

Supporting Information for

**Preparation of Super-Stable Gold Nanorods via Encapsulation into Block
Copolymer Micelles**

Dae Hwan Kim,¹ Alexander Wei,² and You-Yeon Won^{1,*}

¹School of Chemical Engineering, and ²Department of Chemistry, Purdue University, West

¹Lafayette, Indiana 47907

* To whom correspondence should be addressed. E-mail: yywon@ecn.purdue.edu

Figure S1. Mean hydrodynamic diameter of PEO₁₁₃-PnBA₈₉ BCP micelles in a water/DMF mixture, as a function of w_{water} and time. The shaded area represents a solvent composition window in which the BCP molecules aggregate into metastable colloids, signifying a medium for rapid exchange.

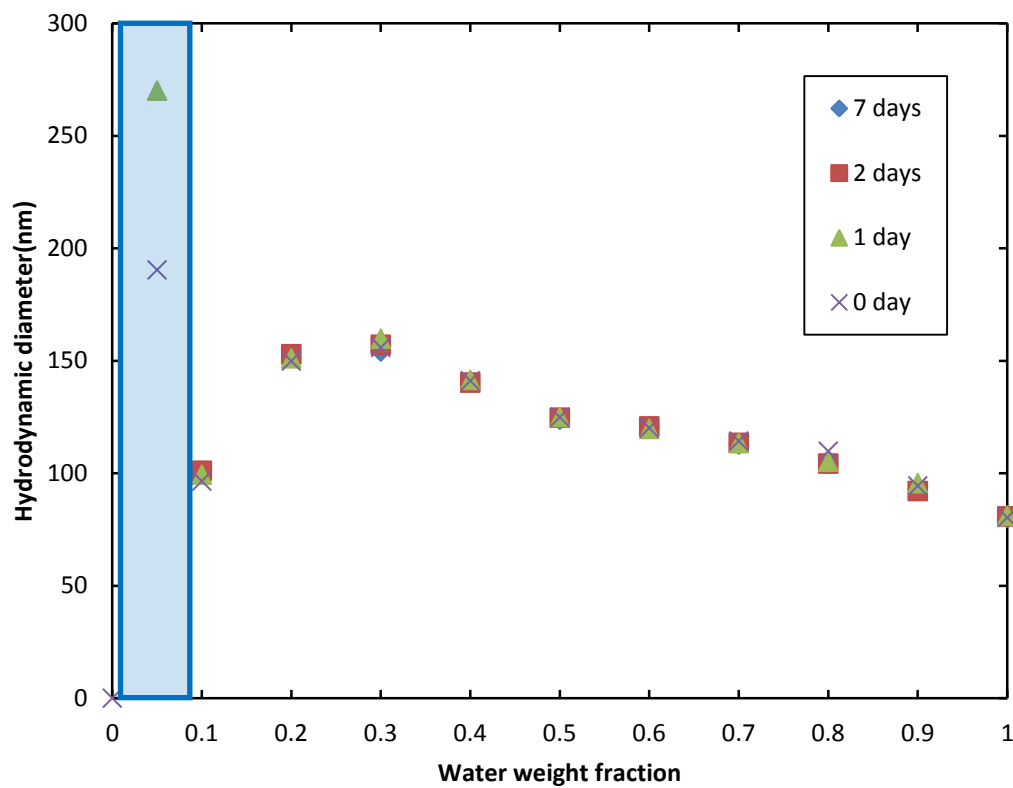
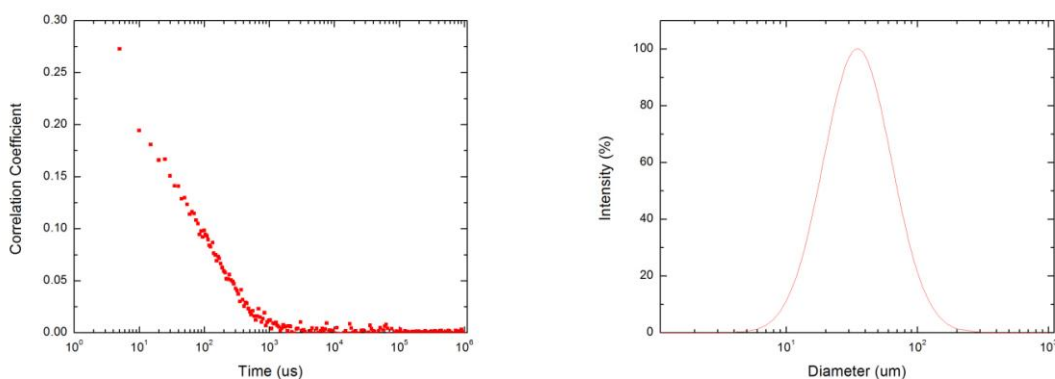


