Supplementary Information

Dynamically tunable nanoparticle engineering enabled by short contact-time microfluidic synthesis with a reactive gas

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Experimental Details

Materials: 3-aminopropyl tris(trimethylsiloxy)silane (APTTS, 99%), hydrogen tetrachloroaurate(III) trihydrate (HAuCl4, 99.99%), tetrakis(hydroxymethyl) phosphonium chloride (THPC, 80% in water), sodium hydroxide (NaOH, Reagent grade, 97%), acetonitrile (CH3CN, HPLC grade 99.9%), potassium carbonate (K2CO3, 99.99%), Octadecafluorodecahydronaphthalene (Perfluorodecalin, Fluka, mixture of cis and trans, 95%) from Sigma-Aldrich Co. Ltd., Singapore, were all used as obtained without any further purification. De-ionized water and glassware washed in aqua regia and rinsed thoroughly in water were used for all experiments.

Synthesis of amino-functionalized silica spheres: 230 nm silica particles were synthesized by the Stöber method.[1] The surfaces of silica spheres were functionalized with APTTS in refluxing acetonitrile. Amino-functionalized silica particles were washed with acetonitrile, ethanol and DI water by sonication and several cycles of centrifugation.[2,3]

Gold-seeded silica particles: 2-3 nm colloidal gold particles used for seeding the amino-functionalized silica was made according to the procedure of Duff et al.[4] Under rapid stirring 1.5 mL of 0.2 mM aqueous NaOH and 1.0 mL of 67.7 mM aqueous THPC were sequentially added to 45.5 mL of DI water followed by addition of 2 mL of aqueous 25 mM $HAuCl_4$. The solution immediately turned brown-red indicative of the colloidal gold formation. 150 µL of amino-functionalized silica particles suspension with 20ml of colloidal gold solution was shaken for 8 hours at room temperature and centrifuged to separate the gold-seeded silica particles. These particles were washed three times with water by cycles of centrifugation to remove the unattached colloidal gold particles.

K-Gold Solution: 3 mL of 1 wt% HAuCl4 was taken with 50 mg K_2CO_3 in 200 mL DI water (1.8mM) and aged for 1 day to produce a colorless gold plating solution, so-called K-gold, containing gold hydroxide ions.[5]

Microfabrication: Microfluidic device patterns were fabricated onto silicon wafers by standard photolithography using negative photoresist SU-8 2050.[6] Devices were subsequently moulded in poly(dimethyl siloxane) (PDMS) using the soft lithography technique. PDMS was molded onto the SU-8 masters at 70˚C for 2 hrs, peeled, cut and cleaned. Inlet and outlet holes (1/16-in. o.d.) were punched into the device. The microchannels were irreversibly bonded to a glass slide pre-coated with a thin layer of PDMS after a brief 35 s air plasma treatment. The bonded devices were then cured for 24 hours at 100˚C. The microchannels have rectangular cross-section and the details of the channel dimensions are: width and depth of the liquid and gas channel are 300 µm and ~124 µm and 100 µm and ~124 µm respectively, and the parallel liquid and gas channels are separated by 200 µm. Devices with lengths of the parallel channel section of 91.5 cm and 21.8 cm were used.

Microfluidic device setup and operation:

CAUTION!! Carbon monoxide is a highly toxic gas. All experiments should be done in a well-ventilated fume hood.

A schematic of the microfluidic device and experimental setup is shown in Figure 2. Syringe pumps (Harvard, PHD 2000) were used to deliver perfluorodecalin ('FO') from three syringes and a mixture of gold-seeded silica particles and K-gold solution ('AQ') from another syringe to the microfluidic device. Carbon monoxide was delivered from a cylinder equipped with a pressure gauge through a PTFE tube leading into the on-chip gas-inlet. The reagent concentration was varied in terms of the volume fraction of gold-seeded silica particles ('f_s') in AQ ('f_s' is the total volume of the silica spheres/total solution volume). The PDMS membrane was pre-saturated by flowing CO in the gas channel for at least 1 hour. For the experiments with different gold-seeded silica volume fractions in AQ (f_s varied from ~ 2.8 x 10^{-5} to 4 x 10^{-5}), we used the device with a length of 91.5 cm and a constant flow rate of AQ: 5 μL/min and total FO: 30 μL/min, corresponding to a residence time of 60 seconds. The residence times were calculated using the superficial velocity of the droplets in the channel and verified by high-speed microscopic observation. For the experiments with a fixed f_s and varying residence times, we used the 21.8 cm long device. We operated at flow rates of AQ: 3 μL/min and total FO: 4 μL/min; AQ: 20 μL/min and total FO: 150 μL/min; AQ: 20 μL/min and total FO: 200 μL/min; AQ: 30 μL/min and total FO: 260 μL/min. Thus we achieved residence times ranging from 70 seconds to ~2 seconds. The carbon monoxide gas pressure was maintained at 10 psig. At the liquid outlet, aqueous colloidal solution was readily phase-separated from fluorinated oil. Carbon monoxide gas was vented out from the gas outlet.

