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High yield synthesis and surface chemistry exchange of small gold hexagonal nanoprisms

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Experimental Section

Chemicals: Cetyltrimethylammonium chloride solution (CTAC, 25% w/w in H_2O), hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$, ≥49% gold basis), sodium iodide (NaI, ≥99.5%, ACS reagent), hydroquinone ($C_6H_6O_2$, ≥99.5%), sodium borohydride ($NaBH_4$, 99%) and poly(vinylpyrrolidone) (PVP, 10, 55, and 360 kDa) were purchased from Sigma-Aldrich. PVP standard (5 kDa) was acquired from American Polymer Standards Corporation. All solutions were freshly prepared before use except for $HAuCl_4$ (stored at 4 °C) and CTAC solutions (100 mM, stored at 28 °C).

Seed-mediated synthesis of gold hexagonal nanoprisms (AuHNPs)

Seed solution. The seed solution was prepared by following the procedure reported by Scarabelli *et al.*[1] First, 25 μL of $HAuCl_4$ (50 mM) was mixed with 4.7 mL of CTAC aqueous solution (100 mM) in a 25 mL vial. Then, 300 μL of $NaBH_4$ (10 mM, ice cold) was injected quickly under vigorous stirring (1000 rpm). The seed solution was aged for 2 h at 25°C and it was diluted 10x in 100 mM CTAC before use.

Growth solutions. Two growth solutions (GS) were prepared GS 1 and GS 2. For GS 1, 1.6 mL of CTAC solution (100 mM) was added to 8 mL of Milli-Q water in a 50 mL Erlenmeyer flask. To this mixture, 40 μL of $HAuCl_4$ (50 mM) was added followed by 15 μL of NaI solution (10 mM). This GS 1 was utilized for the overgrown step of the diluted seed solution. For GS 2, 500 μL of $HAuCl_4$ (50 mM) was mixed with 40 mL of CTAC solution (50 mM) in a 125 mL Erlenmeyer flask followed by 350, 400, 450 or 500 μL of NaI solution (10 mM). Next, 400 μL and 2.5 mL of hydroquinone (100 mM) were added to GS 1 and 2, respectively. The growth solutions were hand-stirred until clear colorless solutions were obtained. Lastly, 150, 200, 250 or

300 μL of diluted seed solution was injected to GS 1 and hand-stirred for 2-3 seconds. Immediately, 3.2 mL of this solution was added to GS 2 and hand-stirred for 10 s. The second growth solution turned red-pink and violet-purple during the first 3-5 minutes of synthesis. The reaction mixture was kept at 25°C for 2 h.

Purification. The mixture was centrifuged once at 8000 rpm for 15 min (50 mL centrifuge tube) and the pellet was redispersed in 4-5 mL of Milli-Q water in a 15 mL centrifuge tube. Then, a certain volume of CTAC 25% w/w was added to the centrifuge tube to precipitate the AuHNPs by depletion flocculation. The final concentration of CTAC varies from 0.06 to 0.35 M and depends on the size of the AuHNPs estimated by the SPR band position. Large AuHNPs require less concentration of surfactant to flocculate. After 16 h at 25°C, the supernatant was removed and the pellet of AuHNPs was redispersed in 10 mM CTAC. For TEM analysis, the sample was purified by one round of centrifugation at 6000 rpm for 15 min.

Synthesis of AuHNPs with PVP of different molecular weights: The growth solutions GS 1 and 2 were prepared as described above. Initially, specific volumes of 0.2 mg/mL 10 kDa PVP were added to GS 2 after 15 min of reaction to achieve 0.1-0.5 μg/mL. Then, stock solutions of 0.2 mg/mL PVP (5, 10, 55, and 360 kDa) were prepared and each molecular weight of PVP was added to GS 2 during the growth reaction (15 min) to obtain 0.05 μg/mL as the final concentration of the additive. The purification step for AuHNPs was performed as mentioned above.

