

## **Supporting Information**

### **Evaporation induced wrinkling of graphene oxide at the nanoparticle interface**

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## Experimental Section

*Chemicals.* All of the DNA samples were purchased from Integrated DNA Technologies (Coralville, IA) and were purified by standard desalting. AuNPs (13 nm) were synthesized on the basis of the standard citrate reduction procedures, and their concentration was estimated to be ~10 nM.<sup>[1]</sup> AuNPs of 5 nm size were purchased from BBI international (Cardiff, UK). 12 nm BPEI NanoXact™ AuNPs (0.05 mg/mL) were purchased from nanoComposix Inc. (San Diego, CA). GO and graphene was purchased from ACS Material, LLC (Medford, MA). Bovine serum albumin (BSA) and KCN were from Sigma-Aldrich. Urea was obtained from Bio Basic Inc (Markham, ON, Canada). 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) and NaCl were from Mandel Scientific (Guelph, ON, Canada). Mill-Q water was used to prepare all the buffers and solution. All other reagents and solvents were of analytical grade and used as received.

*Functionalization of AuNPs with thiol-modified DNA or with BSA.* The typical salt aging method was performed by adding NaCl over 2 days to prepare the polyvalent DNA-AuNP conjugates, regardless of the DNA sequence.<sup>[1]</sup> First, 3  $\mu$ L of thiolated DNA stock solution (100  $\mu$ M in 10 mM HEPES buffer, pH 7.4) was added to 200  $\mu$ L of 13 nm AuNP solutions (10 nM) and the sample was incubated at room temperature overnight. Second, 50  $\mu$ L NaCl (1 M) was added to the AuNP solutions. After brief vortexing, the sample was allowed to incubate at room temperature for 2 h and another 50  $\mu$ L NaCl (1 M) was added to the AuNP solution. After standing for another 24 h, the solution was brought to 0.3 M NaCl and the sample was allowed to incubate for another 2 h at room temperature. Finally, the DNA-AuNP mixture was centrifuged at 15 000 rpm and the supernatant was removed. The pellet was washed four times with 10 mM HEPES buffer. The final DNA-

AuNP conjugate was re-dispersed in 10 mM HEPES buffer for further use. Similar procedure was performed by adding 3  $\mu$ L of HS-A<sub>15</sub> stock solution to 200  $\mu$ L of 5 nm AuNP solutions (83 nM). To prepare the BSA capped AuNP, 10  $\mu$ L BSA stock solution (10 mg/mL) was added to 1 mL of 13 nm AuNP solution (10 nM) and incubated at room temperature overnight.

*Functionalized AuNP/GO complex preparation.* In a typical experiment, 50  $\mu$ L GO (100  $\mu$ g/mL in buffer A: 10 mM HEPES and 100 mM NaCl) was mixed with 100  $\mu$ L various formulation of AuNP (13 nm, 10 nM), such as AuNP/HS-A<sub>15</sub>, AuNP/HS-T<sub>15</sub>, AuNP/BPEI, and AuNP/BSA. For the 5 nm AuNP/HS-A<sub>15</sub>, the concentration is 83 nM. After 30 min incubation, the complex solution was centrifuged at 3 000 rpm and the supernatant was removed. The pellet was washed two times with buffer A and re-suspended in the same buffer for the following experiment. The only exception was to re-suspend GO-AuNP/HS-A<sub>15</sub> in a lower surface tension solvents (e.g. methanol, ethanol, isopropanol and acetonitrile). TEM was used to observe wrinkle formation.

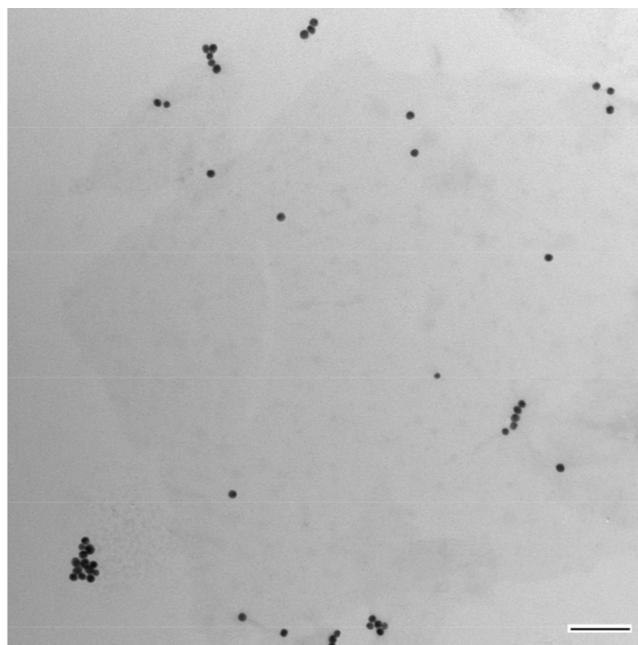
*Graphene-AuNP/HS-A<sub>15</sub> complex preparation.* 50  $\mu$ L pristine graphene (10  $\mu$ g/mL in 100 mM NaCl) were mixed with 100  $\mu$ L AuNP/HS-A<sub>15</sub> (10 nM). After 30 min incubation, the complex solution was centrifuged at 3 000 rpm and the supernatant was removed. The pellet was washed twice with 100 mM NaCl solution and re-suspended for TEM characterization.

