

Supporting information for

Spatially Controlled Reduction and Growth of Silver in Hollow Gold Nanoshell Particles

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Materials

Sodium citrate tribasic dehydrate (99%), gold (III) chloride trihydrate (99.9%), silver nitrate (99%), Hydrochloric acid (37%), Sodium borohydride (98%), Hydroxylamine hydrochloride (98.0%), sodium hydroxide and nitric acid were purchased from Sigma Aldrich, Singapore. All glassware used was cleaned in a bath of freshly prepared aqua regia solution, and then rinsed thoroughly with Milli-Q water before use.

Synthesis of gold nanoshell

The AuNS particles were synthesized via a template method, where the AgNPs served as template modified from previous procedures.¹ In a typical synthesis, AgNPs were first synthesized by reducing AgNO₃. 50 μ L sodium citrate solution (1 M, 50 μ L) was added to AgNO₃ (0.2 mM, 50 mL) at 60 °C. After 5 minutes, NaBH₄ (100 mM, 1 mL) was injected into the solution. The solution was stirred for 2 hours at 60°C and allowed to cool down to room temperature. Galvanic replacement of Ag by Au occurs at room temperature. A 200 mM NH₂OH.HCl solution (1 mL) was added to as prepared AgNPs (47 mL) followed by AgNO₃ (0.1 M, 141 μ L) 5 min later to minimize the formation of AuNPs.² The solution was kept for 2 hours to allow for the reaction to complete. At 60 °C, HAuCl₄ (25 mM, 713 μ L) was added dropwise to the solution under magnetic stirring at 500 rpm. The reactions was stopped after 2 hours by lowering the temperature to 25 °C.

Reduction of silver in gold nanoshell

The reduction of Ag^+ was initiated by increasing the pH of AuNS suspension. In a first time, the pH of suspension was adjusted with NaOH (0.1 M) from pH 3.8 (initial pH) to pH 8.1. In a second set of experiments a silver nitrate solution was added dropwise to final concentration of 0.16 mM and 0.32 mM, respectively. After reaching the final concentration we adjusted the pH of the AuNS suspension to 8.1 by adding NaOH (0.1 M) under magnetic stirring at 500 rpm. AuNS suspensions were kept in amber glassware and stored in the refrigerator at 4 °C.

Reaction in the dark and with laser and white light

The reactions in the dark were performed using Eppendorf tubes wrapped in aluminum foil. The dark control was left to stand in a dark room, while the experiments done under white light and laser control were conducted by illuminating the tubes with white LED light and with a 633 nm HeNe laser with an output power of 20 mW, respectively.

Characterization: UV/Vis, DLS, Zeta potential, TEM, STEM elemental mapping

The UV/Vis absorption spectra of all the samples are measured using Lambda 35 (Perkin Elmer) or Cary 50 (Varian) spectrophotometer. Dynamic light scattering (DLS), and zeta potential (ELS) measurements were performed using Litesizer™ 500 apparatus (Anton Paar) equipped with a 658 nm laser operating at 40 mW. The backscattered light collection angle was set at 90°. The zeta potential cuvette has a Ω -shaped capillary tube cuvette with an applied potential of 150 V. The same suspensions were used for DLS and ELS

measurements. Each sample was analyzed in triplicate and each measurement was an average of three 30 s runs. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100 plus LaB6 (JEOL, Japan) microscope with an acceleration voltage of 200 kV and an Orius 4 K CDD camera (Gatan; USA). STEM mode was used to perform elemental mapping of the two metals (lines: Au-L and Ag-L). Energy-dispersive X-ray (EDX) analysis was realized with an 80 mm² SDD detector (Oxford Instrument) and was treated with Aztec software. The samples were prepared by dropping a dilute suspension onto the carbon-coated copper grids and dried at room temperature before imaging. Size distribution was established by counting a minimum of 400 particles for TEM and was determined using ImageJ Software.

Size distribution and surface charge

The size and surface charges of all the AuNS particles are characterized by DLS, and zeta potential, and the data are shown in Figure S1.

