

Study of organic monolayers' effects on gold-plated surfaces wettability in the interest of biocompatibility

Background

Aerogels, lightweight, micro-porous substances, have been researched (with much success) as implants to promote neural regrowth. [1] Although these implants are biocompatible on their own, gold-coated aerogel implants (which have the benefit of having a non-reactive outer surface and the ability to pass a current along it to further promote neural regrowth) have demonstrated poor biocompatibility in preliminary testing.

There are two potential problems that could be causing this: the gold coating is too thin and is flaking off *in vivo*, or the surface chemistry of the gold doesn't bond properly to certain proteins and therefore results in biological rejection.

To fix the second problem, we hypothesized that a chemical structure called a self-assembled monolayer (SAM) could adhere to the gold coated aerogel and alter the surface chemistry to a more biologically acceptable level. SAMs are preferred due to their ability to alter the surface chemistry of an object without changing bulk properties. [2] Research has documented their effects on cell adhesion [3], along with several biomolecules that can make SAMs [4-5]. One of these biomolecule SAMs is pictured in **Fig. 1**.

In order to test this hypothesis, we used both surface-air and liquid-liquid contact angle measurements to test their wettability, or hydrophilicity/ hydrophobicity, which is a clear indicator of surface chemistry changes. The surface-air contact angle method, where a water droplet is merely deposited on the surface, is the most commonly used and widely accepted. However, the liquid-liquid method, which submerges the slide upside down and floats an octane droplet up to the surface, is in an environment that is similar to physiological conditions and therefore very relevant in this case. [6]

- Goals:**
1. Determine whether SAMs on gold-coated aerogels have similar wettabilities as gold slides.
 2. Design and implement a liquid-liquid contact angle measurement setup.

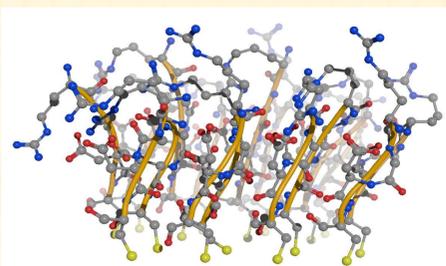


Figure 1. RGDC peptide in SAM formation. The yellow ribbons represent the "backbone" of the molecules, which are all organized.

Methodology

Sample Preparation: Each gold slide was cleaned in piranha solution (70:30 H₂SO₄: 30% H₂O₂) for 15 minutes. After being cleaned, they were rinsed in deionized water, dried in ultra high purity N₂, rinsed in ethanol and methanol, and finally deposited in ~1mM solutions of each of the alkanethiols shown in **Table 1**. SAMs were also formed on pre-cleaned aerogels by placing them into four selected solutions.

	RGDC peptide	S3
	11-mercapto-1-undecanol	S4
	methyl-3-mercapto propionate	S5
	L-cysteine	S6
	S-(4-cyanobutyl) thioacetate	S7
	1-adamantanethiol	S8
	4-bromophenyl thioacetate	S9
	5-tert-butylthioacetate	S10
	1-undecanethiol	S11
	1-octadecanethiol	S12

Table 1. List of the chemicals with their structures, full names, and abbreviations used in **Fig. 6-7**.

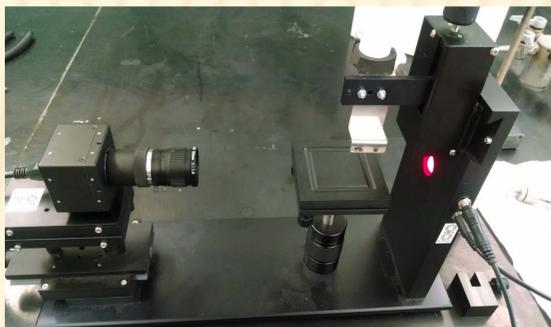


Figure 2. Surface-air contact angle measuring setup.

Contact Angle Measurements: To measure the contact angles of each sample, both the traditional surface-air (air/water/substrate) method and the liquid-liquid (water octane/substrate) method were used. For the surface-air method, a 10μL water droplet is deposited on the surface (**Fig. 2**) while in liquid-liquid tests the slide is submerged upside-down in water and an octane droplet is released upwards from an inverted needle (**Fig 3**).



