Chapter 1

Introductory Chapter: Synchrotron-Based X-Ray Characterization of Nanomaterials

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Additional information is available at the end of the chapter

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The capability of X-rays to analyze the structure and dynamics of almost all forms of matter has been largely demonstrated by scientific researches. Since X-rays are sensitive to structural features with lengths from 10^{-3} to about 1 nm as well as to dynamic properties with characteristic time scales from about 10^{-16} to 10^{3} s, they are a powerful ingredient for exploring nanomaterials and the frontiers of nanoscale characterizations. Developing in beams and optics to produce appropriate and tunable wavelengths/energies and detecting their interactions with matter create new windows to measure the arrangements of atoms (structure) and to track the movements of atoms or molecules (dynamics). The arrangement of atoms inside objects can be determined using several techniques based on scattering, diffraction, spectroscopy, and imaging. Moreover, X-ray interacts weakly with most materials; it is nondestructive and can penetrate deeply into samples. It can also be used for *in situ* studies of materials during processing and under real or extreme conditions of temperature, pressure, and magnetic or electric fields.

The improvements in X-ray diffraction, scattering, spectroscopy, and imaging methods need an increase in the intensity, collimation, and focusing of the beam as well as tuning of the wavelength. Hence, moving from X-ray laboratories to accelerator-based "light sources" facilities is required to obtain the most powerful analysis and characterization tools.

In a synchrotron, charged particles such as electrons are accelerated and injected into a storage ring, where they get energies from 500 MeV to 8 GeV depending on the size of the ring. As the charged particles are bent around the ring (by magnetic devices), energy is dissipated and electromagnetic radiation is emitted from infrared to X-rays. This radiation is highly intense, highly focused, and strongly polarized. Part of this radiation can emerge with energies from 0.1 keV (corresponding to a wavelength of 12.4 nm, known as "soft" X-rays) to 100 keV (0.0124 nm "hard" X-rays), being well suited to investigations at nanoscale (1–100 nm) [1].

The generation of X-rays by accelerators of electrons goes back to about 70 years ago. The first-generation sources were electron storage rings originally designed and operated for high-energy physics experiments. These facilities were adapted for use as synchrotron radiation sources by adding exit ports for the radiation. In the mid-1970s, facilities totally dedicated to synchrotron light were built. These facilities, in which synchrotron light was produced by bending magnets as well as high magnetic field devices, known as wigglers, are called second-generation sources. Afterwards, the optimization of magnetic structures, like in wigglers and undulators, produced new synchrotron radiation sources (named third generation) characterized by a X-ray more brighter than a conventional X-ray sources used in laboratories. The synchrotron X-rays are captured into beamlines where they can be tailored for scattering, diffraction, spectroscopy, and imaging with tailored resolution, intensity, or *in situ* measurements. While improvements in third-generation synchrotron radiation sources are still possible, *fourth-generation sources* are being developed, based on free electron lasers (FELs) that are able to produce very short coherent light pulses of very high peak intensity and brightness. The improvement of brightness for each generation of synchrotron X-ray sources along with a photograph of a synchrotron light source is shown in **Figure 1**.

The researches in nanomaterials are focused on producing nanoscale materials with unique properties for specific applications. Hence, the advanced characterizing methods for determining the structure, composition, and properties of materials at the nanoscale are needed. There is request on real-time and *in situ* monitoring of the synthesis and processing of nanomaterials to find the mechanisms as well as structure-property-processing relationships, which can be obtained by X-ray–based techniques in the areas of scattering, diffraction, absorption, imaging, reflection, and photoelectron emission as shown schematically in **Figure 2**. X-ray diffraction (XRD), X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS), which includes X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS), are well suited to probing synthetic processes at the atomic scale that are difficult or impossible to study with traditional electron imaging or spectroscopy techniques. For instance, *in situ* analysis by synchrotron radiations of vapor phase processing methods (chemical vapor deposition and atomic layer deposition), as well as etching methods such as reactive ion etching (RIE), and solution phase growth methods, such as the sol-gel process, has been performed by researchers [2].

Using synchrotron facilities, another analysis capability is the characterization of materials under specific conditions such as applied pressure, temperature, and fields. *Operando* experiments are the new frontier application of synchrotron-based characterizations, which can be pointed to understand energy storage materials research, such as Li-ion battery materials, which is included in the structural transformation during the fabrication of cathode materials and structural changes in the first lithium loading cycle as well as the investigations during the charging and discharging processes of an entire lithium battery. The fine spot size of the synchrotron X-ray beams together with their bulk penetration lead to study the buried layers in different battery components. The BL28XU beamline at SPring-8 in Japan has been recently installed for *in situ* structural and electronic analysis of rechargeable batteries, providing a powerful tool for the investigation of battery reactions. This beamline makes use of quasi-monochromatic X-ray beams obtained by an in-vacuum tapered undulator, which allows to extend the energy bandwidth to 2 keV [3]. It consists of three hutches: one for the optics allocation and the other two as experimental stations as shown in **Figure 3**.

