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Surface Characterization of Sodium Cholate Treated CVD Graphene

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Abstract* — The advancement of graphene has created a need in exploring its properties for different applications. One way to explore its properties is by reducing its hydrophobicity. To overcome hydrophobicity of graphene, surfactants have been used in functionalization, hence improving the surface properties of the graphene monolayer. Therefore, investigating surfactant treatment for CVD graphene becomes useful in understanding the surface property effects on graphene. This study utilizes CVD graphene on silicon substrates. Its treatment was done with varying concentrations of Sodium Cholate (SC) for different treatment times. These samples were then characterized using Atomic Force Microscopy (AFM) to investigate the surface properties of the samples before and after treatment. To be optimized, the graphene must remain attached to the silicon substrate. The result shows that the integrity of the graphene, which is basically the sp^2 structure, is preserved as there was no delamination from the substrate even after treatment for as long as 2 hours in 1% weight/volume concentration of the SC solution.

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I. INTRODUCTION

The advancement of graphene in recent years has been on the rising amongst researchers particularly in the application of electronic devices. Despite this rising interest, there are concerns associated with hydrophobicity and inertness of graphene. Graphene has been widely used in so many flexible electronic applications and this is due to its attractive and excellent mechanical, chemical, electrical conductivity, and surface properties [1]. Graphene as a flat monolayer has a unique high electron mobility and has been researched as a top list candidate for solar cells, etc. However, for optimization, several pre-treatment processes have been studied even in high temperatures up to 1000^0 C and the result proves that oxides such as copper oxides have been eliminated from the surface without affecting its functionalization [2].

In recent times, the research dynamics of the functionalization of graphene in water purification has also been studied [3]. Electronic and photonic devices are a significant area of research, and it covers a wide range of graphene applications [4]. Although, the hydrophobicity and inertness of graphene during fabrication is a functionality that can be addressed by surface treatment. And so, in addition for varying application of GO in different fields of science and technology, it is expedient to combine graphene with other nanomaterials such as magnetic nanoparticles, carbon dots, carbon nanotubes, nano semiconductors, quantum dots etc. However, before that is done, there is a need for its surface functionalization. This surface functionalization can either be non-covalent functionalization or covalent functionalization [5 - 6, 9]. The non-covalent functionalization of graphene using surfactant is done via technological process to optimize the performance of graphene particularly in sensing applications [7].

This study aims to contribute to knowledge by examining the surface properties of a treated CVD graphene using Sodium Cholate surfactant. This experiment will also show the effect of surfactant on the structure of the nanoparticles. The AFM study of the surfactant-functionalized graphene samples (SFGS) could also show the relationship between the surfactant distribution on CVD graphene and nanoparticles distribution after ALD deposition.

II. MATERIALS AND METHODS

In this study, the graphene sample is CVD graphene on Si/SiO_2 (Graphenea Inc. Cambridge USA). The characterization of the as-received CVD graphene sample to be used includes SEM (Scanning Electron Microscope), AFM (Atomic Force Microscopy) and Optical Microscopy. Sodium Cholate (Sigma-Aldrich, USA) was used as the surfactant for the treatment of CVD graphene in this experiment. The factor variables are varying concentration and varying time. The samples will be rinsed after the surface functionalization using deionized water and then dried using nitrogen. After which characterization will be performed on the samples. Characterization techniques like SEM, AFM, and optical microscopy. We will compare the effects of this Sodium Cholate surfactant treatment to the as received CVD graphene and also, to the previous work done using SDS (Sodium Dodecyl Sulfate) as a surfactant.

III. CURRENT RESULTS

To indicate the basal plane and boundaries for the as received CVD graphene samples, Scanning Electron Microscopy were taken. These features were as a result of the polycrystalline copper substrate employed in the deposition of graphene, which are as seen in Figure 1. At the outset, using a Sodium Cholate (SC) concentration of 1 wt./vol%, a sample of the as received graphene was soaked for a period of 2 hours which was the concentration and

treatment time used in comparison to Sodium Dodecyl Sulfate (SDS) used in the previous work, which is the treatment concentration and duration for carbon nanotube.[7] After treatment of the sample for the stated concentration and time, graphene did not detach from the substrate (Figure 2).

