

Supplementary information

Aqueous-phase synthesis of monodisperse plasmonic gold nanocrystals using shortened single-walled carbon nanotubes

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Experimental Details

Materials: All experiments were performed under ambient conditions. All water used was purified with an EASYpure® RF system (Barnstead, Dubuque, IA; 18.2 Ω). Highly pure HiPco® single-walled carbon nanotubes (SWNTs) were purchased from Carbon Nanotechnologies Inc. (Houston, TX). All other reagents (ACS grade) were purchased from Sigma-Aldrich (Milwaukee, WI).

SWNT sample preparation: The highly pure SWNTs were oxidized, dispersed, shortened, and rendered hydrophilic as described previously⁴ with initial concentration of 1 g/L under appropriate processing time. The SWNT size was controlled by altering the time duration for acid refluxing with sonication in the process: 12 h for highly shortened SWNTs and 3-5 h for a mixture of highly and moderately shortened SWNTs. The processed SWNTs were reconstituted in water in the absence of surfactants. Estimated with atomic force microscopy (AFM), the resultant SWNTs were well dispersed in water with average lengths and diameters of 29.7 (\pm 7.79) nm and 1.2 (\pm 0.19) nm for the highly shortened SWNTs and 59.3 nm (\pm 32.7 nm) and 1.1 (\pm 0.24) for the mixture of highly and moderately shortened SWNTs.

Synthesis of CNT-medicated gold nanoparticle (cGNP): In typical experiments, the reaction medium consisted of 2 mL of the CNT solution and 8 mL of an aqueous solution containing 0.2 mM HAuCl₄ with subsequent addition of 0.2 mL of 102 mM HAuCl₄ (final concentration of 2 mM). The incubation time for each step was 1 h at room temperature (23°C). The resultant products were harvested and washed three times with distilled water after centrifugation at 10,000 g for 5 min to remove the remaining reactants, *i.e.*, residual HAuCl₄ and SWNTs. The resultant hexagonal bipyramidal and triangular cGNPs were further purified by separating them through a simple size-exclusion filtering step using a commercial filtration unit (Millipore Ultrafree MC, VV 0.1 μ m).

Physicochemical characterization: The absorption spectra of samples were obtained using a DU-800 Ultraviolet/Visible/Near-infrared (UV/Vis/NIR) spectrophotometer (Beckman Coulter Inc., Fullerton, CA). Their PA/PT analyses were performed as described previously.^{3a}

The physical characteristics of the processed SWNTs and cGNPs were assessed using atomic force microscopy (AFM) and transmission electron microscopy (TEM). The AFM imaging was implemented with a Veeco Multimode Scanning Probe Microscope with Nanoscope IIIa Controller (Veeco Instruments, Woodbury, NY). The TEM analyses were conducted with FEI Titan 80-300 S/TEM fitted with an image corrector, an X-ray energy dispersive detector (EDAX) and a post-column energy filter (GIF from Gatan). For AFM analysis, samples were scanned in tapping mode in air. For example, the AFM analysis was started with loading 5 μ L of each sample solution on a mica substrate (Novascan, Ames, IA). The mixture with 5 μ L of water was used as a control. The loaded sample was treated with gentle N₂ blow to minimize watermarks after drying, which may cause unwanted noises in the AFM imaging. The AFM tip used was a NanoWorld Pointprobe® NCSTR AFM probe (NanoWorld AG, Neuchâtel, Switzerland), which is designed for soft tapping mode imaging and enables stable and accurate measurements with reduced tip-sample interaction, in order to obtain high-resolution AFM images. The sample scan rate was 1.0 Hz with an aspect ratio of 1:1. The force constant of the tip for scanning was 7.4 Nm⁻¹. The free resonance frequency of the cantilever was automatically tuned by the Nanoscope Software (version v5.30r3sr3; Veeco Instruments).

For TEM analyses, 1.5 μ L of each sample solution was deposited onto a 300 mesh Formvar-coated copper grid (Ted Pella, Redding, CA) except for the energy dispersive X-ray

(EDX) analysis. For EDX, a silicone nitride membrane (Ted Pella) was used to accurately assess the spectrum of SWNTs and their existence in cGNPs. No staining was used to alleviate any possibility of artifacts. After dehydration, the samples were examined using the aforementioned Titan TEM operating at 300 kV.

Particle size: The analyses of particle size and number in AFM images were carried out using the 'Particle Analysis' parameter in the Nanoscope Software. The numbers of particles used for the size analyses were 100 particles for all samples. Particle size analyses with TEM images were also conducted for the cGNPs using Scion Image Software (Alpha 4.0.3.2 version, Scion Corporation, Frederic, MD) as detailed in elsewhere.^{S1} The numbers of particles used for analyses were 75 particles for the size estimation.