Functionalization of AuHNPs with MUTAB: The biggest aspect ratio nanoprisms synthesized with and without 10PVP were utilized for the ligand exchange reaction with 11-mercaptoundecyltrimethylammonium bromide (MUTAB). The nanoprisms surface area was between 9,700 and 10,300 nm^2 (edge length 73-81 nm). AuHNPs solution (1.5 mL) was

centrifuged once at 6000 rpm for 15 min and the pellet was redispersed in 1.5 mL of Milli-Q water in a 2 mL centrifuge tube. Next, 75 μL of 10 mM MUTAB was added to the solution to achieve 0.5 mM and the tube was placed in the rocking platform for 1 day. MUTAB coated AuHNPs were purified twice by centrifugation at 6000 rpm for 15 min and redispersed in 1.5 mL of Milli-Q water.

Instrumentation: UV-Vis spectra were measured with an Evolution 220 UV-Vis spectrophotometer (Thermo Fisher Scientific). Transmission electron microscopy (TEM) was performed with a JEOL 1230 or a JEOL 2100 Field Emission Gun (JEOL) instrument operating at 80 and 200 kV, respectively. Scanning electron microscopy (SEM) images were acquired on an FEI ESEM operating at 15 kV. AuHNPs size distribution calculations (200 hexagonal nanoprisms) were obtained using ImageJ (National Institutes of Health). Zeta potential values were collected by a Zen 3600 Zetasizer instrument (Malvern) on DTS1070 folded capillary zeta cells. The AuHNPs control and functionalized samples were centrifuged and diluted with Milli-Q water before each triplicate measurement.

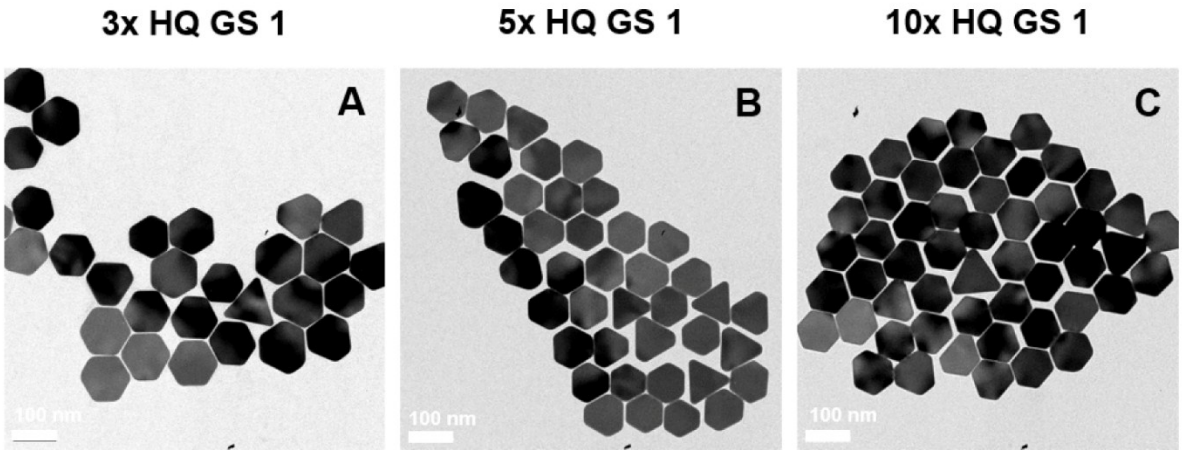

Fig. S1 TEM images of AuHNPs synthesized with (A) 3x, (B) 5x and (C) 10x = 2 mM HQ in GS 1 for 10x = 6 mM HQ in GS 2 for 150 µL seeds. Scale bars are 100 nm.

