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Supporting Information

Efficient Preparation of Size Tunable PEGylated Gold Nanoparticles

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Experimental

Materials

ACS grade tannic acid and gold (III) chloride trihydrate (≥ 99.9% trace metal basis) were purchased from Sigma Aldrich. HPLC grade acetone and ACS grade hydrochloric acid (HCl) was obtained from Fisher Scientific. Phosphate buffered saline without Ca^{2+} and Mg^{2+} was obtained from Lonza. Water was purified by 0.2 μm filtration and four stage deionization to a resistivity of 17 MΩ or greater (NANOpure Diamond, Barnstead International, Dubuque, IA). Block copolymer, polystyrene-*b*-polyethylene oxide (PS1.6kDa-b-PEG5kDa), was from Polymer Source (Dorval, QC, CAN).

PEGylated Gold Nanoparticle Synthesis

FNP was performed using a hand-operated confined impinging jet mixer. The block copolymer and TA were dissolved in acetone, typically at 10 mg/mL and 20 mg/mL, respectively. The acetone stream was rapidly mixed against an aqueous stream containing $AuCl_4.3H_2O$ (2 mg/mL in 0.01M HCl)) and collected into various 4 mL aqueous baths: 0.01M HCl, deionized water, or PBS at pH 7.4. Residual organic solvent was removed by dialysis (Spectra/Por MWCO 6-8 kDa, Spectrum Laboratories, USA) against a 100-fold volume of water or buffer for 24 hours with 4 changes of the bath.

Nanoparticle Characterization

Nanoparticle size distributions and zeta potentials were measured using a Zetasizer Nano-ZS (Malvern Instruments, Malvern, UK) with a backscatter detection angle of 173°. Distributions are reported using the normal resolution mode intensity weighted distribution (average of 4 measurements). Zeta potentials of dialyzed nanoparticle samples in water and dilute PBS were measured in triplicate in a disposable folded capillary cell. TEM samples were prepared by

placing 5 μL of the nanoparticle dispersion on a grid (Ted Pella, Inc., Redding, CA 01824) and dried under ambient conditions. The samples were imaged using a Philips CM100 TEM (Eindhoven, The Netherlands) with an accelerating voltage of 100 kV. The average size and standard deviation of the encapsulated gold nanoparticle were determined by measuring the diameter of 100 particles using ImageJ software (NIH). UV absorbance spectra between 450 and 800 nm of the dispersions were collected at room temperature with an Evolution 300 UV-visible spectrophotometer (Thermo Electron Corporation, Madison, WI, USA). ^{1}H NMR spectra were recorded in D_2O using a Bruker Avance-III 500 MHz (Bruker Biosciences, Inc. Billerica, MA).