Supporting References

S1. R. Sardar and J. S. Shumaker-Parry, *Nano Lett.* 2008, **8**, S1 (Supporting Information).

Supplementary Figures

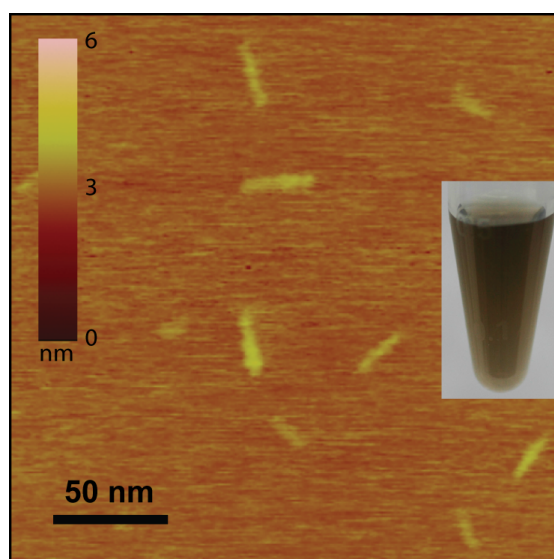


Fig. S1 Topographic AFM image of highly shortened, well-dispersed SWNTs in water. Inset: Photographic image of the processed SWNTs in water. The average length and diameter of the processed SWNTs are 29.7 ± 7.79 nm and 1.2 ± 0.19 nm, respectively.

