Supporting Information

Millifluidics for Time-resolved Mapping of the Growth of Gold Nanostructures

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Experimental Section

Materials: Millifluidic chips (made of polyester terephthalate polymer) were purchased from Microplumbers Microsciences LLC. The chip had serpentine channels with dimensions of 2 mm (W) x 0.15 mm (H) x 220 mm (L) within which the experiments were performed. High precision, fully automated, pulsation free syringe pumps to flow the liquids within the chip were purchased from Cetoni Automation and Microsystems, GmbH. Fluidic connections between the reactor chip and the pump were made using FEP tubing (0.25 mm I.D., 1/16" O.D., Dolomite). The pumps were tested with water as solvent at different flow rates prior to the experiment to optimize the required flow rate.

Chemicals: HAuCl₄ (Aldrich, 99.9%), *meso*-2, 3-dimercaptosuccinic acid (DMSA, Aldrich, 98%), NaBH₄ (Aldrich, 98%), and Nanopure water (18.2 M Ω -cm) was used in all experiments.

Formation of gold nano/microstructures within the millifluidic chip:

(i) *In situ* **XAS:** A standard solution of HAuCl₄ (10 mmol, 118.2 mg/30 ml) was prepared in Nanopure water. Another solution containing DMSA (20 mmol, 109.2 mg/30 ml) and sodium hydroxide (50 mg) in Nanopure water (pH 12) was prepared. The two solutions were fed through two separate syringes into the millifluidic chip at a flow rate of 10 ml/h using the automated pump. For the *in situ* XAS study, the millifluidic chip was coupled to the synchrotron beam line using a metal stage that has access to movement in XYZ directions.

(ii) Time-dependent formation: Standard solutions of HAuCl₄ (10 mmol, 118.2 mg/30 ml), DMSA (20 mmol, 109.2 mg/30 ml) and NaBH₄ (10 mmol, 11.34 mg/30 ml) were prepared in Nanopure water. 10 ml each of HAuCl₄ and DMSA solutions were taken into two separate syringes and were flown within the chip with a uniform flow-rate of 1 ml/h for a fixed amount of time (*i.e.* 1 h, 5 h, and 9 h) which resulted in the formation of $Au_xS_y^-$ structures. The as-formed $Au_xS_y^-$ structures within the chip were later reduced by flowing 10 mmol NaBH₄ within the chip for 15 min at 5 ml/h flow rate. The chip was finally washed with Nanopure water for 30 min at the same flow-rate before conducting the catalysis experiments.

Catalysis reactions: Two catalysis reactions, (1) 4-nitrophenol reduction to 4-aminophenol and (2) hexacyanoferrate (III) reduction to hexacyanoferrate (II) were performed with three sets of gold catalysts (*i.e.* structures formed at 1 h, 5 h and 9 h respectively). In a typical reaction, 15 ml of 9 X 10^{-5} mol solution of 4-nitrophenol was mixed with 3.3 ml of 0.65 mol NaBH₄ solution to form 4-nitrophenolate ion according to reported literature procedure.¹ The resultant solution was passed through the gold structures deposited chip at 5 ml/h flow rate (other flow-rates, *viz.* 20, 40 and 60 ml/h were also used) and the products collected were analyzed using UV-Vis spectrophotometer. Similarly, for the other catalysis reaction, 5 ml of 8.33 X 10^{-4} mol Hexacyanoferrate (III) was mixed with 1 ml of 1 X 10^{-2} mol NaBH₄ solution and the resultant solution was passed through the chips with same flow-rates.

3-D X-ray Tomography: High resolution X-ray tomography images were collected at Louisiana State University, Center for the Advanced Microstructures and Devices (CAMD) Tomography Beamline at 15keV monochromatic X-ray energy. Transmitted X-rays through the samples were

converted to visible light with a synthetic garnet (Ce:YAG) scintillator and scintillator was imaged with a 5.4 X microscope objective focused onto a 16 bit CCD camera (Princeton Instrument PIXIS2KB 2048 x 512 pixels, each 13.5 μ m x 13.5 μ m), yielding an effective spatial resolution 2.5 μ m. The sample was cut into a piece fitted in a field of view and mounted with clay atop the tomography sample rotation stage. Reconstructions of 766 images from 0° to 179.5° by 0.5° angle increment and double imaging with 10 pixels apart were performed using a MatLab program based on filtered back projection and double correlated sampling to reduce the ring artifacts.

