How to Prepare Self-Assembled Monolayers

Theory of Self-assembly

Self-assembly of alkanethiols on gold occurs spontaneously and is driven by the strong interaction between the sulfur group and gold. To prepare self-assembled monolayers (SAMs), a dilute solution of the desired alkanethiol is commonly prepared. Next, a clean gold substrate is immersed into this solution for a period of several hours to a few days. A typical protocol for preparing SAMs is outlined below.

This general protocol is appropriate for most alkanethiols, but some compounds require modifications to the protocol to obtain well ordered SAMs. Examples of these include carboxy-, amine-, and PEG-terminated alkanethiols. For more information, see pages 54 and 56, respectively.

Summary of Protocol 1

Step 1: Determine amounts and concentration of alkanethiol solution.
Step 2: Prepare alkanethiol solution in the desired solvent.
Step 3: Start self-assembly.
Step 4: Stop self-assembly.
Step 5: Store SAMs.

Equipment and Materials

NOTES

Containers: Glass or polypropylene containers can be used for alkanethiol assembly. If glass containers are used, it is often necessary to clean them extensively to avoid solution contamination. One option for glass cleaning is the use of piranha solution (30:70 v/v solution of 30% hydrogen peroxide (H_2O_2) and concentrated sulfuric acid (H_2SO_4)). ***Extreme caution has to be taken when using piranha solution. It is a very strong oxidant and reacts violently with organic matter.***

Containers that can be easily capped and sealed are generally used. Each substrate is placed in its own container to avoid overlap of the samples. This prevents substrates from covering or scratching each others' surfaces and will assure that monolayer formation is not inhibited

Self-assembly containers can be reused, as long as they are rinsed well with ethanol after each use and dedicated to the same alkanethiol to avoid cross-contamination.

Solvent: For most alkanethiols, pure ethanol (200 proof) is required for successful assembly. Solvent purity should be verified due to potential contamination by copper. If the levels of copper are too high, the copper will disrupt the assembly of the alkanethiols and may affect the performance of the resulting SAM.

If 200-proof ethanol is not available, denatured alcohol, containing up to 5% isopropanol and/or methanol, is a suitable substitute. Again, it is important to verify that the solvent does not contain copper.

Dedicated wash bottle: It is best to have a dedicated solvent wash bottle (with squirt spout) for ethanol used for rinsing containers, substrates and SAMs. Store the bottle empty and only fill it with fresh ethanol when needed.

Equipment List

1. Gold coated substrates (For information on gold substrates see the section called "Gold Substrate Preparation" on page 45)
2. Alkanethiol compound(s)
3. Fresh 200 proof ethanol
4. Container for mixing thiol solution
5. Tweezers for sample handling
6. A clean solvent bottle for ethanol (with squirt spout)
7. Parafilm for sealing containers
8. Containers for holding samples during assembly
9. Petri dishes for transporting and storing SAMs
9. Dry nitrogen, for sample drying

Protocol 1: Step-by-step Instructions

Preparation for Self-Assembly

Step 1: Determine necessary amounts and concentration of alkanethiol solution.

Step 1a: Calculate the total volume of alkanethiol solution needed to make the number of samples desired.

NOTE

Self-assembly will occur onto the surface as long as the surface is exposed to the alkanethiol solution, but it is important to minimize exposure to oxygen during the assembly process. For this it is necessary to reduce the head space above the alkanethiol solution and backfill the space with an inert gas, such as nitrogen or argon. To do this, one should plan to use a container that will allow adequate ease of sample handling and minimize the amount of solution necessary with minimal head space. Regardless of the container size, it is recommended to fill the container approximately halfway to reduce the head space above the solution. Some suggested containers are scintillation vials, polypropylene test tubes and centrifuge tubes.

Example Calculation:

If using a 10mL polypropylene test tube for the assembly with 5mL of solution per container, then the total amount of solution needed would be:

[Total volume of solution (mL)] = [total number of samples] **x** [5mL]

Step 1b: Calculate the total amount of alkanethiol needed to prepare desired amount of solution.

NOTE

Most literature refers to 1 mM solutions for performing the self-assembly.

Example Calculation:

To calculate the mass of alkanethiol needed for total volume of a 1mM solution:

[Mass of alkanethiol (g)] = [TotalVolume (mL)] **x** [1L/1000mL] **x** [0.001 mol/L] **x** [MW(g/mol)]

If the thiol is a liquid, you can convert the mass to a volume using the density of the thiol. Use a calibrated micropipet for measuring and dispensing liquid alkanethiols.

