Design and characterization of nanoparticles and their assemblies

Transmission electron microscopy investigations from atomic to mesoscopic length scales

Arnaud Mayence

Department of Materials and Environmental Chemistry
Stockholm University
Cover: The cover illustrates different length scales of matter, from atoms to mesoscopic arrays, illuminated by an electron beam. The experimental data underneath were obtained using different electron microscopy techniques (STEM-HAADF, 3D EDT, EFTEM, EELS and TEM imaging)
Education is learning what you didn't even know you didn't know

Daniel J. Boorstin
Abstract

Transmission electron microscopy (TEM) is a powerful and versatile tool for investigating nanomaterials. In this thesis, various transmission electron microscopy techniques are used to study the chemical and structural features of different types of inorganic nanoparticles of well-defined morphologies as well as their assemblies. The synthesis of spherical and anisotropic nanoparticles (iron oxide nanocubes and other morphologies, gadolinium orthophosphate nanorods, tungsten oxide nanowires and nanorods, palladium nanospheres, and faceted iron-manganese oxides hybrid nanoparticles) using thermal decomposition of metal complex precursors in high-boiling point organic solvents and hydrothermal process are described in details.

Electron diffraction tomography (3D EDT) is a recently developed technique that is used to investigate the 3D structure of crystalline materials. Reciprocal space volume reconstruction of 3D EDT data of thin WO$_3$ nanowires assembled into nanorods revealed single crystal domains of hexagonal symmetry. Moreover, the use of 3D EDT enabled to identify and solve the structures of individual GdPO$_4$ nanorods in a mixed phase powder. The use of 3D EDT was extended using small-angle diffraction mode to investigate the packing arrangements and defects in nanoparticle assemblies. A high concentration of planar defects found in different nanoparticle assemblies highlights the competition between the fcc and hcp arrangements during the assembly process.

Iron-manganese oxides hybrid nanoparticles with different three-dimensional configurations, i.e. core|shell and asymmetric faceted dimers, were investigated using a combination of several electron microscopy techniques (HRTEM, SAED, STEM-HAADF, EFTEM, EELS). The growth of the faceted cubic MnO phase onto preformed Fe$_3$O$_4$ seed particles occurs preferentially along the Fe$_3$O$_4$ nanocube edges forming a well-oriented crystalline interface despite the lattice mismatch and defects. Atomic resolution monitoring of the structural changes in Mn$_3$O$_4$|Fe$_3$O$_4$ and Fe$_3$O$_4$|Mn$_3$O$_4$ core|shell nanoparticles induced by the electron beam revealed a strain relief mechanism at the interface involving inhomogeneous diffusion of cations and defects creation.
List of Publications

This thesis is based on the following publications:

I. **WO₃ nanorods created by self-assembly of highly crystalline nanowires under hydrothermal conditions**

   *Scientific contributions: carried out the TEM characterization and analyses, contributed to writing.*

II. **Phase identification and structure solution by three-dimensional electron diffraction tomography: Gd-phosphate nanorods**

   *Scientific contributions: performed the syntheses, TEM characterization and analyses, lead role in writing.*

III. **Probing planar defects in nanoparticle superlattices by 3D small-angle electron diffraction tomography and real space imaging**

   *Scientific contributions: participated in the self-assembly process, TEM characterization and analyses, lead role in writing.*

IV. **Strain and defects in asymmetric Fe-Mn oxides hybrid nanoparticles**
A. Mayence, M. Wéry, D. Trung Tran, E. Wetterskog, P. Svedlingh, C.W. Tai, L. Bergström, Submitted.

   *Scientific contributions: designed the project, performed the syntheses and TEM characterization and analyses, lead role in writing.*
V. Probing the metastability of core-shell nanoparticle systems at atomic resolution


Scientific contributions: analyses of the STEM-HAADF data, contributed to writing.

† Indicates shared first authorship

Publications not included in this thesis:

VI. Precise control over shape and size of iron oxide nanocrystals suitable for assembly into ordered particle arrays

VII. Controlling orientational and translational order of iron oxide nanocubes by assembly in nanofluidic containers

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<tr>
<td>2D</td>
<td>Two-dimensional</td>
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<tr>
<td>3D</td>
<td>Three-dimensional</td>
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<td>TEM</td>
<td>Transmission electron microscopy</td>
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<td>EDT</td>
<td>Electron diffraction tomography</td>
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<td>HRTEM</td>
<td>High-resolution transmission electron microscopy</td>
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<td>SAED</td>
<td>Selected-area electron diffraction</td>
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<td>NBD</td>
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<td>High-angle annular dark field</td>
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<td>Scanning transmission electron microscopy</td>
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<td>EELS</td>
<td>Electron energy-loss spectroscopy</td>
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<td>EFTEM</td>
<td>Energy-filtered transmission electron microscopy</td>
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1 Introduction

The ongoing research and development in nanomaterials fabrication is driven by the interesting properties they exhibit arising from their unique structures, chemical nature, domain size and morphologies. The small size (i.e. large surface-to-volume ratio) of nanomaterials can also lead to tunable and enhanced functional properties (e.g. optical, electronic and magnetic).\(^1,2\) Numerous methods have been developed to obtain materials on the nanometer scale, and their fabrication can be divided into two main strategies: the 'bottom-up' and the 'top-down' approaches. The 'top-down' approach is based on the controlled removal of material in order to obtain the desired dimensions and geometry (e.g. photolithography, electron beam lithography, etc.). The other approach consists of building-up materials from atoms or ions to larger entities (e.g. chemical vapor deposition, wet-chemistry synthesis, etc.). Nanomaterials have attracted much attention over the past decades because of the possible innovation and value creation in technological developments ranging from materials (e.g. sensors, inks, catalysis, etc.) to life sciences (e.g. drug delivery, cancer therapy, etc.).\(^3,4\) The fabrication of complex functional nanomaterials is currently possible under controlled experimental conditions. Besides, the ability to control the three-dimensional morphology of nanoparticles has opened new possibilities in producing materials with tunable properties.\(^5,6\) Also, the precise control of the size and morphology of nanoparticles is of key importance to assemble them into highly-ordered mesoscopic structures offering a promising and inexpensive way to create devices with unique properties.\(^7\)

Determination of the nanoparticle structures and the investigation of their chemical nature as well as their imperfections (e.g. defects) are crucial in order to understand how the material properties relate to their composition and structure. Powerful characterization tools using different probes (e.g. X-ray, neutrons and electrons) can provide information on the structural features in materials such as the three-dimensional arrangement of atoms from sub-Ångström to sub-micron length scales.\(^8\)–\(^10\) The advent of modern transmission electron microscopes has offered a unique opportunity to investigate nanomaterials structures using various techniques including high-resolution imaging, diffraction and spectroscopy techniques. Moreover, the ever-growing development of transmission electron microscopy techniques has enabled scientists to gain a deeper understanding of the nanomaterials nature at the atomic scale.
1.1 Nanoparticle synthesis

Bottom-up approach using chemical syntheses can yield a large variety of colloidal nanomaterials that are dispersible in polar and non-polar solvents. These processes include hydrothermal synthesis, templated synthesis, sol-gel, co-precipitation, micro and mini-emulsion, chemical reduction and many more. In this thesis, we present two bottom-up methods used to synthesize palladium nanospheres, tungsten oxide nanowires and nanorods, gadolinium orthophosphate nanorods, iron oxide nanocubes and other morphologies, and manganese-iron oxides hybrid nanoparticles.

The first method consists of thermal decomposition of an organometallic or metal complex precursor (e.g. metal carbonyls, metal acetates, metal acetylacetates, metal oleates, etc.) in non-polar high-boiling point solvents (e.g. 1-octadecene, hexadecane, 1,2 hexadecanediol, benzyl ether, etc.) in the presence of amphiphilic molecules (ligands) such as phosphines, fatty acids and long-chain amines. The thermal decomposition route yields crystalline nanoparticles dispersed in an organic phase. For instance, the thermal decomposition of metal-oleate has been widely used to produce a large amount of crystalline monodisperse metal oxide nanoparticles. The size and morphology of the nanoparticles can be controlled by changing experimental conditions such as temperature or ligand and precursor concentration. This method is particularly efficient for producing monodisperse and shape-defined nanoparticles with well-controlled compositions including metals and alloys (e.g. Co, Fe, FePt, CoPt, CoPt3, etc.), semiconductors (e.g. CdS, CdSe, CdTe) as well as metal oxides (e.g. CoO, ZnO, MnO, MFe2O4; M=Fe, Mn, Co). In addition, inorganic multicomponent nanoparticles can be fabricated using a seed-mediated thermal decomposition-based synthesis route. Multicomponent nanoparticles with various chemical composition and configurations (e.g. core|shell, dumbbell and other morphologies) can be obtained by the subsequent growth of another material onto preformed nanoparticles.

The second method, called hydrothermal synthesis, can be used for preparing a wide range of materials in water such as hydroxides, metal oxides, nitrides, carbonates, phosphates, zeolites and many more. Hydrothermal synthesis is a cost effective process carried out in a sealed vessel (e.g. autoclave) at relatively high temperature (typically 100 °C-300 °C) resulting in autogenous high-pressure conditions. The high temperature and pressure conditions infer a change of solvent properties such as solubility, density, viscosity and dielectric constant. For example, the dielectric constant of water decreases with temperature affecting the solubility of polar molecules and ionic species. Organic solvents such as methanol, ethanol and acetone can be used instead of water, in so called solvothermal processes. Hydrothermal synthesis has been extensively used for the preparation of bulk materials.
single crystals. More recently, there has been a growing interest in using hydrothermal synthesis for nanomaterials fabrication.\textsuperscript{36,37}

Chemical synthesis methods can thus yield a large variety of nanomaterials with tunable size and morphology. However, the formation of nanomaterials in solution is still poorly understood.\textsuperscript{38} The classical nucleation theory provides a thermodynamic model that describes liquid condensation from a vapor phase. LaMer and coworkers proposed a theory based upon experimental observations made during monodispersed sulfur colloids formation.\textsuperscript{39} This model elaborates on the nucleation of nanoparticles in solution under supersaturation conditions where nanoparticle nucleation is initiated by a sudden burst period (fast increase of monomer concentration), followed by the growth of small nanocrystals through diffusion of monomers and surface reactions. Nanoparticles may further grow into larger entities through coarsening mechanisms such as Ostwald ripening.

Nevertheless, classical theories are not able to describe universally nanoparticle nucleation and growth, and might not be valid for a large number of cases. In fact, a number of examples of non-classical crystallization have been reported suggesting an alternative mechanism for the nanoparticles’ growth.\textsuperscript{40,41} For instance, oriented attachment has been observed for some biomimetic nanomaterial systems\textsuperscript{42}, but also for nanomaterials produced through hydrothermal synthesis (e.g. anatase\textsuperscript{43}) and thermal decomposition of metal complex precursors (e.g PbSe nanowires\textsuperscript{44}, MnO multipods\textsuperscript{45}, Co$_3$O$_4$\textsuperscript{46}). Oriented attachment mechanisms might play an important role in nanoparticles growth, shown e.g. in a recent \textit{in-situ} investigation that revealed the oriented coalescence of platinum nanoparticles.\textsuperscript{47}

Besides, the size and morphological control of nanoparticles can be achieved through the use of stabilizers that adsorb onto the nanoparticle surface preventing their agglomeration. A large variety of stabilizers such as polymers and long-chain alkyl molecules have been used to guide the nanoparticle growth, and change the growth rate along specific crystallographic facets yielding diverse nanoparticle morphologies.
1.2 Self-assembly of colloidal nanoparticles

Colloidal nanoparticles can be self-assembled into large two-dimensional films or three-dimensional mesoscopic arrays (Figure 1-1), also called nanoparticle supercrystals, supra-crystals, nanoparticle superlattices or nanoparticle assemblies. Like atoms in crystals, nanoparticles exhibit long-range translational order in nanoparticle assemblies. Nanoparticle assemblies can be termed mesocrystals when they exhibit orientational order meaning that the nanoparticle building-blocks exhibit coherent alignment of their crystal axes. The assembly process itself is interesting for fundamental research aspects on crystallization, and nanoparticle assemblies are attractive for the development of complex functional devices. The nanoparticle assembly process is often triggered by the evaporation of a colloidal dispersion under controlled conditions. However other strategies can be used including destabilization of the colloidal dispersion (e.g. depletion and non-solvent destabilization), induced assembly by external magnetic and electric fields or light, and DNA mediated-assembly. Significant research efforts during the last decade have led to the development of nanoparticle assemblies (e.g. 2D films and 3D mesoscopic arrays of single- and multiple-component nanoparticle assemblies) with a large structural diversity.