*GO-AuNP/HS-A<sub>15</sub> treated with KCN.* In order to know whether the wrinkling of GO was caused during the drying process, KCN with a final concentration of 5 mM was added to the as-prepared GO-AuNP/HS-A<sub>15</sub> conjugate (GO = 50  $\mu$ g/mL). The mixture was incubated for 1 h and then washed with buffer A twice before drying on a TEM grid. In

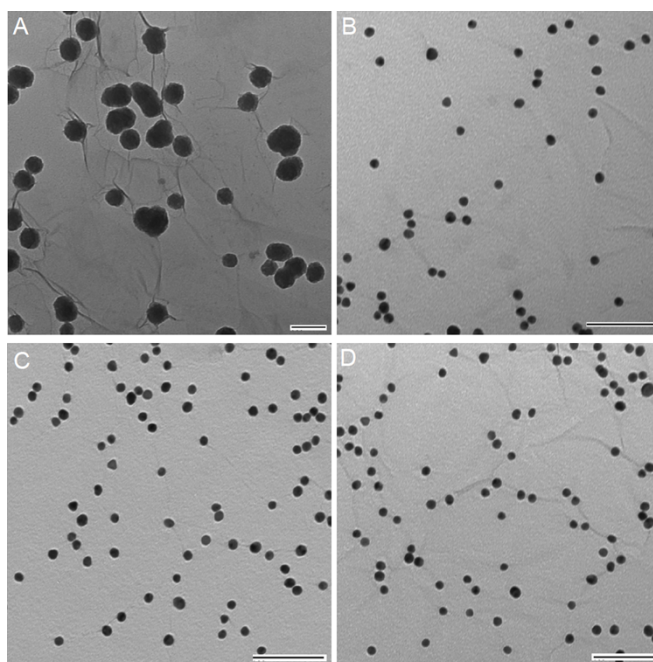
another experiment, the GO-AuNP/HS-A<sub>15</sub> sample (MGO 50 µg/mL) was dried on a TEM grid overnight and then soaked in the KCN (5 mM) for 20 min. After washing with buffer A twice, the carbon grid was dried in air before TEM characterization.

*Adsorption strength using urea treatment.* 100 µL GO-AuNP/HS-A<sub>15</sub> (10 nM AuNPs) was concentrated by centrifugation and dried in air overnight. Then 100 µL buffer A was added to re-suspend the dried sample. 100 µL of 8 M urea was further added (final urea concentration = 4 M) and also to the regular undried 100 µL MGO-AuNP/HS-A<sub>15</sub> (10 nM) for 1 h. Then both of the solutions were centrifuged at 3 000 rpm for 10 min. At this speed, free AuNPs cannot be precipitated, but their conjugate with GO can. The fraction of released AuNP in the supernatant was estimated based on the UV-vis absorption intensity at 520 nm. UV-vis measurement was carried out on an Agilent 8453A instrument.

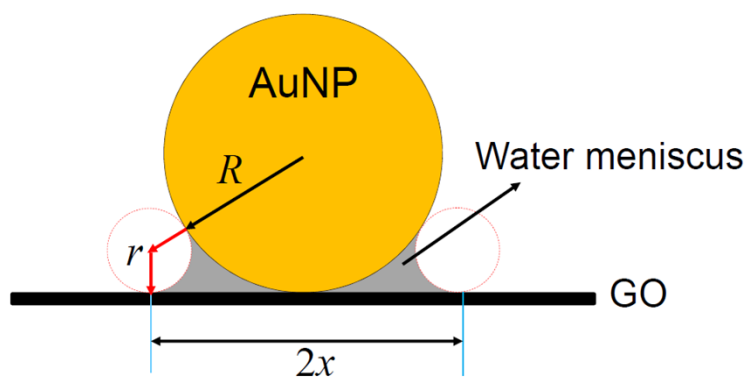
*TEM characterizations.* TEM measurements were performed on a Philips CM10 transmission electron microscope. The samples were prepared by pipetting a drop of the suspension onto a 230 mesh copper holey carbon grid and the samples were allowed to dry in air before measurement.



**Figure S1.** Citrate-capped AuNPs are not adsorbed by GO. After centrifugation at 3000 rpm, the supernatant remained red (not shown) and the TEM micrograph shows that AuNPs are only sparsely associated with GO, while free AuNPs are also present.



**Figure S2.** TEM images of (A) 50 nm SiO<sub>2</sub> nanoparticles dried on GO. TEM image of drying of GO-AuNP/HS-A<sub>15</sub> (13 nm) dispersed in acetonitrile (B), methanol (C) or isopropanol (D). Scale bars = 100 nm.



**Figure S3.** Geometry calculation. Approximately,  $R^2 + (x+r)^2 = (R+2r)^2$ .  $\rightarrow x^2 + 2rx = 4rR + 3r^2$ . Since  $r$  is much smaller compared to  $x$  or  $R$ ,  $x^2 \cong 4rR$ .

#### Additional references

- [1] J. J. Storhoff, R. Elghanian, R. C. Mucic, C. A. Mirkin, R. L. Letsinger, *J. Am. Chem. Soc.* **1998**, *120*, 1959.