NANOPARTICLE FACTORIES IN FLOWING FOAMS

Suhanya Duraiswamy[1] and Saif A. Khan[1,2*]
[1]Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore
[2]Singapore–MIT Alliance,Singapore

ABSTRACT

The availability of robust, scalable and automated nanoparticle manufacturing processes is crucial for the viability of emerging nanotechnologies. Metallic nanoparticles of diverse shape and composition are commonly manufactured by solution-phase colloidal chemistry methods, where rapid reaction kinetics and physical processes such as mixing are inextricably coupled, and scale-up often poses insurmountable problems. Here we show how self-assembly of ordered microscale foams enables a simple yet general solution for remarkably precise, scalable and automated nanoparticle synthesis. We demonstrate this by presenting the first continuous process to synthesize thin gold 'nanoshells' and 'nano-islands' on silica nanoparticle surfaces.

KEYWORDS: Foams, Emulsions, Microfluidics, Nanoshells, Gold, Nanoparticles, Process

INTRODUCTION

Colloidal synthesis methods for nanometer-scale metallic particles have fueled spectacular advances in diverse areas of application including plasmonics, chemical catalysis, optoelectronics and biological sensing. [1, 2] The viability and eventual success of many emerging nanotechnologies now hinges on the availability of robust, reproducible and scalable colloidal synthesis methods that yield larger quantities of material.[3] However, innovations in scalable processing have thus far lagged behind rapid advances in proof-of-concept applications. One of the key reasons for this impasse is the fact that colloidal chemistry often involves rapid, autocatalytic, diffusion-controlled processes; reagent addition and mixing, which are method and operator dependent, are inextricably *coupled* to the chemistry. Reagent homogenization and chemical reaction proceed simultaneously in the reaction vessel, thus making it very difficult to tightly control the final outcome.[4] Continuous flow-based microfluidic synthesis methods provide an alternative, promising superior control over reaction conditions while operating at steady-state, thus simultaneously ensuring reproducibility.[5] In this paper we demonstrate extremely robust, scalable and automated nanoparticle processing in self-assembled flowing foams. We generate an ordered *composite* foam lattice in a simple microfluidic device, where the lattice cells are alternately aqueous drops containing reagents or gas bubbles. Microfluidic foam generation enables precise reagent dispensing and mixing, and the ordered foam structure facilitates compartmentalized nanoparticle growth. We present the first *continuous* process for the manufacture of gold nanoshells on silica nanoparticle surfaces, where we are able to modulate nanoshell morphology and the resulting optical resonances.

EXPERIMENTAL

Syringe pumps (Harvard, PHD 2000) were used to deliver silicone oil (Dow Corning DC50, viscosity 10 cSt), a mixture of gold-seeded silica particles and gold plating solution and reducing agent solution to the microfluidic device while nitrogen gas was delivered from a cylinder equipped with a two-stage pressure regulator through circular PEEK tubings (60 μm, 1.5 m long) leading into the on-chip gas-inlet. The plating solution was aged (>24 hrs) gold hydroxide formed by the addition of 249 mg (1.8 mM) of potassium carbonate in 1L (0.435 mM) of hydrogen tetrachloroaurate (III) trihydrate solution . The $[Au^{3+}]$ in plating solution was varied from 0.43 mM to 0.29 mM, and the volume fraction of gold-seeded silica particles (f_S) in S was varied from ~0.003 % to 0.01%. Freshly prepared hydroxyl amine hydrochloride (4 mM) was used as the reducing agent in all experiments. Flow rates of the individual streams were S: 8 μL/min, R: 2 μL/min each and the volumetric flow ratio of aqueous reagents (S+R) to oil was maintained at 2. The nitrogen gas pressure was maintained at 17 psig. Approximately 1 mL of the aqueous sample was collected from the reactor outlet, for every experimental condition and were analyzed with a UV-Vis spectrometer (Shimadzu UV-2450) and TEM (JEOL 2010, acclerating voltage 200 kV) or FESEM (JEOL JSM-6700f, acclerating voltage 4-25 kV)

RESULTS AND DISCUSSION

Microfluidic composite foams: salient features

Fig. 1(a) is a two-dimensional schematic illustrating the basic features of the foams used in this work. The foam is an ordered alternation of gas and liquid cells (hence the term 'composite'[6]) dispersed in an immiscible oil phase flowing within a microchannel. The overall foam structure resembles the compact 'bamboo' structures observed in confined cylindrical foams. Operation between the dry and wet foam limits leads to characteristic flattening of adjacent fluid interfaces and sharp Plateau border curvatures (Fig. 1(b)).[7] Flowing microscale composite foams possess a unique set of structural and functional features that make them attractive for nanoparticle processing. Aqueous reagents for colloidal synthesis can be controllably dispensed as liquid cells of identical size that serve as individual reaction 'flasks' and are effectively isolated from other reagent-filled cells and the microchannel walls during their transit through the microchannel. Gas bubbles and reagent-filled aqueous drops are alternately formed at a microfluidic T-junction and subsequently assemble downstream into an ordered foam lattice. Reagents are dispensed during the process of foam generation, as shown in Fig. 1(c). The injected gas periodically clears reagents from the T-junction, thereby preventing

