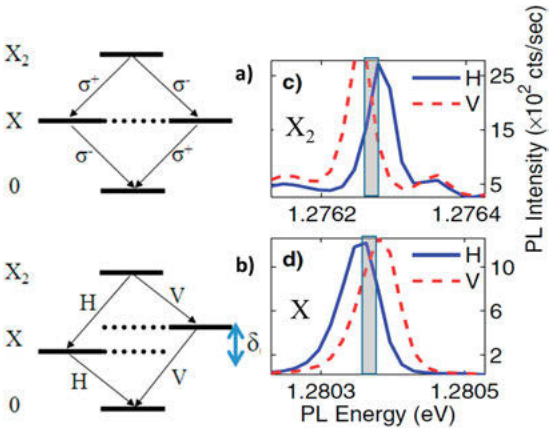

Figure 2.1.4: (a) Perfect scheme for an entangled state due to the biexciton-exciton recombination cascade. (b) A more realistic case with a splitting of the exciton state. (c) Spectral selection in gray of the "right" biexciton and (d) exciton photons for having an entangled state. Reprinted with permission from Ref. [36].

Tuning the fine structure splitting was also realized using a magnetic field [37], using an electric field [38, 39], and by mechanical stress [40]. Besides the micropillars already mentioned, other resonators have been considered such as ring resonators. In fact, the first observation of a single-photon emission with an epitaxially grown QD was realized with a QD inserted within a ring resonator and coupled to a whispering gallery mode (WGM) of a microdisk [29]. Although presenting high quality factors,

these types of resonators are not very practical for SPSs in order to efficiently extract the light: micropillars and PhCs are much more appropriate for that, and ring resonators are used more for lasing devices [41]. Epitaxial QDs are very important quantum emitters considering the degree of control we have over them in terms of positioning and coupling them to photonic structures, but also to use them as efficient spin/photon interfaces [14].

2.1.4.4 Photonic crystals

As we will see, if one wants to go towards future integration of quantum systems (quantum photonics), then one needs not only to be able to extract the light efficiently but also to be able to integrate a given quantum system within a network of other quantum systems, with many types of sources and detectors being possible to fabricate. In terms of extracting as much light as possible, the idea of controlling its propagation has been around for some time, but it was only during the late 1980s that researchers thought of engineering materials such that light would bend and reflect in a specific way. The concept of PhCs was thus born out of two seminal articles published in 1987 [42, 43]. In a nutshell, the idea is that if one carefully engineers a certain material, one can create photonic bands for light, very much the same way that atoms in a periodic lattice tend to modify the propagation of electrons within a solid. For light, the atoms are for example holes that act as scatterers. In simple terms, we use the Snell–Descartes law many times and for many periodic occurrences. Then holes (say in a thin membrane) will make a periodic array of a different index ($n_{\text{air}} \sim 1$ in this case) into materials made of Si or GaAs with a high refractive index and will thus engineer a system that guides the light. This strong index contrast will modify the light propagation. Like with electrons, if the spacing between holes is chosen carefully, roughly on the order of the wavelength of the light for a PhC, then a band structure for the dispersion of light will appear, alongside with photonic band-gaps where light cannot propagate.

The first 3D PhC was realized in diamond by Yablonovich's group (one of the two discoverers of PhCs) in 1991 by drilling holes into it to be resonant in the microwave regime [44]. This is called a Yablonovite. It did not take long before people started to make these structures for optical wavelengths using e-beam lithography in order to prepare membranes. PhCs would be "drilled" into these membranes, and an emitting material in the membrane would be inserted for more complex PICs. Lasing emission from quantum wells was obtained at first [45] before Noda et al. introduced defects into PhCs in order to create high-Q cavities and to approach a system like the one presented in Figure 2.1.5 [46, 47]. In this work, they realized a silicon-based 2D photonic-crystal slab with a nanocavity with a quality factor of $Q \sim 45{,}000$ and a cavity mode volume of $V \sim 7.0 \times 10^{-14}\,\text{cm}^3$. Figure 2.1.5a presents the resonant spectra of different cavities formed by simply adjusting a couple of holes nearby the cavity (Fig. 2.1.5b) [47].

