

Product Information

Technical Bulletin AL-266

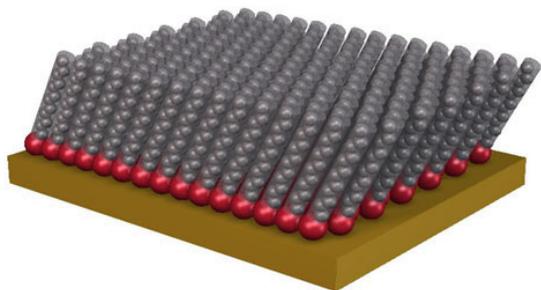
Preparing Self-Assembled Monolayers (SAMs) A Step-by-Step Guide for Solution-Based Self-Assembly

Description

Self-assembled monolayers (SAMs) of thiols are prepared by immersing a clean gold substrate into a dilute solution of the desired thiol.

Figure 1.

Schematic showing an ordered self-assembled monolayer of densely packed alkane thiols.



Although self-assembly takes place rapidly, good experimental procedures are needed to produce consistent, highly ordered films. This technical bulletin outlines a recommended protocol for preparing SAMs.

Reagents and Equipment Recommended

- Gold coated substrates
- Thiol compound(s)
- 200 proof ethanol (Catalog Number 459844)
- Calibrated micropipettes
- Container for mixing thiol solution
- Tweezers for sample handling
- A dedicated ethanol solvent bottle
- Parafilm® (Catalog Number P7793) for sealing containers
- Containers for sample preparation
- Petri dishes for transporting and storing SAMs
- Dry nitrogen gas
- Analytical Balance
- Sonicator
- pH paper

Precautions and Disclaimer

Please consult the Material Safety Data Sheet for information regarding hazards and safe handling practices.

Environment - A clean environment is key to preparing high-quality SAMs. Even low levels of contaminants can affect monolayer quality. Avoid rooms or hoods in which silanes or poly(dimethylsiloxane) (PDMS) have been used. These compounds easily cross contaminate a variety of surfaces. Iodine adsorbs readily onto gold and should also be avoided. All thiols should be handled in a fume hood.

Containers - Appropriate containers include glass or polypropylene (e.g., scintillation vials, polypropylene test tubes and centrifuge tubes). If glass containers are used, they must be cleaned thoroughly to avoid solution contamination.¹ One option for glass cleaning is the use of piranha solution [30:70 v/v solution of 30% hydrogen peroxide (H₂O₂) and concentrated sulfuric acid (H₂SO₄)].

Note: Extreme caution must be taken when using piranha solution. It is a very strong oxidant and reacts violently with organic matter.

Containers should be easily sealable. For the highest quality films, oxygen exposure should be minimized during the assembly process. This is achieved by reducing the headspace above the thiol solution and backfilling with an inert gas. Each substrate is placed in its own container to avoid interactions that would be detrimental to film quality.

Containers can be reused, as long as they are rinsed well with solvent after each use and dedicated to the same thiol to avoid cross-contamination.

Solvent - For most thiols, 200 proof ethanol (Catalog Number 459844) is required for successful assembly.

Note: Elevated levels of copper disrupt the assembly of the thiols and may affect the performance of the resulting SAM.

Sample Slides – Gold-coated slides (Catalog Numbers 643246 and 643203) must have an adhesion layer of chromium (Cr) or titanium (Ti) under the gold layer. If this layer is missing, the gold will delaminate and ruin the monolayer during sonication.

Procedure

This procedure was adapted from an article in *Material Matters*TM Vol. 1 No. 3, written by Dr. Dan Graham from Asemblon and Dr. Sean Dingman from Sigma-Aldrich. It is appropriate for most thiols. Thiols containing amine or carboxy groups require slight modifications described in the procedure. The properties of PEG thiol monolayers depend on the method of self-assembly. Researchers should review the literature before using these materials.⁵⁻⁷

A. Determine necessary amounts and concentration of thiol solution.

1. Calculate the total volume of thiol solution needed to make the number of samples desired:

[Total volume of solution (mL)] = [total number of samples] × [Sample solution volume (mL)].

2. Calculate the total amount of thiol needed to prepare desired amount of thiol solution.

[Mass of thiol (g)] = [Total Volume (mL)] × [C] × [10⁻⁶ mol/ml] × [MW (g/mol)]

Where MW is the Molecular Weight of the thiol, and C is the concentration in mM (typically 1–5 mM).

If the thiol is a liquid, convert the mass to a volume using the density. Use a calibrated micropipette to measure and dispense liquid thiols.

B. Prepare Thiol Solution - Prepare enough solution for all samples to ensure the solution concentration is constant across the sample set. When preparing mixed thiol solutions, prepare a stock solution of each thiol separately, then mix them at the proper proportions for the final stock solution.

1. Rinse all assembly containers with 3–5 mL of solvent. Repeat 2–3 times and re-cap each container. Also rinse all beakers, tweezers, etc., to be used in the experiment.
2. Measure the appropriate volume of solvent into a clean solution container.

3. Dispense the mass (or volume) of thiol into the solvent.

Note: If carboxy or amine terminated thiols are being used, the pH of the thiol solution needs to be adjusted accordingly. For carboxy-terminated thiols, adjust the pH to ~2 by adding a few drops of concentrated HCl (Catalog Number 320331). For amine-terminated thiols, adjust the pH to ~12 by adding concentrated NH₄Cl (Catalog Number 213330) or triethylamine (Catalog Number T0886).

4. Sonicate solution for 5–10 minutes to dissolve.
5. Once dissolved, dispense the planned volume of solution into each sample container.

C. Sample Self-Assembly

1. Immerse gold substrate in container containing thiol solution. Handle gold substrates with tweezers and minimize exposure to air.
2. Backfill each container with dry nitrogen gas, seal the cap and wrap with Parafilm.
3. Store the sample for 24–48 hours. Longer assembly times tend to result in better monolayer packing.

D. Terminate Self-Assembly

Note: Functional groups on thiols can affect self-assembly termination.

1. For simple alkane thiols, hold sample with clean tweezers and rinse with solvent for 10–15 seconds using a clean solvent bottle. Note: For thiols with hydrogen-bonding, polar or bulky head groups, hold sample with clean tweezers and rinse with solvent for 10–15 seconds from a clean solvent bottle.
2. Dry sample with a stream of dry nitrogen gas.
3. Place each sample in a container with fresh solvent and close the cap.
4. Sonicate the samples for 1–3 minutes.
5. Remove the samples individually and rinse again for 10–15 seconds under a steady stream of ethanol. At this stage no pH adjustment is necessary. Use pure solvent.
6. Dry sample with a stream of dry nitrogen.

E. Sample Storage

1. Place in clean Petri dish or desiccator.
2. Backfill Petri dish with dry nitrogen.
3. For long-term storage - Place Petri dishes in a jar backfilled with dry N₂ and sealed with Parafilm. If you are going to use the monolayers for further experimentation, plan your experiments so you can rinse the samples right before use. Minimize time between preparation and use, since SAMs can oxidize over time.

References

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