

Electronic Supporting Information for:

“Gold nanoparticles become stable to cyanide etch when coated with hybrid lipid bilayers”

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Materials and Methods.

HAuCl₄ (Strem Chemicals) and 95% phosphatidylcholine (PC) from soybean (Avanti Polar Lipids) were used as received. CH₂Cl₂ (Sigma-Aldrich) was filtered through basic alumina prior to use. H₂O was from a Milli-Q ultra pure system. All other chemicals and reagent grade solvents were purchased from Sigma-Aldrich and used as received. Absorbance measurements were performed with an Ocean Optics USB2000 UV-Visible spectrophotometer using a 1.0 cm path length quartz cell.

Method 1 for HBN Synthesis – Steps (i) through (iv) in Scheme 1

Synthesis of PC-coated Nanoparticles - step (i).

PC-coated gold nanoparticles were prepared as previously reported with a slight modification.¹ Briefly, a CH₂Cl₂ (10 mL) solution of PC (0.064 g, 0.084 mmol) was added to an aqueous solution of HAuCl₄ (0.029 g, 0.084 mmol in 10 mL of H₂O) while stirring rapidly to form an emulsion. A freshly prepared aqueous solution of NaBH₄ (0.016 g, 0.42 mmol in 5 mL of H₂O) was added dropwise. The solution was stirred for 1 h and was then stored overnight at 4°C followed by removal of both solvents by rotary evaporation. The sample was dissolved in a minimum amount of CH₂Cl₂ and washed

with H₂O (2 x 5 mL). The remaining solvent was removed by rotary evaporation and the product was dried *in vacuo* for 12 h.

Solubility Conversion of Au-PC Nanoparticles – step (ii) and (iii).

Au-PC nanoparticles were dissolved in CH₂Cl₂ (1.0 mL), diluted to an optical density of 1.2 a.u. at 526 nm and dispensed into vials. Uniform thin films were produced by rotating the vials under a stream of N₂. The films were further dried *in vacuo* for 12 h followed by re-suspension in H₂O (1 mL) to produce water-soluble nanoparticles. Samples re-suspended to an optical density of 1.2 a.u. at 526 nm indicating no loss of material.

Formation of HBNs – step (iv).

1-decanethiol (1, 3, 5, 10, or 15 µl of a freshly prepared 1 mM ethanol solution) was added to a dilute aqueous solution (1 mL) of resuspended nanoparticles (OD at 526 nm=1.2 a.u.) and the mixtures were stirred for 5 min. Samples were used for KCN stability studies within 1 h of preparation.

Transmission Electron Microscopy.

Samples were prepared for Transmission Electron Microscopy (TEM) by drop casting dilute solutions of nanoparticles onto carbon-coated (300 Å) Formvar films on copper grids (Ted Pella). Samples were dried in air for at least 1 h before images were obtained. Transmission electron micrographs (Figure S1a) were acquired on an FEI Tecnai F-20 at an acceleration voltage of 200 kV using a CCD detector. Nanoparticle size analysis

(Figure S1b) was performed using ImageJ Software after applying a band pass filter to the images and adjusting the threshold. Images were collected of PC-coated nanoparticles as synthesized, after addition of 10 μ l of 1 mM 1-decanethiol, and 3 months after addition of KCN. The average size of the nanoparticles did not change significantly between these steps. The TEM taken after addition of cyanide revealed a portion (\sim 35%) of nanoparticles in distinct clusters, suggesting that a sub-population of the hybrid bilayers may encapsulate multiple nanoparticles.