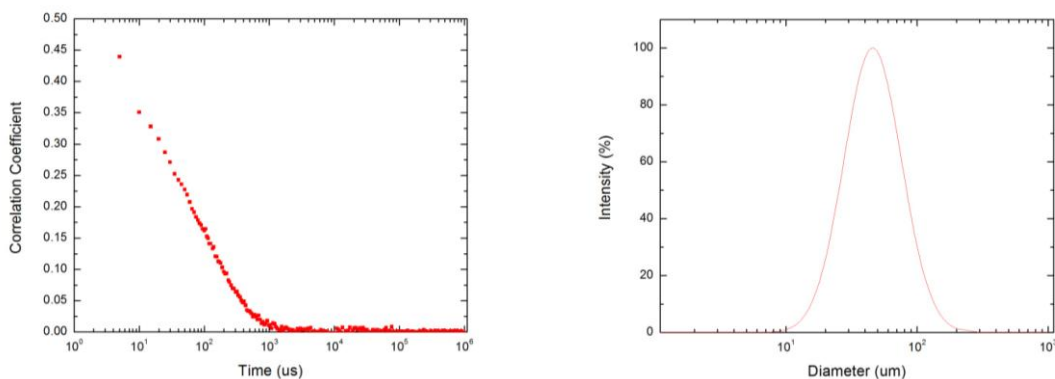
Figure S2. Representative DLS intensity autocorrelation functions and intensity-weighted size distributions (obtained by log-normal analysis) for **(A)** PEO₁₁₃-PnBA₅₇-coated GNRs (prepared by surfactant exchange at $w_{\text{water}} = 0.35$) in pure water (DLS data taken at $t = 0$, ~3 and ~6 months after preparation), **(B)** PEO₁₁₃-PnBA₅₇-coated GNRs (prepared by surfactant exchange at $w_{\text{water}} = 0.35$) in 150-mM NaCl solution (at $t = 0$, ~3 and ~6 months after exposure to 150 mM NaCl), and **(C)** CTAB-coated GNRs in 150-mM NaCl solution (at $t = 0$, 1 and 2 days after exposure to 150 mM NaCl).

(A)

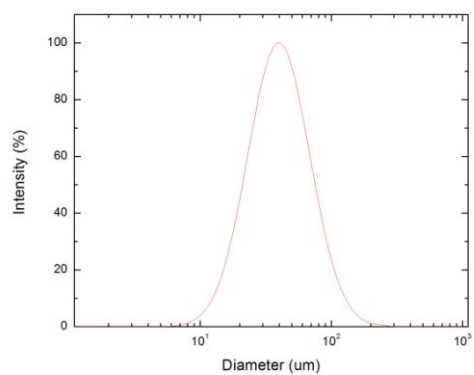
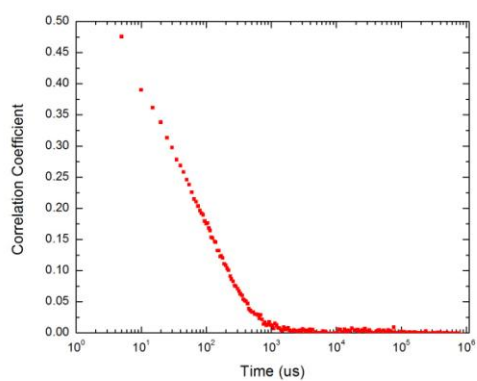
$t = 0$



$t = \sim 3$ months

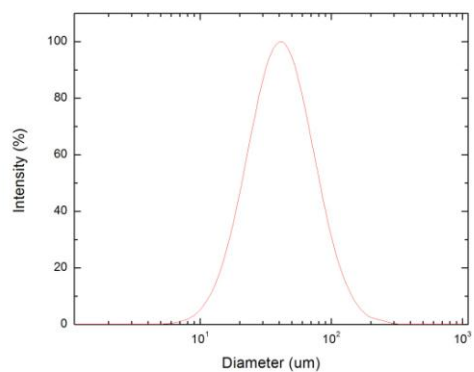
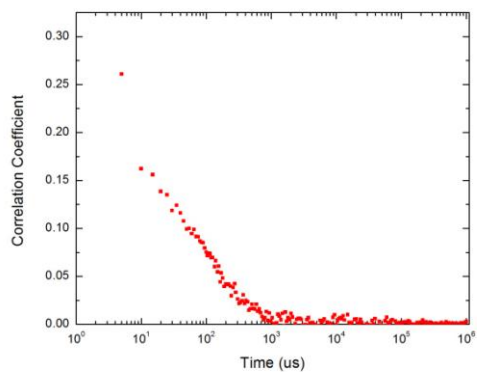


