Citrate-Stabilized Gold Nanorods: Supporting Information

*Jonathan G. Mehtala, Dmitry Zemlyanov, Joann P. Max, Naveen Kadasala, Shou Zhao, and Alexander Wei**

Department of Chemistry and Birck Nanotechnology Center, Purdue University, West Lafayette, IN USA

Surfactant exchange protocol: Experimental details

All reagents were obtained from commercial sources and used as received. CTAB-stabilized GNRs were prepared on a gram scale using seeded growth conditions mediated by $AgNO_3$, as described by Zubarev.[20] Optical densities (O.D.) of GNR solutions were measured on the basis of their plasmon resonance peak at extinction values below 1.0; the O.D. of concentrated samples were extrapolated after serial dilution. Deionized water was obtained using an ultrafiltration system (Milli-Q, Millipore) with a measured resistivity above 18 MΩ·cm.

Preparation of PSS-stabilized GNRs. In a typical batch process, 40 mL of CTAB-GNRs (O.D. ~13) were diluted with water to 160 mL. In Stage 1, the GNR suspension was concentrated to approximately 10 mL in a stirred ultrafiltration cell using a cellulose membrane filter (MWCO 100 kDa). The retentate was transferred to two centrifuge tubes (Becton-Dickinson, 50 mL), then diluted with water to a final volume of 100 mL (O.D. 5.1). In Stage 2, the GNR suspensions were subjected to centrifugation at 6,500 *g* for 60 min. Nearly 95% of the supernatant was decanted, and the retentate was redispersed in 0.15 wt% Na-PSS to a final volume of 100 mL (O.D. 4.1), and allowed to sit for at least 1 hour prior to the next step. In Stages 3 and 4, the GNR suspensions were subjected to centrifugation at 7,500 *g* for 30 min, then decanted from the supernatant and redispersed in 0.15 wt% Na-PSS to a final volume of 100 mL (O.D. 3.9 after Stage 4). Alternatively, PSS-GNR dispersions could be prepared at higher concentrations (O.D. >10) in 0.7 wt% Na-PSS, and diluted for later use. The PSS-GNR dispersions were stable at room temperature for at least several weeks.

Preparation of citrate-stabilized GNRs. In Stage 5, GNRs suspended in 0.15 wt% Na-PSS (30 mL, O.D. 3.9) was centrifuged as described above in 15-mL plastic tubes. The supernatant was decanted until 0.2 mL of the retentate remained, and the GNRs were redispersed into 30 mL of 5 mM sodium citrate and allowed to sit for 12 hours. The GNR suspension was subjected to a

second C/R cycle in the same manner, yielding 30 mL of GNRs dispersed in 5 mM Na_3-citrate (O.D. 3.8). The cit-GNR dispersions were stable at room temperature for at least several months.

GNR characterization data

Optical absorbance spectra were recorded using a Cary Bio50 spectrophotometer and quartz cuvettes. Transmission electron microscopy (TEM) images were obtained using a FEI/Philips CM-10 with an accelerating voltage of 100 kV; samples were prepared by depositing 10 μL of GNR suspension onto Formvar-coated copper grids (400 mesh), then blotting the grid edge after 25 minutes and allowing the residual wetting layer to dry in air.

XPS data were obtained by a Kratos Ultra DLD spectrometer using monochromatic Al Kα radiation (1486.58 eV), with samples mounted on a double-sided adhesive Cu conductive tape. The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 and 20 eV, respectively. The binding-energy scale was calibrated using Au $4f_{7/2}$ = 84.00 eV and Cu $2p_{3/2}$ = 932.67 eV (standard deviation in peak position <0.05 eV); the charge reference was also calibrated against the Au $4f_{7/2}$ peak.[*] A Kratos charge neutralizer was used to achieve a Au $4f_{7/2}$ peak linewidth (full width at half-maximum) of 0.65–0.75 eV. XPS data were analyzed with CasaXPS (v. 2.3.16 PR 1.6) with individual peaks fitted to a Gaussian/Lorentzian function. The atomic concentrations of the elements in the near-surface region were estimated after the subtraction of a Shirley type background, taking into account the corresponding Scofield atomic sensitivity factors and inelastic mean free path of photoelectrons.