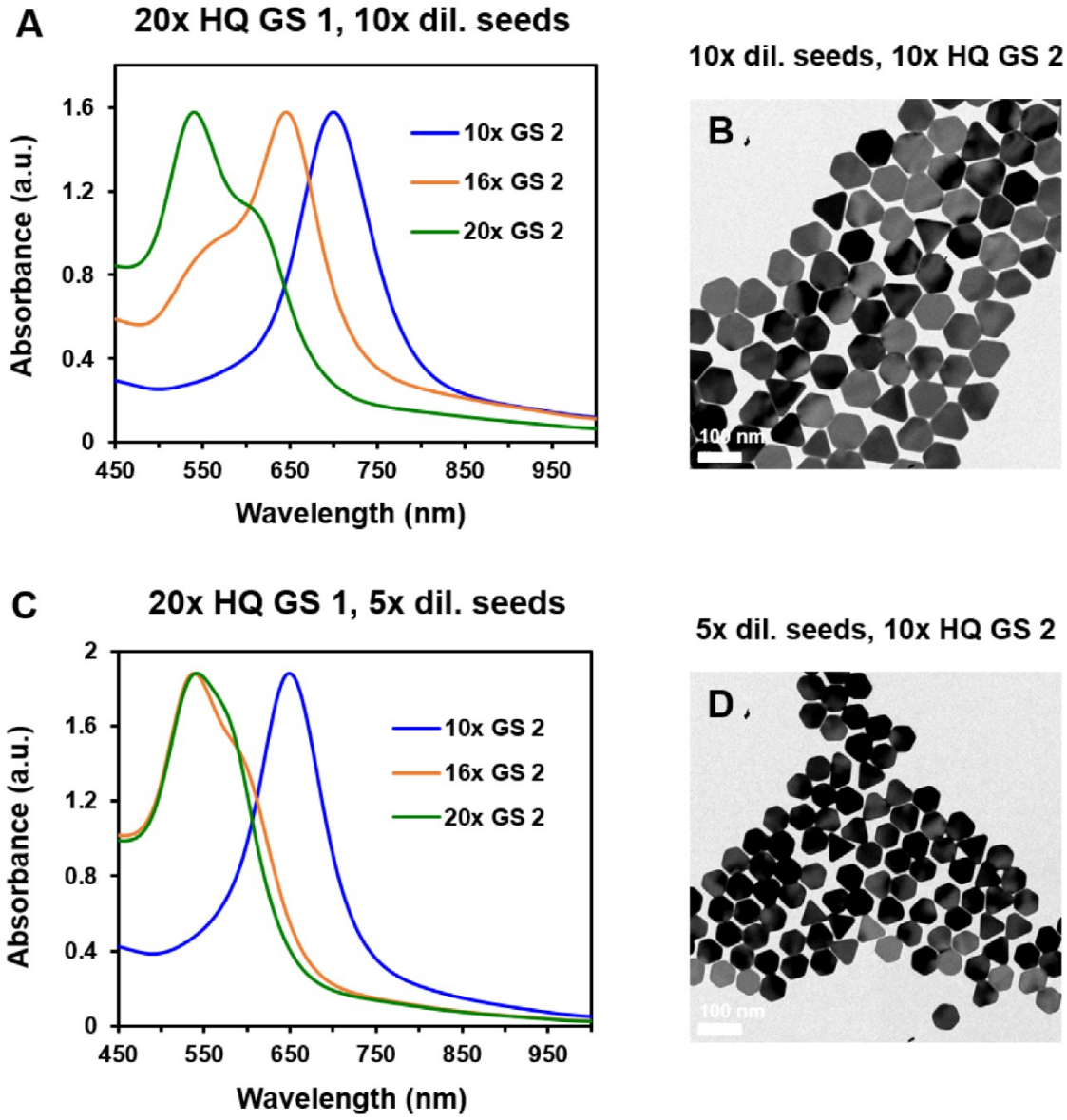

Fig. S2 Normalized UV-Vis spectra of AuHNPs synthesized with distinct amounts of HQ in GS 2 with 20x HQ in GS 1 for (A) 10x diluted seeds and (C) 5x diluted seeds. TEM images of AuHNPs for 10x HQ in GS 2 with (B) 10x diluted seeds and (D) 5x diluted seeds. Scale bars are 100 nm.