$t = \sim 6$ months

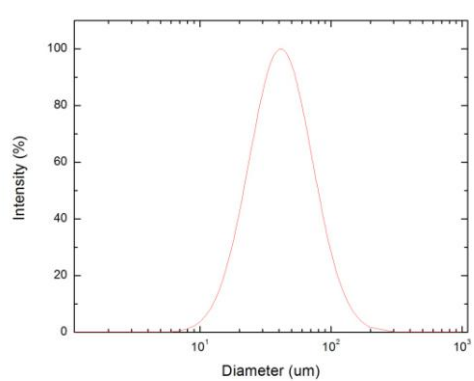
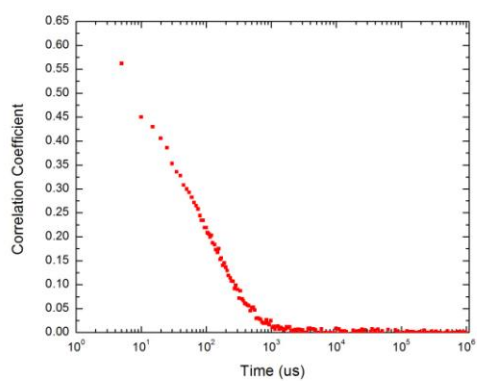


(B)

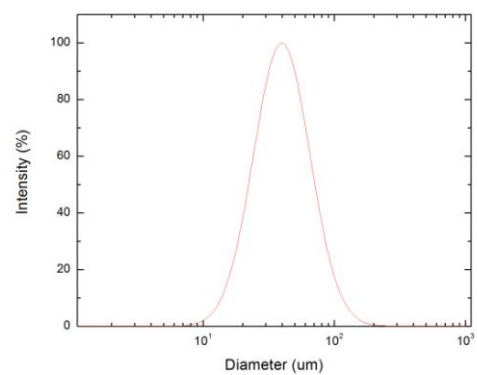
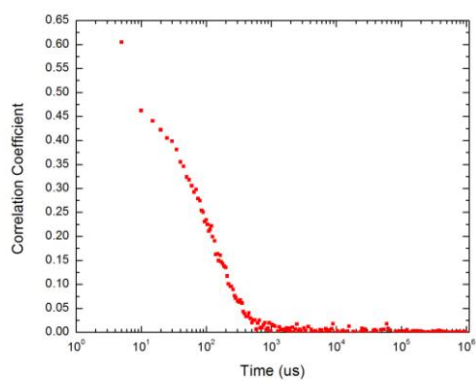
$t = 0$



$t = \sim 3$ months

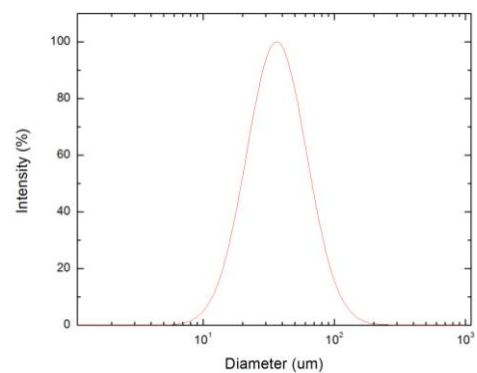
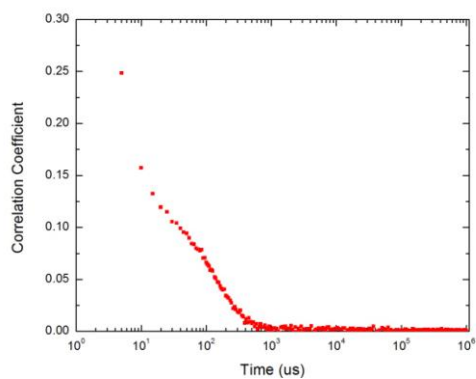


