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

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Abstract Magnetic nanoparticles with average size 30 nm were utilized to build three-dimensional framework structures—nanotrusses. In dual-phase Ni/NiO nanoparticles, there is a strong correlation between the amount of magnetic Ni and the final size and shape of the nanotruss. As it decreases, the length of the individual nanowires within the trusses also decreases, caused by a higher degree of branching of the wires. The position and orientation of the non-magnetic material within the truss structure was also investigated for the different phase compositions. For lower concentrations of NiO phase, the electrically conducting Ni-wire framework is maintained through the preferential bonding between the Ni crystals. For larger concentrations of NiO phase, the Ni-wire framework is interrupted by the NiO. The ability to use nanoparticles that are only partly oxidized in the growth of nanotruss structures is of great importance. It opens the possibility for using not only magnetic metals such as pure Ni, Fe, and Co, but also to use dual-phase nanoparticles that can strongly increase the efficiency of e.g. catalytic electrodes and fuel cells.

Keywords Ni · NiO · Nanotruss · Nanoparticle · Magnetic assembly

Introduction

The ability to design structures with a huge surface area to volume ratio is vital for many energy-related applications of nanomaterials (Zhou et al. 2011), such as different electrodes for capacitors, batteries, fuel cells, and electrochemical catalysis (Ning et al. 2016; Royston et al. 2008; Li et al. 2012; Debe 2012). Assemblies of nanoparticles can have such interesting properties. However, they are mostly effective on 2D surfaces as the surface area exposed to reactants is limited in thicker layers and among agglomerated particles. One way to circumvent this is to use a 3D support matrix (Somorjai and Park 2008) or assembling the nanoparticles into more open structures. The latter can be achieved, by using magnetic¹ nanoparticles combined with an applied magnetic field which allows the nanoparticles to self-assemble into nanowires or frameworks of nanowires—so-called nanotrusses. This can be achieved using magnetic particles in a liquid suspension (Kralj and Makovec 2015) or by direct generation and assembly of nanoparticles using plasma-based methods (Ekeröth et al. 2018). The latter has the advantage of avoiding impurities, such as surface oxidization. In a previous work, we have shown that Fe nanoparticles can be generated and assembled, onto a variety of substrates, into long (> 100 µm)

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¹ The term magnetic is used for ferromagnetic, ferrimagnetic as well as superparamagnetic materials in this article as all of them allow magnetic collection and assembling of nanoparticle by the method used in this article. The term non-magnetic is used for antiferromagnetic, paramagnetic, and diamagnetic materials.

nanotrusses through a plasma where the particles are generated followed by magnetic collection (Ekeröth et al. 2018). The low packing density of these trusses makes the material suitable for electrocatalysts since reactants can reach a high fraction of the exposed surface. Other benefits include no extra process steps associated with support structure, the entire structure is composed of active material, and there are electrical pathways to the substrate.

In the present work, nanowires and nanotrusses are formed through direct self-assembly of dual-phase magnetic Ni/NiO nanoparticles. The magnetic property of the nanoparticles is needed for the self-assembly of the nanotrusses in the magnetic field applied. We here investigate the amount of magnetic material needed in the individual nanoparticles for the assembly to occur. This knowledge is essential when designing nanostructures containing materials that are non-magnetic for different applications, e.g., catalytic electrodes. Some interesting materials include CuNi (Kimi et al. 2018), FePt (Adamski et al. 2018), and NiPt (Pham et al. 2017). The growth of individual dual-phase nanoparticles of Ni and NiO has been demonstrated previously, where various oxygen flow rates, 0 to 0.08 sccm, produced particles from pure Ni to (almost) pure NiO particles (Ekeröth et al. 2019). Ni nanoparticles have ferromagnetic properties (at size > 20 nm) (Ishizaki et al. 2016) and NiO (with a size > 4 nm) is antiferromagnetic (Rinaldi-Montes et al. 2014). This allows us to investigate magnetic collection into nanowires and nanotrusses from particles with varying amount of magnetic material. When the NiO fraction in the nanoparticles increases, their ability to form individual nanowires decreases while, at the same time, the occurrence of intrawire branching and inter-wire interlinking increases.