Sample collection and analysis

The outlet from each microfluidic device was connected via fluoropolymer (FEP) tubing to a 2 mL centrifuge tube. Approximately 1 mL of the aqueous sample was collected in the tube for every experimental condition. The aqueous phase was separated from the oil phase by simple decantation. Aqueous samples containing nanoparticles were analyzed with a UV-vis spectrometer (Shimadzu UV-2450). A drop of this sample was placed onto a 200 mesh formwar protected copper grid and allowed to dry overnight. The copper grid was then analyzed using TEM (JEOL 2010, accelerating voltage 200 kV).

Colloidal gold synthesis

A PDMS device, with the parallel channel section length of 91.5 cm was used for gold sol synthesis experiments. We used flow rates of AQ: 3 μL/min and total FO: 9 μL/min, corresponding to a residence time of 170 seconds. Droplets of aqueous 0.3 mM $HAuCl_4$ were generated in FO and transported in parallel to the CO-filled channel (CO pressure = 10 psig). At the outlet a pink aqueous phase was collected and analyzed by UV-Vis spectroscopy; an absorbance spectrum characteristic of colloidal gold (Figure S1) was obtained. The sizes of the particles were measured from TEM micrographs to be in the range of 10±2 nm (Inset in Figure S1). In this gas-liquid microfluidic system sufficient amount of CO diffused through the PDMS membrane and the intervening oil phase to induce reduction of gold ions to colloidal metallic nanoparticles within the droplets.

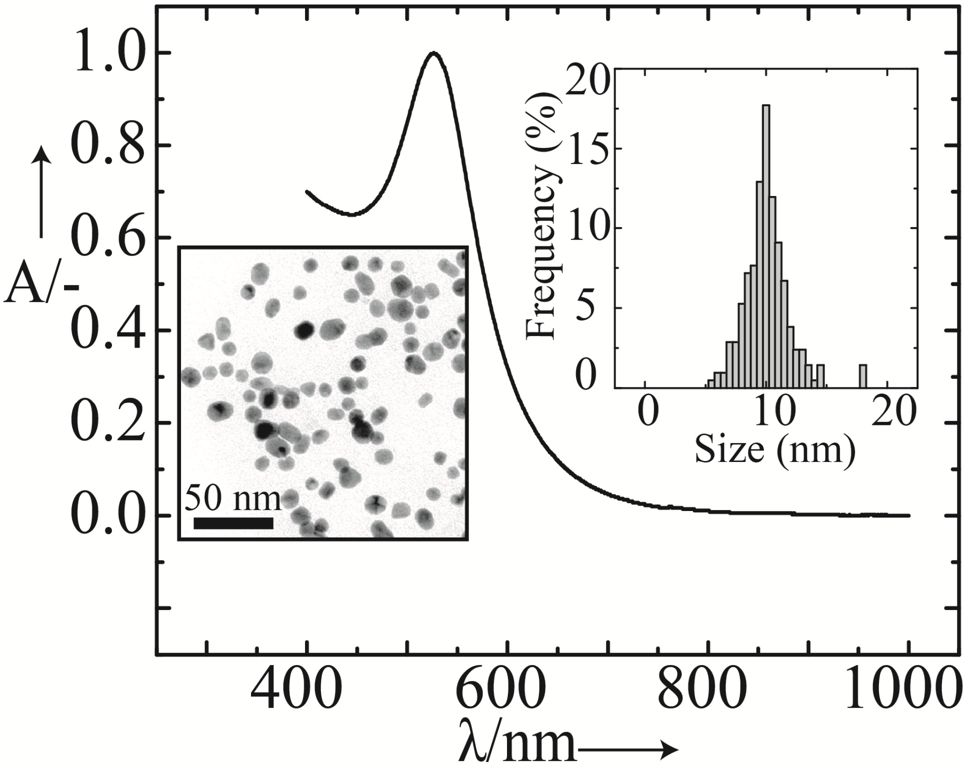

Figure S1: UV-Vis absorbance spectrum of colloidal gold synthesized using the microfluidic device. *Insets:* TEM image of gold nanoparticles and measured particle size distribution.

