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# Determination of Functional Head and Tail Groups of Self-Assembled Monolayer (SAM) Formed by 2-Mercaptoacetate on Aluminium Oxide Substrate

Indragandi Subramani[1], RM Ayub[1*], SCBGopinath[1], MK Md Arshad[1], RDAA Rajapaksha[1] and C Ibau[1]

[1]*Institute of Nano Electronic Engineering, Universiti Malaysia Perlis, Taman Pertiwi Indah, Seriab. 01000 Kangar, Perlis, Malaysia.*
[2]*Nano-technology Research Laboratory, Department of Electronics, Faculty of Applied Sciences, Wayamba University of Sri Lanka, 60200 Kuliyapitiya, Sri Lanka.*

**ABSTRACT**

*In order to immobilize the biological receptor, aluminium oxide surface was functionalized by introducing a linker named 2-mercaptoacetate, which contains thiol and carboxylate functional groups. 2-mercaptoacetate will form orderly packed monolayer known as Self Assembled Monolayer (SAM) on the aluminium oxide surface. The aim of this work is to investigate and determine the head and tail of this SAM formed by the aforementioned linker on the aluminium oxide surface. The bare and the 2-mercaptoacetate modified aluminium oxide surface were compared and analyzed under X-ray photoelectron spectroscopy (XPS) to determine the head group. For further verification, 50 nm gold nanoparticle (GNP) was deposited on the 2-mercaptoacetate modified aluminium oxide to confirm thiol as a tail group of SAM layer. GNP deposition on 2-mercaptoacetate modified aluminium oxide surface was characterized by scanning electron microscope (SEM) and Atomic force microscope (AFM). XPS analysis indicates that native oxide has been grown on aluminium thin film. It also confirms the SAM structure; carboxylic and thiol as a head and tail group respectively.*

**Keywords:** Self-Assembled Monolayer (SAM), 2-Mercaptoacetate, Aluminium Oxide.

## 1. INTRODUCTION

Recently, Point of Care (POC) electrochemical biosensor in a medical application has replaced the conventional analytical method for disease screening due to its huge benefits such as high sensitivity, specificity, the possibility of miniaturization and cost-effective. Improvement and development are being done in every part of the biosensor to produce a better device that can diagnose disease efficiently[1].

A typical biosensor is consisting of two main components; a biological recognition element which is a bioreceptor, and a transducer part that converts this recognition into a detectable, measurable and quantifiable output [2]. In the former, the immobilization of analyte for biorecognition is the most vital aspect of biosensor construction. The later part mostly concerns with transforming and amplifying the signal resulting from the interaction bioreceptor and biomarker into an easily measured and quantified output. The transducer could be in the form of Field Effect Transistor (FET) or Interdigitated Electrodes (IDE), which made up of noble metals such as gold, silver and platinum [3]. This element can be engineered according to designer desire that can perform an adequate function.

Cost wise, aluminium is the cheapest metal as compared to other metals, therefore it was chosen as transducer material in this study.The transducer could be in the form of Field Effect

* Corresponding Author: *ramzan@unimap.edu.my*

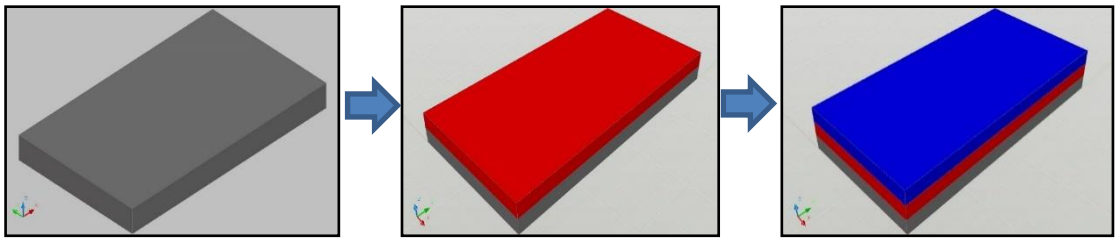
Transistor (FET) or Interdigitated Electrodes (IDE), which made up of noble metals such as gold, silver and platinum [3]. This element can be engineered according to designer desire that can perform an adequate function. Cost wise, aluminium is the cheapest metal as compared to other metals, therefore it was chosen as transducer material in this study. Aluminium can simply be oxidized to form aluminium oxide or well known as alumina which is biologically inert and also compatible be used in the human body [4].

