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Non-Covalent Functionalization of Graphene Films for Uniform Nanoparticle Deposition via Atomic Layer Deposition

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NON-COVALENT FUNCTIONALIZATION OF GRAPHENE FILMS FOR
UNIFORM NANOPARTICLE DEPOSITION VIA ATOIC LAYER
DEPOSITION

NON-COVALENT FUNCTIONALIZATION OF GRAPHENE FILMS FOR UNIFORM
NANOPARTICLE DEPOSITION VIA ATOMIC LAYER DEPOSITION

An Undergraduate Honors College Thesis

In the

Department of Mechanical Engineering

College of Engineering

University of Arkansas

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By

Ty Conner Seiwert

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1. ABSTRACT

Graphene functionalized with platinum (Pt) and palladium (Pd) has proven to be highly effective as a hydrogen sensor. Deposition methods such as Atomic layer deposition (ALD) can be further enhanced by pretreating the graphene with a non-covalent surfactant prior to nanoparticle deposition. In this study, graphene-based sensing devices will be fabricated by ALD deposition. The graphene will be non-covalently functionalized using sodium dodecyl sulfate (SDS) anionic surfactant prior to ALD deposition. The aim of this study is to test the deposition pattern achieved by varying the amount of time that graphene is treated with the SDS surfactant. Initially, ALD deposition of Zinc-Oxide (ZnO) will be performed and the resulting patterns will be analyzed using SEM imaging. The resulting patterns will then be used to aid in the deposition of Pt and Pd onto graphene using ALD in future work.

2. INTRODUCTION

In the ongoing push for environmental protection, hydrogen has demonstrated its potential as a cleaner alternative than traditional petroleum fuels. Hydrogen combustion produces clean emissions and is highly efficient due to its high energy content and low ignition energy [1]. Despite these advantages, hydrogen is also extremely flammable, and will burn at a concentration of only 4% volume in air [2]. It is also inherently susceptible to leaks due to its size, making safety a major concern for applications involving hydrogen. A reliable and efficient means of detecting potential leaks is therefore paramount to the future success of hydrogen. Extensive research has gone into improving the capabilities of modern hydrogen sensors in an effort to eventually achieve the performance targets set by the Office of Energy Efficiency and Renewable Energy (EERE) [3].

In this pursuit, resistive type sensors made from graphene have shown significant promise [4, 5]. Graphene is highly conductive with a low level of electrical noise and optimal specific surface area thanks to its highly ordered hexagonal lattice. These properties make it highly effective in sensing applications allowing for minute surface interactions to be picked up by monitoring resistance changes in the graphene [6]. In order to selectively isolate hydrogen interactions, however, further surface functionalization is necessary. Platinum and Palladium are extremely effective in this pursuit as they both exhibit a high affinity towards hydrogen. While pristine graphene is inert itself, small defects such as grain boundaries serve as bonding sites that allow Platinum and Palladium to be deposited [4]. As a result, deposition of Platinum and Palladium nanoparticles is inconsistent as it is heavily influenced by the arbitrary morphology of the graphene.

More recently, atomic layer deposition (ALD) has been adopted to better control the distribution pattern and deposition size of the nanoparticles. The process uses two sequential

self-limiting half reactions that allow for atomic scale size control [7]. Furthermore, uniform deposition is also possible with ALD. This can be achieved by selecting a highly reactive precursor, which can break the strong carbon bonds and introduce point defects in the graphene. These point defects serve as anchor sites for nanoparticle growth to occur [4, 7]. While this technique allows for deposition to occur beyond preexisting defects in the graphene, it can also have adverse effects on the properties of the graphene. This is because it requires physical alteration of the graphene lattice.

An alternative method of achieving uniform distribution is to pre-treat the graphene surface with a noncovalent surfactant. One surfactant that has previously been implemented is sodium dodecyl sulfate (SDS). SDS consists of a hydrophobic long-chain hydrocarbon tail with a hydrophilic sulfate head group [7]. When dispersed in an aqueous solution at a concentration above its critical micelle concentration of 8.1 mM, SDS will aggregate at the graphene interface [8]. The long-chain hydrophobic tails of the SDS bond to the graphene surface by van der Waals attractions while the hydrophilic head groups are repulsed from the surface exposing them to serve as ALD nucleation sites [7].

Research Purpose

The purpose of this thesis is to non-covalently functionalize CVD grown pristine graphene by treating it with SDS anionic surfactant. The effect of treatment time on the resulting deposition patterns of nanoparticles following atomic layer deposition will be observed and understood.

3. EXPERIMENTAL SETUP

Graphene Samples

Two samples of monolayer graphene film were purchased from two different suppliers, Advanced Chemical Supplier (ACS) and Graphene Supermarket. Both samples were grown by chemical vapor deposition (CVD) onto a SiO₂ substrate with an oxide thickness of 300 nm for the ACS sample and 285 nm for the other. The quality of the graphene samples can be characterized by the Raman Spectroscopy data which was specified by the manufacturer for each sample. There are three bands that pertain to graphene which are the D, G, and 2D bands. Both the G band and the 2D band are significantly influenced by the layer thickness while the D band intensity directly correlates to the amount of defects present in the graphene sample [9].

The quality of the graphene samples were confirmed by observing the Raman band characteristics shown for each sample in Figure 1a and 1b. For both samples, it is apparent that the 2D bands have sharp and symmetrical shapes. The 2D bands are also significantly larger than the corresponding G bands, which is a strong indication of single layer graphene. Further, the D bands for each sample are minimal indicating a lack of defects in the graphene lattice. It is worth mentioning however that the D band seen in Figure 1b for the Graphene Supermarket sample appears to be larger than the ACS sample in Figure 1a. This suggests that the ACS sample likely contains less defects.

