

## Supporting Information

### Synthesis and characterization of plasmonic peptoid nanosheets

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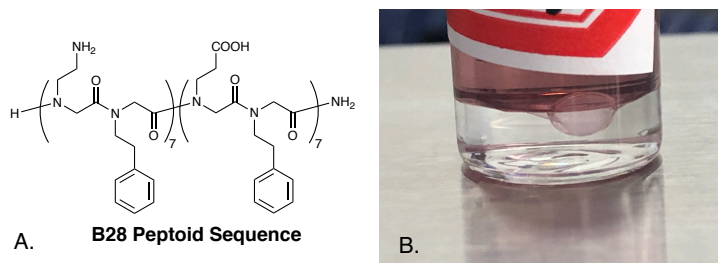
## 1. Nanosheet Synthesis

The peptoid used in these studies was synthesized at The Molecular Foundry as part of a user proposal.<sup>1</sup> Water used in solution preparation was obtained from an Elga PureLab Ultra Water Polishing System and had a resistivity of 18.2 M $\Omega$ -cm. Working peptoid solutions (20  $\mu$ M) were prepared by diluting a stock solution (2 mM peptoid in 2:1 DMSO:water) in a pH 8 solution of 10 mM Trizma base (Sigma Aldrich). Dried 5.2 nm gold nanoparticles (AuNPs) functionalized with dodecanethiol ligands were purchased from nanoComposix. The AuNP stock solution was prepared by dispersing the dried AuNPs in anhydrous toluene (Sigma Aldrich, 99.8%) to a concentration of 5 mg/mL. AuNP solutions used in nanosheet formation ( $\sim$ 0.25 mg/mL) were prepared by diluting the stock solution in toluene to a final volume of 500  $\mu$ L. The absorbances of these solutions were measured at 518 nm using an Agilent 8453 UV/Vis diode array spectrophotometer. The concentrations were calculated using an extinction coefficient of  $9.29 \times 10^4$  M<sup>-1</sup>cm<sup>-1</sup> as described by Sharma et al.<sup>2</sup> The displayed spectrum of the AuNPs dispersed in toluene is a representative spectrum from a 2  $\mu$ M sample. The average LSPR peak position was calculated from spectra of 8 different samples. All work performed with dry AuNPs or AuNPs dispersed in toluene was performed in a fume hood or well-ventilated area with appropriate PPE.

To prepare the AuNP-embedded nanosheets, 500  $\mu$ L of the aqueous peptoid solution was gently dispensed into a 1-dram vial, followed by the 500  $\mu$ L AuNP solution. After allowing a few minutes for the co-assembly of the peptoid and AuNPs at the toluene-water interface to occur, the nanosheets were formed by gently agitating the vials, which caused the sheets to detach from the toluene-water interface and partition to the aqueous phase. Vials were agitated approximately every 10 minutes for at least an hour. Following the formation, the toluene phase was removed from the vial and the surface was washed at least three times with pure toluene to remove free nanoparticles from the surface. Peptoid nanosheets in the absence of AuNPs were formed as described above. The peptoid nanosheet solutions were dialyzed against water for at least 12 hours using 100 kD Float-A-Lyzer dialysis kits to remove free peptoid.

## 2. Peptoid Sequence Studies

Peptoid nanosheets have typically been prepared at the air-water interface using the amphiphilic peptoid sequence<sup>1</sup> (B28) shown in Fig. 1A. We initially attempted to prepare AuNP-embedded nanosheets with B28 at hexane-water and toluene-water interfaces but were not successful. What we observed in these studies was a highly elastic-like composite film that descended into the aqueous phase after agitation (Fig. 1B). However, this film did not collapse to produce nanosheets. We proceeded our studies with the peptoid sequence described in the manuscript, which readily produced AuNP-embedded nanosheets at the toluene-water interface. We believe that B28 does not readily form AuNP-embedded nanosheets because the intermolecular interactions between the B28 hydrophobic groups and the AuNP hydrophobic ligands in the composite monolayer are too strong. These interactions prevent the B28-AuNP monolayer from collapsing and partitioning into the aqueous phase in the form of nanosheets. The extent of interactions between the peptoid reported in the manuscript and the AuNPs in the composite monolayer are not significant enough to prevent monolayer collapse, which is supported by the small effect that the AuNPs have on the surface pressure of the peptoid monolayer at the toluene-water interface (see Fig. 5A in the manuscript).



