Electronic Supplementary Material (ESI) for Chemical Communications

Near-infrared light-responsive vesicles of Au nanoflowers

Jie He[a], Peng Zhang[a,b], Tarrika Babu[a], Yijing Liu[a], Jinlong Gong[b], Zhihong Nie[a]*

[a] *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA.*
[b] *Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China.*

E-mail: znie@umd.edu

1. Materials

Gold(III) chloride hydrate ($HAuCl_4$, 99.999%), sodium citrate tribasic dihydrate (98%), and 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid (HEPES), were purchased from Sigma-Aldrich. All the chemicals were used as received unless otherwise noted. Deionized water (Millipore Milli-Q grade) with resistivity of 18.0 MΩ was used in all the experiments.

2. Synthesis of AuNFs

The 20-nm AuNP seeds (0.025 mg/mL) were synthesized according to the procedures reported previously.[1] AuNFs were prepared using a seed-mediated growth. Typically, 10 mL of above AuNP solution was mixed with predetermined amount of $HAuCl_4$ and then diluted to 50 mL. Then, 5 mL of 0.5 mg/mL weak reductant HEPES were quickly injected into this mixture under strong stirring. After stirred for 30 s, the mixed solution was kept for 6 hrs. The AuNF was further purified by centrifuged at 6000 rpm for two cycles. By varying the amount of $HAuCl_4$ from 1.5 μmol (39 nm) to 15 μmol (72 nm), various sizes of AuNFs can be synthesized as shown in Figure S4.

3. Surface modification and self-assembly of AuNFs

The synthesis of thiol-ended BCP of PEO-*b*-PS was reported elsewhere.[2] The surface modification of AuNFs by BCPs was performed via a ligand exchange method. Briefly, 5 mg of thiol-ended BCP was first dissolved in 10 mL of DMF. Then, ~100 μL of a concentrated solution of AuNFs (from 50 mL of original solution) was slowly added into the above solution under vigorous shaking. Subsequently, the mixture was sonicated for 1 hr to avoid the aggregation of AuNFs, and then kept steady for overnight to complete the ligand exchange. The BCP modified AuNFs were purified by centrifuged for 6-8 times and redispersed in THF. The self-assembly of BCP modified AuNFs was achieved by the film rehydration method. After drying the AuNF solution in a glass vial, the film was sonicated in pure water to prepare vesicles.

4. Characterizations

The extinction spectra of AuNFs and vesicles were recorded on a PERKIN LAMBDA 35 UV/Vis System. The morphologies of assemblies were imaged using a Hitachi SU-70 Schottky field emission gun

Scanning Electron Microscope (FEG-SEM) and a JEOL FEG Transmission Electron Microscope (FEG-TEM). Samples for SEM were prepared by casting a 5-10 μL of NP aqueous solution on silicon wafers, and dried at room temperature. TEM samples were prepared from the casting on 300 mesh copper grids covered with carbon film, and dried at room temperature.

Rhodamine B (RB) was used as a model molecule to examine the control release. RB was firstly dissolved in water and then sonicated with BCP tethered AuNFs. The vesicle solution was then dialyzed against pure water for 2 days to remove the unloaded dye molecules. To monitor the light-triggered release of RB, the solution was exposed to the NIR pulse laser at 800 nm (60 mW). The release of RB was measured at an excitation wavelength of 540 nm using a fluorescence spectrometer.