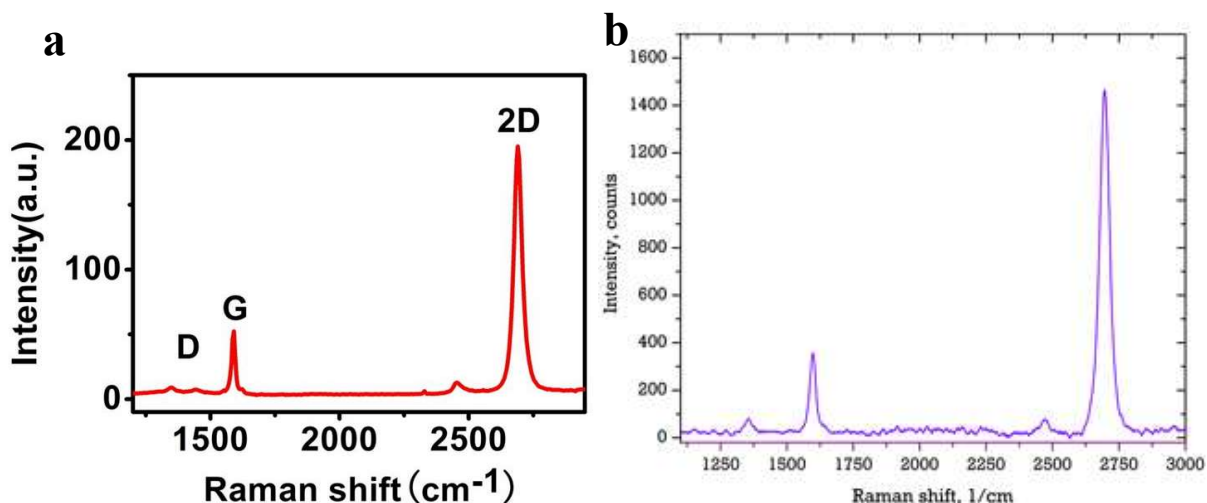


Figure 1: Raman spectrum data of graphene sample purchased from (a) ACS and (b) Graphene Supermarket

Sodium Dodecyl Sulfate (SDS) Treatment

Sodium dodecyl sulfate (SDS) anionic surfactant was obtained from Polysciences Inc. An aqueous solution of 1 wt% SDS was prepared by dissolving 0.25 g of SDS in a volumetric flask containing 25 ml of deionized (DI) water. This concentration is above the critical micelle concentration identified by previous experiments [8, 10]. Both samples, each purchased from different manufacturers, were initially cleaved into five individual pieces using a diamond tipped blade. The associated pieces from each sample were designated as two separate batches to undergo SDS treatment. All of the samples were then cleaned by sonication in deionized (DI) water prior to treatment. This was done to remove any impurities from the graphene surface that might interfere with the adherence of the SDS surfactant.

Four of the samples from each batch were dipped into the SDS solution and allowed to soak. The fifth sample remained untreated to serve as the control for comparison. In 30-minute increments, a single sample from each batch was removed from the solution and placed into a separate beaker containing DI water and sonicated for 3 minutes. Once the sonication was

completed, the samples were removed from the DI water and allowed to air dry. This process was repeated for each sample at the subsequent time interval resulting in two batches containing samples treated for 30, 60, 90, and 120 minutes as well as a control sample.

Atomic Layer Deposition

Atomic layer deposition was achieved using a Veeco Savannah S200 that was both controlled and monitored by a computer. For deposition of Zinc Oxide (ZnO), the precursors used were diethyl zinc (DEZn) and H₂O. The trap, exhaust line, and valve manifold inside the ALD were kept constant at a temperature of 150°C while the actual deposition temperature itself was 100°C. Reactor pressure was held at 0.276 Torr during deposition and the flow rate was 20 sccm. For all samples from both batches, ZnO was deposited for a total of 100 cycles. Each individual cycle consisted of a 0.015 second pulse of DEZn, a 5 second flush, a 0.015 second pulse of H₂O, and finally another 5 second flush.

To avoid access contamination, the ALD equipment was located in a seal and pressurize glove box. The pressure inside the glovebox was held constant at 200 psi and could only be entered through an intermediary pressurization chamber. Therefore, the samples had to be placed in the glove box in order for them to be transferred into the ALD deposition chamber. Once the process was completed, the samples were placed back into their labeled containers and depressurized so that they could be removed from the glove box and characterized.

4. RESULTS

Optical Imaging

Following ZnO deposition of 100 cycles in the ALD, the samples from both batches were initially observed using an optical telescope. In order to have a basis for comparison, imaging of the graphene was performed prior to any modification by SDS treatment or ALD. The unmodified ACS graphene is shown in Figure 1. The teal portion located in the bottom right portion of the image is the monolayer graphene film while the lighter green area represents the bare SiO₂ substrate. Initially the graphene is clean and uniform as was expected.

