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Adsorption of Fluorescently Tagged Self-Assembled Monolayers onto Zinc Selenide Thin Films through Microcontact Printing

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Self-assembled monolayers, Zinc Selenide, Microcontact printing

ABSTRACT

Self-assembled monolayers (SAMs) are a spontaneously formed, organized, single layer of organic molecules adsorbed onto a surface. SAMs have many applications, one of which is in the development of biosensors. In the current work, polydimethylsiloxane (PDMS) stamps were utilized to microcontact print fluorescein tagged 11-amino-1-undecanethiol SAMs onto zinc selenide thin films. Initial experiments were run using non-tagged 11-amino-1-undecanethiol hydrochloride to determine an alkanethiol concentration for microcontact printing. A 0.3 mM concentration resulted in successful microcontact printing on both ZnSe and gold thin films and a pattern was visualized using steam imaging at a macroscopic level. The formation of self-
assembled monolayers was confirmed by contact angle goniometry, with angles changing from 24.9(±1.8)° to 39.7(±2.1)° for ZnSe films and 46(±4.4)° to 61(±2.6)° for gold films. Microcontact printing using a 0.3 mM concentration of 1:9 fluorescein tagged 11-amino-1-undecanethiol to non-tagged 11-amino-1-undecanethiol resulted in a pattern initially visualized under a fluorescent microscope. After an ethanol rinse, the pattern was no longer observed. Steam imaging was inconclusive due to a poorly visualized pattern and contact angles changed from 19.8(±5.3)° to 48.6(±5.6)°. Additional experiments are required to determine the cause for the observed loss of a fluorescent pattern after rinsing with ethanol. Future work utilizing this procedure will enable the formation of patterned, functionalized SAMs which can be used in developing biosensors for disease detection.

INTRODUCTION

Self-assembled monolayers (SAMs) are a type of nanostructure formed from the organized and spontaneous adsorption of a single layer of organic molecules onto the surfaces of a substrate.1,2 The first reported observations on the self-assembly of monolayers was by W.A. Zisman and his coworkers in the late 1940s, however, extensive research on this phenomenon did not begin until the 1980s.2,3 SAM formation is similar to the self-assembly of molecules that occurs in nature to produce biological compounds.4 Studying the thermodynamic process of SAM formation could give insight into how biological compounds like proteins and enzymes can form and function in cells. Beyond these sorts of fundamental insights, the study of SAM formation also opens the possibility for generating molecularly designed surfaces and investigating interfacial and surface phenomena.1,2
SAMs can be characterized as having four general parts: the (usually metal) substrate with which the organic molecule chemically or physically interacts, the headgroup of the organic molecule which binds to the metal substrate, the spacer which is an alkane chain that follows the headgroup, and finally the end of the organic molecule which is the terminal functional group (Figure 1).\textsuperscript{1} The headgroup of the SAM is a functional group that can interact or react with a metal substrate and this results in the organic molecule’s attachment to the metal surface.\textsuperscript{1} The end functional group is the part of the molecule that can be manipulated and changed in order to change the properties of the SAMs, and allows the SAMs to be used in various applications such as biosensing.\textsuperscript{1,2} By employing various headgroups and end functional groups the molecule-substrate and molecule-solvent interactions can be studied.\textsuperscript{1,2}

\textbf{Figure 1.} The general structure of a self-assembled monolayer.

The formation of a SAM is a thermodynamically favorable process that occurs due to a chemical or physical interaction between the metal and the adsorbate. The presence of a SAM can be advantageous in some cases because it protects the metal from other common chemical reactions, such as oxidation. This interaction between the surface and adsorbate tends to lower
the surface energy of the metal, decreasing the likelihood the system will spontaneously react with its environment.\textsuperscript{1}

