

Controlling bubbles using bubbles – Microfluidic synthesis of ultra-small gold nanocrystals with gas-evolving reducing agents

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Single phase microfluidic experiments

Single phase flow studies which involve premixing the aqueous solution of CTAB and HAuCl_4 and passing them through one of the reactor inlets at flow rate of $7.5 \mu\text{L}\cdot\text{min}^{-1}$ and flowing NaBH_4 through the other inlet at a flow rate of $1 \mu\text{L}\cdot\text{min}^{-1}$ were conducted. The experiments show that the uncontrolled out gassing in the aqueous NaBH_4 solution resulted in nucleation of bubbles that adhere to the channel walls as shown in Figure S1 (b) leading to flow disruption, heterogeneous particle nucleation and deposition on the channel walls as shown in Figure S1 (a) and eventually to clogging within an hour of experiments.

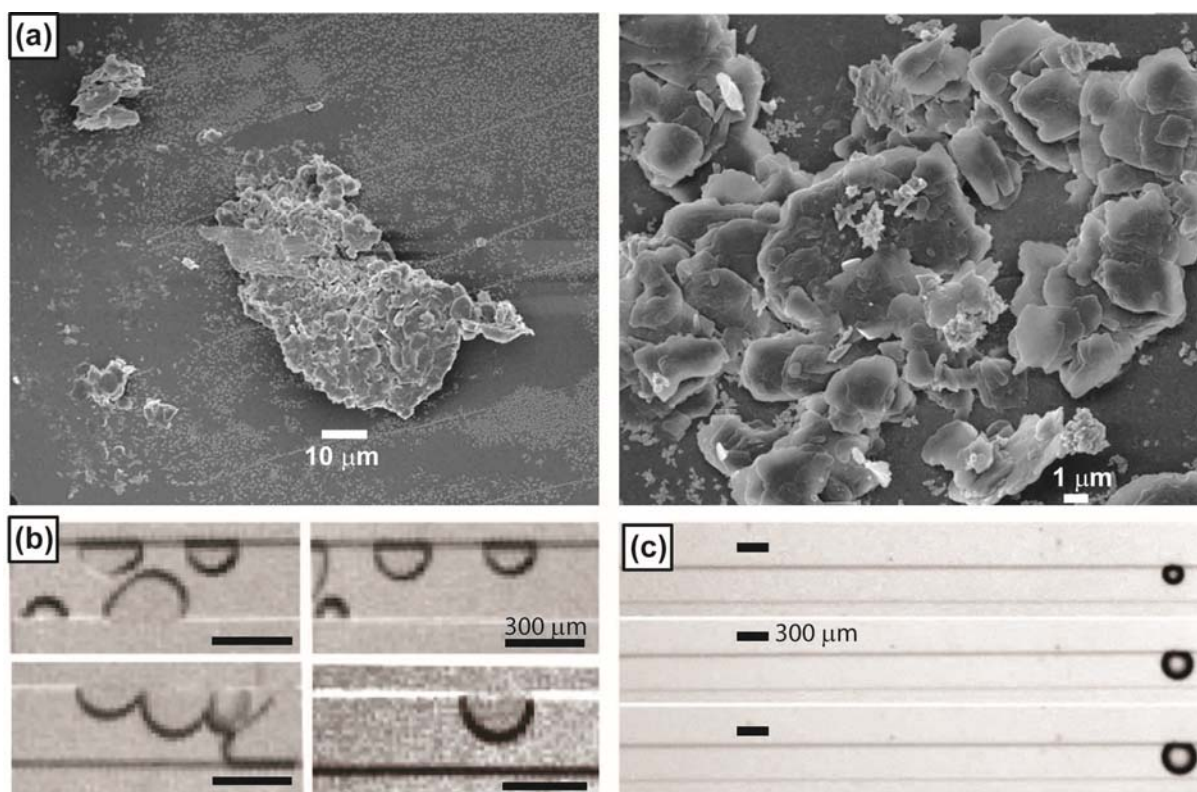


Figure S1. (a) Scanning electron microscope images of the reactor after 1 hour of experiment using the single phase flow method. (b) Stereomicroscope images of bubbles formed and adhered to the walls of the channel (c) Stereomicroscope images of the growth of a single bubble adhered onto the reactor wall over a period of 5 mins.