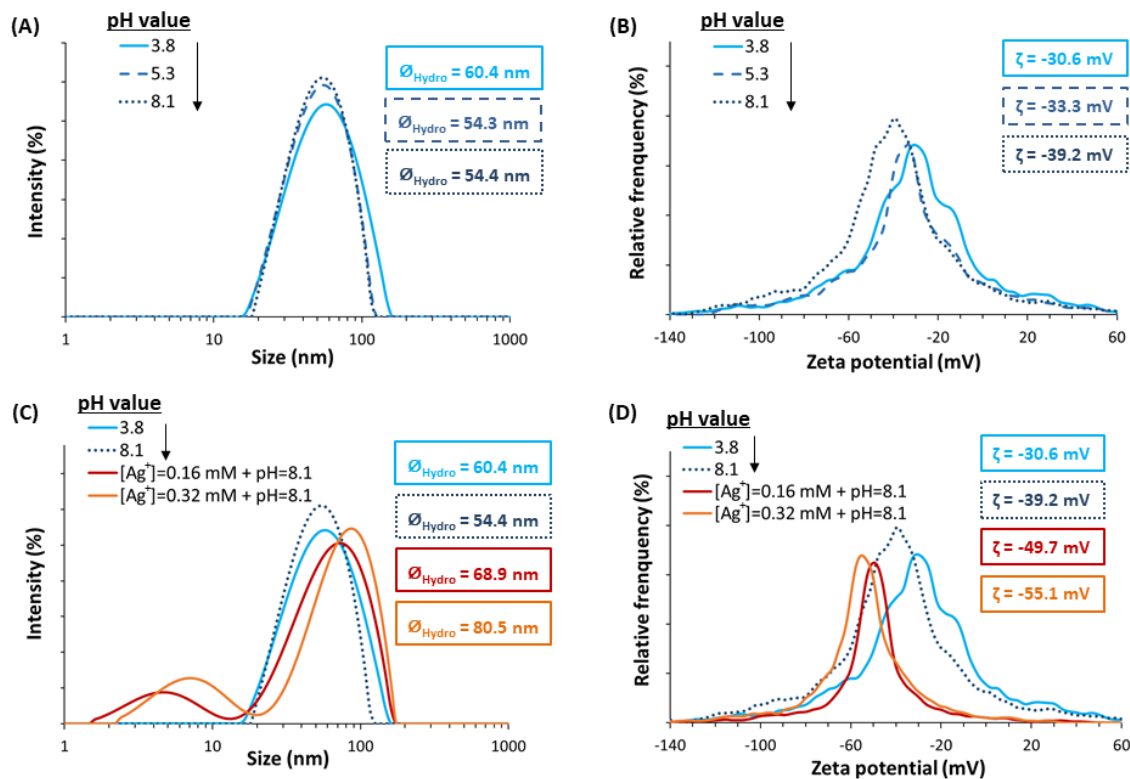


Figure S1. (A) Dynamic light scattering (DLS), and (B) zeta potential (ELS) measurements at different pH: pH 3.8, pH 5.3 and pH 8.1. (C) Dynamic light scattering (DLS), and (D) zeta potential (ELS) measurements at pH 8.1 after adding the silver nitrate ($[\text{Ag}^+] = 0.16 \text{ mM}$ and $[\text{Ag}^+] = 0.32 \text{ mM}$) in suspension at pH 3.8.

AuNS composition

The composition of all the AuNS particles are locally characterized by EDX, and the EDX readings are shown along with images in Figure S2.