Experimental setup

Nanoparticles are created by generating a high-density flux of Ni ions from a hollow cathode sputtering source using high-power pulses. The Ni cathode (99.98% purity; inner diameter 5 mm and length 54 mm) is placed in a high vacuum chamber with a base pressure of 3×10^{-7} Torr (4×10^{-5} Pa) where nanoparticles nucleate and grow. Through the hollow cathode, an Ar sputter gas (99.9997% purity) is flown into the vacuum chamber at a rate of 30 sccm. Diluted O₂ (99.5% Ar) is added to the process through a separate gas inlet in the vacuum

chamber wall, located approximately 30 cm downstream of the cathode. The O₂ gas flow is the only parameter that is changed for the different growth conditions. Four growth conditions are used, with effective O₂ flows of 0, 0.02, 0.04, and 0.06 sccm. In Table 1, each condition is given a roman numeral for easier description throughout the paper. The experimental setup has been described earlier (Ekeröth et al. 2019), with the only difference being the position of the substrates. In the present work, the substrate is placed on a permanent magnet with a magnetic flux density of 0.36 T and dimensions of 9 mm in diameter and a height of 7 mm. The magnet is placed inside the mesh at the same height as the anode, see Fig. 1. This allows the substrate to be close to the nanoparticle generation zone, but away from the most intense plasma region. In control experiments, nanoparticles are also collected at the same position, but without a magnet. Substrates are Ti-coated (200 nm) Si wafers.

Scanning electron microscopy (SEM) images are taken using a LEO 1550 instrument equipped with electron high tension (EHT) and in-lens detectors. To investigate the structure of the nanotrusses as well as the particle-particle bonding, suitable samples for transmission electron microscopy (TEM) analysis are prepared. First by placing the deposited sample in isopropyl alcohol in an ultrasonic bath for 5 min to create a suspension of the nanotrusses. Then a small drop (approx. 50 µl) of the suspension was dried onto a TEM grid covered with an amorphous carbon film. The TEM analysis is obtained with a FEI Tecnai G2 operated at 200 kV using high angle angular dark field (HAADF) and energy dispersive X-ray spectroscopy (EDS) combined with scanning TEM (STEM) analysis. The HAADF images are collected with the annular detector spanning an angular range from 80 to 260 mrad.

Grazing incidence X-ray diffraction (GIXRD) measurements are performed using an Empyrean diffractometer in a parallel beam configuration with a line-

Table 1 Growth conditions and phase composition of the nanoparticles grown

Growth condition	O ₂ flow (sccm)	Phase composition (Ni/NiO)
i	0.00	100:0
ii	0.02	91:9
iii	0.04	32:68
iv	0.06	0:100

Fig. 1 Schematic drawing of the system setup, highlighting the placement of magnet and substrate

focused copper anode source (Cu K α , $\lambda = 0.154$ nm), operating at 45 kV and 40 mA. The primary beam is conditioned using a parallel beam mirror and a $1/4^\circ$ divergence slit and in the secondary beam path a 0.27° parallel plate collimator is used. A PIXcel-3D detector is used as an open detector for the data acquisition. The grazing incidence X-ray diffraction scans are performed at an incidence angle of 1° in a 2θ range of $30\text{--}80^\circ$ using a step size of 0.015° and a data collection time of 0.88 s/step.

Calculations of the magnetic orientation within nanoparticles is done with the “Magnetic Fields, No Currents” module within COMSOL Multiphysics version 5.4 (COMSOL Multiphysics 2019). A cylindrical calculation domain with a diameter of 300 nm and a length of 323 nm is used with the nanoparticle in the center, aligned with the cylinder axis. Magnetic energy is calculated as $W_m = \int_V \frac{1}{2} \vec{H} \cdot \vec{B} d\tau$ where the integration is performed over the entire calculation domain τ .

Results and discussion

A series of nanoparticles were grown, and collected on substrates, using conditions with different levels of oxygen added, Table 1. Their phase composition is

estimated using semi-quantitative reference intensity ratios of the two phases observed using the grazing incident XRD measurements, Fig. 2.