Figure 1-1. Self-assembly of spherical nanoparticle into ordered mesoscopic nanoparticle assemblies.

In this thesis, nanoparticle assemblies are produced by a destabilization strategy where ethanol (non-solvent) slowly diffuses into a dispersion of spherical nanoparticles in toluene to produce highly-ordered mesoscopic nanoparticle assemblies. TEM investigation of nanoparticle assemblies and their planar defects will be presented in Chapter 4.
1.3 Transmission electron microscopy – a powerful tool to investigate nanomaterials

Transmission electron microscopy (TEM) has undoubtedly become a powerful and versatile tool for the study of material structures, particularly nanomaterials. Using electrons as a source is advantageous because they interact strongly with matter.\textsuperscript{73} This makes electrons suitable to probe small individual crystals or atomic clusters in the range of several Ångström to hundreds of nanometer in size. The interaction of electrons with matter produces various signals (e.g. elastic/inelastic scattered electrons, photons, etc.) that can be exploited to obtain information on the structure, the chemical nature of a material, as well as its physical properties (e.g. optical, magnetic and electrical properties). Conventional high-resolution imaging together with electron diffraction has been extensively used for the structural analysis (e.g. phase identification, structure determination and interfacial defects localization) of a wide range of materials.\textsuperscript{74–76} Recent technological developments in TEM optics (e.g. monochromators, aberration correctors and detectors) and novel TEM-based techniques involving the implementation of robust algorithms enable researchers to probe material structures at atomic resolution.\textsuperscript{77–79} Recently, three-dimensional TEM-based techniques (in real and reciprocal space) have demonstrated their reliability obtaining the three-dimensional structure model of nanocrystals.\textsuperscript{77,80,81} For example, the three-dimensional core structure of an edge dislocation could be identified in multiply-twinned Pt nanoparticles.\textsuperscript{82} Also, electron diffraction tomography has been successfully used for structure determination of complex sub-micron crystals.\textsuperscript{83,84} The development of image analysis methods has opened up new possibilities for extracting useful information on the atomic arrangement and local structural inhomogeneities in nanoparticles (e.g. lattice strain). For instance, 3D measurement of the lattice strain in Au nanoparticles was demonstrated using atomic resolution electron tomography.\textsuperscript{85} Scanning transmission electron microscopy (STEM) imaging combined with either energy-dispersive X-ray spectroscopy (EDS) or electron energy-loss spectroscopy (EELS) demonstrated chemical mapping at atomic resolution.\textsuperscript{86–92} In addition, transmission electron microscopes can be used to investigate the physical properties such as the magnetism of nanomaterials by electron holography\textsuperscript{93} or electron magnetic circular dichroism (EMCD)\textsuperscript{94,95}.

The TEM techniques used in this thesis are described in the next chapter and cover a handful of techniques including electron diffraction, imaging and spectroscopy.
1.4 Scope of the thesis

The synthesis of nanoparticles with well-defined chemical composition, structure and morphologies is of key importance to tailor systems with desired properties that can be used for technological applications. In this thesis, ligand-assisted syntheses through bottom-up chemical processes (i.e. hydrothermal synthesis and thermal decomposition of metal complexes) are used to fabricate a number of different nanoparticles with various morphologies and chemical compositions (iron oxide nanocubes and other morphologies, gadolinium orthophosphate nanorods, tungsten oxide nanowires and nanorods, palladium nanospheres and facetted iron-manganese oxides hybrid nanoparticles). The characterization of their structures together with their interfaces and defects is essential to gain a better understanding on how the synthesis pathways affect the quality and functional properties of the nanoparticles.

The advent of transmission electron microscopy has offered the opportunity to investigate the atomic order in a wide range of materials. The first part of the thesis deals with the structural characterization of nanomaterials using a recently developed technique, three-dimensional electron diffraction tomography (3D EDT). This technique has been developed to simplify the electron diffraction data collection process yielding high-quality 3D electron diffraction volumetric data. The 3D EDT technique is used to investigate and solve the crystal structure of individual nanocrystals at the atomic scale as described in Chapter 3. Chapter 4 introduces how the use of 3D EDT is extended, using small-angle diffraction mode, to probe mesoscopic materials consisting of self-assembled nanoparticle arrays offering an alternative to real-space tomography.

Inorganic hybrid nanoparticles are an important class of materials, which offers potential interesting enhanced and/or multifunctional properties. The investigation of Fe-Mn oxides hybrid nanoparticles (i.e. facetted dimers and core|shell nanoparticles), presented in Chapter 5, through different TEM-based techniques highlights the presence of defects and strain at their interface. Atomic resolution characterization using scanning transmission electron microscopy reveals inhomogeneous cation diffusion and a strain relaxation mechanisms associated to the transformation of the manganese oxide spinel region in core|shell nanoparticles.
2 Characterization of nanocrystals with transmission electron microscopy

2.1 The transmission electron microscope

The first electron microscope was conceived in the early 1930’s in Berlin by Max Knoll and Ernst Ruska. The idea behind the development of such a microscope was to achieve a better resolution than that of the light microscopes. At the time, the smallest object that scientists could observe was in the micrometer range, as dictated by the limitations of visible light resolution, i.e. the optimal resolution relies on the wavelength of the illumination source. However, the use of electrons as a source of illumination leads to a significantly smaller wavelength than that of the light if sufficiently accelerated. In 1925, Louis de Broglie postulated that electrons exhibit a wave-like behavior. In 1927, the wave nature of electrons was demonstrated through electron diffraction experiments conducted by two independent groups of scientists: Thompson and Reid, and Davisson and Germer. A few years later, the first prototype electron microscope was built, and successfully magnified a platinum grid x17.4. Today, quantitative information on the elemental distribution of a material down to the atomic scale is possible to obtain as a result of the enduring technological development of TEM optics and electron detectors.

A transmission electron microscope is a complex setup in which a high-energy electron beam passes through a very thin specimen in order to be subsequently analyzed. The transmitted portion of the electron beam is focused and magnified by means of electromagnetic lenses to form either a diffraction pattern or an image. A typical transmission electron microscope can be described for the sake of simplicity by three main components: the illumination system, the objective lens/stage, and the imaging system (Figure 2-1a). The first part of the illumination system is composed of a source where electrons are extracted from a filament and subsequently focused by the condenser lenses. The role of the condenser lenses is to deflect and focus the beam so as to obtain suitable illumination conditions (e.g. spot size and convergence angle). The user can adjust the strength of the condenser lenses to obtain either parallel (e.g. HRTEM, SAED) or convergent (e.g. CBED, NBED, STEM) beam conditions. A condenser aperture placed underneath the condenser lenses is useful to decrease the convergence angle and, to reduce
the spherical aberration. The specimen holder is inserted into the objective lens and can be tilted along one or two main axes to align the material with respect to the electron beam. The objective lens is considered the most important lens of the entire microscope because the final image quality is closely related to its performance. The role of all the lenses below the objective lens (i.e. intermediate and projector lenses) is to provide adequate magnification (up to x1.5 million) and to project either a diffraction pattern or an image on the detector plane; a phosphorescent screen or detector. Two apertures are found in the imaging system: the objective aperture and the selected-area aperture. A schematic representation of the ray paths of the electron beam in the two conventional diffraction and imaging modes using parallel illumination is shown in Figure 2-1b.

Figure 2-1. Transmission electron microscope. (a) Transmission electron microscope JEOL JEM-2100F at Stockholm University. (b) Schematic of the electron ray path of the two conventional operation modes in a TEM; the imaging mode on the left and the diffraction mode on the right.
2.2 TEM imaging techniques

2.2.1 High-resolution transmission electron microscopy

High-resolution transmission electron microscopy (HRTEM) has been extensively used to investigate the crystal structures, interfaces, and defects such as dislocations, stacking faults and grain boundaries of various types of crystalline materials.\textsuperscript{101–104} HRTEM imaging is based on the acquisition of an image that carries information on the lattice fringes of a crystal. The contrast in a TEM image arises mainly from two contribution types, namely, the amplitude contrast and the phase contrast. The former includes the mass-thickness contrast that is observed with a variation of thickness and/or atomic number across the crystal. The latter is related to the phase change of the electron wave which results in the appearance of the lattice fringes of a thin crystal at high magnification and, therefore, enables high-resolution imaging. The electromagnetic lenses in an electron microscope are not perfect and therefore affect the electron waves as they pass through the electron microscope column. The information carried by the electron waves is modulated as the electron beam passes through a series of lenses and apertures in the microscope. The contrast transfer function (CTF), describes how the electron wave phase shift, \( \chi(u) \), is modulated and damped as the electrons pass through the objective lens, see Equation (2-1). The phase contrast in the HRTEM image is dependent on the manipulation of the CTF, \( \sin \chi(u) \), where \( u \) is the reciprocal space vector.

\[
\chi(u) = \pi \Delta f \lambda u^2 + \frac{\pi}{2} C_s \lambda^3 u^4 
\]

where \( \lambda \) is the electron wavelength
\( C_s \) is the third-order spherical aberration coefficient of the objective lens
\( \Delta f \) the lens defocus

Typically, contrast reversal in HRTEM images can be observed by changing the defocus value (\( C_s \) and \( \lambda \) are usually fixed during the experiment). HRTEM images can be used to determine the structure of thin crystals (e.g. nanoparticles). In fact, HRTEM image contains information on projected crystal potential.

In this thesis, HRTEM imaging is used to investigate the structural features (e.g. defects) of several nanocrystals including \( \text{WO}_3 \) nanorods and Fe-Mn oxides dimers using a JEOL JEM-2100F microscope (200 kV, Schottky field-emission gun, ultra-high resolution pole-piece, \( C_s = 0.5 \text{ mm} \), point resolution 1.9 Å).
2.2.2 Scanning transmission electron microscopy

Another TEM technique that can be used for imaging is scanning transmission electron microscopy (STEM). It scans the region of interest with a fine focused electron beam (i.e. 0.05 – 0.5 nm probe size) collecting the scattered electrons using a detector (Figure 2-2). The advantage of STEM over HRTEM imaging is the absence of contrast reversal which enables a direct interpretation of the contrast in a STEM image. In STEM bright-field (STEM-BF), a detector is used to intercept electrons scattered at low-angle (such as the direct and diffracted beams) whereas an annular dark-field (ADF) detector collects the electrons scattered at higher angles excluding the low-angle scattered electrons (e.g. the direct beam). A STEM-BF image results from the interference of the direct beam with low-angle scattered electrons (i.e. elastic and inelastic electrons). STEM-BF using an annular detector has shown promising results in imaging light elements.\textsuperscript{105,106} On the other hand, high-angle annular dark-field (HAADF) in STEM has attracted much interests because it produces image contrast that is sensitive to the atomic number (I \propto Z^2), sometimes called Z-contrast imaging.\textsuperscript{107} Modern transmission electron microscopes using STEM provide a spatial resolution at the atomic scale.\textsuperscript{78,108–110}

![Scanning transmission electron microscopy imaging](image)

Figure 2-2. Scanning transmission electron microscopy imaging. (a) Schematic of the electron ray path for STEM imaging showing the position of BF, ADF and HAADF detectors, as well as their relationship with the scattering angle \( \alpha \). (b) Simulated STEM-BF and (c) STEM-HAADF images of FeO along a <001> zone axis where the atomic columns are revealed in black (BF image) and white (HAADF image), respectively.

In this thesis, STEM-HAADF is used to investigate the 3D morphology of Fe-Mn oxides hybrid nanoparticles through tomography reconstruction using a JEOL JEM-2100F microscope at Stockholm University. Also, STEM-HAADF using a Cs-corrected microscope is used to follow the structural change in core|shell nanoparticles using a fifth-order aberration corrected Nion Ultra STEM 200 microscope equipped with a cold field-emission gun at Oak Ridge National Lab.
2.3 Electron crystallography

2.3.1 Unit cell and crystal symmetry

A crystal can be thought of as a periodic arrangement of a three-dimensional network of atoms that can be divided into a set of identical units, called unit cell. The unit cell of a crystal is characterized by three non-coplanar vectors \((a, b, c)\) where \(\alpha, \beta, \gamma\) are the angles between the pairs of vectors \(b\) and \(c\), \(a\) and \(c\), and \(a\) and \(b\), respectively. The basic vectors and their associated angles define the unit cell dimensions but also the crystal lattice type (e.g. cubic, hexagonal, etc.). There are 14 distinguishable crystal lattices, called Bravais lattices, which describe the three-dimensional configuration of atoms in space. Bravais lattices are divided into 7 crystal systems: cubic, hexagonal, rhombohedral, tetragonal, orthorhombic, monoclinic and triclinic, which have one or several lattice type (e.g. primitive (P), body-centered (I), face-centered (F), base-centered (A, B or C)). For each individual crystal systems, atomic planes are described by three integers named Miller indices. The Miller indices, \(h\), \(k\) and \(l\), describe how the planes cut the lattice. Examples of some lattice planes in a cubic lattice presented with their Miller indices are shown in Figure 2-3. The crystallographic directions can also be described using \(h\), \(k\) and \(l\) indices in squared brackets.