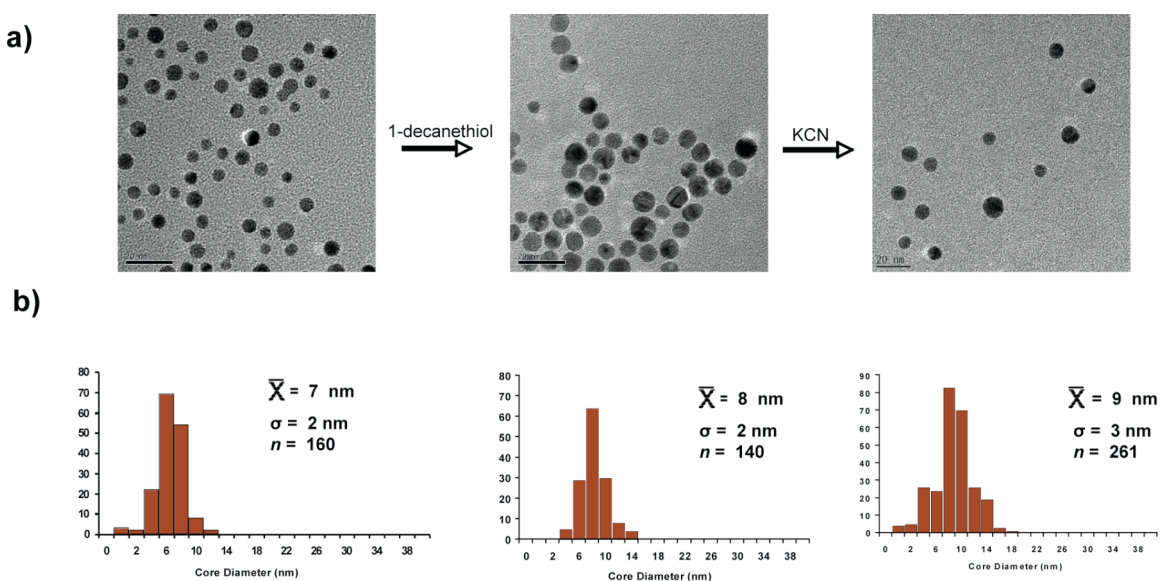


Figure S1. TEM analysis of PC-coated nanoparticles as synthesized (left), after addition of 10 μ l of a 1 mM ethanol solution of 1-decanethiol (center), and 3 months after addition of KCN (right). Scale bars = 20 nm.

Method 2 for HBN synthesis – switching step (ii) and (iv).

1-decanethiol (1, 3, 5, 10, or 15 μ l of a 1 mM ethanol solution) was added to a dilute (1.2 a.u. at 526 nm) CH_2Cl_2 solution of PC-coated nanoparticles (from step (i), Method 1) and the mixture was stirred for 5 min. KCN (1 mg) was added to a portion of these mixed-monolayer organic-soluble nanoparticles and the UV-Vis was monitored for 8 hours as the KCN dissolved (Figure S2). CH_2Cl_2 was removed from another portion by rotary

evaporation and the film was dried *in vacuo* for 12 h. These thin films were re-suspended into water and stability to KCN was measured (Figure S3).

Estimating the Quantity of Thiols on Each Nanoparticle. The nanoparticle sample synthesized in step (i) contains 0.084 mmol of gold. The absence of Au³⁺ in the UV absorption spectrum after the addition of sodium borohydride is evidence of a quantitative conversion of HAuCl₄ to nanoparticulate gold. In step (ii), the samples are diluted 200-fold to 1.2 a.u. (at 526 nm) resulting in a sample that contains 420 nmol of gold. We estimate a quantitative conversion in steps (ii) and (iii) based on the observation that the solubility change occurred without loss of material.¹ The number of gold atoms in a 7 nm diameter nanoparticle with a truncated cuboctahedral shape is estimated (using $N = 283.7r^3$, where r is the nanoparticle radius) to be 12,164 with ~15% of those atoms on the surface.^{2,3} Therefore, a 1.2 OD sample of 7 nm nanoparticles contains approximately 63 nmol of surface gold atoms. When 10 nmol of 1-decanethiol is added to this sample, there are ~6 times more surface gold atoms available than thiols and ~42 times more total gold atoms than thiols indicating that the thiol is present in sub-monolayer quantities.

Stability Studies Using Various Thiols

Thiols were added to dilute aqueous solutions of re-suspended PC-coated nanoparticles (OD at 526 nm=1.2 a.u.) as follows. 6-mercaptohexanol was added in 10 μ l of ethanol and stirred for 5 min. 2-mercaptoethanol was added in 10 μ l of ethanol and stirred for 5 min. Sodium 2-mercaptoethanesulfonate was solubilized in minimal water, added with

10 μl of ethanol, and stirred for 5 min. 1-Decanethiol was added in 10 μl of ethanol and stirred for 5 min. For detergent stability studies (Figure S4), 1-decanethiol in 10 μl of ethanol was added and stirred for 5 min followed by addition of Triton X-100 (10.2 μl) and 15 min of stirring. KCN was added to each sample (6mM final concentration) and the UV-Vis was collected every minute for one hour. The average intensity of the $\lambda_{\text{max}} \pm 2 \text{ nm}$ was calculated at 1 min intervals. 2-mercaptoethanol itself can act as an etchant causing a red-shift in the plasmon resonance of gold nanoparticles.⁴ We exposed a sample of HBNs to 6 mM 2-mercaptoethanol and no substantial change was observed after one hour (Figure S5). In contrast, PC-coated nanoparticles aggregated when exposed to 6mM 2-mercaptoethanol as indicated by a red-shift of 20 nm in the plasmon resonance.