The O₂ gas flow is the only process parameter altered. The XRD acquired phase composition is calculated from the peaks shown in Fig. 2.

An overview of the structures obtained is presented in Fig. 3, displaying top-view SEM images of samples grown using the four different growth conditions investigated. It shows that nanotrusses are formed from particles grown at the lower oxygen flow rates (conditions i–iii), but not for the highest flow rate investigated (condition iv).

In order to elucidate the 3D structure, SEM and TEM investigations of samples grown using conditions i through iii are shown in Fig. 4. A matrix system is used to describe the specific image, Fig. 4 (x, y), where x determines the row and y the column. Each column represents a specific growth condition (in accordance with Table 1) and the rows display increasing magnification of SEM and TEM images of the three different samples.

Comparing the present results for pure Ni (condition i) with previously published results using Fe nanoparticles (Ekeröth et al. 2018), similarities are observed with trusses highly oriented along the growth direction, i.e.,

Fig. 2 XRD data, linear scale, of the peaks around 43.2° (NiO) and 44.4° (Ni), showing the gradual transition from Ni to NiO with the introduction of more O₂ into the process. i–iv represent the different growth conditions described in Table 1

Fig. 3 SEM images of Ni and Ni/NiO nanoparticles collected with the aid of an external magnet in the attempt to grow nanotrusses. **a–d** show increasing O₂ flows, from 0 to 0.06 sccm for **a** to **d**. Only the nanoparticles grown with O₂ flows of up to 0.04 sccm show the nanotruss structures. The apparent tilts of the nanotrusses are caused by their orientation with the applied magnetic fields and will vary at different locations on the substrate

the magnetic field orientation of the external magnet. The nanotrusses, with lengths of up to 100 μm , are made up of nanowires that interlink. Differences between the Fe and Ni are seen in the size of the individual nanoparticles within the trusses. Fe nanoparticles with sizes of less than 10 nm have been seen to participate in nanotruss formation (Ekeröth et al. 2018). However, no individual Ni nanoparticles smaller than 20 nm are found within the trusses. Fe has a significantly higher saturation magnetization as compared to Ni (217.6 and 55.1 Am^2/kg , respectively) (Crangle and Goodman 1971). This means that Ni particles need to grow bigger as compared to Fe particles for the attractive force of the magnet at the substrate to overcome the diffusive motion of the nanoparticle in the plasma. Please, see Ekeröth et al. (2018) for details on magnetic capturing of nanoparticles.

As oxygen gas is added to the process, Ni/NiO-composite nanoparticles are expected to be formed (Ekeröth et al. 2019), which should affect how the nanoparticles are collected and nanostructures formed. For the lowest oxygen gas flow investigated, condition ii, the SEM images (Fig. 4a (ii) and b (ii)) reveal only a small difference compared to growth without oxygen (Fig. 4a (i) and b (i)). The individual nanowires are no

longer easily distinguishable and the bundles seem to be denser, but the overall appearance is still fibrous. From the TEM image (Fig. 4c (ii)), we can see a higher degree of interlinking between the nanowires compared to the pure Ni nanoparticles (Fig. 4c (i)). This can be one explanation to why the individual wires are not clearly seen in Fig. 4b (ii). At higher magnification, a clear trend is observed within the nanoparticles themselves. With no oxygen, the particles are monodispersed with an average diameter of approximately 35 nm and show a hexagonal projection in the TEM image (Fig. 4d (i)). Adding the oxygen flow, the particles themselves become increasingly polydisperse both in terms of their size and shape (Fig. 4d (ii)). This is due to the formation of mixed-phase nanoparticles consisting of both metallic/magnetic Ni and insulating/non-magnetic NiO. The different phases are easily distinguished in the STEM-HAADF images of Fig. 5a, b, d where the higher average atomic mass of Ni gives it a higher contrast compared to NiO. EDS mapping confirms this, and in Fig. 5c NiO (blue) is clearly visible between larger and smaller Ni (green) particles. The NiO domains are typically 20 nm by 10 nm in size, as seen in the 2D projections of the TEM. They are cone-shaped crystals formed on a larger (30–40 nm) Ni particle.

