Plasma Synthesis and Self-Assembly of Magnetic Nanoparticles

Sebastian Ekeroth
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Cover image: Fe nanoparticles collected into nanotrusses on top, and around the edges, of a Si wafer.
Abstract

Nanomaterials are important tools for enabling technological progress as they can provide dramatically different properties as compared to the bulk counterparts. The field of nanoparticles is one of the most investigated within nanomaterials, thanks to the existing, relatively simple, means of manufacturing. In this thesis, high-power pulsed hollow cathode sputtering is used to nucleate and grow magnetic nanoparticles in a plasma. This sputtering technique provides a high degree of ionization of the sputtered material, which has previously been shown to aid in the growth of the nanoparticles. The magnetic properties of the particles are utilized and makes it possible for the grown particles to act as building blocks for self-assembly into more sophisticated nanostructures, particularly when an external magnetic field is applied. These structures created are termed “nanowires” or “nanotrusses”, depending on the level of branching and inter-linking that occurs.

Several different elements have been investigated in this thesis. In a novel approach, it is shown how nanoparticles with more advanced structures, and containing material from two hollow cathodes, can be fabricated using high-power pulses. The dual-element particles are achieved by using two distinct and individual elemental cathodes, and a pulse process that allows tuning of individual pulses separately to them. Nanoparticles grown and investigated are Fe, Ni, Pt, Fe-Ni and Ni-Pt. Alternatively, the addition of oxygen to the process allows the formation of oxide or hybrid metal oxide – metal particles. For all nanoparticles containing several elements, it is demonstrated that the stoichiometry can be easily varied, either by the amount of reactive gas let into the process or by tuning the amount of sputtered material through adjusting the electric power supplied to the different cathodes.

One aim of the presented work is to find a suitable material for the use as a catalyst in the production of H$_2$ gas through the process of water splitting. H$_2$ is a good candidate to replace fossil fuels as an energy carrier. However, rare elements (such as Ir or Pt) needs to be used as the catalyst, otherwise a high overpotential is required for the splitting to occur, leading to a low efficiency. This work demonstrates a possible route to avoid this, by using nanomaterials to increase the surface-to-volume ratio, as well as optimizing the elemental ratio between different materials to lower the amount of noble elements required.
Populärvetenskaplig sammanfattning


En nyhet som presenteras i denna avhandling är att nanopartiklar tillverkas av flera olika material genom att använda flera cylindrar som består av olika tillväxtn materialet. Genom att styra hur hög elektrisk spänning som läggs på respektive cylinder kan man justera hur mycket atomer
som sputtras ut från respektive material. På så sätt styrs sammansättningen hos nanopartiklarna.

Ett mål med denna avhandling är att hitta ett lämpligt material som ska fungera som katalysator vid vätgasframställning via vattenklyvning. En katalysator är ett material som gör att det inte krävs lika hög aktiveringsenergi för att en kemisk reaktion ska genomföras. Anledningarna till att detta undersöks är flera. Dels kan vätgas ersätta fossila bränslen i många transportmedel, och vid förbränning av vätgas bildas enbart vattnånga. Dels så kräver sådana reaktioner idag stora mängder av material som inte är så vanligt förekommande på jorden. Några exempel på material som används idag är iridium och platina. I den här avhandlingen visar vi hur det är möjligt att framställa vätgas via vattenklyvning utan vare sig stora mängder sällsynta metaller eller hög energiförbrukning. Detta görs genom att optimera förhållandet mellan olika material vid tillverkningen av nanopartiklar, samt utnyttja de fackverksstrukturer som bildas vid sammansättningen av dessa nanopartiklar.
Preface

This thesis is the result of my doctoral studies in material science, in particular the research on nanoparticle growth and collection in the Plasma & Coatings Physics division at the department of Physics, Chemistry and Biology (IFM) at Linköping University. The work was carried out between January 2015 and December 2019.

The main goal of my research has been to study the growth of magnetic nanoparticles through a pulsed hollow cathode plasma discharge, as well as investigating the possibilities to collect said particles into advanced nanostructures using magnetic collection. The catalytic studies have been performed by colleagues at Umeå University.

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To all members of the Plasma Group, both present and former. Thank You for fruitful discussions during meetings, interesting topics of conversation at lunches and fun and giving company in general. A special thanks to Robert Boyd for always providing excellent microscope images and to Tetsuhide Shimizu for helping me explore the Japanese cuisine.

Rickard Gunnarsson deserves a special thank you. Both for the support during our Bachelor and Master years, for introducing me to the Plasma and Coatings division and for all support and help both inside and outside the lab.

Thank you Peter Münger for your help with calculations and simulations of magnetic and electric fields.

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To other collaborators throughout my years as a PhD student at IFM, e.g. Jens Eriksson, Marius Rodner and Jianwu Sun. Thank You for the nice cooperation and helping me to broaden my view on the possible applications of nanoparticles.
Thanks to all of my friends at IFM with whom I had many nice discussions and fun fika moments. A special thank you to Ana, Martin and Katherine for the interesting excursions and figments.

The 9 O’CCC (9 o’clock coffee club). I believe I was the last one into this morning coffee group, and now I’ll be the last one to leave. Thank You all for the nice and relaxing morning coffees together.

I would like to thank my friends from bachelor and master years at LiU, together with whom I’ve spent numerous hours in “Avogadro”, studying physics and math. A special thanks to Karl and Natalie for staying in touch over the years.

To all my friends from the Hemvärnets Musikkår Östergötland and Cykelorkestern. Thank You all for giving me something to focus on outside work (and at some occasions also during). I believe an active social life outside work is important, and You have certainly provided this.

Finally, I wish to thank my family for all of the support and encouragement throughout this work, and my entire life.
included publications

Paper 1
Catalytic Nanotruss Structures Realized by Magnetic Self-Assembly in Pulsed Plasma
Nano Letters 18 (2018) 3132

I was involved in planning and designing the experiments, performed the nanoparticle deposition experiments and performed some of the characterization. I wrote a major part of the first draft and contributed to the final paper. I did not carry out any of the electrocatalysis measurements nor theoretical force calculations.

Paper 2
Growth of semi-coherent Ni and NiO dual-phase nanoparticles using hollow cathode sputtering
Journal of Nanoparticle Research 21 (2019) 37

I planned and designed the experiments. I supervised and/or performed the experiments as well as the SEM and XRD characterization. I prepared the first draft and wrote major part of the paper.

Paper 3
Impact of nanoparticle magnetization on the 3D formation of dual-phase Ni/NiO nanoparticle-based nanotrusses
Journal of Nanoparticle Research 21 (2019) 228

I planned and designed the experiments. I supervised and/or performed the experiments as well as the SEM and XRD characterization. I prepared the first draft and wrote major part of the paper.
Paper 4
Self-assembly of Fe, Ni and FeNi-alloy nanoparticles into highly active nanotruss catalysts for the oxygen evolution reaction
Submitted

I was involved in designing and creating the dual source cathode holder. I planned, designed and performed the experiments, excluding the electrocatalysis. I did the SEM and XRD characterization. I prepared the first draft and wrote major part of the paper.

Paper 5
Acid-stable Platinum Nickel alloys – mechanistic insight into low noble metal content catalysts for hydrogen evolution reaction
In manuscript

I planned and designed the experiments. I supervised and/or performed the experiments as well as the SEM and XRD characterization, excluding the electrocatalysis. I prepared the first draft.
Related but not included publications

I  
**Modified Epitaxial Graphene on SiC for Extremely Sensitive and Selective Gas Sensors**  
Materials Science Forum **858** (2016) 1145

II  
**Performance tuning of gas sensors based on epitaxial graphene on silicon carbide**  

III  
**Graphene Decorated with Iron Oxide Nanoparticles for Highly Sensitive Interaction with volatile Organic Compounds**  
Sensors **19** (2019) 918

IV  
**A nanostructured NiO/cubic SiC p-n heterojunction photoanode for enhanced solar water splitting**  
Journal of Materials Chemistry A **7** (2019) 4721
Acronyms and variables

DC Direct Current
EDX (EDS) Energy-Dispersive X-ray Spectroscopy
HER Hydrogen Evolution Reaction
HiPIHCS High-Power Impulse Hollow Cathode Sputtering
HiPIMS High-Power Impulse Magnetron Sputtering
OER Oxygen Evolution Reaction
PEC PhotoElectroChemical (water splitting)
SEM Scanning Electron Microscopy
TEM Transmission Electron Microscopy
VOC Volatile Organic Compound
XRD X-Ray Diffraction

B
Diameter of a flow channel [m]
d
F_B Magnetic force [N]
K_a Knudsen number
m Magnetic moment [Am^2 = Nm/T = J/T]
p Pressure [Pa, torr]
r_NP Nanoparticle radius [m]
T_e Electron temperature [eV]
T_i Ion temperature [eV]
W_th,kin Translational kinetic energy [J]
\eta Plasma density [1/m^3]
\eta_e Electron density [1/m^3]
\eta_i Ion density [1/m^3]
\lambda Mean free path [m]
\sigma_{atom} Collision cross section, atoms [m^2]
\sigma_{ion} Collision cross section, ions [m^2]
\phi_B Magnetic potential energy [J]
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Chapter 1

1. Introduction

Nanoparticles are today heavily used in the development of nanotechnology. There are many reasons for this. One is the fact that the property of a nanoparticle depends heavily on its size and shape. Therefore, many interesting properties can be found in a nanoparticle, which is not found in its bulk counterpart. [1] Another reason for focusing on nanoparticles is their surface-to-volume ratio. As the size of a particle decreases, its surface-to-volume ratio increases. This means that a larger fraction of the atoms forming the nanoparticle sits at the particle surface. [2] As the surface is the most accessible part of a material, a large surface-to-volume ratio can be important to a vast range of applications.