![Figure 2-3. Examples of different crystallographic planes and their associated Miller indices in a cubic lattice. Representation of (100), (110) and (200) crystallographic planes.](image)

The lattice type is not sufficient to describe the three-dimensional atom position in a crystal. In fact, different atomic arrangements are possible within a given unit cell and lead to different symmetry. The symmetry of a (perfect) crystal is described by one of the 230 distinct space groups that result from the combination of all symmetry operations in three-dimensions.
2.3.2 Diffraction and the reciprocal lattice

Diffraction patterns are interesting because of the information they carry on the symmetry of crystals. Electron diffraction in crystal occurs when electrons of a given wavelength, $\lambda$, are scattered by a set of lattice planes having an inter-planar spacing, $d_{hkl}$, leading to constructive interferences (Figure 2-4). This is observed when the difference in path lengths, $2d_{hkl}\sin\theta$, between two parallel in-phase electron waves is equal to an integer multiple of the incoming wavelength of the electrons, $n\lambda$. Diffraction spots (reflections) are observed on a diffraction pattern as long as the Bragg condition is fulfilled, see Equation (2-2).

$$2d_{hkl} \sin\theta = n\lambda$$  \hspace{1cm} (2-2)

Figure 2-4. **Bragg diffraction.** Bragg diffraction occurs when the difference in path lengths, $2d_{hkl}\sin\theta$, between two parallel in-phase waves is equal to an integer multiple of the incoming wavelength of the radiation, $\lambda$.

The Ewald sphere is another geometrical representation that is a convenient way to describe the occurrence of diffraction in reciprocal space. Figure 2-5 illustrates the geometrical relationship between the incident electron wave vector $k_0$ (incident beam) and the scattered wave vector $k$ (diffracted beam in Bragg condition). The scattering vector $g_{hkl}$ corresponds to the difference between the scattered wave vector $k$ and the incident electron wave vector $k_0$. The reciprocal lattice geometry depends on the orientation and the lattice parameters of the crystal. Diffraction occurs whenever the Ewald sphere crosses a reciprocal lattice “point”, which is more accurately described by relrods. Reflections in an electron diffraction pattern are sometimes observed even if the Bragg conditions are not exactly met (i.e. excitation error, $s$, describes how far it deviates from the exact Bragg condition). The intensity of the reflections in a diffraction pattern decreases as the Ewald sphere cuts the relrod out of its center, which is at the exact Bragg condition. An electron diffraction pattern is a section of part of the reciprocal lattice that is projected on a detector, and its origin is $000$ (indexing of the transmitted beam, $k_0$).
Figure 2-5. **Schematic in 2D of the Ewald sphere construction with two different orientations of the reciprocal lattice with respect to the incident electron beam.** (a) Along a crystallographic zone axis of the crystal and (b) off-zone axis. A diffraction spot is observed for (a) 002 reflection, but in (b) 002 reflection is absent.

A large number of reflections of the reciprocal lattice can be covered when the crystal is properly oriented along one of its zone axis (see Figure 2-5a). Other reflections in reciprocal space can be sampled by changing the crystal orientation so that the Ewald sphere will intercept different reciprocal lattice relrods (compare Figure 2-5a and Figure 2-5b). In a typical TEM experiment, the crystal orientation is changed by rotating the crystal using the goniometer and sample tilting holder. Alternatively, beam tilt can be used in a limited range of few degrees. The relationship between the length of the reciprocal lattice vector, $g_{hkl}$, the lattice plane spacing, $d_{hkl}$, and the scattering angle, $\theta$, can be described as follows:

$$|g_{hkl}| = \frac{1}{d_{hkl}} = 2\frac{1}{\lambda} \sin \theta \quad (2-3)$$

where $|g_{hkl}| = |k - k_0|$

Each reciprocal lattice point can be described as follows:

$$g_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad (2-4)$$

where $hkl$ are the Miller indices

$\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$ are the reciprocal lattice vectors

The position of the reflections in an electron diffraction pattern gives information on the equivalent set of lattice planes whereas the intensities depends on the types of atoms and their positions in the unit cell, as well as
other factors such as crystal size and thickness. The structure factor describes the diffraction intensities from a known crystal structure. Electron diffraction patterns carry only the amplitude of the resultant interference and the phase of the structure factor is lost. The structure factor can be expressed as follows:

\[ F(hkl) = \sum_j f_j e^{2\pi i (hx_j + ky_j + lz_j)} \]  

(2-5)

where \( f_j \) is the atomic scattering factor of the \( j^{th} \) atom  
\( hkl \) the Miller indices  
\( x_j, y_j \) and \( z_j \) are the atomic coordinates of the \( j^{th} \) atom  

However, the phase of the structure factor can be recovered using ab initio structure determination methods such as direct methods or charge-flipping. The kinematical relationship between the intensity of diffracted beams and the structure factor is the following:

\[ I(hkl) \propto |F(hkl)|^2 \]  

(2-6)

2.3.3 Crystallography using electron diffraction

Electron crystallography requires collecting enough electron diffraction patterns along different crystallographic orientations of one or several single crystal(s) in order to perform the unit cell determination, quantitative intensities extraction and structure solution at the atomic scale. The conventional approach to collect an electron diffraction data set involves selecting a suitable crystallographic axis of a single crystal followed by tilting of the crystal around this axis. A final three-dimensional data set can be obtained after recording sufficient individual electron diffraction patterns along different zone axes. The crystal lattice type and/or symmetry elements (e.g. glide planes, screw axes) can be inferred from the diffraction symmetry and the extinction conditions in an electron diffraction pattern. The approach of recording along the major zone axes provides a relatively high number of reflections at such directions and the structure solution using reflections from zone axis patterns often leads to good atomic projections. However, this approach is tedious and time consuming. In fact, the completion of the data set often requires gathering the data from several crystals, especially for the low symmetry crystal systems such as monoclinic or triclinic systems. Moreover, the dynamical effects are stronger in diffraction patterns obtained along the zone axes of a crystal, in particular for thick crystals. The recent development of techniques using automated acquisition of a three-dimensional electron diffraction data set have eased the way to collect and process electron diffraction data set. Several similar techniques have been
developed to provide 3D data set; automated diffraction tomography (ADT)\textsuperscript{112,113}, rotation electron diffraction (RED)\textsuperscript{114,115} and three-dimensional electron diffraction tomography (3D EDT)\textsuperscript{83,116} are currently used to solve challenging crystal structures at the atomic scale. In our investigations, the 3D EDT technique is used to probe nanomaterial structures at the atomic scale and we extend its use to probe the packing arrangement of nanoparticle in ordered mesoscopic assemblies using a special “small-angle diffraction” mode.

2.3.4 Electron diffraction tomography

Three-dimensional electron diffraction tomography (3D EDT) is a technique that allows the acquisition of a large amount of individual diffraction patterns from one unique crystal by combining the electron beam tilt and mechanical goniometer tilt (see Figure 2-6). This technique presents several advantages over the conventional approach where two-dimensional diffraction patterns are recorded in-zone. The crystal alignment along a particular zone axis is not required for data collection. This allows to drastically reduce the acquisition time and the dynamical effects. The fine cut of reciprocal space allows the reciprocal volume to be fully covered, including high indexed reflections. This improves the reflection number and intensity quality, which are used for ab initio structure solution.

![Schematic diagram of 3D EDT](image)

Figure 2-6. **Schematic illustrating the different steps in structure determination using 3D EDT.** (a) The data collection consists of recording individual electron diffraction patterns by combining beam tilt and mechanical goniometer tilt. (b) 3D reciprocal volume reconstruction enables unit cell determination and hkl reflections indexing (c) Atomic structure determination after intensities extraction and ab initio structure determination.

2.3.4.1 Data collection

Individual electron diffraction patterns are recorded by fine sampling of reciprocal space using a combination of mechanical goniometer tilt (large, >2°) and beam tilt (fine, 0.02-0.1°) along the goniometer axis (x-tilt). The use of this technique does not require any additional hardware and, therefore, can be used on most transmission electron microscopes. The acquisition procedure
takes about 45 minutes up to 2 hours depending on the beam tilt step and the total angular tilt range. The maximum tilt range that can be obtained depends on the type of goniometer used. We typically used a single tilt-holder covering 150° of the reciprocal space (-75° to +75°). Acquisition of electron diffraction patterns can be performed using either selected-area (SAED) or nano-beam (NBED) electron diffraction mode. All experimental data of electron diffraction presented in this thesis were obtained using a JEOL JEM-2100 (Cs = 1.4 mm, Cc = 1.8 mm, point resolution = 2.5 Å) electron microscope equipped with LaB₆ filament operated at 200 kV and Analitex EDT-COLLECT software is used for data collection. Conventionally, the nominal camera length used to collect electron diffraction patterns is set between 40 to 100 cm enabling to access the reflections which have spatial frequencies up to few Å⁻¹. However, an unusually long camera length of 5 meters has been used to probe the inter-spacing between nanoparticles in mesoscopic arrays equivalent to spatial frequency range of few nm⁻¹ in reciprocal space. In this thesis, the term small-angle is therefore used to characterize such large camera length.

2.3.4.2 Data processing

The series of electron diffraction pattern collected using EDT-COLLECT are processed to yield a three-dimensional reciprocal volume. The unit cell parameters of the crystal can be found, and the information on the symmetry of the crystal is obtained by looking at systematic absences (i.e. extinction conditions) in the 3D reciprocal volume. The reflections conditions are found by inspecting the 3D volume along specific directions. For example, if the lattice parameters found correspond to a cubic lattice and the 3D reciprocal volume reveals systematic absences only along one direction (reflection conditions: 00l =2n) then the space group can be identify as either P2₁3 or P4₃2₁.

2.3.4.3 Structure solution and refinement

Structure solution can be determined ab initio using the intensities collected by 3D EDT. There are several methods that can be used for structure solution including direct methods (e.g. FOX¹¹⁷ and SIR2011¹¹⁸ programs) and charge flipping (e.g. Superflip¹¹⁹ and JANA2006¹²⁰). Structure solution often requires prior knowledge on the chemical nature of the material studied. All possible space groups found based on systematic absences can be tested, and structure solution is found once the model (i.e. potential map depicting the atom positions within the unit cell) obtained is consistent with the chemical and topological knowledge we have of the crystal studied. The refinement can be performed using a least-squares refinement procedure using for example SHELX¹²¹ or JANA2006 program. In this thesis, we used direct methods implemented in SIR2011 to solve the crystal structure and JANA2006 for the refinement.
2.4 Spectroscopic TEM techniques used for chemical mapping

Conventional TEM imaging (e.g. HRTEM) does not allow the chemical composition of materials to be examined. For this purpose, several spectroscopic techniques have been developed using different types of signal detection and acquisition principles. The interaction between the incident electron beam and matter in a TEM produces, for instance, characteristic X-rays which can be exploited for chemical analysis. The technique using characteristic X-rays is known as energy dispersive X-ray spectroscopy (EDS). Besides, energy-filtered transmission electron microscopy (EFTEM) and electron energy-loss spectroscopy (EELS) have also emerged as powerful TEM-based techniques for chemical mapping of materials. Unlike EDS, these techniques rely on the detection of specific inelastically scattered electrons that passed through the material. Detection of such signal requires the transmission electron microscope to be equipped with a spectrometer, installed either in-column or post-column. The spectrometer consists of a magnetic prism that deflects electrons according to their intrinsic energies. A specific energy window can be set to discriminate electrons so that only electrons of the selected energy window (e.g. from $E_0$ to $E_0-\Delta E$) will reach the detector yielding an electron energy-loss spectrum (see Figure 2-7a). The electron energy-loss spectrum obtained contains information on the chemical fingerprint of atoms and their surrounding in a material and depicts the quantities of scattered electrons as a function of their energy loss. A typical EEL spectrum contains (i) the zero-loss peak found around 0 eV (i.e. elastic electrons), (ii) the low-loss region (<100eV) which includes plasmon peaks, and (iii) the core-loss region contains the core-loss features (i.e. ionization edge that depends on the electronic structure of the atom), which includes near edge structure (i.e. contains information on the bonding of atoms) and extended fine structure (i.e. provides information on the electron density of states revealing the coordination and interatomic distances).

