

STUDY OF SILVER NANOPARTICLES PREPARED VIA PHYTOSYNTHESIS ON MICROFLUIDIC PLATFORM AS FILLERS FOR GRAPHENE NANOCOMPOSITES

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*Tilia cordata* and many other plants as well as siliceous algae were used for a period in our laboratory for gold and silver nanoparticles **biosynthesis** [1]. These nanoparticles are then mostly used in disinfection in the case of silver [2] or as catalyst for gold [3]. For **nanosilver** particles there is further emerging application as agents to **enhance conductivity and antimicrobial property of graphene**.

Because of some issues of batch synthesis, typically kinetics of reaction, heterogeneity of nanoparticles, etc., we are focusing now on **biosynthesis of nanoparticles on microfluidic 3D printed chips** with phytochemicals contained in plants and serving as reducing agents and stabilizers in once. Low reproducibility of bionanotechnology is well known and microfluidics may tackle this challenge in future especially in nanoparticulate systems design and control.

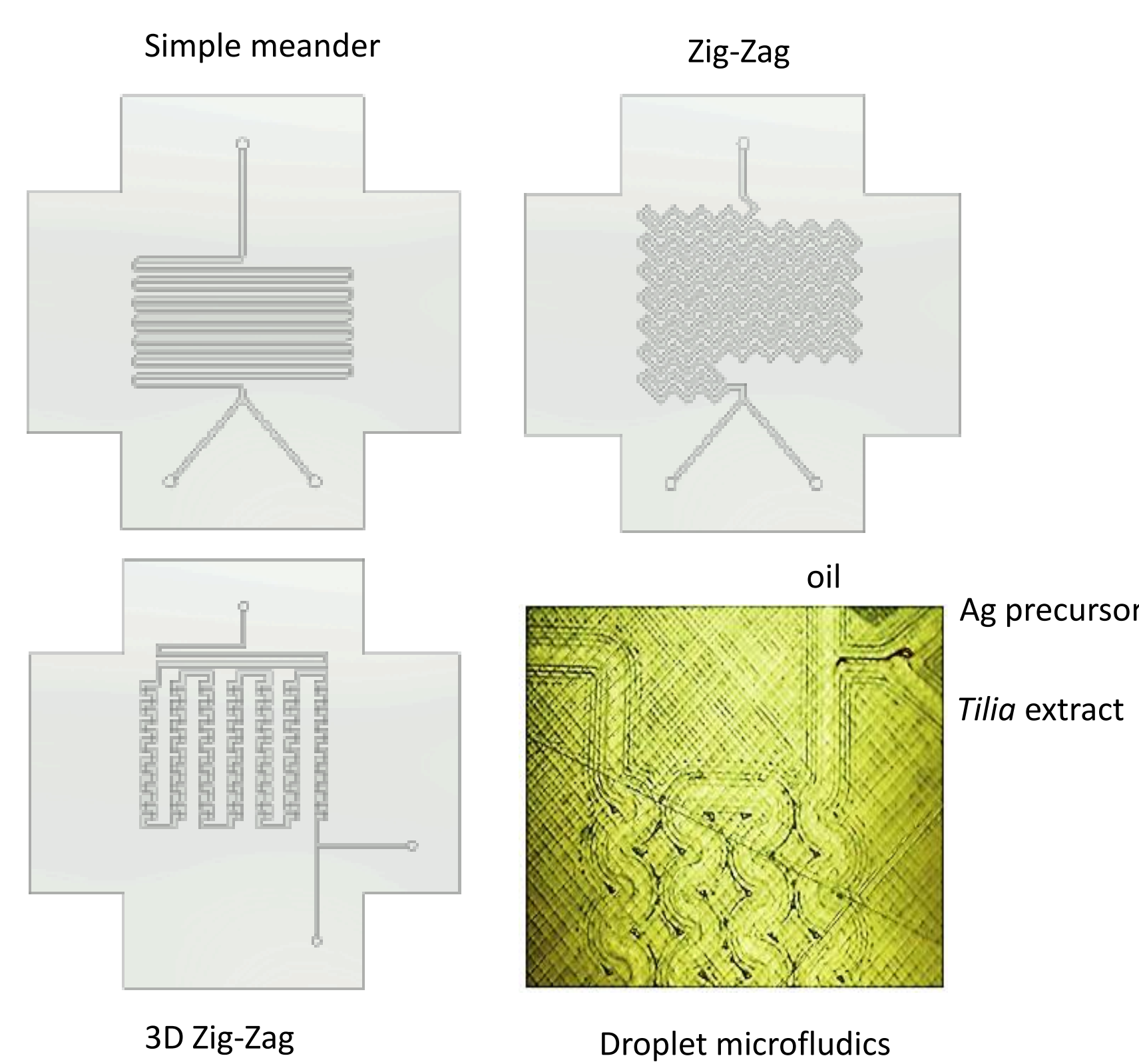
Preliminary tests and electron microscopy survey revealed that different flow rates on the same chip have no great effect on silver nanoparticles morphology and size. However, when chip with **more complicated channels geometry** (Zig-Zag or 3D Zig-Zag) and **micro-mixing system** is used, phytosynthesized nanoparticles seem to be **smaller and better stabilized by phytochemicals**.