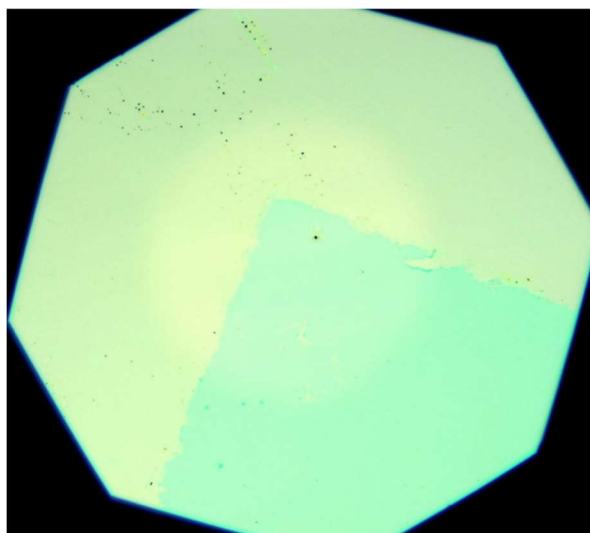


Figure 2: Optical image of unmodified CVD graphene purchased from ACS

Following SDS treatment and ZnO deposition, it was obvious that the SDS had significantly influenced the deposition pattern achieved with the ALD. Below, Figure 2a shows the control sample which was left untreated in comparison to the 30-minute SDS sample shown in Figure 2b. A significant difference in color can be seen at the graphene boundary while smaller patches mirroring the same yellow tint can be observed further in on the graphene film. This same characteristic is not observed in the control sample. Overall, it appears the control more closely resembles the unmodified graphene apart from some minor discoloration seen at

the boundaries. This suggests that ZnO deposition was not achieved on the inert pristine graphene and is only present around the lattice borders which was expected.

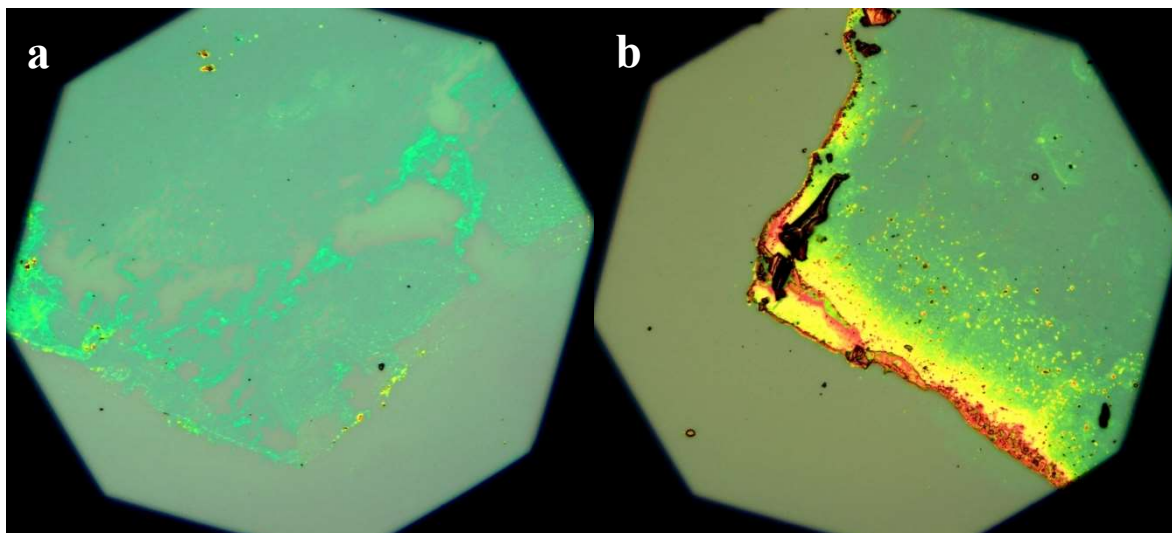


Figure 3: Optical image of (a) untreated control sample from batch 1 and (b) 30-minute SDS sample from batch 1

Further analysis of the optical imaging results suggested that the amount of ZnO deposited was in fact influenced by the amount of time each sample was treated with SDS. This is shown in Figure 3 by comparing the 30-minute SDS sample (a) to the 90-minute sample (b). The 90-minute sample shows more defined patterning with a more distinct yellow tint than the 30-minute sample. It is also significant that both samples appear to exhibit very similar patterning on their corresponding films, which suggests that SDS treatment time does not play a significant role in the resulting distribution.

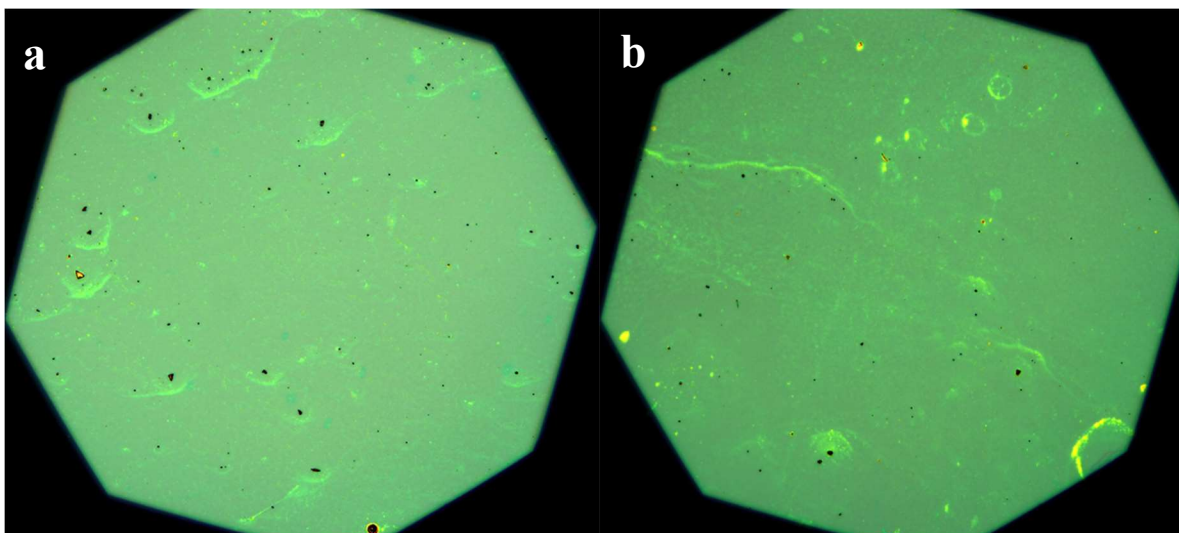


Figure 4: Optical image of (a) 30-minute SDS sample from batch 1 and (b) 90-minute SDS sample from batch 1