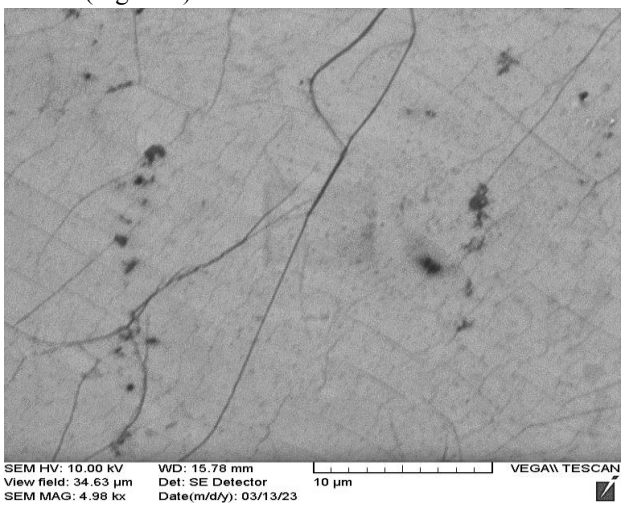

Figure 1. SEM image of as-received CVD graphene sample at 5000x magnification.

SC concentration was varied from 1 wt./vol% down to 0.06 wt./vol% and this was done to establish the genesis of graphene delamination from substrate. Figure 3 shows the optical images of different concentrations for the same treatment time of 2 minutes. The obtained results clearly reveal the non-effect of the surfactant concentrations on the CVD graphene sample as compared to the SDS samples in the previous work.

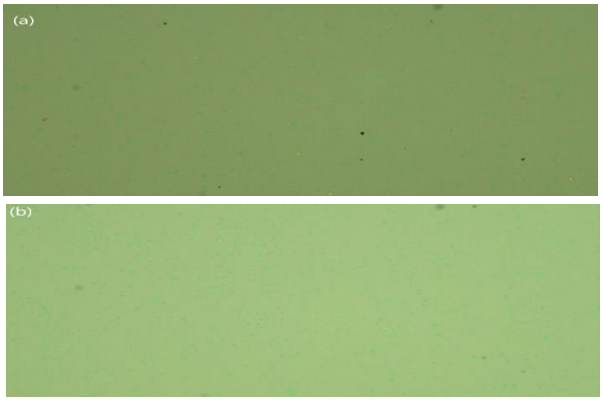

Figure 2. Graphene did not detach from the substrate post 1 wt./vol% SC treatment for 2 hours. (a) Area with CVD graphene-treatment (b) Area with graphene post-treatment.

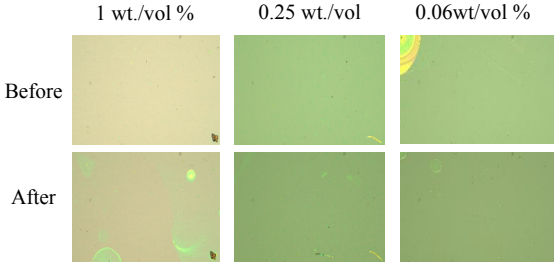

Figure 3. High concentration of SC made no prominent changes to the graphene to detach from the substrate. 0.06 wt./vol% was seen to clean dirt off the surface of the CVD graphene. Images depict the pre-treatment and post-treatment at varying concentrations.

Selecting 0.25 wt./vol% concentration and varying the treatment time from 30 minutes down to 2 minutes, we examined the effect of the treatment time with graphene and surfactant. It was observed that the shorter the CVD graphene remained in the solution, the cleaner the surface optically became. Most stains on the as-received CVD graphene were cleaned and a cleaner area was discovered.

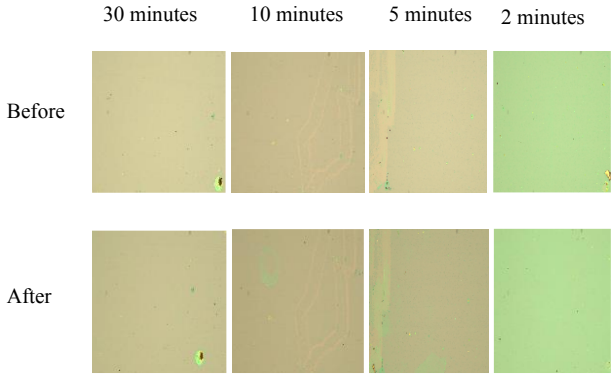

Figure 4. Shorter SC treatment time leads to a cleaner graphene surface area. All samples were treated with 0.25wt./vol% of SC for the times shown. The shorter treatment times and lower concentration will lead to a cleaner substrate.

Emphasizing the above results, it is necessary to find the ideal surfactant treatment time for the CVD graphene. The SC surfactant was initially dissolved in 5ml of water and the required volume for a desired concentration was achieved with isopropyl alcohol (IPA). This was done to obtain a higher concentration of SC. The IPA solvent was used because of its non-delaminating effect on graphene from substrate and its use in the cleaning of graphene. What's more, IPA, a polar compound with 3 carbons, is soluble in water because of its polar nature and few numbers of carbon atoms [8]. The SC/water/IPA treatment of the CVD graphene also resulted in a non-delamination of the graphene off the substrate for both 0.25 wt./vol% and 0.125 wt./vol% at 2 minutes and 4 minutes.