The method used for growing nanoparticles within this thesis is called high-power pulsed hollow cathode sputtering. It has previously been shown to give fast nanoparticle growth as well as a good nanoparticle size and stoichiometry control thanks to the large number of controllable parameters within the growth process. The most common use of nanoparticles grown using this technique is to collect them onto a 2D surface using electric fields from a substrate bias. [3] [4] [5] [6] [7] In this thesis, the aim is to investigate the possibilities to assemble a 3D structure using individual nanoparticles as the building blocks. The idea is to even further increase the reachable surface of e.g. catalytic materials. Here, the approach is to grow magnetic nanoparticles and use magnetic fields in order to collect said particles onto substrates. Instead of just landing on top of each other and basically creating a “film” of nanoparticles, as in electrical collection, magnetically collected nanoparticles forms nanowires and interlink into nanotrusses. These nanotrusses are strongly bound to each other and follow the magnetic field lines of where they are assembled. This gives a stable, yet “airy”, 3D structure where electrolytes get access to a large part of the structure surface.

One issue with growing these structures is of course to choose materials that are magnetic enough to collect using this method, yet still catalytically interesting. Big parts of the thesis are therefore focused on investigating how much magnetic material that is needed for a nanoparticle
to be collected magnetically, as well as looking into different methods of growing nanoparticles of several elements to increase their catalytic performance. The latter is done in two different ways. Both by introducing different amounts of a reactive gas in order to grow nanoparticles through reactive sputtering, and by using two hollow cathodes of different materials. In the thesis, it is also shown that by using different pulse sequences and powers to the two cathodes, the elemental ratios of individual nanoparticles can be controlled.

To ease the understanding of the results of this work, several chapters are provided to guide the reader through the whole process of what is required in order to create the nanostructures, and how to use them. This starts with the fundamentals of the sputtering process to grow the desired nanoparticles, through to magnetic collection in order to collect and assemble the particles into nanotrusses, and finally some applications are discussed.
2. The sputtering process

This section will cover the basics of the sputtering process, as well as some of the physics required to achieve sputtering for thin film and nanoparticle growth.

2.1 Plasma Physics

Plasma is its own state of matter, together with the solid, liquid and gas states. To go from a state with more tightly bond particles to one with more free movement, the addition of energy is needed. A plasma is an ionized gas, which means that one or more electrons has been removed from a gas molecule, leaving a positively charged ion. How much of a gas that needs to be ionized for it to be classified as a plasma can be defined as: “A plasma is a quasineutral gas of charged and neutral particles which exhibits collective behaviour”. Here “quasineutral” means that there needs to be similar numbers of ions and electrons per unit volume, so that the total charge of the plasma is zero. This number is usually called the plasma density and can be written as

\[ n \cong n_i \cong n_e \]  

(1)

where \( n_i \) and \( n_e \) is the ion and electron density, respectively. In a normal gas, particles interact mainly by physically colliding and changing trajectory. However, because the plasma particles have an electric charge, it is not only the random collision that causes these particles to interact but also their electric forces. Local concentrations of such charges give electric fields. And as the charges move, currents are generated which in hand create magnetic fields. For the condition of “collective behaviour” to be fulfilled, the motion of the charged particles must be dominated by these electromagnetic forces, rather than collisions with neutral atoms.

From this it can be understood that, for a plasma to exist, a low concentration of gas particles is needed. In space this is no problem, and most of the visible universe consists of plasma. However, in the ambient atmosphere of the earth a plasma would be cooled by the air and cause the ions
and electrons to recombine into neutral atoms and molecules. To achieve and maintain a plasma, an artificially created vacuum is often needed. [8]
2.2 Vacuum science

Vacuum is defined as the absence of material. A total vacuum is not possible to create since not all gas molecules can be removed, and the gas pressure in a volume is therefore used to define the level, or regime, of the vacuum. Table 1 displays the name and pressure regimes of some commonly used “levels of vacuum” in plasma processes.

Table 1 | Definition of some vacuum regimes, their pressure ranges in Pa and torr, and their mean free paths.

<table>
<thead>
<tr>
<th>Vacuum level</th>
<th>Pressure range (Pa)</th>
<th>Pressure range (torr)</th>
<th>Mean free path, λ (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>(10^3 &gt; p &gt; 3.3\times10^3)</td>
<td>(760 &gt; p &gt; 25)</td>
<td>(10^{-8}-10^{-6})</td>
</tr>
<tr>
<td>Medium</td>
<td>(3.3\times10^3 &gt; p &gt; 10^{-1})</td>
<td>(25 &gt; p &gt; 10^{-3})</td>
<td>(10^{-6}-10^{-2})</td>
</tr>
<tr>
<td>High</td>
<td>(10^{-1} &gt; p &gt; 10^{-7})</td>
<td>(10^3 &gt; p &gt; 10^9)</td>
<td>(10^2-10^4)</td>
</tr>
<tr>
<td>Ultra high</td>
<td>(10^{-7} &gt; p &gt; 0)</td>
<td>(10^9 &gt; p &gt; 0)</td>
<td>(&gt;10^4)</td>
</tr>
</tbody>
</table>

Vacuum is usually achieved in a laboratory using pumps to remove air from sealed metal containers. Different levels of vacuum require different types of pumps, seals and containers. The reason why not one single type of pump can be used is because of the way gas molecules interact with each other. The average distance a particle can travel without interaction (collision) with another particle is known as the mean free path, denoted \(\lambda\). This distance is inversely proportional to the pressure since the number of gas molecules in a volume determines how often they will collide. There are two main types of gas flows, and they are separated by the most likely type of collision for the gas particle: a collision with a wall, or with another particle. This is symbolized through the Knudsen number:

\[
K_n = \frac{\lambda}{d} \tag{2}
\]

where \(d\) is the diameter of a flow channel. With \(K_n < 0.01\), the flow is said to be in viscous (continuous) flow. This means that the gas particles are most likely to interact with each other and the gas moves in a similar way to a liquid. To transport particles in this type of flow, it is enough to remove particles from one part of the volume and the constant interaction of the remaining particles will make sure that they are evenly distributed. The type of pumps used in this regime is called positive displacement pumps, such as scroll pumps, roots pumps and rotary vane pumps. In the range \(K_n > 0.5\), the number of particles in a volume is so low that it is
more likely that they will hit a wall of their container rather than another particle, i.e. the mean free path is larger than half the distance between the walls. The regime $K_n > 0.5$ is known as the *molecular flow* and means that one can no longer remove some particles and expect others to take their place. Instead, each particle to be removed from the volume is given its energy to leave from the pump itself. These pumps are referred to as kinetic pumps, and some examples are turbomolecular pumps, diffusion pumps and propellant jet pumps.\(^*\) In between these two regimes, $0.01 < K_n < 0.5$, there exists a third one called the *Knudsen flow*. This is basically a mixture between the viscous and the molecular flows. [9]

The higher the vacuum (lower pressure), the purer materials are possible to achieve when doing thin film deposition. This is because impurities such as gas particles can attach to the substrate surface during film deposition, thus embedding itself in the growing film. The unit to measure this is called the *monolayer formation time*, and this is basically the time it takes for a clean surface to be covered by a monolayer of particles. Higher vacuum means fewer gas particles and a longer monolayer formation time. [10]

\(^*\) Note: these are not all types of vacuum pumps, merely the ones used within this thesis. There are also other pumps, e.g. entrapment pumps which works on the principle of preventing particles from moving in the volume.
2.3 Sputtering

Sputtering is the process of removing particles of a material from its surface through bombardment of energetic particles from a gas or a plasma. The material one wishes to sputter from is called a target, while the gas/plasma particles are referred to as the sputter gas. The gas used is usually a noble gas, such as argon, to avoid reactions between the target material and the sputter gas. The way to collide the sputter gas particles into the target with enough energy to cause sputtering is commonly to ionize the gas and accelerate it using an electric potential. When the ion hits the target, surface species of the target material can be sputtered out. The number of atoms being sputtered by a single ion is called the sputter yield and depends on the surface binding energy of the target, the energy of the incoming ion and the mass ratio between said ion and a target atom. [11] The sputtered species can be atoms, but also ions and electrons. These can then aid in the ionisation of more sputter gas atoms, which in turn gets accelerated towards the target and sustain the process. To ionize the sputter gas as efficiently as possible, the electrons should be kept close to the target. This can be done in several ways, two of which will be discussed here.