$t = \sim 6$ months

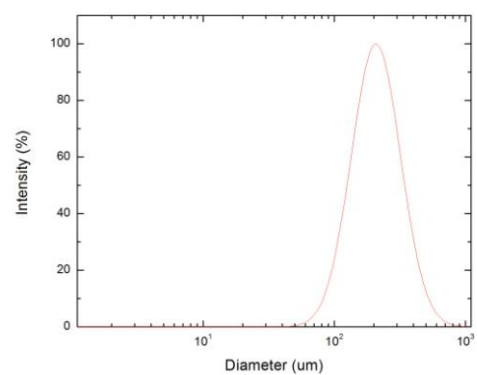
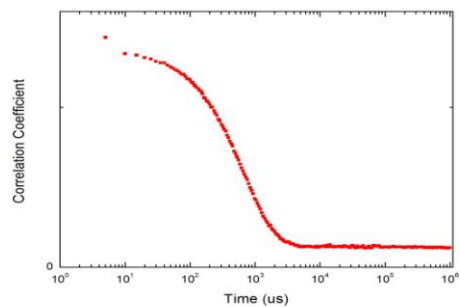


(C)

$t = 0$



$t = 1$ day



$t = 2$ days

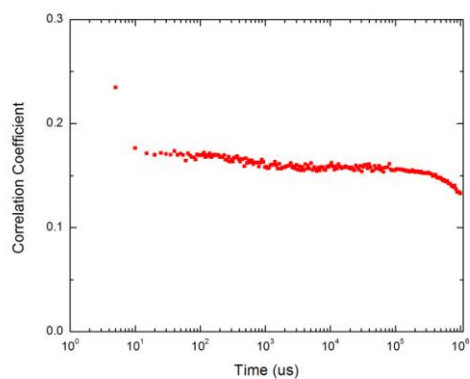
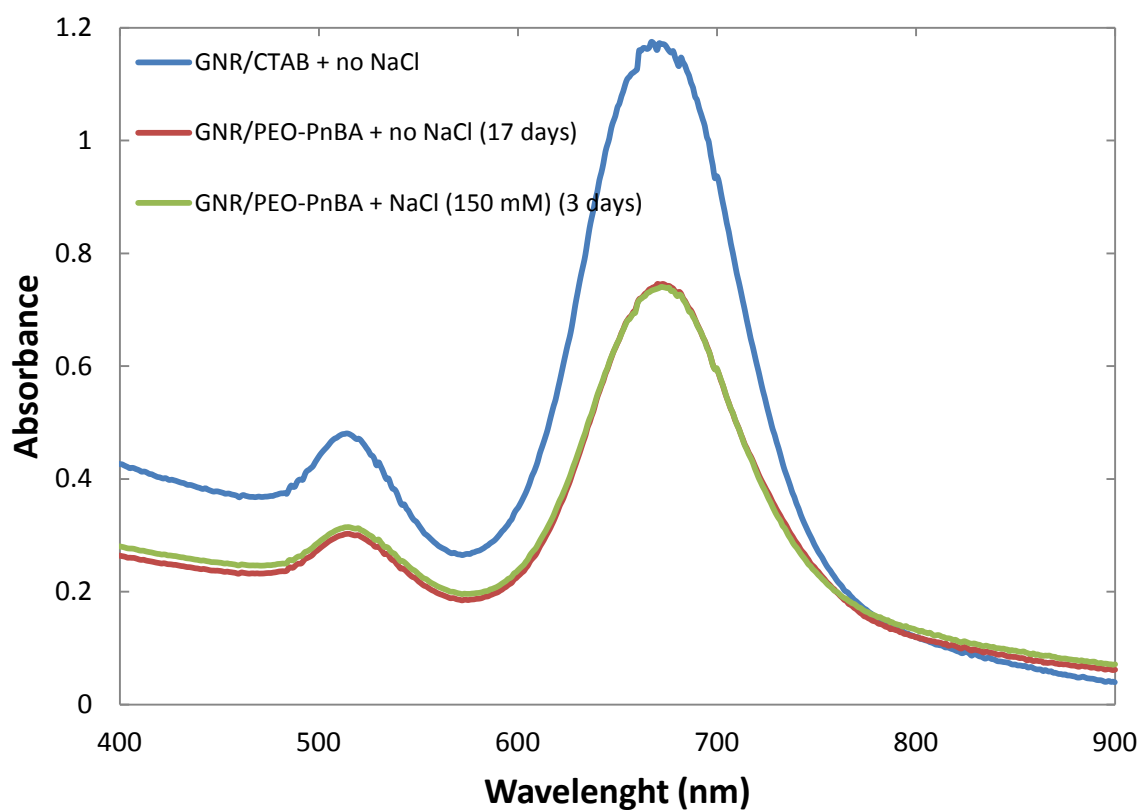


Figure S3. Representative UV-vis absorption spectra **(A)** for PEO₁₁₃-PnBA₅₇-coated GNRs (prepared by surfactant exchange at $w_{water} = 0.35$) in pure water (absorbance data taken at $t = 17$ days after preparation), PEO₁₁₃-PnBA₅₇-coated GNRs (prepared by surfactant exchange at $w_{water} = 0.35$) in 150-mM NaCl solution (at $t = 3$ days after exposure to 150 mM NaCl), and CTAB-coated GNRs in pure water (as synthesized), and **(B)** for CTAB-coated GNRs in 150-mM NaCl solution (at $t = 0, 1$ and 3 days after exposure to 150 mM NaCl).