The main differences between elemental mapping done by EELS in STEM and EFTEM rely on the acquisition procedure as illustrated in Figure 2-7b and c. Chemical mapping using STEM-EELS allows to collect different edges simultaneously as the fine-focused electron beam scans the area of interest. The resultant elemental map consists of a specific energy range electron energy-loss spectrum recorded at each pixel in the image as illustrated in Figure 2-7b. On the other hand, EFTEM imaging enables chemical mapping of one specific chemical element at a time. The elemental map of a material is obtained from a series of energy-filtered images recorded around the core-loss edge of the element of interest (cf. $\Delta E_1$ and $\Delta E_2$ energy window on Figure 2-7c), and in the pre-edge region to estimate the background. An overlay image of several elemental maps can be obtained by summing up individual
elemental maps of the area of interest. EFTEM and EELS techniques display a higher sensitivity towards light element detection as compared to EDS.

![Image](image.png)

Figure 2-7. **EFTEM and EELS elemental mapping.** (a) Schematic representation of the post-column filter used to record EEL spectra. (b) STEM-EELS elemental mapping where each pixel contains an EEL spectrum. (c) One image of a specific range of energy loss can be recorded at a time and elemental maps can be obtained by overlay of each individual EFTEM image.

In this thesis, EELS and EFTEM are used to produce elemental maps of Fe-Mn oxides hybrid nanoparticles (i.e. core|shell and asymmetric configurations) looking at the L$_{2,3}$ edge of Mn and Fe and O-K edge.

### 2.5 Image processing of high-resolution TEM images

#### 2.5.1 Geometric phase analysis

High-resolution electron microscopy provides information on the atomic scale and, therefore, can be used to investigate defects and strain in nanomaterials. Geometric phase analysis (GPA)$^{122,123}$ is a quantitative method that measures strain and local deformation (i.e. variation of the lattice spacing at a specific position) by the analysis of the lattice fringes displacement in an image. This technique quantifies the strain in a material with respect to a non-distorted lattice (reference area). GPA is used in our work to evidence lattice deformation in nanoparticles that display chemical inhomogeneity across its structure.

A HR-TEM image of an ideal crystal along a zone axis can be interpreted as a summation of periodic planar waves corresponding to the atomic planes in the crystal. Therefore, the intensity, I(r), in an image can be expressed as the sum of the each Fourier component over all reciprocal lattice vectors;
\[ I(r) = \sum_g I_g(r)e^{2\pi ig \cdot r} \]  
\[ (2-7) \]

where \( g \) is the reciprocal lattice vector.

For the sake of simplicity, the one dimensional case is considered where only one reflection is used for GPA. The local Fourier component is selected by filtering a specific reflection in reciprocal space (see green mask on b). The filtered signal (local Fourier component) is:

\[ I_g(r) = A_g(r)e^{iP_g(r)} \]  
\[ (2-8) \]

where \( A_g \) is the amplitude and \( P_g(r) \) the geometric phase.

The geometric phase image of the local Fourier component is essential for GPA because it is used to calculate the displacement field, which is the lattice difference between the region of interest and the area of reference defined by the user (Figure 2-8c). The relationship between the geometric phase, \( P_g(x) \), and the displacement field, \( u(x) \), is given by:

\[ P_g(r) = -2\pi g \cdot u(r) \]  
\[ (2-9) \]

A deformation map along one direction, \( \varepsilon_x \), is obtained (Figure 2-8d):

\[ \varepsilon_x = \frac{\delta u}{\delta x} \]  
\[ (2-10) \]

The color variation in the color map indicates the strain (i.e. variation of the lattice spacing) in the image with respect to the reference area.

Figure 2-8 Schematic of geometric phase analysis along one direction of a core|shell \( \text{Mn}_3\text{O}_4|\text{Fe}_3\text{O}_4 \) nanoparticle. (a) High-resolution STEM-HAADF image along [1\(-1\)0] zone axis. (b) Fourier transform of the image shown in (a) using 004\(_{\text{Fe}_3\text{O}_4}\) reflection. The green masks inset highlight the spatial frequencies used for filtering. (c) Geometric phase image. (d) Deformation map obtained using 004\(_{\text{Fe}_3\text{O}_4}\) reflection. (e) Schematic depicting the lattice spacing variation across the nanoparticle along [001].
2.5.2 Particle image velocimetry analysis

Particle image velocimetry (PIV) analysis is a technique, usually used to study complex flow phenomenon, that quantifies the particles’ displacement as a function of time.\textsuperscript{124} The average particle displacement is calculated on selected regions of interest (i.e. interrogation windows). The iterative procedure involving cross-correlation computation between two images recorded at subsequent exposure time leads to a displacement map (see Figure 2-9). The procedure is based on the following steps: (i) selection of an image window, (ii) correlation analysis, (iii) displacement peak identification, and (iv) calculation of the velocity map. During the procedure, the spurious displacement vectors (i.e. having a low correlation values) are replaced by the median value of the neighbouring vectors.

![Figure 2-9. Particle image velocimetry.](image)

Figure 2-9. **Particle image velocimetry.** (a) Image depicting a regularly spaced lattice. (b) Shearing of the image in (a). (c) Displacement map where colored vectors depict the displacement.

In this work, PIV analysis implemented as a plugin of ImageJ software package\textsuperscript{125} is used to investigate the cations displacement in a core|shell nanoparticle during the transformation of its core.
3 Synthesis of nanoparticles and determination of their structures using electron diffraction tomography

Investigating structural features of materials is an important step in understanding the nature of their physical and chemical properties. Electron diffraction presents a major advantage over X-ray based diffraction techniques by offering the possibility to probe the structure of individual nanomaterials. This chapter describes the synthesis of WO$_3$ and GdPO$_4$ nanorods using hydrothermal process and we show how the use of a recently developed TEM-based technique, 3D electron diffraction tomography (3D EDT), provides information on the crystal structure of individual nanocrystals.

3.1 Synthesis of tungsten oxide nanowires and nanorods

Tungsten oxides are particularly interesting for their electro-optical properties. Their optical responses (i.e. color change) make them suitable for electrochromic devices (e.g. smart windows and switchable sunroof glazing). Development of tungsten oxide nanocrystals and control of their nanometric domains is a promising approach to increase the charge insertion density, which controls the color change. In this thesis, we report a simple way to control the width of tungsten oxide nanorods using different organic ligands having a common functional group (i.e. –COOH).

WO$_3$ nanorods with a high aspect ratio are obtained by hydrothermal synthesis (180 °C for 3 hours under constant stirring) using sodium tungstate (Na$_2$WO$_4$·2H$_2$O) as a precursor in the presence of three different organic acids; oxalic acid, citric acid, or poly(methacrylic acid) (see chemical formula in Figure 3-1). The resulting tungsten oxide nanocrystals display a large difference in their width as shown in Figure 3-2. The largest nanorods, having about 100 nm in width (Figure 3-2a), are obtained in the presence of oxalic acid. Interestingly, these nanorods are composed of a large number of small nanowires that assemble together to form larger entities. This stacking effect has been observed in similar systems. Thinner nanorods are obtained using citric acid as ligand resulting in a drastic width reduction (Figure 3-2b). The use of poly(methacrylic acid) (PMAA) results in thin tungsten oxide nanowires that are inclined to form wire coils (Figure 3-2c). Stirring during
the synthesis is crucial to obtain a small width (compare Figure 3-2c and Figure 3-2d).

Figure 3-1. Chemical formulas of the acids used for the hydrothermal synthesis of WO$_3$ nanorods. Figure and caption reproduced from paper I.$^{130}$

Figure 3-2. TEM images of the WO$_3$ nanorods and nanowires obtained at 180 °C under constant stirring with (a) oxalic acid, (b) citric acid and (c) poly(methacrylic acid). (d) WO$_3$ nanorods synthesized without stirring in the presence of poly(methacrylic acid). Figure and caption reproduced from paper I.$^{130}$
3.2 Structural analysis of tungsten oxide nanorods

TEM images of a WO$_3$ nanorod synthesized in the presence of PMAA are shown in Figure 3-3. WO$_3$ nanorods have a hexagonal lattice (space group: $P6_{3}/mmm$) with lattice parameters of $a = 7.3339(5)$ Å and $c = 3.8721(3)$ Å as shown by powder X-ray diffraction (see paper I). The rod has a relatively high aspect ratio and the electron diffraction pattern inset Figure 3-3a shows that the preferred growth direction of the WO$_3$ nanorod corresponds to the hexagonal $c$-axis. HRTEM images of the WO$_3$ nanorod recorded along [1−10] zone axis (Figure 3-3b, c) reveal structural discontinuities (see Figure 3-3b) suggesting that WO$_3$ nanorods consist of an assembly of thin nanowires packed along their common crystallographic $c$-axis. Three-dimensional electron diffraction tomography (3D EDT) performed on WO$_3$ nanorod demonstrates that WO$_3$ subdomains (i.e. nanowires) display a high degree of alignment along the $c$-axis whereas diffuse scattering features are observed along the $a^*-b^*$ plane (see Figure 3-4). The diffuse features depict a disorder that is most likely related to a misorientation of the WO$_3$ nanowires during their assembly into a rod. This indicates that the growth may occur through orientated attachment of thin nanowires.$^{131}$ A similar stacking effect among tungsten oxide nanowires has been reported earlier with a lower degree of alignment.$^{132}$

Figure 3-3. TEM images of a nanorod synthesized with PMAA without stirring. (a) Low-magnification image (inset, SAED pattern) and (b, c) HRTEM images of the tagged area in panel (a) along [1−10] zone axis (insets, FFT of the corresponding HRTEM image). Figure and caption reproduced from paper I.$^{130}$
3.3 Synthesis of gadolinium orthophosphate nanorods

Lanthanide orthophosphates are chemically stable and display good thermal stabilities. They have been considered for nuclear waste disposal due to their radiation resistance and chemical durability properties. Gadolinium phosphates are interesting contrast agent for magnetic tumor imaging but also for their optical properties when doped with other lanthanides (e.g. Eu$^{3+}$). Gadolinium orthophosphates nanorods suspended in water are synthesized under hydrothermal conditions at 180 °C. In a typical synthesis, gadolinium nitrate (Gd(NO$_3$)$_3$·6H$_2$O) and ammonium phosphate monobasic (NH$_4$H$_2$PO$_4$) are mixed in water and transferred to a Teflon lined stainless steel autoclave. The nanorods widths can be narrowed down from about 300 nm to 15 nm using poly(methacrylic acid) (PMAA) as a ligand (Figure 3-5).
3.4 Phase identification and structure solution of gadolinium orthophosphate nanorods

GdPO$_4$ nanorods synthesized in the presence of PMAA were used for structural investigation. Powder X-ray diffraction (PXRD) performed on the purified GdPO$_4$ nanorods powder reveals the presence of two different phases; a hexagonal form (ICDD 39-0232) and a monoclinic phase (ICDD 32-0386) that belongs to a monazite structure type (Figure 3-6a). The two most ubiquitous rare-earth orthophosphates found in nature are the monazite$^{139}$ ($P2_1/n$, monoclinic crystal system) and xenotime$^{140}$ ($I4_1/amd$, isostructural to the tetragonal zircon type) structures. However, synthetic conditions such as temperature, precursor type and pH have a strong influence on the final structure type of rare-earth orthophosphates formed.$^{141,142}$ For instance, low temperature synthesis conditions (20-90 °C) can yield hexagonal form (rhabdophane structure). This hexagonal form dehydrates under thermal treatment, and transforms into the stable monazite phase.$^{143}$ In fact, previous studies report the crystals structures of some rare-earth orthophosphates (La, Ce, Pm, Nd, and Sm)$^{144,145}$ Mooney was the first to identify that CePO$_4$ is dimorphic and crystallizes in a monoclinic phase isomorphous with the monazite mineral and a hexagonal form that can be transformed to the monoclinic form at relatively high temperature.$^{58}$ The hexagonal structure was identified to belong to either $P6_222$ or $P3_12_1$ space groups. However, later studies including IR spectroscopy investigations of several rare earth phosphates were rather inconclusive regarding the space group determination.$^{146,147}$ Prior to our publication,$^{138}$ no single crystal data on the hexagonal form of gadolinium orthophosphate had been reported and its structure solution was never obtained.