2.3.1 Magnetron sputtering

A magnetron is a devise where magnetic fields are used to limit the movement of the electrons and keep them close to the target. The most common way to generate this magnetic field is with permanent magnets, and a cross section view of such a magnetron in a circular setup is displayed in Fig. 1a. The magnets are placed with a center magnet with one pole facing the target and a ring magnet surrounding it with the other pole towards the target. This gives rise to magnetic field lines as displayed in the figure, which helps keeping the electrons near the target surface. [12] As a result, the sputter gas is more ionized in this region, giving more bombardment of the target surface and higher sputtering rate (this is displayed as a denser plasma in Fig. 1a. Because of this, the target is more heavily consumed in a circular pattern between the two magnets. This is called the race track and is displayed in Fig. 1b for a used 2″ Ti target.
2.3.2 Hollow cathode sputtering

Another way to keep the electrons close to the target and interacting with the sputter gas is through the hollow cathode design. Here, the target has a tube shape, as displayed in Fig. 1d, and the sputter gas is passing through the tube. An electron generated at one side of the target wall will be repelled from the same because of the negative charge of the target. With respect to the plasma, all walls of the target are negatively charged, and will therefore contain the electrons within said plasma. This causes an oscillation of the electron inside the tube, as illustrated in Fig. 1c. Because the sputter gas is flown through the cathode, the oscillating electron has a high probability to interact with gas atoms and ionize them. This is known as the hollow cathode effect and gives a high cathode current with corresponding increase in plasma density. [13], [14] Another important feature of the hollow cathode design is the fact that the gas is trapped and cannot become rarefied as in an open magnetron, which makes it possible to achieve a super-saturated metal vapor in the hollow cathode. [15] This high density of sputtered material is especially important for the growth of nanoparticles, as will be explained in the section on nanoparticle growth.
Fig. 1 | (a) Illustration of the cross section view of a magnetron, displaying the orientation of magnets and magnetic fields, as well as densest plasma region. (b) 2″ Ti planar target that has been used in a magnetron. (c) Illustration of the cross section of a hollow cathode. (d) Fe hollow cathode target that has been used in the present work.

Recently, there are studies done which seek to combine the hollow cathode effect with the entrapment of electrons through magnetic fields, to further increase the efficiency of the hollow cathode sputtering technique. [16] Although interesting, this is not a topic of this thesis, and will therefore not be discussed further.

As mentioned above, an electric potential is needed to accelerate the ions towards the target. This can be done in a number of different ways, but the ones discussed here will be DC and HiPIMS discharges.
2.3.3 DC sputtering

*Direct current* sputtering is the simplest way of applying an electric potential to a target. Here, a constant negative voltage is kept on the target to attract the ionized gas species. The technique is relatively cheap since the requirements of the power supply is quite low, and the reproducibility is high due to the simplicity of its layout. [17]

2.3.4 HiPIMS

*High Power Impulse Magnetron Sputtering* HiPIMS is a deposition technique for sputtering from magnetrons. This technique merges the benefits from DC magnetron sputtering with that of high-power deposition techniques. [18] The way to achieve this higher energy of the deposition material is to increase the electric power of sputtering. However, if this is done in DC, the total power would heat up and melt the target material, as well as damaging the magnetron. This is avoided in HiPIMS by the use of pulses (i.e. short bursts) where the power reaches very high levels, referred to as on-time. This is then followed by longer periods where no power is supplied, keeping the average power acceptably low, called off-time. See Fig. 2 for a schematic illustration of the difference in power over time for DC and HiPIMS.

Throughout the papers in this thesis, the HiPIMS technique has been used to power the sputtering process. However, since hollow cathodes are used and not magnetrons, the correct term for the technique would be High Power Impulse Hollow Cathode Sputtering (HiPIHCS, “pronounced high-picks”). [16] The reason for using this pulsed technique is the large fraction of ionized species generated, and extracted, compared to DC. [15] The benefits of having ionized species for nanoparticle formation is discussed in the section “Nucleation and growth of nanoparticles”.

2.3.5 Reactive sputtering

In the *reactive sputtering process*, in addition to the sputter gas, a second gas is used. Unlike the sputter gas, this one is meant to react with the target material, and is therefore called the *reactive gas*. The idea is to form e.g. metal oxides through sputtering the metal from the target and adding the oxygen through the gas supply. By controlling the ratios of metal to oxygen, the stoichiometry of the deposited material can be tuned. However, the introduction of a reactive gas has a major impact on the sputtering process, and its flow will influence both deposition rates and composition. [19] This is because the reactive gas atoms will not only react with the sputtered species and the deposited film, but also with the target surface atoms, effectively influencing all discharge parameters of the target. When a compound layer from the reactive gas forms on the target surface, it is called *target poisoning*. Because of the higher bond strength of compounds compared to metals, the poisoning of the target will lead to a lower deposition rate. It is therefore a balance to find the right amount of reactive gas to use in a process, to achieve the desired film stoichiometry while still maintaining a sufficient deposition rate. This process window is called the *transition region*, and lies between the metal and the poison modes. [20]

Because of its design, the hollow cathode setup used throughout this thesis is less susceptible to target poisoning. The reason is that the sputter gas flown through the cathode will make it less likely for the reactive gas
molecules to be able to reach the target surface.* However, it is of course possible to drive the hollow cathode setup into poison mode as well, especially for materials more keen to form compounds, e.g. titanium and oxygen. [4], [5] More on the specific use of reactive gases on compound nanoparticle growth is discussed in the section “Nucleation and growth of nanoparticles/Reactive growth”.

This chapter has been covering sputtering in general. The method can be used to remove a material from a surface, so called etching, but also to transfer particles of one material in order to use it for e.g. thin film deposition or nanoparticle growth.

* Note: this is only true if the reactive gas is let in downstream of the hollow cathode, as in the setup for this thesis. If the reactive gas is fed through the hollow cathode along with the sputter gas the situation changes, as the reactive gas atoms are released closer to the cathode and have a higher probability to reach the target surface.
3. Magnetism

Because magnetism is used to guide the nanoparticles in this work, some basic understanding on what makes a material magnetic, along with some nomenclature, is given below.

One of the easiest ways to classify a material is through its magnetic moment in zero applied field. For a **diamagnetic** material, the moment in each atom is zero. If subjected to an applied magnetic field, an opposite magnetic field is induced, creating a repulsive force between the diamagnetic material and the source of the applied magnetic field. The diamagnetic magnetic field is caused by electron movements around the nucleus. If there is no other form of magnetism in the material, it is called a diamagnet. In a **paramagnetic** material, the magnetic moment is non-zero when looking at single atoms, but is (for zero applied external field) averaged out to zero as the moments on the average are randomly directed and cancel each other out. However, if an external magnetic field is applied to the material, the moments become aligned with the external field, inducing a magnetic field in the paramagnetic material which gives an attractive force to the source of the applied field. As for a **ferromagnetic** material, each atom has a non-zero magnetic field, and the average is not zero even in zero applied field. This is because the moments of the individual atoms interact in such a way that they can partly align with each other even without the help of an applied field. [21]

For more details on the mechanisms of magnetic nanoparticle collection, please see the section “Nanoparticle collection/Magnetic collection”.

Chapter 3
4. Nanoparticles, nanowires and nanotrusses

Chapter 2 described how atoms and ions can be ejected from a target material. In this chapter we will focus on how these can grow into nanoparticles within the plasma phase, and how these particles can then be used as building blocks to create more advanced nanostructures.

4.1 Nucleation and growth of nanoparticles

For the sputtered atoms of a target to form nanoparticles, there are several steps of transformation. These are described in the following sections.