Due to silver reactivity in the final colloid and agglomeration tendency, further experiments of **oil microfluidic phytosynthesis** were performed and showed that enclosure of reaction mixture in a drop leads to the formation of even smaller particles than in previous cases.

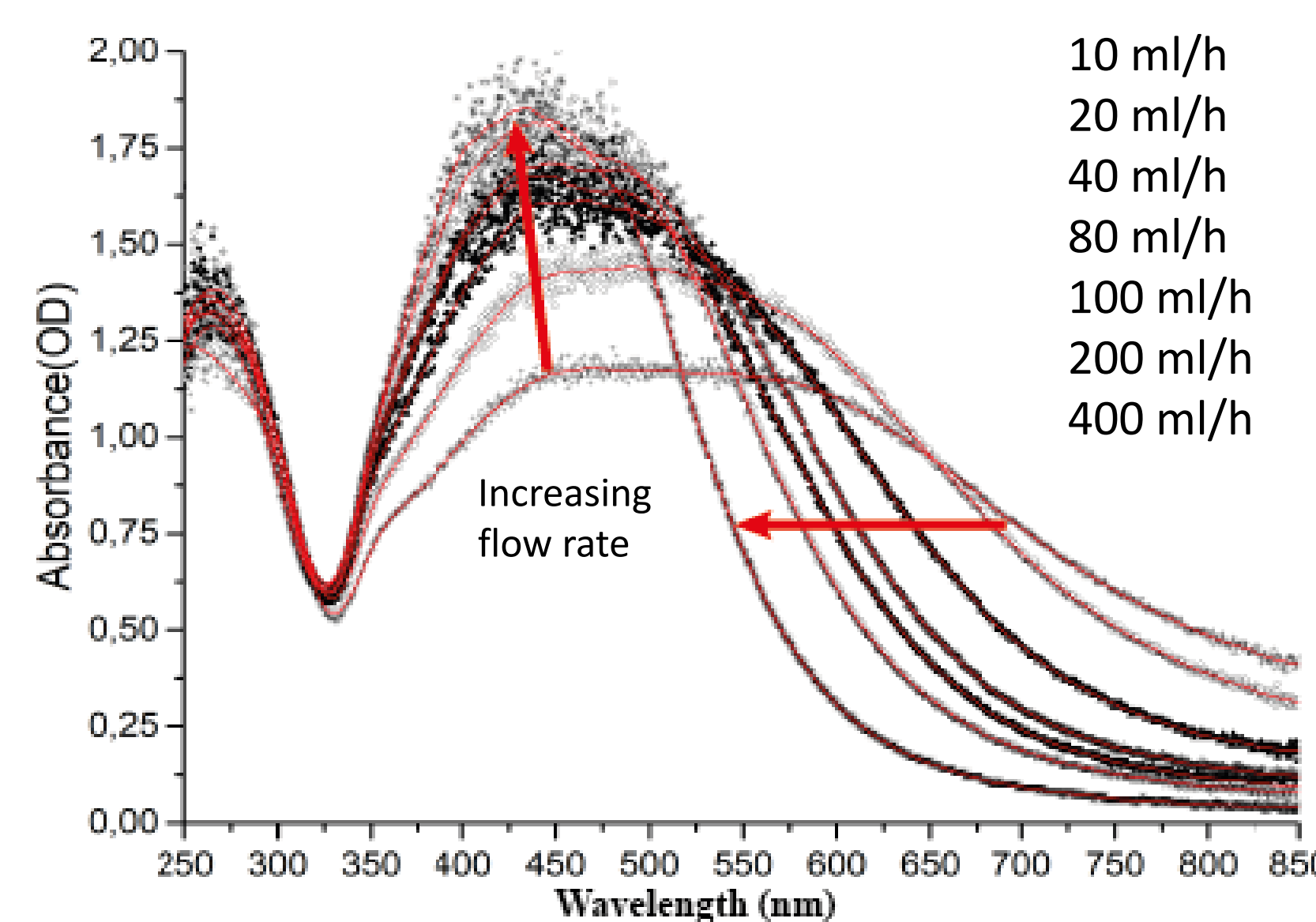
In general, applying **microfluidics** completely **different results regarding shape, size and stability of nanoparticles may be achieved compared to the batch synthesis**. Further, more in depth studies with some preferred experimental conditions set on the base of these experiments will be conducted with the main goal to prepare stable and homogenous silver nanoparticles and functional graphene-nanosilver composites.