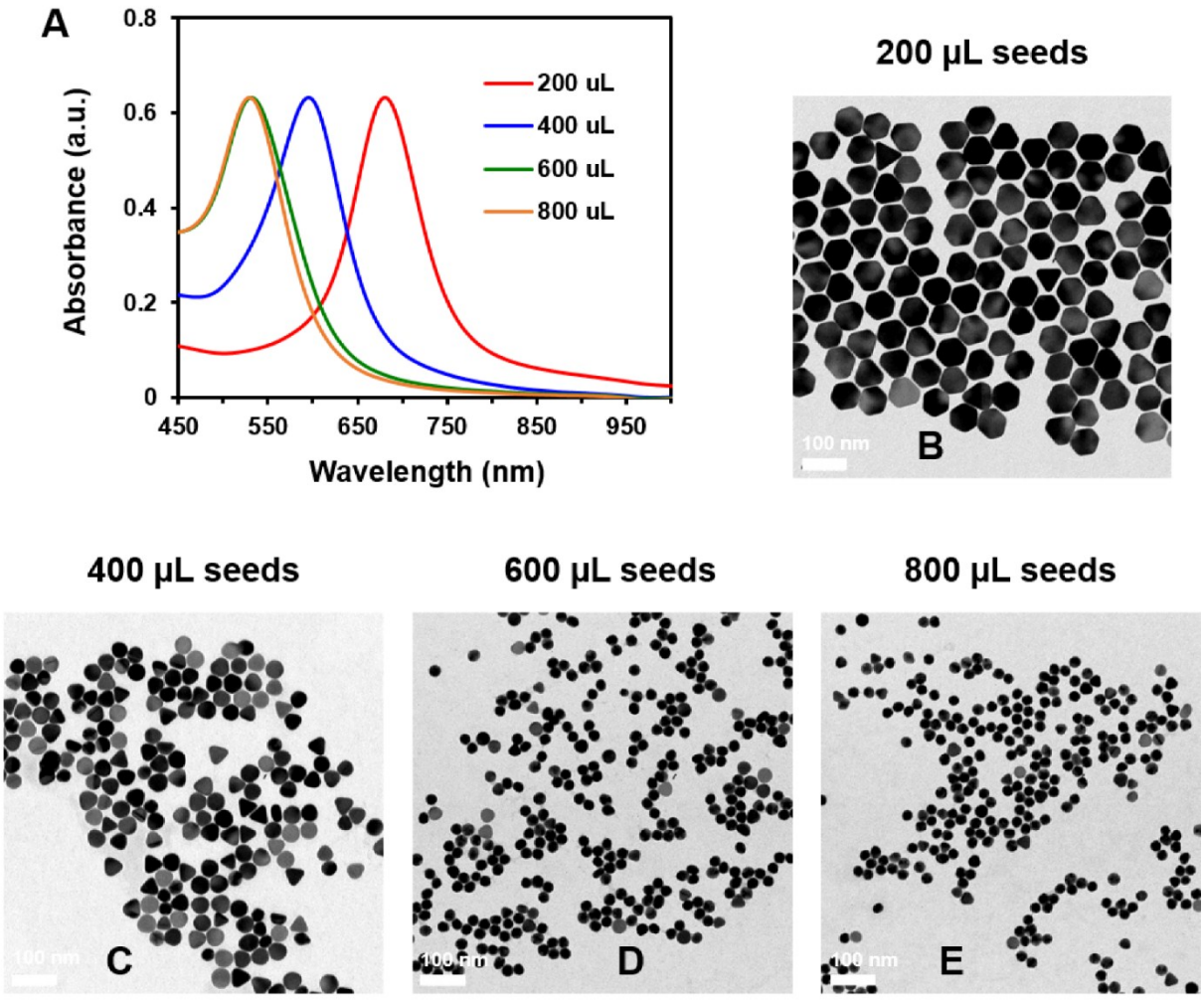

Fig. S3 (A) Normalized UV-Vis spectra of AuHNPs synthesized with distinct volumes of 10x diluted seeds (200-800 µL) added to GS 1 for 20x HQ in GS 1 and 10x HQ in GS 2. TEM images of AuHNPs for (B) 200 µL, (C) 400 µL, (D) 600 µL and (E) 800 µL seeds. Scale bars are 100 nm.