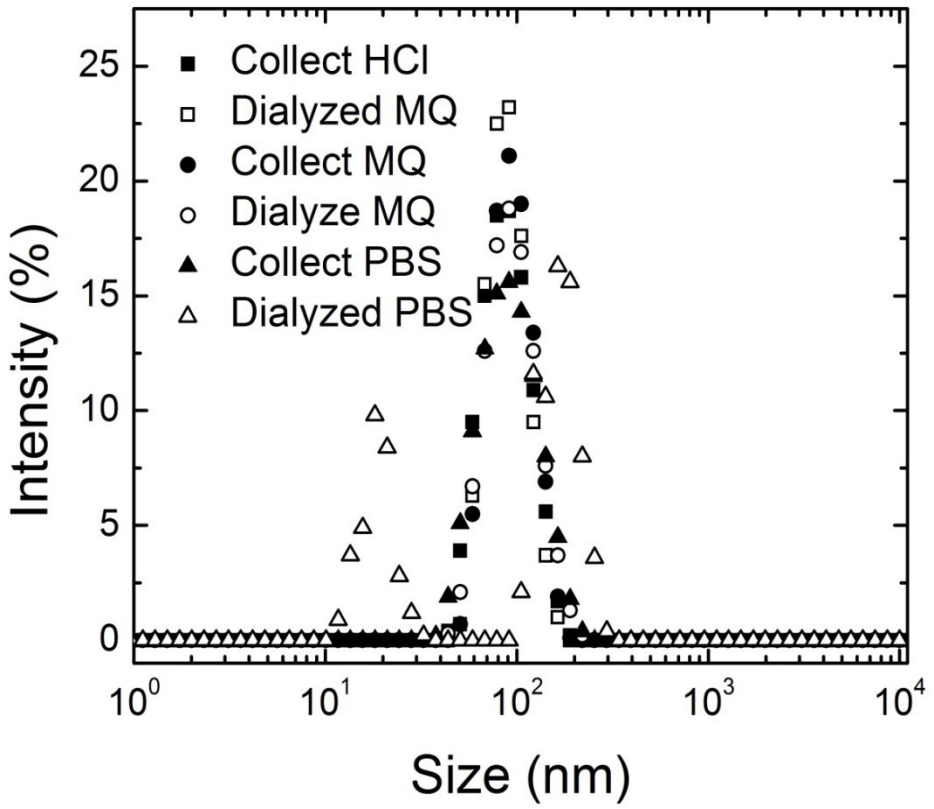

Figure S.1. Nanoparticle size distributions of TA produced at pHs between 2 and 7.4 (HCl, water (MQ), or PBS buffer) immediately after mixing and after dialysis measured by DLS.

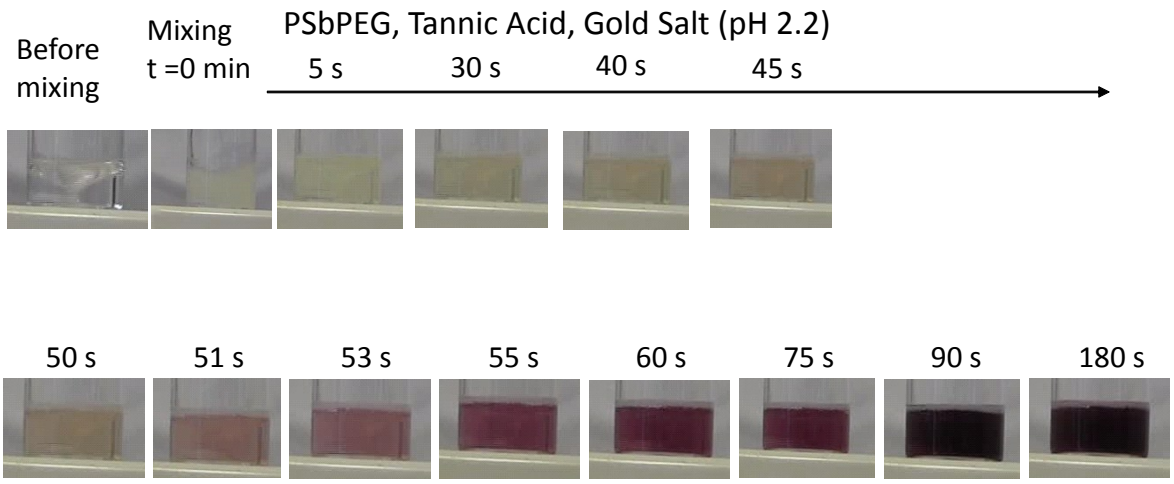

Figure S2. Representative images from video analysis of gold nanoparticle synthesis. The aqueous gold stream is initially at pH 2 and the reaction takes place at pH 3 (FNP with dilution in deionized water. At pH 2, the color evolution occurred over 7 minutes and at pH 6 the color evolution occurred over 20 seconds.