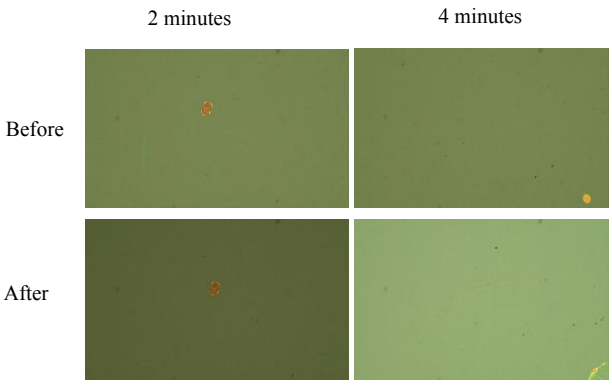

Figure 5. Optical images before and after SC/water/IPA 0.25wt./vol% treatment of the CVD graphene resulted in a no delamination of the graphene for 2-minutes and 4-minutes treatment times.

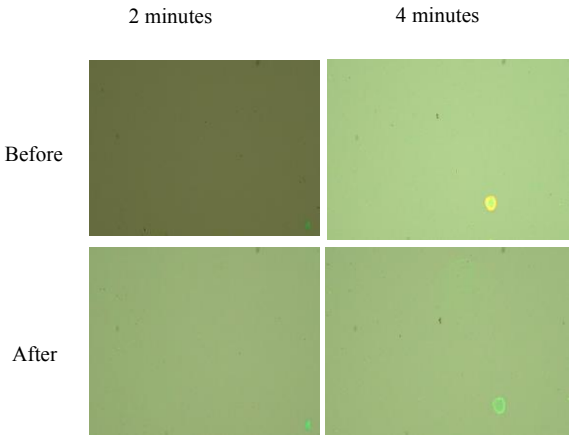

Figure 6. Optical images before and after SC/water/IPA 0.125wt./vol% treatment of the CVD graphene resulted in a no delamination of the graphene for 2-minutes and 4-minutes

3 µm x 3 µm AFM images for the samples were taken for different concentrations and times. Figure 7 and Figure 8 show the AFM images for the concentrations of 0.25 wt./vol% and 0.125 wt./vol% respectively. The values for the root-mean-square (RMS) roughness of the scanned areas were evaluated. The surface treatment effects were measured by evaluating the difference between the RMS values pre and post treatment. Considering the samples treated with 0.25 wt./vol% SC concentration for 2 minutes, the RMS roughness pre and post treatment were **0.184 nm** and **0.275 nm** respectively which results in a difference of **0.091 nm**.

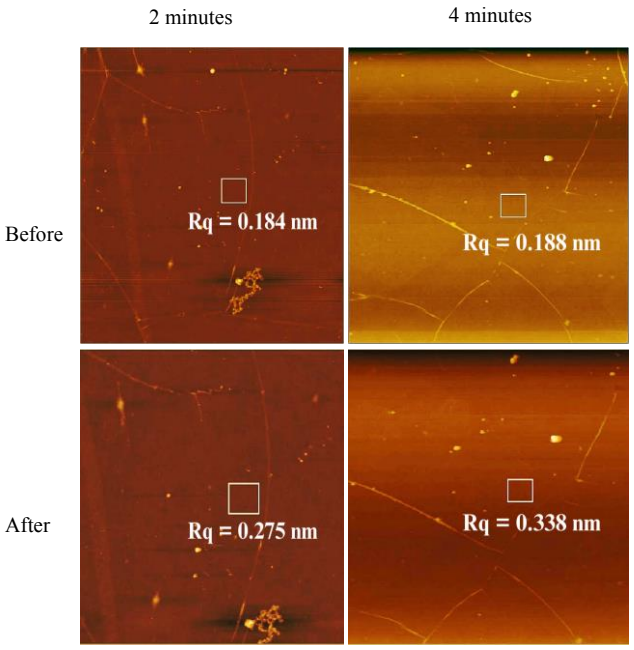

Figure 7. The RMS roughness evaluated for similar area (squares) after the treatment with 0.25wt./vol% SC/Water/IPA for 2 and 4 minutes.