[Total volume alkanethiol (mL)] = [Mass alkanethiol (g)] ÷ [density (g/mL)]

Step 2: Preparing the alkanethiol solution.

Step 2a: Rinse all equipment used for self-assembly.

- Fill clean solvent squirt bottle with ethanol (or solvent used for self-assembly, if different than ethanol)
- Rinse all assembly containers with ethanol by squirting ~3 to 5 mL around the inside of the containers. Empty container and dispose of ethanol.
- Repeat 2-3 times and then re-cap each container.
- Rinse all beakers, tweezers, etc., to be used in the experiment with ethanol.

NOTE

It is important to be as clean as possible in SAM preparation. Even low levels of contaminants can affect your results. Be especially careful to avoid rooms or hoods in which someone has been doing silane or poly(dimethylsiloxane) (PDMS) chemistry. If these compounds are in the room, they are likely to be on your surface as well. Additionally, iodine adsorbs readily onto gold and should be avoided.

Step 2b: Label all containers.

Step 2c: Measure the appropriate amount of ethanol into a clean container.

Step 2d: Measure needed alkanethiol.

- Weigh out the amount of alkanethiol, as calculated in step 1b (on an accurate scale) if the alkanethiol is a solid.
- Dispense appropriate amount of alkanethiol, as calculated in step 1b, using a calibrated micropipette if alkanethiol is a liquid.

WARNING

Be sure to open all alkanethiol containers and dispense all alkanethiols ***IN A HOOD***. Alkanethiols have an obnoxious smell and many are toxic (***check MSDS before using***).

Step 2e: Add the alkanethiol to ethanol.

NOTE

Depending on the alkanethiol and the solution concentration used you may need to sonicate or heat the solution to get the alkanethiol to dissolve. Alkanethiols with a chain length greater than 17 carbons have this problem.

Step 2f: Once dissolved, dispense the planned volume of solution into each vial.

NOTE

Prepare enough solution for all samples used in one experiment so that the solution concentration is constant across the sample set. When preparing mixed alkanethiol solutions first make up a stock solution of each alkanethiol separately and then mix them at the proper proportions for the mixture.

The Assembly Process

Step 3: Start Self-Assembly

Step 3a: Immerse gold substrate in container containing the alkanethiol solution.

Handle gold substrates with tweezers and minimize expose to air, to reduce surface contaminants.

Step 3b: Backfill each container with dry N_2 and seal the cap.

Step 3c: Wrap the cap of each container with Parafilm.

Step 3d: Store the sample for the desired assembly time.

NOTE

Varying assembly times have been reported in the literature, but if a well assembled, fully annealed monolayer is desired, it is recommended to assemble for at least 24 to 48 hours. In general, longer assembly times tend to result in better packed monolayers. It is true that a monolayer most likely forms after a few minutes or a couple hours, but this initial layer is probably not well packed. It takes time for the chains to anneal out gauche defects and assume an all trans configuration. Also there is some evidence that SAMs formed from dilute solutions for longer times form better packed SAMs.

Step 4: Stop self-assembly.

Step 4a: If you are working with simple methyl terminated SAMs:

- Hold the sample with clean tweezers and rinse with copious amounts of ethanol for 10 to 15 seconds from a clean solvent bottle.
- Dry sample with a stream of dry nitrogen.

Step 4b: If you are working with SAMs with hydrogen-bonding, polar or bulky head groups:

- Hold the sample with clean tweezers and rinse with copious amounts of ethanol for 10 to 15 seconds from a clean solvent bottle.
- Place each sample in a container with fresh ethanol and close the cap.
- Sonicate the samples for 1 to 3 minutes.
- Remove the samples individually and rinse again for 10-15 seconds under a steady stream of ethanol.
- Dry sample with a stream of dry nitrogen.

IMPORTANT

If you have to sonicate a SAM sample, you 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 your monolayer will be ruined.

Step 5: Store SAMs.

Step 5a: Place in clean petri dish.

Step 5b: Backfill petri dish with dry N_2.

NOTE

- 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.

- **If samples must be stored** place the petri dishes in a jar backfilled with dry N_2 and sealed with Parafilm. This should allow long-term storage.

Chemical Waste Disposal:

Waste should be disposed of according to standard operating procedures for your laboratory.