(A)



(B)

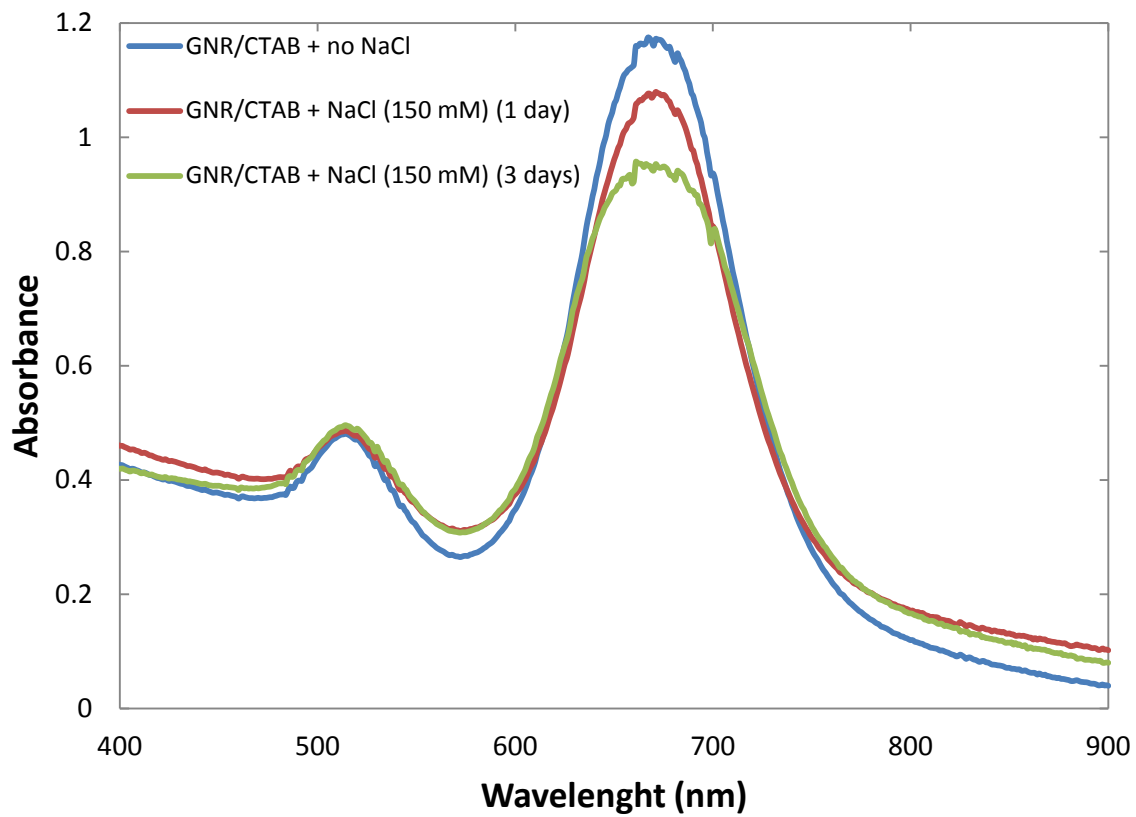


Figure S4. Additional TEM images of PEO₁₁₃-PnBA₅₇ BCP-coated GNRs (prepared by surfactant exchange at a solvent composition of $w_{\text{water}} = 0.35$) stored in pure water for 17 days after preparation. The TEM specimens were negatively stained with 2% uranyl acetate.

