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Supplementary Information for

Defying Symmetry: A 'flowery' Architecture with Augmented Surface Area from Gold Coated Polymeric 'NanoBlooms'

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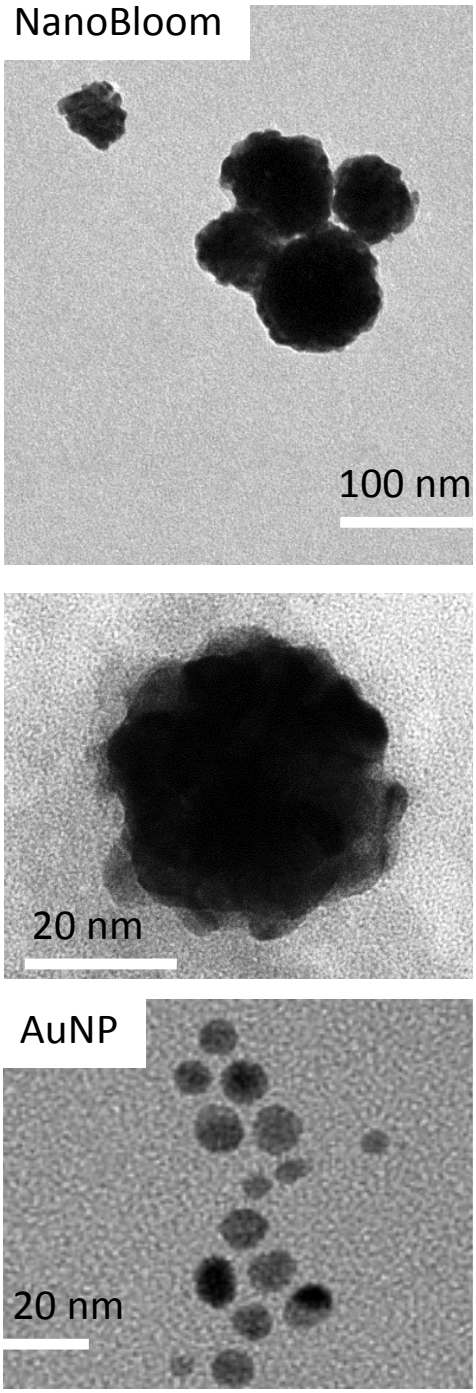

Figure S1. TEM images of nanoblooms and AuNPs.

Materials

Unless otherwise listed, all solvents and reagents were purchased from Aldrich Chemical Co. (St. Louis, MO) and used as received. Anhydrous chloroform and methanol were purchased from Aldrich Chemical Co. Poly(styrene-*b*-acrylic acid)[1] (PS-*b*-PAA) was purchased from Polymer Source Inc. (Montreal, Canada). Polyoxyethylene (20) sorbitan monooleate, manganese acetate was purchased from Aldrich. Argon and nitrogen (Ultra High Purity: UHP, 99.99%) were used for storage of materials. The Spectra/Por membrane (Cellulose MWCO: 20 000 Da) used for dialysis was obtained from Spectrum Medical Industries, Inc. (Laguna Hills, CA).

Typical procedure for the preparation of nanoblooms

To a testube, 1 mg of PS-b-PAA was added and was dissolved in 1ml of THF and 1ml of MeOH combined through vortex. The dissolved solution was then rodaevaporated slowly to form a lipid film. The film was then dried for an hour. 20 ml of deionized and 0.2 μm filtered water was then added to the film and was probe sonicated lightly (power -1), and within less than a minute, gave a uniform, slightly grey transparent solution. To this 10 ml of the solution, 1 mg of PLH-HCl, dissolved in 1 ml of 0.2 μm filtered deionized water was added drop wise. After an hour of notating the solution, precipitate was visible within the solution. 1 ml of the solution was then taken out and was added to 15 ml vortex tube. Along with it, 1 mg of Gold Chloride Trihydrate dissolved in 1 ml of 0.2 μm filtered deionized water, was added to the 1ml of solution. The pH was checked and was initially 3.5. Then 1 M NaOH solution, added dropwise (~3 drops) gave a pH of 9.5. The resulting solution was notarized for 30 minutes.