The analytical performance of the biosensor is greatly influenced by the effectiveness of immobilization technique [5]. Thus, the chosen immobilization approach is vital in order to ensure the proper function of the constructed biosensor. There are many available immobilization chemical techniques that have been developed such as covalent bonding, non-covalent technique, amine coupling, Self-Assembled Monolayer (SAM) and so on [6],[7].

This study deals with the construction of an electrochemical biosensor for early Prostate Cancer (PCa) detection. In this biosensor construction, lectin which is a type of protein has been chosen as a bioreceptor. In this work, aluminium oxide surface was functionalized with 2-mercaptoacetate for lectin immobilization. 2-mercaptoacetate acts as a linker that could help to hold lectin and the aluminium oxide surface together. It introduced two functional groups which are thiol and carboxylic. Once the 2-mercaptoacetate has been deposited onto the aluminium oxide surface by following a certain procedure, an orderly packed layer formed spontaneously on it. This layer is known as a self-assembled monolayer (SAM). The molecules or ligands that form SAMs have a chemical functionality, or "headgroup", with a specific affinity for a substrate; in many cases, the headgroup also has a high affinity for the surface and displaces adsorbed adventitious organic materials from the surface. There are a number of headgroups that bind to specific metals, metal oxides, and semiconductors. The main objective of this research is to identify the functional head group and a tail group of 2-mercaptoacetate towards aluminium oxide. There are a lot of studies has shown that, the carboxylic group has more affinity towards aluminium oxide[8],[9],[10].

## 2. MATERIAL AND METHODS

A 4-inch p-type silicon wafer with the resistivity of 10-20 ohm-cm was cleaned by immersing the wafer inside the piranha mixture of $H_2SO_4$:$H_2O_2$ (3:1) for about 15 minutes as per the standard operation procedure (SOP) of piranha cleaning. Piranha solution is highly oxidative and helps to remove metals and organic, inorganic contaminations. Then, dry oxidation was carried out in order to grow approximately 600 Å of silicon dioxide layer. After that, the sample was deposited with aluminium thin film through thermal evaporation technique. By setting to a current of 50 mA for 10 minutes with 5.3 nm/s deposition rate and vacuum background pressure rate at 50 uTorr, the thickness of deposited aluminium was calculated to be around 2000 Å. The aluminium deposited wafer was exposed in a cleaned environment so that oxide layer can grow naturally. Finally, the wafer is cut into 2 cm x 2 cm. The fabrication process flow is illustrated in Figure 1.



a) Cleaned silicon wafer b) Oxide layer is grown c)Deposition of Aluminium Thin film

**Figure 1.** Fabrication process flow where three major steps are displayed.

Trimethylolpropane tris or 2-mercaptoacetate linker was treated ultrasonically in order to avoid any precipitation. Prior to the deposition process, the substrate was washed with deionized water (DIW) and ethanol. 200 µl of 3.5M linker was carefully dropped on aluminium thin film coated substrate. 200 µl is pretty enough to cover the whole 2x2 cm surface. Then, the substrate was incubated for 24 hours in dry and clean ambient. Washing with DIW was done to remove any unbound 2-mercaptoacetate. Physical characterization was performed mainly using XPS to identify the attached functional group on the aluminium oxide surface. 50 nm carboxylic acid functionalized goldnanoparticles (GNP) was subsequently deposited on the 2-mercaptoacetate modified aluminium oxide surface. Followed by washing was done with DIW to remove any unbound GNP.