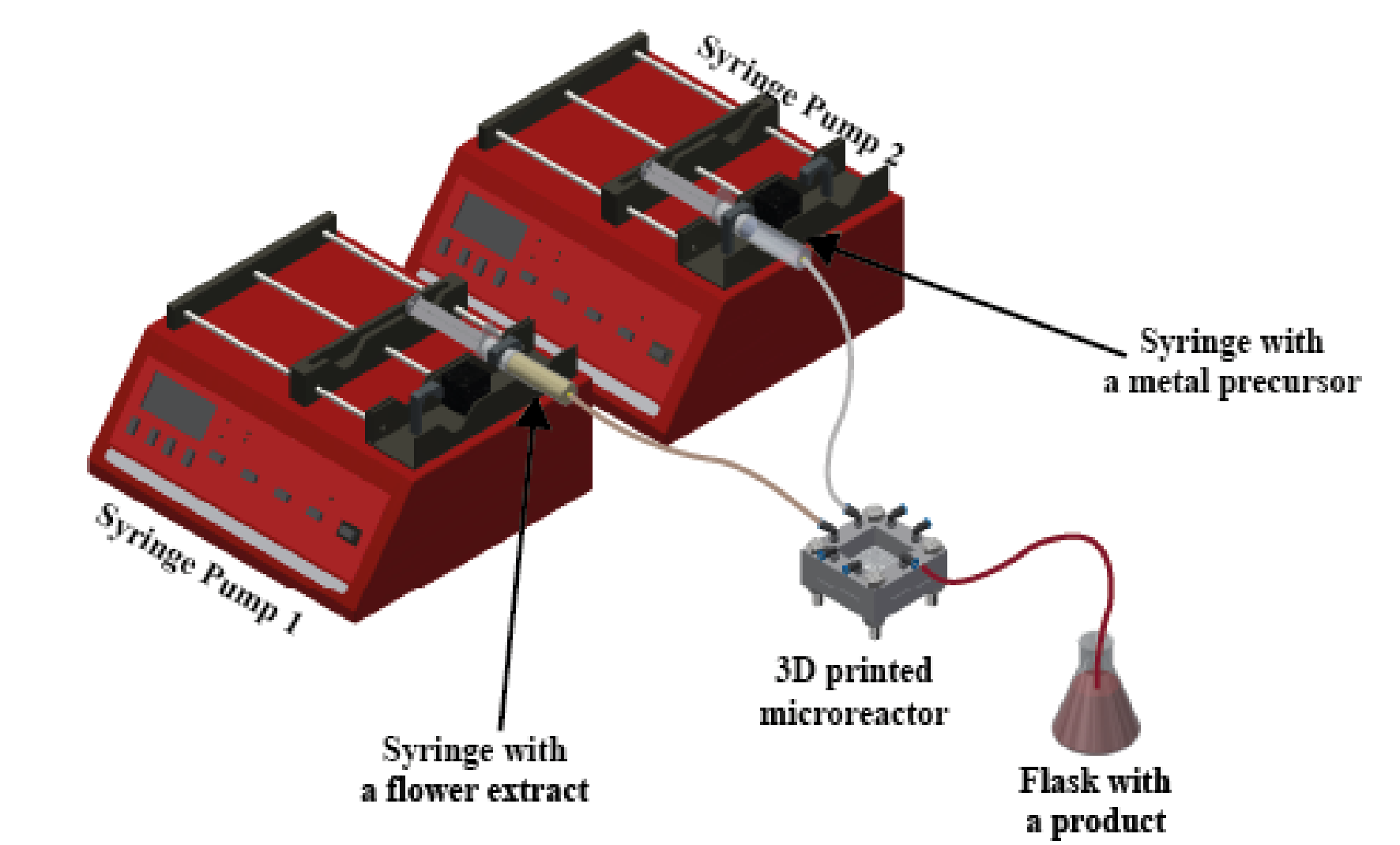
Left – Ag NP reduced and stabilized by *Anabaena mendotae*, Middle - *Mallomonas kalinae* with AuNP (colored in Photoshop), Right - Au NP reduced on the *Diademsis gallica* siliceous frustule, modified with ferrofluid (scale 100 nm)