reagent buildup and nanoparticle deposition. These features are a significant advance over current droplet-based microfluidic synthesis methods, where droplet formation is sensitive to fluid properties such as interfacial tension and downstream droplet coalescence is a frequent occurrence.[8] Relative motion between liquid-filled foam cells and the microchannel walls, mediated by the intervening oil, generates recirculating fluid motion within the cells and cause rapid mixing of the contents (Fig. 1(d)). The mixing patterns within the aqueous foam cells are extremely robust, and display little cell-to-cell variation at any given downstream location (Fig. 1(e)). *In situ* foam generation therefore crucially enables controllable and reproducible reagent dispensing and rapid mixing. Furthermore, the intense mixing does not entail high shear rates, which can often lead to irreversible colloidal aggregation in macroscale methods involving mixing by agitation.
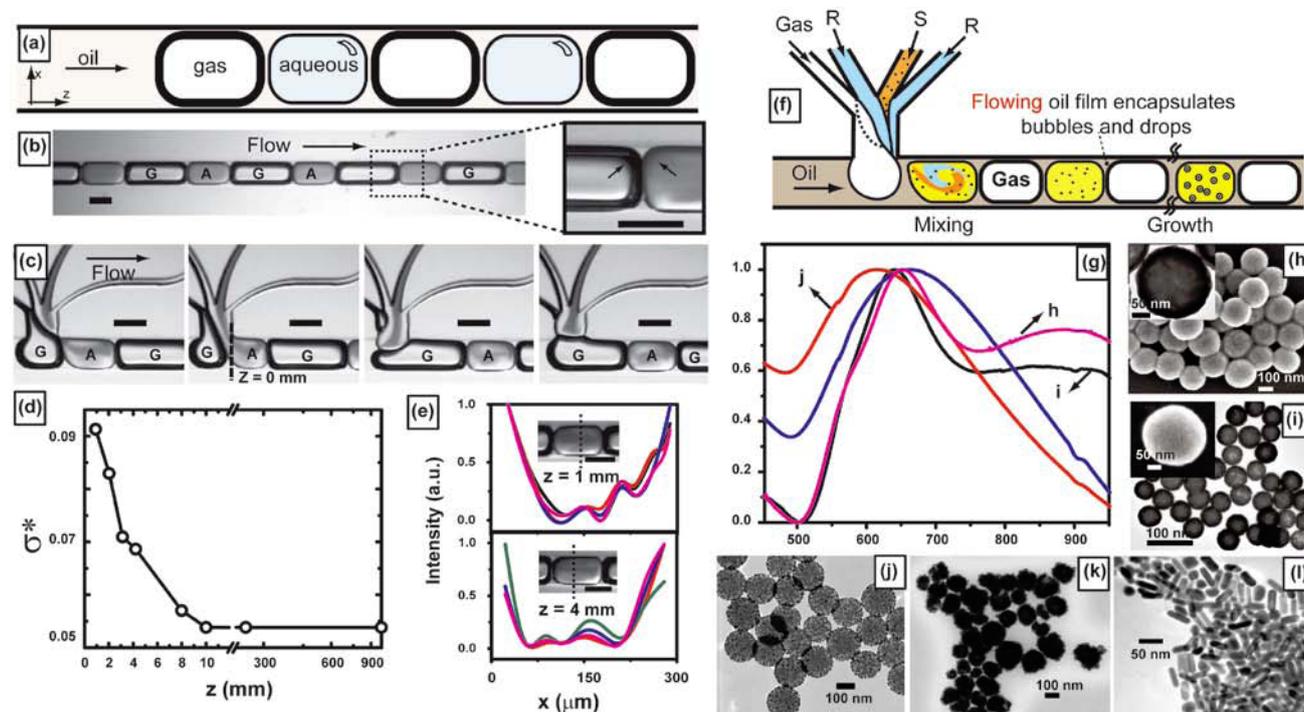
Figure 1.(a) Two dimensional schematic of flowing composite foams (b) Stereomicroscope images of the microfluidic composite foam (c) Series of stereomicroscope images showing the breakup and formation of composite foams at a microfluidic T-junction, G representing gas and A the aqueous phases (d) Mixing within a foam cell, quantified by the normalized standard deviation $\sigma[I(y)]$ of dye intensity $I(y)$; $\sigma^* = \sigma[I(y)]/ <I(y)>$ (e) Cross-sectional intensity profiles (along the dotted lines of the inset stereomicroscope images) within the aqueous foam cell at two different axial positions (z = 1 mm and 4 mm) along the microchannel. (f) Two dimensional conceptual schematic of our method (g) Ensemble UV-Vis absorbance spectra of corresponding gold nanoshells and nano-islands (h) - (i) TEM and SEM images of gold nanoshells of thickness (h) 15 nm and (i) 22 nm (j) TEM image of silica-supported gold-nanoislands each of 10 nm size (k) - (l) TEM image of (k) gold nanorods and (l) silver nanoshells.

