

## Design of novel microreactors for the continuous synthesis of metal nanoparticles with tuneable sizes and compositions

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### Highlights

- Novel manufacturing technology for the continuous synthesis of nanoparticles
- Fluid dynamic simulations guide the design of microreactors to promote transitional flows.
- Exquisite control of size, chemical composition and morphology of nanoparticles.

### 1. Introduction

In this paper, we present an innovative approach for the design of microreactors, guided by fluid dynamic simulations, for the continuous synthesis of metal nanoparticles with tuneable sizes and compositions thanks to the spatio-temporal opportunities offered by microsystems.

Metal nanoparticles have stimulated the interest of the scientific community during the last decades due to their unique catalytic, optical, electronic, magnetic, etc. characteristics. These intrinsic chemical and physical properties are strongly dependent on the size and shape of the metal nanoparticles with a huge scientific effort dedicated to the development of reproducible and reliable synthetic routes. A number of liquid phase routes such as reduction methods have been developed [1] with a high size control in the presence of organic capping agents such as PVP, surfactants such as CTAB, etc. However, the presence of these molecules on the nanoparticle's surface not only can have detrimental effects on the final application (e.g. diffusion limitations in catalysis, toxicity in biomedicine,) but they also determine the final nanoparticle size, limiting its tuneability.

Microscale have been presented in the last decade as a production tool for the continuous synthesis of metal nanoparticles due to their unrivaled heat and mass transfer advantages [2]. In this work, we reveal a new capability of these new systems: their characteristic laminar flow regime allows the production of nanoparticles in the absence of steric capping ligands, leading to unprecedented control of not only their size but also chemical composition.

### 2. Methods

Silver nanoparticles are synthesized using silver nitrate as metal precursor and sodium borohydride as reducing agent. Large excess of NaBH<sub>4</sub> with an Ag/NaBH<sub>4</sub> molar ratio of 1:6 is used in all cases to avoid any changes on the reduction kinetics due to the NaBH<sub>4</sub> potential hydrolysis. Both solutions are introduced in bespoke continuous PFA (perfluoroalkoxy) tubular reactors using syringe pumps and T-mixer. The geometry of the reactor (e.g. curvature, length, pitch distance) is precisely controlled using 3D-printed supports.

### 3. Results and discussion

In this work, we demonstrate the synthesis of silver nanoparticles with tunable sizes between 4 – 20 nm. For this, we exploit the opportunities offered by the laminar flow regime characteristic of micro-devices to prevent the agglomeration of the particles in the absence of capping ligands. By careful design of the reactors geometry, and precise curving of the channels, Dean vortices are promoted on the cross section of the channels leading to the rotation of the fluid, reducing the residence times distributions (Figure 1) [3]. By increasing the curvature of the reactor, the velocity profile of is not only shifted outwards the center of the curvature but also the maximum velocity value slightly decreases. This effect is directly translated into small particles (< 4 nm) with narrow size distributions [4].

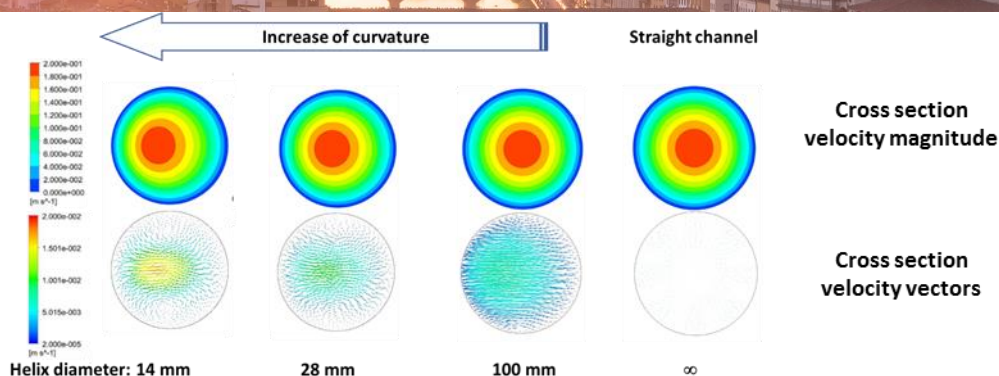


Figure 1. Fluid dynamic simulations of the effect of helix diameter on the formation of secondary transverse flows

In addition, the absence of ligands in the surface of the particles also allows the separation of the seed formation and growth stages. In this way, further addition of silver precursor downstream the reactor, leads to an exquisite growth control, allowing the production of nanoparticles with selective sizes between 5-10 nm, while conserving the narrow size distributions presented by the original seeds as shown in Figure 2.

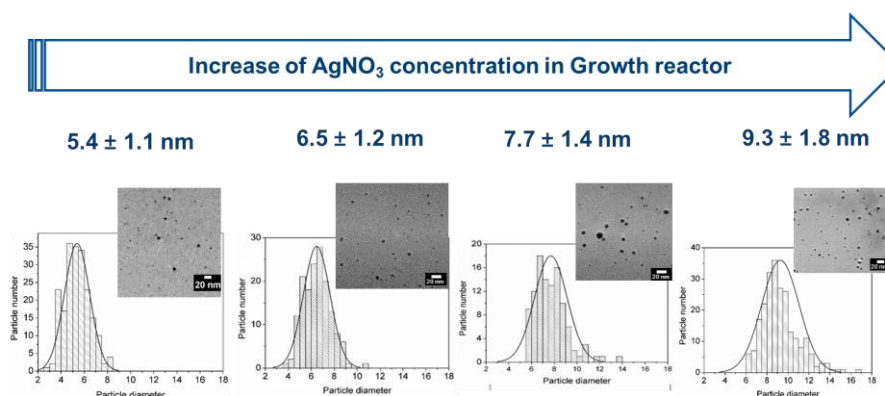


Figure 2: Careful control of silver nanoparticle sizes by varying the silver concentration downstream the reactor.

This spatio-temporal capability offered by microreactors also allows the introduction of a second metal in our ambition to produce controllable bi-metallic systems. If the second metal has a lower reducing potential, (for example, palladium), galvanic displacement of silver is produced leading to hollow bi-metallic particles where the thickness of the shell is a function of the size of the original silver seed.

#### 4. Conclusions

In this work, we present a novel manufacturing technology for the continuous synthesis of metal nanoparticles with tuneable sizes (4 – 20 nm) and compositions (bi-metallic, core-shell, hollow shells). For this, microreactors have been carefully designed guided by fluid dynamic simulations to promote transitional flows to narrow the size distributions while avoiding agglomeration even in the absence of capping ligands.

#### References

- [1] B. L. Cushing, V.L. Kolesnichenko and C.J. O'Connor, *Chemical Reviews*, 2004. 104(9): p. 3893-3946.
- [2] S. Marre and K.F. Jensen, *Chemical Society Reviews*, 2010. 39(3): p. 1183-1202.
- [3] S. Vashisth, V. Kumar and K.D.P. Nigam, *Industrial & Engineering Chemistry Research*, 2008. 47(10): p. 3291-3337.
- [4] K. Wu, G.M.D. Bohan, and L. Torrente-Murciano, *Reaction Chemistry & Engineering*, 2017. 2(2): p. 116-128.

#### Keywords

“microreactors”, “continuous synthesis”, “metal nanoparticles”, “transitional flow”