Investigating the Creation of Self-Assembled Monolayers for UV-Initiated Cross-Linking of Quantum Dot Polymer Composite Films

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Patrick Hynes

Year 1 Undergraduate Student Researcher
College of Health and Science
School of Engineering & Physical Sciences
University of Lincoln

Abstract

Self-Assembled Monolayers (SAMs) are one-molecule-thick films that form spontaneously and have properties that are useful in the field of nanotechnology, such as for biosensors or molecular electronics, which has gained traction in recent years. Delamination is the peeling away of a layer of material from the substrate, this stops the substrate from being used to form the SAM. It is important to limit this delamination for the self-assembly of molecules to work, and for the long-term stability of the monolayers. Self-assembled monolayers also stabilise colloidal nanocrystals, providing additional functionality. It has been proposed that a mixed monolayer of thiobenzoic acid (TBA, a photo-initiator) and 2-propene-1-thiol (PTA, a cross-linking agent) or tert-Dodecyl mercaptan (TDM, a different cross-linking agent) on nanocrystals can facilitate UV-initiated cross-linking when the nanocrystals are in polymer solution. To test the compatibility of TBA and PT in a mixed self-assembled monolayer, we aimed to deposit such mixed SAMs on the silver substrates.

The research began by sputtering an adhesion layer of Titanium (Ti) on substrates of Fine Quartz (FQ) or Indium Tin Oxide (ITO) so that a layer of Silver (Ag) could be layered on top. Different thicknesses were tested to see which layers have minimal delamination and maximum wetting as well as different conditions to see which ones survive ultrasonication.

Keywords: Quartz, Titanium, Silver, ITO, Delamination, Cross-Linking, Self-Assembled Monolayers

Introduction

This project is part of a competitive undergraduate research scheme which is both supported and funded by UROS (Undergraduate Research Opportunities Scheme) to grant the opportunity for undergraduate students to partake in research with academics at the University of Lincoln, as co-researchers under the Student as Producer model. The first aim was to investigate the best materials to use for the substrate, either ITO or FQ, surface layer and the adhesion layer of the SAM them to work as efficient as possible, also determining the optimal thickness of the layers. The second aim was to determine which cross-linker, TDM or PT, works better with TBA, and then which ratio of the two works best for creating the most effective SAMs for quantum dot polymer composite films.

This was conducted by trying different materials, Ti, Ag, ITO, or FQ, thicknesses, as seen in Table 2, and conditions, such as spinning or heated, and checking for delamination after ultrasonication, which is a necessary cleaning stage before SAMs can be formed, often leading to delamination. Then, once the substrates were made, different combinations of the molecules were coated onto them to see which works best.

Project Background

This research was conducted to confirm the compatibility of the two molecules, in aid of a government grant proposal investigating UV-initiated cross-linking using TBA and PT for next generation labelling for food traceability.

There are several viable options for both the adhesion layer and the metal layer. Ti was chosen over Cr as Cr tends to diffuse through the Ag layer, forming a Cr-Ag Alloy (Rairden et al., 1971; Guo et al., 2024). Ti is beneficial as it improves the wetting properties, how uniform and continuous the layer is, of the Ag layer (Todeschini et al., 2017). The presence of the Ti layer facilitates the formation of Ag layers with a more monodisperse grain size and predominant crystal orientation, decreasing the nucleation energy barrier and increasing the number of nucleation sites, leading to a faster formation of a continuous Ag layer (Liang et al., 2022). Most research is conducted using Gold (Au) (Love et al., 2005) for the metal layer, but Ag has several of the same properties (Laibinis et al., 1991), is more accessible and was favoured for this research.

The TBA is a much longer molecule compared to PT, which may affect how the two interact, so in addition a third molecule TDM which is more equal in length to the TBA was also tested to see if they interact more effectively.

This could be done using a variety of experimental techniques with further research, such as Raman or Infrared (IR) spectroscopy, which are used to see how IR radiation is absorbed by the system and the chemical structure of the SAM.

Literature Review

The building of SAMs on conductive substrates such as ITO has gained considerable interest due to their applications such as in molecular electronics (Aswal et al., 2006), engineering (Onclin et al., 2005) and biosensors (Wink et al., 1997). SAMs provide a means of tailoring the properties of a surface through chemisorption of functionalised organic molecules, like thiols, which assemble into ordered molecular structures. While Au has been used in most SAMs as it's relatively unreactive compared to other metals and has a high affinity for thiols. Since both Ag and thiols are soft acids/bases (Pearson., 1963), more recent efforts have shown that alternative conductive materials such as ITO or Ag can be just as useful, but they come with their own unique challenges.

