Synthesis of silver nanoparticles in a continuous flow microreactor

Background

Silver nanoparticles are used in a variety of applications, e.g. as antibacterial and antifungal agents in medical applications. The synthesis of these nano-sized metal particles through 'wet chemistry' serves as the most practical laboratory technique, as silver salts are easily reduced using common reducing agents in solution. While still being made in batch vessels most of the time, continuous flow can offer significant advantages since precise control of reaction parameters is often necessary to obtain high-quality nanoparticles with good size uniformity.

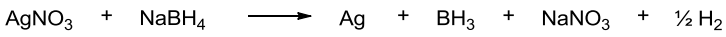

Figure 1: Synthesis of silver nanoparticles scheme

Using continuous flow chemistry, precise control over the size (diameter) of the formed nanoparticles is possible by varying the residence time, temperature or molar ratio of reagents. In continuous flow, a silver nitrate solution and a sodium borohydride solution are introduced into the microreactor, where they react to form the corresponding nanoparticles.

Setup and method

Material

- *Flow*Start B-200
- B-230 Pump Module
- B-242 Inlet Module
- Basic Quench Microreactor (internal volume $V_{\mu R}$ = 92 µL)

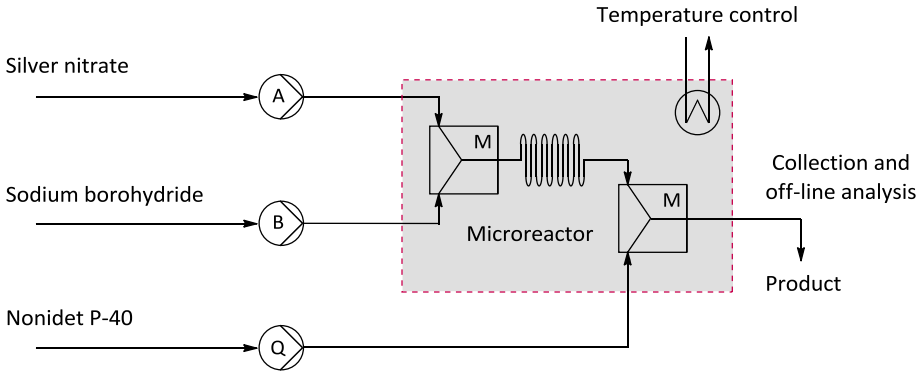

Figure 2: FlowStart setup for the Synthesis of silver nanoparticles

Chemicals

Recommended grade: *pro analysi* (p.a.) or *reagent grade*.

- Sodium borohydride
- Silver nitrate
- Sodium hydroxide
- Nonidet P-40

Stock solutions

- **A.** Silver nitrate (5.7 mg, 310 µmol) dissolved to a total volume of 1.0 L with water (corresponding to 310 µM)
- **B.** Sodium borohydride (38 mg, 1.0 mmol) dissolved to a total volume of 100 mL with 10 mM NaOH (corresponding to 10 mM)
- **Q.** Nonidet P-40 (1% v/v in water)

Stock solutions are to be prepared at the beginning of the experiments, or can be prepared beforehand by the instructor (large volumes are stable for a long time when stored in the fridge).

Analysis

Analysis of the reaction mixture is done using UV-vis. Analyse your samples and calculate the particles' diameter by using the response curve which can be found in the analysis section.

Optimisation experiment

The goal of this experiment is to identify the influence of reaction parameters on particle diameter in the synthesis of silver nanoparticles using flow chemistry. Optimisation in a three-dimensional space can be done using various mathematical techniques, of which are commonly used: univariate analysis, full-factorial design, 3D simplex.

Flow parameters

Using flow chemistry, reaction parameters can be easily varied by adjusting the flow rates and temperature. The latter parameter speaks for itself, while both B/A molar excess ratio and reaction time are controlled by setting different flow rates. The reaction parameters and their useful ranges are listed in Table 2. Parameters should not be chosen outside these ranges, as the pump's flow rate and the substrate's boiling point impose some of these limits. Also, the reaction has been extensively screened to yield a good experimenting region within these limits.

Table 1: Reaction parameter ranges

Parameter	***Minimum value***	***Maximum value***
Reaction time (t_R)	7 s	24 s
Sodium borohydride/silver nitrate molar excess ratio ($ME_{B/A}$)	1	1000
Temperature (T)	20°C	80°C

The stabilisation time for this reaction is around 1 min. Roughly 100 µL of the microreactor outflow is collected and diluted to 1.0 mL (10 x dilution), which can be measured directly on a UV-vis spectrophotometer. The quenching flow is kept at roughly 5% of the sum of flow A and B (that is: $\phi_Q = 0.05 * (\phi_A + \phi_B)$). The used setup can be seen in Figure 2.

Synthesis of silver nanoparticles optimisation setup

Preparation:

- Using one of the above optimisation techniques (or a different one), choose the parameter sets you want to investigate.
- For all the points in the parameter sets, calculate the flow rates and collection time. Then conduct the experiments in the same way as the introductory experiment.

- If you have obtained all measurement data and the results look valid (e.g. duplicates show the same wavelength maximum), present your data graphically.

Analysis:

- Measure the samples using UV-vis, find the absorption maximum for each sample, and report the obtained data in a graphical way. Also, find *parameter trends* for performing the synthesis of silver nanoparticles in flow.

Questions

1. **Preparation of the experiment:**
    a. **Roughly calculate the cost of the experiment from the prices of the chemicals. In other words, calculate the price (e.g. per gram) of the product. For these calculations, assume that chemical yield of the silver nanoparticles with respect to silver nitrate is 100%.**
    b. **Find the safety aspects (including R/S values) of the used chemicals.**

2. **What advantages in performing the synthesis of silver nanoparticles in continuous flow can you think of? Also, can you think of any disadvantages?**