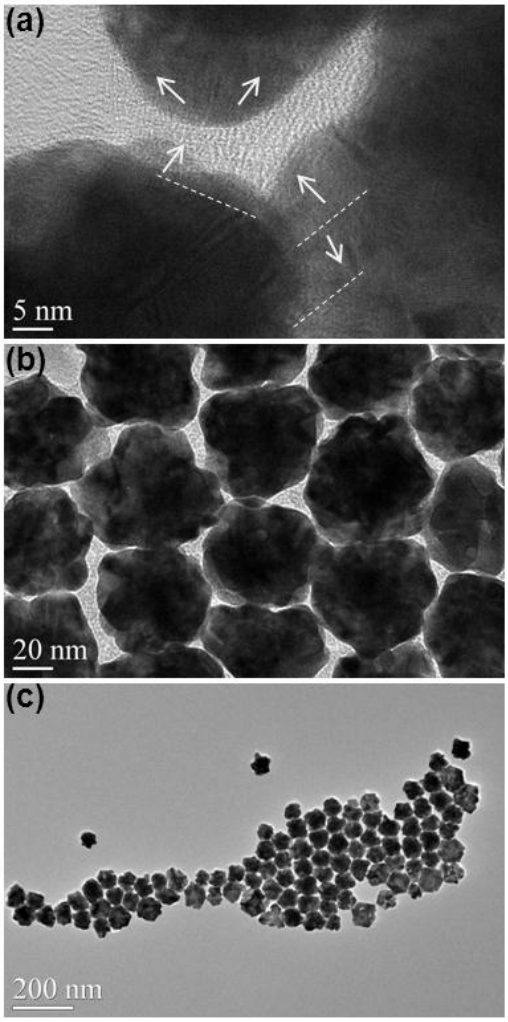

Figure S1. Representative TEM images of 63-nm AuNFs. The arrows in high resolution image in (a) indicates the growth direction of (200) facets and the dash lines are twin boundaries.

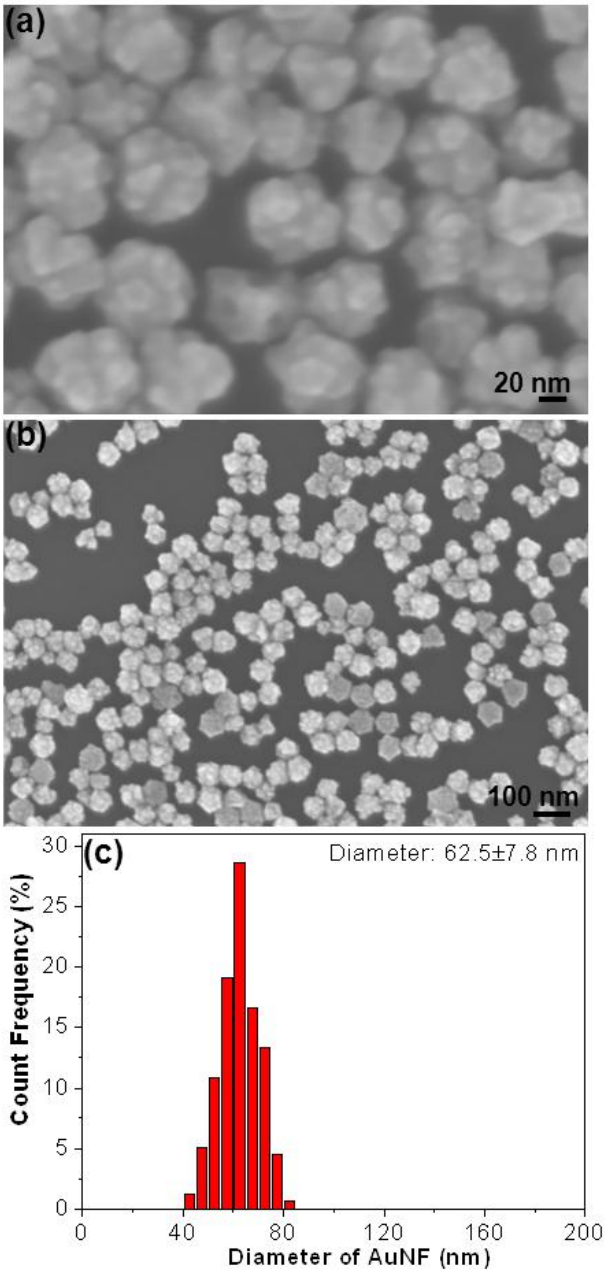

Figure S2. (a,b) Representative SEM images of 63-nm AuNFs. (c) The size and size distribution of 63-nm AuNFs.