4.1.1 Nucleation

The first step for a nanoparticle to start to grow from atoms is the formation of a dimer. This is a first cluster, consisting of two atoms which are bonded together. For this to happen, it is not enough that two atoms collide. The internal vibrational energy between these atoms will be too high to be able to form a stable bond, as the conservation of energy within the system must be maintained. The extra energy needs to be passed on to a third atom, which can then carry it away. [22] This is referred to as the three-body collision and can take place e.g. between two target atoms and a sputter gas atom, as displayed in Fig. 3. Because of this required collision, a higher pressure (i.e. more gas and metal atoms within a specific volume) leads to a higher rate of collisions and dimer formations. This is one reason why a higher pressure is used for the growth of nanoparticles, compared to the pressure set for e.g. thin film growth. The same reasoning goes for using hollow cathodes to reach super-saturated metal vapours, as sputter gas atoms alone will not be enough to form the desired dimers. As described above, the metal target ions are also needed for the three-body collision. However, there are also other ways of forming a first dimer. It has e.g. been suggested that a two-body collision between a target atom and a water molecule could be enough for a dimer to form,
as the target atom binds to the oxygen while a hydrogen molecule is ejected to release the excess energy. [23]

Fig. 3 | Schematic image of three-body collision as two target atoms and a sputter gas atom collides. The target atoms bind to form a dimer as the sputter gas atom carries away the excess energy.

4.1.2 Growth

Once a stable dimer has formed, the cluster can continue to grow by collision with new target atoms. The energy from such a collision can now be adsorbed through internal vibrations since there are more bonds to share the energy. It is also possible for the cluster to grow through collision with a target ion, however the following recombination with an electron may again break the bond to one of the atoms due to the high recombination energy. At this stage the cluster can either grow or decrease in size depending on the particles it interacts with. The probability to evaporate an atom from the cluster is, below a critical size, higher than the probability to add an atom, meaning that most dimers will not grow to large clusters. This is because a cluster which has an atom added to it will heat up and needs time to cool down before another atom can be added. However, once a cluster reaches a certain size the probability to evaporate one atom will be the same as the probability for the cluster to be able to cool down before the evaporation. Above this size the cluster will, on average, only grow bigger, and it is defined as being nucleated. [23]

The probability of an atom to interact with a cluster depends on the size of the cluster as well as density and motion of the atoms. A larger cluster will have a larger “target surface” and is more likely to be hit by an atom. This is called the *collision cross section* and is for a neutral atom given by

$$\sigma_{\text{atom}} = \pi r_p^2$$  \hspace{1cm} (3)

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where $r_{NP}$ is the radius of the nanoparticle in the plasma. [6] The growth of particles in a plasma, due to atom collection, is a slow process. Growth rates of less than 3 nm/s has been reported. [7] However, a particle in a plasma will charge up due to interaction with charged plasma species, ions and electrons. Because of the higher mobility of the electrons, the particle will obtain a negative charge. [24] This charge causes ions to collide with the particle with a higher probability than atoms, due to the electric attraction between the particle and the ion. The collision cross section of an ion can be written as

$$\sigma_{ion} = \pi r_{NP}^2 \left( 1 + K_1 \frac{T_e}{T_i} \right) \quad (4)$$

where $T_e$ and $T_i$ is the electron and ion temperatures, respectively. $K_1$ is a factor that depends on the ion mass and the temperature ratio of electrons and ions, here assumed to be constant at 2.41 in the case of $T_e/T_i \approx 100$ ($T_e = 2 eV$ and $T_i = 0.03 eV$). [6] The electric attraction increases the growth rate of the particles significantly, and growth rates as high as 470 nm/s has been reported in the case of using HiPIMS in combination with a hollow cathode setup. [7] This can be achieved because both the HiPIMS and the hollow cathode gives high plasma densities, resulting in a high degree of ionized species compared to neutrals in the plasma. This means that a larger fraction of the growth material can be collected through the more efficient ion collection. See Fig. 4 for a schematic illustration of the difference in particle trajectories for neutrals vs ions. The region of dense plasma (large amounts of free ions and electrons) is called the growth zone and is primarily located between the anode and the cathode.

Fig. 4 | Schematic drawing of particle trajectories as (a) neutral atoms and (b) ions pass by a negatively charged nanoparticle. The collision cross sections for neutrals and ions are displayed by the pink ellipse in (a) and (b) respectively.
4.1.3 Reactive growth

This section relates back to the one on reactive sputtering, but here concentrates on the effect of reactive gas on nanoparticle growth. This is the main focus of Paper 2, hence the results described here derive from this paper.

In the setup used throughout this thesis, the reactive gas (O$_2$) inlet is placed downstream from the hollow cathode, closer to the pump outlet. (See the “Experimental setup” section for a more detailed overview). As the O$_2$ molecules reach the growth zone, they can contribute to the nanoparticle growth by collision with clusters, similar to the target atoms described in the earlier section. However, this new element will affect the growth of the nanoparticle, changing its crystal structure. E.g., if Ni is used as target material, and O$_2$ as reactive gas, the amount of O$_2$ used in the deposition process will determine the final nanoparticle properties. As shown in Fig. 5, no O$_2$ in the process will give pure Ni nanoparticles, with NiO shells only forming because of the later exposure to the ambient atmosphere. At really high O$_2$ flow rates on the other hand, the whole nanoparticle has grown as a NiO crystal. At intermediate O$_2$ gas flows, dual-phase Ni/NiO nanoparticles can be grown, with varying phase compositions determined by this gas flow. As two crystal lattices overlap, Moiré fringes can sometimes be visible in the TEM images. Note that this behaviour of only two, distinct, clearly separable phases is due to the lattice forming properties of Ni and O. In the growth window of nanoparticles for these two elements, there exists only two phases, Ni and NiO. If other elements are used, e.g. Fe and O, also other phases are to be expected, like Fe, FeO, Fe$_3$O$_4$ and Fe$_2$O$_3$. 

Fig. 5 | TEM image of Ni and NiO nanoparticles. Increase in O₂ flow shifts the growth from dominantly pure Ni towards dominantly NiO crystals. Images borrowed from Paper 2.

4.1.4 Dual target growth

To understand how it is possible to grow alloyed nanoparticles using growth material from two different targets, we first need to have a closer look at how the pulsing of a target effects the nanoparticle growth. From earlier studies [6], we already know that it takes several pulses from the hollow cathode to grow the nanoparticles. As a pulse of growth material (atoms and ions) is ejected from the cathode, and the pulse frequency is sufficiently high, the cloud of atoms from the previous pulse will be in the region between the hollow cathode and the anode ring. (See the experimental setup in Fig. 13 for detailed positioning of the anode and cathode). The ions in the cloud moves much faster than the atoms, as they are subjected to ambipolar diffusion. This means that the ion cloud of a pulse will, at some point, move through the atom cloud of the previous pulse. As a result, subsequent pulses will have a direct interaction of overlapping sputtered material. Adding to this, there is also an indirect interaction as the discharge current of subsequent pulses travels from the cathode to the anode. This can potentially ionize some of the neutral atoms and affect the nanoparticle growth rate. [6]

From this we realize that, through alternating between different cathodes between pulses, one can create a growth zone of mixed growth species. This is the topic of Paper 4 and 5, and here this mix of growth species is achieved by placing two hollow cathodes in the vicinity of each other and
using two different pulse generators connected to a synchronization unit in order to deliver a single pulse to one cathode before switching to the other. See Fig. 6a for an illustration of the pulsing pattern applied to the different cathodes. By controlling the power delivered to each cathode, it is then possible to tune the ratio of the two target materials in the produced nanoparticle. There are of course also other possible ways of changing the material ratio within the nanoparticles. One would be to use different pulse lengths to the different cathodes to regulate the amount of growth material present in the growth zone at any given time. This is an interesting topic for future work, however not covered within the scope of this thesis.

If the desired nanoparticles are not alloys, but instead single element particles of the different materials, this is possible to achieve as well. The easiest way is simply to change the pulse sequence and deliver a number of pulses to one cathode before switching to the other. In this way the nanoparticles can grow to their final size before the material in the growth zone is changed. To ensure that no mixture of materials occur, it is possible to put a short “resting time” in, called off-time, before turning on the other cathode, to ensure that there is nothing left of the other species of growth material. See Fig. 6b for an illustration of this pulse pattern. This mode of pulse delivery is called pulse train and the effect of it is illustrated in Paper 4. As a result, the individual nanoparticles grown are only consisting of a single element, but there coexist two sorts of nanoparticles of different elements within the same sample.