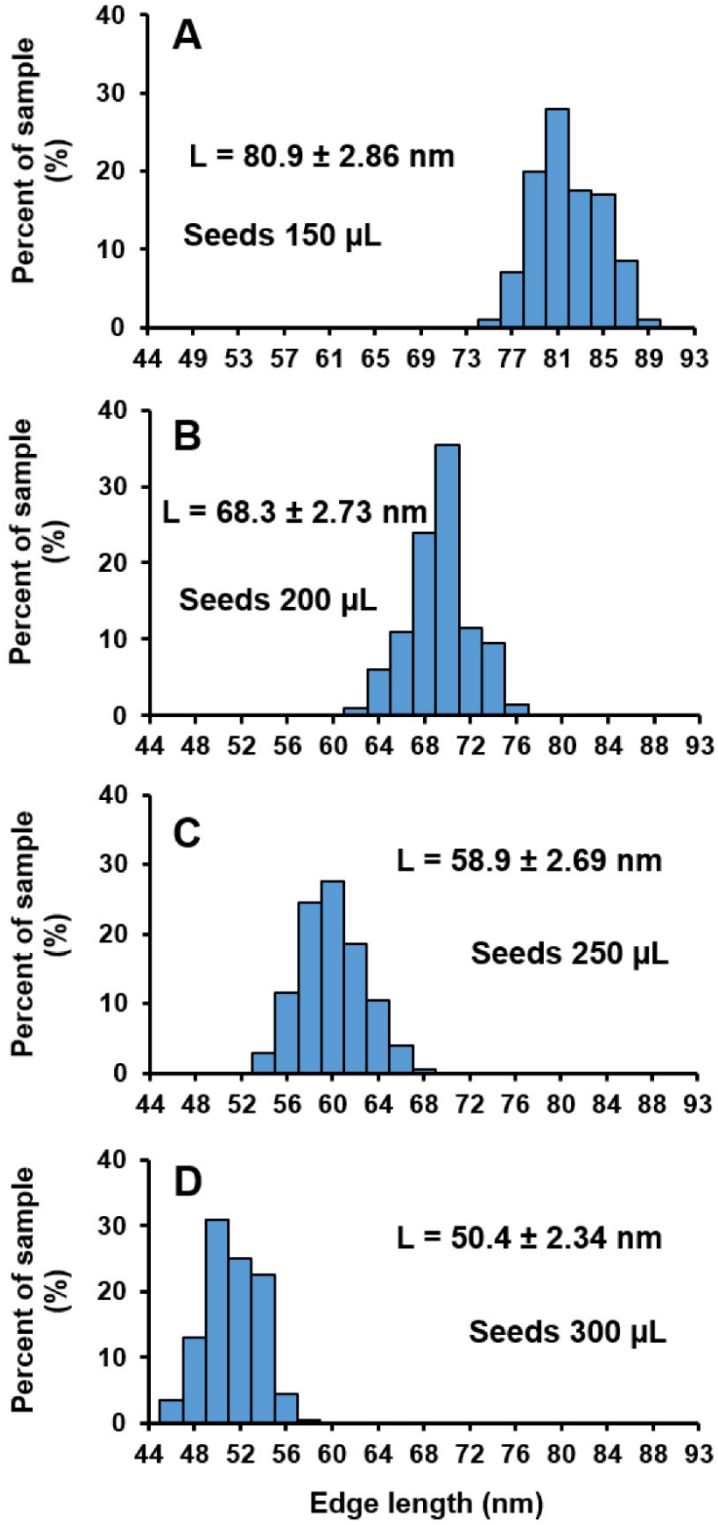

Fig. S4 Histograms of edge length (L) distribution of AuHNPs for syntheses with (A) 150 µL, (B) 200 µL, (C) 250 µL and (C) 300 µL seeds added to GS 1.