Finally, the last significant observation worth mentioning is that corresponding samples from both batches tested exhibited similar patterning and characteristics. This can be seen in Figure 4 which compares the image taken of the 90-minute sample from batch 1 (a) alongside the 90-minute sample from batch 2 (b). The red color seen in the batch 2 image also stands out as an obvious difference between the two batches, however, this is attributed to the thickness of the oxide layer grown on the silicon substrate during manufacturing. The samples from batch 1 were purchased from ACS who specified an oxide layer thickness of approximately 300 nm. This is slightly thicker than the 285 nm oxide layer for the batch 2 samples manufactured by graphene supermarket. The thicker oxide layer causes the substrate surface to appear greener in the batch 1 samples and redder in the batch 2 samples. Despite this distinction, the color of the graphene film is almost exactly the same for both batches indicating they are of similar high quality.

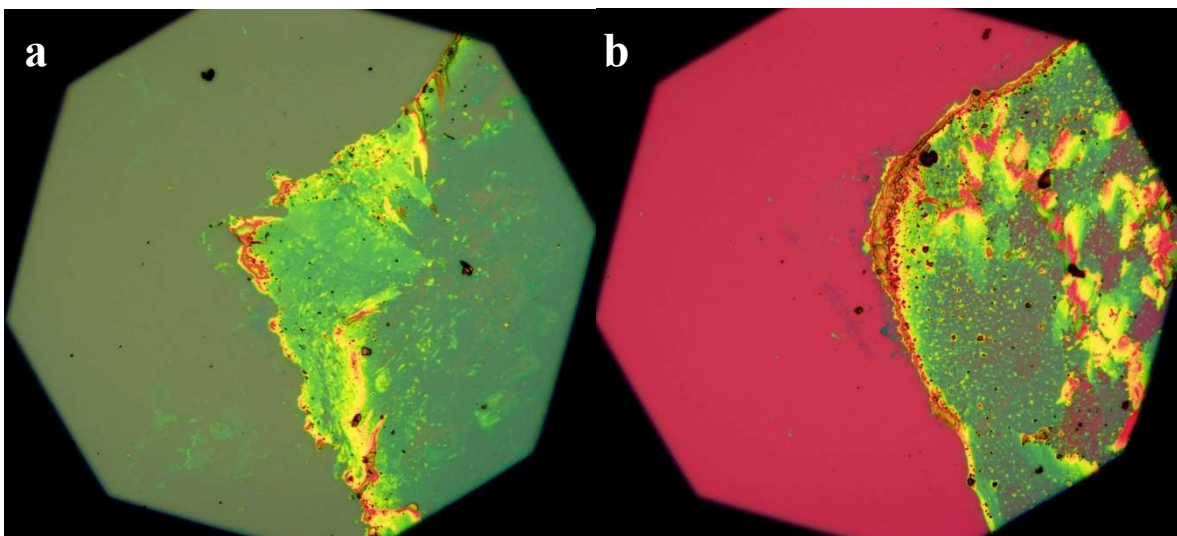


Figure 5: Optical image of (a) 90-minute SDS samples from batch 1 and (b) 90-minute SDS sample from batch 2

SEM and EDX Characterization

In order to gain further insight into the ZnO deposition characteristics, a combination of scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX) were used. Figure 5a and 5b show SEM images that were taken of the 120-minute SDS treated sample from batch 1. At a resolution of 2 μm , a fairly consistent and uniform distribution of ZnO appears to be deposited on the graphene film. The deposition pattern is not completely uniform however as small darker spots can be seen throughout the film. Increasing the resolution to 200 nm, it is observed that the darker spots corresponded to areas where ZnO deposition did not occur. At this range, it is also possible to distinguish individual contours of the nanoparticles which are both tightly packed and approximately equal in size. Based on these images, it was seen that the SDS had successfully allowed for uniform deposition across the otherwise inert CVD graphene.

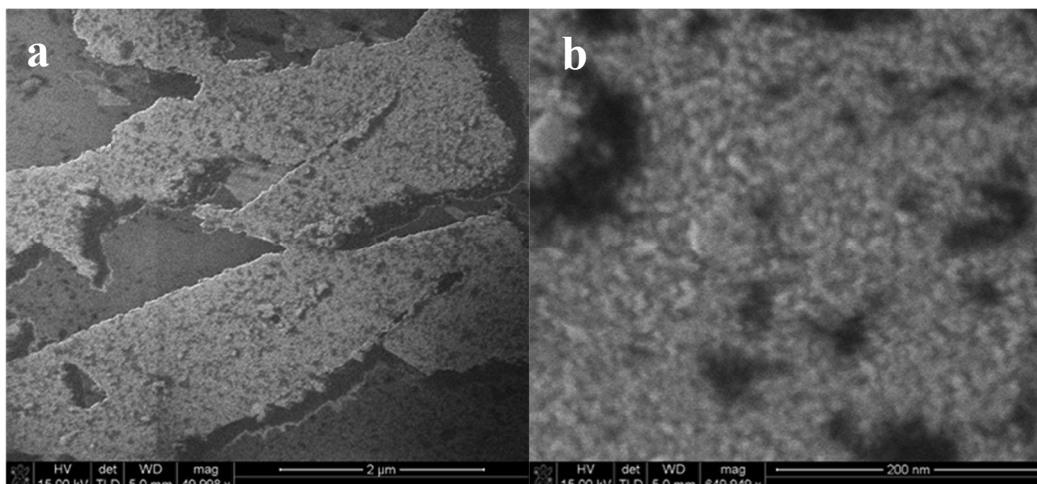


Figure 6: SEM images of the 120-minute SDS sample from batch 1 at resolutions of (a) 2 μm and (b) 200 nm