X-ray Absorption Spectroscopy: The X-ray absorption measurements were performed at two different synchrotron radiation facilities *viz*. Advanced Photon Source (APS) and Center for Advanced Microstructures and Devices (CAMD). The *in situ* XANES and EXAFS measurements of Au L₃-edge were performed with ionization chamber in Stern-Heald geometry at the insertion device beam line at Sector 10, Materials Research Collaborative Access Team (MRCAT, 10-ID) of the APS, Argonne National Laboratory.² The X-ray beam was 0.05 mm x 0.05 mm and data was collected in fluorescence geometry. Au foil spectrum for energy calibration was obtained simultaneously with the samples. The Si (111) double crystal monochromator was scanned continuously and data was collected in quick EXAFS mode. The incident ion chamber was filled with 50% nitrogen mixed with 50% helium gas while the fluorescence detector was filled with Argon gas. The collected data were processed using WinXAS software ³ by extracting the EXAFS oscillations $\chi(k)$ as a function of photoelectron wave number k following standard procedures. Experimental scattering paths were generated from Au foil (12 Au-Au at 2.88 Å) and NaAuCl₄ (4 Au-Cl at 2.28 Å) for Au-S and the fit models

were optimized in R-space in the conventional way. Experimental values of $\Delta\sigma^2$ are relative to the references, which assume a value of 0.000. The XANES experiments on other samples were carried out at the WDCM beamline of the synchrotron radiation source at CAMD, Baton Rouge, USA, with an energy of 1.3 GeV using Ge(220) crystals for the Double Crystal Monochromator (DCM). For calibration, the energy of the Au-L₃ edge was set to 11919 eV using the first maximum of the first derivative of the metal foil spectrum. XANES spectra were measured with 3 eV equidistant energy steps in the pre-edge region of 11750 eV to 11900 eV, with 0.7 eV in the edge region of 11900 eV to 11200 eV and with 1.0 eV in the post-edge region of 12000 eV to 12400 eV. Data were normalized using a first-order fit for pre-edge and third-order polynomial in the post-edge regions and analyzed using the ATHENA program of the IFFEFIT package.⁴

Scanning Electron Microscopy (SEM): Hitachi S-4500II cold field emission scanning electron microscope equipped with EDS detector, was used to investigate the surface morphology of gold structures formed within the millifluidic channels. The SEM was also equipped with large stage with motion ranges of 360° continuous rotation, -5° to 45° tilt, 0 to 100 mm in X, 0 to 50 mm in Y and 3 to 28 mm in Z direction, and could be used to image features at magnification from 20x to 500,000x, with resolution of 1.5 nm (at 15 kV accelerating voltage and working distance of 4 mm) or 4.0 nm (at 1 kV accelerating voltage and working distance of 3 mm). The EDAX compact detector unit, with super ultra-thin window that could be used for light elemental analysis down to beryllium, was employed to analyze their chemical composition.

Transmission Electron Microscopy (TEM): JEOL 2010 High-resolution Transmission Electron Microscope (HRTEM) with an integrated EDAX EDS system was used for TEM

analysis. The samples were prepared by dissecting the portion of the chip (zones on the chip) and collecting the sample from the portion using solvent. The solution was later placed on carbon coated-copper grids for analysis.

UV-Visible Spectroscopy: Optical absorbance of the catalysis samples were recorded using Shimadzu, UV-3600 spectrophotometer. 3 ml of sample was collected for each catalytic run and introduced into 10 mm Quartz cuvette and the absorbance was measured from 250 nm to 500 nm. The absorbance bands for respective samples were assigned based on the standard reference samples of 4-nitrophenol and 4-aminophenol.