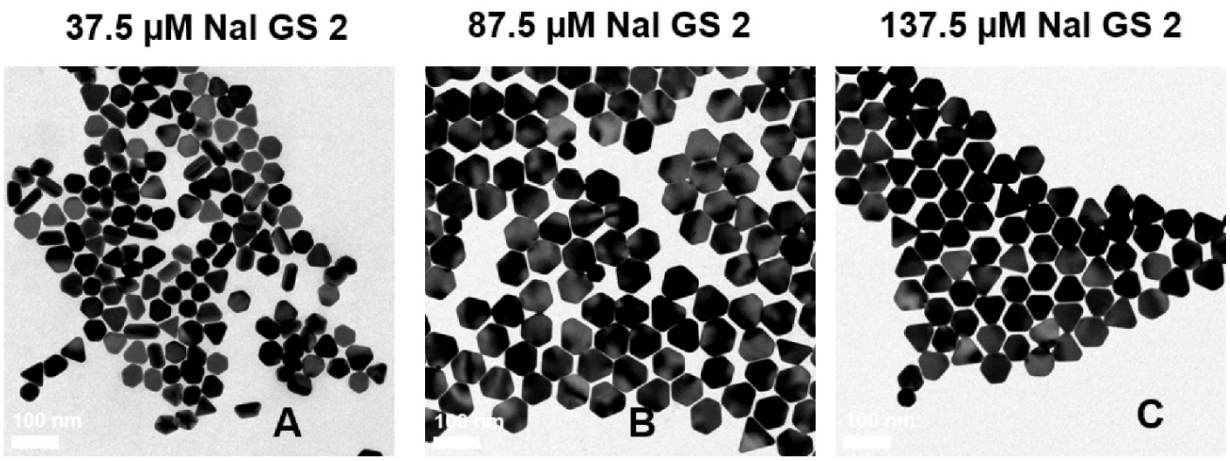

Fig. S5 TEM images of AuHNPs synthesized with (A) 37.5 µM, (B) 87.5 µM and (C) 137.5 µM NaI added to GS 2 for 150 µL seeds. Scale bars are 100 nm.

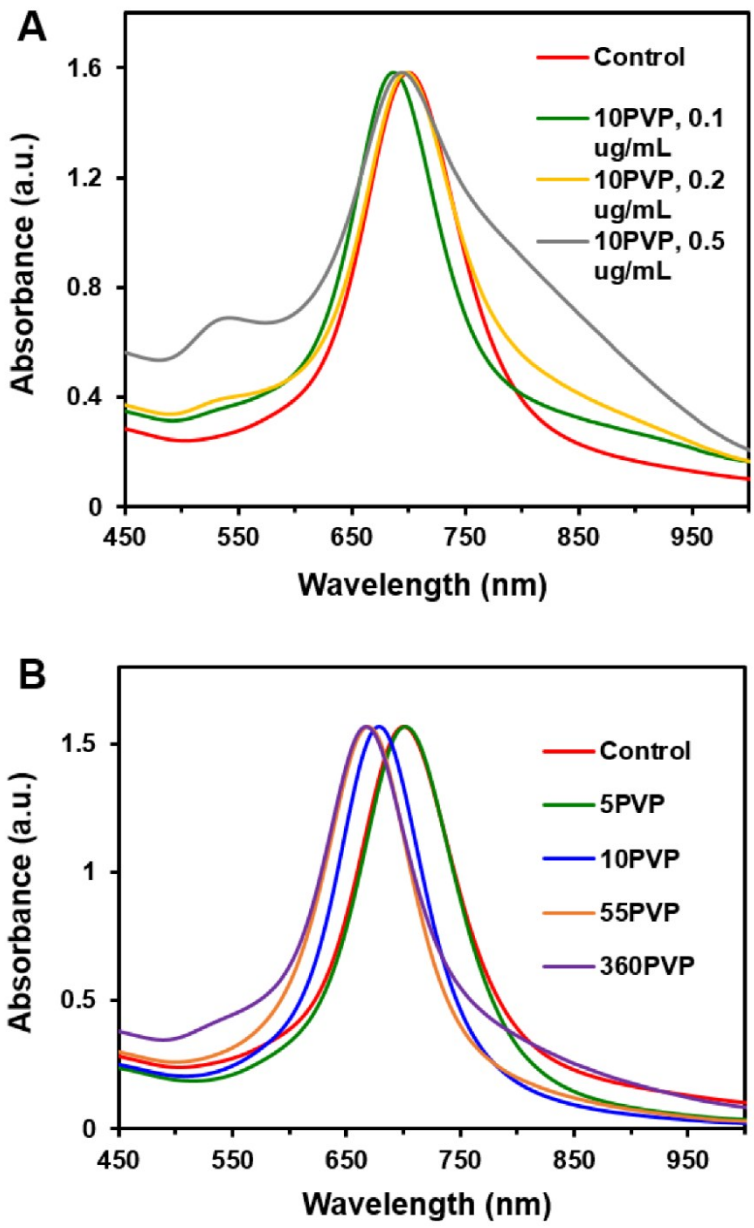

Fig. S6 Normalized UV-Vis spectra of AuHNPs synthesized without and with PVP for 150 µL seeds. (A) Distinct concentrations of 10PVP (0.1-0.5 µg/mL) and (B) different molecular weights of PVP (0.05 µg/mL) added at 15 min of growth (GS 2).