Fig. 6 | Pulse sequence as delivered for growing a) alloyed or b) single element nanoparticles from a dual source.
4.2 Nanoparticle collection

In the previous chapter, the nucleation and growth of nanoparticles in a plasma was described. In this section, a closer look into how these particles can be extracted from the plasma and collected onto a substrate is made.

4.2.1 Random collection

The simplest way of getting nanoparticles onto a substrate is to place the substrate in the vicinity of the growth zone and wait until the intrinsic movement of the particles has caused some of the nanoparticles to end up on the substrate. Note that the movement of the particles in a hollow cathode generated plasma is not completely random since the direction of the gas flow will influence the nanoparticles and cause them to move away from the cathode opening. This technique is here called random collection and can be useful if a very small amount (less than a monolayer) of nanoparticles is desired. It can also work for insulated substrates where no bias can be supplied.

4.2.2 Electric collection

The most common way to collect the nanoparticles from the plasma phase is through electric collection. Here, the fact that the nanoparticles obtain a negative charge in the plasma is used to attract them to the substrate. A positive bias is put on the substrate and the particles are then drawn towards it. Particles will however only be affected by the substrate bias close to the substrate since electric fields cannot penetrate far into the plasma. This is the same technique as used when a substrate bias is used to draw ions towards a substrate to grow thin films. However, since the individual ions has a positive charge, the substrate bias of such a setup needs to be negative, the opposite of the nanoparticle case. The electric collection method is the one used in Paper 2.

4.2.3 Magnetic collection

This method can only be used for magnetic particles, as a magnet is placed behind the substrate to attract the nanoparticles. An important issue when dealing with magnetic nanoparticles is the risk that these will agglomerate in the plasma, due to magnetic attraction, before being
collected onto a substrate. In the plasma, however, there exists an electrostatic repulsion of the negatively charged nanoparticles that will suppress agglomeration. The question is then which of these forces that is strongest. In Paper 1, the limit for agglomeration is investigated through calculation of the force between two charged spherical nanoparticles with perfectly aligned magnetic moments. Here it is shown that the electrostatic repulsion dominates at larger distances while the magnetic attraction is stronger at shorter distances. This gives an energy barrier for two nanoparticles that approach each other. Agglomeration is suppressed if the random thermal kinetic energy is lower than this barrier. This energy is given by the gas temperature, 300 K. The height of the barrier is dependent on the electron temperature, and for fully magnetized Fe nanoparticles agglomeration was found to be suppressed if the electron temperature of the plasma exceeds 0.15 eV. Counterintuitively, and of large importance, this result was found to be independent of the sizes of the involved nanoparticles. This suppression of agglomeration in the plasma is represented by the encircled number (1) in Fig. 7.

Fig. 7 | Schematic illustration of the involved physics in magnetic collection. Encircled numbers show: (1) suppression of agglomeration in the plasma, (2) alignment of the magnetic moment, (3) no escape from the capture zone and (4) attraction to the magnet.
In contrast to electric fields, magnetic fields can penetrate a plasma, and the magnetic collection can therefore take place while nanoparticles are still in their growth regime in the plasma volume. With respect to the magnetic capture, this volume can be divided into two regions. Within the capture zone, defined below, the nanoparticles align their magnetic moment $\mathbf{m}$ with the external magnetic field $\mathbf{B}$ and a magnetic force drags them to the magnet,

$$F_B = -m\mathbf{vB}.$$

This force will only have minor effects on the nanoparticles while outside the capture zone. The process of magnetic capture is denoted in Fig. 7, by the encircled numbers 2-4. These numbers represent: (2) alignment of the magnetic moment of the nanoparticle to the external magnetic field, (3) no escape from the capture zone possible as the translational kinetic energy is smaller than the escape barrier due to magnetic force and (4) attraction to the permanent magnet.

**Capture zone**

The capture zone is defined from the following energy argument. The particles will experience a magnetic potential energy of

$$\Phi_B = -\mathbf{m} \cdot \mathbf{B}$$

where $\mathbf{m}$ is the magnetic moment of the nanoparticle and $\mathbf{B}$ is the magnetic field of the external magnet. When nanoparticles rotate, the largest possible value is $\Phi_{B,\text{max}} = -mB$, and occurs when the nanoparticle is aligned with the external magnet. Nanoparticles can rotate freely in the plasma if the field $B$ is below a critical field strength for alignment with the external magnet, given by combining $\Phi_{B,\text{max}}$ with the average thermal rotation energy. It can be written as

$$B_c = \frac{9}{8} \frac{k_BT_g}{\pi \bar{r}_3 N_p M}$$

where $k_B$ is Boltzmann’s constant, $T_g$ is the process gas temperature and $M$ is the magnetization of the nanoparticles. If $B > B_c$, the rotational energy is too small for totally free rotation to occur, and the magnetic moment of the particles will tend to be aligned with the applied magnetic field. To lower the average magnetic energy, the nanoparticle is now drawn towards the external magnet. However, the nanoparticle also has a
translational kinetic energy, $W_{th,kin}$, which pushes the nanoparticle to continue on a specific path. The nanoparticle will end up on the substrate (i.e. be “captured”) if $W_{th,kin} < mB$. Because the thermal energies of kinetic and rotation is the same at thermal equilibrium, the critical field strength of the magnetic capture is the same as the critical field strength for alignment, $B_c$. We call the volume when $B > B_c$ the capture zone and it is determined by the magnetic properties and size of the nanoparticle, as well as the external magnetic field strength.

In Fig. 7, a region named the *Near Capture Zone* is displayed. This region represents where short-range forces act upon the nanoparticles as they get close enough. In the present case, this region is typically much less than 1 mm from the substrate. The short-range magnetic force is that experienced by a nanoparticle as it approaches a substrate where nanowires have already started to assemble. Provided that the nanoparticles in the wire have similar sizes, an approaching nanoparticle will experience an attractive force that will make it attach primarily to the free end of the nanowire where the magnetic flux that is trapped within the nanowire escapes. In the case where a nanowire is built up of very unequal sizes of nanoparticles there also exists attracting positions along the wire, i.e. not only at the wire ends. These are locations where the magnetic flux is no longer fully confined within the wire. This gives rise to the branching of the nanowire, and thereby interlinking into nanotrusses. Examples and simulations of this can be found in the next section, on the assembly of nanowires and nanotrusses.

In the magnetic capture process above, a stationary gas is assumed in the growth zone. However, in a real experiment the gas flow will be non-zero and also varies both in space (with distance to the cathode opening) and in time (as the power is pulsed). [15] Therefore, a nanoparticle might be dragged out of the capture zone and lost if the gas drag force is larger than the magnetic force. On the other hand, during the pulse there exists a discharge electric field which exerts a force on the negatively charged nanoparticles towards the anode. From the experimental setup, Fig. 13, it can be seen that this tends to keep the nanoparticles inside the magnetic capture zone.

If a magnet is placed close enough, the nanoparticle can grow in the plasma and be drawn to the substrate as soon as a large enough size is
reached to fulfil the criterias described above. This is the main collection method used in Papers 1, 3, 4 and 5.
4.3 Assembly

The types of collection of nanoparticles onto a substrate will not only be different in the way the particle is drawn to the substrate, it will also influence how they arrange in relation to each other on the substrate. For non-magnetic nanoparticles, both the random and electric collection will end up with nanoparticles evenly spread on top of each other over a surface, much like how balls arrange in a ball pool for children. Fig. 8 shows such a structure. Here Ti nanoparticles have been collected onto an Au surface using electric collection.

However, because of their magnetic properties, the magnetically collected nanoparticles will arrange into more complex structures. Each nanoparticle acts as its own magnet, with a north and a south pole, and their positions on the substrate will be influenced by both other nanoparticles and the field of the external magnet. In this work, two different structures have been identified, and are described below.
4.3.1 Nanowires

When the nanoparticles attach to each other, one after the other, to form a single, long thread of particles, we refer to it as a nanowire. For individual nanowires to form, the nanoparticles that constitute the wires need to be of similar size. As described in paper 1, this is achieved through not using an external magnet, but instead allowing the wires to form spontaneously. This can happen in different ways. One option is that the nanoparticles reaches a region where the electron temperature is low enough, i.e. their charge low enough, for the magnetic attraction between individual nanoparticles to overcome their electric repulsion. Another is that wires, already attached to a grounded or positively biased surface, has lost their charge and hence the electrostatic repulsion disappears towards an arriving nanoparticle which still holds its charge. In these ways, the wires can grow simply by the north of one particle attaching to the south of another, as already described as the Near Capture Zone in the previous section. The result is long, individual, nanowires which are entangled without any general orientation. In Fig. 9a, such an entanglement of nanowires is displayed. The wires have then been separated by ultrasonication for easier display in the TEM. An individual wire is displayed in Fig. 9b and 9c.
Fig. 9 | Nanowires grown without an external magnet. (a) SEM of a bundle of nanowires, (b) TEM of a single nanowire after ultra-sonication to separate the wires and (c) a zoom in of a section of the nanowire, showing the narrow size distribution of the nanoparticles. Adapted with permission. Copyright American Chemical Society 2018.
4.3.2 Nanotrusses

Using an external magnet to collect magnetic nanoparticles will result in a broader size distribution than what is seen in the previous example for the nanowires, which were not collected using an external magnet. The reason for this size distribution increase is that the nanoparticles are dragged out of the plasma at different sizes, depending on where in the plasma they are formed. From Eq. (7) follows that a particle that is formed further from the external magnet needs to grow to a larger size before being attracted by the $B$ field, compared to a particle that forms closer to the magnet. We call this the capture zone, and it is in Fig. 10 displayed for an external magnet with a $B$ field of 0.36 T where the dashed black lines represent the capture zones for different sizes (diameter) of fully magnetized Fe nanoparticles.