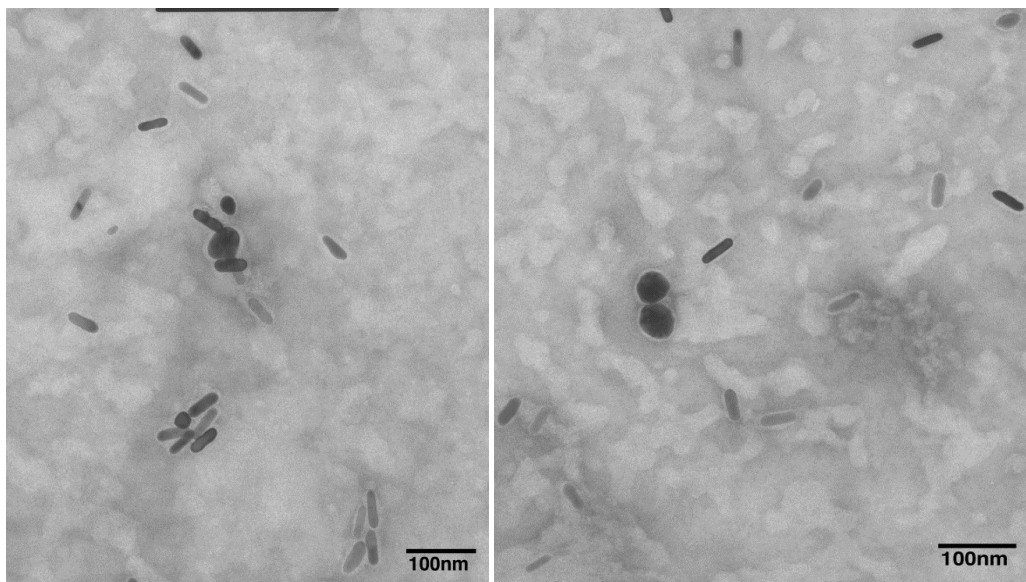
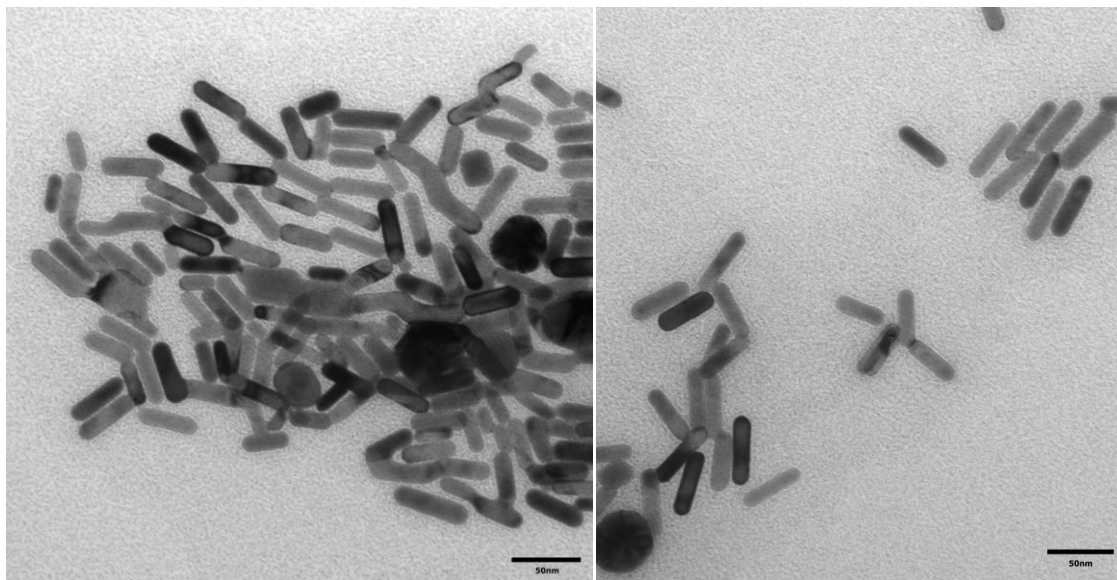


Figure S5. Additional TEM images of CTAB-coated GNRs **(A)** as synthesized in water or **(B)** stored in 150 mM NaCl for 3 days. The TEM specimens were negatively stained with 2% uranyl acetate.

(A)



(B)