TEM Size Analysis

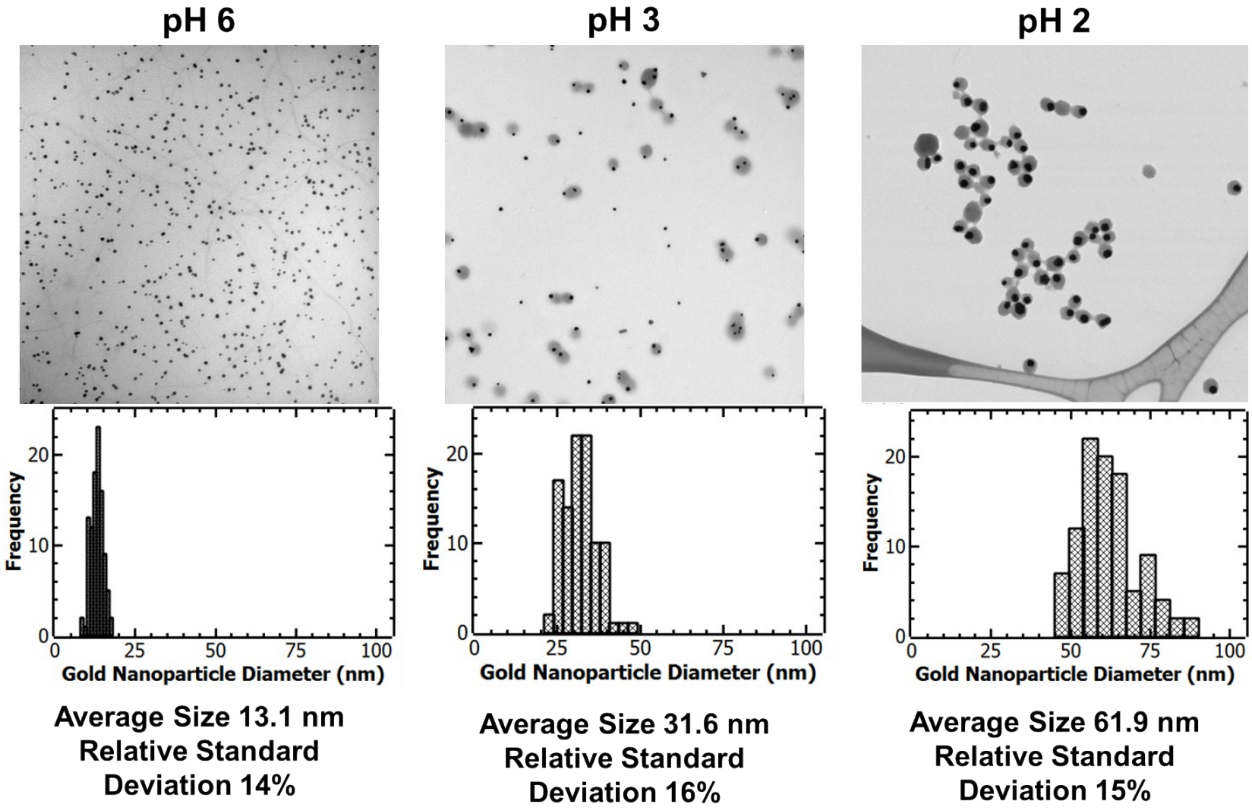

Figure S2. Representative low magnification TEM images to demonstrate gold particle uniformity. The relative standard deviation for gold nanoparticles synthesized at pH 2 and pH 6 are below 15% indicating monodisperse gold nanoparticles.

NMR Analysis

For NMR analysis, the solvent switched to D_2O for using Amicon Ultra-2 Centrifugal devices with a 50 kDa molecular weight cutoff (Millipore, Billerica, MA) according to the manufacturers specifications. ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were recorded in D_2O with 4,4-dimethyl-4-silapentane-1-sulfonic acid DSS as an internal standard (Cambridge Isotopes, Tewksbury, MA) using a Bruker Avance-III 500 MHz (Bruker Biosciences, Inc. Billerica, MA). Analysis with NMR demonstrates the presence of PEG and TA on the surface of the nanoparticle construct. The amount of PEG were estimated based on the internal standard DSS. The amount of TA was estimated based on a sample with a known concentration of TA and

internal standard DSS. Representative NMR spectra are included in Figure S.1. The broadening of the PEG peak in the case of the PSbPEG/TA/Au nanoparticles made using MQ as the collection bath may be due to PS-b-PEG associated with a gold nanoparticle and empty micelles of PS-b-PEG.