**Figure 1.** (A) Peptoid sequence (B28) typically used in nanosheet synthesis at the air-water interface. (B) Vial containing B28 in the aqueous phase and 5 nm dodecanethiol-functionalized AuNPs in the toluene phase. Upon agitation, a composite film descended into the aqueous phase but did not collapse to form AuNP-embedded peptoid nanosheets.

### 3. Nanosheet Characterization

Absorbance spectra of the aqueous phase containing the AuNP-embedded nanosheets were measured using an Agilent 8453 UV/Vis diode array spectrophotometer. The reported spectrum is an average from four samples. The AuNP-embedded nanosheets were prepared for imaging by dispensing 20  $\mu\text{L}$  drops of the aqueous phase onto thermal silicon oxide wafers (300 nm  $\text{SiO}_2$  layer on Si(100), MTI Corp.) that had been washed with acetone and subsequently cleaned in a Harrick Plasma Cleaner. The drops containing the solvated AuNP-embedded nanosheets were imaged using an Olympus BX51 optical microscope. After the drops dried, the wafers were washed to remove excess peptoid by gently dipping the wafer in a vial of water, removing, and allowing to air-dry. Thermal silicon oxide wafers allow for imaging nanoscale materials using optical microscopy<sup>3</sup>. Specifically, very thin layers of material (on the order of nanometers) appear as a color red-shifted from the color of the bare substrate. The thicker the deposited material, the greater the red shift. Dry samples of the peptoid nanosheets and AuNP-embedded nanosheets were imaged using the optical microscope, a Zeiss EVO MA-15 scanning electron microscope (SEM), and an Asylum Research MFP-3D atomic force microscope (AFM). AFM images were collected under ambient conditions in tapping mode using commercially available silicon AFM probes with aluminum reflex coatings (resonant frequency of 150 kHz and force constant of 5 N/m).

### 4. Nanosheet Image Library

Figure 2 displays optical microscopy images of solvated AuNP-embedded nanosheets, which demonstrate a variety of sheet shapes.