The transformation of the hexagonal form into monoclinic structure was followed by in-situ XRD (Figure 3-6b). Two characteristic peaks marked by stars in Figure 3-6b indicate that the stability range of the hexagonal form extends from room temperature up to 800 °C. The diffraction pattern recorded at 900 °C reveals the complete conversion of the hexagonal into the monoclinic phase.
Figure 3-6. Powder X-ray diffraction of GdPO$_4$ nanorod powder synthesized with PMAA. (a) (top) Experimental PXRD pattern of a dimorphic GdPO$_4$ powder synthesized with PMAA and (middle and bottom) simulated PXRD patterns of both hexagonal and monoclinic forms. (b) PXRD patterns of the GdPO$_4$ powder at different heating temperatures. The peaks marked with stars depict the hexagonal form present in the powder. Figure and caption reproduced and adapted from paper II.$^{138}$

In order to perform data collection on a single nanorod, no pre-alignment along a low-index zone axis is required. The nanocrystal must be isolated so as to collect uniquely diffraction reflections that belong to the crystal of interest. A low concentration dispersion of GdPO$_4$ nanorods is prepared, and a small aliquot is retrieved from water dispersion and subsequently drop-casted onto a TEM grid. Electron diffraction data sets were collected from individual nanorods using electronic beam tilt series of 0.15° steps covering the range of ±1.5° with a 3° goniometer tilt angle. In less than an hour, over 1000 unique electron diffraction frames were recorded in the nanobeam (NBD) mode using a 50 µm condenser aperture. After data processing, a three-dimensional reciprocal volume was obtained as shown in Figure 3-7. The nanorod consists of a hexagonal structure, as evidenced by the three different reciprocal space volume projections in Figure 3-7a, b and c. A second phase was identified by collecting another dataset on a different crystal confirming the presence of a monoclinic phase as shown in Figure 3-8. The reconstructed reciprocal space volume shows several systematic absences, ($h0l$, $h + l = 2n + 1$) and ($0k0$, $k = 2n + 1$), that correspond to $P2_1/n$, a well-known monoclinic space group.$^{140}$
Figure 3-7. **Projections of reconstructed three-dimensional reciprocal space volume of the hexagonal form of an individual GdPO$_4$ nanorod along (a) [001], (b) [1-10], and (c) [010] zone axes.** Figure and caption reproduced from paper II.\textsuperscript{138}

Figure 3-8. **Projections of reconstructed three-dimensional reciprocal space volume of the monoclinic form of an individual GdPO$_4$ nanorod along (a) [100], (b) [010], and (c) [001] zone axes.** Figure and caption reproduced from paper II.\textsuperscript{138}

The systematic extinction condition found in the reciprocal space volume of the hexagonal phase (00$_l$, $l = 3n$) allowed us to identify a set of different space groups; \{P$_6$2$_2$, P$_6$42$_2$\} and \{P$_6$, P$_6$4\} which belong to the hexagonal crystal system whereas \{P$_3$1$_2$, P$_3$2$_1$\} and \{P$_3$, P$_3$2\} are trigonal. The structure of the hexagonal GdPO$_4$ form is obtained *ab initio* by means of *direct methods* using the extracted intensities from 3D EDT data set. The experimental parameters related to the data collection and structure determination of the hexagonal GdPO$_4$ form are shown in Table 3-1. We found that the GdPO$_4$ nanorods have a hexagonal lattice with the P$_6$222 space group based on the R$_1$ factor calculated and the chemical and topological knowledge. Atomic coordinates in the hexagonal lattice are found as listed in Table 3-2. A projection of the structure model in Figure 3-9a describes a network of alternately connected chains formed by Gd surrounded by eight oxygen (blue) and phosphate tetrahedra (grey) along the $c$-axis. The three-dimensional structure results from the chain linked to each other in such a manner as to create channels that can accommodate water. The potential map obtained experimentally (Figure 3-9b) shows the high-quality recovery of the atomic potential of all elements (Gd, P and O). The comparison with the monoclinic
structure projections shown in Figure 3-9c reveals that the hexagonal structure display a lower density than that of the monoclinic phase.

Table 3-1. Experimental parameters for the GdPO₄ hexagonal form. (Table and caption reproduced from paper II)

<table>
<thead>
<tr>
<th>Experimental Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Tilt range (deg)</td>
<td>-73.0° to + 65.9°</td>
</tr>
<tr>
<td>Total reflections</td>
<td>791</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>86</td>
</tr>
<tr>
<td>Resolution (Å)</td>
<td>0.9</td>
</tr>
<tr>
<td>Reflection coverage (%)</td>
<td>84</td>
</tr>
<tr>
<td>R_{sym}</td>
<td>15.3 %</td>
</tr>
<tr>
<td>R (Sir2011 solution)</td>
<td>6.8 %</td>
</tr>
<tr>
<td>R₁ (Jana2006 refinement)</td>
<td>13.1 %</td>
</tr>
</tbody>
</table>

Table 3-2. Crystallographic data for the GdPO₄ hexagonal form. x, y and z are the atomic coordinates and U is the thermal parameter. Table and caption reproduced from paper II.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd</td>
<td>0.5</td>
<td>0</td>
<td>0.5</td>
<td>0.022</td>
</tr>
<tr>
<td>P</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0.027</td>
</tr>
<tr>
<td>O</td>
<td>0.303</td>
<td>0.860</td>
<td>0.152</td>
<td>0.014</td>
</tr>
</tbody>
</table>

Figure 3-9. **Crystallographic models of gadolinium orthophosphate.** (a) Projection of the hexagonal GdPO₄ structure model along [001] showing the polyhedra–tetrahedra network and (b) the potential map obtained from the direct methods solution using the 3D EDT data set. (c) Projection of the monoclinic GdPO₄ structure model along [010]. Figure and caption reproduced from paper II.

Hydrothermal syntheses of WO₃ nanoparticles using different organic ligands described a simple way to control the width of WO₃ nanowires and nanorods. 3D EDT has been successfully used to retrieve information on the crystallographic alignment of WO₃ nanowires and the crystal structures of individual GdPO₄ nanocrystals were determined.
4 Characterization of order and defects in nanoparticle assemblies by transmission electron microscopy

This chapter first describes briefly the synthesis of monodisperse Pd nanospheres, which are further used as building blocks for the formation of mesoscopic arrays (i.e. nanoparticle assemblies). We show how the combination of real-space imaging and electron diffraction tomography enables to probe the packing arrangement, quantify distortion and identify planar defects in Pd nanosphere assemblies. Electron diffraction tomography is used in small-angle diffraction mode in order to probe distances on the nanometer scale. This approach provides an alternative to real-space tomography.

4.1 Monodisperse Pd nanospheres synthesis for self-assembly

Palladium nanoparticles are effective catalysts for a number a chemical reactions,\textsuperscript{148} and they also exhibit plasmonic properties.\textsuperscript{149} A wide variety of morphologies can be obtained by careful control of synthetic conditions (e.g. precursor concentration, reductants and stabilizers).\textsuperscript{150} Monodisperse spherical Pd nanoparticles, with an average hard core size of 6.1 ± 0.6 nm, were synthesized through thermal decomposition of palladium acetylacetonate (Pd(C\textsubscript{5}H\textsubscript{7}O\textsubscript{2})\textsubscript{2}) in 1-octadecene (C\textsubscript{18}H\textsubscript{36}) in the presence of 1,2-hexadecanediol (C\textsubscript{16}H\textsubscript{34}O\textsubscript{2}), trioctylphosphine (P(C\textsubscript{8}H\textsubscript{17})\textsubscript{3}) and oleic acid (C\textsubscript{18}H\textsubscript{34}O\textsubscript{2}) at 316 °C (see Figure 4-1). The Pd nanospheres were used as building blocks to produce 3D highly-ordered nanoparticle assemblies. In this study, the nanoparticle assemblies result from a solvent mediated destabilization process where ethanol slowly diffuses into a stable dispersion of Pd nanoparticles in toluene.\textsuperscript{60} The nanoparticle concentration range and the assembly time were carefully selected in order to obtain well-ordered thin nanoparticle assemblies. The nanoparticle concentration used in our experiment is 1.3 mg of Pd per ml of toluene. Thin nanoparticle assemblies are formed after several hours of slow ethanol diffusion and larger nanoparticle assemblies are formed upon prolonged diffusion time. Large
nanoparticle mesoscopic arrays can be obtained upon 72 hours of ethanol diffusion as shown in Figure 4-2.

Figure 4-1. TEM images of spherical Pd nanoparticles. (a) TEM image of spherical Pd nanoparticles. (b) HRTEM image of Pd nanoparticles. (c) Histogram depicting the size distribution of Pd nanoparticles. Figure and caption reproduced and adapted from paper III.¹⁵¹

Figure 4-2. Large nanoparticle assemblies built from Pd nanoparticles. (a-f) TEM images of facetted Pd nanoparticle assemblies obtained after 72 hours of ethanol diffusion. (a, b, c) nanoparticle assemblies with hexagonal platelet morphology. (d, e, f) nanoparticle assemblies deviating from a perfect hexagonal morphology. Figure and caption reproduced from paper III.¹⁵¹
4.2 Probing order and defects in nanoparticle assemblies by combining real and reciprocal space TEM

The properties and performance of materials are often influenced by the presence of defects. Likewise, the collective properties in nanoparticle assemblies can be dependent on the packing symmetry and the nanoparticle ordering. For instance, coherent Raman scattering has been evidenced in ordered silver fcc supra-crystals whereas it vanishes for disordered nanoparticle assemblies.\textsuperscript{152} Also, the magnetic properties of Co nanoparticle assemblies can vary upon the degree of order in nanoparticle assemblies.\textsuperscript{153} It is therefore important to identify which defects are predominantly found in nanoparticles arrays. Previous investigations on binary nanoparticle assemblies using real-space TEM imaging enabled to characterize and classify different types of defects found in nanoparticle assemblies.\textsuperscript{154,155} However, studies on defects in nanoparticle assemblies remain scarce.\textsuperscript{156}

The investigation of the packing arrangement of nanoparticles within the assemblies by TEM requires arrays that are relatively thin. 3D EDT was used in a special mode, called “small-angle electron diffraction”, which requires the microscope to have a large camera length (i.e. distance between the sample and the camera), as high as 5 meters. The acquisition of a three-dimensional small-angle electron diffraction dataset together with imaging of the nanoparticle assemblies along one direction allowed us to obtain a 3D model of the nanoparticle packing arrangement. Nanoparticle assemblies formed during the first 24 hours of ethanol diffusion were retrieved for subsequent TEM investigation. Figure 4-3a shows a typical pseudo-hexagonal mesoscopic nanoparticle assembly which consists of several nanoparticles packed layers.

![Figure 4-3. TEM images of a Pd nanoparticle hexagonal assembly recorded along [001]\textsubscript{hcp}. (a) Low magnification TEM image showing a pseudo-hexagonal morphology in-plane and the corresponding small-angle electron diffraction pattern (SA-EDP). (b) Intermediate magnification TEM image of the area tagged in (a). (c) Higher magnification TEM image from the area tagged in (b). (d) 3D model of the hexagonal assembly indexed with hcp arrangement. Figure and caption reproduced from paper III.\textsuperscript{151}](image-url)
The small-angle electron diffraction pattern recorded from the nanoparticle assembly (see inset of Figure 4-3a) reveals that the nanoparticles are packed with a high degree of translational order. The TEM images of the nanoparticle assembly recorded at intermediate and higher magnification confirm the high translational order where each nanoparticle shares 6 nearest neighbours on the plane (see Figure 4-3b and c) separated from each other by ~2.0 nm of soft organic ligands. From this two-dimensional projection, we can expect either face-centered cubic (fcc) (also known as cubic close-packed) (ccp), or hexagonal close-packed (hcp) symmetry since both are characterized by a 6-fold symmetry along either \(<111>_{fcc}\) or \(<001>_{hcp}\) directions, respectively. The three-dimensional small-angle electron diffraction tomography (3D SA-EDT) volume reconstruction reveals the presence of diffuse streaking observed along the \(c^*\)-axis suggesting the presence of a large number of defects in the nanoparticle assembly perpendicular to the basal plane of the hexagonal lattice (see Figure 4-4a, b and c). The nanosphere packing symmetry can be ascribed to a mixture of hcp arrangement (unit cell dimensions of \(a = b = 7.9\) nm and \(c = 12.0\) nm) and fcc unit cell \((a = 11.2\) nm).