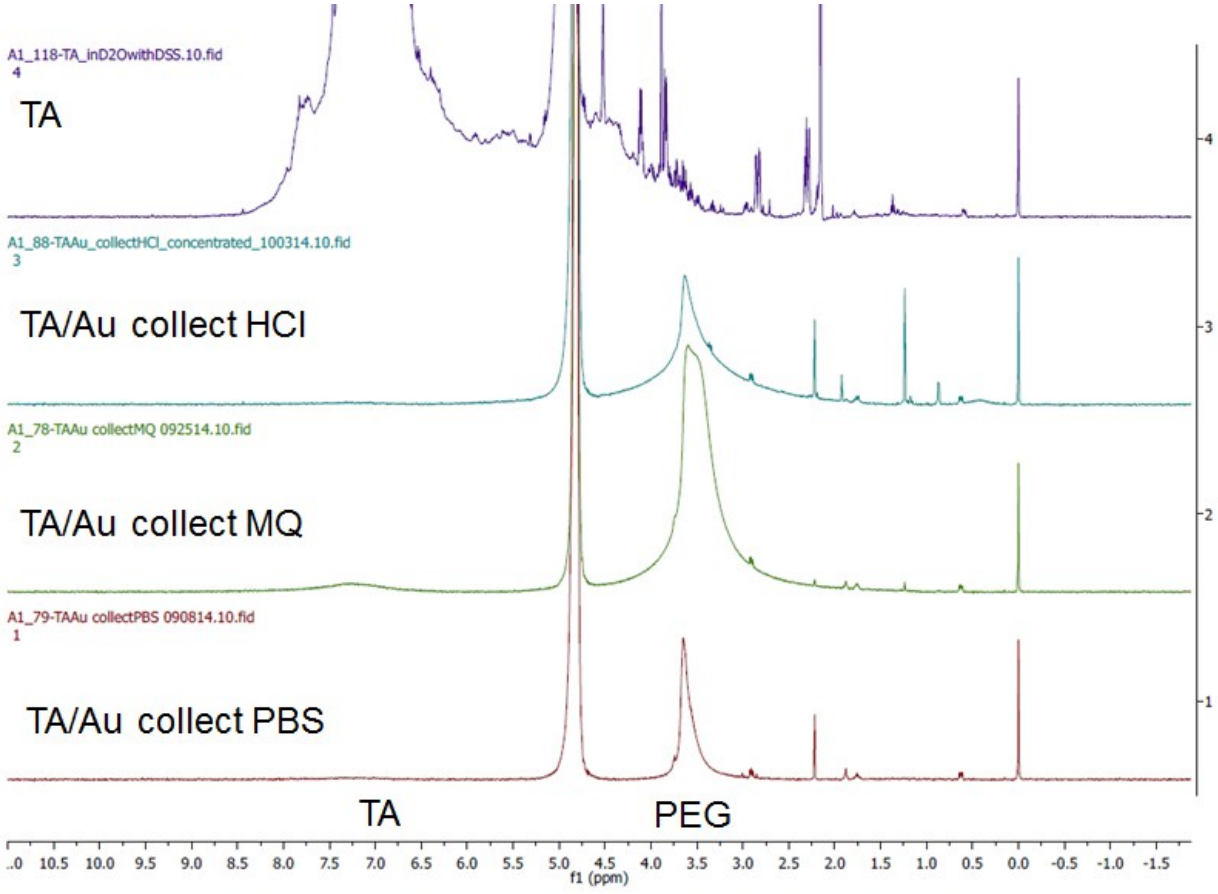

Figure S.3. 1H-NMR spectra of TA and PSbPEG/TA/Au nanoparticles dispersed in D2O using DSS as an internal standard.