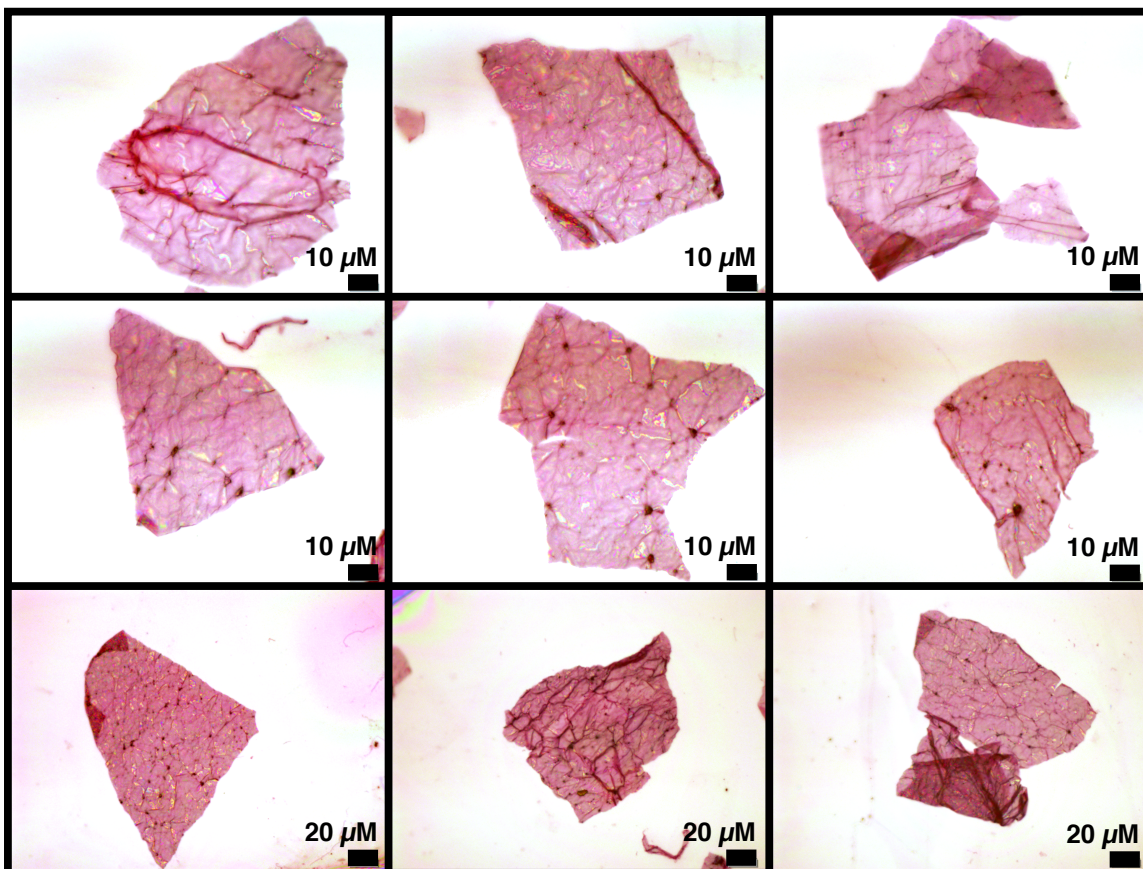


Figure 2. Optical microscopy images of AuNP-embedded nanosheets in solution.

## 5. Pendant Drop Interfacial Tension Measurements

Interfacial tension data were collected using a Theta Lite Optical Tensiometer. In these measurements, a 5-10  $\mu\text{L}$  drop of the toluene phase was suspended from a 1 mL Hamilton threaded plunger syringe equipped with a 22-gauge hooked needle into a 1 cm quartz cuvette containing the aqueous phase. Prior to data collection, the syringe system was copiously rinsed with clean toluene and the cuvette was copiously rinsed with water (18.2M  $\Omega\text{-cm}$ ) until the neat toluene-water interface was measured to be within 1 mN/m of 36 mN/m for 10 minutes. Data collection began within a second after drop formation and images of the drop profile were collected at a rate of 0.2 frames per second. Using the OneAttension software, images of the drop profile were fit to the Laplace-Young equation to obtain the shape factor,  $\beta$ . The interfacial tension,  $\gamma$ , was subsequently calculated using eq. 1.

$$\gamma = \Delta\rho g \frac{R_0}{\beta} \quad (1)$$

Here,  $\Delta\rho$  is the difference in densities between the aqueous and toluene phases,  $g$  is the gravitational constant, and  $R_0$  is the radius of the drop curvature at the apex. The data are reported as surface pressure vs. time and are averages of at least three trials.

## 6. Surface Pressure vs. Surface Area Measurements

Surface pressure vs. surface area measurements were performed using a KSV NIMA Langmuir-Blodgett system equipped with a trough top with a surface area of 197  $\text{cm}^2$  (model KN 2007). Prior to each use, the trough was wiped with ethanol and dried. Water (18.2M  $\Omega\text{-cm}$ ) was cycled through the trough until the air-water surface tension was measured to be between 70-75 mN/m using a paper Wilhelmy plate. The trough was determined to be clean if the surface tension value did not change more than 1 mN/m upon compressing the surface area from 197  $\text{cm}^2$  to 51  $\text{cm}^2$ . Surface pressure vs. surface area isotherms of the peptoid monolayer, AuNP monolayer, and composite layer were collected at the air-water interface. The subphase used in all experiments consisted of 10 mM Trizma base at pH 8. Isotherms were collected as the trough area was compressed at a rate of 50 mm/min from the initial trough area of 197  $\text{cm}^2$  to a final trough area of 51  $\text{cm}^2$  and then expanded back to the initial trough area. Peptoid samples were prepared by dispersing 6  $\mu\text{L}$  of the 2.0 mM peptoid stock solution (corresponding to  $7.2 \times 10^{15}$  peptoid chains) in 50  $\mu\text{L}$  of ethanol, which was spread onto the aqueous subphase. AuNP solutions were prepared by dispersing 4.5  $\mu\text{L}$  of a 76  $\mu\text{M}$  AuNP stock solution (corresponding to  $2.0 \times 10^{14}$  particles) in 1 mL of toluene, which was spread onto the aqueous subphase. For experiments of the composite layer, the peptoid solution was first spread on the aqueous subphase, followed by the AuNP solution. Solvents were allowed to completely evaporate before the start of each experiment. The reported surface pressure vs. surface area isotherms are averages from three separate trials.