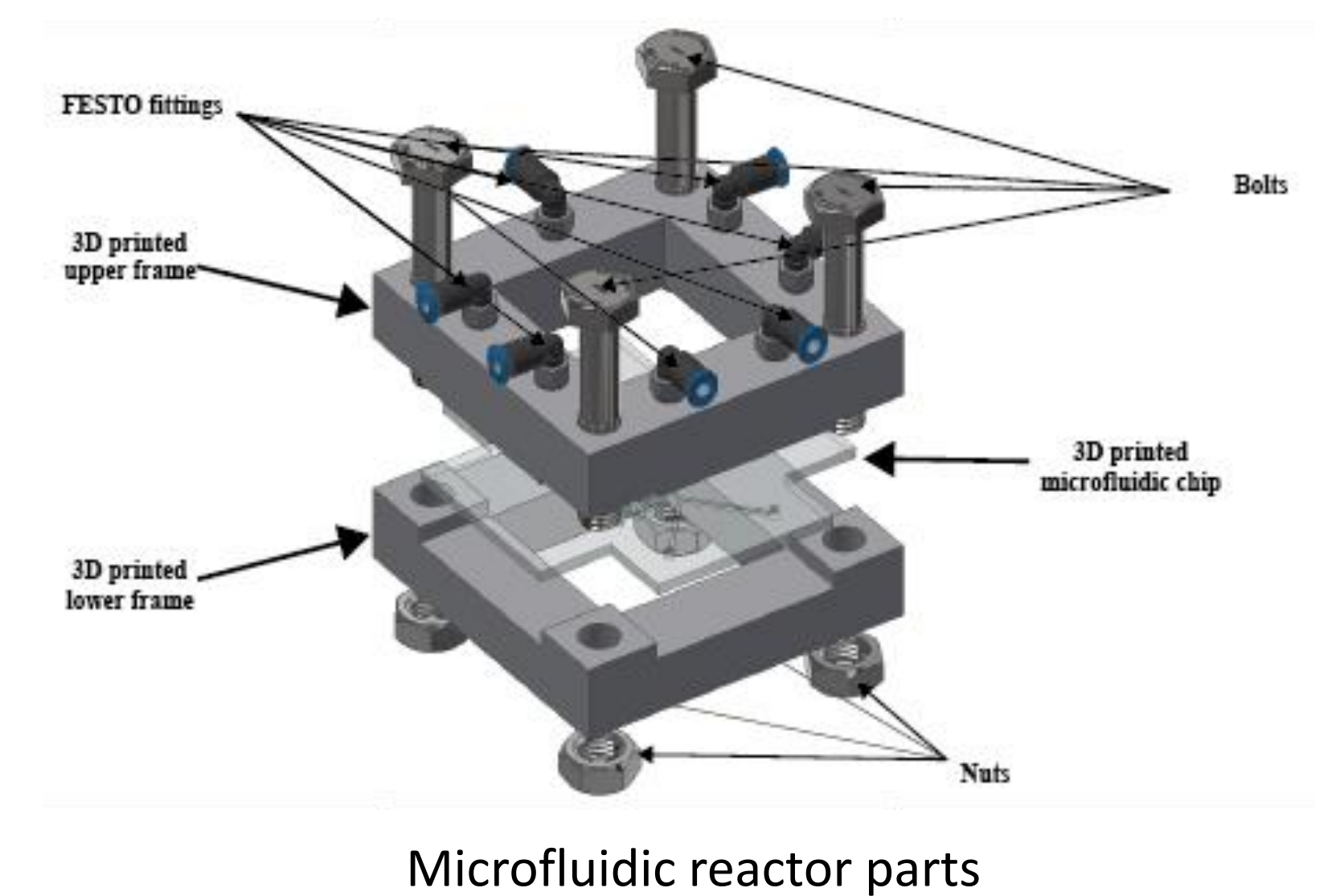
Types of 3D printed microfluidic chips for phytosynthesis of nanosilver