![Figure 4-3](image)

**Figure 4-3.** 3D SA-EDT volume reconstruction of the nanoparticle array shown in Figure 4-3 projected along: (a) [001]_{hcp}, (b) [−110]_{hcp} and (c) arbitrary crystallographic orientation. Figure and caption reproduced from paper III.151

Disorder in nanoparticle assemblies was further confirmed by probing different nanoparticle assemblies that grew along different orientations. A striking example of such an assembly is imaged in Figure 4-5. The nanoparticle assembly also exhibits high translational order along one direction (see Figure 4-5a). However, a high concentration of stacking faults propagating parallel to the substrate are found across the nanoparticle assembly as outlined by the zigzag white lines in Figure 4-5a. The stacking sequence is altering from a predominant hcp (...ABABA... sequence) to an fcc (...ABCABCABC... sequence) packing (see Figure 4-5b).
Figure 4-5. TEM images of a Pd nanoparticle assembly showing stacking faults propagation along one direction. (a) High concentration of stacking faults in nanoparticle assembly highlighted by the traced white zigzag features. (b) Higher magnification image of the tagged area in (a) showing the two possible unit cell projections of the close-packed arrangements as outlined by the cubic fcc and hexagonal hcp unit cell. The sequence alternation of the nanoparticle close-packed planes is described using A, B, and C symbols in blue, red and green respectively. Figure and caption reproduced from paper III.\textsuperscript{151}

The 3D SA-EDT volume reconstruction (goniometer tilt from -43° to +65° covering 216° of reciprocal space) obtained from the nanoparticle assembly exhibits diffuse streaking that is associated with the high concentration of stacking faults in the nanoparticle assembly (Figure 4-6a). The simulated 3D reciprocal space volume of a hexagonal packed arrangement (space group: P6\textsubscript{3}/mmc, unit cell ratio c/a=1.91) shown in Figure 4-6a, c and e was used as a reference in order to assess the deviation from the perfect close-packed arrangement. We found a contraction of ~20\% along [100]\textsubscript{hcp} and a decrease of the hexagonal basal plane angle of 5°(see Figure 4-6c and d). Therefore, the nanoparticle assembly results in a monoclinic packing arrangement with unit cell dimensions of \( a = 5.5 \text{ nm} \), \( b = 6.9 \text{ nm} \), \( c = 13.2 \text{ nm} \) and \( \alpha = 90° \), \( \beta = 90° \) and \( \gamma = 115° \). Interestingly, the 3D SA-EDT data set shown in Figure 4-6 reveals that the inorganic cores of the Pd nanoparticles (~5.3 nm) close to each other with each other (see model in Figure 4-7), suggesting that the ethanol destabilization process may induce surfactant desorption from the Pd surface. Previous investigations have indeed revealed distortions in nanoparticle assemblies upon drying.\textsuperscript{154,157} Deviations from the perfect packing of hard spheres can be attributed to the nature of the soft shell capping the inorganic hard core of the nanoparticles. Other effects leading to substantial contraction such as desorption of the capping agent during the
assembly process or the high vacuum conditions used for TEM experimental are also possible. We also found that the average nanoparticle size can vary from one nanoparticle assembly to another suggesting a local size segregation/fractionation during the self-assembly process. In fact, a Monte Carlo simulation investigation on freezing of polydisperse hard spheres concluded that precipitation from a fluid phase cannot occur when polydispersity in spheres diameter exceeds 5.7% unless fractionation takes place.\textsuperscript{158}
Figure 4-6. (right) 3D SA-EDT volume reconstruction of the nanoparticle assemblies shown in Figure 4-5a and (left) simulated 3D reciprocal volume of a hexagonal packed arrangement using $P6_3/mmc$ space group viewed along; [100]$_{hcp}$ (a) simulated and (b) experimental, [001]$_{hcp}$ (c) simulated and (d) experimental and [001]$_{hcp}$ (e) simulated and (f) experimental. Figure and caption reproduced from SI of paper III.\textsuperscript{151}
Figure 4-7. **Distortion in nanoparticle assemblies.** Crystallographic model along [001]_{hcp} depicting the lattice distortion occurring in the nanoparticle assembly shown in Figure 4-5. The monoclinic lattice axes are drawn in red. Figure and caption reproduced from paper III.\textsuperscript{151}

Other interesting anomalous features are found in nanoparticle assemblies along <001>_{fcc} directions. Regular square lattices matching a pure fcc packing are disrupted by linear features that repeat across the whole nanoparticle array (Figure 4-8).

![Figure 4-8. TEM bright-field images of square lattice disrupted by line defects.](image)

The appearance of regularly spaced line defects (~15–60 nm) can be attributed to out-of-plane stacking faults propagating at 54.7° (angle between [111]_{fcc} and [001]_{fcc}) with respect the viewing direction. Defect free nanoparticle assemblies were rarely found in our experiment. Figure 4-9 highlights the difference between a defect free nanoparticle assembly and a nanoparticle assembly containing a high concentration of planar defects viewed along [001]_{fcc}. The diffuse features found close to Bragg reflections in the SA-DP (Figure 4-9d) demonstrate the presence of defects that disrupt the ideal fcc packing. The red and blue models of spheres in Figure 4-9 found inset outline the fcc and hcp subdomains in the nanoparticle assemblies.
Figure 4-9. Slanted stacking faults in Pd nanoparticle assemblies. TEM bright-field images, crystallographic models and SA-EDPs of Pd nanoparticle assemblies along [001]_{fcc}; (a, c) without and (b, d) with planar defects. The crystallographic models viewed from the side, along [110]_{fcc}, are provided below each images; the blue and red spheres depict hcp and fcc domains, respectively. Figure and caption reproduced from paper III.\textsuperscript{151}

Some nanoparticle assemblies display more complex features that are caused by the combination of multiple planar defects propagating along different directions. Figure 4-10 shows a few examples of such assemblies.
Figure 4-10. TEM bright-field images of Pd nanoparticle assemblies exhibiting multiple stacking fault propagation directions. (a, b, c) Two nanoparticle assembly domains, highlighted in blue and red, showing in-plane stacking faults running along two different directions outlined by the zigzag white lines. (d) Combination of stacking faults propagating along two different directions; in-plane stacking fault (traced by zigzag line) and out-of-plane stacking fault. The 2D crystallographic models of the nanoparticle packing are provided along two projections, and the model inset shows the side view of the nanoparticle packing. (e) Complex combination of stacking faults in a nanoparticle assembly. The red and blue regions discriminate domains with different stacking fault propagation directions. Figure and caption adapted from paper III.\textsuperscript{151}
This study reveals that planar defects (i.e. stacking faults) are ubiquitous in Pd nanoparticle assemblies and are found regardless of the crystallographic orientation of the Pd nanoparticle assemblies. In fact, only few assemblies are defect free which consist of fcc packing arrangement. Stacking faults found in Pd nanoparticle assemblies are analogous to defects found in close-packed metal structures\textsuperscript{159,160} and noble-gas clusters\textsuperscript{161,162}. They are characterized as Shockley partial dislocations along the $<112>_{fcc}$ directions as illustrated in Figure 4-11. The stacking faults found in Pd nanoparticle assemblies usually propagate along one unique direction (Figure 4-10a, b). This is particularly true if the nanoparticle assemblies present a high occurrence of variation of the stacking order. In fact, an hcp system allows only slip along one unique direction (see Figure 4-41a). Sometimes, stacking faults running along two perpendicular directions are observed as shown in Figure 4-10c. This is possible only if the adjacent domain corresponds to an fcc packing. In fact, fcc lattice allows the slip of closed packed planes along four different and equally probable directions (see Figure 4-11b).

The combination of 3D EDT using the small-angle diffraction mode and conventional TEM imaging enabled to investigate order in nanoparticle assemblies. The predominant defects found in nanoparticle assemblies highlights the competition between fcc and hcp packing during the assembly process.

**Figure 4-11.** Crystallographic models of close-packed arrangements and their respective slip systems. (a) The hcp system with a single slip plane; (001). (b) The fcc system contains 12 independent slip systems, and 4 different slip planes; (111), (−111), (1−11) and (11−1). The red vectors depict the slip directions of the close-packed plane in both structures. Figure and caption reproduced from paper III.\textsuperscript{151}
5 Synthesis and structural characterization of iron oxide nanoparticles and Fe-Mn oxides hybrid nanoparticles

The first part of this chapter deals with the synthesis of iron oxide nanoparticles with different morphologies as well as the synthesis of facetted iron-manganese oxides hybrid nanoparticles. The second part describes the structural characterization of iron-manganese oxides hybrid nanoparticles using different TEM techniques (STEM-HAADF imaging and tomography, EFTEM imaging, SAED, HRTEM imaging). Investigation of the structural features (e.g. defects and strain) in non-confined asymmetric nanoparticles is first described. The last part elaborates on in-situ atomic resolution monitoring of the structural changes in Fe₃O₄|Mn₃O₄ and Mn₃O₄|Fe₃O₄ core|shell nanoparticles induced by the electron beam.

5.1 Synthesis of iron oxides nanocubes and other morphologies

Iron oxide nanoparticles have been extensively investigated for a variety of applications including ferrofluids, cancer therapy, catalysis, and many others.¹⁶³,¹⁶⁴ A typical synthetic route to produce iron oxide (i.e. Fe₃O₄) nanocubes dispersed in non-polar solvents is the thermal decomposition (300 °C-325 °C) of iron-oleate complex in 1-octadecene in the presence of a mixture of oleic acid and sodium oleate.¹⁶⁵ Sodium oleate plays an important role in shaping Fe₃O₄ into {100} facettted nanocubes.¹⁶⁶ Figure 5-1 shows Fe₃O₄ nanocubes of 12.5 ± 1.3 nm, which are typically obtained by thermal decomposition of iron-oleate precursor. The Fe₃O₄ nanocubes display a well-defined morphology along with a narrow size distribution, which makes the nanocubes suitable building blocks for self-assembly. In fact, this material has been used for confinement studies in nanofluidic containers.¹⁶⁷ Additionally, the Fe₃O₄ nanocubes are used as seeds for the growth of MnO phase through a seed-mediated thermal decomposition process yielding iron-manganese oxides hybrid nanoparticles (see next section of this chapter).
We have investigated how the presence of benzyl ether as solvent during the thermal decomposition affects the final morphology of Fe$_3$O$_4$ nanoparticles, at a decomposition temperature of $T = 298$ °C (temperature elevation of 3 °C/min) with a precursor to ligands ratio of 20:1, for different volume ratios of 1-octadecene and benzyl ether. We found that the presence of benzyl ether in the solution affects the morphology of Fe$_3$O$_4$ nanoparticles. In fact, the thermal decomposition of iron-oleate in 1-octadecene systematically led to nanocubes with {100} exposed facets (see Figure 5-2a). The addition of benzyl ether up to a range of 4:1 (1-octadecene:benzyl ether) in the solution does not significantly change the final morphology of the nanoparticle, although the cubes are found with a higher degree of truncation (see Figure 5-2b). Lower volume ratios lead to a drastic change of the morphologies of Fe$_3$O$_4$ nanoparticles. In fact, octahedral nanoparticles are predominantly found in addition to hexagonal and triangular platelets (see Figure 5-2c, d). Such nanoparticles have {111} exposed facets (see Figure 5-3). Further investigations are necessary to gain a deeper understanding of the effect of benzyl ether on the formation of faceted Fe$_3$O$_4$ nanoparticles.
Figure 5-2. Fe$_3$O$_4$ nanoparticles with different morphologies. TEM images of Fe$_3$O$_4$ nanoparticles synthesized through thermal decomposition of iron oleate at 298°C using high-boiling point solvents (1-octadecene and benzyl ether) with different volume ratios. (a) Fe$_3$O$_4$ nanocubes synthesized in 1-octadecene. (b) Fe$_3$O$_4$ nanocubes exhibiting truncation at their edges synthesized in a mixture of 1-octadecene and benzyl ether (4:1 volume ratio). (c) Fe$_3$O$_4$ octahedra and other morphologies synthesized in a mixture of 1-octadecene and benzyl ether (1:1 volume ratio). (d) Fe$_3$O$_4$ octahedral nanoparticles and other morphologies synthesized in benzyl ether.
Figure 5-3. Different morphologies of Fe₃O₄ nanoparticles produced by thermal decomposition of iron-oleate in high-boiling point solvents (1-octadecene and benzyl ether) and their crystallographic relationship. (Top panel in a, b, c, d) HRTEM images of (a) octahedral, (b) triangular and (c) hexagonal nanoparticles recorded along [111] zone axis and (d) a cubic nanoparticle recorded along [001] zone axis. (Middle panel a, b, c, d) Fourier transform of the HRTEM images, and (down panel) crystallographic orientation of the nanoparticles.

