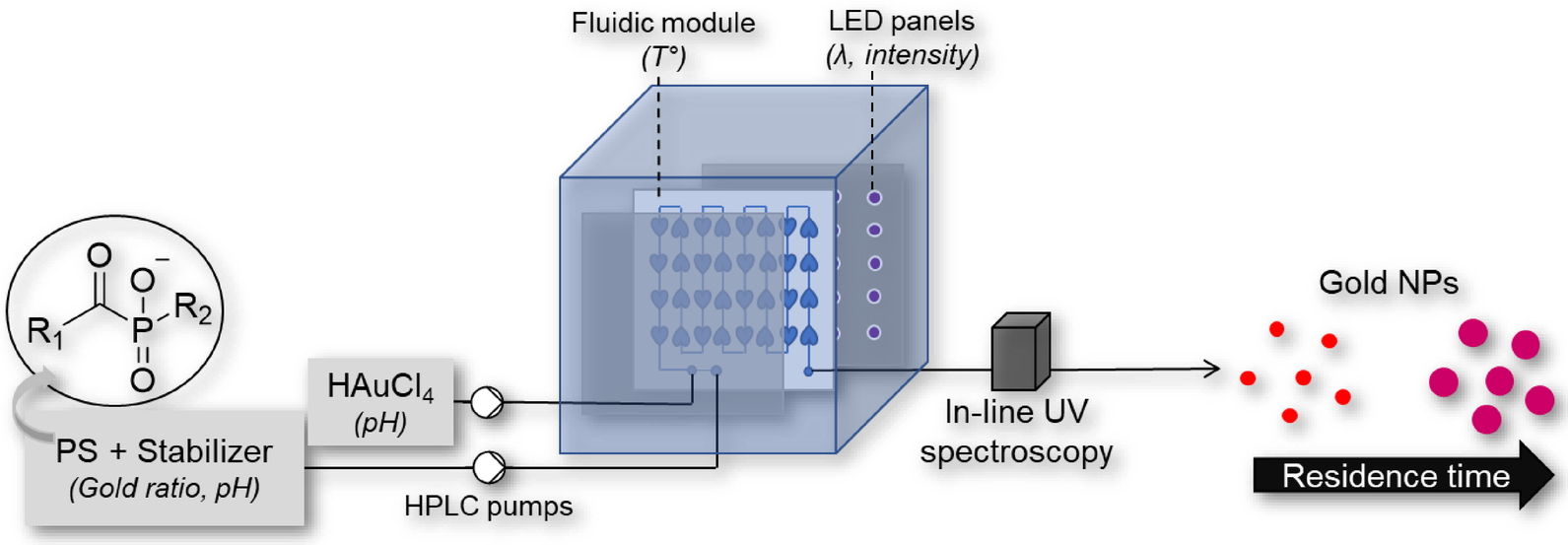
CONTINUOUS FLOW TECHNOLOGY FOR THE PHOTOCHEMICAL SYNTHESIS OF SPHERICAL GOLD NANOPARTICLES

Pauline Bianchi, Guillaume Petit, Jean-Christophe Monbaliu*

Center for Integrated Technology and Organic Synthesis (CiTOS), MolSys Research Unit, University of Liège, B-4000 Liège (Sart Tilman), Belgium
e-mail: pauline.bianchi@student.uliege.be



Gold nanoparticles (Au NPs) are used in a wide range of applications because of their localized surface plasmon resonance (LSPR), leading to shape- and size-dependent optical properties. The **photochemical generation of gold NPs** has emerged as a potential alternative to the well-known Turkevitch method since it offers a **spatial and temporal control**.

We present herein a **continuous flow process** for the controlled photochemical synthesis of spherical gold NPs. The implementation of a continuous flow setup **overcomes issues related to batch synthesis**, namely poor mixing efficiency, poor light penetration and inefficient control of the local parameters. After optimization, the NPs size is only **dictated by the irradiation time**.