**Figure 3.** Photograph of a peptoid-AuNP composite monolayer at the air-water interface after compression in a Langmuir trough, revealing surface features that are perpendicular to the force of the compression.

These Langmuir trough studies revealed the formation of wrinkles and folds in the peptoid-AuNP composite monolayer at the air-water interface, which run parallel to each other and perpendicular to the direction of the compression force (Fig. 3). The image of this compressed monolayer suggests that the parallel surface features that appear on the surfaces of the AuNP-embedded peptoid nanosheets likely form during the compression of the composite monolayer at the toluene-water interface.

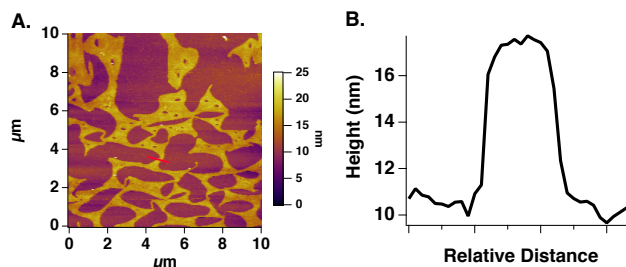


## 7. AFM Image Analysis

AFM images were leveled using the open-source software Gwyddion (version 2.56). These leveled images were imported into Igor Pro 8 (version 8.04) and plotted. Line profiles of each image were obtained between relatively flat regions of the bare substrate and the edge of the sample. In addition, image statistics were obtained in relatively flat regions of interest (ROI) of the nanosheet and bare substrate near the nanosheet edge. Nanosheet thicknesses were determined by subtracting the average height of the bare substrate from the average height of the nanosheet that were determined from the image statistics. The reported average thickness of the AuNP-embedded nanosheets was calculated from AFM images of five different samples and the average peptoid nanosheet thickness was calculated from AFM images of three different samples.

## 8. AFM Analysis of Gold Nanoparticles

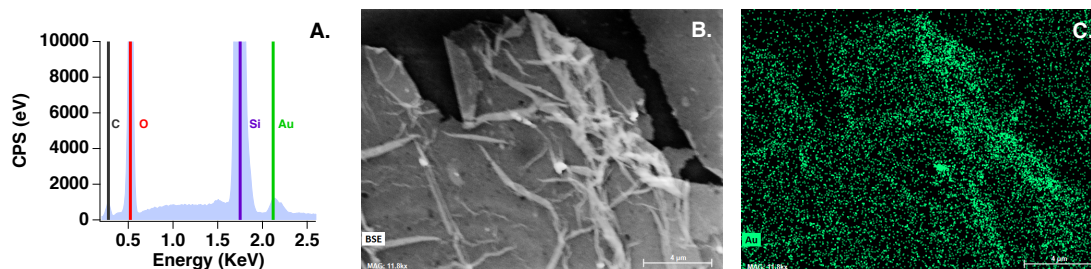
AFM images were obtained of the 5.2 nm dodecanethiol-functionalized AuNPs (Fig.4). The AFM sample was prepared by depositing the AuNPs from the air-water interface to a thermal silicon oxide wafer at a surface pressure of 37 mN/m using the Langmuir trough described above. Analysis of the image shows an average height of  $6.9 \pm 0.4$  nm, which is consistent with the 5.2 nm gold core plus the dodecanethiol ligands.



**Figure 4.** AFM image analysis of 5.2 nm dodecanethiol-functionalized AuNPs. (A) The red line on the AFM image shows where the line profile was obtained. (B) The line profile shows a thickness of  $6.9 \pm 0.4$  nm.

## 9. EDX analysis of composite films

Energy dispersive X-ray analyses (EDX) of the peptoid-AuNP films were performed using a Bruker Quantx 200 EDX system (Fig. 5). The EDX spectrum shows the characteristic K  $\alpha$  X-ray emission line for carbon from the peptoid and AuNP ligand, oxygen and silicon from the thermal silicon oxide wafer, and gold from the AuNPs (Fig. 5A). Comparison of an SEM image of a peptoid-AuNP composite film (Fig. 5B) to the corresponding elemental map for gold (Fig. 5C) shows a higher density of gold where the sheet has folded on itself.



**Figure 5.** Elemental mapping of a peptoid-AuNP composite film. (A) EDX spectrum, (B) SEM image, and (C) gold elemental map for an AuNP-embedded nanosheet.

## **10. References**

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