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Engineering the Structure and Optical Properties of Gold Nanostars with Microfluidics

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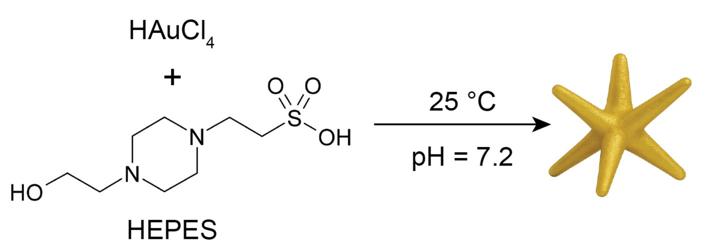
Introduction

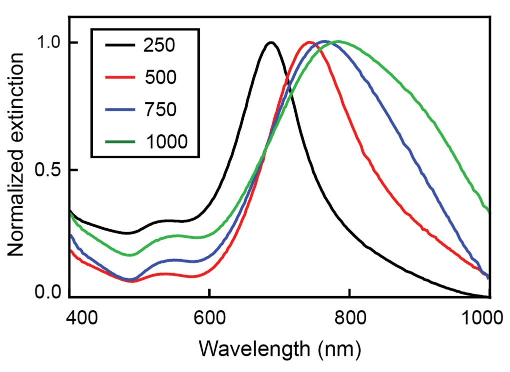
Gold nanostars (AuNS) are anisotropic gold nanoparticles with structure-tunable optical properties.[1] Most synthetic protocols rely on multi-step procedures and on the use of cytotoxic and/or strongly bound chemicals, which can hamper AuNS applications.[2] While the synthesis of AuNS with HEPES overcomes these limitations by using a biocompatible buffer that acts both as a shape-directing and reducing agent, the resulting nanoparticles are highly heterogeneous and polydisperse.[3] Here, we use a microfluidic chip to manipulate the morphology and optical properties of AuNS, while significantly improving their monodispersity. Notably, by adjusting microfluidic parameters, including viscosity of the organic phase, flow rate ratio (FRR), and buffer-to-gold ratio (R value), this protocol can manipulate the growth mechanism of the nanoparticles, switching between seedless and seed-mediated-like growth, and it does so without the need to add a pre-synthesized seed. Such control is not possible with one-pot bench synthesis.