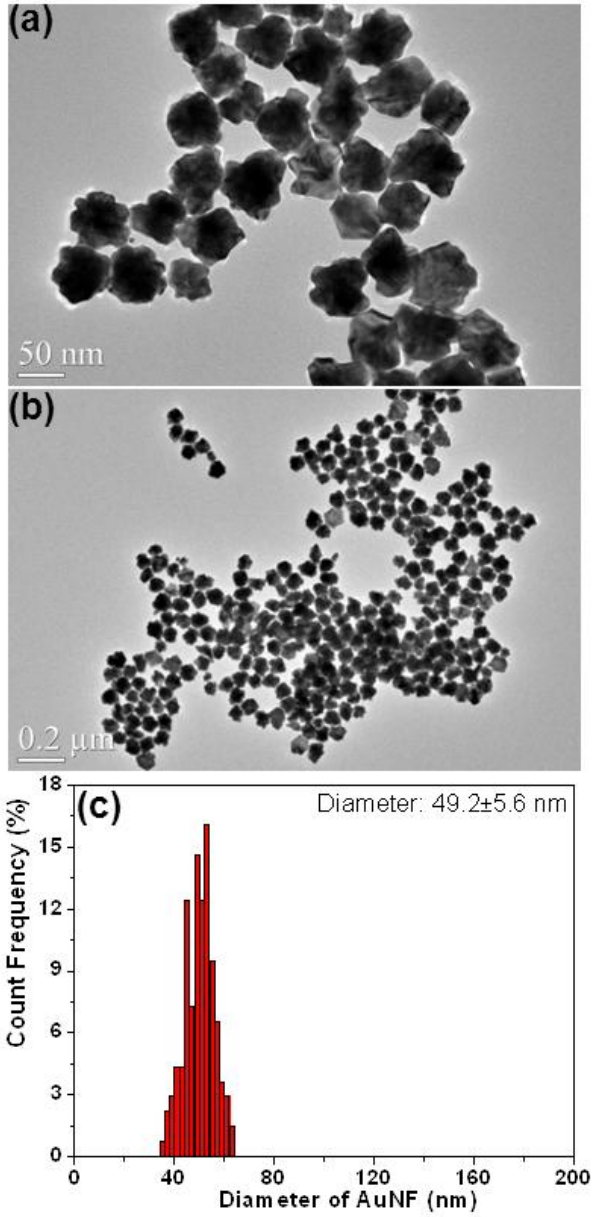

Figure S3. (a,b) Representative TEM images of 49-nm AuNFs. (c) The size and size distribution of 49-nm AuNFs.