To confirm the pattern observed by the SEM was indeed ZnO particles on the surface, the 120-minute batch 1 sample was further characterized using EDX. The green box shown in Figure 6a indicates the area on the sample that was analyzed. As expected, the two most significant peaks correspond to silicon and oxygen which can be attributed to the composition of the underlying substrate. The next largest peak seen indicates that a significant amount of zinc is present within the area specified. This confirms that the contours seen during SEM imaging are indeed successfully deposited nanoparticles of ZnO.

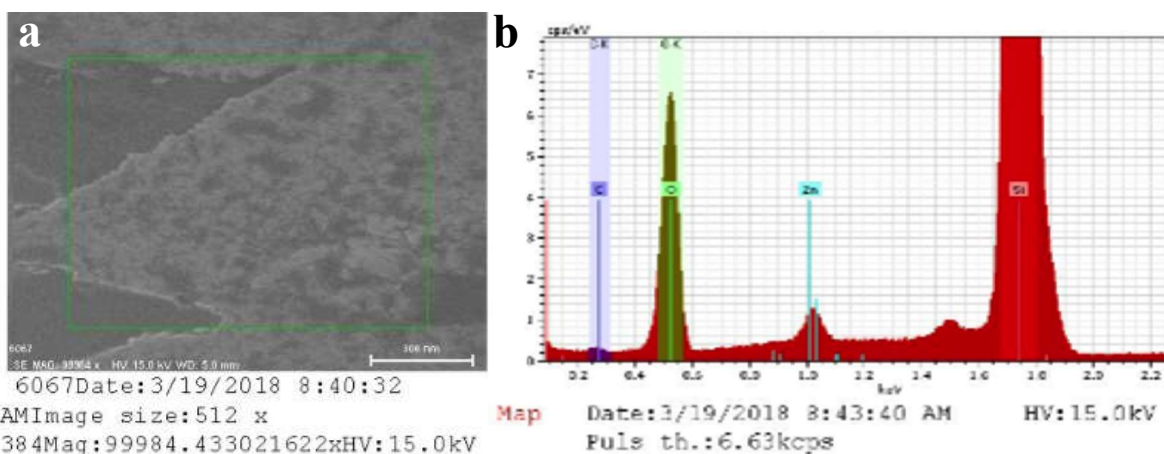


Figure 7: (a) image of graphene surface being analyzed by EDX (b) EDX graph of measured energy peaks showing elements located on the sample

5. CONCLUSIONS

In summary, it was found that sodium dodecyl sulfate anionic solution can be used as an affective pretreatment to non-covalently functionalize pristine monolayer graphene for achieving uniform nanoparticle deposition. Analysis showed that varying the amount of time that graphene is treated with SDS can influence the amount of ZnO deposited for samples that have undergone equal numbers of ALD cycles. The overall uniformity in the distribution pattern remained fairly consistent across all samples regardless of varying SDS treatment times. These results show promise that uniform deposition of platinum and palladium using ALD may also be achieved without physical alteration of the graphene lattice. To this extent, further research is recommended.

6. FUTURE RESEARCH

In the future, this research can be continued by depositing platinum or palladium nanoparticles in place of zinc-oxide. Due to the success observed with depositing ZnO, it is most likely expected that similar patterns would be obtained for platinum and palladium. Although this work aimed to observe the deposition characteristics of ZnO on SDS functionalized graphene, more concrete and numerical characterization would need to be done once platinum and palladium were deposited. Analyzing aspects such as nanoparticle size, growth rate, as well as aggregation and distribution would be necessary to begin analyzing how the process can be adjusted to achieve the desired nanoparticle characteristics. Once uniform deposition of Pt and Pd has been achieved, another important aspect for future work is to integrate and test the hydrogen sensing capabilities. The fabrication precision associated with ALD combined with the possibility of uniform nanoparticle deposition that also preserves the graphene lattice could hopefully improve the capabilities of modern hydrogen sensors.

Another aspect that deserves more attention in the future is the procedure used during the SDS treatment. Allowing the samples to air dry once they were removed from the sonication bath often resulted in a small ring that was visible on the sample where a tiny droplet of DI water had dried and evaporated. Ideally, the process would benefit from being optimized so that the sample requires a minimal amount of handling and no remnant amount of DI water droplets remain on the graphene surface prior to drying. Observing the deposition patterns associated with varying concentrations of SDS would also serve as a novel focus for future work. Previous studies have been done to observe how concentration affect SDS aggregation at the graphene interface in an aqueous solution but not after the sample is dried [10].