Fig. 4 SEM and TEM images of nanotrusses grown using process conditions with 0–0.04 sccm of O₂ flow. The SEM images (rows **a** and **b**) were taken with a sample tilt of 54° to allow side-on view of

the structures. In the TEM images (rows **c** and **d**), the trusses have been sonically detached from the substrate. If there is only one scale bar in a row, it applies to all images in that row

Fig. 5 HAADF-STEM images of sections from the nanotrusses showing the wires from growth conditions ii (a–d) and iii (e–h). **b** and **f** are enlargements of the areas marked in **a** and **e**, respectively. **c** and **g** are STEM-EDS maps of the same areas as **b** and **f**, respectively. Green indicates Ni and blue oxygen

These domains are then capped by a smaller (8–10 nm) Ni crystal. The generation of these multiphase nanoparticles is more carefully explored and discussed in our previous work (Ekeröth et al. 2019).

The nanowires formed by these multiphase nanoparticles produced under growth condition ii mainly constitute a main wire-structure of the larger Ni particles connected to each other, as seen in Fig. 5a. The NiO cone

(with the Ni-cap) points out from the wire. This should increase the probability of interlinks forming between wires, as is seen in Fig. 5d. Here the Ni-cap of a multiphase particle seemingly connected to the larger Ni particle of another multiphase. These extra branching sites give rise to the formation of the distinctive nanotruss structures seen in Fig. 4b(ii). How the dual-phase nanoparticles assemble into wires, with the capped NiO to the

Fig. 6 Color-coded magnetic flux density in a symmetry plane along the symmetry line (dashed) for a three-domain particle. The NiO domain joining the Ni domains is unmagnetized. Dark red indicates a strong field of 6.5 T while light blue indicates zero field. Field lines are depicted in red. For **a**, the large Ni domain in the

bottom is fully magnetized with the field direction to the left in the figure while the smaller Ni domain on top is fully magnetized with the field direction to the right, while for **b** the large Ni domain in the bottom and the smaller Ni domain on top are both fully magnetized with the field direction upwards in the figure

side or along the wire, can be understood by studying the magnetic configuration within the mixed-phase nanoparticles when formed in the plasma. To investigate the probable magnetic configuration, calculations of two prospective magnetization orientations were performed

on a model geometry using COMSOL Multiphysics (COMSOL Multiphysics 2019). The model geometry consists of two differently sized spheres of Ni joined by a coaxial truncated cone of NiO. The Ni spheres were truncated to form flat interfaces with the NiO. Figure 6a

Fig. 7 SEM images showing the effect of using an external magnet on Ni nanoparticles (top) vs NiO nanoparticles (bottom)

Fig. 8 SEM image of a NiO nanoparticle assembly from growth condition iv

and b depict the magnetic flux density in a cross section along the symmetry line for two different magnetizations of the particle. The two magnetizations were along and perpendicular to the symmetry axis (dashed line), with opposing magnetic orientation in the two Ni domains for the perpendicular case, see Fig. 6. These two configurations were chosen since other configurations are likely to have higher magnetic energy due to lower symmetry. A magnetization of 5.1×10^5 A/m was used in Ni while NiO was treated as air magnetically in the calculations. The calculations show that the configuration in Fig. 6a is favorable as the magnetic energy, W_m , is lower than for the configuration in Fig. 6b, 4.79 versus 5.03 eV. The results from the calculations explain the observed formation, with the larger Ni particle taking part in the main structure and the NiO cone with the Ni-cap sticking out.