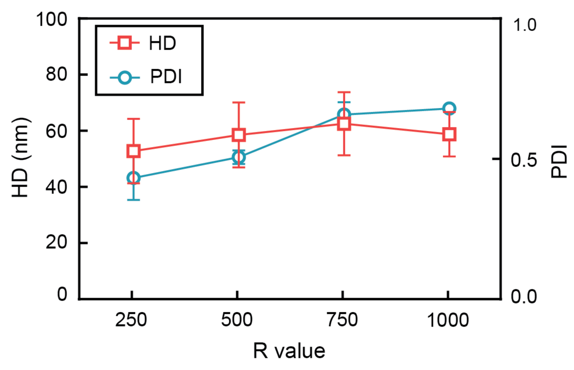
Results

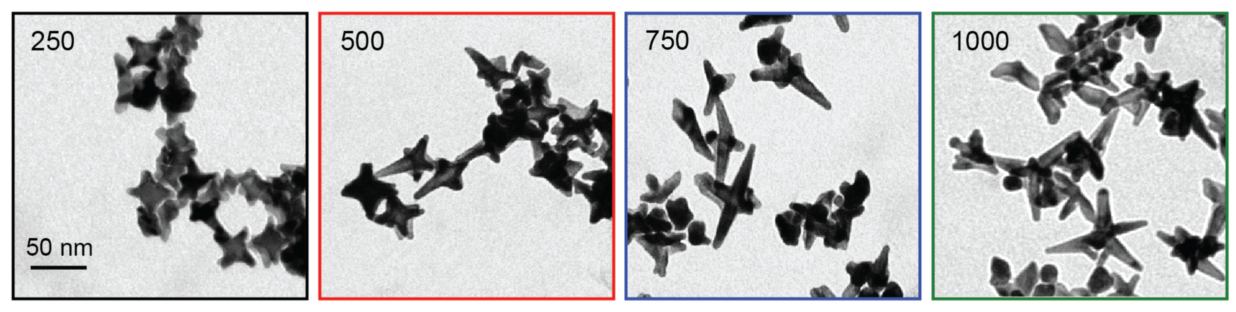
Bench Synthesis



R values: 250, 500, 750, 1000
Vortex for 30 seconds

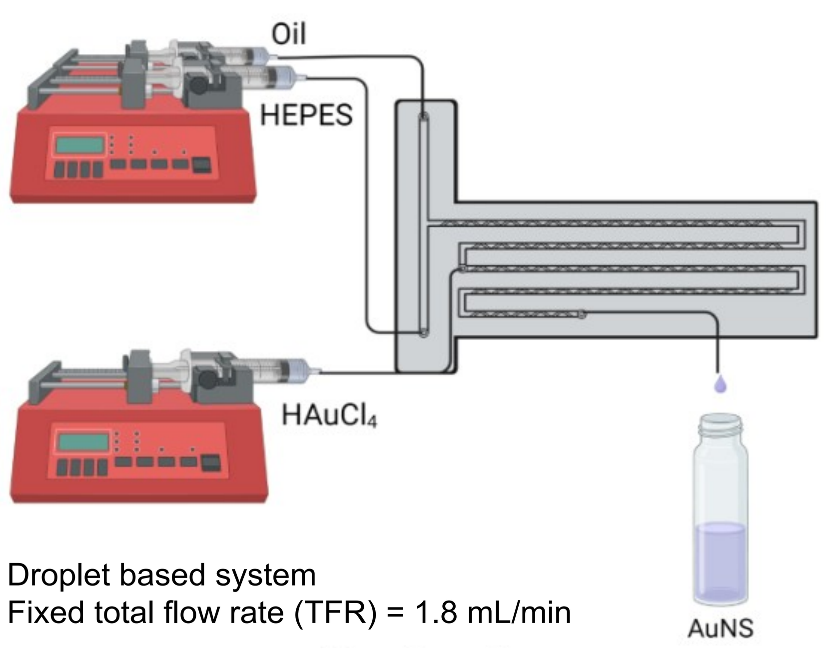






Optically tuneable AuNS with **seedless morphology**, red shifting LSP peak, increasing size and branch length with increasing R value.

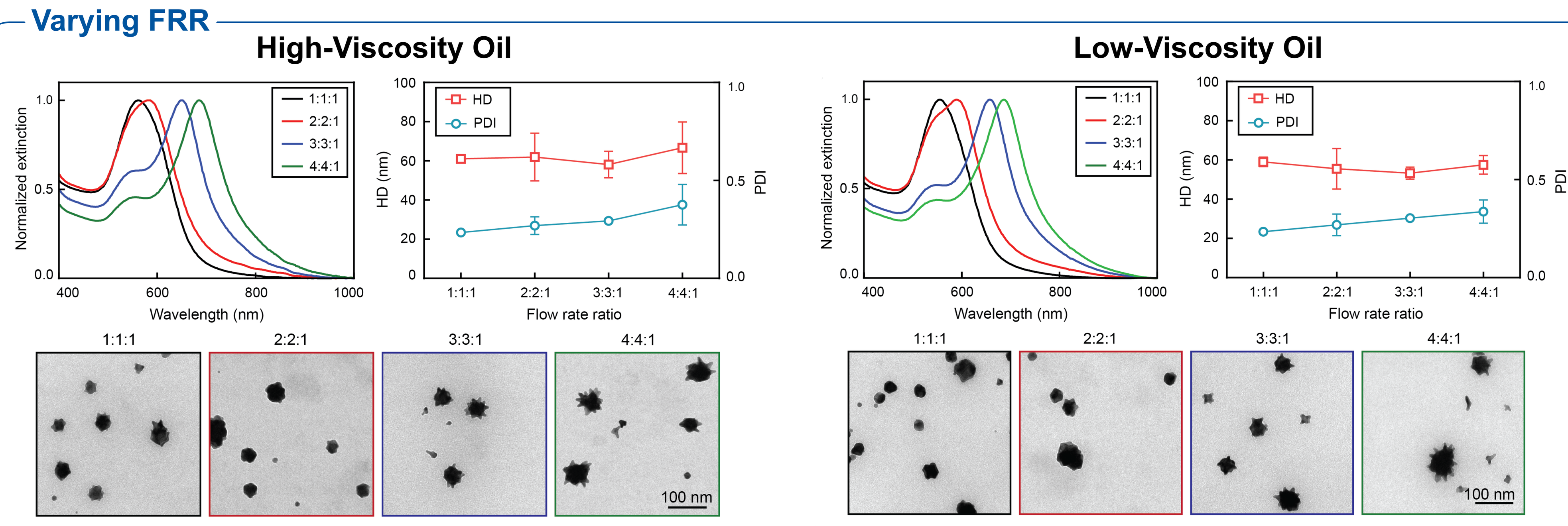
Microfluidic Synthesis



Parameters varied
- Viscosity of oil: 500 cSt (high) and 100 cSt (low)
- FRR: HEPES:Oil:$HAuCl_4$ 1:1:1, 2:2:1, 3:3:1, 4:4:1
- R values: 200, 400, 600, 800