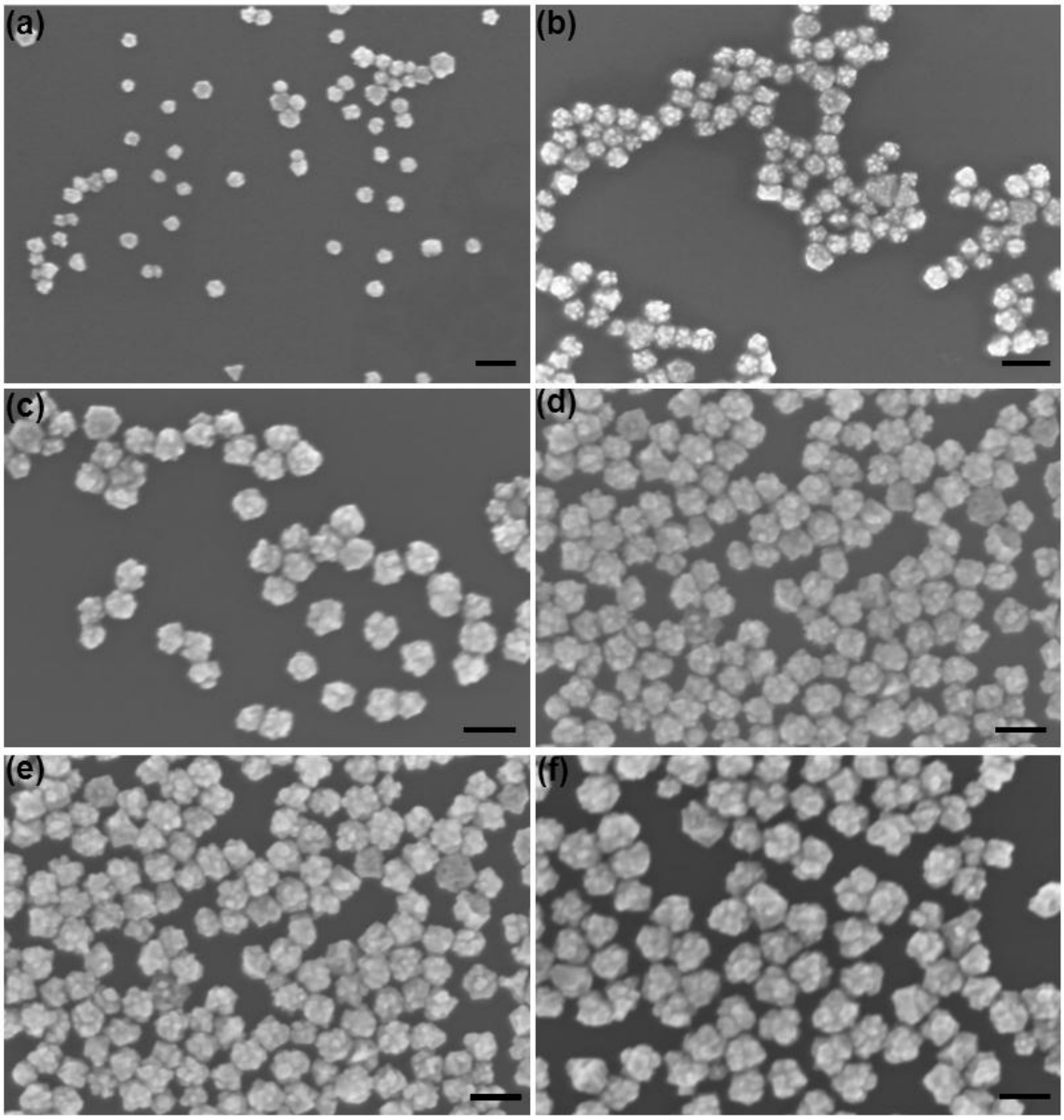

Figure S4. SEM images of AuNFs with various sizes by varying the concentration of $HAuCl_4$. (a) 39.1 nm; (b) 45.3 nm; (c) 54.6 nm; (d) 62.3 nm; (e) 66.4 nm; and (f) 72.8 nm. Scale bars are 100 nm in (a-f).

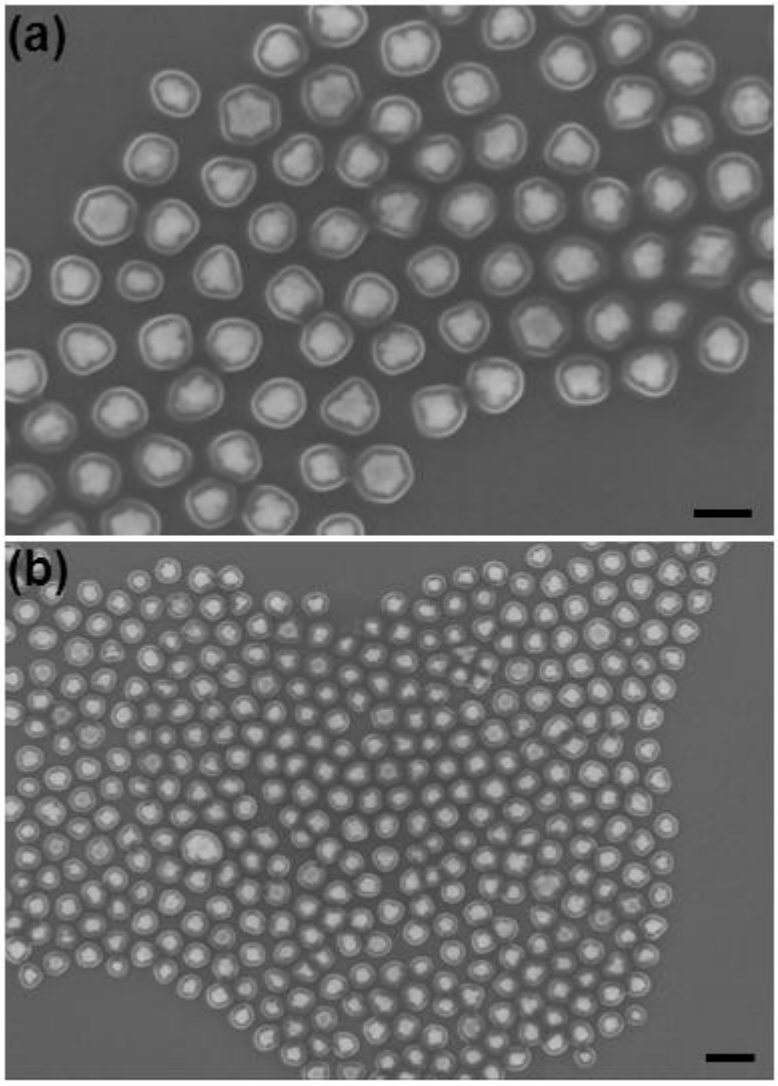

Figure S5. SEM images of 63-nm AuNFs tethered with BCP of PEO_{45}-*b*-PS_{455}. The high resolution SEM image clearly indicates the polymer shell on AuNFs. The grafting volume of BCP was estimated by approximating AuNFs as standard spheres, using the reported method.[3] Scale bars are 100 nm in (a) and 200 nm in (b).