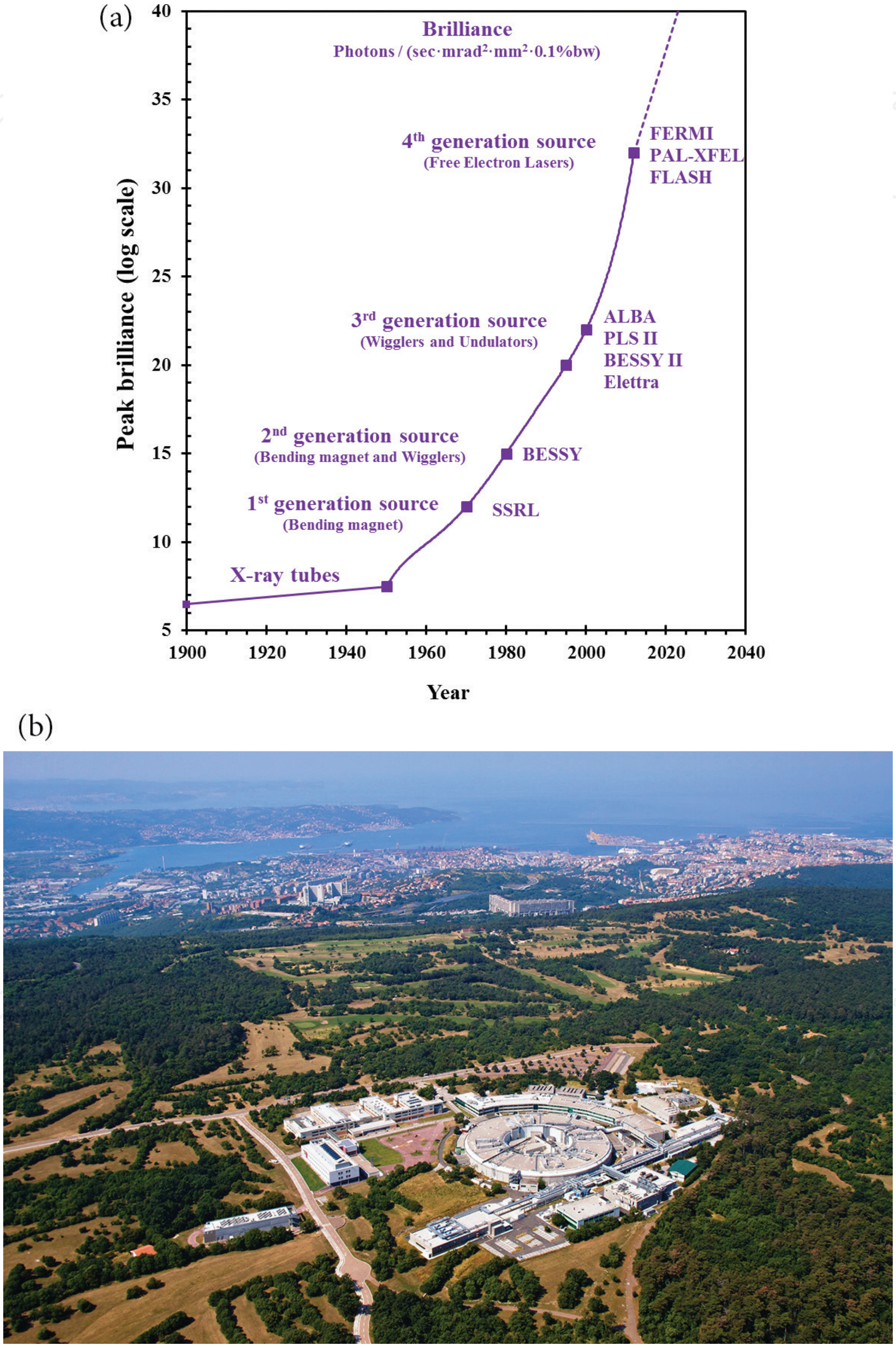

Figure 1. (a) Brightness of different generations synchrotron radiation sources, (b) aerial view of the Elettra synchrotron facility (Courtesy of Elettra Sincrotrone Trieste, ph. Gabriele Crozzoli).

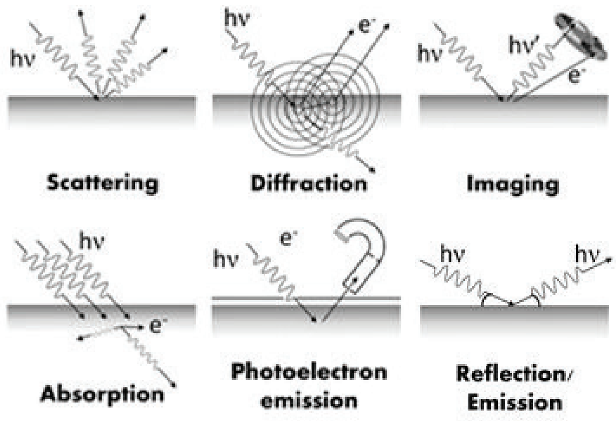

Figure 2. Schematic representation of some X-ray–based techniques due to the interaction of synchrotron radiation with matter (Courtesy of Elettra Sincrotrone Trieste).