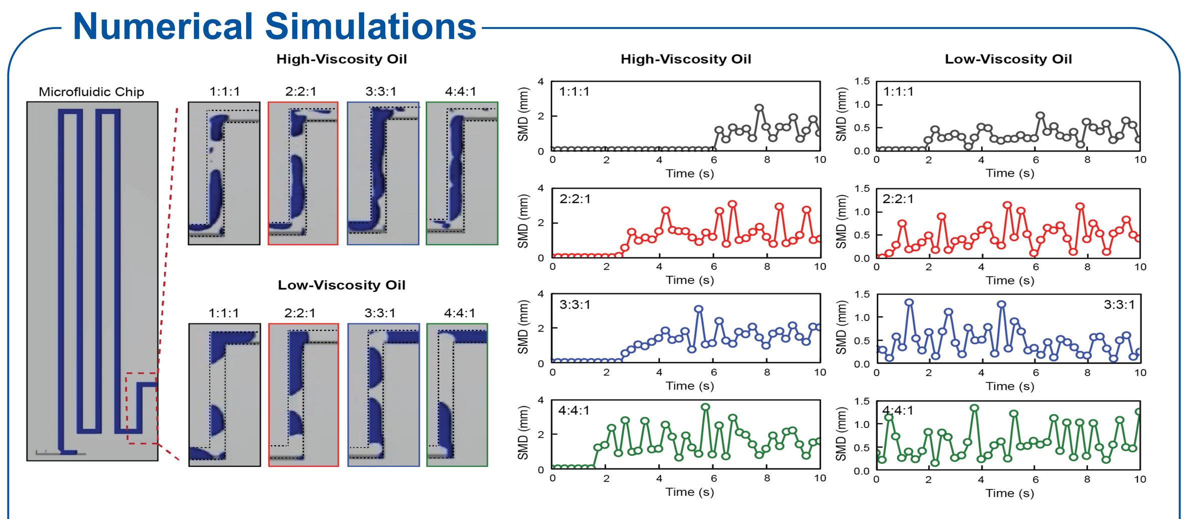
Droplet based system
Fixed total flow rate (TFR) = 1.8 mL/min

Varying FRR



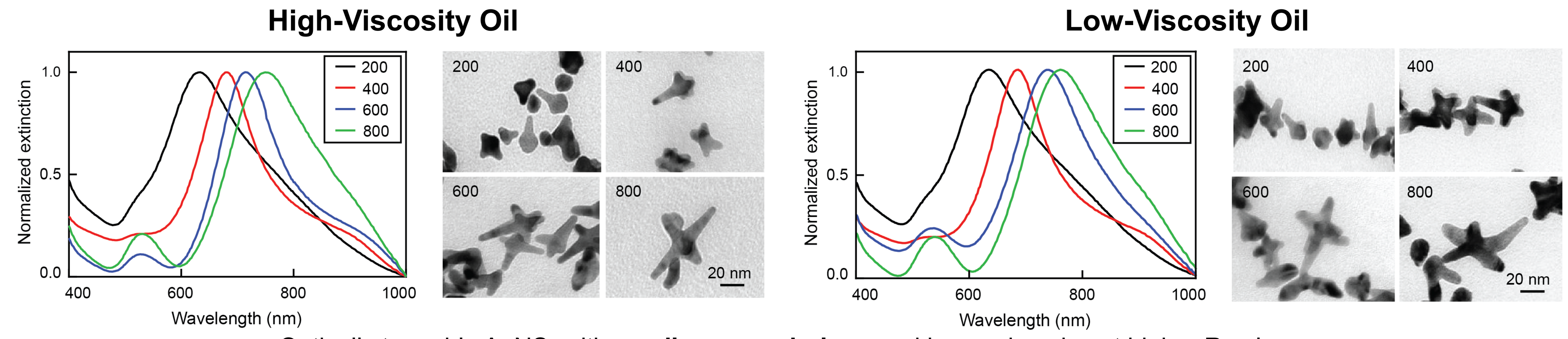
Optically tuneable AuNS, with **seedless and seed-mediated-like morphology** even in the absence of pre-synthesized seeds. Higher fraction of seed-mediated-like AuNS was obtained with lower viscosity oil at low and moderate FRR.

