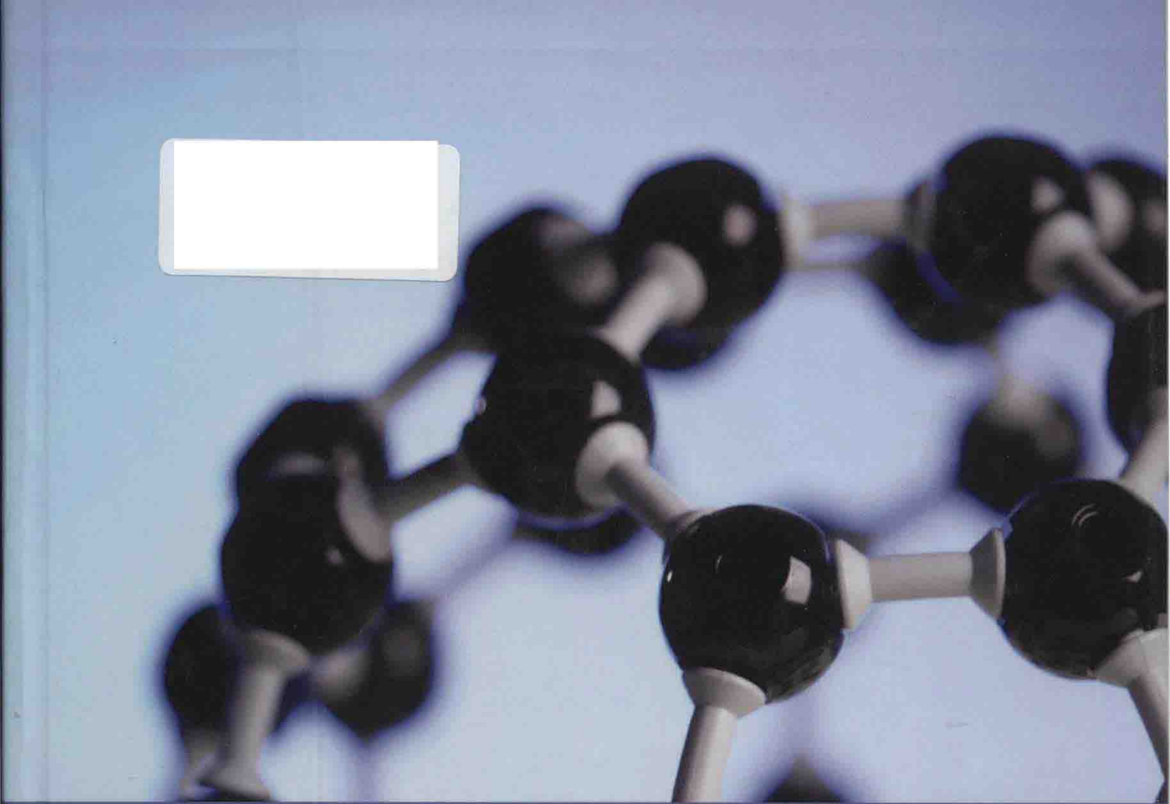

Nanotechnology:

Science, Innovation and Opportunity

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Preface

Nanotechnology is the art and science of manipulating matter at the atomic or molecular scale and providing significant improvements in technologies for protecting the environment. It is a branch of technology dealing with the manufacture of objects with dimensions of less than 100 nanometres and the manipulation of individual molecules and atoms. The text Nanotechnology Science, Innovation and Opportunity covers the latest in nanotech science, technology, and applications. First chapter provides basic notions as to grazing incidence small angle X-ray scattering (GISAXS), a technique typically used to study nanostructured surfaces. Second chapter discusses how nanotechnologies enhance the use of active phytochemicals. Carbon nanofiber concrete for damage detection of infrastructure has been presented in third chapter. In fourth chapter, we focus on the synthesis of nanofibers with different composition, and the design and preparation of electrospun nanofibers with novel secondary structures. Laser based fabrication of graphene has been introduced in fifth chapter. A review on carbon nanofibers and their composites has been proposed in sixth chapter. Last chapter deals with surface optical mode in semiconductor nanowires.

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Contents

Chapter 1

ASSEMBLED NANOSTRUCTURED ARCHITECTURES STUDIED BY GRAZING INCIDENCE X-RAY SCATTERING

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ABSTRACT

In this chapter, we will focus on a specific X-ray- based technique among those employed in surface science and which is especially suitable for the study of self-assembled nanocrystals: Grazing Incidence Small Angle X-ray Scattering (GISAXS). We will first introduce the main field of investigation considered herein, with basic notions of X-ray scattering from surfaces, and then address basic concepts about GISAXS. Finally, we will describe a few relevant examples of studies, of nanostructured architectures, through ex situ and in situ experiments of grazing incidence X-ray scattering. This manuscript is focused on the former, showing that they can be performed by using laboratory instruments. In situ investigations still need synchrotron radiation sources in most cases; therefore, only a few examples selected from the literature are reported here, for the sake of completeness. The experiments described are mainly performed in the small angle range, providing information on the size and shape of nanocrystals, together with their spatial arrangement. Both 2D and 3D architectures are considered. In particular, GISAXS

measurements of 2D superlattices of nano-octapods, performed both at a third generation synchrotron beamline and with a table-top set-up, are compared; the employed table-top set-up is described in a dedicated paragraph. Further examples of grazing incidence studies as performed by the authors with a table-top set-up are reported: a GISAXS study of 3D iron oxide nanocrystal superlattices, showing the importance of modelling in order to obtain structural information from data; a combined small/wide angle scattering (GISAXS/GIWAXS) study of 3D PbS nanocrystal superlattices; and a GIWAXS study of P3HT nanofibres, showing how the ordering at the molecular and atomic length scales can be obtained by exploring different angular ranges in the same grazing incidence geometry. Finally, selected examples of in situ GISAXS studies, performed with synchrotron radiation sources, are described.