7. APPENDIX A – FIGURES

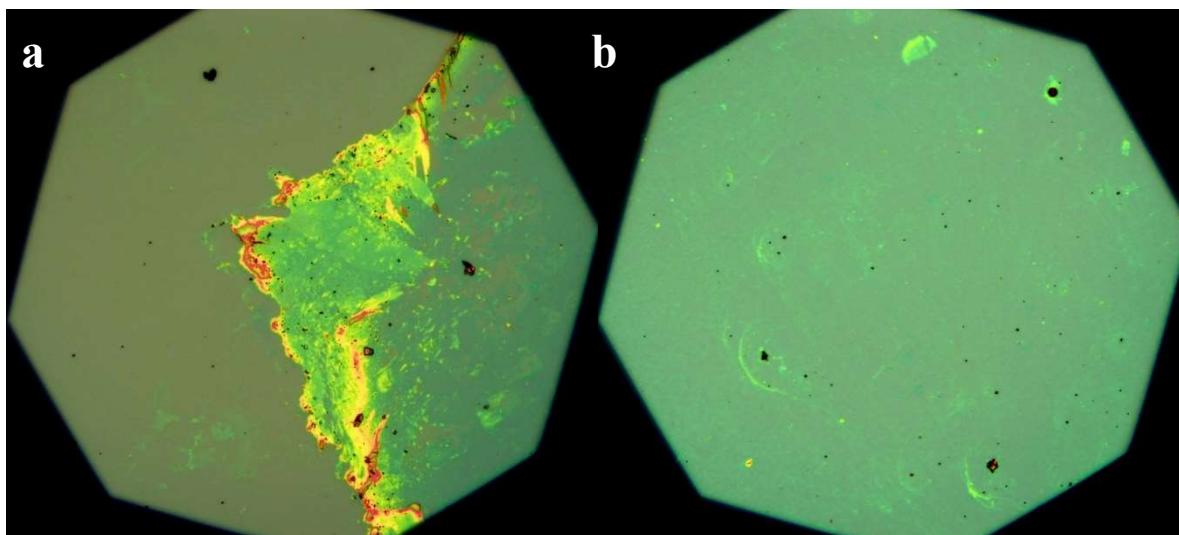


Figure 8: Optical image of 60-minute SDS sample from batch 1 at (a) graphene lattice border and (b) central location on graphene film

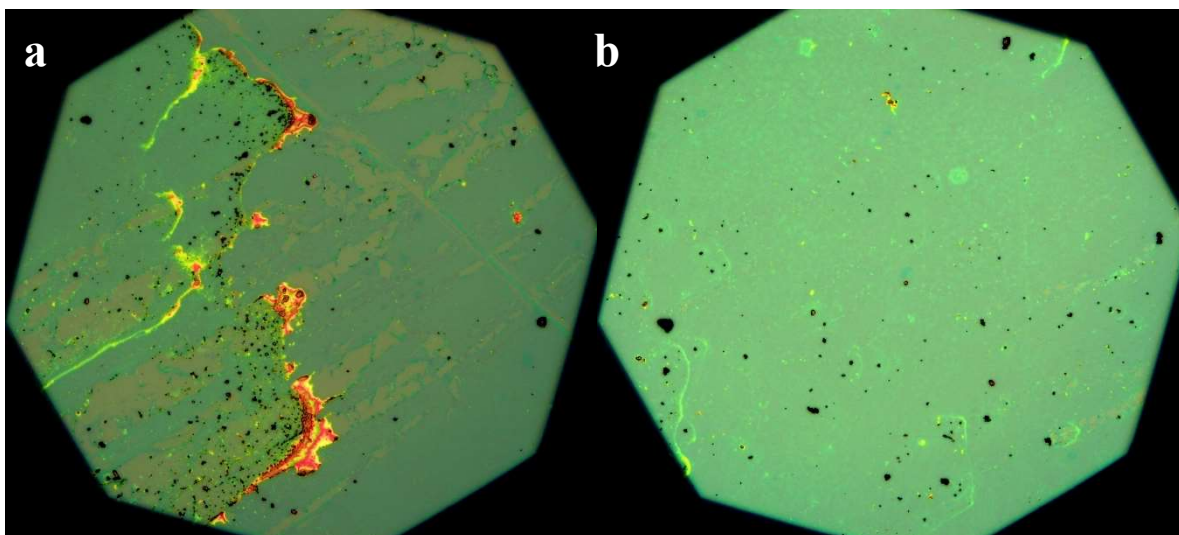


Figure 9: Optical image of 120-minute SDS sample from batch 1 at (a) graphene lattice border and (b) central location on graphene film