At the ESCA, microscopy beamline of the Elettra synchrotron, a dynamic high pressure (DHP) system, has been recently developed. This setup is a solution adaptable to existing synchrotron-based XPS spectroscopes and microscopes, which allows to overcome the pressure constraints of photoemission technique (high vacuum or ultra-high vacuum) and to operate up to mbar range. The success of the first near ambient pressure scanning photoelectron microscopy experiment manifests that the developed novel solutions can pave the road to ambient pressure photoelectron spectromicroscopy, allowing for instance the characterization of catalytic systems near real condition [4].

In this book, five chapters on synchrotron-based characterization of nanostructured materials related to energy applications have been collected.

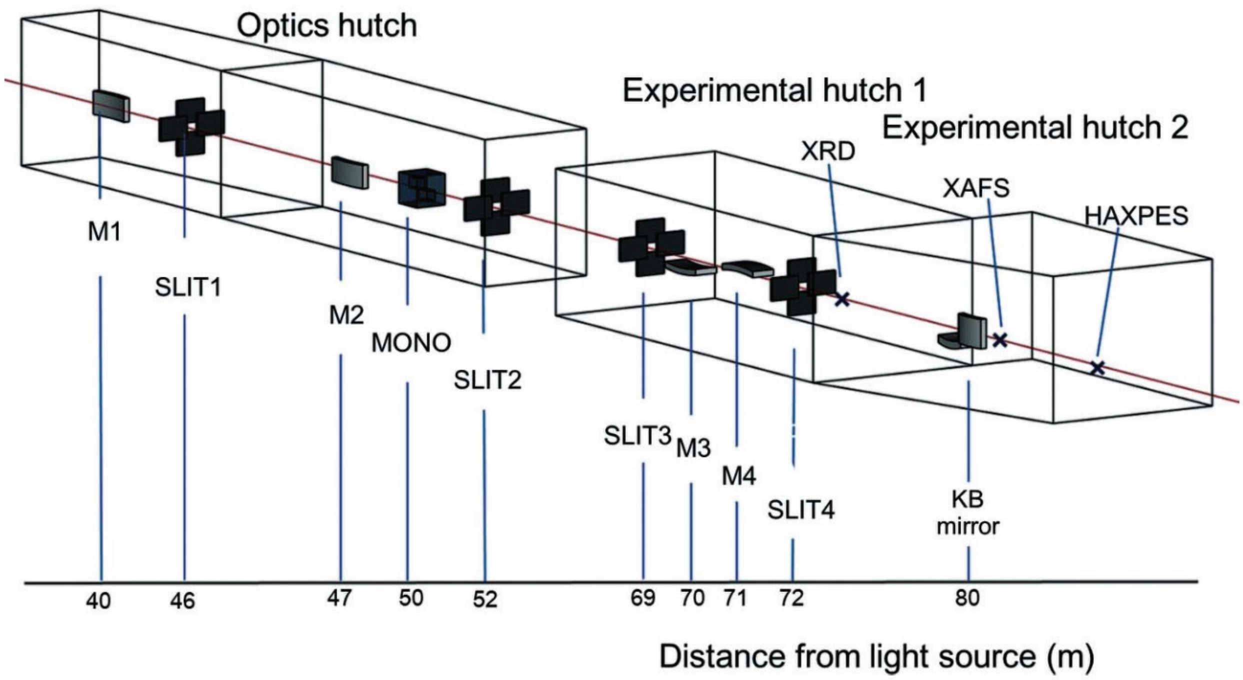

Figure 3. Schematic of beamline BL28XU at SPring-8 in Japan [3].

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The chapter "Nanocrystallization of Metallic Glasses Followed by in situ Nuclear Forward Scattering (NFS) of Synchrotron Radiation" is about metallic glass materials, which have applications in energy transformation and sensor devices. Structural transformations in metallic glasses including nanocrystallization are investigated by Nuclear Forward Scattering (NFS) of synchrotron radiation to fine details that are completely hidden when conventional analytical tools are employed. The following chapter illustrates the operando structural characterization by surface X-ray diffraction (SXRD) of the electrochemical atomic layer deposition of semiconductor ultra-thin films, which have applications in nanoelectronics and photovoltaics. Last three chapters are dedicated to energy storage and battery materials, especially on Li-ion batteries, and their synchrotron-based characterization by X-ray absorption spectroscopy and X-ray microscopy.

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