Infrared (IR) spectra were acquired using a Nexus 670 spectrometer (Thermo) equipped with a grazing-angle attenuated total reflectance module (GATR, Harrick), purged with dry nitrogen; GNR samples were concentrated by centrifugation, then deposited on a ZnSe window. Surface-enhanced Raman scattering (SERS) spectra were acquired at an excitation wavelength of 785 nm using a confocal Raman microscope with a 20X objective lens (Olympus, N.A.=0.4) and 180° backscattering collection, which was relayed by a fiber-optic bundle to a charge-coupled device camera (2 cm^{-1} resolution). Exposure times of 10–30 seconds with a laser power of 20 mW at the sample were used.

[*] Seah, M. P. *Surf. Interface Anal.* **1989,** *14*, 488.

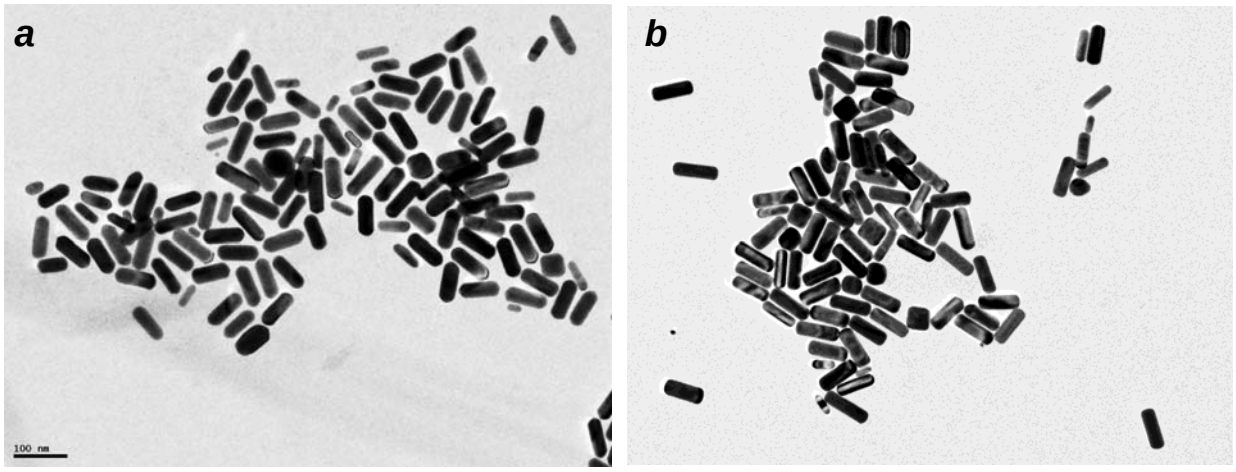

Figure S1. TEM images of (a) CTAB-stabilized GNRs (68.2 × 26.2 nm; *N*=102) and (b) citrate-stabilized GNRs (68.5 × 25.7 nm; *N*=134). Bar = 100 nm.

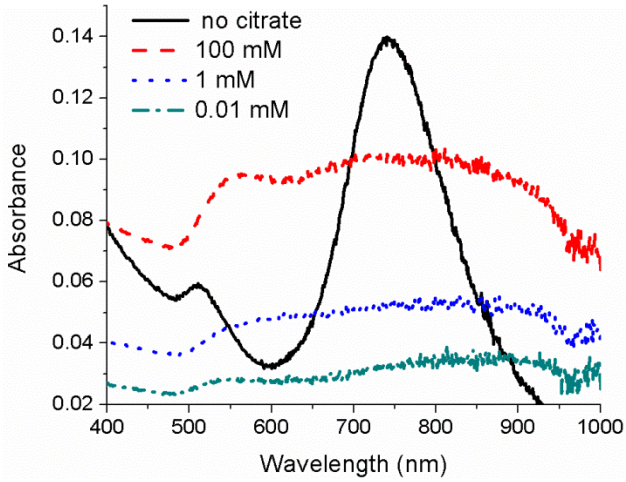

Figure S2. Absorbance spectra of GNR dispersions stabilized in 100 mM, 1 mM, or 0.01 mM CTAB, before and after treatment with 5 mM sodium citrate. All GNR dispersions were strongly aggregated after several hours' exposure to citrate, in the absence of PSS treatment.