Numerical Simulations



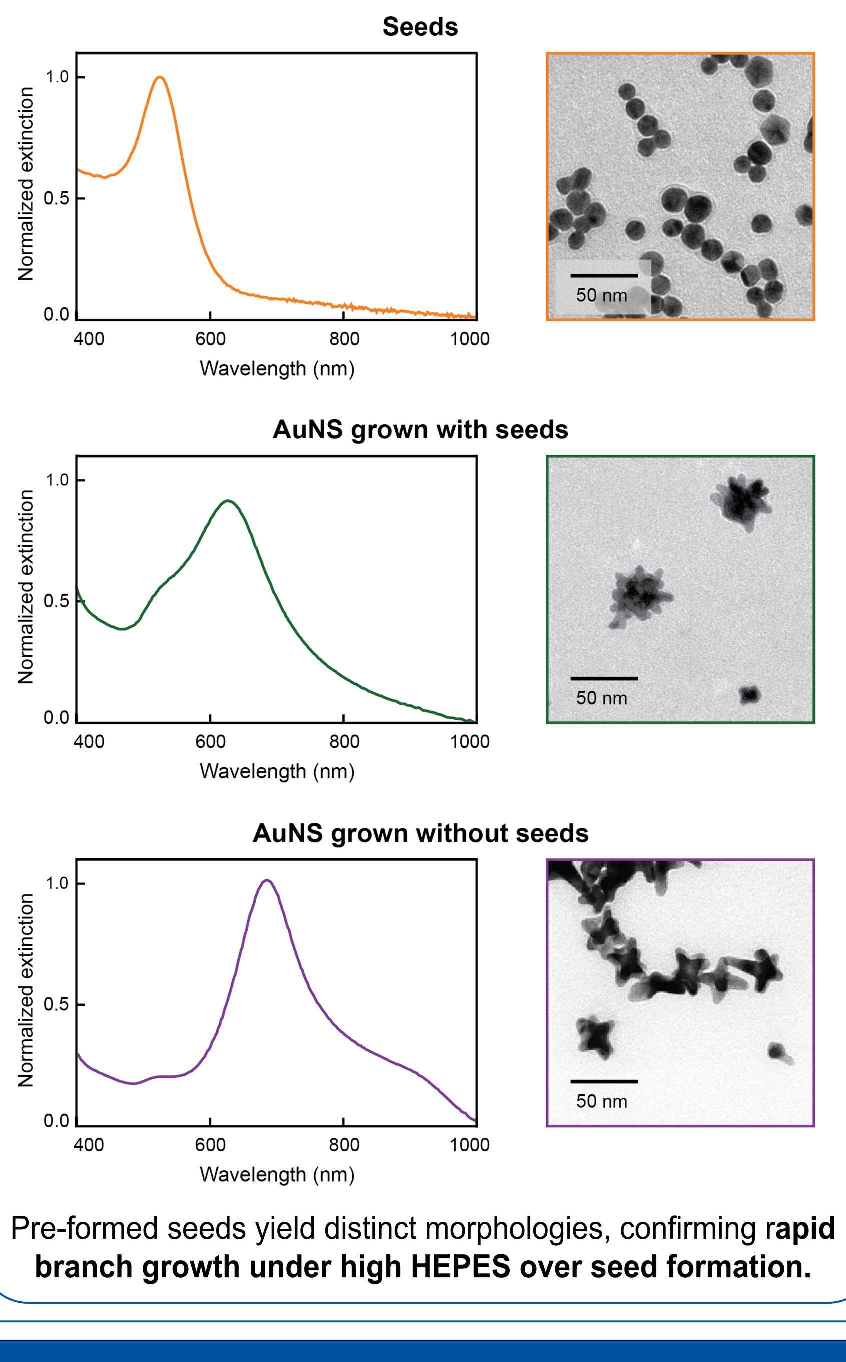
More efficient mixing at lower FRRs and oil viscosity due to smaller droplet size.