References:

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- (3) Ressler, T. J. Synchrotron Rad. 1998, 5, 118-122.
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Supporting Information S1. Photograph showing the millifluidic chip with serpentine channels connected to the manifold.



Supporting Information S2. Experimental set-up showing the millifluidic chip coupled to synchrotron beam line for the *in situ* XAS analysis at Advanced Photon Source, Argonne National Lab.



Supporting Information S3. TEM image of $Au_x S_y$ nanoclusters.



Supporting Information S4: (a) Matrix assisted laser desorption ionization (MALDI) spectra of the $Au_xS_y^-$ nanoclusters in negative ionization at varying laser fluence. The laser fluence was increased from top to bottom.



Supporting Information S4. (b) MALDI spectra of the $Au_xS_y^-$ nanoclusters in positive ionization mode at varying laser fluence. The laser fluence was increased from top to bottom. Au: DMSA = 11:7 = 3441 (cal.); = 3438 (Exp. – negative mode).



Flow Rate			1 ml/h	10 ml/h	60 ml/h
Color	Zone	Spatial Resolution (mm)	Time Resolution	Time Resolution	Time Resolution
	1	0.05	54 mS	5.4 mS	0.9 mS
	2	15	16.20 S	1.62 S	0.27 S
	3	35	37.80 S	3.78 S	0.63 S
	4	55	59.40 S	5.94 S	0.99 S
	5	75	81.00 S	8.10 S	1.35 S
	6	95	102.60 S	10.26 S	1.71 S
	7	115	124.20 S	12.42 S	2.07 S
	8	135	145.80 S	14.58 S	2.43 S
	9	160	172.80 S	17.28 S	2.88 S

Supporting Information S5. Calculated time-resolution for the millifluidic chip at three different flow-rates for a beam size of 0.05 mm X 0.05 mm.



Supporting Information S6. SEM images of the gold structures formed after 3 h and 7 h showing intermediate structures.



Supporting Information S7. SEM image of the Au_xS_y ⁻ structures formed after 9 h before NaBH₄ reduction.



Supporting Information S8. SEM image of the gold hemispherical structures with a smaller size formed at 12 ml/h flow rate.



Supporting Information S9. Au L₃-edge XANES spectra of the chip coated with precursors, after NaBH₄ reduction and after catalysis: (a) Gold sulfide powder reference, (b) before NaBH₄ reduction: experimental data (—), linear combination fitting (---), (c) after NaBH₄ reduction: experimental data (—), linear combination fitting (---), (d) after catalysis: experimental data (—), linear combination fitting (---), (e) bulk gold as gold foil reference.



Supporting Information S10. Photograph of the chip after 9 h flow-time and reduced with NaBH₄.



Supporting Information S11. EDS spectra (EDAX) of the gold structures formed for 9 h duration after $NaBH_4$ reduction showing the presence of Au and S. The sulfur peak was overlapped by the Au peak.



Supporting Information S12. Flow-rate dependent catalysis of the gold structures formed with a flow-time of 9 h. The UV-Vis spectra indicating phenolate ion conversion at four different flow-rates with highest conversion taking place at the lowest flow-rate of 5 ml/h.

Ferricyanide to ferrocyanide conversion reaction:

$$BH_4^- + 8 [Fe(CN)_6]^{3-} + 3H_2O \longrightarrow H_2BO_3^- + 8[Fe(CN)_6]^{4-} + 8H^+$$



Supporting Information S13 (A). UV-Vis spectra of (a) ferricyanide and ferrocyanide (b) Conversion of ferricyanide to ferrocyanide in a millifluidic chip reactor with and without gold. The partial conversion observed for chip without gold was due to the presence of NaBH₄.



Supporting Information S13 (B). Flow-rate dependent catalysis of the gold structures formed with a flow-time of 9 h. The UV-Vis spectra indicating ferricyanide conversion at four different flow-rates with highest conversion taking place at the lowest flow-rate of 5 ml/h.