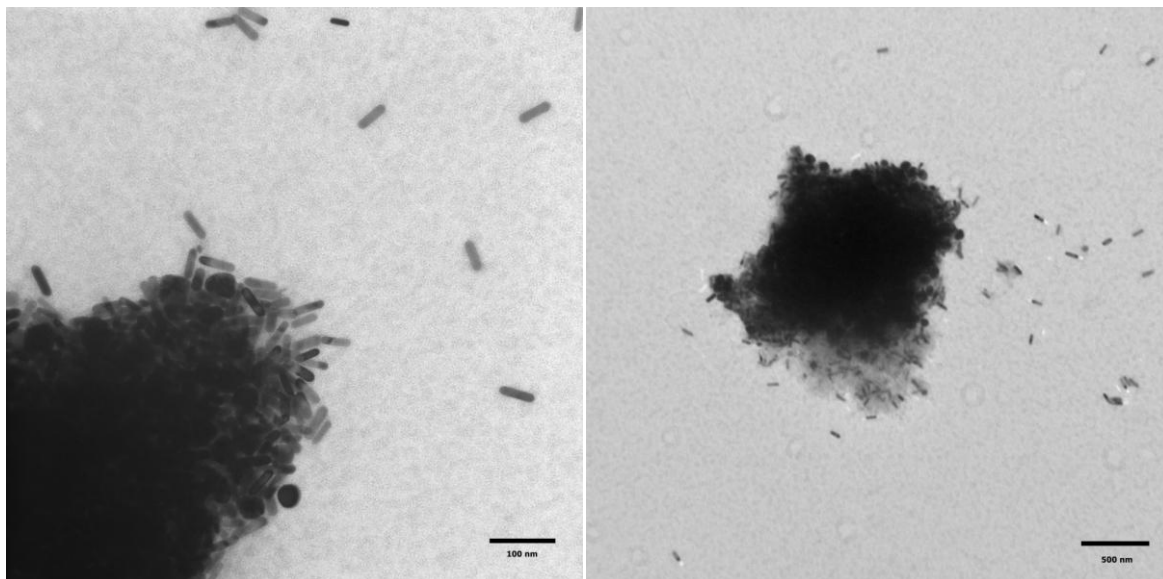


Figure S6. TEM images demonstrating an unsuccessful BCP encapsulation trial conducted at a solvent composition outside the determined range for optimal CTAB exchange (discussed in Section 2.2). In this example, the surfactant exchange process was undertaken with PEO₁₁₃-PnBA₅₇ at a solvent composition of $w_{\text{water}} = 0.20$. The TEM specimens were negatively stained with 2% uranyl acetate. The specific sample preparation procedure used is as follows: A solution containing 0.01 mg/ml GNR (coated with CTAB) was prepared in a water/DMF mixture at $w_{\text{water}} = 0.40$. A 1.0 mg/ml solution of PEO₁₁₃-PnBA₅₇ in pure DMF was also separately prepared. Equal amounts (by weight) of these two solutions were mixed so that the final solvent composition was a water weight fraction of 0.20. The resultant mixture was sonicated for 30 minutes in a bath sonicator. Additional 1.2 g of water was added to make final solvent composition $w_{\text{water}} = 0.50$, again followed by 30 minutes of sonication. The GNR suspension was then dialyzed in a dialysis bag (molecular weight cutoff 3,000) for 2 days against a large volume of deionized water (regularly replaced with fresh water) in order to remove residual DMF and CTAB.