Table S1 AuHNPs size characterization (nm) for n=35 and Zeta potential values for AuHNPs (150 µL seeds) control and sample with 0.05 µg/mL 10PVP before and after surface functionalization with MUTAB (*P<0.05, **P<0.01).

Sample	Control	With 10PVP
Size characterization (nm)		
Thickness	15.1 ± 0.76	12.7 ± 0.75*
Side length	38.8 ± 3.30	36.7 ± 2.88
Volume x 10^3 (nm^3)	59 ± 4.0	44 ± 3.0**
Zeta potential values (mV)		
CTAC	46.7 ± 1.00	44.7 ± 0.82
MUTAB	46.3 ± 2.77	61.2 ± 0.53**

Table S2 Thickness, side length and volume of AuHNPs control and sample with 10PVP for different amounts of seeds (200-300 µL). Vertically aligned AuHNPs (n=35) were analyzed from TEM images.

Volume of seeds (µL)	200	250	300
Thickness-Control (nm)	15.0 ± 1.67	13.1 ± 0.75	13.4 ± 0.47
Thickness-*10PVP (nm)	13.3 ± 1.10	13.7 ± 0.51	13.2 ± 0.86
Side length (nm)	34.4 ± 2.25	29.9 ± 1.69	22.9 ± 1.51
*Side length (nm)	32.3 ± 1.57	29.3 ± 1.41	22.7 ± 1.16
Volume x 10^3 (nm^3)	46 ± 4.0	30 ± 1.7	18 ± 0.9
*Volume x 10^3 (nm^3)	36 ± 2.4	30 ± 1.3	18 ± 0.8

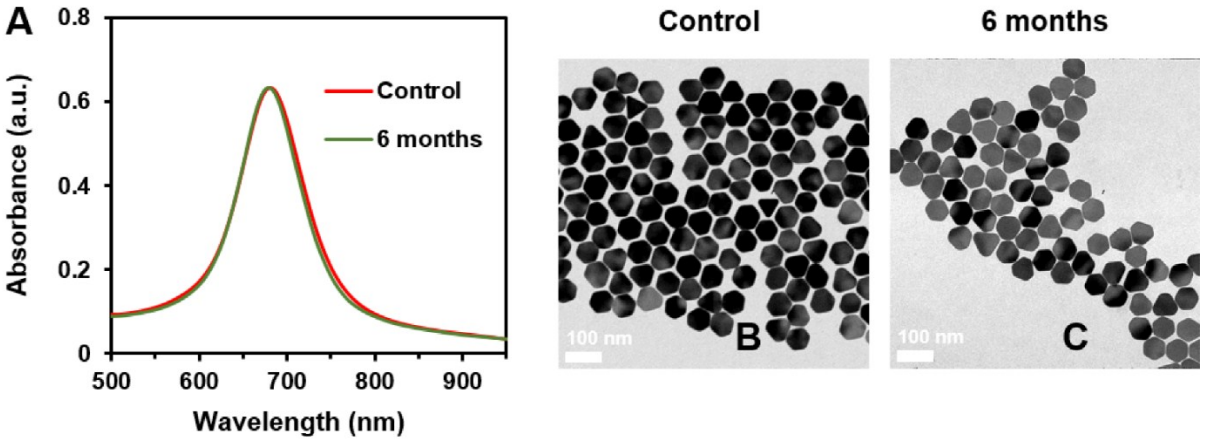

Fig. S7 Comparison of normalized UV-Vis spectra of AuHNPs prepared with 200 μL seeds and 10PVP immediately after the synthesis and after 6 months of storage (A). TEM images of AuHNPs (B) after the synthesis and (C) after 6 months of shelf-life. Scale bars are 100 nm.