STEP 1 : Identification of the best photosensitizer (PS)

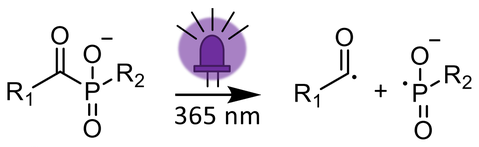
Tests with different PS:

Type I PS:
Unimolecular reaction
May be water soluble
Better stabilization

Type II PS:
Bimolecular reaction
Need of a co-initiator
Water solubility issues
Bad stabilization

Identification of a new, water-soluble acylphosphinate PS : generation of free radicals acting as internal reductants of chloroauric acid ($HAuCl_4$) into Au(0)

Photocleavage



Gold reduction

STEP 2 : Avoiding gold coating

The formation of a gold coating on the internal surface of the reactor decreases the light intensity and leads to a less efficient photoredox process

Solutions:

~~Coating the glass with Sigmacote® before the synthesis~~

~~Working under biphasic conditions~~

Adding some **electrostatic repulsions** by working at slightly basic pH and with a deprotonated stabilizer

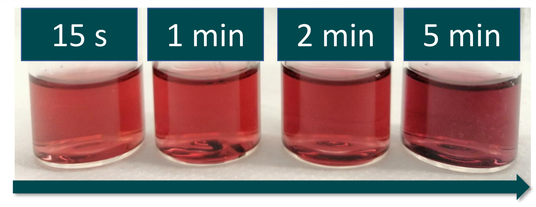
➡ The selection of the most appropriate stabilizer is critical

STEP 3 : Optimization

Tuning experimental parameters : Monitoring with in-line UV spectrometry

Increase of	Light intensity	T°	pH	C_{stab}
Maximum intensity	↗	↗	↘	↗
Maximum wavelength	↘	↗	↗	↘

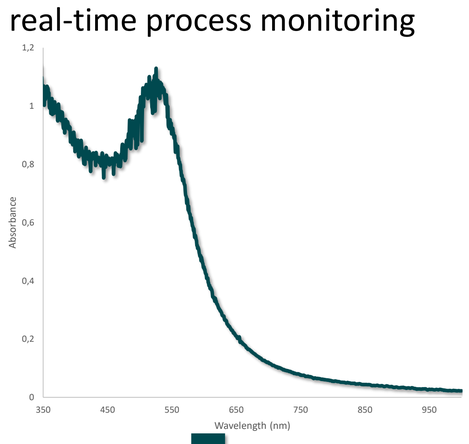
Residence time : bigger NPs obtained when the irradiation time increases



Stability : The addition of an external stabilizer and the optimization of some parameters enable the production of **stable** NPs up to several weeks

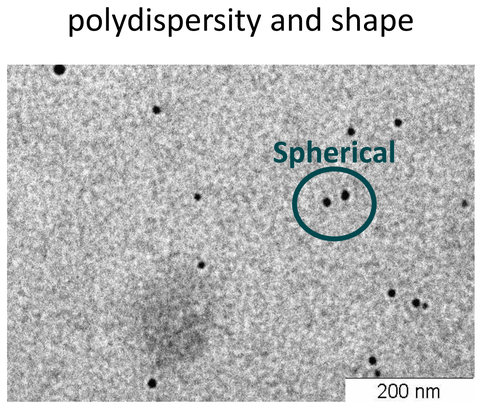
NPs characterization : size and shape

In-line UV spectroscopy :
real-time process monitoring



Particle or crystallite size

TEM : information about polydispersity and shape



Crystallite size radius

CONCLUSION AND PERSPECTIVES

- ✓ Fast photogeneration of **spherical gold NPs : control of the size** only by tuning the irradiation time
- ✓ Use of the **flow technology** to overcome issues related to batch synthesis
- ✓ Identification of the parameters **avoiding gold coating**
- ✓ Identification of the best conditions to obtain **stable** NPs
- ✓ **Real-time monitoring** with in-line UV spectroscopy

Perspectives : scale-up

3. G3 : Industrial production (400 to 2000 mL/min)

2. G1 : Scalability test (10 to 200 mL/min)

1. Lab photo reactor : Optimization (2 to 10 mL/min)