Varying R value



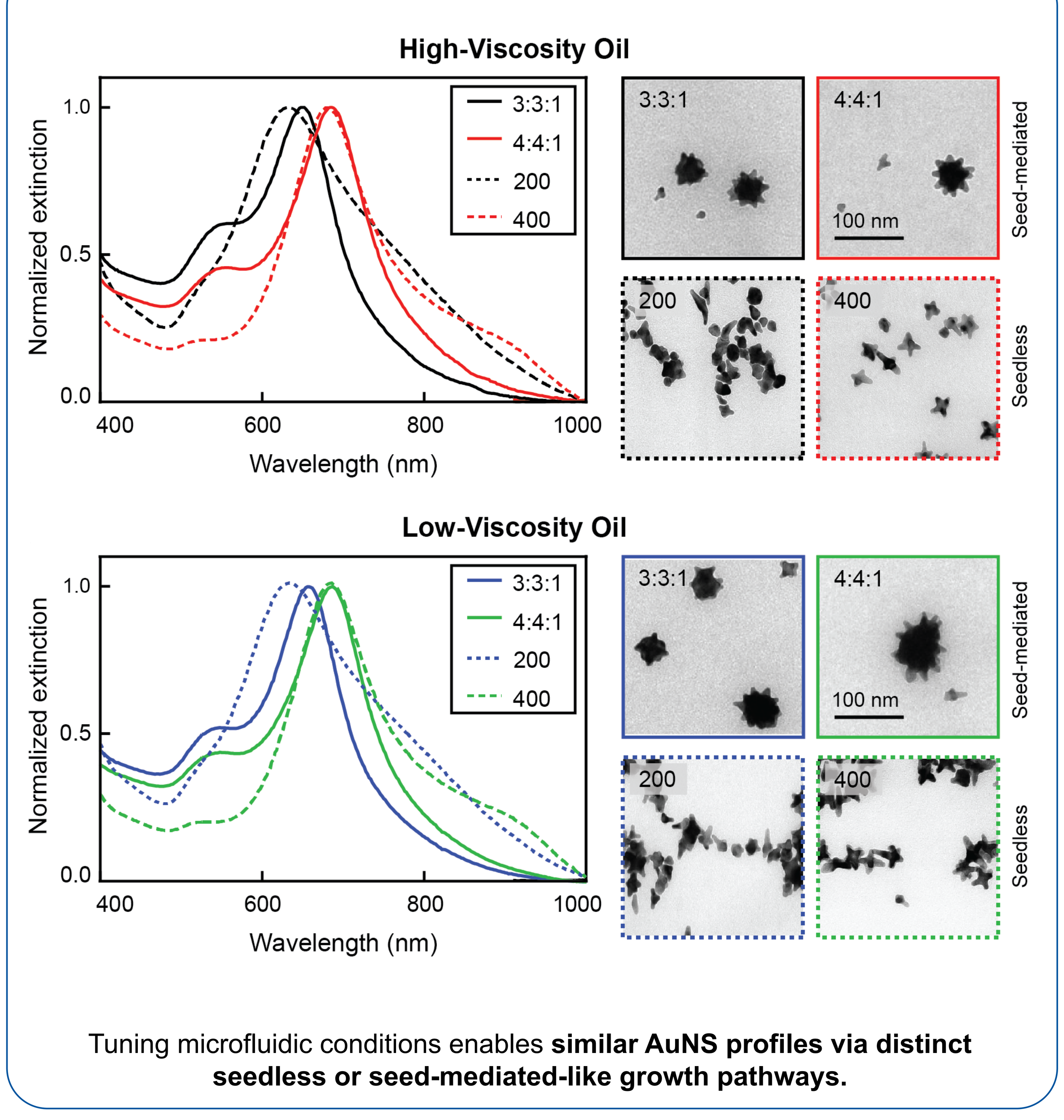
Optically tuneable AuNS, with **seedless morphology** and increasing size at higher R values. Larger tunability with lower viscosity oil showing more elongated branches.