## 3. RESULTS AND DISCUSSION

### 3.1 2-Mercaptoacetate/Aluminium Interface Characterization

**Table 1** Atomic concentration (%) of the unmodified and 2-mercaptoacetate modified aluminium oxide surface acquired from XPS analysis

| Surface | C (%) | O (%) | Al (%) | N / F / Cl (%) | S (%) | Au (%) |
|---|---|---|---|---|---|---|
| Bare Alumina | 16.23 | 56.75 | 26.00 | 1.02 | - | - |
| Alumina + 2-mercaptoacetate | 16.87 | 56.31 | 25.39 | 0.35 | 1.09 | - |
| Alumina + 2-mercaptoacetate + GNP + EDC/NHS | 28.69 | 48.83 | 20.44 | 0.52 | 1.42 | 0.10 |

XPS analysis is implemented on the bare/unmodified aluminium oxide surface and 2-mercaptoacetate modified aluminium oxide surface. This technique measures sample at the depth of 5-20 Å, thus the degree of surface coverage is depending on the concentration of the aluminium. Deposition of 2-mercaptoacetateresulted in slight decrease in the Al atomic concentration from 26.00% to 25.39 % as shown in Table 1. XPS analysis on bare/unmodified aluminium oxide surface is employed to confirm the growth of oxide layer on top of the physically evaporated aluminium surface. Figure 4 shows the high-resolution spectra of Al2p where the atomic concentration of aluminium oxide and aluminium is 80.69% and 19.3% respectively. This indicates that the surface is almost covered by aluminium oxide but the coverage is not uniform. This supported by the XPS high resolution spectra of aluminium in Figure 4. XPS analysis also was performed in order to elucidate the interaction between 2-mercaptoacetate and aluminium thin film. Figures 2 and 3 show the survey spectra of XPS analysis before and after deposition of 2-mercaptoacetate respectively. As expected, both spectra show almost similar major peaks of elements such as oxygen, carbon and aluminium. The very obvious differences in both spectra are the presence of Sulphur element. The spectra in Figure 2 show that there is some fluorine contamination on the sample as well. This result says that the interaction between 2-mercaptoacetate and aluminium has occurred.