5.2 Synthesis of Fe-Mn oxides hybrid nanoparticles

Multicomponent nanomaterials bring new possibilities in creating novel and enhanced functionalities such as tunable magnetism (e.g. tunable coercivity, saturation magnetization and blocking temperature). Bi-magnetic Fe-Mn based oxides core|shell nanoparticles (e.g. MnₓFe₃₋ₓO₄|FeₓMn₃₋ₓO₄ core|shell nanoparticles) exhibit exchange bias at their interfaces. Typically, Fe-Mn oxides core|shell nanoparticles are synthesized using a seed-mediated growth method. So far, there have been only reports on Fe-Mn oxides core|shell nanoparticles with onion-like configurations that do not exhibit well-defined or homogeneous morphologies.

Two types of iron-manganese oxides hybrid nanoparticles (i.e. pseudo-core|shell and asymmetric hybrid nanoparticles) were synthesized using thermal decomposition of manganese (II) acetate tetrahydrate (Mn(CH₃COO)₂·4H₂O). In these syntheses, Fe₃O₄ nanocubes of well-defined morphologies are used as seeds (cf. Figure 5-1) for the subsequent growth of
MnO. Typically, 50 mg of the Fe₃O₄ cubes (~50% of inorganic material) are dispersed in a solution of either benzyl ether or 1-octadecene in the presence of 0.25 mmol of sodium oleate and 0.25 mmol of oleic acid under vigorous stirring. The solution is heated up to 250 °C after degassing at 120 °C with a heating rate of 3 °C/min. The thermal decomposition process was held at 250 °C for 1 hour before cooling to room temperature. The synthesis of iron-manganese oxides hybrid nanoparticles in 1-octadecene yields nanoparticles displaying no particular faceting (Figure 5-4). The use of benzyl ether as a solvent plays an important role in shaping the iron-manganese oxides nanoparticles. In fact, thermal decomposition of manganese acetate using benzyl ether instead of 1-octadecene as a high-boiling point solvent, at the same experimental conditions as the one presented above, yields asymmetric hybrid nanoparticles that are facetted as inter-grown cubes (Figure 5-5).

Figure 5-4. TEM images of Fe-Mn oxides hybrid nanoparticles synthesized using 1-octadecene as solvent. (a) Low magnification TEM image of Fe-Mn oxides nanoparticles. (b) TEM image of a single Fe-Mn oxides nanoparticle recorded at higher magnification. (c, d) TEM images of small individual Fe-Mn oxides nanoparticles.

Figure 5-5. TEM images of Fe-Mn oxides hybrid nanoparticles synthesized using benzyl ether as solvent. (a, b, c, d) TEM images showing dimers and different geometrical configurations of trimers.
5.3 TEM analysis of asymmetric Fe-Mn oxides hybrid nanoparticles

Further TEM investigations on the faceted Fe-Mn oxides hybrid nanoparticles were carried out. Two dimers and one trimer of Fe-Mn oxides hybrid nanoparticles synthesized in the presence of benzyl ether are shown Figure 5-6a, b and c. All nanoparticles exhibit sharp \{100\} facets. Both oxides share oriented interfaces (see Fourier transforms in Figure 5-6d, e and f). Each of the distinct phases can be identified based on the difference of their lattice spacing (see Figure 5-6g, h, i, j, k and l) as evidenced by the Fourier analysis of HRTEM images of the dimers and trimer using $200_{\text{MnO}}$ reflection of the rock-salt MnO structure and $400_{\text{Fe}_3\text{O}_4}$ reflection of the spinel Fe$_3$O$_4$ structure.\(^1\)

Both MnO and Fe$_3$O$_4$ structures are cubic and contain oxygen fcc-sublattice ($a = 8.39$ Å for bulk Fe$_3$O$_4$ and $a = 4.44$ Å for bulk MnO). However, in magnetite, iron (Fe$^{2+}$, Fe$^{3+}$) occupy octahedral and tetrahedral sites whereas Mn$^{2+}$ occupies octahedral sites in MnO. Their structural similarities (i.e cubic lattice and oxygen fcc-sublattice) make them in principle compatible for the growth of one structure onto the other. However, a coherent interface is inhibited by the significant lattice mismatch (5.5 %) between MnO and Fe$_3$O$_4$.

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1 FeO is found in a small portion in iron oxide nanocubes and is disregarded in this section
EFTEM images of manganese and iron L\textsubscript{2,3} edges shown in Figure 5-7 reveal that the dimers, in fact, consist of two distinct regions, which are MnO and Fe\textsubscript{3}O\textsubscript{4} respectively.

Figure 5-7. EFTEM elemental mappings of Fe-Mn oxides dimers. (a) Unfiltered TEM images of two nanodimers highlighted by red squares. (a, b, c) EFTEM elemental maps (b) overlay of iron (red) and manganese (blue) L\textsubscript{2,3} edges and (c) oxygen K-edge. Scale bars: 20nm. Figure adapted from paper IV.

STEM-HAADF tomography performed on a nanodimer highlights the 3D morphology of a nanodimer where Fe\textsubscript{3}O\textsubscript{4} and MnO inter-grown nanocubes share their edges. This indicates that the growth of MnO onto Fe\textsubscript{3}O\textsubscript{4} nanocubes occurs along <110> (Figure 5-8).

Figure 5-8. STEM-HAADF tomography of a Fe-Mn oxides nanodimer. (a, b) Iso-surface rendering of the three-dimensional tomogram of a Fe-Mn oxides dimer displayed in two different orientations. (c) STEM-HAADDF image of the Fe-Mn oxides dimer nanoparticle. Scale bars: 10nm. Figure adapted from paper IV.

The HRTEM image (Figure 5-9a) reveals that the dimers display a high crystallinity where the size and shape of iron oxide nanocube is preserved. The MnO shares a common crystallographic orientation with Fe\textsubscript{3}O\textsubscript{4} nanocube together with a slight lattice rotation. The lattice mismatch is found to be about
5 % (Figure 5-9b), which is pretty close to the theoretical value (5.5 %). Figure 5-9 shows that the dimer exhibits interfacial strain of about 5 to 15 % (see blue squares in Figure 5-9a, b and d) as well as defects (see green and pink squares in Figure 5-9a, b, c and e) as highlighted by GPA and Fourier-filtered imaging. The defects found at the interface correspond to misfit dislocations, which decrease the interfacial energy owing to the lattice mismatch between MnO and Fe₃O₄ structures. The defects characterize a shift of ½ of the MnO (or ¼ of Fe₃O₄) unit cell along <100>. The defects found at the dimer interface are not regularly spaced as for epitaxially grown films.¹⁷⁴

![Figure 5-9. Strain and defects at the Fe-Mn oxides dimer interface.](image)

5.4 Structural transformation in Fe₃O₄|Mn₃O₄ and Mn₃O₄|Fe₃O₄ core|shell nanoparticles

Fe₃O₄|Mn₃O₄ and Mn₃O₄|Fe₃O₄ core|shell nanoparticles were synthesized using a two steps seeded-mediated growth thermal decomposition of iron and manganese complexes in high-boiling point organic solvents.¹⁷⁵ Both systems were characterized by high-resolution STEM-HAADF imaging to investigate their structural inhomogeneities. High-resolution STEM-HAADF images of Fe₃O₄|Mn₃O₄ and Mn₃O₄|Fe₃O₄ core|shell nanoparticles, recorded at early stage of electron exposure along [0-11]Fe₃O₄ zone axis (for more details on the chemical mappings, see paper V), reveal a high crystallinity with a coherent spinel structure. A change of contrast is observed upon prolonged electron exposure (compare Figure 5-10a and b), which evidences the selective
reduction of $\text{Mn}_3\text{O}_4$ to $\text{MnO}$. This transformation occurs topotaxially\textsuperscript{176} meaning that the oxygen $\text{fcc}$-sublattice is persevered during the Mn cation redistribution from the tetrahedral to the octahedral sites. Typically, the reduction of $\text{Mn}_3\text{O}_4$ to $\text{MnO}$ takes place at relatively high temperature and/or pressure.\textsuperscript{177} The comparison of Figure 5-10a and b shows that the reduction process is accompanied by a volume reduction of the Mn-rich shell related to oxygen loss and inwards cation diffusion during transformation.

Figure 5-10. **Electron-induced shell transformation ($\text{Mn}_3\text{O}_4$ to $\text{MnO}$) in $\text{Fe}_3\text{O}_4|\text{Mn}_3\text{O}_4$ core|shell nanoparticles.** (a, b) STEM-HAADF images of a $\text{Fe}_3\text{O}_4|\text{Mn}_3\text{O}_4$ core|shell nanoparticle recorded along [1-10]$_{\text{Fe}_3\text{O}_4}$ (a) at early stage and (b) after 10 minutes of electron beam exposure. (c, d) Magnified STEM-HAADF images highlighted by the (c) red and (d) blue squares in (a) and (b) images, respectively. (e, f) Fourier-filtered images of the STEM-HAADF in (c) and (d) using 004$_{\text{Fe}_3\text{O}_4}$/002$_{\text{MnO}}$ reflections. (g, h) Deformation maps of (a) and (b) using 004$_{\text{Fe}_3\text{O}_4}$/002$_{\text{MnO}}$ reflections. Scale bars: 2nm. Figure adapted from paper V.
The transformation from Mn$_3$O$_4$ to MnO in Fe$_3$O$_4$|Mn$_3$O$_4$ core|shell nanoparticles leads to a lattice rotation of 5° between MnO (shell) and Fe$_3$O$_4$ (core), which enables to keep a defect-free interface (Figure 5-10c, e, d and f). In fact, misfit dislocation are not found at the nanoparticle interface. Moreover, the deformation maps obtained by GPA show a relatively homogeneous strain across the Fe$_3$O$_4$|Mn$_3$O$_4$ core|shell nanoparticle’s interface (Figure 5-10g and h).

This transformation occurs in both Fe$_3$O$_4$|Mn$_3$O$_4$ and Mn$_3$O$_4$|Fe$_3$O$_4$ core|shell nanoparticles. The transformation of Mn$_3$O$_4$ to MnO in Mn$_3$O$_4$|Fe$_3$O$_4$ core|shell nanoparticles was followed at early stage of reduction in order to gain a better understanding of the reduction process. The reduction process was followed in-situ by recording 100 subsequent high-resolution STEM-HAADF images every 2 seconds. Interestingly, the analysis of the subsequent STEM-HAADF images using particle image velocimetry (PIV) reveals an inhomogeneous cation diffusion towards the nanoparticle’s core with a maximum displacement value of 1.5 Å (Figure 5-11), which is not observed in Fe$_3$O$_4$|Mn$_3$O$_4$ core|shell nanoparticles. The displacement of cations across the nanoparticle is associated to the volume loss of the core due to oxygen removal during reduction. In fact, an outwards diffusion of oxygen is necessary for Mn$_3$O$_4$ to transform into MnO. This observation indicates that the mechanism of reduction in Fe$_3$O$_4$|Mn$_3$O$_4$ core|shell nanoparticles might be different than in the case of Mn$_3$O$_4$|Fe$_3$O$_4$ core|shell owing to geometric constrain of the MnO core imposed by the Fe$_3$O$_4$ shell.