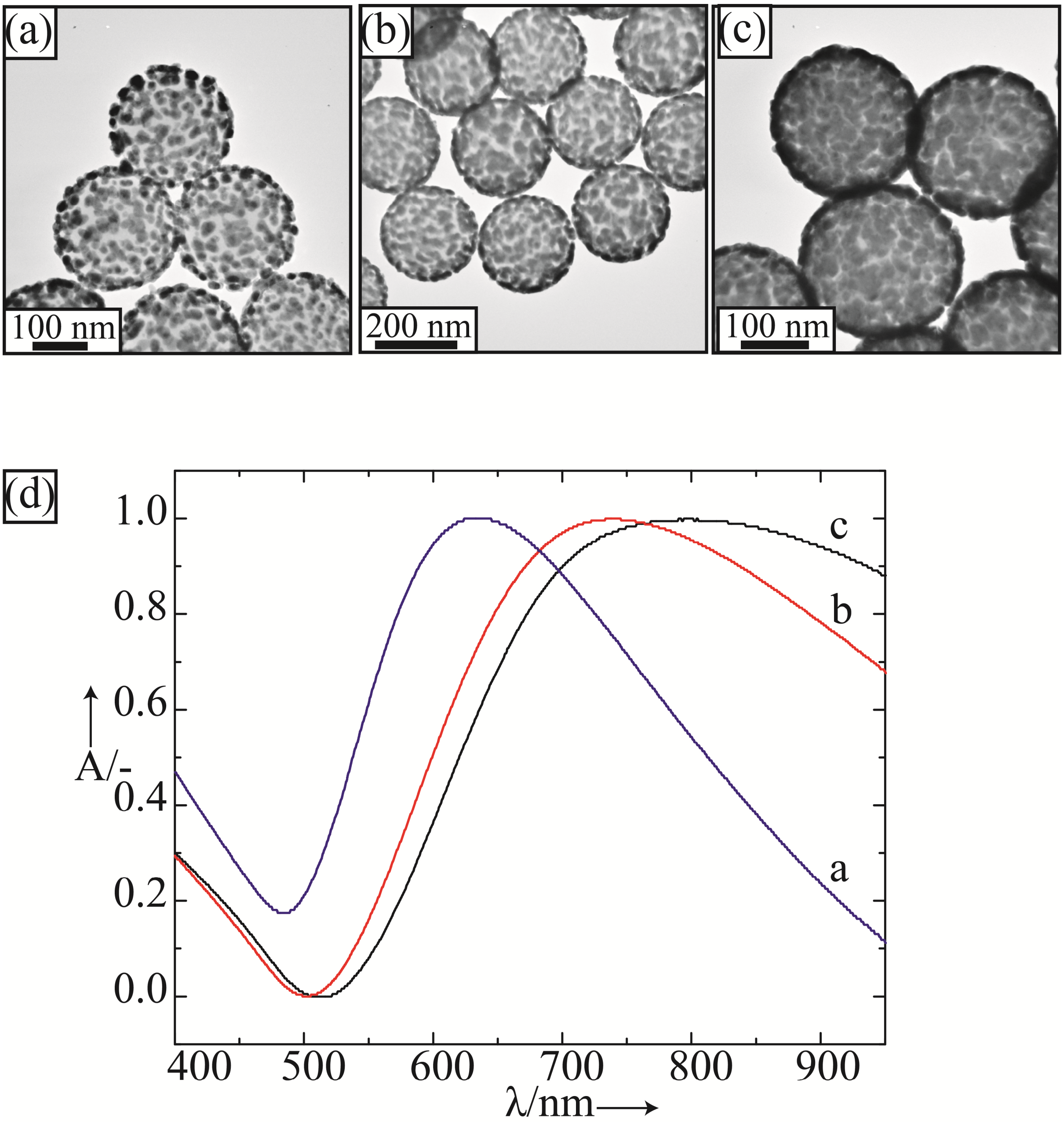

Figure S2 : Gold-silica core-shell particles obtained by changing only the silica volume fraction in the reagents at a fixed residence time of 60 sec: TEM images of 230±20 nm silica particles with: **(a)** nano-islands (f_s=4 x10^{-5} in 0.36 mM K-Gold), **(b)** almost coalesced nanoislands (f_s= 3.4 x10^{-5} in 0.37 mM K-Gold). **(c)** complete nanoshell (f_s= 2.8 x10^{-5} in 0.37 mM K-gold). **(d)** Ensemble UV-Vis spectra for all particles **(a)**-**(c)**.