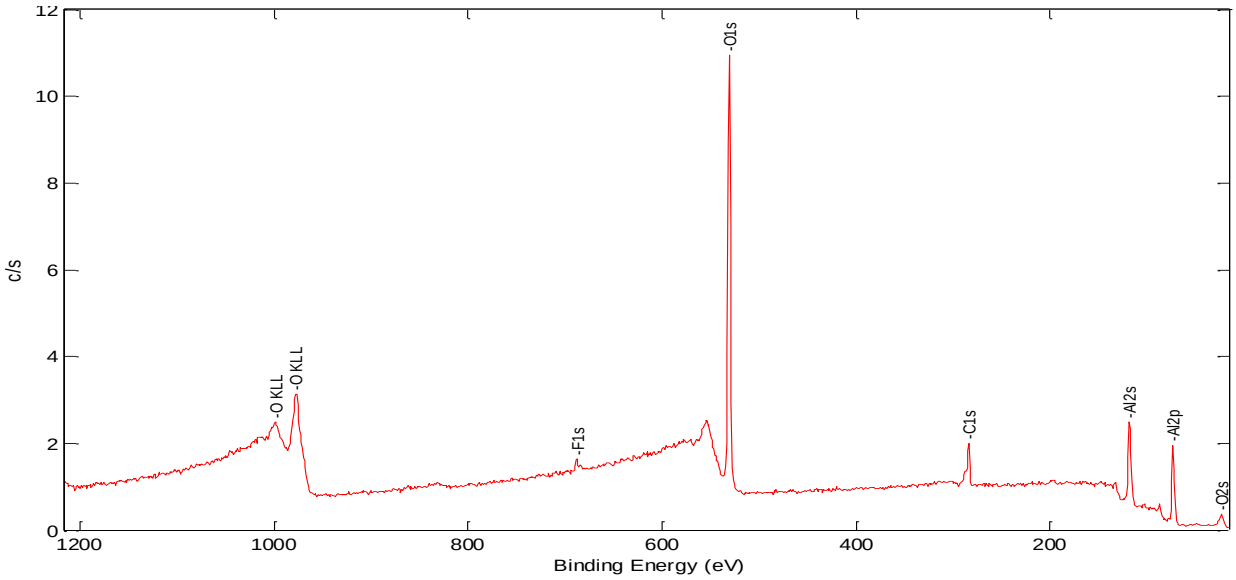



**Figure 2.** XPS survey spectrum of clean bare aluminium thin film.

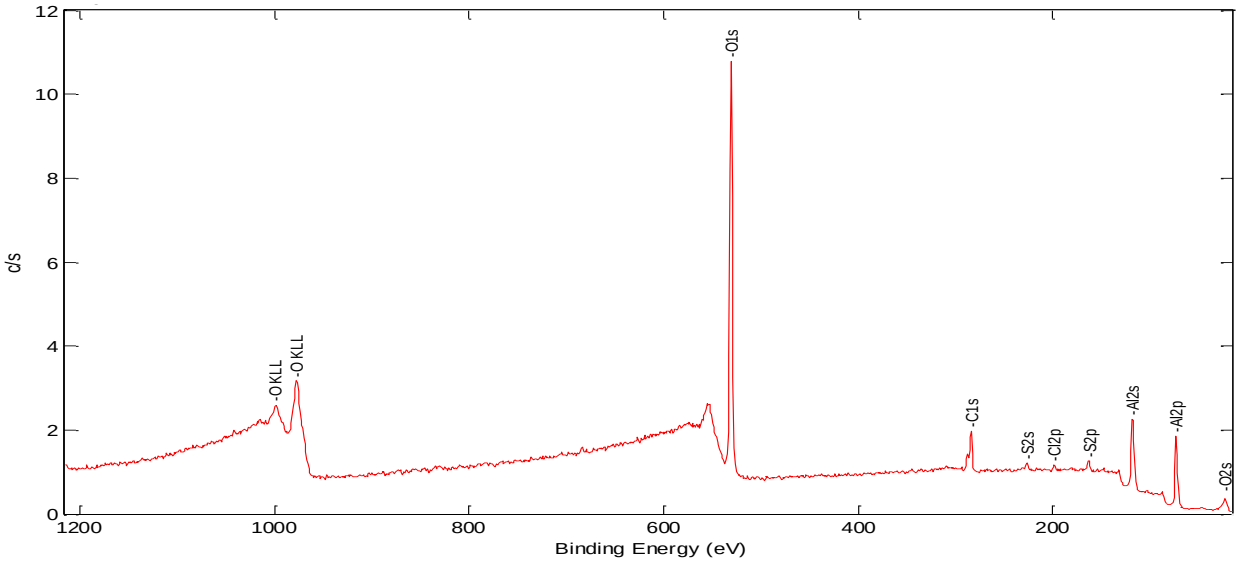



**Figure 3.** XPS survey spectrum of 2-mercaptoacetate treated aluminium thin film.

For the sample that been incubated with 2-mercaptoacetate, the high-resolution analysis was implemented in the region of S2p as shown in Figure 5. There are three peaks that can be observed in the envelope during the curve fitting process. The 163.45eV (orange) peak binding energy corresponds to the S-H bond which verifies the presence of unreacted 2-mercaptoacetate on the aluminium thin film surface. The peak at 164.74eV (blue) is attributed to the S-S bond and the peak at 168.81eV (green) is corresponds to SO2 bond as shown in Figure 5. The XPS analysis indicates that there is no sulphur-aluminium interaction since it has been stated in literature that metal sulphur bond should have lower binding energies than the S-H bond energy[11]. In other word, it can be understood that thiol group are didn't bind to the aluminium oxide surface and behave as a tail group of the SAM, therefore carboxylate group attached to the surface of the aluminium oxide as a head group. Carboxylate group has a higher binding affinity to aluminium oxide surface compared to thiol [12].