Figure S2. UV-Vis of PC-coated gold nanoparticles in CH_2Cl_2 (red). The same sample 8 hours after addition of 10 μl of 1 mM 1-decanethiol followed by addition of 15 mM KCN (blue).

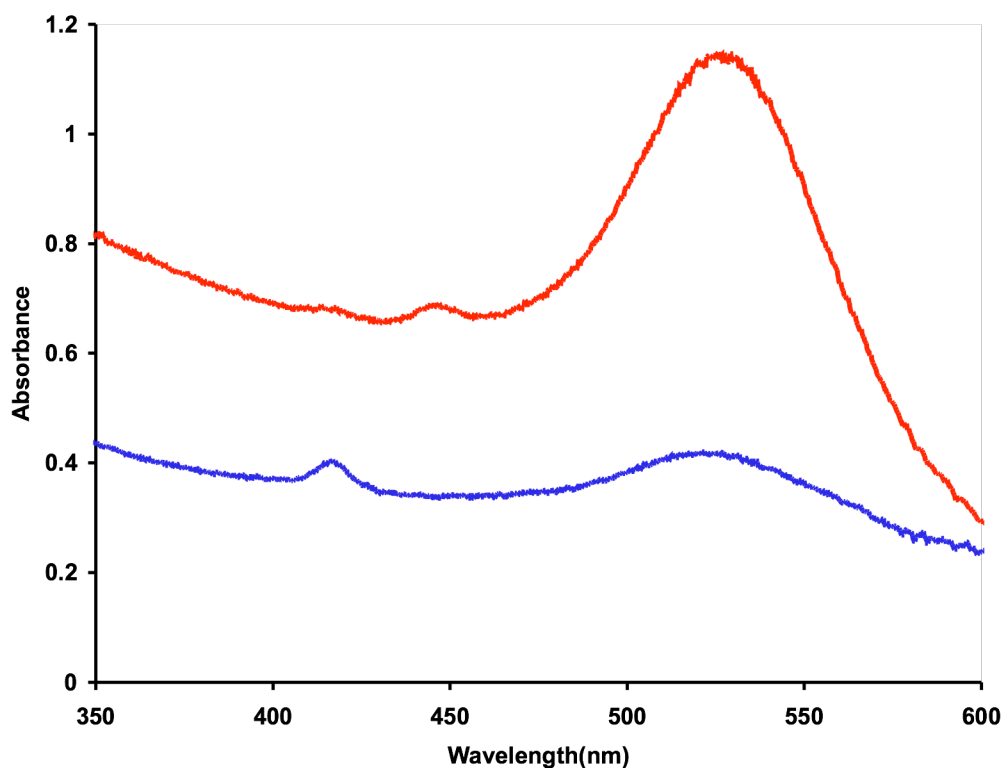


Figure S3. KCN stability of HBNs formed by method 2 with 1-decanethiol at 10 μM (\blacklozenge), 5 μM (\blacktriangle), 3 μM (\blacksquare), and 1 μM (\blacklozenge). Average intensity of the $\lambda_{\text{max}} \pm 2$ nm was calculated each minute after addition of 6 mM KCN.

