Variations in the Assembly Protocol for Carboxy- and Amine-Terminated Alkanethiols

Most thiols can be assembled successfully using the protocol described in our "General Self-Assembly Procedure" online (http://asemblon.com/sc/tutorials). However, some thiols have been found to form better SAMs by using a modified protocol. Variations for the assembly of carboxy- (COOH) and amine-terminated alkanethiols are listed below. Asemblon does not guarantee that the protocols listed below will work for all COOH and amine- terminated alkanethiols, but provides them as a starting point for the creating of high-quality monolayer surfaces.

Carboxy- (COOH) terminated Alkanethiols

Some researchers have reported that monolayers of carboxy-terminated alkanethiols form more highly ordered layers when assembled from and/or rinsed with acidic ethanol solutions.[1, 2] Assembly from or rinsing with an acidic solution assures that the carboxy terminus remains protonated and reduces multilayer formation. It has also been suggested that using a polar aprotic solvent can reduce multilayer formation and increase ordering in COOH SAMs.[3] We have found the following simple modifications to our standard protocol to work well for COOH terminated SAMs.

Variations from the standard protocol: "General Self-Assembly Procedure"

(See http://asemblon.com/sc/tutorials)

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

- Use a 0.5 mMol solution instead of a 1 mMol solution in ethanol.

Step 4a and b: Rinsing solvent modification

- Place a sample into fresh ethanol in a new container
- Vortex the sample for 20 to 30 seconds
- Place the sample into ethanol that has been acidified by adding a few drops of acid (pH~2)
- Vortex the sample for 20 to 30 seconds
- Place the sample in neutral ethanol
- Vortex the sample for 20 to 30 seconds
- Dry the samples with a stream of N_2 gas

Amine-terminated Alkanethiols

Some researchers have reported that monolayers of amine terminated thiols form more complete and well ordered monolayers when assembled from and/or rinsed with basic ethanol solutions.[2,4] Assembly from basic solution assures that the amine terminus remains deprotonated and reduces multilayer formation. We have found the following simple modifications to our standard protocol to work well for amine terminated SAMs.

Variations from the standard protocol:

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

- Use a 0.5 mMol solution instead of a 1 mMol solution in ethanol.

Step 4a and b: Rinsing solvent modification

- Place a sample into fresh ethanol in a new container
- Vortex the sample for 20 to 30 seconds
- Place the sample into basic ethanol solution (10%v/v NH4OH)
- Vortex the sample for 20 to 30 seconds
- Place the sample in neutral ethanol
- Vortex the sample for 20 to 30 seconds
- Dry the samples with a stream of N_2 gas

Chemical Waste Disposal:

Follow standard protocols established in your lab for handling and disposing of acidic and basic solutions.

References:

1. Arnold, R.; Azzam, W.; Terfort, A.; Woll, C., *Langmuir* **2002**, *18*, 3980-3992.
2. Wang, H.; Chen, S. F.; Li, L. Y.; Jiang, S. Y., *Langmuir* **2005**, *21*, 2633-2636.
3. Noh, J.; Konno, K.; Ito, E.; Hara, M., *Jpn. J. Appl. Phys. Part 1 - Regul. Pap. Short Notes Rev. Pap.* **2005**, *44*, 1052-1054.

4. J.E. Baio, T.Weidner, J. Brison, D.J. Graham, Lara J. Gamble, David G. Castner, J. Electron. Spectrosc. Relat. Phenom. **2009**, 172, 2-8.