Relationship between flow-rates and in-situ UV-Vis data pointing the aggregation/stability and size distribution of colloidal system



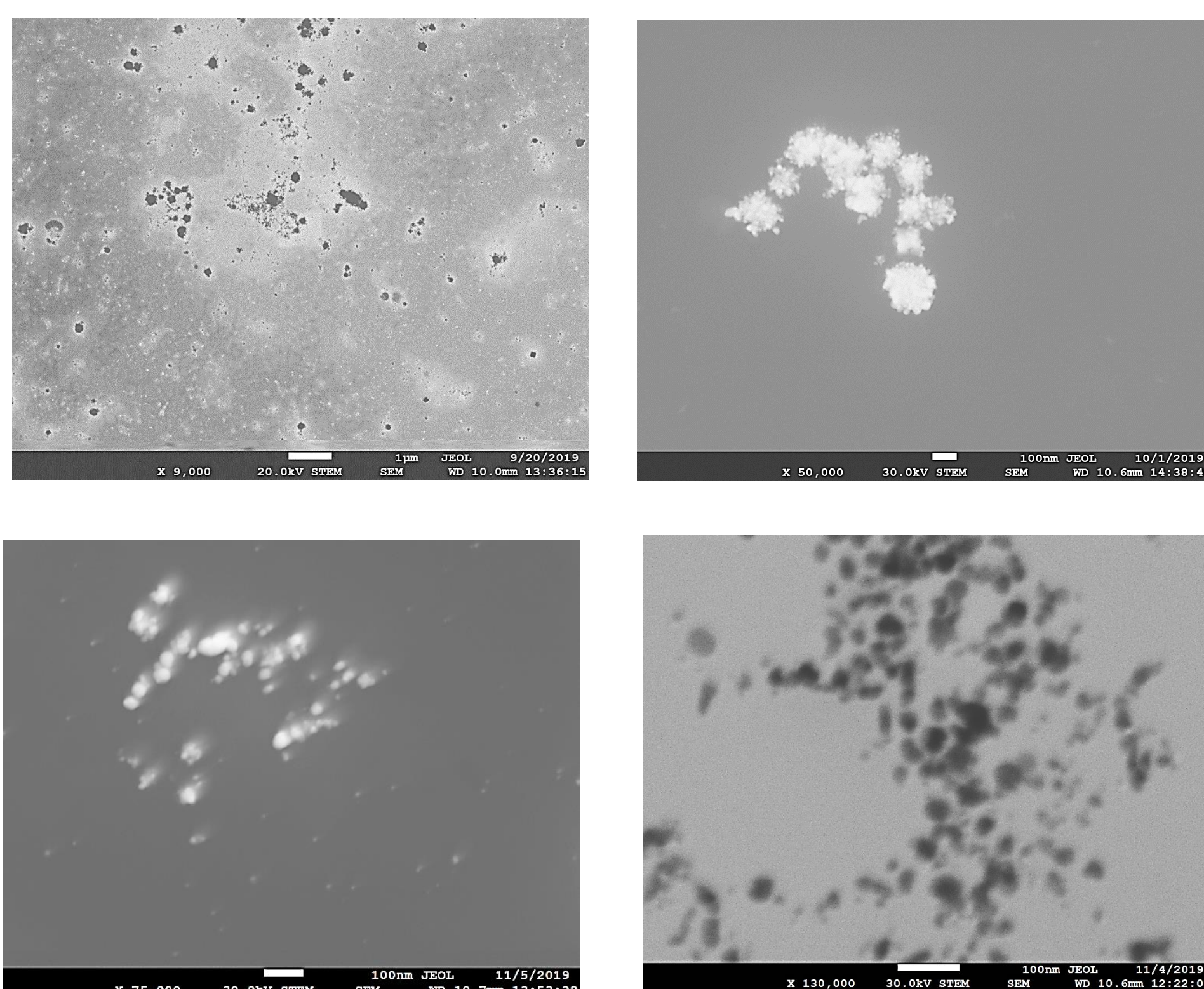
Laboratory set for continuous flow biosynthesis of nanoparticles