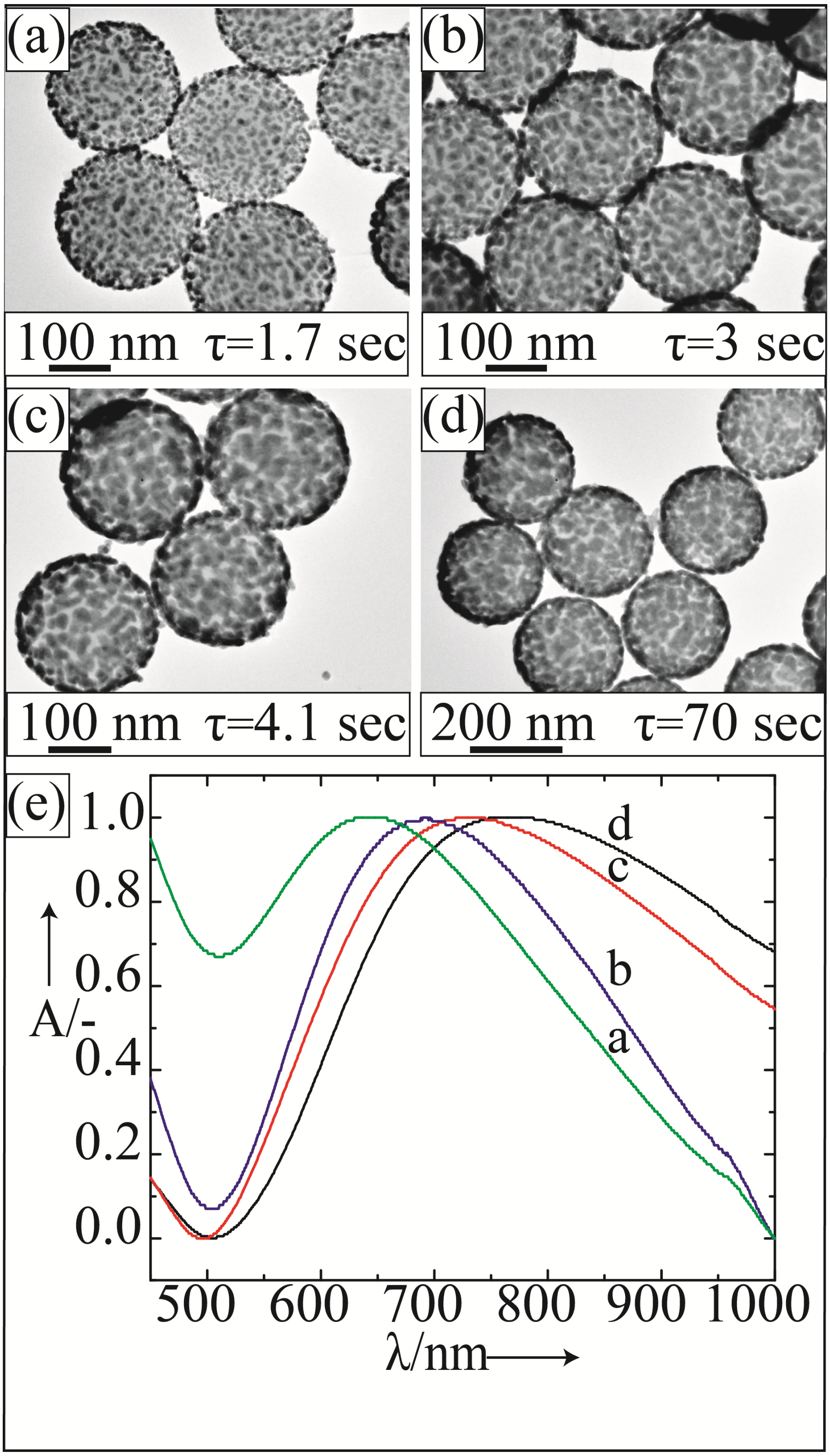

Figure S3: Gold-silica core-shell particles obtained by changing the residence times with a fixed f_s=3.1 x10^{-5} in 0.37 mM K-Gold : TEM images of 230±20 nm silica particles with: **(a)** sparse nano-islands, **(b)** nanoislands, **(c)** almost coalesced nanoislands **(d)** complete nanoshell. **(e)** Ensemble UV-Vis spectra for all particles **(a)**-**(d)**.