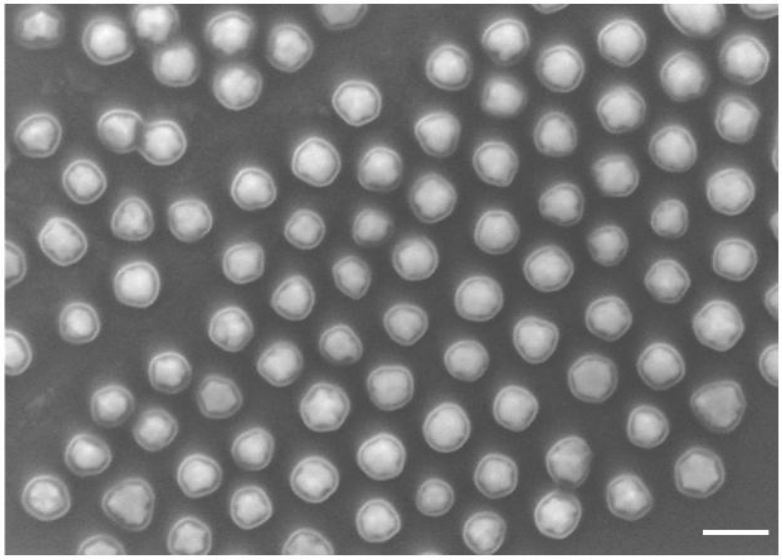

Figure S6. SEM image of 49-nm AuNFs tethered with BCP of PEO_{45}-*b*-PS_{455}. Scale bar is 100 nm.

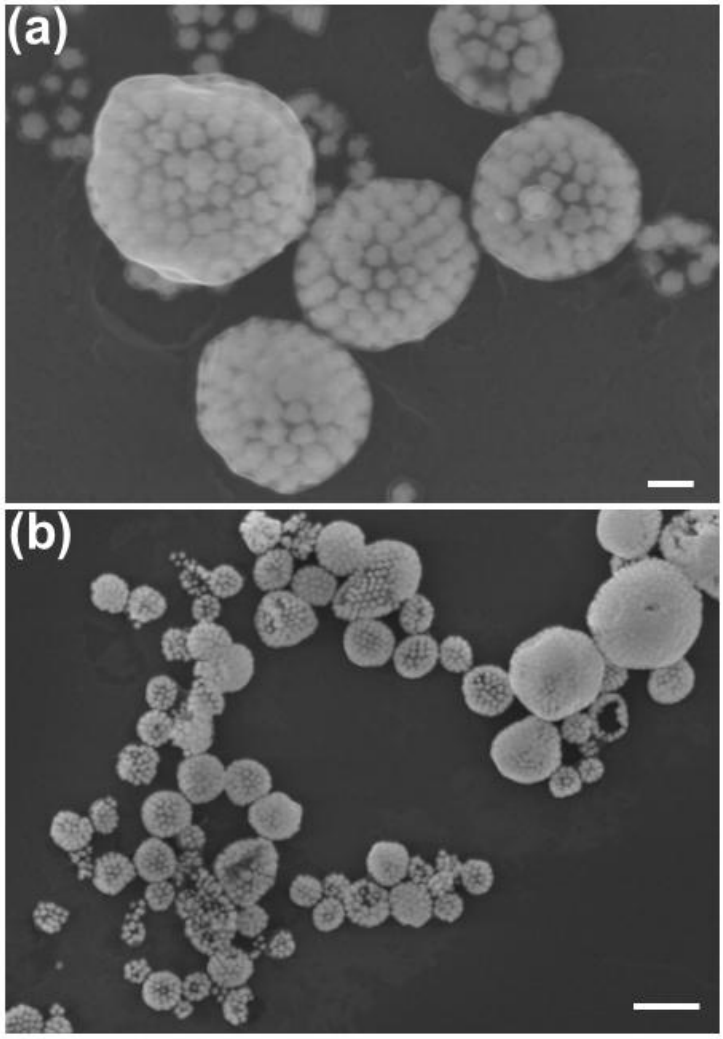

Figure S7. SEM images of vesicles from 49-nm AuNFs. Scale bars are 100 nm in (a) and 500 nm in (b).