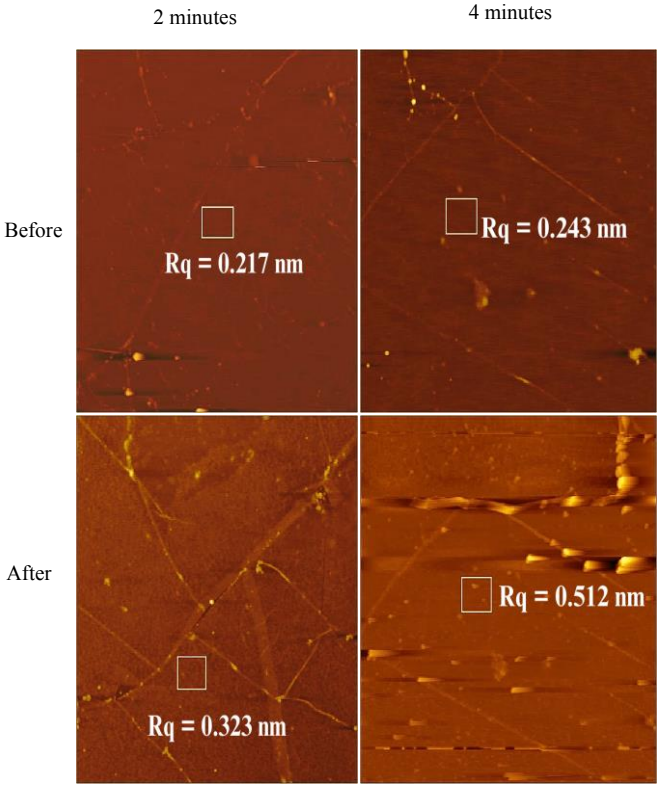

Figure 8. The RMS roughness evaluated for similar area (squares) after the treatment with 0.125wt./vol% SC/Water/IPA for 2 and 4 minutes.

For the sample treated for 4 minutes with the same concentration of 0.25 wt./vol%, the RMS roughness pre and post treatment were **0.188 nm** and **0.338 nm** respectively, with a difference of **0.15 nm**.

The sample treated with the lower SC concentration of 0.125 wt./vol% for 2 minutes, the RMS roughness pre and post treatment were **0.217 nm** and **0.323 nm** respectively which results in a difference of **0.106 nm**. Then, the sample treated for 4 minutes with the same concentration of 0.125 wt./vol%, the RMS roughness pre and post treatment were **0.243 nm** and **0.512 nm** respectively, with a difference of **0.269 nm**.

The RMS roughness difference pre and post treatment for the 2-minutes and 4-minutes treatments were **0.015 nm** and **0.119 nm** respectively.

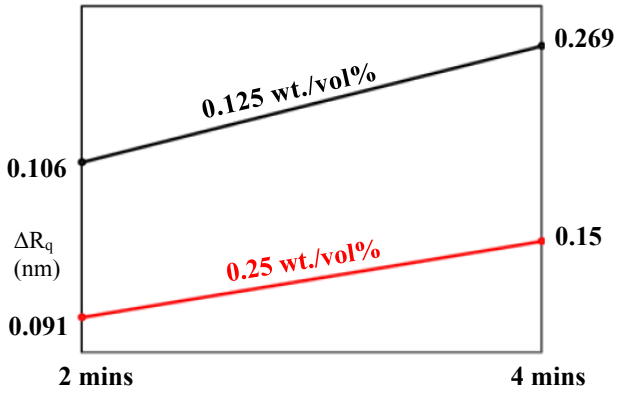

Figure 9. ΔRq for the two SC concentrations and time show an increase in ΔRq for longer treatment time and lower treatment concertation.

IV. Discussion and Future Work

Results shown above indicated that the treatment of CVD graphene with SC was not affected, i.e., no delamination from the substrate, even with high concentration and a long soaking time. Although, as the concentration was varied, some grits were observed to be taken off the surface and this intensified as the concentration was increased with increased soaking time from 2 minutes to 2 hours. Again, Figure 1 revealed that the structure of graphene remains the same after treatment as there was no distortion in the lattice structure which could have been evident by delamination of the CVD graphene on the substrate, as observed with SDS. However, with the mixture of the SC, water and IPA, we observed that the lower concentration of 0.125wt./vol% was more efficient with surface cleaning of the CVD graphene as compared to the 0.25wt./vol%. Additionally, the 0.125wt./vol% solution was observed to have increased the root-mean-square surface roughness of the as-received CVD graphene as compared to the 0.25wt./vol% solution which is an interesting observation. Also, the surface roughness of the samples, compared to the previous work with SDS, was observed to have increased with each SC concentration treatment. Increase in the surface roughness, as observed in Figure 7 and Figure 8, would directly affect the functionality of the thin film CVD graphene. Existing literature shows that an increase in surface roughness of 2D materials has a direct effect on electrical transport properties, considering electrical conductivity. To better this phenomenon, when the thickness of thin film decreases and gets comparable to the mean free path of the electron, the effect of surface roughness on the electrical conductivity increases, thus leading to an increase in surface residence [10]. Hence, this increase in surface roughness will have an undesirable effect on the conductivity of the surface functionalized/treated graphene.

For further investigation, more concentration of the SC surfactant may be varied with increasing treatment time. Additionally, surfactants such as SOS (Sodium Octyl Sulfate) can be and will be explored in future research.

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