Discussion of Gas-Liquid mass transfer

The synthesis of metal-dielectric core shell nanoparticles such as gold/silver-silica nanoshells is carried out using electroless plating which involves the autocatalytic deposition of gold on colloidal silica pre-seeded with gold nanoparticles. Such electroless plating reactions are known to be extremely fast, making the process mass transfer limited. Since the PDMS membrane separating the gas and liquid channels is thin (200 um) and highly permeable to gas, it offers no significant resistance to the mass transfer of CO. Further, we pre-saturate the membrane by flowing CO in the gas channel for at least 1 hour in our experiments. To support our assumption, we compare the membrane mass transfer and the liquid phase mass transfer resistances. Under steady state conditions the flux across the membrane and from the wall to liquid phase will be equal. A simple mass transfer model can be written to determine the flux (mol/m^2-sec).

Membrane side flux:

$$N = \frac{P}{z}\left(P_{GAS} - P_i\right) \qquad \text{...... (1)}$$

Since the kinetics is rapid, assuming instant consumption of CO within droplets, liquid side flux is given as

$$N = k_L\left(C_S - 0\right) \qquad \text{...... (2)}$$

Where P is the permeability of CO through PDMS, P_{GAS} is the pressure in the gas channel (10 psig), P_i is the pressure at the solid-liquid interface and C_S is the solubility of CO in the aqueous phase. A relation between the two can be given using Henry's law

$$P_i = {C_S}/{H} \qquad \text{...... (3)}$$

Henry's law constant (H) for carbon monoxide and water is 9.9 x 10^{-6} mol/m^3-Pa.[7]

Adding equations 1 and 2 and using relation 3 we get

$$N\left(\frac{1}{k_L H} + \frac{z}{P}\right) = P_{GAS}$$

$$N = \frac{P_{GAS}}{\dfrac{1}{k_L H} + \dfrac{z}{P}} \qquad \text{...... (4)}$$

This equation is of the form Flux= Driving force/Resistance

Thus the total resistance can be written as the sum of the membrane and liquid phase resistances

$$R_{TOTAL} = \frac{1}{k_L H} + \frac{z}{P}$$

The permeability of CO through PDMS has been reported to be in the range of 400 barrer.[8] In SI units this is equal to 1.34 x 10^{-13} mol-m/m^2-s-pa. Typical volumetric wall-to-liquid mass transfer coefficients ($k_L a$) are tremendously accelerated in such microscale segmented flows compared to conventional gas liquid contacting methods, and are in the range of ~ 0.1 s^{-1}.[9] Here *a* is the area per unit volume available for mass transfer. Using *a* for the specific geometry of our system, we obtain k_L= 3.93 x 10^{-6} m/s.

Using these values we determine the two individual resistances. We find that the liquid phase resistance (2.6 x 10^{10} m^2-s-pa/mol) is an order of magnitude higher than that of the membrane (1.5 x 10^9 m^2-s-pa/mol). Therefore, we safely assume that 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. The flux of CO through the membrane using equation 4 is calculated to be 6.2 x 10^{-6} mol/m^2-sec. Mixing is extremely rapid within the aqueous droplets due to intense internal convection; the mixing time t_m (~ 0.1 s) decreases with increasing droplet speed[10] and is smaller by at least an order of magnitude compared with the residence times used. It is also smaller by at least two orders of magnitude when compared to the characteristic time for CO homogenization via pure diffusion ($t_D \sim w^2/D_{CO}$ = 45 s, where w = 300 μm is the width of microchannel and D_{CO} = 2 x 10^{-9} m^2/s is the aqueous diffusivity of CO) – a fact that highlights the advantage of using moving microscale droplets for multiphase synthesis. Thus the CO that enters the droplets from the wall gets rapidly homogenized and is consumed extremely fast in the ensuing reaction. We note that these are order-of-magnitude estimates, and represent a lower bound on the amount of CO entering the droplets. CO can also enter the aqueous droplets via the oil phase; however, since this involves a two-step mass transfer process (wall-to-oil and oil-to-aqueous), we make the reasonable assumption assume that the dynamics are slower than the direct wall-to-aqueous transfer of CO.

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