

# DROPLET MICROFLUIDICS WITH INTEGRATED GAS-PERMEABLE MEMBRANES FOR NANOMATERIALS SYNTHESIS WITH REACTIVE GASES

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## Abstract

We present a continuous microfluidic method that achieves unique and exquisitely controlled gas-liquid contacting in utilizing a gaseous reducing agent (carbon monoxide), for the broadly tunable synthesis of plasmonic silica-gold nanoparticles. Our method enables tunable gas-liquid contact times with sub-second time resolution, allowing us to precisely regulate the dosage and mixing of CO into microscale droplets thereby enabling dynamic tunability of surface morphology, without changing reagent concentrations or the need for a reaction quench. Such truly 'on-demand', dynamically tunable nanoparticle engineering is nearly impossible to realize in conventional gas-liquid batch chemistry and is the first demonstration of its kind.

## Introduction

Nanoparticles exhibit a wide range of properties not seen in their bulk counterparts and are of much interest in several promising applications. Nanoparticle properties are highly dependent on their size, shape and composition. Therefore the development of facile, efficient, reproducible and scalable processes for nanomaterials synthesis has attracted considerable interest over the past decade. The use of reactive gases such as carbon monoxide (CO) as reagents in plasmonic nanomaterials chemistry has been known for more than a hundred years [1], and is of much interest due to the exceptional stability of gases when compared to aqueous reagents and the ease with which they can be separated and reused [2]. However, due to the extremely fast nucleation and growth kinetics often involved with nanoparticles synthesis, implementation of gas-liquid materials chemistry in conventional batch processes poses significant reproducibility and scale-up challenges. In addition, CO is highly toxic, and large gas volumes pose inherent process safety risks. Continuous flow droplet-microfluidics is a promising technology for synthetic and analytical chemistry as it enables automated, well-controlled reagent dispensing, efficient mixing leading to rapid (multiphase) mass-transfer, and excellent thermal control. Here we present a continuous-flow microfluidic process that achieves exquisitely controlled gas-liquid contacting in utilizing carbon monoxide (CO), a known reducing agent for metal ions [3], for the robust, safe and broadly tunable synthesis of plasmonic nanoparticles.

## Experimental and Results

We use a poly(dimethylsiloxane) (PDMS) based microfluidic reactor in which a segmented train of monodisperse reagent-filled aqueous drops (AQ) is first created at a T-junction in an immiscible fluorinated oil (FO) and then transits through a parallel-channel network situated downstream of the T-junction (Figure 1a, b). CO is delivered into the other parallel (and 'co-serpentine') channel where it rapidly diffuses through the thin PDMS membrane separating both the channels and into the droplet via the oil. The CO that diffuses into each droplet gets rapidly homogenized due to intense internal convection within translating droplets. We exert temporal control over the gas-liquid contacting by controlling the residence time of the droplets, which, coupled with the inherently accelerated mass transfer in such microscale systems, allows us to precisely regulate the amount of CO infused into the aqueous droplets – a capability that is simply unrealizable at the macroscale, and has crucial implications in enabling reactive gas-assisted nanoparticle synthesis.

We illustrate the utility of our method in the synthesis of an important class of plasmonic nanomaterials obtained by decorating dielectric nanoparticles (silica) with small gold islands ('nanoislands') or by complete encapsulation with a thin shell of gold ('nanoshells'). Optical properties of such materials depend on the core sizes, island coverage and shell thickness. Therefore tight control over particle attributes and size distribution becomes imperative for applications in sensing, bio-imaging and cancer therapy, and plasmonic metamaterials [4].

