HIGH THROUGHPUT SYNTHESIS OF NI(*0*) NANOPARTICLES USING COAXIAL MIXING PRINCIPLES

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Introduction

Nickel nanoparticles (NP) are used as catalysts in chemical reactions and as essential parts for electrodes in multilayer ceramic capacitors, which can be found in nearly every electronic device. Countless ways of producing those particles were investigated, e.g. the carbonyl method, spray pyrolysis, sonochemical decomposition etc. Wet chemical routes for production of non-agglomerated nanoparticles are also well known to literature. The two major routes are the polyol-process and the reduction with strong reducing agents like hydrazine or borhydride. Commonly known methods for mass production with wet chemical processes have to cope with bad reproducibility in batch reactors or blockage and fouling of mixing chambers in continuously operated reactors. Usually blockage and fouling is avoided by high diluted reactants, which results in long reaction times and difficult postprocessing. Rising demand in quality and quantity for nickel NPs asks for novel approaches to mass-produce those particles.

We have come up with two different ways of high throughput synthesis using coaxial micromixing principles. A cone channel nozzle providing an *ex chamber* microdroplet mixing with batchwise heating and a coaxial injection mixer giving the opportunity to carry out the synthesis in a fully continuous way using *in chamber* mixing and the novel process window.

Reaction

- Two step reaction in water
- Mixing nickel(II)sulfate solution with aqueous alkaline hydrazine solution
- Formation of blue $Ni[N_2H_4]_3SO_4$ complex (1) & (2)
- Heating in batch to form Ni(*0*) NPs (3)
- (4) & (5) are side reactions due to slow heat & mass transfer (overheating)

- The highly reactive intermediate can be isolated via the fully continuous process. TEM investigation (not shown) identifies the different nature of the intermediate as source for varying nanoparticle shapes

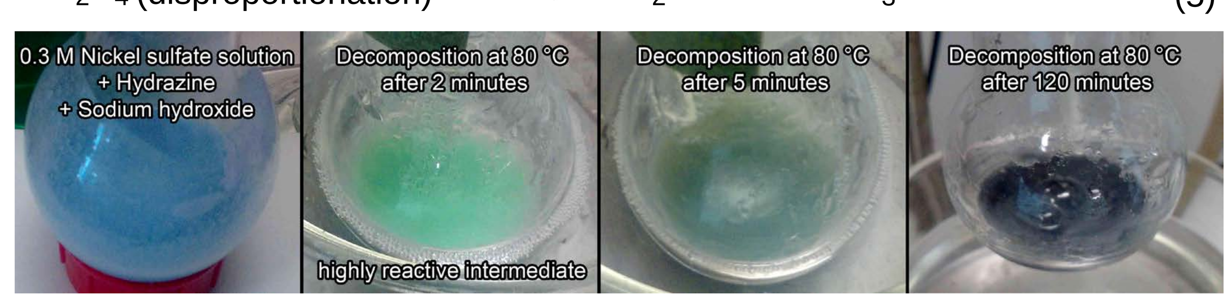
$$NiSO_4 + 3\,N_2H_4 \longrightarrow Ni[N_2H_4]_3SO_4 \quad (1)$$

$$Ni[N_2H_4]_3SO_4 + 2\,NaOH \longrightarrow Ni(OH)_2 + 3\,N_2H_4 + Na_2SO_4 \quad (2)$$

$$2\,Ni(OH)_2 + N_2H_4 \xrightarrow{\Delta} 2\,Ni(0) + N_2 + 4\,H_2O \quad (3)$$

$$N_2H_4 \text{ (decomposition)} \xrightarrow{\Delta} N_2 + 2\,H_2 \quad (4)$$

$$3\,N_2H_4 \text{ (disproportionation)} \xrightarrow{\Delta} N_2 + 4\,NH_3 \quad (5)$$



Top: occuring reactions, bottom: foto of the flask at each reaction step, the highly reactive intermediate can be synthesized with the fully continuous process.