SEM images of the channel

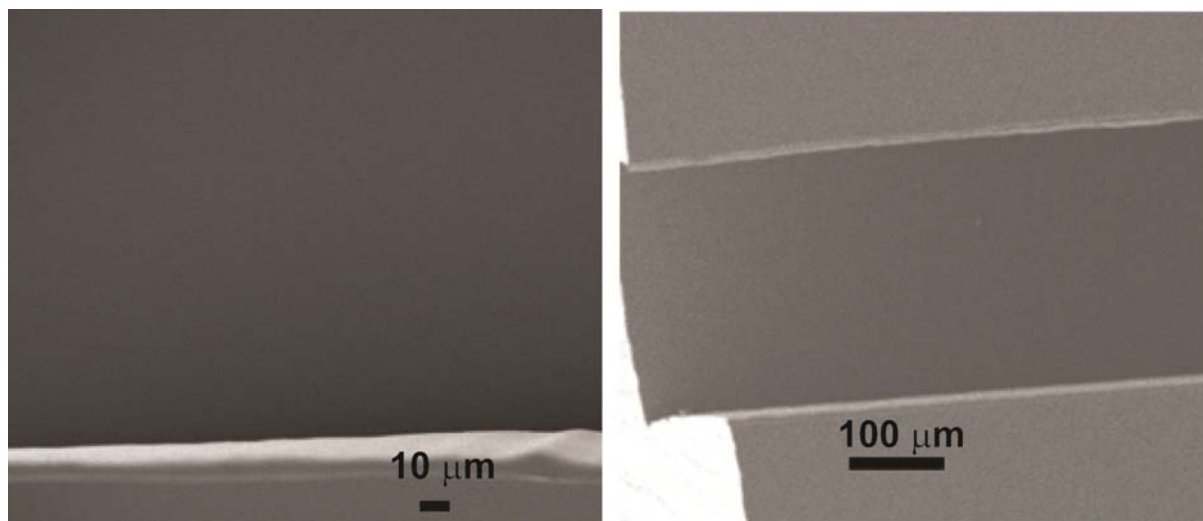


Fig. S2 SEM images of the device walls after 8 hrs of continuous synthesis using the segmented-flow method

Seeded growth of gold nanorods using chemically modified NaBH_4

Experimental

Chemical modification of NaBH_4 solution

A stock solution was prepared by adding 0.038 g of NaBH_4 to 30 mL of 1 M NaOH and 70 mL of DI water. 3 mL of this stock solution was then mixed with a solution containing 0.1 g of NaBH_4 in 30 mL of iso-propanol.

Seed synthesis

Nearly spherical gold nanoparticle seeds (<4 nm in size) were synthesised by adding freshly prepared, ice cold sodium borohydride solution (0.6 mL of the above mentioned solution) to a mixture of aqueous $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.25 mL of 10 mM) and CTAB (7.5 mL of 100 mM) solution, while stirring vigorously (700 rpm, Heidolph) using a magnetic stirrer (teflon, 2 mm) in a borosilicate vial (20 mL, scintillation, Kimble glass Inc., Singapore). The solution was brownish yellow and was maintained at 35°C to prevent CTAB from crystallizing.