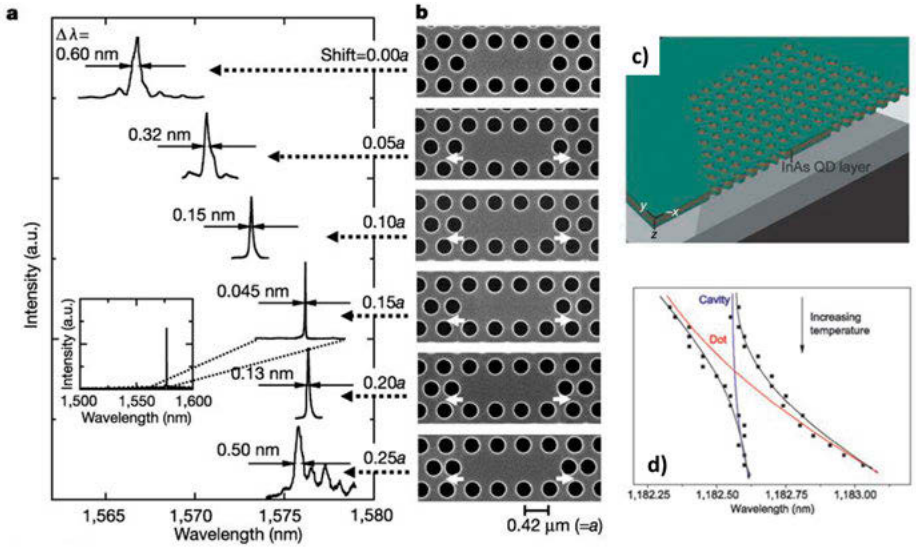

Figure 2.1.5: (a) Resonance spectra of different cavities formed by simply adjusting a couple of holes nearby the cavity. (b) SEM images of the corresponding cavities. Reprinted with permission from Macmillan Publishers Ltd.: Noda et al., *Nature*, vol. 425, 944 (2003) [47]. Copyright 2003. (c) Scheme of a layer of QDs within a photonic crystal. (d) Experimental observation of the Rabi splitting of a single quantum dot in a PhC. Reprinted with permission from Macmillan Publishers Ltd.: Yoshie et al., *Nature*, vol. 432, 200–203 (2004) [48]. Copyright 2004.

One can see a maximum of the sharpening of the spectrum for a shift of $0.15a$, where a is the period of the PhC. This was done at around a telecom wavelength at 1.57 μm or so.

In order to make active quantum devices, the next step was thus to insert quantum emitters. Once again, people knew how to make QDs out of III-V semiconductors such as InAs QDs in a GaAs matrix. It was then natural to grow such a structure and then construct a PhC very much like it was done with a micropillar. Figure 2.1.5c illustrates the experiment where a layer of QDs is inserted into a PhC. The regime of strong coupling was reached with such structures as can be seen in Figure 2.1.5d, where Rabi splitting for photons and cavity modes was observed [48].

This experiment was central to many others to come, and it is still up to these days a very much studied system even in other materials such as diamond. The idea of using diamond as a platform is essential for quantum information purposes. It is well known that deep defect centers in diamond such as the nitrogen vacancy (NV) defect (where one N atom replaces one C atom next to the vacancy of another C atom) has a fine structure that is very well suited for quantum processing and quantum communications [49]. It would be thus ideal to fabricate photonic structures directly within bulk diamond already containing these NV centers. The first experiment of a PhC in a single crystal diamond was done by the Becher group in 2011 [50]. Since then, we know

how to create and address single-color centers such as silicon vacancy (SiV) centers [51]. This work from Harvard University consisted in fabricating an integrated platform for scalable quantum nanophotonics where SiVs were coupled to nanoscale diamond devices. These SiV centers were placed inside diamond PhC cavities, in order to realize a quantum optical switch controlled by a single-color center. This single photon transistor is very important for quantum simulators and communications. We refer the reader to some review articles on color centers in diamond for quantum networks and quantum photonics for further reading [52].

