

Grow with the flow: Bottom-up synthesis of anisotropic plasmonic nanoparticles within microfluidic channels

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Abstract: Bottom-up colloidal synthesis is the “gold standard” approach for preparing plasmonic gold nanomaterials with select compositions, sizes, and shapes, with high uniformity.¹ Here, we take a chemical approach towards translating traditional colloidal synthesis to *in situ* growth – the direct formation of morphology-controlled nanostructures directly on a substrate surface.

While *in situ* growth has been explored in the past, the quality of the fabricated nanostructures tends to have lower quality – low shape yield, high polydispersity, and limited control over the plasmonic response – compared to colloiddally prepared nanostructures.² Additionally, many *in situ* growth schemes still rely on the implementation of colloidal seeds.³ In this work, we aim to address this gap in synthetic know-how, with the specific goal of developing methods for fabricating gold nanostars and nanorods *in situ* on the internal walls of microfluidic channels without the use of colloidal synthesis or self-assembly. Taking a systematic approach, we were able to identify that increasing the competition between colloidal nanoparticle formation in the flowing growth solution and nucleation on the surface is necessary to facilitate successful formation of the desired nanoparticles on the substrate surface (**Figure 1A**).

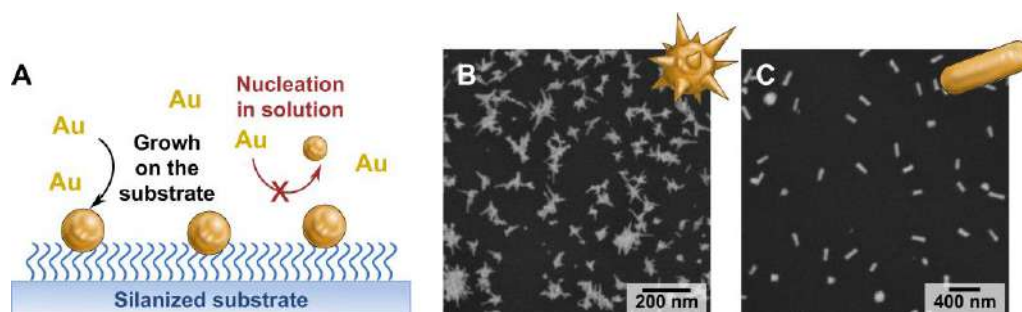


Figure 1. A: Schematic of the competition between colloidal nucleation and *in situ* growth of nanoparticles on the substrate. **B,C:** Scanning electron microscopy images of the gold nanostars (**B**) and nanorods (**C**) grown *in situ*.

Moreover, we identified key aspects of the growth conditions affecting shape yield, *i.e.*, nanoparticle density, growth solution composition, and flow rate. The extinction of the nanoparticles could also be modified *in situ* (~600 nm to 1100 nm) by changing the composition of the growth solution. Overall, tuning the chemical environment, we attain >90% shape yield for nanostars and ~80% for nanorods (**Figure 1B,C**), which in the latter case, represents a significant improvement, with previous reports obtaining only ~20-37% yield.

Ultimately, the fabricated plasmonic-microfluidic chips have the potential to be implemented in applications such as biological and chemical sensors and in microfluidic platforms incorporating 2D and 3D *in vitro* cellular models.

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