Now focus is turned to the growth condition with more oxygen, condition iii. Here, the general direction of the main structures (micrometer scale) is along the external magnetic field direction, as is the case for growth conditions i and ii. This can be seen in Fig. 3. However, the general appearance of these structures grown under condition iii is fluffier than the corresponding structures of grown under condition i or ii, which display more fibrous structures. See Fig. 4 (row a) for this comparison. The reason for this appearance can be found when comparing the structures at a higher resolution, Fig. 4 (row b). The ends of the nanotrusses at growth condition iii have a high tendency to deviate from direction of the external magnetic field (Fig. 4b (iii)). This results in trusses and wires of extending up to a few hundred nanometers in all directions from the main structure. For growth condition ii, there is a similar tendency. However, here the trusses and wires extend only short distances (less than 100 nm, Fig. 4b (ii)). With no added oxygen, condition i, such features are rare (Fig. 4b (i)). The TEM of structures grown under condition iii (Fig. 4c (iii)) shows a high degree

of branching of the nanowires, creating relatively large voids between the wires. As can be seen in the TEM micrograph with higher resolution (Fig. 4d (iii)), the typical shape of the nanoparticles has, for growth condition iii, shifted from spheres to cube-like structures, with small (1–2 nm) features covering the surfaces. From the STEM-HAADF images (Fig. 5e, f, h), it can be seen that the NiO (darker contrast) is both cubic and incorporated in the main wire-structure. EDS studies (Fig. 5g) confirm that the different phases are Ni (green) and NiO (blue). A previous study has shown that these structures appear when NiO is dominating with cubically shaped nanoparticles, having multiple small Ni satellites attached to it (Ekeröth et al. 2019). This change in the particle composition is a probable explanation for the change observed in the microstructure, with highly branched structures as seen in Fig. 4a–d (iii). However, even if a large fraction of the nanoparticles is of the non-magnetic NiO phase, the fact that trusses are still formed is an indication that the amount of metallic Ni is high enough to magnetically collect the particles.

For even higher flow rates of oxygen (0.06 sccm, condition iv), it is no longer possible to form truss structures. There are still some nanoparticles collected at the substrate; however, they do not assemble into the characteristic nanotruss-structure. To validate that it is the magnetic properties of the nanoparticles that determines the formation of nanotrusses, control experiments, where the permanent magnet was removed, were also performed and compared to samples collected with a magnetic field present. The results are presented in Fig. 7 with growth condition i in the top row and condition iv in the bottom row. The influence of using a magnet is very clear for condition i but no effect is observed for condition iv. For the latter condition, particle distribution is similar to earlier experiments done with electrically collected metallic nanoparticles (Gunnarsson et al. 2015; Gunnarsson et al. 2016; Pilch et al. 2013a, p. 102; Pilch et al. 2013b, p. 103).

Higher magnification images of samples grown at condition iv, with or without a magnet present (see Fig. 8 for an example), reveal that the individual particles have changed both in shape and size, compared to the particles in growth conditions i–iii with or without a magnet. Here the particles consist of large assemblies with many crystals of cubical shape, similar to what was seen for higher oxygen flow rates in earlier work (Ekeröth et al. 2019). These assemblies appear to be formed in the gas phase, without the aid from a magnetic field, before arriving at the substrate surface.

Conclusion

The technique of using magnetic fields for direct assemble of vapor phase formed ferromagnetic nanoparticles into nanotrusses can be applied also to complex multiphase nanoparticles. Through different levels of oxidation, Ni/NiO dual-phase nanoparticles are generated which assemble into nanostructures (nanotrusses) unless the ferromagnetic Ni-fraction becomes too low. The NiO content of the nanoparticles has a significant effect on the overall nanostructures. With an increasing fraction of NiO, more nanowire branching occurs within the nanotruss. At the highest NiO content studied, only very small domains of Ni remain, and the nanoparticles do not assemble into extensive nanotrusses. The possibility to include non-magnetic phases in the otherwise ferromagnetic nanoparticles opens possibilities to generate nanostructures with improved or altered properties that might find applications in different fields, e.g., as active electrodes in electrocatalysis.

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Compliance with ethical standards

Conflict of interest There are no conflicts of interest to declare.