2.1.4.5 Optical fibers and quantum systems

Ideally, in order to harness single photons from quantum systems, the simplest thing to do would be to couple photons from emitters directly into optical fibers as once the photons are in an optical fiber, they can propagate for long distances and interact with other quantum systems. This can be done, for example, using the nanomanipulation of a QD in a photonic wire that is then attached to an optical fiber as seen in Figure 2.1.6a and b. By this technique, photons emitted from a QD are directly cou-

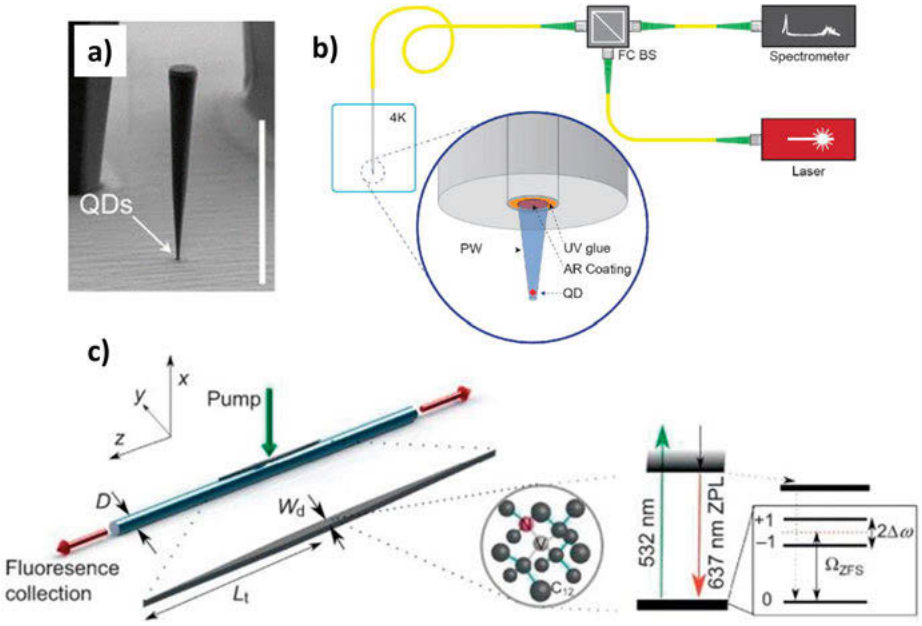

Figure 2.1.6: (a) Quantum dot in a photonic wire (b) that is then attached to an optical fiber and coupled to a Hanbury Brown and Twiss setup. Reproduced from [53], with permission from AIP Publishing. (c) NV center inside a single-mode tapered diamond waveguide that is itself integrated on a tapered silica fiber. Reprinted with permission from Macmillan Publishers Ltd.: Patel et al., *Light: Science & Applications*, vol. 5, e16032 (2016) [54]. Copyright 2016.

pled into the fiber by adiabatic mode coupling from the photonic wire to the optical fiber [53]. By the same token, a group at MIT managed to couple single photons emitted from an NV center inside a single-mode tapered diamond waveguide that was itself integrated on a tapered silica fiber as shown in Figure 2.1.6c [54]. A similar idea was demonstrated with epitaxial QDs in a nanophotonic directional coupler physically coupled to an optical fiber with a 6 % coupling demonstrated [55]. It was also demonstrated that optical fibers can be used for controlling the flow of light when they are used as nanophotonic waveguides [56]. Petersen et al. showed that thanks to the strong transverse confinement of guided light, a spin–orbit interaction of light occurs, and they observed the breaking of the mirror symmetry of the scattering of light by a gold nanoparticle on the surface of a nanofiber [56]. This makes a chiral waveguide coupler in which the handedness of the incident light determines the propagation direction in the waveguide [56]. The same effect was observed using an epitaxial QD within a III-V nanobeam with the interesting perspective that spin state selection from a QD can be controlled that way [57]. This is very important for quantum information processing.