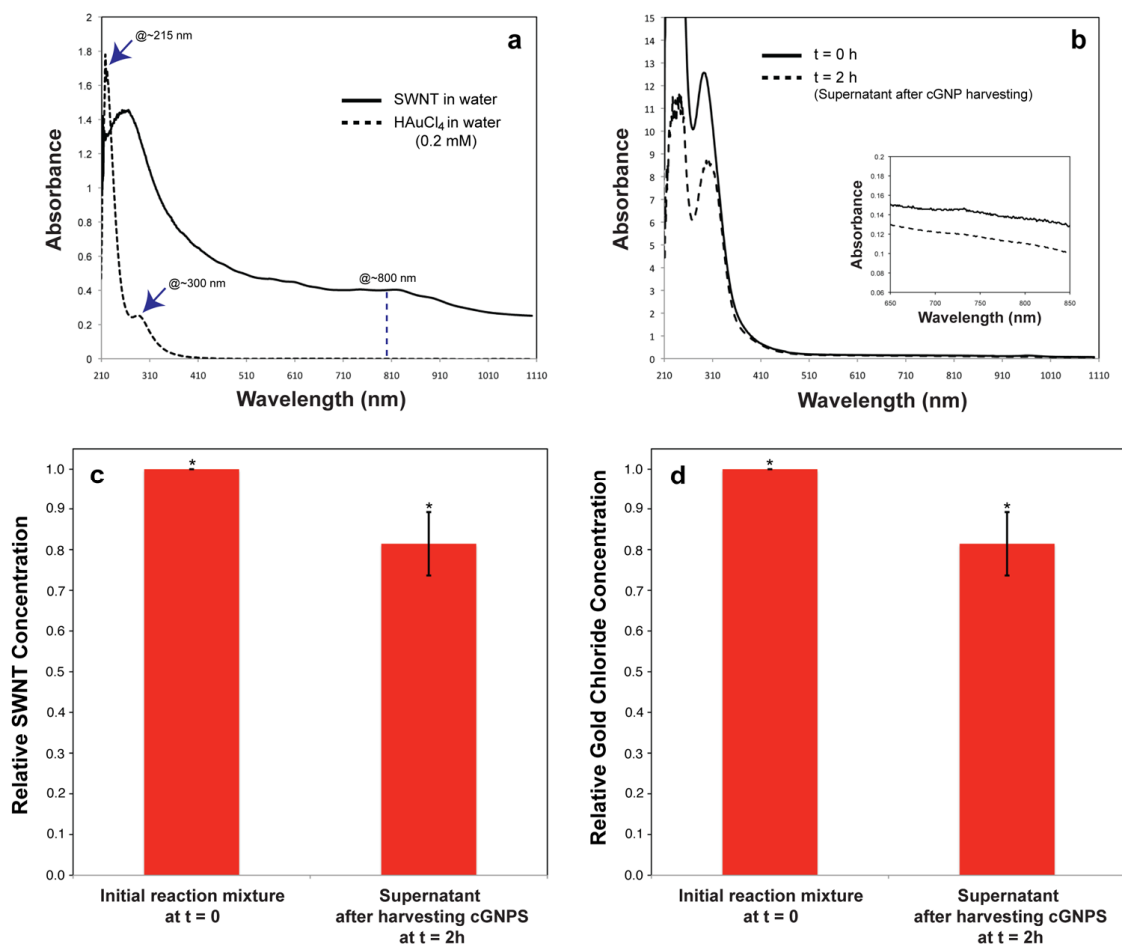


Fig. S2 Comparison of the concentrations of SWNTs and AuCl₄⁻ before and after cGNP synthesis. (a) Typical UV/Vis/NIR absorption spectra of highly shortened SWNTs in water and AuCl₄⁻ in water. The AuCl₄⁻ yielded two distinct peaks at ~215 nm and ~300 nm. (b) An example of UV/Vis/NIR spectra of the reaction mixture at t = 0 h and the supernatant after harvesting cGNPs at t = 2 h. (c) Comparison of SWNT concentration before (at t = 0 h) and after (at t = 2 h) SWNT-driven synthesis of cGNPs. The absorbance at 800 nm was compared between the reaction mixture at 0 h and the supernatant after harvesting cGNPs at 2 h (*i.e.*, no or little cGNPs in the supernatant). The wavelength of 800 nm was used because no or little absorbance of HAuCl₄, which is only other major reagent present in the two samples, occurs at the NIR wavelength as exemplified in Fig. S2a. The SWNT concentration was estimated on the basis of Beer's law using the measured absorbance at 800 nm and the SWNT's estimated molar extinction coefficient of $\sim 7.65 \times 10^6 \text{ M}^{-1}\text{cm}^{-1}$ at 800 nm. **P* < 0.05. (d) Comparison of AuCl₄⁻ concentration before (at t = 0 h) and after (at t = 2 h) SWNT-driven synthesis of cGNPs. The absorptions at 215 nm and 300 nm for the reaction mixture at 0 h and the supernatant after harvesting cGNPs at 2 h were used to estimate the changes in gold chloride concentrations. **P* < 0.05.

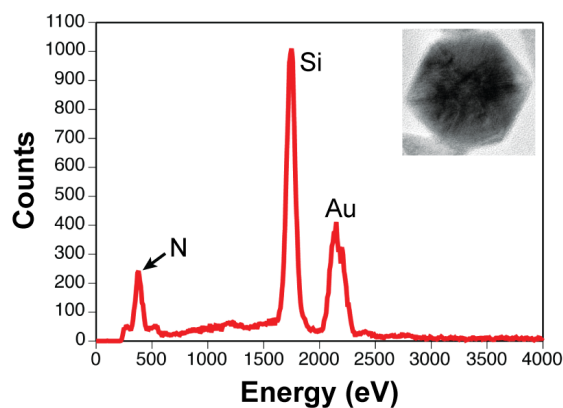


Fig. S3 EDX spectrum of a bipyramidal cGNP. Samples were on Si_3N_4 TEM membranes.

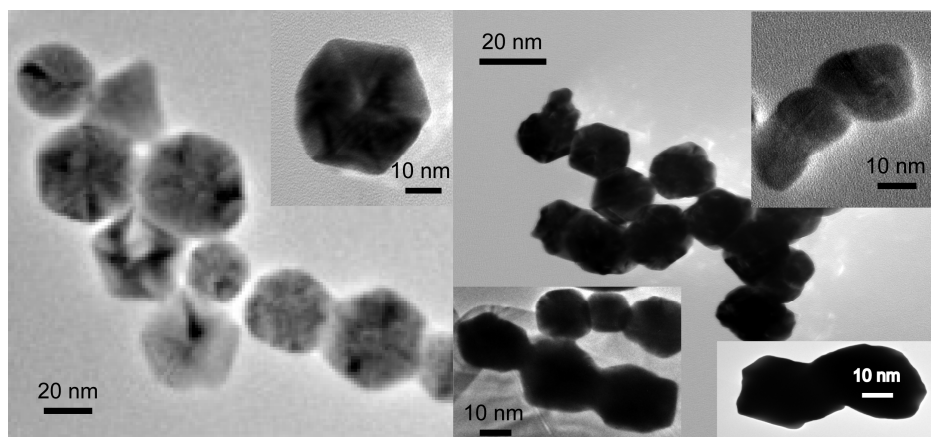


Fig. S4 HR-TEM images of the products of SWNT-driven reaction with SWNTs containing mixture of highly and moderately shortened ones, *i.e.*, average length and diameter of 59.3 nm (± 32.7 nm) and 1.1 (± 0.24). The growth of both cGNPs (*i.e.*, single Au NPs) and GNTs (*i.e.*, rod-shape NPs with linear arrays of 2 to 3 Au NPs) were observed. More variations in the sizes of cGNPs as well as GNTs were resulted in due to more variations in the sizes of SWNTs. This indicates the significance of the size uniformity of CNTs for the controlled synthesis of NPs, including both cGNPs and GNTs, with well-defined size and shape.