Electroless plating of dielectric nanoparticles: synthesis of gold 'nanoshells' and gold 'nano-islands'

Nitrogen gas, an aqueous mixture of gold-seeded silica particles in gold plating solution (labeled S) and aqueous reducing agent solution (labeled R) are delivered continuously to a microfluidic T-shaped junction, where the reagents are dispensed as aqueous cells within a composite foam lattice (Fig. 1(f)). The plating solution and reducing agent used were originally proposed by Graf and van Blaaderen in a study exploring the controlled synthesis of nanoshells.[9] The flowing foam cells spend ~120 s in the long microchannel downstream of the T-junction, and subsequently enter a collection vial where the gas escapes, and the aqueous and oil phases spontaneously form two immiscible fluid layers.

We conducted a series of nanoshell growth experiments by exploring the parameter space comprised by the volume fraction of gold-seeded silica particles f_S (%) and ionic metal concentration ([Au^{3+}] (mM)) while keeping all other parameters fixed. Uniformly sized particles with complete, smooth gold shells were obtained in a subset of the parameter space (Fig. 1(h)-(i)), where we could tune shell thicknesses from ~10 nm - 40 nm. (The minimum complete shell thickness depends on the average spacing between gold nanoparticle seeds attached to the silica nanoparticle surface. For the gold-seeded silica used in our experiments, we estimate this spacing to be ~6 nm.) Ensemble UV-visible absorbance measurements (Fig. 1(g)) clearly indicates the presence of two spectral resonance peaks, with a sharp lower wavelength peak at ~ 650 nm that blue-shifts with increasing shell thickness, and a broad shouldered peak at 900 nm. These peaks may be thought of as resulting from a hybridization of inner and outer shell plasmons.[10] These ensemble measurements are in qualitative agreement with Mie theory calculations for light scattering from single nanoshells, made

using measured average particle sizes, thus complementing electron microscopy in indicating the presence of narrowly distributed particle populations.[11]

By operating in the gold-limited region of the f_S -[Au^{3+}] parameter space, we were able to synthesize tightly controlled populations of silica nanoparticles decorated with gold islands of various sizes (Fig. 1(j)). Electron microscopy analysis of these particles also indicates a possible mechanism of nanoshell growth, in which growing seed particles first coalesce into large, irregularly shaped islands that eventually coalesce to yield a complete shell. Further, we observe that island growth is anisotropic; being more pronounced in-plane along the silica surface than in the radial direction, leading to large flattened islands. The combined effect of anisotropy in island shape and localized surface plasmon interactions between islands is to red-shift the absorption maximum (Fig. 1(g)), with further peak broadening due to finite island size distributions.[11]

This microfluidic method is simple to implement; reagent dispensing and rapid mixing is accomplished in robust, automated fashion with no operator intervention, and uniformly sized unaggregated particles requiring no post-synthesis treatment are obtained. The method is not limited merely to electroless plating chemistries, and can be readily adapted to a broad range of colloidal syntheses. As a further example, we have successfully synthesized silver nanoshells (Fig. 1(k)) using the same recipe as gold nanoshells and gold nanorods involving seeded growth of small gold seed crystals in relatively concentrated surfactant solutions (Fig. 1 (l)). In addition, the gas cells of the foam lattice may also carry a gas-phase reagent for colloidal chemistry, further broadening the spectrum of possibilities. However, we are currently limited to room-temperature aqueous-based colloidal chemistry due to the material used for device fabrication (PDMS). Extension to higher-temperatures and non-aqueous syntheses will require microfabrication in materials such as glass or silicon, and appropriate selection of the carrier 'oil' phase, which has to be immiscible with the solvent(s) used, while preferentially wetting the microchannel surfaces. We are able to operate continuously at single-device throughputs of ~1 mL/hr with silica volume fractions of up to 0.015% with the current generation of devices, and have tested device operation for up to 12 hours per run. Even relatively modest parallelization can therefore yield preparative quantities of material.

CONCLUSION

We thus present a crucial advance in the area of continuous processes for nanomanufacturing. We are currently working towards scaling of such foam-based reactors for larger volumes of production. The inherently digital nature of foam-based nanoparticle processing also raises the possibility of autonomous logic-based processing for high-throughput applications such as, for example, rapid parameter-space exploration of colloidal syntheses.

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CONTACT

*Saif A. Khan, tel: (65) 6516 5133; chesakk@nus.edu.sg