SUMMARY

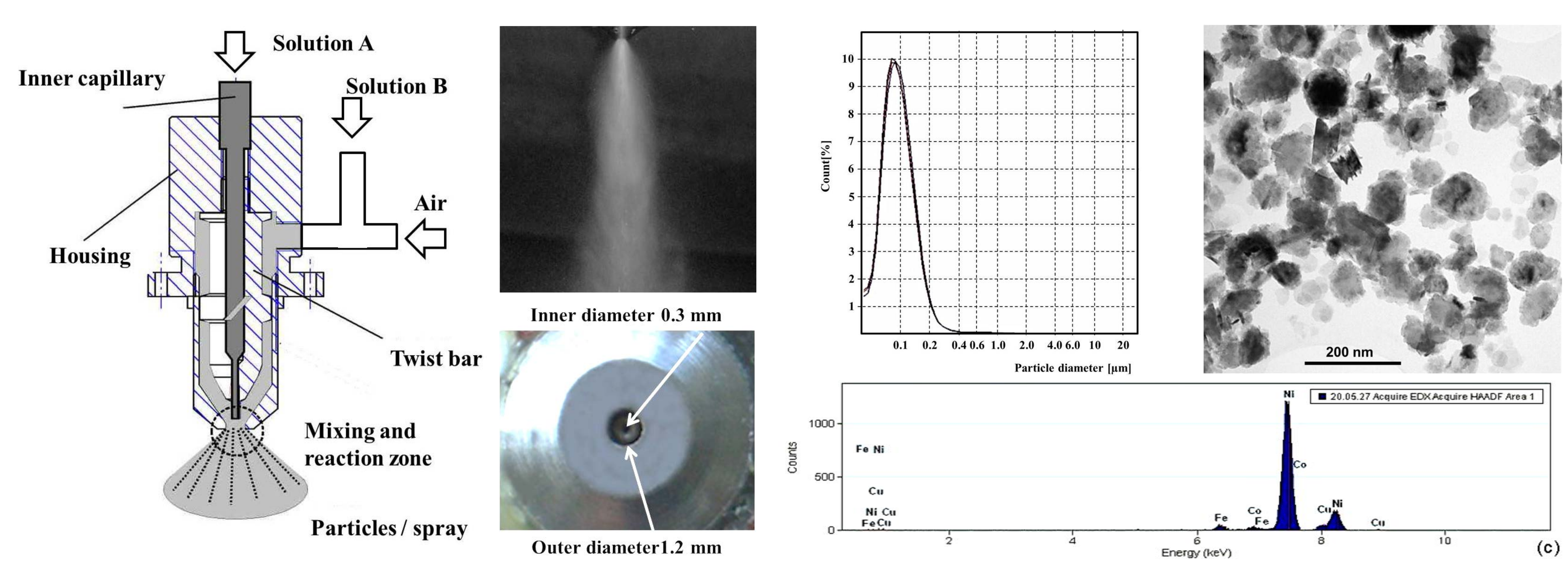
- **Two different setups able to produce 1 kg nickel nanoparticles per day**
- **Uncloggable microdroplet reactor yields 95 nm sized round/flat shaped particles with batchwise heating**
- **Fully continuous injection reactor yields 82 nm sized flat shaped particles**
- **Batchwise operation of injection reactor yields 270 nm hedgehog shaped particles**

Microdroplet reactor

+ Very good mixing in small droplets
+ Excellent reproducibility of NP size
+ Impossible to clogg
+ Operation at atmospheric pressure (1 bar)
+ Insight in reaction (glass vessels)
- Semi batch operation
  → Collecting the wet precursor & heating in a separated step
- Need for air filtratrion (exhaust air)
- Uniformity of particles not always given

- Yielding 95 nm nickel NPs with narrow size distribution (see DLS graph)
- 100% chemical purity (see EDX; Fe, Co & Cu are artifacts)
- Heated batchwise at 80 °C without stirring for ~2 hours
- Washed with ethanol and water