![Fig. 10 | Magnetic capture zones for different sizes of fully magnetized Fe nanoparticles, for an external magnet of 0.36 T. Reused with permission. Copyright American Chemical Society 2018.](image)

As the nanoparticles are captured and dragged to the substrate, they will start to line up in a similar way as for nanowire growth, with the north pole of one particle attaching to the south pole of another. However, since the size distribution of these particles are much broader than for the wire case, there will be spots of magnetic leak fields from the larger particles, i.e. locations where the magnetic flux is not fully contained by the nanowire, as discussed in the previous section. This is due to the fact that the smaller nanoparticles cannot sustain as large magnetic fields as the larger ones, causing parts of the magnetic field to leak out from the wire formed.
These sites, in the near capture zone of Fig. 7, will attract new particles which attach there, lowering the magnetic potential. This is illustrated in Fig. 11a-c, where magnetic field strength simulations of differently shaped nanowires are displayed. Here, stronger magnetic fields can be seen both at the ends of the nanowires and along the sides of the larger nanoparticles incorporated in the nanowires. Capture at the latter sites results in a branching of the nanowires into a strongly interlinked web of wires, named nanotrusses. Fig. 11d displays a TEM image of such a nanowire that is branching into several wires, due to the difference in nanoparticle size. This can be compared to Fig. 9c where all particles are of a similar size. A characteristic feature of the nanotrusses is their preferred orientation, since they will, generally, grow in the magnetic field direction of the external magnetic field.

Fig. 11 | (a-c) Magnetic field strength simulations illustrating magnetic leak fields along nanowires with nanoparticles of different sizes, and how the sites of stronger leak fields gives rise to branching and interlinking of the nanowires. (d) TEM of a wire with different particle sizes, resulting in branching of the wire. Adapted with permission. Copyright American Chemical Society 2018.
Chapter 5

5. Applications

Over the last 30 years, there has been a growing interest in the field of nanoparticles to be used in industrial applications. A lot of different applications can be found, suitable for a vast range of different shapes and sizes of nanoparticles. [25] [26] One major production technique for the nanoparticles is through gas phase synthesis, where the particles are formed using the bottom-up method of building the nanoparticles from individual atoms or molecules. [27] As this is also the basic technique used in this thesis, this chapter will aim to point out the unique features of the nanostructures created using the current setup. Also, some applications of the nanoparticles, both created with this setup and investigated in papers outside the scope of this thesis, are discussed to give a general idea of areas of application.

The most characteristic feature studied in this thesis is the nanotruss structure, which is the subject of 4 out of 5 papers. The main properties of these trusses are:

- high surface-to-volume ratio
- high degree of branching and interlinking

A large surface is important when the material is to be used for e.g. catalytic reactions, as the contact of the reactant with the surface of the material can assist in lowering the energy barrier for a chemical reaction to take place (i.e. serve as a catalyst). If an expensive or rare material is needed for this, a lot can be saved if the amount (volume) of said material can be decreased. Another reason for wanting to reduce the volume of a material is to save space and/or weight. This can be important for e.g. transportation applications.

The branching and interlinking of the nanotrusses have several benefits. The mechanical strength is increased with more interlinking, and so is the ability for the structure to carry electrical currents.
Combined, the properties of the nanotrusses give a 3D structure that allows catalytic liquids to flow over large surfaces. As the reactions take place, electrons can flow freely within the trusses and into a current-distributing substrate. Some suitable applications are discussed below.

During the course of this thesis work, several collaborations other than those included in the thesis have been carried out in order to investigate how nanoparticles can help improve chemical reactions as the particles are spread over a surface rather than forming 3D structures. Some of these investigations can be found in the “Related but not included publications” section, and are briefly described here.

5.1 Hydrogen production

The basic principle of hydrogen production is that energy is used to split liquid water into gaseous H₂ and O₂, such as

\[ H_2O(l) + \text{Energy} = H_2(g) + \frac{1}{2} O_2(g) \]  \( (8) \)

Here, clean energy without pollution emission can be achieved. [28] There are several reasons for doing this, but one of the most recent ones is to produce H₂ for later use in hydrogen fuel cells. Here we look at two different ways of performing the water splitting.

5.1.1 Electrocatalysis

In Papers 1, 4 and 5, the electrocatalytic water splitting is used as a method to investigate the H₂ production efficiency of the produced nanotrusses. Here, the “Energy” in Eq. (8) comes from electricity as a high voltage is applied from a DC power supply between the positive electrode (anode) and the negative electrode (cathode). Depending on the elements used, the produced electrode material can be better suited as either cathode, i.e. the hydrogen evolution reaction (HER), or as anode, the oxygen evolution reaction (OER). [28] Even if H₂ is commonly the desired gas, both the HER and the OER reactions are important as one will not take place without the other. In Paper 1, Fe nanotrusses were investigated for the HER reaction. In Paper 4 and 5, different alloys of FeNi and PtNi were used for OER and HER reactions, respectively.
5.1.2 Photocatalysis

Solar driven photoelectrochemical (PEC) water splitting is a method for converting solar energy into $\text{H}_2$ and $\text{O}_2$. A semiconductor material is used to form an excited electron-hole pair from the absorption of a solar photon. The hole must then reach a surface to drive the OER, while electrons will be consumed in the HER. [29] In a work using cubic SiC (3C-SiC) as the semiconductor, NiO nanoparticles similar to the ones grown in Paper 2 were deposited. NiO was chosen because its wide bandgap gives an optical transparency in the visible sunlight region. [30] The need of transparency together with a desire of a single layer of nanoparticles meant that only electric collection of the nanoparticles was done. Compared to a bare 3C-SiC substrate, a substrate coated with NiO displayed a 33.6 times higher photocurrent. Together with a reduced overpotential, high fill factor (57%) and photo-corrosion protection, the NiO nanoparticles significantly enhanced the water splitting performance of the 3C-SiC. [30]

5.2 Gas sensors

Gas sensors of different types has been used for decades in order to detect gases which are flammable or hazardous. There exists a big variety of technological solutions for these sensors, which all has different principles of operation. Because of this, they all have different advantages and disadvantages. [31] Due to its high surface-to-volume ratio, graphene can often be used as a base material of a gas sensor to improve its sensitivity and at the same time reduce the size and power consumption of the sensor. [32] [33] These graphene-based gas sensors have been used for over 10 years, as they have ultra-high sensitivity to a range of molecules. [34] However, because of this sensitivity the selectivity is low and the response and recovery times slow. This can be enhanced by nanostructured metallization layers being deposited on top of the graphene. The desired electronic properties of the graphene are preserved, while sensitivity, selectivity and response speed are improved by the modified surface chemistry of the sensor. [35] An effective way of getting a small and controlled amount of metal onto the graphene, without damaging its sensor properties, is to deposit metallic nanoparticles grown in a plasma. In several papers, it has been shown that Fe and Fe$_3$O$_4$ nanoparticles can be used to
enhance the efficiency of gas sensors towards toxic volatile organic compounds (VOCs). Quantitative measurements of VOCs were performed on concentrations down to a single part per billion (ppb). This, together with response times of less than a minute, makes the Fe nanoparticle coated, graphene-based gas sensor a promising candidate for air quality monitoring. [36], [37], [38]
6. Experimental setup

This section gives an overview of the experimental setup used throughout the papers of this thesis. Some images depicting one of the setups (that of Paper 5) is seen in Fig. 12. Specific details on the precise setup of each paper can be found in its “Experimental” section.
Fig. 12 | Images of the hollow cathode setup. Left: Ni and Pt plasmas ignited inside the vacuum chamber. Upper right: Side image of the setup displaying the copper block, gas inlet, mesh, anode ring, shutter and substrate table. Lower right: Bottom view of the setup, displaying the two cathodes side by side, as well as the opening in the bottom of the mesh.
6.1 Hardware

The main components for growing and assembling the nanoparticles described in this thesis are a vacuum chamber, a system that provides electricity, gas and cooling water to the hollow cathodes, and power supplies capable of delivering the high-power pulses.