The adsorption and formation of a SAM can occur through either of two main pathways: physisorption or chemisorption. Physisorption, or physical adsorption, is adsorption caused by van der Waals interactions between the headgroup and substrate.\textsuperscript{5} Chemisorption, or chemical adsorption, is adsorption due to a covalent or ionic force between a substrate and adsorbate.\textsuperscript{5} SAMs are typically formed by chemisorption in which the organic adsorbate is in solution or a gas phase and through physical contact between the metal substrate and organic adsorbate, monolayers form. Once the organic molecules adsorb to the metal, they organize into dense crystalline structures due to the van der Waals forces between the chains.\textsuperscript{1,6} Since the organization of the SAMs depends on the intermolecular forces between the chains, longer, linear chains of the organic adsorbate form at quicker rates and increase in their stability with each additional carbon in the chain.\textsuperscript{1,2,6} Depending on the type of metal to which the organic molecules adsorb, the molecules will display a different tilt angle, which is the angle the molecule chain is in with respect to the line perpendicular to the substrate (Figure 2).\textsuperscript{1} This angle usually remains consistent as long as the organic molecule chain does not have strong polar bonds near the surface of the substrate.\textsuperscript{1} In order to functionalize the end group, it is important to have a longer chain in order to have a stable structure, and to make sure the end group does not react with the surface.\textsuperscript{1,6}
Figure 2. The tilt angle, $\theta$, is the angle the chains are from a perpendicular line to the substrate.

Alkanethiols, which are made up of an end group, an alkane chain, and a thiol group (-SH), are one of the most commonly studied organic molecules in SAMs due to thiol’s high affinity to metals. One of the most commonly studied interactions is between thiols and gold. Thiols attach to gold via a Lewis acid-base reaction, where the sulfur, a Lewis base, forms a bond with gold, which is a soft Lewis acid.

Much of the research done on SAMs has used gold as a substrate, but that is not the only possible substrate. Research has also been done with other metals like copper, silver, palladium, and platinum. One of the possible substrates that has been tested is Zinc selenide. Studies have been done in the formation of thiols with ZnSe and this research has found that thiols readily adsorb to Zinc selenide. One of the advantages of using ZnSe is that it allows for transmission in the infrared region making it a very useful tool in the study of the organic molecule structures. If a SAM formed on the ZnSe surface, the presence of the organic molecule could be determined by running a transmission FT-IR. Additionally, ZnSe is hydrophilic while the organic molecules are hydrophobic. The formation of SAMs can be determined by the change in water contact angles. To observe these changes, the monolayers would first need to adsorb onto the ZnSe surface. One method commonly used for adsorption of the molecules is immersion in
which the molecules are dissolved in a solution, and the substrate is left in the solution allowing for the monolayers to form.\textsuperscript{2} Another method of monolayer formation is through microcontact printing which involves the inking of a small featured stamp with the monolayer solution and placing the stamp on the surface of a clean substrate.\textsuperscript{10,11} Through microcontact printing, monolayers can be placed on the surface in a pattern.

The goal of the following experiment was to successfully microcontact print fluorescently tagged SAMs onto ZnSe thin films. The experiments performed in the formation and microcontact printing of fluorescein tagged alkanethiols were based on Dr. Alison Noble’s work performed at Linköping University. Successfully microcontact printing fluorescently tagged SAMs is an important step in utilizing ZnSe as a biosensor.

**EXPERIMENTAL METHODS**

**Cleaning ZnSe slides.** ZnSe thin films were placed into a UV-ozone chamber for twenty minutes. The slides were then alternatively rinsed with 200 proof ethanol and dried with nitrogen gas three times. The entire process was repeated twice more to fully clean the slides. Contact angles of the clean slide were measured.

**Microcontact printing.** To microcontact print, a solution of 0.1-0.3 mM 11-amino-1-undecanethiol hydrochloride in 200 proof ethanol was prepared. 11-amino-1-undecaenthiol hydrochloride was obtained from Sigma-Aldrich. A PDMS stamp was inked by dipping a sterile q-tip in the alkanethiol solution and coating the stamp. The stamp was left to dry in normal room conditions for 30-45 seconds and then dried with N\textsubscript{2} gas for 15 seconds. The stamp was then placed on a clean ZnSe thin film for 30 seconds (Figure 3). The thin film was rinsed with ethanol
and dried with N\textsubscript{2} gas. The contact angles were taken. The pattern on the slide was visualized by steam imaging at a macroscopic level.

**Figure 3.** A PDMS stamp is inked with the organic molecule in solution and placed on the substrate, zinc selenide, leaving behind SAMs in the shape of the stamp.\textsuperscript{23}

**Fluorescently tagged microcontact printing.** An EDC-NHS coupling reaction was utilized to tag a primary amine alkanethiol molecule with fluorescein. A 1 ml solution of 50.4 mM 11-amino-1-undecanethiol and 76.5 mM NHS-fluorescein was prepared and placed covered in an orbital shaker for one hour at room temperature at 400 rpm. NHS-fluorescein was obtained from Thermo-Fisher. Molecules were assumed to be tagged and a 0.3 mM solution of 1:9 fluorescently tagged to non-tagged molecules was prepared. The microcontact printing procedure was followed emitting the ethanol rinse. The film was imaged using a fluorescence microscope. The film was then rinsed with ethanol and reimaged.