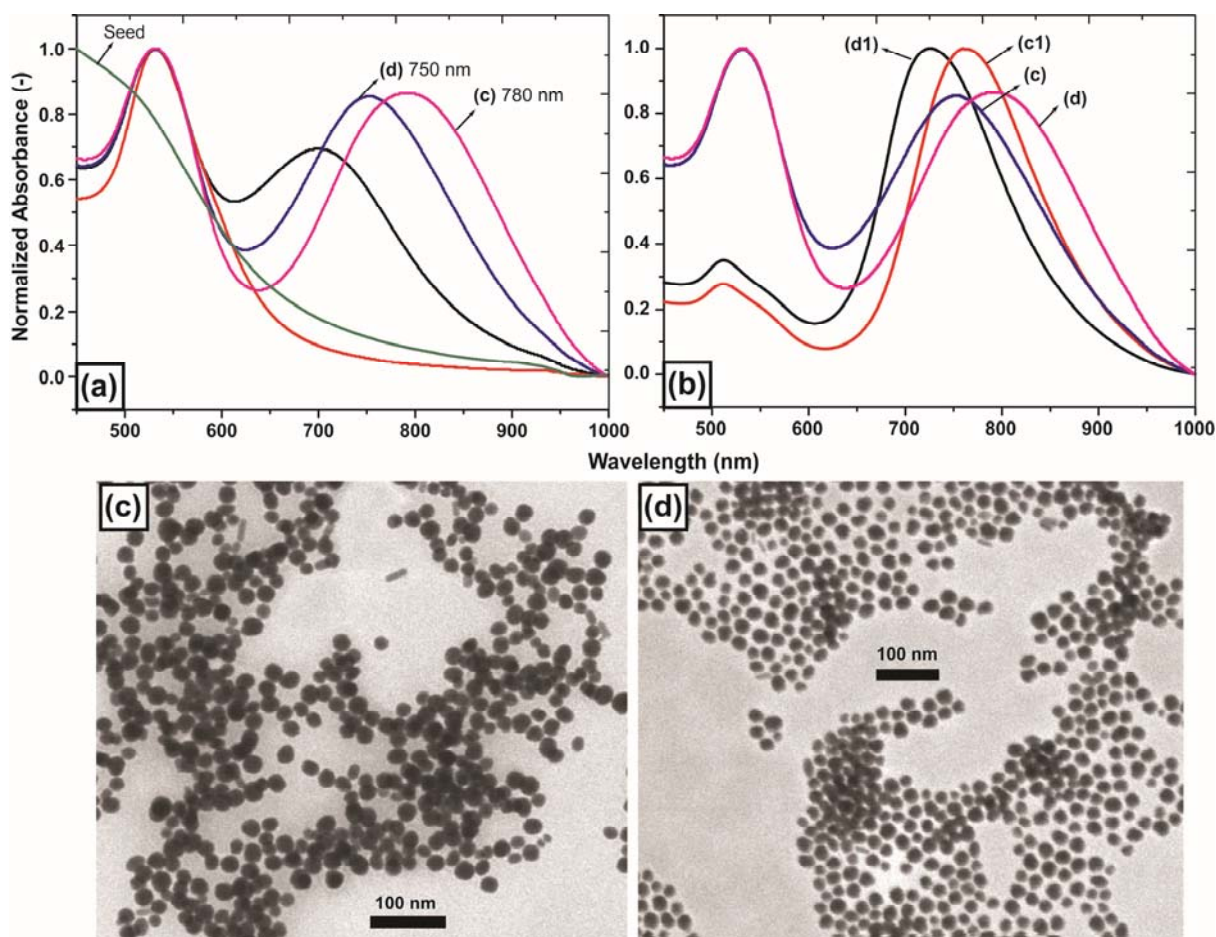


Figure S3. UV-vis absorbance spectra of (a) GNR synthesised using chemically modified NaBH_4 solution (b) Comparison of the spectra of GNR samples synthesised using seeds prepared from (c) and (d) chemically modified NaBH_4 solution and (c1) and (d1) unmodified NaBH_4 solution. TEM images of GNR samples synthesised using chemically modified NaBH_4 solution with silver ion content (c) 0.08 mM and (d) 0.1 mM.

Table 1 : Other reactions that can be performed using our approach

1. Generation, separation, and reaction of diazomethane gas.¹
2. Enzymatic reactions evolving CO₂, O₂, CH₃ and H₂.²⁻⁴
3. Bromine gas by oxidation of bromide by bromate.⁵
4. Nitrogen and nitrous oxide by the oxidation of hydrazoic acid with bromate.⁶
5. Reactions involving strong acids evolving gases such as SO₂, CO₂.⁷

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