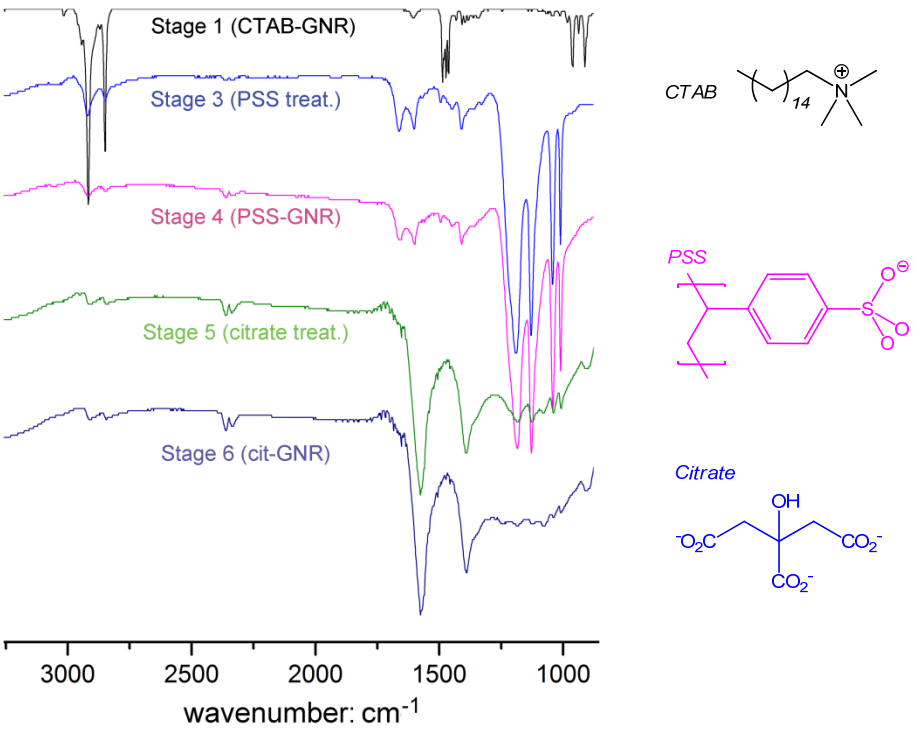

Figure S3. ATR-IR spectra acquired from pelleted GNR samples after each step. Stage 1: CTAB-GNRs (after ultrafiltration); Stage 4: PSS-GNRs; Stage 6: cit-GNRs.

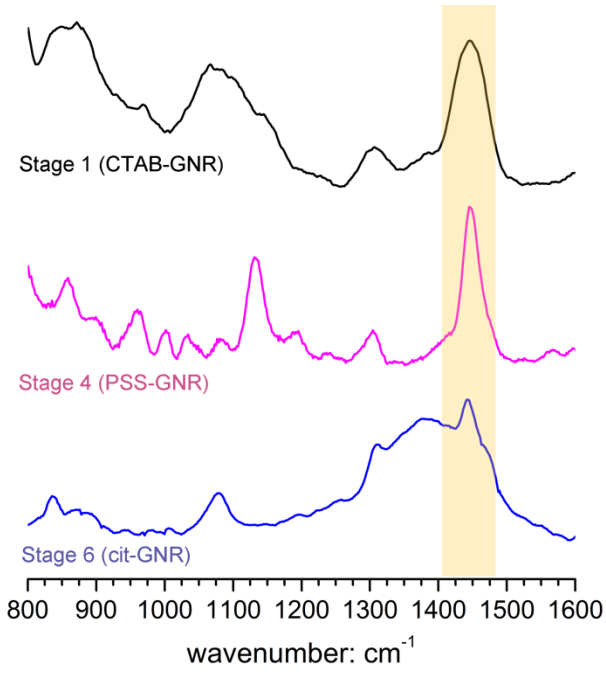

Figure S4. SERS spectra acquired from pelleted GNR samples after Stage 1 (ultrafiltration), Stage 4 (PSS-GNRs), and Stage 6 (cit-GNRs). Colored band (1420−80 cm^{-1}) represents C−H bending mode common to all surfactants.