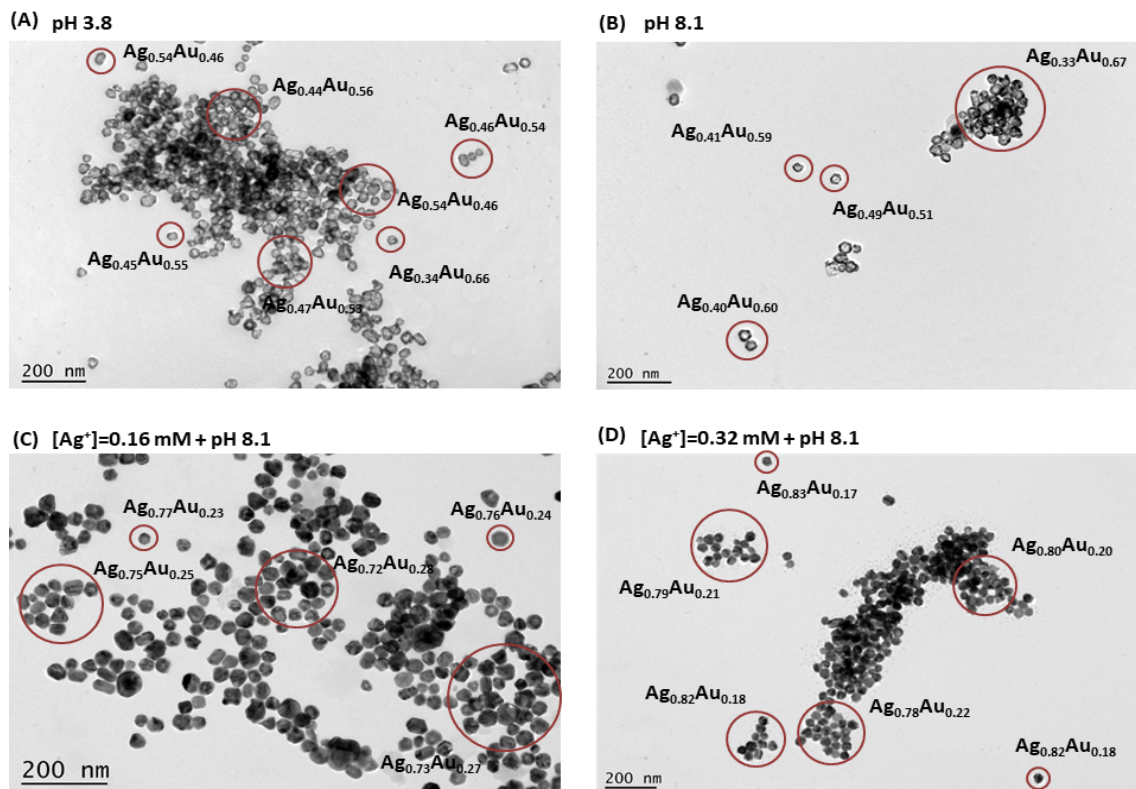


Figure S2. TEM images with energy-dispersive X-ray (EDX) analysis at (A) pH 3.8, (B) pH 8.1 and (C-D) after adding the silver nitrate ($[\text{Ag}^+] = 0.16 \text{ mM}$ and $[\text{Ag}^+] = 0.32 \text{ mM}$, respectively) to the suspension at pH 3.8 and then, raising the pH until pH 8.1.

pH-dependent kinetics

The kinetics of reaction for a sample whose pH was raised to 5.3 was slower than that of sample at pH 7, cf Figure 2C. The sample at pH 5.3 eventually ended up at the same chemical state as the one at pH 8. A sample kept at pH 3.6 and stored overnight did not show any shift in peak position.

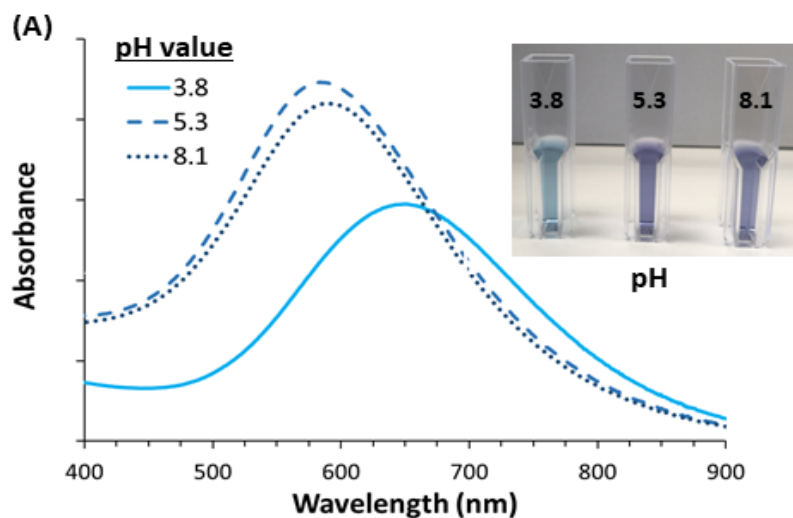


Figure S3. (A) Absorbance spectra of AuNS in pH 3.8, pH 5.3 and pH 8.1 realized 24 h after adjusting the pH of the suspension with NaOH (0.1 M) from pH 3.8 to pH 8.1. (B)

Reversibility

We tested whether the optical response of the huge blue shift is reversible by lowering the pH value with HNO_3 . Specifically, the pH of suspension was decreased by adding HNO_3 (0.1 M) drop by drop until the pH reaches the initial pH value ~ 3.8 . UV-Vis spectra of suspension were recorded after 24 hr incubation. The absorption spectra did not change significantly. Peak position shows slightly red shift of < 7 nm. Compared to the 76 nm blue shift induced by Ag deposition, this small amount of red shift is more likely due to changes in refractive indices.