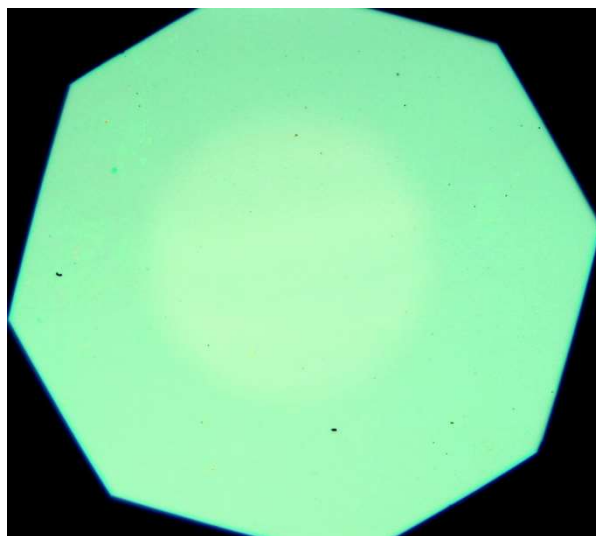


Figure 10: Optical Image of CVD grown graphene film purchased from ACS

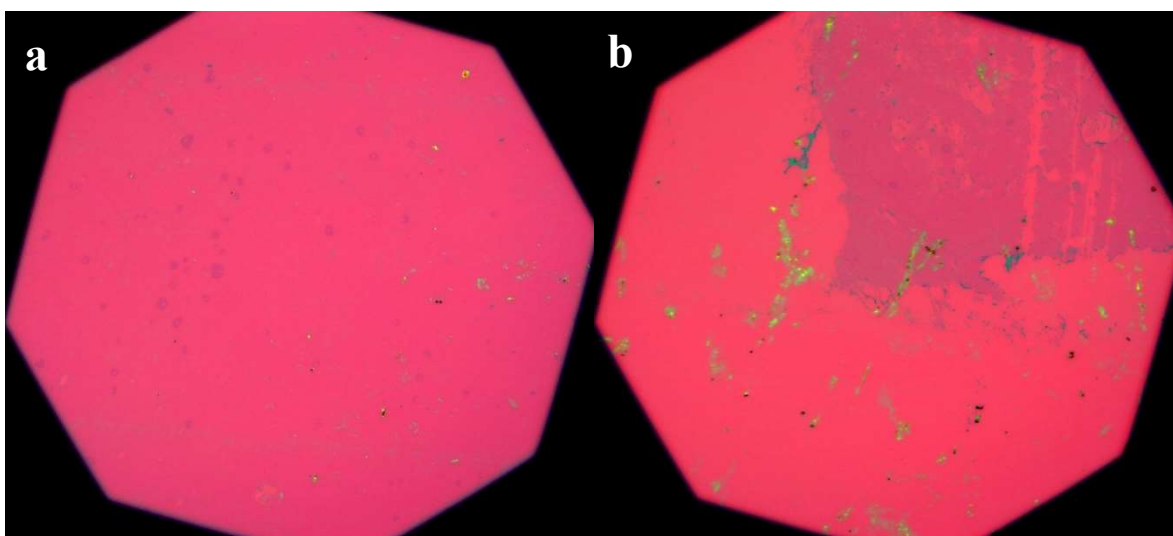


Figure 11: Optical image of control sample from batch 2 at (a) graphene lattice border and (b) central location on graphene film

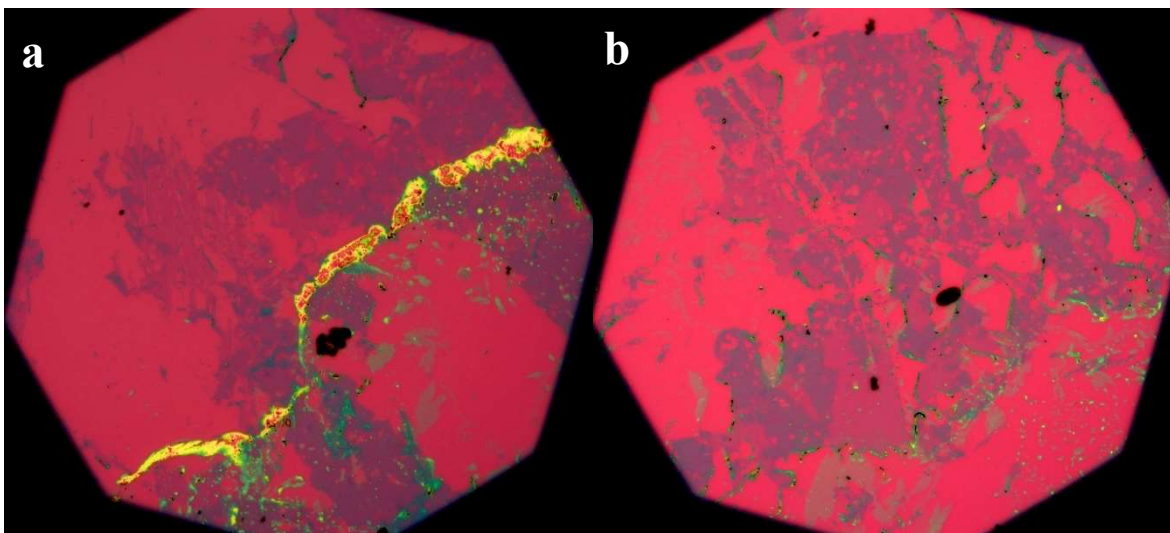


Figure 12: Optical image of 30-minute SDS sample from batch 2 at (a) graphene lattice border and (b) central location on graphene film