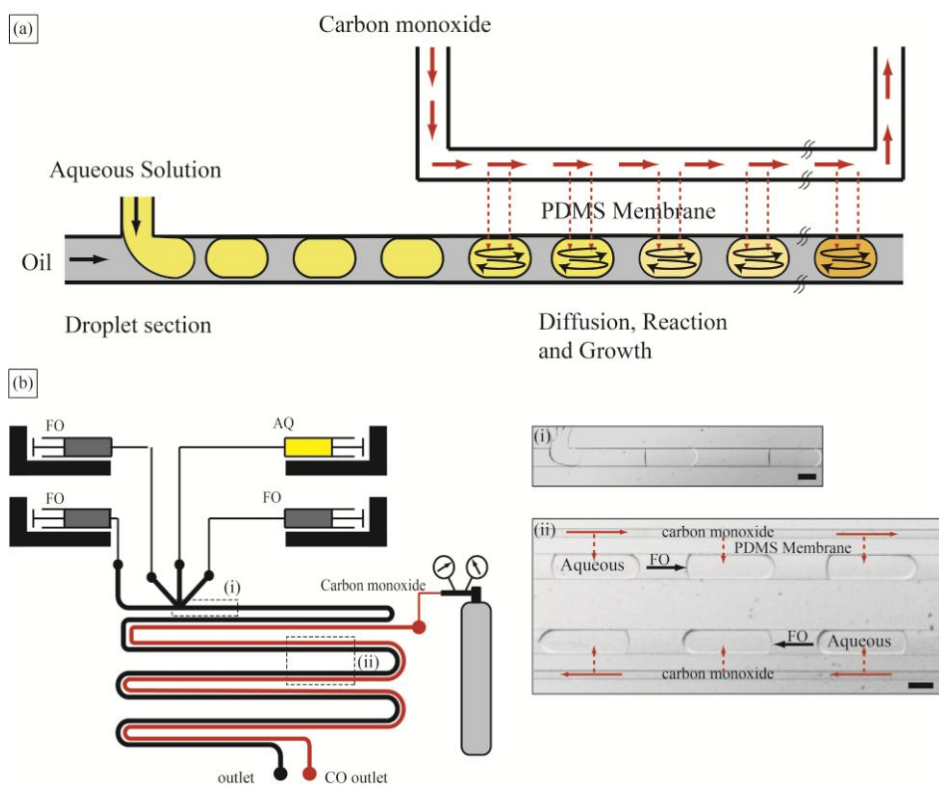


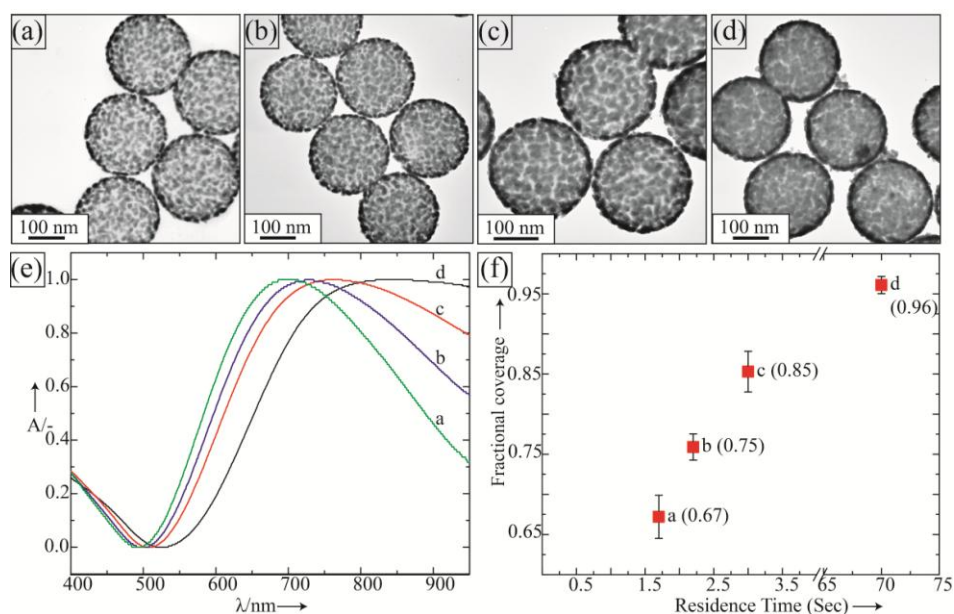
Figure 1: (a) Conceptual schematic of gas-liquid contacting in the parallel channel microfluidic device. (b) Schematic of the microfluidic reactor setup. Insets: stereomicroscopic images of (i) segmented aqueous droplet formation in fluorinated oil (FO) and (ii) segmented flow of aqueous droplets in the gas-liquid channel network. Scale bars: 300  $\mu\text{m}$ .

Such particles are typically synthesized using electroless plating, in which gold-seeded silica particles are dispersed in an aqueous gold salt plating solution ( $\text{HAuCl}_4 + \text{K}_2\text{CO}_3$ ) and the reduction of  $\text{Au}^{3+}$  to  $\text{Au}^0$  onto the silica surface is initiated by a reducing agent [3]. We synthesized silica-gold ‘nanoshells’ and ‘nanoislands’, by dosing CO into the aqueous droplets containing silica particles and  $\text{Au}^{3+}$ . These aqueous droplets act as individual reaction flasks and are of equal volume and subject to nearly identical reaction conditions. Hence, in all droplets nearly equal amounts of CO take part in reducing gold ions onto existing gold seeds on silica spheres to give either nanoislands or complete coverage, depending on the original silica/ $[\text{Au}^{3+}]$  ratio. Conventionally in batch syntheses and in our previous work using liquid phase reagents, the final plasmon resonance (gold coverage) is strictly controlled by changing the initial [silica]/ $[\text{Au}^{3+}]$  ratio in the aqueous feed solution ( $f_s$ ) [5].