ITO suffers from limited reactivity with thiol-based SAMs. To avoid this, multilayered electrode structures incorporating Ti and Ag have been investigated. Introducing a Ti adhesion layer between the ITO substrate and the Ag to form an ITO-Ti-Ag structure enhances chemical stability and facilitates a more uniform SAM formation.

Notably, the addition of an Ag top layer offers the advantage of thiol-compatible chemistry, improving SAM density and order. Nonetheless, Ag is susceptible to oxidation, depending on the amount of sulphur compounds in the air, which could compromise the SAM's longevity, prompting investigation into deposition conditions (Gilmer et al., 1998). Furthermore, SAMs can incorporate functional groups capable of initiating or directing UV-induced reactions, making them ideal for QD polymer network formation during cross-linking, although these were tested on flat macroscopic substrates, not QDs directly.

The majority of the literature referenced indicates that there is a growing consensus that multi-metallic substrates such as ITO-Ti-Ag or ITO-Ti-Au offer an optimal balance of conductivity, stability and chemical compatibility for SAM integration.

Quantum Dots (QD) are small particles whose properties change when their size is increased or decreased (Bagher., 2016). They have many applications in biomedicine due to their photo-physical properties (Reshma and Mohanan., 2019), in electrical displays, photoconductors and photodetectors (Cotta., 2020) as well as labelling for food traceability (Ezati et al., 2022).

Methodology

The first task was to create the substrates, using either ITO or FQ for the base, Ti for the adhesion layer and Ag for the metallic top layer, this was done by sputtering the Ti and Ag onto the suspended substrate using Argon (Ar) plasma. Sputtering is the process where atoms are ejected from a solid surface when it's hit by high-energy particles, used to deposit thin films of metals onto surfaces. Several different thicknesses were tested to see which one experiences the least amount of delamination and de-wetting after ultrasonication. Thicknesses were determined using a quartz crystal microbalance, which measures by detecting changes in its vibration frequency; as material accumulates on the crystal, the frequency decreases proportionally to the mass that gets deposited.

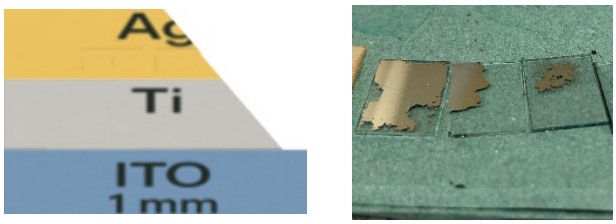

Figure 1: A) Diagram showing delamination of the layers B) An image of how that looks in practice.

All relevant thicknesses tested experienced some level of break down on the surface, as seen in Figure 1, so the deposition conditions were changed to limit this. Thicker layers, slower deposition rates and heat was added to remove any organic residue on the ITO and better control the deposition.

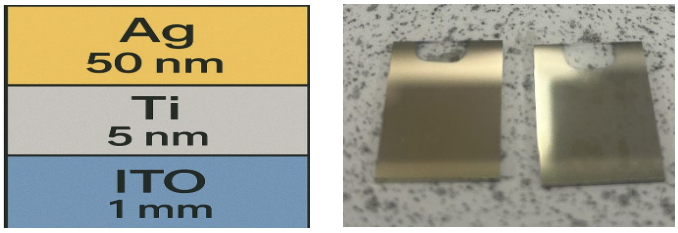

Figure 2: A) Diagram showing how the elements should layer B) An image of how that looks in practice.

After the chamber where the sputtering takes place was pumped, reducing the pressure inside to the chamber as low as possible, and creating a near vacuum, it was heated to 300°C and left at that temperature for an hour, before clearing the oxidised layer on top of the targets and depositing the materials onto the substrate. The Ti and Ag were deposited at a rate of 0.5Ås^{-1} on a spinning platform to ensure uniform deposition across the substrate. Once deposited the chamber was left to vent and cool before the substrates were removed and stored.

Combination	PT-%	TDM-%	TBA-%
1	100	0	0
2	0	100	0
3	0	0	100
4	50	0	50
5	0	50	50
6	70	0	30
7	0	70	30
8	80	0	20
9	0	80	20

The next stage was to create the SAMs made using TBA as the photo-initiator and either TDM or PT as the cross-linker, to work out which combination of the two was the most efficient.