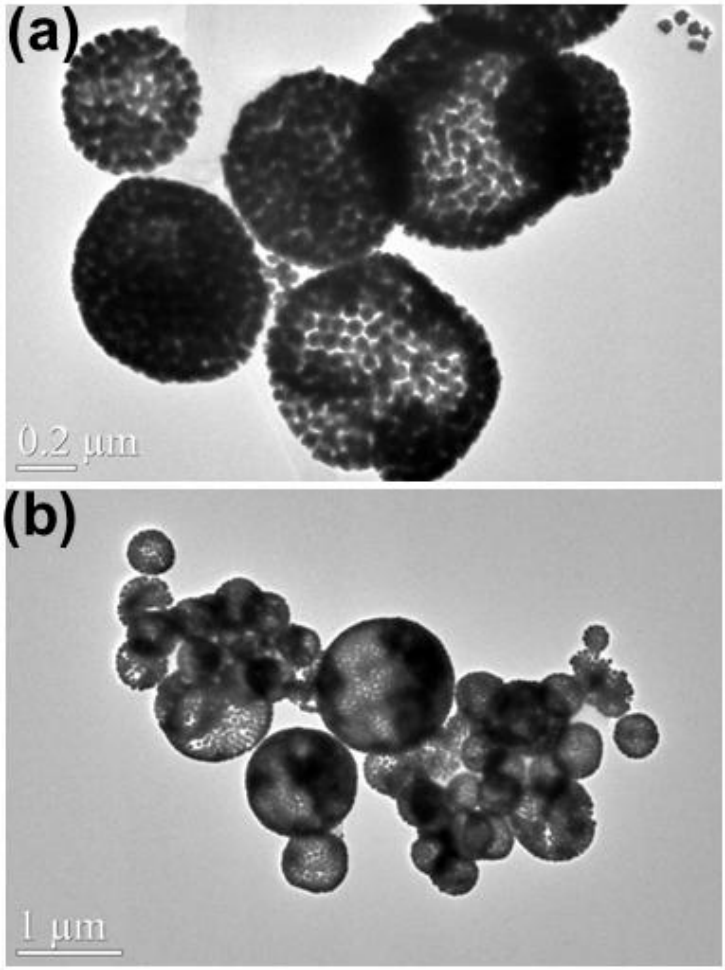

Figure S8. TEM images of vesicles from 49-nm AuNFs.

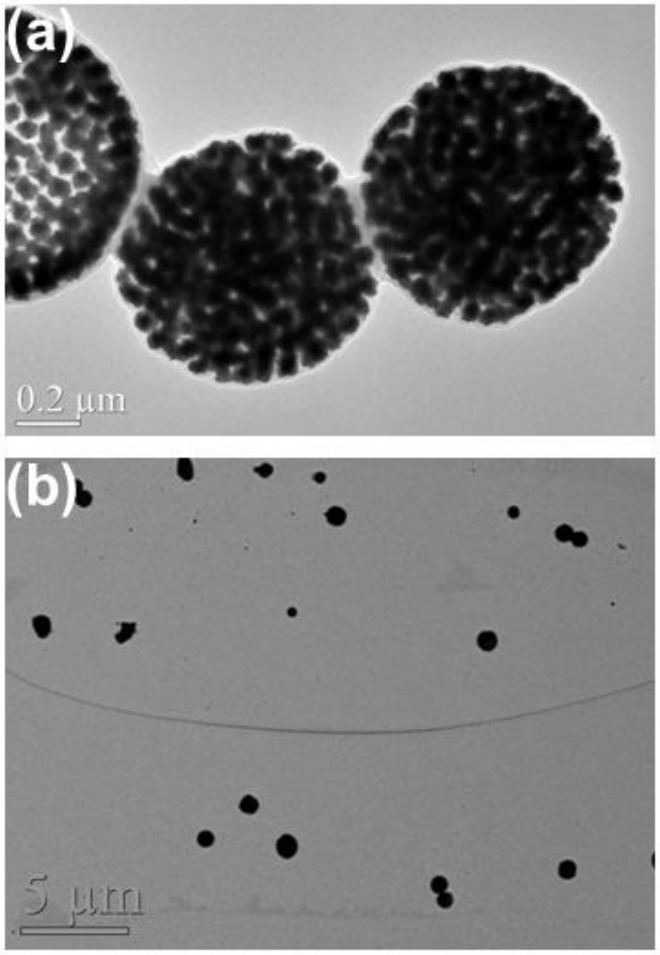

Figure S9. TEM images of vesicles assembled from 63-nm AuNFs.

References

(1) Frens, G. *Nat Phys Sci* **1973**, *241*, 3.
(2) He, J.; Liu, Y.; Babu, T.; Wei, Z.; Nie, Z. *J Am Chem Soc* **2012**, *134*, 11342.
(3) Nie, Z. H.; Fava, D.; Rubinstein, M.; Kumacheva, E. *J Am Chem Soc* **2008**, *130*, 3683.