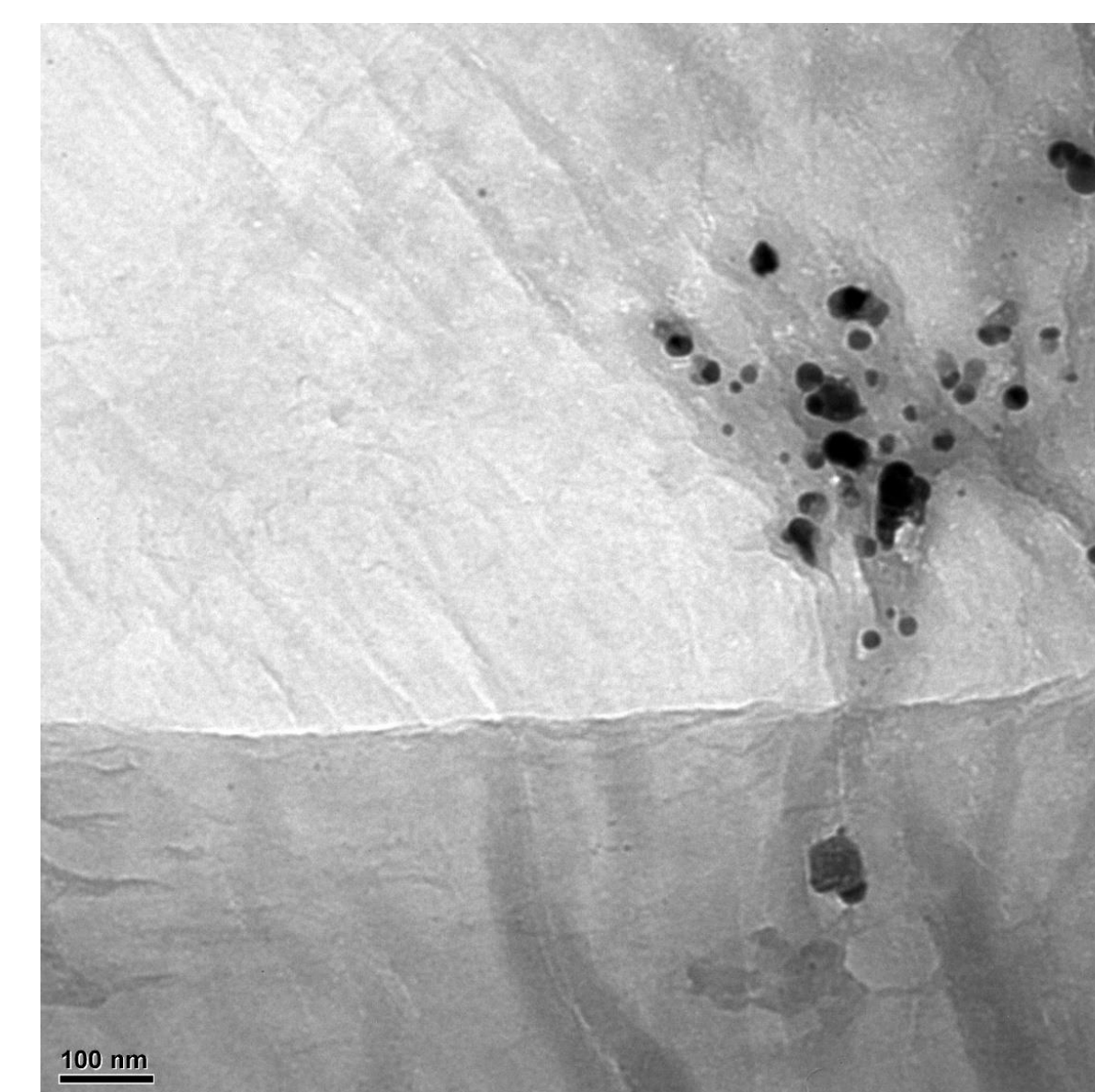
Microfluidic reactor parts

Silver nanoparticles parameters: batch vs. microfluidic phytosynthesis. Ag NPs prepared on chip have better stability, uniform shape and have lower size variance.

Sample	Ag(batch)	Ag(15)	Ag(30)	Ag(60)
$\lambda$ (nm)	443	448	448	445
$d_{max}$ (nm)	55	34	33	27
$d_{min}$ (nm)	7	12	15	12
$d_n$ (nm)	19	19	24	19
Size range (nm)	7 - 55	11 - 34	15 - 33	12 - 27
Shape of NPs	Spherical, rods	Spherical	Spherical	Spherical
Zeta potential (mV)	-23.5	-44.5	-38.9	-38.5



Ag NPs produced in simple meander aggregated into spherical or pseudo-cubic clusters and minimal effect of flow rate on particles character was observed. The best results in particles/aggregates formation were obtained on 3D ZigZag chip (left, middle). Single, no aggregated nanoparticles were then achieved applying droplet microfluidics (right) with the flow rates 5 ml/h oil, 5 ml/h 5 mM silver nitrate and 10 ml/h plant extract and further other ratios of flow rates were tested (5:5:20, 10:10:20) with similar results.



Silver nanoparticles prepared on-chip decorate irregularly the graphene oxide surface. Combining GO suspension with Ag NPs colloid the re-growing of small particles could be observed that is visible as cookies shapes. There is presumed Ostwald ripening as a phenomenon observed in solid solutions or liquid sols that describes the change of an inhomogeneous structure over time, i.e., small crystals or sol particles dissolve, and redeposit onto larger crystals or sol particles.

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REFERENCES

- [1] Kratošová G, Holišová V, Konvičková Z, Ingle AP, Gaikwad S, Škrlová K, Prokop A, Rai M, Plachá D, Biotechnology Advances, 1(2018) 154-176
- [2] Vilamová Z, Konvičková Z, Mikeš P, Holišová V, Mančík P, Dobročka E, Kratošová G, Seidlerová J, Scientific Reports, 1(2019) 1-10
- [3] Holišová V, Natšinová M, Kratošová G, Chromčáková Ž, Schröfel A, Vávra I, Životský O, Šafařík I, Obalová L, Arabian Journal of Chemistry, 7 (2019) 1148-1158

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