Table 1: A table showing the percentage of each molecule in the coating mixture for each combination tried. Combinations 1-3 are controls to gauge how well it coats.

Combinations 1-3 were used as control mixtures to see how well each bind to the substrate on its own. TBA has less of a percentage in the non-even ratios as it has been shown in the past that it binds very well to the silver (López-Ramírez, 2021).

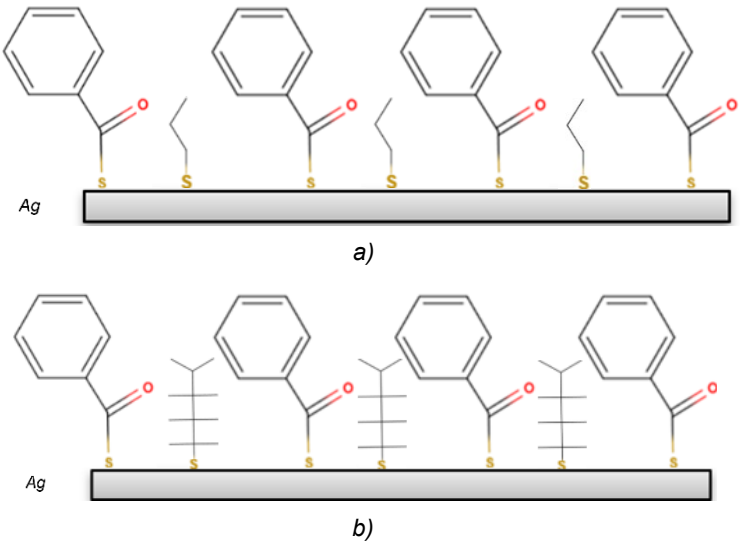

Figure 3: a) Molecules of TBA and PT on an Ag electrode in a perfect uniform scenario. b) Molecules of TBA and TDM on an Ag electrode in a perfect uniform scenario.

The first step was to prepare stock solutions of each molecule so that the mixtures can be obtained without having to go back and forth to the bottles of molecules. We needed a volume of 0.05L at an advised concentration of 0.005 $\mathrm{molL^{-1}}$ (5 $m\mathrm{molL^{-1}}$) (Sigma-Aldrich, 2025).

The amount of TBA that needs to be added to $10\ \mathrm{mL}$ of ethanol was found by the following:

Number of Moles	= Volume × Concentration	(1)
Number of Moles	= (0.05L) (0.005 $\mathrm{molL^{-1}}$)	
Number of Moles	= 0.00025 mol	
Number of grams	= Molar Mass × Number of Moles	(2)
Number of grams	= (74.15 $\mathrm{gmol^{-1}}$) (0.00025 mol))	
Number of grams	= 0.019g	
Volume required	= mass/density	(3)
Volume required	= (0.019g)/(0.898 $\mathrm{gmL^{-1}}$)	
Volume requied	= 0.021mL	

By modifying equations 1-3 we found that the desired TDM and PT stock solutions require $0.029\ \mathrm{mL}$ and $0.059\ \mathrm{mL}$ of TDM and PT, respectively.

Once the stock solutions were made, they were purged with nitrogen in order to remove any trapped oxygen. The susbtrates were ultrasonicated to clean the top layer, and placed in a container. A pipette/syringe was used to add the desired mixture of the ethanolic stock solutions of TBA and/or TDM and/or PT, totalling $10\ \mathrm{mL}$ in order to coat the substrate. We used a nitrogen jet in order to remove the oxygen from the container each time before putting the lid on and sealing it to limit oxidation.

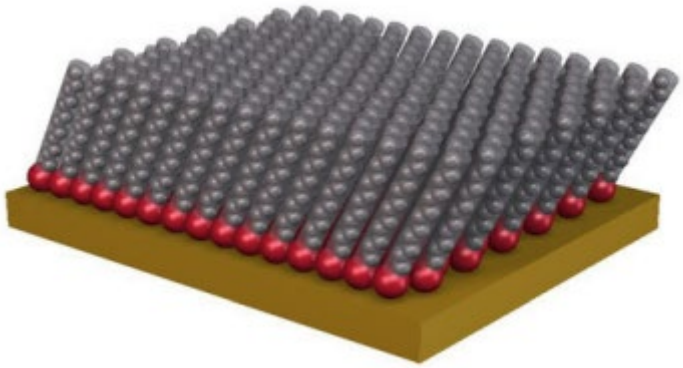

Figure 4: Schematic showing an ordered self-assembled monolayer of densely packed thiols (Sigma-Aldrich, 2025).