AuNS with and without pre-synthesized seeds



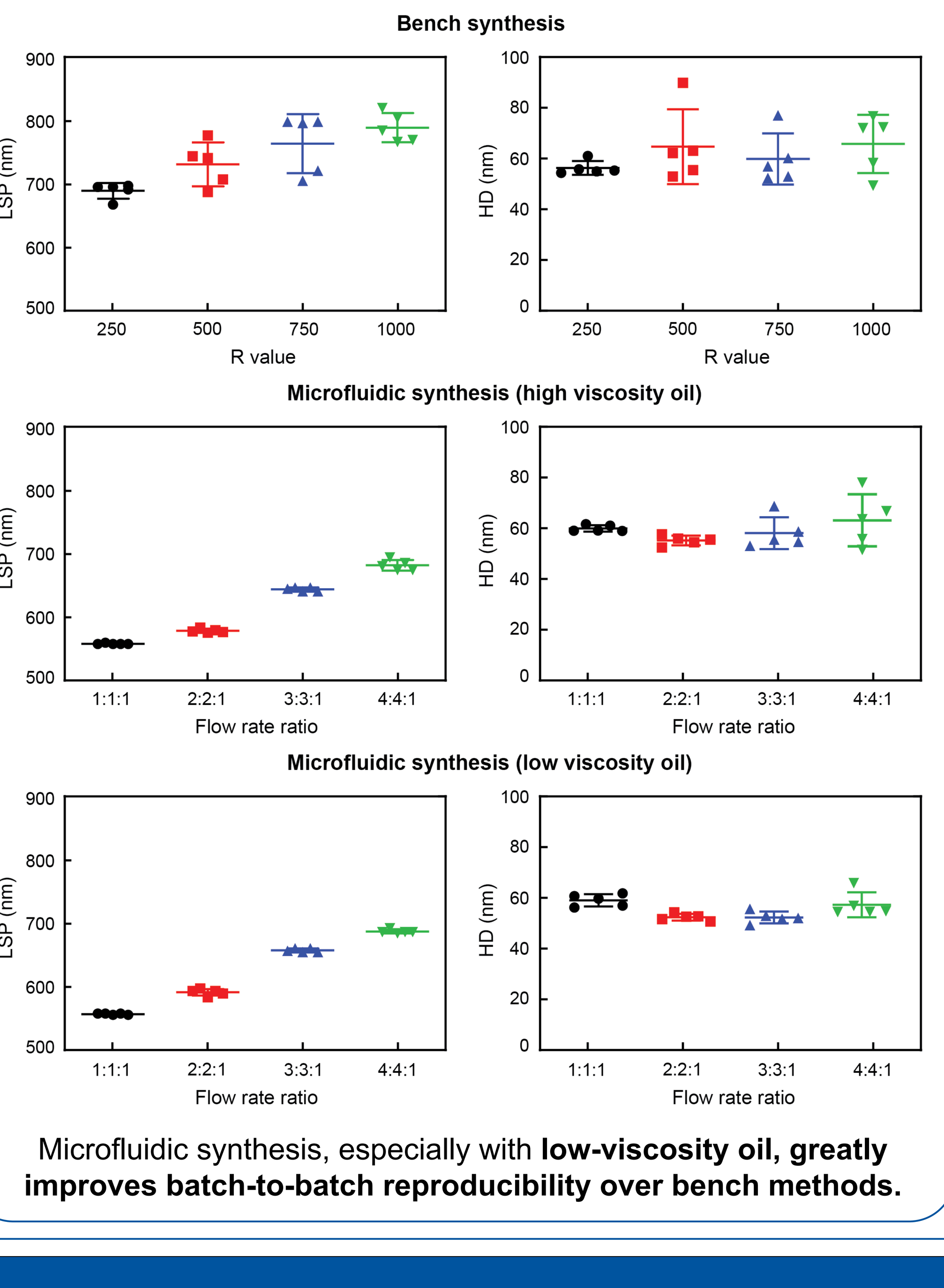
Pre-formed seeds yield distinct morphologies, confirming **rapid branch growth under high HEPES over seed formation.**

Tuning of AuNS properties with microfluidics



Tuning microfluidic conditions enables **similar AuNS profiles via distinct seedless or seed-mediated-like growth pathways.**

Batch-to-batch variability



Microfluidic synthesis, especially with **low-viscosity oil, greatly improves batch-to-batch reproducibility over bench methods.**

Conclusions

We developed a microfluidic method to precisely control AuNS morphology and optical properties using HEPES buffer. This approach improved monodispersity compared to bench synthesis. By tuning flow and viscosity parameters, growth mechanisms could be selectively modulated. The protocol enables seedless and seed-mediated-like synthesis, offering potential for sensing and biomedical applications.

References

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Acknowledgements

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