2.1.4.6 Quantum photonic circuits

Ultimately, the goal remains to go towards fully integrated quantum photonic circuits, and preferably without optical excitation, but with an electrically driven light source. A first proof-of-concept was shown by the group of Wolfram Pernice where they reported the observation of photon antibunching from an electrically driven carbon nanotube embedded within a photonic quantum circuit. The single photons were detected by waveguide-integrated superconducting single-photon detectors (SSPDs) [58]. Figure 2.1.7a presents a schematic of this experiment where several carbon nanotubes and several superconducting detectors are integrated on a chip. This is an example of an all-integrated quantum photonic circuit. This approach is a rather bottom-up one where the components are brought together.

Other approaches are studied such as the all-epitaxial approach one with III-V semiconductors [59, 57]. This is a rather top-down approach with QDs being grown and waveguides then etched down in order to guide single photons emitted from the QDs. The main advantage of using III-V semiconductors is the fact that they are high-refractive-index materials and thus guide the light very tightly when surrounded by air [59]. Figure 2.1.7d presents an SEM image of such a structure. A similar experiment was realized by the Finley group from the Walter Schottky Institute [60] with a schematic of the integrated photonic system shown in Figure 2.1.7c. In this example, InGaAs QDs emit photons waveguided along a GaAs ridge waveguide that are detected by a NbN nanowire (SSPD made of niobium nitride). This is a mix of top-down (for the light source and the waveguide) and bottom-up approaches (with the integration of the SSPD). Using this geometry, resonant fluorescence was observed, and a line width of

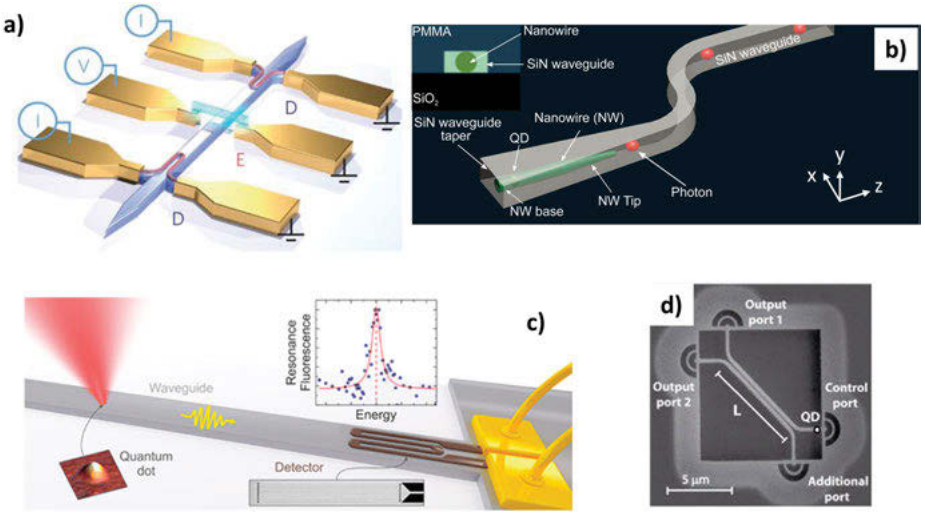

Figure 2.1.7: (a) Carbon nanotubes and superconducting detectors integrated on a chip. Reprinted with permission from Macmillan Publishers Ltd.: Khasminskaya et al., *Nature Photonics*, vol. 10, 727 (2016) [58]. Copyright 2016. (b) QD in a photonic nanowire, embedded in a silicon nitride (Si_3N_4) waveguide. Reprinted with permission from Zadeh et al., *Nano Letters*, vol. 16, 2289–2294 (2016) [62]. Copyright 2015 American Chemical Society. (c) Integration of an epitaxially grown quantum dot with a superconducting detector. Reprinted with permission from Reithmaier et al., *Nano Letters*, vol. 15, 5208 (2016) [60]. Copyright 2015 American Chemical Society. (d) Quantum dot grown in GaAs embedded in an etched-down waveguide. Reproduced from [59] with permission from AIP Publishing.