Meanwhile, a solution containing 1.4 mg of hydroxylamine dissolved in 1 ml of 0.2 μm filtered deionized water was made. After 30 minutes, 1 drop of the hydroxylamine solution was added and then the solution immediately turned black, and then gave a purple color. Two additional drops was added and notarized for another half an hour. DLS was then checked again:

D_{av} (Number-averaged; DLS) =49±4 nm; polydispersity (PDI) = 0.13; Zeta (electrophoretic potential, ζ) = -50±5 mV.

Measurements

Dynamic light scattering measurements (DLS)

Hydrodynamic diameter distribution and distribution averages for the polymeric particles in aqueous solutions were determined by dynamic light scattering. Hydrodynamic diameters were determined using a Brookhaven Instrument Co. (Holtsville, NY) Model Zeta Plus particle size analyzer. Measurements were made following dialysis (MWCO 10 kDa dialysis tubing, Spectrum Laboratories, Rancho Dominguez, CA) of nanoparticle suspensions into deionized water (0.2 μM). Nanoparticles were dialyzed into water prior to analysis. Scattered light was collected at a fixed angle of 90°. A photomultiplier aperture of 400 mm was used, and the incident laser power was adjusted to obtain a photon counting rate between 200 and 300 kcps. Only measurements for which the measured and calculated baselines of the intensity autocorrelation function agreed to within +0.1% were used to calculate nanoparticle hydrodynamic diameter values. All determinations were made in multiples of five consecutive measurements.

Electrophoretic potential measurements (Zeta Potential)

Zeta potential (ζ) values for the polymeric particles were determined with a Brookhaven Instrument Co. (Holtsville, NY) model Zeta Plus zeta potential analyzer. Measurements were

made following dialysis (MWCO 10 kDa dialysis tubing, Spectrum Laboratories, Rancho Dominguez, CA) of nanoparticles suspensions into water. Data were acquired in the phase analysis light scattering (PALS) mode following solution equilibration at 25°C. Calculation of ζ from the measured nanoparticle electrophoretic mobility (μ) employed the Smoluchowski equation: $\mu = \varepsilon\zeta/\eta$, where ε and η are the dielectric constant and the absolute viscosity of the medium, respectively. Measurements of ζ were reproducible to within ±4 mV of the mean value given by 16 determinations of 10 data accumulations.

Transmission Electron Microscopy Measurements (TEM)

Glow discharged carbon/formvar coated nickel grids were floated on a drop of sample for 2 mins. Grids were blotted, rinsed quickly in water, and stained in 1% aqueous uranyl acetate (UA) for 1 min. Samples were blotted, air dried, and viewed on a Zeiss 902 Electron Microscope, and recorded with Kodak E.M. film. Micrographs were collected at 100,000x magnification.

Scanning electron microscopy (SEM) imaging and Energy dispersive X-ray (EDX) analysis

The samples on Si wafer were imaged using a Nova NanoSEM 230 EDAX Genesis in high vacuum mode at 10 kV and at a working distance of 5 mm. Samples were prepared as follows: One drop of nanoblooms suspension in nanopure water was deposited on a piece of clean Si wafer (Si wafer was rinsed and sonicated in nanopure water, ethanol and acetone respectively). After 1 min, excess liquid was removed by touching the edge of the liquid bead using a piece of filter paper. The sample was allowed to air dry for 1 hour before sputter coating, and then was sputter coated with Au-Pd for 15 seconds at 25mA.

References

1. Pan, D.; Williams, T. A.; Senpan, A.; Allen, J. S.; Scott, M. J.; Gaffney, P. J.; Wickline, S. A.; Lanza, G. M. *J Am Chem Soc.* **2009**, *131*, 15522-7.