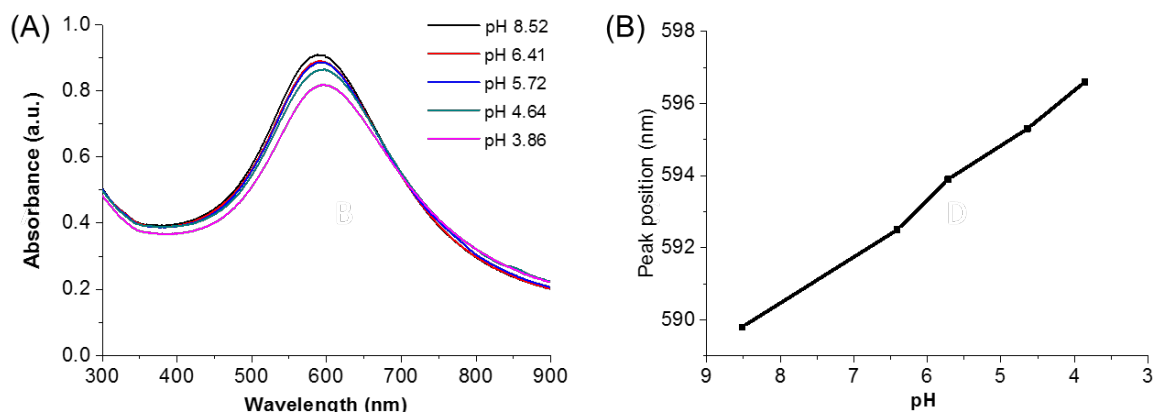


Figure S4. (A) Absorbance spectra of the AuNS particles shown in Figure 2B measured by lowering pH values to 3.86. (B) Summary of peak position of the spectra at pH values from 8.52 to 3.86.

Ascorbic Acid

Alternatively, the reduction of Ag^+ can also be triggered by ascorbic acid, a stronger reducing agent than citrate.³ Figure S5 shows the evolution of absorption spectra in 10 min after adding 1 mM ascorbic acid (pH 3.5). The same trends in peak shift and intensity change are observed as that of increasing the pH of sodium citrate.

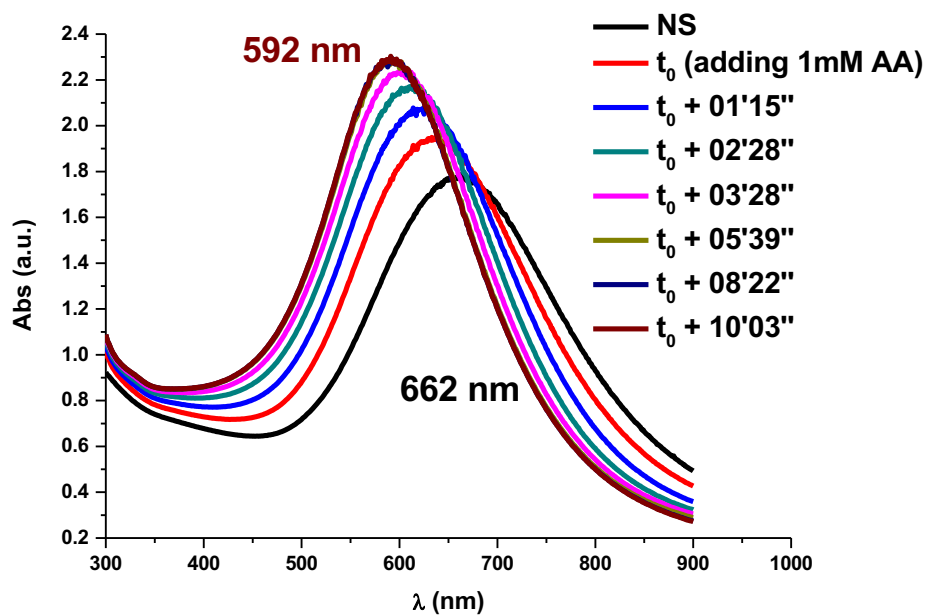


Figure S5. Absorption spectra of AuNS solution after adding 1 mM ascorbic acid with time.

Reference

- (1) Piñero, S.; Camero, S.; Blanco, S. In *Journal of Physics: Conference Series*; IOP Publishing: 2017; Vol. 786, p 012020.
- (2) Ma, Y.; Liang, X.; Tong, S.; Bao, G.; Ren, Q.; Dai, Z. *Adv. Func. Mater.* **2013**, 23, 815.