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References

- Adamski J, Qadir MI, Serna JP, Bernardi F, Baptista DL, Salles BR, Novak MA, Machado G, Dupont J (2018) Core-shell Fe-Pt nanoparticles in ionic liquids: magnetic and catalytic properties. *J Phys Chem C* 122:4641
- COMSOL Multiphysics, version 5.4. COMSOL 2019, URL: <https://www.comsol.com>. Accessed 9 Apr 2019
- Crangle J, Goodman GM (1971) The magnetization of pure iron and nickel. *Proc Roy Soc Lond A* 321:477
- Debe MK (2012) Electrocatalyst approaches and challenges for automotive fuel cells. *Nature* 486:43

- Ekeröth S, Ikeda S, Boyd R, Shimizu T, Helmersson U (2019) Growth of semi-coherent Ni and NiO dual-phase nanoparticles using hollow cathode sputtering. *J Nanopart Res* 21:37
- Ekeröth S, Mürner EP, Boyd R, Ekspong J, Wågberg T, Edman L, Brenning N, Helmersson U (2018) Catalytic nanotruss structures realized by magnetic self-assembly in pulsed plasma. *Nano Lett* 18:3132–3137
- Gunnarsson R, Helmersson U, Pilch I (2015) Synthesis of titanium-oxide nanoparticles with size and stoichiometry control. *J Nanopart Res* 17:353
- Gunnarsson R, Pilch I, Boyd RD, Brenning N, Helmersson U (2016) The influence of pressure and gas flow on size and morphology of titanium oxide nanoparticles synthesized by hollow cathode sputtering. *J Appl Phys* 120:044308
- Ishizaki T, Yatsugi K, Akedo K (2016) Effect of particle size on the magnetic properties of Ni nanoparticles synthesized with trioctylphosphine as the capping agent. *Nanomaterials* 6(9):172
- Kimi M, Jaidie MMH, Pang SC (2018) Bimetallic Cu-Ni nanoparticles supported on activated carbon for catalytic oxidation of benzyl alcohol. *J Phys Chem Solids* 112:50
- Kralj S, Makovec D (2015) Magnetic assembly of superparamagnetic iron oxide nanoparticle clusters into nanochains and nanobundles. *ACS Nano* 9:9700
- Li L, Nan C, Lu J, Peng Q, Li Y (2012) α -MnO₂ nanotubes: high surface area and enhanced lithium battery properties. *Chem Commun* 48:6945
- Ning F, Shao M, Xu S, Fu Y, Zhang R, Wei M, Evans DG, Duan X (2016) TiO₂/graphene/NiFe-layered double hydroxide nanorod array photoanodes for efficient photoelectrochemical water splitting. *Energy Environ Sci* 9:2633
- Pham VV, Ta V-T, Sunglae C (2017) Synthesis of NiPt alloy nanoparticles by galvanic replacement method for direct ethanol fuel cell. *Int J Hydrog Energy* 42:13192
- Pilch I, Söderström D, Brenning N, Helmersson U (2013a) Size-controlled growth of nanoparticles in a highly ionized pulsed plasma. *Appl Phys Lett* 102:033108
- Pilch I, Söderström D, Hasan MI, Helmersson U, Brenning N (2013b) Fast growth of nanoparticles in a hollow cathode plasma through orbit motion limited ion collection. *Appl Phys Lett* 103:193108
- Rinaldi-Montes N, Gorria P, Martínez-Blanco D, Fuertes AB, Fernández Barquin L, Rodríguez Fernández J, de Pedro I, Fdez-Gubieda ML, Alonso J, Olivi L, Aquilanti G, Blanco JA (2014) Interplay between microstructure and magnetism in NiO nanoparticles: breakdown of the antiferromagnetic order. *Nanoscale* 6:457
- Royston E, Ghosh A, Kofinas P, Harris MT, Culver JN (2008) Self-assembly of virus-structured high surface area nanomaterials and their application as battery electrodes. *Langmuir* 24:906
- Somorjai GA, Park JY (2008) Colloid science of metal nanoparticle catalysis in 2D and 3D structures. Challenges of nucleation, growth, composition, particle shape, size control and their influence on activity and selectivity. *Top Catal* 49:126
- Zhou Z-Y, Tian N, Li J-T, Broadwell I, Sun S-G (2011) Nanomaterials of high surface energy with exceptional properties in catalysis and energy storage. *Chem Soc Rev* 40:4167

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