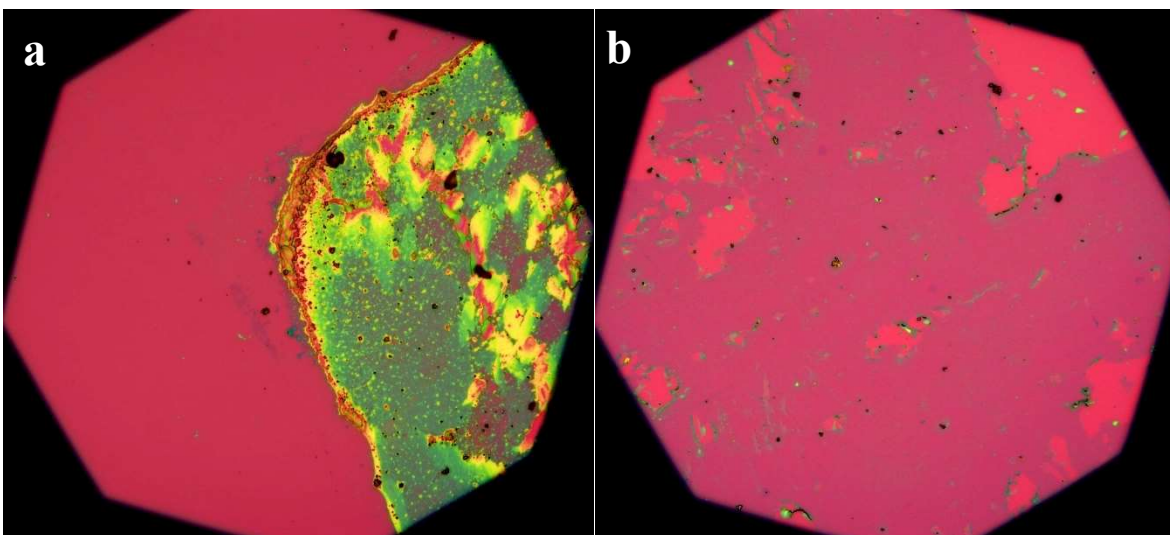


Figure 13: Optical image of 60-minute SDS sample from batch 2 at (a) graphene lattice border and (b) central location on graphene film

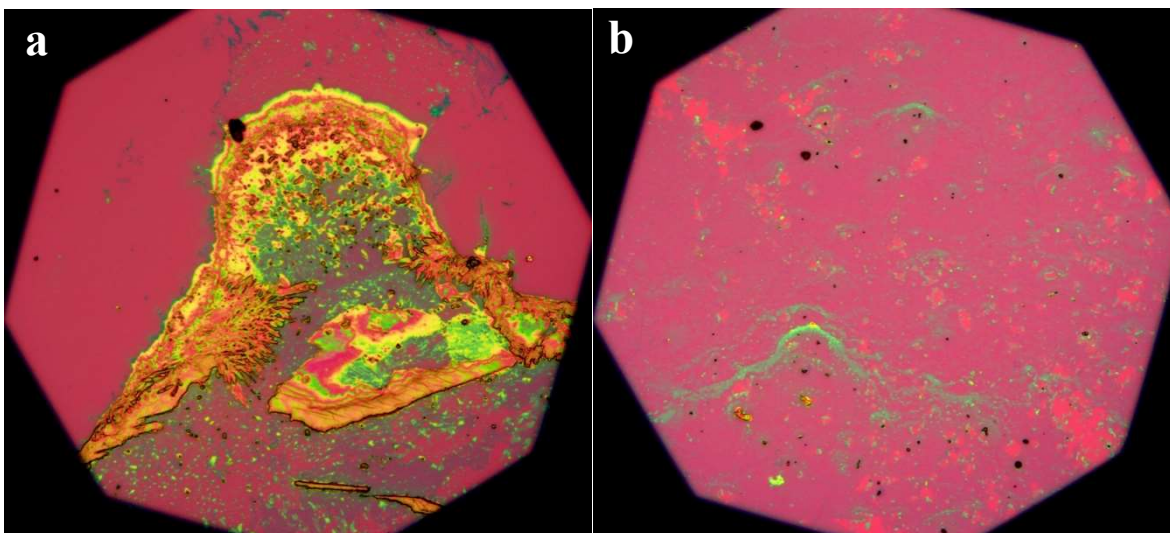


Figure 14: Optical image of 90-minute SDS sample from batch 2 at (a) graphene lattice border and (b) central location on graphene film

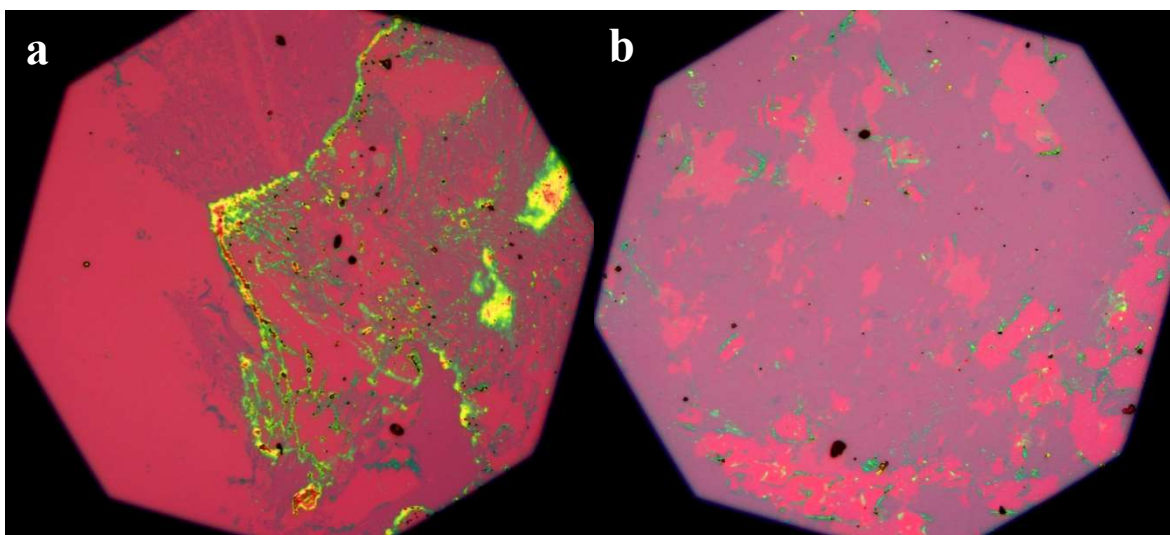


Figure 15: Optical image of 120-minute SDS sample from batch 2 at (a) graphene lattice border and (b) central location on graphene film

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