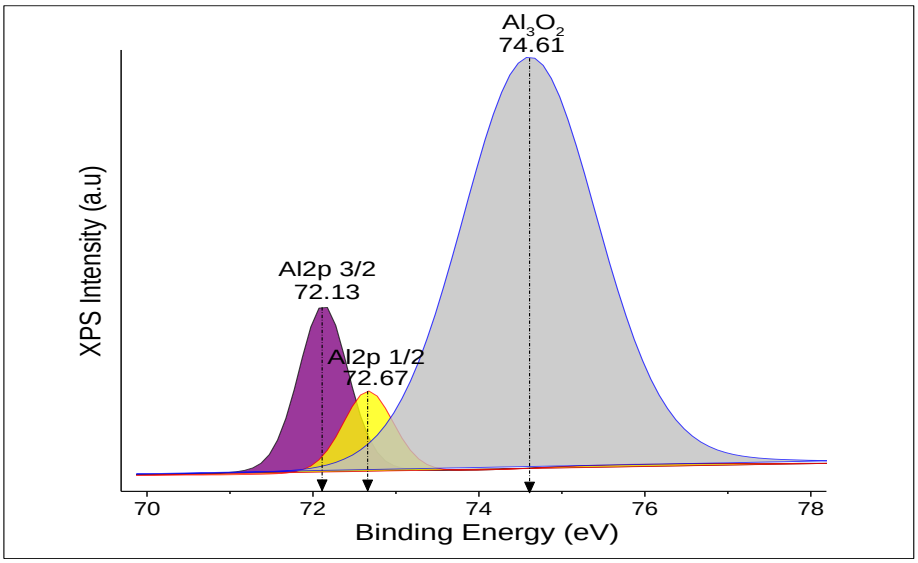



**Figure 4.** High resolution spectrum of Al2p region of unmodified aluminium surface.

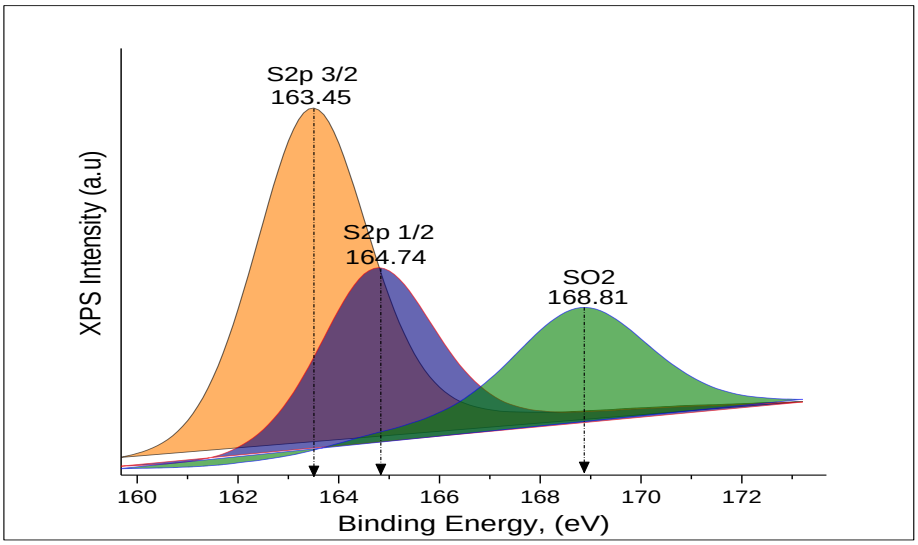



**Figure 5.** High-resolution spectrum of S2p region of the 2-mercatoacetate modified aluminium surface.

### 3.2 Gold Nanoparticle (GNP) Characterization

Gold nanoparticles (GNPs) have a strong affinity towards thiol group and usually they bind together through covalent bond [13]. Thus, GNP is used here to prove that the thiol group is free of binding on the aluminium surface and will give a path to the subsequent GNP binding. Carboxylic group functionalized GNP was used for later amine coupling process. Before interacting with the layer of 2-mercaptoacetate, GNP solution was analyzed by UV-visible spectroscopy. Figure 6 shows the peak at 535.14 nm, indicating the presence GNP of 50 nm.