We first synthesized complete silica gold shells using a  $f_s$  such that the gold ions are sufficient to completely cover the silica. Using a residence time of 60s, rapid microfluidic mass transport ensures sufficient dosage into each droplet with enough CO to reduce all the existing  $\text{Au}^{3+}$  onto silica. Now, since the PDMS membrane is thin and highly permeable to gas, the transport of CO from the membrane wall to the droplets represents the rate-limiting step for the growth of gold seeds on the silica particles. Typical volumetric wall-to-liquid mass transfer coefficients ( $k_{l,a}$ ) are tremendously accelerated in such microscale segmented flows, and are in the range of  $\sim 0.1 \text{ s}^{-1}$  [6]. The solubility of CO in water ( $C_s$ ) is  $\sim 1 \text{ mM}$ . Further, mixing is extremely rapid within the aqueous droplets due to intense internal convection; the mixing time  $t_m$  ( $\sim 0.1 \text{ s}$ ) decreases with increasing droplet speed and is smaller by at least an order of magnitude compared with the residence times used [7]. Hence, a simple mass transfer model that assumes instantaneous mixing and reaction of CO within the aqueous drops predicts that the number of moles of CO dosed into each droplet varies linearly with time as  $N_{\text{CO}} = k_{l,a} C_s V_d t \sim 2.5 \times 10^{-12} t$ , where  $V_d$  is the volume of each droplet ( $\sim 25 \text{ nL}$ ). Now, since at least  $14 \times 10^{-12}$  moles of CO are required for complete reduction of  $\sim 9.25 \times 10^{-12}$  moles of  $\text{Au}^{3+}$  in each droplet (at  $0.37 \text{ mM}$ ), we infer that at low enough residence times we can operate in the *CO limiting regime*. To exploit this regime, instead of the conventional gold limiting regime as mentioned above, we shorten the gas-liquid contact time to well below 60 s, and thereby regulate the extent of gold plating for *fixed silica* /  $[\text{Au}^{3+}]$  ratio. This represents a facile *on demand* route to plasmon engineering by simply tuning the gaseous reagent supply into the liquid phase.

To examine this idea, we performed synthesis of particles with varying gold coverage at fixed silica/ $[\text{Au}^{3+}]$  ratio, by varying only droplet residence times (Figure 2). By appropriately tuning the relative flow rates of the aqueous and oil two phases, we were able to access high droplet speeds and therefore low residence times in the 1 – 5 s range. Figure 2(a)-(d) show TEM images of particles synthesized at silica particle volume fraction  $f_s = 2.8 \times 10^{-5}$  and aqueous gold

concentration ( $\sim 0.37$  mM), which are just sufficient to ensure complete coverage of all particles by a thin layer of gold at high residence times ( $>10$  s). Remarkably, we were able to synthesize particles with tunable, reduced fractional gold coverage ranging from  $\sim 0.65 - 0.85$  (Figure 2(e)) with *sub-second* residence time resolution in the  $\sim 1-5$  s range. The plasmon band of the gold-silica particles with increasing gold coverage shifts progressively towards longer wavelengths (Figure 2(f)) – these results highlight the remarkable tunability of plasmon resonances over more than 200 nm with small changes in gas-liquid contact time in the 1-5 s range



**Figure 2:** Silica-gold particles obtained by changing the residence times with fixed reagent concentrations: TEM images of  $230 \pm 20$  nm silica particles (volume fraction  $f_s = 2.8 \times 10^{-5}$  in 0.37 mM K-Gold) with: (a) sparse nanoislands, (b) nanoislands, (c) almost coalesced nanoislands (d) complete nanoshell. (e) Ensemble UV-Vis spectra for silica-gold particles (a)-(d), (f) Plot showing fractional coverage of gold over the silica cores of particles (a)-(d) obtained by TEM image analysis using MATLAB<sup>TM</sup>

## Conclusion

We demonstrate the use of a reactive gas for continuous nanomaterials synthesis and tunable *process-based* engineering of plasmon resonances. Exquisite temporal control of gas-liquid contacting and mass transfer enabled by a hybrid droplet-based microfluidic platform enables dynamic tuning of the morphology (and plasmon resonance) of the nanomaterials simply by varying the residence times of the droplets in the microchannel. Such truly ‘on-demand’ nanoparticle engineering is nearly impossible to realize in conventional gas-liquid batch chemistry or in solution-based continuous processes, and is the first demonstration of its kind.

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