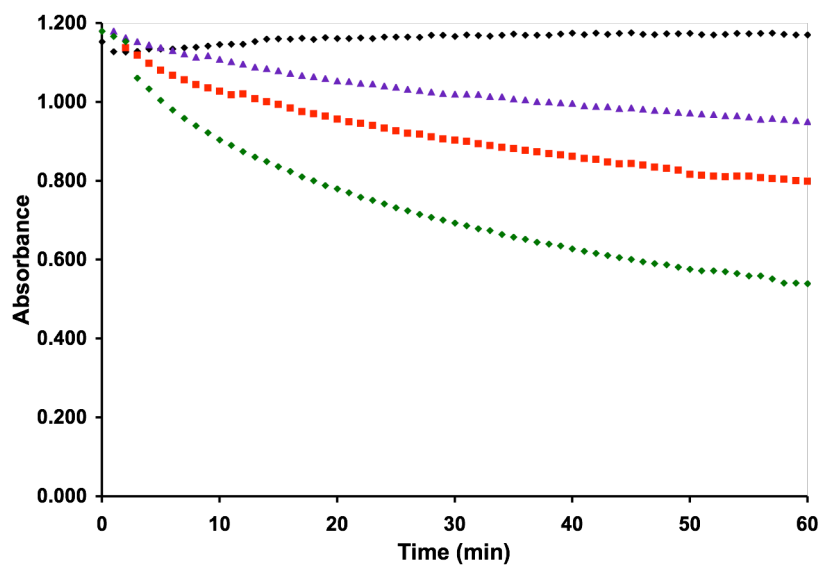


Figure S4. 1-Decanethiol HBNs after addition of 1% Triton (blue), 2 h after addition of 6 mM KCN (red), and 24 h after addition of 6 mM KCN (green).

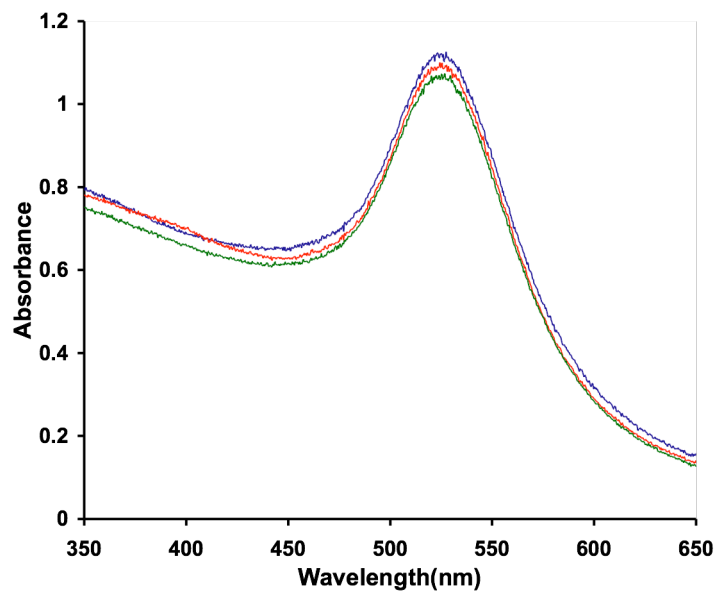
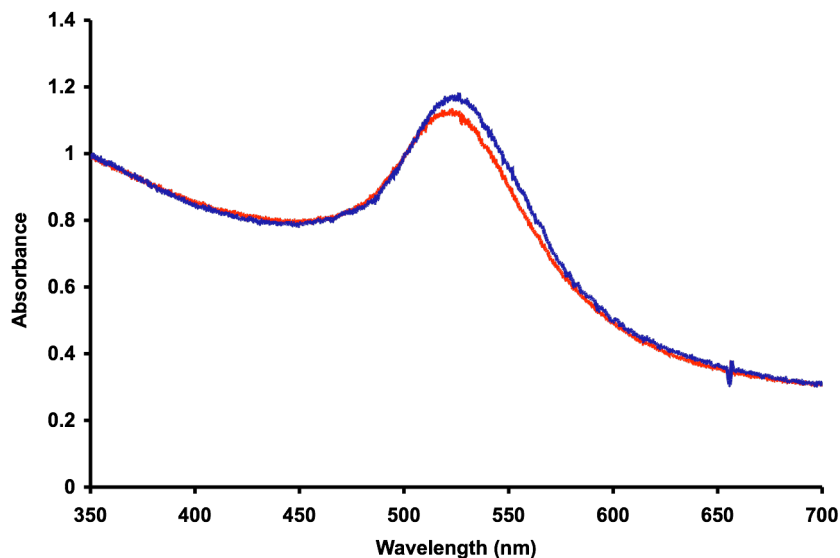


Figure S5. Reaction of HBNs with 2-mercaptoethanol. UV-Vis of HBNs prior to 2-mercaptoethanol addition (blue). UV-Vis of HBNs after 1 hour exposure to 6mM 2-mercaptoethanol (red).



¹ M. R. Mackiewicz, B. R. Ayres and S. M. Reed, *Nanotechnology*, 2008, **19**, 115607.

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⁴S-J. Chen and H-T.Chang, *Anal. Chem.*, 2004, **76**, 3727 – 3734.