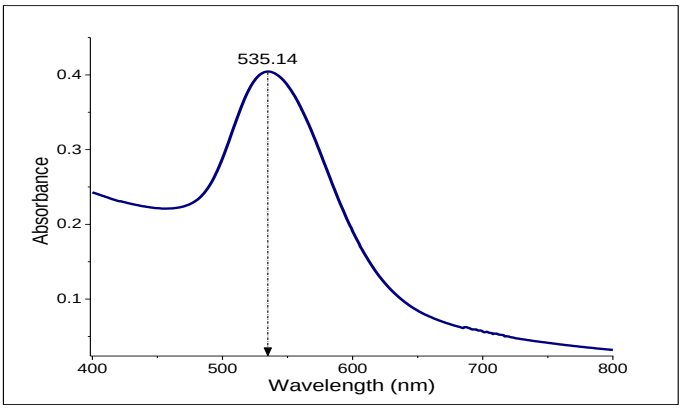



**Figure 6.** UV-visible spectrum of 50 nm sized GNP.

GNP presence and distribution on 2-mercaptoacetate modified aluminium oxide surface was confirmed with scanning electron microscope (SEM) and XPS. Table 1 shows the atomic concentration of Au presence on top of the 2-mercaptoacetate functionalized aluminium oxide surface. Figure 7 shows SEM images of 50nm GNP at different magnifications. This analysis confirms the presence of the GNP on the 2-mercaptoacetate modified aluminium surface. The surface topography image produced by AFM also supports this. Thus, the orientation of functional groups formed via SAM is shown in Figure 9.