![Inhomogeneous displacement of cations in Mn$_3$O$_4$|Fe$_3$O$_4$ core|shell nanoparticle during its core transformation.](image)

Figure 5-11. Inhomogeneous displacement of cations in Mn$_3$O$_4$|Fe$_3$O$_4$ core|shell nanoparticle during its core transformation. (a) Sum of 5 subsequent high-resolution STEM-HAADF images of a Mn$_3$O$_4$|Fe$_3$O$_4$ core|shell nanoparticle at early stage of electron exposure. (b) Displacement map obtained by PIV analysis of the corresponding high-resolution STEM-HAADF images shown in (a) and (c). The arrows indicate the cation displacement directions and the false color scale depicts the displacement in Å. (c) Sum of 5 subsequent high-resolution STEM-HAADF images of a Mn$_3$O$_4$|Fe$_3$O$_4$ core|shell nanoparticle after 3.5 minutes of electron exposure. Scale bars: 2 nm. Figure adapted from paper V.
Mn₃O₄ is a normal spinel structure that has a tetragonal lattice \( (a = 5.76 \, \text{Å}) \) and \( c = 9.44 \, \text{Å} \) for bulk Mn₃O₄) in contrast with Fe₃O₄ (shell) which has a cubic lattice \( (a = 8.39 \, \text{Å} \) for bulk Fe₃O₄). The expanded lattice of Mn₃O₄ is \( a' = \sqrt{2}a = 8.15 \, \text{Å} \). The theoretical lattice mismatch between Fe₃O₄ and Mn₃O₄ along the \( a \)-axis of Mn₃O₄ is relatively low (2.9 %), whereas it is large (10.7 %) along the \( c \)-axis. At early stage of exposure, both Fe₃O₄|Mn₃O₄ and Mn₃O₄|Fe₃O₄ core|shell nanoparticles exhibit a change of their lattice parameters along the \( c \)-axis across the nanoparticle (i.e. \( \Delta c \approx 12 \, \% \) and \( \Delta c \approx 5 \, \% \) between Mn₃O₄ and Fe₃O₄ region in Fe₃O₄|Mn₃O and Mn₃O₄|Fe₃O₄ core|shell nanoparticle, respectively) confirming the inhomogeneous cation distribution across the nanoparticles.¹⁷⁸

Mn₃O₄|Fe₃O₄ core|shell nanoparticle (Figure 5-12a, b, c and d) reveals important structural changes during its core reduction including the formation of a void at the core|shell interface (cf. region of reduced intensity highlighted by the white arrows in Figure 5-12b). In contrast with Fe₃O₄|Mn₃O₄ core|shell nanoparticles, the transformation of the core in Mn₃O₄|Fe₃O₄ core|shell nanoparticles leads to misfit dislocation creation owing to lattice mismatch between the Fe₃O₄ shell and the MnO core, as evidenced by Fourier-filtering (Figure 5-12e, f). In fact, misfit dislocations act as a strain relief at the core|shell nanoparticle interface allowing the nanoparticle to maintain its interface stable. In this case, lattice rotation is not possible due to the confinement of the core.

Surprisingly, a global lattice expansion of about 4 % along the \( c \)-axis (\( c \approx 9.4 \, \text{Å} \) is observed upon the core reduction whereas no significant difference in the lattice spacing along the \( a \)-axis is observed (see more details in paper V). In fact, the lattice spacing along the \( c \)-axis of the nanoparticle core (bulk Mn₃O₄, \( c = 9.44 \, \text{Å} \)) should in principle decrease during the reduction process in order to match the lattice spacing of the MnO bulk (\( 2a \approx 8.88 \, \text{Å} \)) and Fe₃O₄ bulk (\( a \approx 8.39 \, \text{Å} \)), and thus reduce the interfacial strain between the core and the shell. This lattice expansion observed in Mn₃O₄|Fe₃O₄ core|shell nanoparticle probably occurs to compensate for the volume loss associated to oxygen removal and diffusion of cations in the nanoparticle’s core. This explains why the nanoparticle’s core sustains a relatively high strain with respect to Fe₃O₄ shell (see Figure 5-12g and h). Upon prolonged electron exposure, MnO phase is no longer stable as cation redistribution across the interface and the core is observed. In fact, the relatively large strain along the \( c \)-axis found in the nanoparticle core together with the uneven cation distribution may promote the cation redistribution across the interface and the core (see more details in paper V).

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Figure 5-12. **Electron-induced core transformation (Mn₃O₄ to MnO) in Mn₃O₄|Fe₃O₄ core|shell nanoparticles.** (a, b) STEM-HAADF images recorded along [1-10]Fe₃O₄ of Mn₃O₄|Fe₃O₄ core|shell nanoparticles (a) at early stage and (b) after 10 minutes of electron beam exposure. (c, d) Magnified STEM-HAADF images highlighted by the (c) red and (d) blue squares of (a) and (b) images, respectively. The orange overlaid regions in (b and d) outline the MnO core region. (e, f) Fourier-filtered images of the STEM-HAADF in (c) and (d) using 004 Fe₃O₄/002MnO reflections. (g, h) Deformation maps of (a) and (b) using 004 Fe₃O₄/002MnO reflections. The dashed lines depict the nanoparticle boundary. Scale bars: 2nm. Figure adapted from paper V.

The synthesis of facetted asymmetric Fe-Mn oxides nanoparticles was demonstrated and their structural characterization revealed the presence of interfacial strain and defects. The preformed Fe₃O₄ nanocubes share their edges with the MnO overgrown structures, which leads to different geometrical configuration of the trimers. The *in-situ* investigation of the selective electron-beam reduction of Mn₃O₄ to MnO in Mn₃O₄|Fe₃O₄ and Fe₃O₄|Mn₃O₄ core|shell nanoparticles revealed different transformation mechanisms through either lattice rotation or misfit dislocation formation.
6 Conclusions

This thesis describes the synthesis of various types of inorganic nanoparticles with well-defined morphologies using two synthetic pathways (i.e. hydrothermal synthesis and thermal decomposition of metal complexes) to produce metal, metal oxides and iron-manganese oxides hybrid nanoparticles. Their structures and defects were revealed by means of different TEM techniques.

Electron diffraction tomography (3D EDT) is a powerful technique to investigate the three-dimensional structure of nanoparticles, in particular for multiphase nanomaterials. 3D EDT has also been used to provide information on the alignment of nanoparticles stacked together along a common crystallographic axis. Moreover, small-angle 3D EDT together with conventional TEM imaging allows to probe the packing symmetry of nanoparticle assemblies as well as their defects. The high concentration of planar defects (i.e. stacking faults) highlights the competition between fcc and hcp arrangement during the nanoparticle assemblies formation. The type of stacking faults present in nanoparticle assemblies are analogous to planar defects found in crystal structures of close-packed metals.

Lastly, the synthesis of Fe-Mn oxides hybrid nanoparticles with well-defined morphologies through a facet specific growth of manganese oxide nanoparticle onto iron oxide nanocubes was demonstrated. It was found that the interface of asymmetric nanoparticles contains misfit dislocations together with large interfacial strain. Finally, the electron-induced selective reduction of manganese oxide in Mn$_3$O$_4$|Fe$_3$O$_4$ and Fe$_3$O$_4$|Mn$_3$O$_4$ core|shell nanoparticles was investigated in-situ using high-resolution STEM-HAADF. The reduction is accompanied by a strain relaxation mechanism that is seemingly different in Mn$_3$O$_4$|Fe$_3$O$_4$ than in Fe$_3$O$_4$|Mn$_3$O$_4$ core|shell nanoparticle systems.
7 Outlook

Bottom-up approach using chemical processes for the fabrication of nanoparticles are excellent synthetic pathways to produce highly crystalline nanoparticles with controlled morphologies and chemical composition. However, more detailed investigation on how experimental conditions impact on the growth of nanoparticles is needed. For example, while monodisperse iron oxide nanocubes can be produced with a high shape selectivity, the fabrication of other morphologies such as octahedron, triangular and hexagonal platelets remains a challenge. Further investigations on how benzyl ether guides the growth of iron oxide nanoparticles as well as the growth of facetted Fe-Mn hybrid nanoparticles have to be carried out in order to gain a better understanding on the nanoparticle formation mechanisms.

Transmission electron microscopy is an important tool for the characterization of nanoparticle structures and their defects. Electron diffraction tomography can be applied to study a larger number of nanoparticle structures. It might be also a very useful method to solve crystalline structure of organic crystals such as proteins or self-assembled polymer crystals using cryo-TEM. Although these structures are very beam sensitive, the approaches based on merging 3D electron diffraction data recorded from different crystal may be applied to recover a complete 3D reciprocal volume. The investigation of defects in nanoparticles could be conducted using 3D electron diffraction tomography. However, diffuse scattering arising from disorder in crystals are currently difficult to characterize without aid of imaging techniques. Therefore, the development of computational methods could help in the quantification of defects through the analysis of the experimental diffuse scattering in three-dimensions. This would enable to build more accurate structural model of actual crystals. The method could be extended to mesoscopic structures such as nanoparticle self-assemblies for structure determination and defect quantification. Moreover, 3D EDT can be used to investigate the packing arrangement together with the orientational order in nanoparticle mesocrystals by combining 3D data using wide-angle and small-angle modes.

Further investigation by STEM-HAADF together with EELS is needed to follow the transformation of manganese oxide in order to gain a better understanding on the influence of the chemical inhomogeneity and confinement of the core on the transformation and defects formation.
Populärvetenskaplig sammanfattning


Denna avhandling beskriver syntes av nanopartiklar via våtkemiska processer, såsom hydrotermal syntes och termiskt sönderfall av metallkomplex, och karaktäriseringen av dessa nanopartiklar genom transmissionselektronmikroskop (TEM). Våtkemiska processer för syntes av nanopartiklar innebär ofta en måttligt hög värmebehandling av upplöst eller suspenderat utgångsmaterial i vatten eller något opolärt lösningsmedel. Denna process resulterar i suspenderade nanopartiklar som kan bli kemiskt eller fysiskt processade till en önskad form eller funktionalitet.

Utvecklingen av ny TEM-baserad karaktäriseringsteknik och andra tekniker med mycket hög upplösning har hjälpt forskare att utforska nanopartiklars struktur ner till atom-nivå. I den här avhandlingen beskrivs bland annat hur TEM-baserade tekniker används för att undersöka den kemiska sammansättningen och defekterna i nanopartiklar. Med hjälp av en ny metod baserad på konventionell avbildnings och tredimensionell elektronidiffractionrekonstruktion (3D SA-EDT) visas också hur sfäriska nanopartiklar är packade i tillsammans och hur de dominerande defekterna i dessa självorganiserade strukturer ser ut.

Vi har även undersökt defekter och strukturella förändringar i nanopartiklar bestående av två olika faser, d.v.s. strukturer med olika kemisk sammansättning. Denna typ av nanopartiklar kallas ofta för hybridnanopartiklar och kan ha olika tredimensionella former, t.ex. assymetriska facetterade dimerer och kärn/skal-morfologier. Hybrida nanopartiklar är intressanta då nya egenskaper uppstår som ett resultat av kombinationen av två olika strukturer i samma partikel. kombinationen av två olika strukturer i samma partikel.
Popular scientific summaries

Nanoparticles are a class of materials, which exhibit interesting properties. A nanoparticle ranges in size from hundreds of nanometers to just a few which is roughly 1,000 to 10,000 times smaller than a strand of hair. The challenge of fabricating these particles lies in being able to tailor their size, morphologies and chemical composition with a high precision and reproducibility. Moreover, the precise control of their final morphologies and sizes offers the possibility to use these nanoparticles as building blocks for the fabrication of larger ordered entities. These entities are interesting for the novel and/or collective properties they exhibit which are promising for potential technological applications.

This thesis deals with the synthesis of nanoparticles through chemical processes and their characterization by transmission electron microscopy (TEM). Chemical processes involving nanoparticle fabrication often requires moderately high thermal treatment of dissolved and/or dispersed precursors yielding dispersed nanoparticles in water or organic solvents. The dispersed nanoparticles can be chemically and/or physically processed to achieve desirable forms and functionalities.

The development of characterization tools and the ongoing research and development of novel TEM-based characterization techniques have helped scientists to investigate the nanoparticle structures with unprecedented accuracy down to the atomic scale. In this thesis, various TEM-based techniques are used to investigate structural features such as the chemical composition and defects of well-defined nanoparticles. We also examine how spherical nanoparticles are packed in nanoparticle assemblies and determine the predominant defects present in these assemblies using a novel approach based on conventional imaging and three-dimensional electron diffraction reconstruction (3D SA-EDT).

Lastly, we investigate the defects and structural changes in nanoparticles composed of two different phases (i.e. different chemical compositions), which also have different three-dimensional configurations (i.e. asymmetric facetted dimers and core|shell morphologies). These types of nanoparticles, sometimes called, hybrid nanoparticles, are interesting for the new functionalities they may exhibit owing to the combination of two dissimilar structures.
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