Figure 3. Liquid-liquid contact angle measurement setup

Contact Angles

Glass Slide versus Aerogel: Gold coated aerogel surfaces are by no means ideal, which is why there were doubts that the SAMs would not adhere properly. Aerogels have a vast network of microscopic tunnels that make it difficult for an ideal, perfectly uniform lattice to form. Also, during the preparation of the aerogel slides, rough saw cuts created a macroscopically uneven surface. Finally, as you can see in **Fig. 4**, the gold coating on the aerogel is very thin (only 14 nm) and uneven, resulting in high deviations in SAM adherence that could cause contact angles to differ almost 20 degrees on some samples. In future testing, and if these gold plated aerogels ever become implants, ensuring a thick coat of gold and a clean cut of the surface will be paramount to its effectiveness.



Figure 4. Gold slide (left) and aerogel (right)

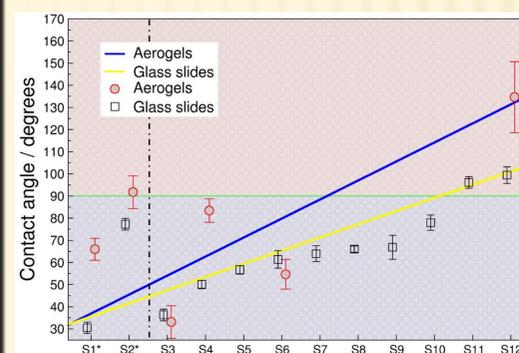


Figure 5. Surface-air contact angles for both glass slides and aerogels.

Graph Notes: The x-axis labels represent SAM-forming compounds, with the asterisked first two representing the controls of non-gold plated glass/aerogel (S1*) and gold-plated glass/aerogel (S2*).

The red and blue areas represent hydrophobic and hydrophilic contact angles, respectively. The liquid-liquid colors are reversed because it is based on an octane droplet in water, effectively inverting the angles.

Graph Notes (contd.): The blue and yellow lines are a visual aid to represent the general trends of the data points.

The increased variations of the glass slide measurements in the liquid-liquid tests are possibly due to surface chemistry alterations in an aqueous environment, with potential protonation and solvation altering how the octane droplet adhered to the surface. [7]

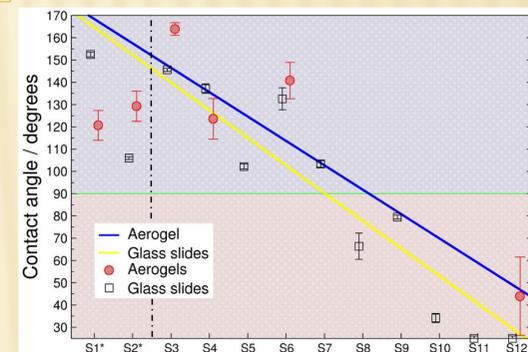


Figure 6. Liquid-liquid contact angles for both glass slides and aerogels.

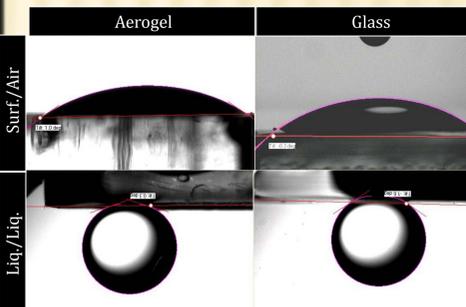


Figure 7. A comparison of RGDC peptide on glass versus aerogel.

RGDC Peptide: RGDC peptide is by far the most promising aerogel coating. In surface-air tests it matched the gold slide's contact angles, and even more importantly it created an even more extreme contact angle in the liquid-liquid tests (**Fig. 7**). This increase in effectiveness may have been due to protonation of the RGDC peptide in water, as it contains two NH₂ groups and two COOH groups.

Concluding Remarks

I was able to create a liquid-liquid contact angle measuring system for our goniometer using an inverted needle, a glass cuvette full of water, and a custom 3D printed inverted slide holder. Because of this other projects will benefit from the addition of a new contact angle measuring technique.

RGDC peptide and L-cysteine are effective at altering surface chemistry on gold-plated aerogels, suggesting that with further research they may be able to increase the biocompatibility of gold-coated aerogel implants. However, any effects they may have are totally dependant on the quality of preparation and the thickness of the gold layer.

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