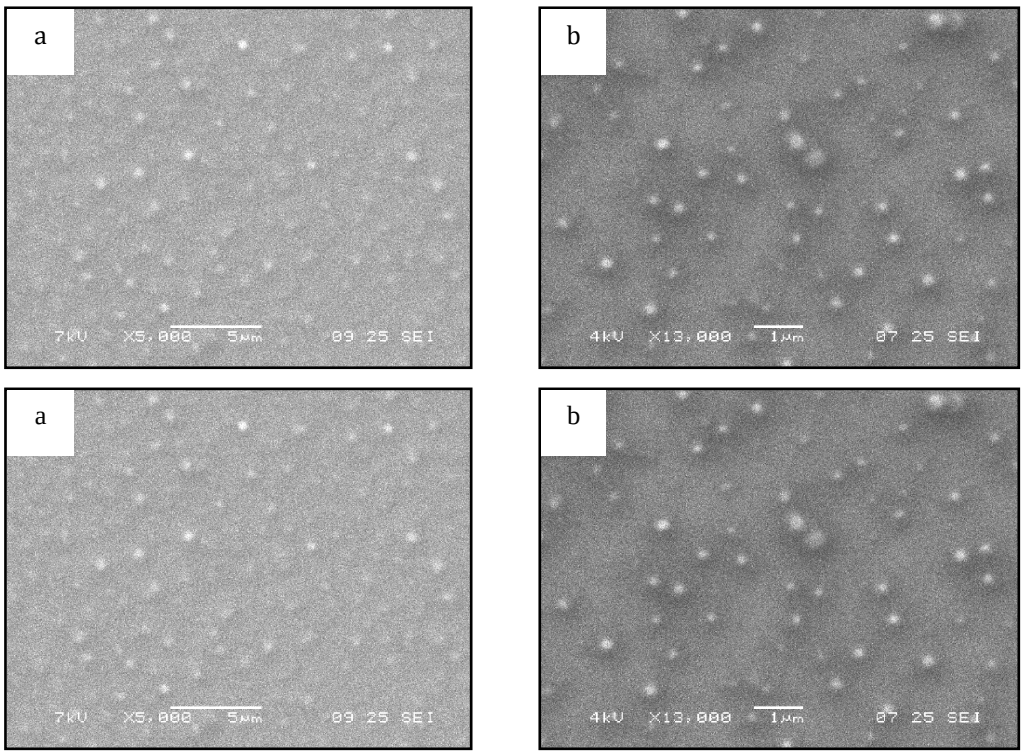



**Figure 7.** SEM images of 50nm GNP at a) x5000 and b) x13000 magnifications.

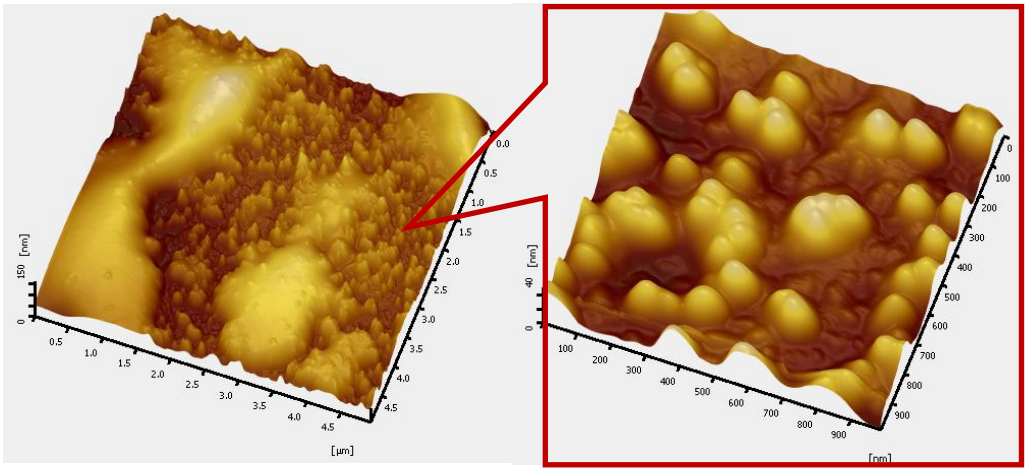


**Figure 8.** AFM images of 50nm GNP.

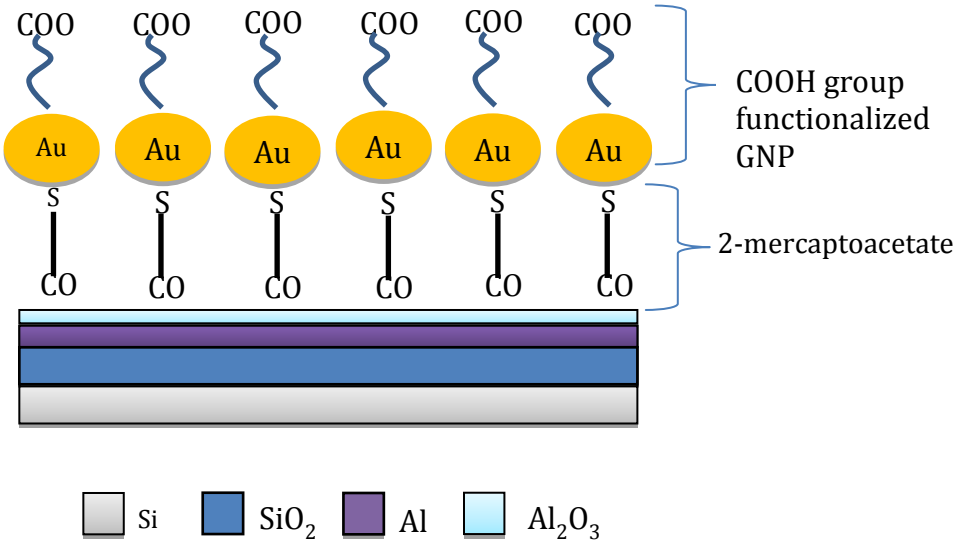



**Figure 9.** Surface functionalization by 2-mercaptoacetate and 50 nm GNP.

## 4. CONCLUSION

In conclusion; SAM can be formed on the native oxide of aluminium using 2-mercaptoacetate. Carboxylate group will be preferentially bound to the aluminium oxide surface over the thiol species. Thus, the carboxylic group will act as a head group while thiol being the tail group of the SAM. This formed SAM layer can effectively act as coupling system where the subsequent desired functional group can be tailored according to the purpose.

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