10 µeV or so was measured from a single QD, reinforcing the concept of artificial atoms with very narrow line widths [60]. We can mention the Zwiller approach using yet again a QD embedded into a photonic wire in a trumpet shape [61] in Figure 2.1.7b that was nanomanipulated and then embedded into a Si_3N_4 ridge waveguide. This material has a fairly high refractive index and is also compatible with silicon technology, which makes it particularly interesting for applications [62]. Once again, a hybrid approach bottom-up/top-down was used where grown emitters are inserted into more complex networks.

There are nowadays several platforms that can claim complete integration, and Table 2.1.1 provides a broad overview of these platforms with their different characteristics whether you work in the visible or in the telecom region (1550 nm or so). The platforms are mostly glass-based such as optical fibers, laser-written waveguides, lithium niobate, and ion-exchange waveguides, but also include high band-gap semiconductor-based platforms such as GaAs, diamond, SOI, or silicon nitride. Then quantum states of light are either created in the material, as already mentioned in the case of deep defect centers in diamond, or with the growth of QDs in III-V semiconductors. There are also hybrid solutions to these problems using different materials

Table 2.1.1: Overview of the different photonic platforms for quantum systems.

	λ range (nm)	**Losses @ 600 nm (dB/cm)**	**Losses @ 1550 nm (dB/cm)**	**Index n (at 600 nm/ 1550 nm)**	**Compatible with fibers**	**Active**
Silica-on-silicon (SOI)[a]	>1100	>100 dB/cm	3.6 dB/cm [67]	2.7/2.46 [68, 69]	Yes	Yes
Silicon nitride (Si_3N_4)	200–10,000	5 dB/cm	1 dB/cm	1.92/1.87 [70]	No	Yes
Laser-written in glass	300–5500	0.5–1 dB/cm	0.1 dB/cm	Δn: 0.0001–0.002 (multimode)	Yes	No
Optical fiber	300–5500	10 dB/km	0.25 dB/km	1.458/1.444	Yes	Yes
Lithium niobate	300–5500		<0.5 dB/cm [71]	2.29/2.21 [69]	No	Yes
Diamond	300–10,000	>70 % (1 mm thick)	$k = 0.009$	2.41/2.39 [69]	No	Yes
Gallium arsenide (GaAs)	>870	>100 dB/cm	<1 dB/cm	3.91/3.37 [69]	No	Yes
Ion-exchange waveguide	300–5500	0.3 dB/cm	0.1 dB/cm	Δn: 0.001–0.03 [72]	Yes	Yes

[a]We recall that silica = silicon dioxide = SiO_2.

and/or using plasmonic structures [63]. A roadmap on integrated quantum photonics now exists where all the different platforms are discussed in terms of current and future challenges [64], and we refer to some review articles for more on the subject of nanoscale quantum optics [65] and integrated quantum photonics [66].

2.1.4.7 Plasmonic antennas

As already seen in previous chapters, e. g., in Volume 1, Section 3, plasmonic resonances in metal can be used to control light emission from quantum emitters in various ways, using either localized surface plasmons (LSPs) or propagating surface plasmons (PSPs). Structures supporting the first type of plasmonic resonance can act as optical nanoantennas for visible light and can strongly influence parameters such as the quantum efficiency, the Purcell effect, and the fluorescence enhancement of an emitter; see Volume 2, Section 6. Figure 2.1.8a presents an example of a nanoantenna made of a bowtie geometry using gold, where molecules were inserted within the bowties [73]. Very high fluorescence enhancement factors were found in this work, more than 1000 times for some single molecules. The authors could affirm the fact that