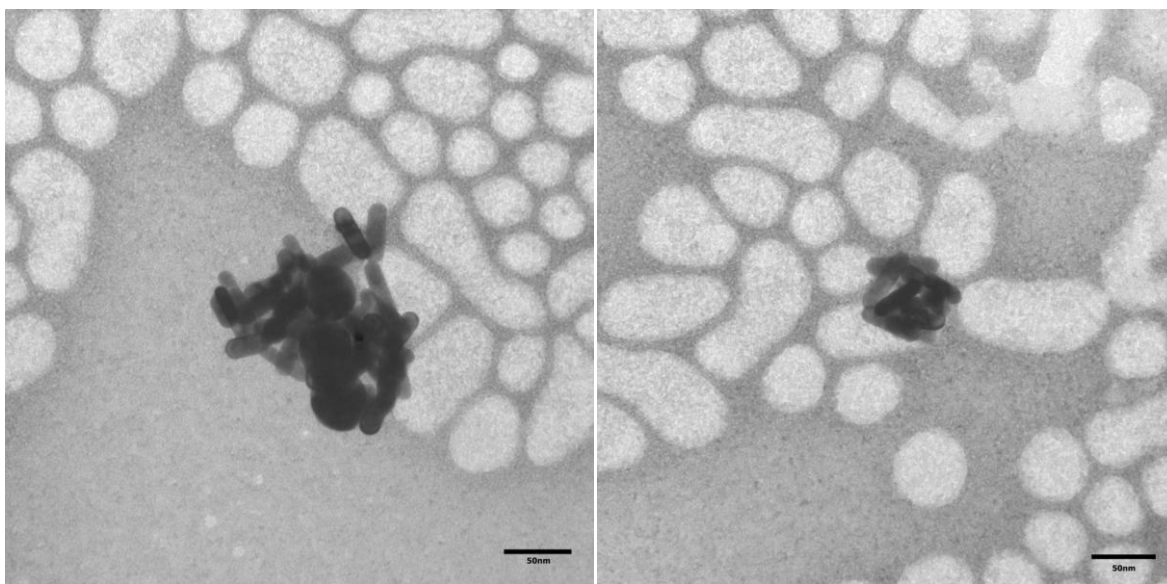


Figure S7. TEM images demonstrating an unsuccessful BCP encapsulation trial conducted at a solvent composition outside the determined range for optimal CTAB exchange (discussed in Section 2.2). In this example, the surfactant exchange process was undertaken with PEO₁₁₃-PnBA₅₇ at a solvent composition of $w_{water} = 0.50$. The TEM specimens were negatively stained with 2% uranyl acetate. The specific sample preparation procedure used is as follows: A solution containing 0.01 mg/ml GNR (coated with CTAB) was prepared in a water. A 1.0 mg/ml solution of PEO₁₁₃-PnBA₅₇ in pure DMF was also separately prepared. Equal amounts (by weight) of these two solutions were mixed so that the final solvent composition was a water weight fraction of 0.50. The resultant mixture was sonicated for 60 minutes in a bath sonicator. The GNR suspension was then dialyzed in a dialysis bag (molecular weight cutoff 3,000) for 2 days against a large volume of deionized water (regularly replaced with fresh water) in order to remove residual DMF and CTAB.

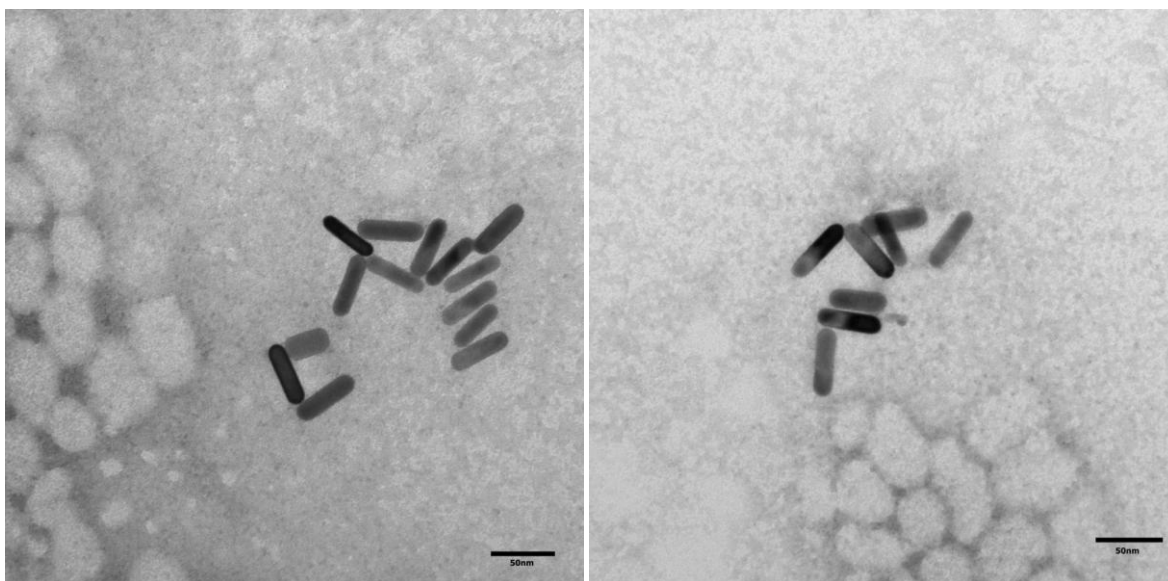


Figure S8. TEM images demonstrating an unsuccessful BCP encapsulation trial conducted at a solvent composition outside the determined range for optimal CTAB exchange (discussed in Section 2.2). In this example, the surfactant exchange process was undertaken with PEO₁₁₃-PnBA₈₉ at a solvent composition of $w_{\text{water}} = 0.05$. The TEM specimens were negatively stained with 2% uranyl acetate. The specific sample preparation procedure used is as follows: A solution containing 0.01 mg/ml GNR (coated with CTAB) was prepared in a water/DMF mixture at $w_{\text{water}} = 0.10$. A 1.0 mg/ml solution of PEO₁₁₃-PnBA₈₉ in pure DMF was also separately prepared. Equal amounts (by weight) of these two solutions were mixed so that the final solvent composition was a water weight fraction of 0.05. The resultant mixture was sonicated for 30 minutes in a bath sonicator. Additional 1.8 g of water was added to make final solvent composition $w_{\text{water}} = 0.50$, again followed by 30 minutes of sonication. The GNR suspension was then dialyzed in a dialysis bag (molecular weight cutoff 3,000) for 2 days against a large volume of deionized water (regularly replaced with fresh water) in order to remove residual DMF and CTAB.