TOWARDS THE SELF-ASSEMBLY OF NANOSTRUCTURED ARCHITECTURES

As of today, the synthesis of nanoparticles, nanocrystals and nanostructured architectures can be realized, on the one hand, by physical approaches, such as Molecular Beam Epitaxy, Laser Ablation, Sputtering and Metal Organic Vapour Phase Epitaxy; and on the other hand, by chemical routes, such as Chemical Vapour Deposition (the reaction of metal-organic species in the gas phase) or colloidal synthesis (the formation of free-standing nanoparticles in liquid media in the presence of organic stabilizers), the latter being the main approach considered here. A relatively large range of colloidal nanomaterial platforms have been successfully fabricated.[1-5] Independently of the specific synthesis approach, the physical and chemical properties of nanostructured materials are indeed distinctly different from those of bulk matter with the same chemical composition. This difference is related to the reduced size, which leads to quantum confinement and/or to structural phase changes. As a consequence, novel electronic configurations (and thus magnetic and optoelectronic responses) and different chemical reactivity (e.g., catalytic properties) are obtained for nanostructures, compared to their bulk material counterparts. A material made of small nanocrystals is expected to be more reactive than the same mass of material made up of larger particles, as the smaller the nanocrystals, the larger the overall exposed surface area. The fraction of atoms at the surface of a nanometre-sized domain significantly increases with the surface area per unit volume, changing - for instance - from ~100% for nanocrystals as small as 1 nm in diameter, to about 15% for 10 nm nanocrystals.[6] A variety of intriguing solid-state properties coupled with facile post-synthesis processability make NCs a major class of attractive "man-made" materials, aimed at achieving specific functionalities. In particular, colloidal NCs are suitable vehicles to bring about the functions of crystals in a solution phase. They are composed of an inorganic crystalline core and a surface shell of surfactant or ligand molecules that coordinate to unsaturated surface atoms. Due to such organic surface capping, NCs can be solubilized in a variety of solvents, embedded in a polymeric matrix, immobilized on substrates, integrated into electrical circuits, or have their surface functionalized with biological molecules or with another inorganic material. The advantages arising from the peculiar behaviour of nano-sized matter can be combined - and, hence, further extended - by fusing various single-component NCs into a unique multifunctional nano-object, thanks to the association of material sections with, e.g., magnetic, optical or catalytic properties.[7-10] "Smart" platforms can then be engineered so that they are able to accomplish multiple actions (e.g., in biomedicine, environmental clean-up, catalysis, sensing).[10, 11] Last generation breeds of so-called hybrid NCs (HNCs) are structurally elaborated multi-material colloidal nanostructures, consisting of two or more different material domains interconnected through permanent chemical bonding, possibly forming heteroepitaxial interfaces. For example, Au-Fe_3O_4, Au-FePt and Ag-Fe_3O_4 heterodimers have been exploited as dual functional probes upon site-selective functionalization with different biomolecules. The processed HNCs have been made simultaneously hydrophilic, fluorescent, responsive to magnetic forces and capable of binding to specific receptors.[12, 13] The creation of asymmetrically functionalized material sections has been also envisioned as a strategy for promoting the self-assembly of HNCs into functional mesoscopic NC-based "superstructures". [7-10] Self-assembling is among the most innovative and creative concepts of modern nanotechnology: carefully designed building blocks, either separated or linked, spontaneously form complex ordered aggregates,14 their interactions usually being non-covalent (e.g., electrostatic interactions, hydrogen bonds, van der Waals' forces, coordination interactions, etc.).[15] The assembled superstructures typically behave as more than the sum of their individual parts or else exhibit completely new types of behaviour.[16] Self-assembling is centrally important in life science: cells contain a large range of self-assembled complex structures (lipid membranes, folded proteins, structured nucleic acids, protein aggregates, molecular machines).17 Self-assemblies are at the base of novel smart materials with regular structures, such as molecular crystals,18 liquid crystals19 and semicrystalline and phase-separated polymers.[20] Its great potential in materials and condensed matter science[21,22] is mainly due to the particular behaviour of assembled superstructures, which typically consist of more than the sum of their individual nanostructures contributions or else exhibit completely new types of behavior.16 In colloidal synthesis, a diverse range of sizes and shapes of building blocks are accessible today, leading to, e.g., spheres, rods, cubes, wires, tetrapods and octapods,[23] whose self-assembling allows them to fabricate new hierarchically-ordered materials ('nanocrystal solids').[24,25,26] In the 1890s, three mathematicians (Federov, Schoenflies and Barlow) independently discovered the number of ways that exist to periodically distribute identical objects of an arbitrary shape in 3D space. Thanks to their work, it is well known in crystallography that there exist 230 different space groups for three- dimensional crystal lattices.

A similar question is under discussion today in view of predicting how polyhedra of nanometric size can self-assemble into complex structures. Very recently, Damasceno[27] published theoretical predictions about 145 convex polyhedra, whose assembly arises solely from their anisotropic shape. Depending on the "coordination number" in the fluid phase (the number of nearest neighbours surrounding each polyhedron) and the isoperimetric quotient (the deviation of the actual polyhedron shape from the sphere), the assembly of hard polyhedra can result in crystals (periodic arrays with long range positional and orientational order), plastic crystals (periodically ordered structures with positionally blocked sites but with building units which are free to rotate), liquid crystals (structures with positional disorder but a strong orientational order) and fully disordered structures (amorphous). NC properties are strongly influenced by their size and shape with respect to both the inner core and the surface ligands, and several tools have to be combined to characterize both parts in detail. Meanwhile, synthesis proceeds from

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