Nozzle geometry, reaction steps and particle analysis



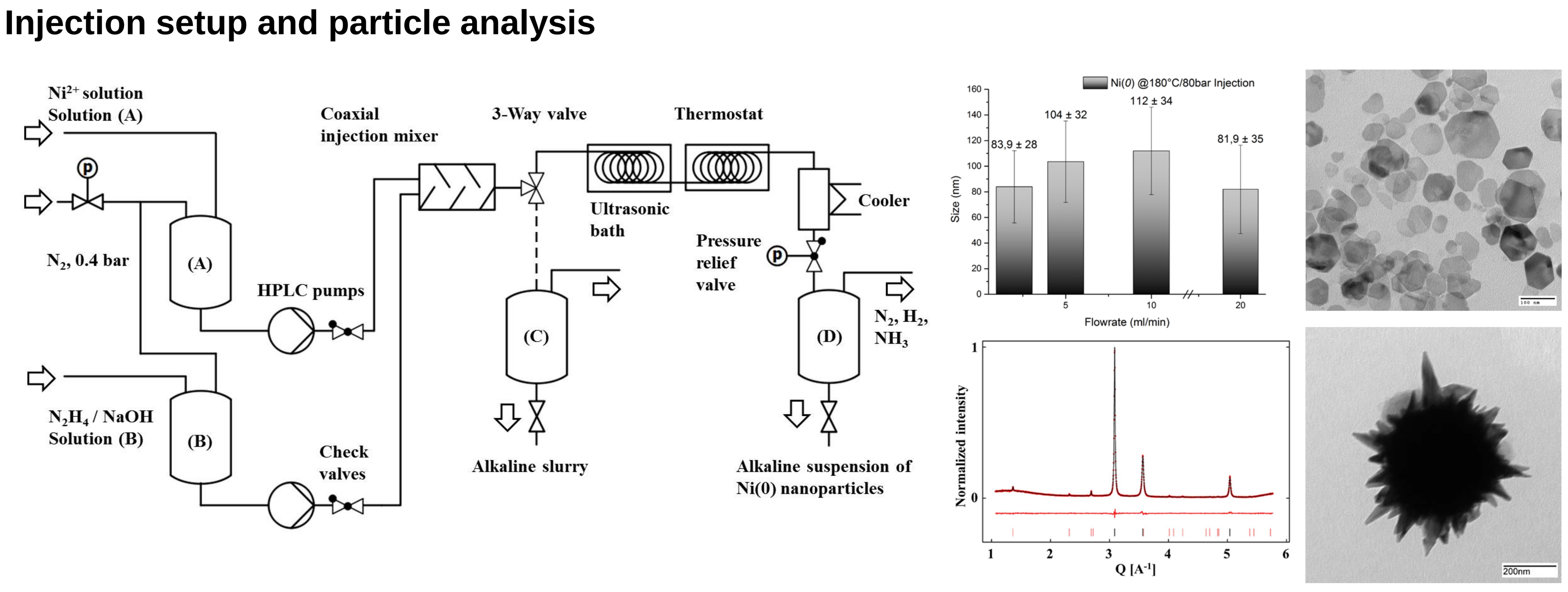
Left: nozzle geometry with indicated mixing zone; middle: spray pattern of the nozzle (with water & 30 l·min⁻¹ air) and mixing area geometry; right: DLS graph and TEM picture of pilot plant sample (~1 kg NPs) showing a mixture of round and flat shaped particles. EDX results below show 100% purity, Fe, Co & Cu EDX-peaks are artifacts from automated analysis

Injection reactor

+ Fully continuous operation possible
+ No fouling observed (although technically possible)
+ Utilization of novel process windows (H_2O @ T=160 °C, p=80-85 bar)
  → Very fast reaction (< 10 minutes)
+ No air filtration necessary
+ Isolation of unstable intermediate possible
+ High "shape purity" of particles
- Operation at high pressure and temperature
- No "insight" in reactor and reaction

- Two operation modes:
  - Fully continuous with heating (vessel (D))
  - Semi batch without heating (vessel (C))
- Fully continuous mode yields ~80 nm sized flat particles without further purification
- Semi batch mode yields hedgehog shaped particles with an avergage size of 270 nm and high surface area
- Heated batchwise at 80-100 °C without stirring
- Washed with ethanol and water

Injection setup and particle analysis



Left: reaction setup for fully continuous (product in (D)) and batchwise operation (slurry in (C)), right top: size distibution against flowrate and TEM image of NPs without purification showing perfectly flat shaped particles, right bottom: XRD results of hedgehog nickel NPs (fundamental parameters approach, anisotropic reflection broadening model) with TEM picture showing a ~270 nm big nickel hedgehog NP with 30*100 nm spikes

Literature

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