6.1.1 Vacuum chambers

Two different High Vacuum (HV) systems were used for the experiments performed throughout the papers in this thesis. Their layout, size, pumping speeds and base pressures are fairly similar, and a schematic drawing for one of the systems can be seen in Fig. 13. The base pressure of the systems is around $3 \cdot 10^{-7}$ torr ($4 \cdot 10^{-5}$ Pa). Both systems consist of stainless steel walls, and the seals are all rubber based.

6.1.2 System setup

As targets for the nanoparticle growth, hollow cathodes were used. These has a length of 54 mm and an inner diameter of 5 mm. The diameter was chosen to achieve a steady operation of the hollow cathode discharge, which ranges 0.1-10 Torr.cm, depending on operating gas, geometry and electrode material. [39] The cathode was incapsulated in a copper block and mounted on a magnetron, with the magnets removed, for the supply of water cooling and electric connection. For the processes where two cathodes were used, Papers 4 and 5, the copper block was split in two and electrically insulated using sheets of mica to ensure that the cathodes could operate at different electrical potential.

A grounded anode ring of stainless steel, with a diameter of 30 mm, is placed 20-40 mm from the exit of the hollow cathode. This is done in order to flow the discharge current through the growth zone of the nanoparticles, which will influence the plasma parameters. [6]

Surrounding the cathode exit and the anode ring sits a mesh cage of stainless steel. This is used to electrically entrap the plasma species while still allowing neutral gas particles to expand freely out from the cathode opening.

Substrates were placed in one of two places. For electrically collected nanoparticles, a rotatable substrate table was placed at an opening in the lower part of the mesh. This substrate table was able to hold 6 or 7
substrates at the time, depending on which of the two chambers that was used. The substrate table has a lid with a small opening, ensuring that only one of the substrates is deposited at the time (not displayed in Fig. 13). For magnetically collected samples, the substrates were placed on top of a permanent magnet and attached to the inside of the mesh, at the same height as the anode ring. This location was chosen to make sure that the substrates were out of the most intense plasma, between the anode and the cathode, but still close enough for the magnetic capture zone of the permanent magnet to be able to reach into said plasma region. Magnets of different materials and field strengths were used, see each paper for details on magnetic properties.
Fig. 13 | Experimental setup for one of the vacuum systems used. Drawn to scale.
6.1.3 Power supply and pulse parameters

To deliver the HiPIMS pulses of the experiments performed, HiPSTER 1 units from Ionautics AB were used, powered by MDX-1K dc power supplies from Advanced energy. When more than one cathode was used, a HiPSTER Sync unit from Ionautics was used to coordinate the pulses to the different targets. In general, a pulse frequency of 1200 Hz and a pulse length of 80 µs has been used for the experiments. Other parameters have been tried, but the chosen ones have shown the most consistent particle growth for all materials deposited, and are therefore used throughout the experiments in the papers. As two cathodes are used, the sync is set to 600 Hz/cathode to ensure that the pulse frequency of 1200 Hz is obtained in the growth zone.

The software of the HiPSTER 1 allows for the control of constant voltage, current or power. As a rule, constant power was used, and this power was kept below 75 W to avoid cathode overheating.
6.2 Growth conditions

6.2.1 Gases, flows and pressures

Throughout the experiments, the process pressure has been kept quite high, at 0.8 torr (105 Pa). The reason for this is the fact that nanoparticles need quite a high pressure in order to nucleate and grow in the plasma regime created outside the hollow cathode. (See the section on “Nucleation and growth of nanoparticles” for details on how gas pressure influences the nanoparticle growth). As a sputtering gas, Ar with a purity of 99.9997%, was used. The gas flows have been regulated from 30 to 120 sccm, see respective paper for details, and the pressure has been kept stable through throttling the pumps. In the cases where O₂ was used, the gas was diluted with Ar in order to more accurately control the low O₂ flows required.
Chapter 7

7. Material Characterization

The underlying physics of the characterization techniques used in this thesis have been covered in extensive detail elsewhere and so will not be discussed in this section. For the interested reader, more on these topics can be found in e.g. [40], [41] and [42]. Instead, the focus will here be on the sample preparation, characterization and data analysis of nanoparticles and nanotrusses when being investigated by the respective technique.

7.1 Scanning Electron Microscopy (SEM)

For most samples analyzed within this thesis, a field emission microscopy (LEO 1550 Gemini) was used. They were analyzed directly without any additional sample preparation. This, along with its relatively high resolution and ease of use, makes the SEM an ideal investigation tool to resolve individual nanoparticles and the structure of their associated nanotrusses. This is dependent on the resolution of the instrument and the size of the nanoparticles, but it is possible to resolve individual nanoparticles larger than 10 nm in diameter.

7.1.1 Energy-dispersive X-ray spectroscopy (EDX/EDS)

Energy-dispersive X-ray spectroscopy was used within the SEM described above. This technique is used for elemental analysis and/or chemical characterization of a specimen. Analysis software is used to calculate the composition from the raw detected X-ray intensities and assumes a homogeneous composition. One needs to be cautious when evaluating nanoparticles using EDX as it probes both the substrate and sample (the nanoparticles), as their different compositions make it possible that the ratio of some elements is over- or underestimated. One way to circumvent this is to only use the data acquired from the nanoparticles themselves, to qualitatively measure compositional change. This only works for elements that are only present in either the nanoparticles or the substrate. E.g. in Paper 2 the oxygen level of the Ni/NiO nanoparticles would be difficult to quantify using the SEM EDX, as oxygen will also be present...
both as TiO on the substrate surface and as contamination in the vacuum chamber itself.

7.2 Transmission Electron Microscopy (TEM)

One drawback of SEM is that it cannot probe the internal structure of nanoparticles nor resolve the interface between two attached particles. For higher resolution images, in order to map out atomic layers and elements within individual nanoparticles, a FEI Tecnai G2 TEM instrument was used. Prior to analysis samples are placed on an amorphous carbon coated copper grid. There are different ways of transferring the sample to the grid, depending on its collection approach.

If a nanoparticle is electrically collected, the grid can be placed inside the deposition chamber on top of an ordinary substrate. Then, the nanoparticles are collected directly onto the grid. Here it is important not to deposit too much material, less than a monolayer of nanoparticles is desired. This is because the electrons used to project an image in a TEM needs to travel through the whole sample in order to form the image. Or in other words, 2D projection of a 3D object. [43] Therefore, if particles are deposited on top of each other, features from overlapping particles can complicate image analysis.

If the nanoparticles are magnetically collected, the high rate of collection together with the fact that particles prefer to attach to one another calls for a different approach when preparing TEM samples. Here, the samples are placed in isopropanol and sonicated to detach the nanotrusses formed during deposition. The trusses can then be transferred onto TEM grids either through dipping the grid in the suspension or by using a pipette to place a drop of the suspension onto the grid. As the isopropanol evaporates, only the nanotrusses will remain. Using this method, it is important to remember that the shape and interlinking of the nanotruss structures are likely to be altered by the rough handling. Therefore, one should be careful with the conclusions one draws from TEM images of samples prepared using this method.
7.3 X-ray diffraction (XRD)

For all XRD measurements performed in the papers of this thesis, an Empyrean diffractometer in a parallel beam configuration with a line-focused copper anode source (Cu Kα, λ=0.154 nm), operating at 45 kV and 40 mA is used. A PIXcel-3D detector is operated as an open detector for the data acquisition. The primary beam is conditioned using a parallel beam mirror and in the secondary beam path a 0.27° parallel plate collimator is used. As the amount of nanoparticles on a substrate is generally quite low, grazing incidence X-ray diffraction (GIXRD) measurements are performed as this probes a larger surface area at a smaller depth compared to e.g. 0/20 measurements. [44]
Chapter 8

8. Summary of the results and contributions to the field
In this chapter, the main results from each paper in this thesis is presented.