In the end the SAM should look like Figure 4, with no gaps between molecules in order for maximum efficiency when cross-linking.

Results

After the first four substrates were ultrasonicated, it was clear that more needed to be done to improve the wetting of the silver. Therefore, the substrates were heated before deposition to remove organic contamination, and thicker layers were attempted.

Thickness	Delamination	De-wetting
2nm Ti and 20nm Ag	Y	Y
10nm Ti	N	N
1nm Ti and 10nm Ag	Y	N
1nm Ti and 20nm Ag	N	Y
5nm Ti and 50nm Ag	N	N
10nm Ti and 100 Ag	N	N

Table 1: A table showing the thicknesses of layers for the substrate and whether each experienced delamination or de-wetting

Some degree of delamination and de-wetting occurred in all the first four depositions. The two depositions following heating and spinning the substrate sight, showed no delamination and de-wetting after being ultrasonicated and so were chosen. Nine more were created under the same conditions to be used for the next part of the experiment, along with seven spares. They were placed in airtight substrate containers, not ultrasonicated as this is saved for right before the molecules are coated on top of the silver.

The stock solutions of both the TBA and PT must be sealed and stored in a fridge in order be kept safe and only opened and used in a fume cupboard.

These were used to create the SAMs using pipettes to get the correct percentages of each.

The SAMs were then also sealed tight and stored in a fridge so that they last as long as possible without their properties being lost.

Overall, the results show that careful optimisation of substrate composition and deposition conditions are essential for the successful formation of stable SAMs. Now the process for eliminating delamination and de-wetting is clear and can be followed in the future, without the need for further testing. The stability of the SAM is a critical aspect of ensuring the reliability of the SAM and subsequent molecular

functionalisation. These findings are an important step towards UV-initiated cross-linking in quantum dot polymer composite films.

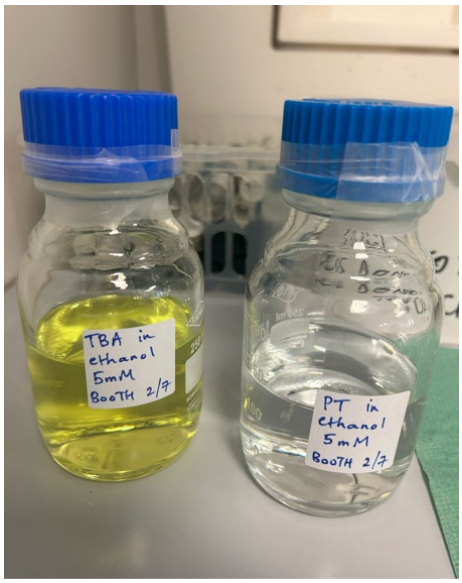

Figure 5: *An image showing the stock solutions of 5mM of TBA in ethanol on the left and 5mM of PT in ethanol on the right.*

UROS Experience

Participating in the UROS project has been an incredibly rewarding experience for me, that has added to both my academic and professional skills. From the beginning, I found the process engaging and enjoyable, offering a unique opportunity to work alongside my lecturers while contributing to a real-world scientific project. I gained valuable insight into professional laboratory practice, learning the importance of meticulous preparation, attention to detail, and strict adherence to safety protocols. I got the opportunity to learn and follow laboratory rules and regulations, from handling hazardous materials to maintaining accurate records, which reinforced the discipline required for high-quality scientific work.

The process of drafting, revising, and refining this IMPact journal in line with academic standards has improved my writing confidence and taught me how to present research effectively to a range of different audiences. Overall, my UROS experience not only expanded my technical abilities but also provided me with the professional foundations essential for a future career in science, making it a valuable step in my academic journey.

Conclusion

This work identified optimal substrate compositions and deposition conditions for stable self-assembled monolayers suitable for UV-initiated cross-linking of quantum dot polymer composites. A Ti adhesion layer with Ag provided a durable, thiol-reactive surface, while controlled deposition minimised delamination and improved wetting. Testing of TBA, PT, and TDM mixtures highlighted the role of molecule length compatibility, with TDM suggesting promise for cross-linking. These results confirm the viability of the ITO–Ti–Ag system for advanced applications such as food traceability labelling, paving the way for further optimisation and scale-up, such as mass production and making it more widespread and affordable for all stages of the food and beverage industry supply chain.

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