**RESULTS AND DISCUSSION**

**Microcontact Printing.** Unsuccessful microcontact printing resulted in no visualized pattern after steam imaging, while successful printing showed the PDMS stamp’s pattern (Figure 4). A change in contact angles confirms the presence of hydrophobic substances on the substrate.
Several experiments were conducted with varying 11-amino-1-undecanethiol concentrations and experimental setups. Contact angles of the clean ZnSe thin film were 27.3(±4.5)°. After microcontact printing using a grid PDMS stamp and a 0.1 mM alkanethiol concentration, the contact angles were 40(±4.2)°. No pattern was visualized after steam imaging. In the second experimental setup, the solution concentration remained the same, but the stamp and thin film were changed. A penny PDMS stamp and a gold thin film were used. The clean gold film angles were 42.3(±1.5)° and the angles following microcontact printing were 58.7(±6.8)°. No pattern was visualized after steam imaging. In the third experiment, the gold thin film and penny PDMS stamp were used and the contact angles of the cleaned film were 46(±4.4)°. The alkanethiol concentration was adjusted until a pattern was visualized during steam imaging. The initial concentration was 0.1 mM of 11-amino-1-undecanethiol and an image was visualized when the concentration was increased to approximately 0.3 mM. The final contact angles were 61(±2.6)°. A final experiment was run utilizing a ZnSe thin film, a dime PDMS stamp, and a 0.3 mM 11-amino-1-undecanethiol concentration. The contact angles changed from 24.9(±1.8)° to 39.7(±2.1)° and a pattern was visualized after steam imaging.

Figure 4. SAMs were microcontact printed onto a clean ZnSe thin film
**Fluorescently tagged microcontact printing.** A 0.3 mM solution containing a 1:9 ratio of fluorescein tagged 11-amino-1-undecanethiol to non-tagged 11-amino-1-undecanethiol was made. A grid patterned PDMS was used to microcontact print onto a clean ZnSe film (Figure 5). The film contact angles prior to microcontact printing were 19.8(±5.3)°. The grid pattern was seen under a fluorescent microscope following microcontact printing but prior to the ethanol rinse. The pattern was no longer perceived following an ethanol rinse (Figure 6). An indistinct grid pattern was visualized on the thin film during steam imaging (Figure 7). The final contact angles were 48.6(±5.6)°.

**Figure 5.** Grid patterned PDMS stamp.
**Figure 6.** ZnSe thin film visualized under a fluorescent microscope following microcontact printing using a solution containing fluorescein tagged and non-tagged 11-amino-1-undecanethiol molecules A. prior to ethanol rinse and B. following ethanol rinse.

![Figure 6](image)

**Figure 7.** Ethanol rinsed fluorescently microcontact printed ZnSe film A. under a microscope and B. under a microscope during steam imaging.

**SUMMARY AND CONCLUSIONS**

Successful microcontact printing was observed when using a concentration of 0.3 mM 11-amino-1-undecanethiol. A pattern was visualized on the gold film, which had contact angles of 46(±4.4)° prior to printing and 61(±2.6)° following printing. Microcontact printing on ZnSe also resulted in successful pattern visualization during steam imaging and a change in contact angles from 24.9(±1.8)° to 39.7(±2.1)°. Microcontact printing using fluorescein tagged 11-amino-1-undecanethiol resulted in a pattern that was initially visualized under the fluorescent microscope but disappeared following an ethanol rinse. The contact angles changed from 19.8(±5.3)° to 48.6(±5.6)° and steam imaging resulted in an indistinct pattern. Rinsing the ZnSe thin films following fluorescent microcontact printing resulted in a loss of a fluorescently visualized pattern. Additional experiments will need to be performed in order to determine if the fluorescein
is successfully bonding with the 11-amino-1-undecanethiol. Once the fluorescent microcontact printing process is fully perfected, the SAMs will be functionalized to perform as a biosensor.

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ABBREVIATIONS

SAMs, Self-assembled monolayers; HDT, Hexadecanethiol; ZnSe, Zinc selenide; PDMS, Polydimethylsiloxane; FTIR, Fourier-transform infrared spectroscopy

REFERENCES