Paper 1
Catalytic Nanotruss Structures Realized by Magnetic Self-Assembly in Pulsed Plasma

In this study, we show that it is possible to assemble nanotruss structures through magnetic guidance of nanoparticles grown in a pulsed plasma process. It is discovered that a magnetic collection of nanoparticles yields a larger size distribution of nanoparticles collected, compared to particles that were grown with similar methods but collected using electric fields. This occurs because magnetic fields can, unlike electric fields, penetrate the plasma and drag particles that have not yet reached their final size out from the growth zone. As a magnetic field drops with distance, the position of the nanoparticle inside the plasma will determine how large it will need to grow before being attracted by the magnetic field and collected to the substrate. The wide size distribution was discovered to be very advantageous, as it allowed the nanoparticles to attach not only to form nanowires, as was shown to be the case for similarly sized particles. Instead the growth structure became a web of highly interlinked and branched wires, which we named nanotrusses (after the interlocking support system of the truss bridge). The magnetic collection technique was shown to be highly effective, as nanotrusses of thicknesses up towards 200 µm were grown within a 10 min deposition. The truss formation was also tested for electrocatalysis through water splitting, which enabled an effective production of H₂ gas. The reason for the effectiveness of the material can be attributed to several features. The fact that the nanoparticles are not densely packed, but instead forms the 3D truss structure, means that the large, active surface is easily reached by the catalyst. The interlinking of the many nanowires also ensures both mechanical stability and electrical conductivity. In Paper 1 it was also shown that electrostatic repulsion
hinders unwanted agglomeration of the nanoparticles while in the plasma phase, as one could otherwise suspect that the use of magnetic nanoparticles would result in uncontrollable particle agglomeration.

Paper 2

**Growth of semi-coherent Ni and NiO dual-phase nanoparticles using hollow cathode sputtering**

In the second paper, nanoparticles are grown with varied amounts of reactive gas, O$_2$, in order to control and tune the composition of Ni/NiO within the particles. It has been shown before that pure Ni nanoparticles can be oxidized and then turned into NiO through a second step of heating in an oxygen rich atmosphere. However, here we show that this is possible to achieve in a single-step approach, as the Ni and O atoms co-exist in the growth regime of the nanoparticles and participate in the continuous growth of the particle. Using this approach, multiple particles of Ni and NiO typically assemble, in the gas phase, into complex structures. Here, it is the fluxes of Ni and O atoms arriving at the nanoparticle surface which determine if a crystal will grow as Ni or NiO. As the conditions and ratio of the two elements will vary throughout the system, due to the geometrical relations of Ni sputtering and O$_2$ gas inlet, so can the growth of the nanoparticle. This can result in particles containing crystals of both Ni and NiO, in a variety of size, shape and volume ratio. The largest assemblies of nanoparticles seen in Paper 2 are the fully oxidized ones. Here, several 10s of crystals are seen to form assemblies which stretch over 100 nm in size, with all of their crystal lattices aligned.
Paper 3

**Impact of nanoparticle magnetization on the 3D formation of dual-phase Ni/NiO nanoparticle-based nanotrusses**

The aim with this work is to investigate to which level a nanoparticle needs to be magnetic in order to be collected using the magnetic collection technique. To do so, the same process conditions and similar nanoparticles as those of **Paper 2** are used, and the particles are collected magnetically. The reason for using these materials is that Ni is ferromagnetic, while NiO is antiferromagnetic (at sizes >20 nm and >4 nm, respectively). This makes it possible to change the magnetic properties of the nanoparticles simply by changing the amount of O\textsubscript{2} introduced into the nanoparticle growth zone. It is shown that a decrease of the amount of magnetic material within the particles results in a decrease in the length of individual nanowires. This is caused by a higher tendency of nanowire branching. As the O\textsubscript{2} content is increased, the position and orientation of the NiO phase within a nanoparticle is shown to change, which influences how the nanoparticles assemble into nanotrusses.

Paper 4

**Self-assembly of Fe, Ni and FeNi-alloy nanoparticles into highly active nanotruss catalysts for the oxygen evolution reaction**

In this paper, a second cathode of a different material is added to the system setup and it is shown how changes in pulse sequences can be used to grow single element nanoparticles of the different materials, or alloys of the two. A way of tailoring the ratio of the different elements in the alloy by regulating the power into the two cathodes separately is also illustrated. The elements used here are Fe and Ni, i.e. two magnetic materials. Again, magnetic collection of the nanoparticles into nanotrusses is utilized. For single element nanoparticles it is shown that single-species Fe and Ni nanoparticles can coexist in the same nanotruss. The nanotrusses of alloyed nanoparticles are tested for electrocatalytical performance. It is shown that by changing the elemental ratio in the alloy, and optimizing the amount of deposited material, the water splitting performance of the nanotrusses can be improved. Actually, a required overpotential for OER
even lower than that of the benchmark IrO$_2$ sample is displayed for one of the sample conditions.

Paper 5

**Acid-stable Platinum Nickel alloys – mechanistic insight into low noble metal content catalysts for hydrogen evolution reaction**

The goal with this paper is to find suitable materials and structures for minimizing the amount of noble metals needed in the HER reaction of electrochemical water splitting. This is achieved through the growth of alloyed Pt$_x$Ni$_{1-x}$ nanoparticles, which are assembled into nanotruss structures through magnetic collection. Very competitive results are shown for Pt quantities as low as $x = 0.05$, displaying an onset potential of 25 mV and an overpotential of 62 mV to reach 10 mA/cm$^2$ in 0.5 M H$_2$SO$_4$. As for Paper 4, two separate cathodes are here used to grow the alloyed nanoparticles. Since Pt is not magnetic, magnetic collection is shown not to be effective at $x > 0.25$. However, through a combination of electric and magnetic collection, it is shown that growth of the nanoparticles is possible for $0 \leq x \leq 1$, i.e. from pure Ni to pure Pt.
Chapter 9

9. Future outlook

As previously discussed, several process parameters (which could possibly influence the growth of the nanoparticles) are kept constant through the experiments performed within the scope of this thesis. This is done in order to limit the number of samples required within a study. Here follow some suggestions on future work, and ideas on how it could influence the nanotruss formation.

Gas flow and gas pressure

It has been shown, by Gunnarsson et al, that the process gas pressure and flow can influence the size and morphology of TiO nanoparticles. With an increasing process gas pressure, the nanoparticles grew in size and changed shape from spherical, through cubic, and eventually to a cauliflower shape. [5] Although this work was made on TiO, one can assume similar behaviour from the materials used in this thesis. A change in nanoparticle shape towards cubic would most likely have an interesting effect on the nanotruss structure, as the possible angles between two particles would be severely restricted. This is of course assuming that the direction of the magnetic field of the particle aligns parallel to the normal of a surface of the cub.

Pulse frequency, pulse width and pulse trains

As the overlapping of subsequent pulses is crucial for the growth of alloyed nanoparticles in the dual cathode setup, changing the width and frequency of the pulses is very interesting. It offers the possibility to understand how fast a cloud of ions and atoms moves and spreads through the growth zone. Applying pulse trains of different numbers of pulses to each cathode could also give an insight in the number of pulses (or amount of material) needed to grow a nanoparticle.

Pulse amplitude

Because of concerns of overheating the target holders, the pulsed power to the cathodes has rarely exceeded 1 kW. By increasing the power even
further, one can expect the nanoparticles to grow even faster. Both be-
cause there will be more growth material in the growth zone due to more 
sputtering, but also because a higher current would most likely give a 
higher degree of ionization of the sputtered material. With this increased 
growth, the size distribution of the collected nanoparticles can be af-
affected. This would in turn change the branching and interlinking of the 
nanotrusses, as previously discussed.

Scaling size
As there is an optimum relation between hollow cathode size and process 
pressure to achieve the hollow cathode effect, as well as an optimum pres-
sure for nanoparticle growth, it is not so straight forward to scale up the 
hollow cathode source. Some interesting solutions could be:
1. to make a linear source through the use of two parallel plates as 
cathodes. A drawback here would be that the confinement of the 
electrons would only be in 1 direction, while the hollow cathode 
offers that confinement in 2D.
2. to design a source with a matrix of hollow cathodes, i.e. a “shower 
head”. However, there might then be issues with how the different 
cathodes, or plasmas thereof, would influence each other.

Scaling of the magnetic collection could also be a challenge. As the na-
oparticles are attracted in the direction of the strongest magnetic field 
strength gradients of a magnet, a homogeneous deposition over a surface 
is difficult to reach. This could possibly be circumvented by the use of 
several smaller magnets, or by moving the magnet in relation to the sub-
strate during deposition.
Bibliography


Papers

The papers associated with this thesis have been removed for copyright reasons. For more details about these see:

http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-161300
Plasma Synthesis and Self-Assembly of Magnetic Nanoparticles

Sebastian Ekeroth