Growth of graphene on stainless steel by chemical vapor deposition using soybean oil as a carbon source

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Abstract. Graphene is a 2-dimensional material which consists of carbon atoms arranged in a flat honeycomb lattice. Graphene has many outstanding properties such as high electron mobility, superb strength, and great flexibility. Although graphene film can be fabricated by economical method such as chemical vapor deposition, the utilization of flammable gas (such as methane, acetylene) in the graphene growth process is still dangerous therefore the safe flammable gas storage and gas line installation are needed. Soybean oil is available vegetable oil which contains carbon, hydrogen and oxygen. Utilization of soybean oil as a carbon source instead of hydrocarbon gas for graphene growth by chemical vapor deposition can avoid an explosion of flammable gas and save the installation cost of gas system. However, the presence of oxygen in soybean oil may obstruct the growth of graphene by chemical vapor deposition. Fortunately, annealing stainless steel with carbon at high temperature can eliminate oxygen from the surface. In this study, the growth of graphene on stainless steel by chemical vapor deposition using soybean oil as a carbon source has been study. The presence and quality of graphene are investigated by Raman spectroscopy. The morphology and element analysis are measured using scanning electron microscope and energy-dispersive X-ray spectroscopy, respectively.

1. Introduction

Graphene is 2-dimensional material which consists of carbon atoms arranged in flat honeycomb lattice. Graphene has considerably attracted researcher’s attentions due to its exotic properties such as, high flexibility [1-2], large specific surface area [3-4], high electron mobility [5-6] and great mechanical properties [7]. Moreover, the coating graphene film on metal can increase corrosion resistance [8-9], electrical conductivity [8] and surface hardness [10] of the metal. Graphene film can be fabricated by many methods such as annealing SiC [11-15], chemical vapor deposition (CVD) [16-18] and so on. CVD is a simple and economical method for graphene growth on large-scale production. Generally, hydrocarbon gas (such as methane or acetylene) is preferred to use as a carbon source in the CVD process for the growth of graphene film on metal. However, methane and acetylene gases are flammable gases therefore the safe gas storage and gas line installation are needed. Soybean oil is carbon-rich liquid which is available and cheap. Thus, the utilization of soybean oil as a carbon source instead of hydrocarbon gas for graphene growth by CVD can avoid an explosion of flammable gas and save the installation cost of gas piping system. In this report, the growth of graphene on stainless steel by CVD
using soybean oil as a carbon source is studied. The effect of soybean oil quantity on the growth of graphene film on stainless steel is emphasized.

2. Experimental
A s304 stainless-steel sheet with a size of 30×40×0.85 mm³ was precleaned by ultrasonic sonication in acetone for 5 minutes and then put into a quartz tube. Thereafter, the quartz tube was first evacuated until the base pressure in the quartz tube reached ~3 Pa and then the stainless-steel plate was heated to the graphene growth temperature (900°C) by furnace. At the growth temperature, the soybean oil with the quantities of 1-25 ml was heated at 400°C to evaporate soybean oil. The vapor of the soybean oil was introduced into the quartz tube for 30 minutes. After that the sample was cooled down rapidly to room temperature.

The formation of graphene film on stainless-steel plates was confirmed by Raman spectroscopy measured at room temperature with a 50x objective and a 532 nm laser. The laser beam size is ~1 μm in diameter. Exposure time and accumulations are set at 10 seconds and 10 accumulations. Surface morphology and element analysis were investigated by field-emission scanning electron microscope (FE-SEM) equipped with an energy dispersive X-ray spectrocope (EDX) at incident beam of 15 keV.

3. Results and discussion
Figure 1 (a)-(f) show the morphology of the samples annealed at 900 °C for 30 minutes under the vapor of soybean oil quantities of 1 ml, 5 ml, 10 ml, 15 ml, 20 ml, and 25 ml, respectively. In case of 1 ml, 5 ml and 10 ml samples (Figure 1 (a)-(c)), the surface roughness increases with increase in the quantity of soybean oil. For 15 ml sample (Figure 1 (d)), many islands appear on the sample surface and they disappear when the samples annealed under the vapor of soybean oil quantities of 20 ml and 25 ml as shown in Figure 1 (e) and (f), respectively. Figure 1 (g) displays Raman spectra of the samples annealed at 900 °C for 30 minutes under vapor of various quantity of soybean oil. In general, graphene has 2 main specific peaks in the Raman spectra at ~1580 cm⁻¹ (G band) and ~2700 cm⁻¹ (2D band). G band and 2D band are originated from E₂g vibrational mode and second-order two-phonon mode, respectively [19]. However, The D band at ~1350 cm⁻¹ is the third specific peak of Raman spectra of graphene. The D band will appear where the symmetry of graphene structure is broken by edge or deflect [20]. In the case of 1 ml, 5 ml and 10 ml samples, there is no significant peak appears in the Raman spectra while the Raman spectrum of 15 ml sample displays D band and G band at 1359 cm⁻¹, 1592 cm⁻¹, respectively. The absence of 2D band reveals that there is no graphene on the surface of the 15 ml sample. The D and G bands of the 15 ml sample may be originated from amorphous carbon on its surface. For 20 ml and 25 ml samples, the G and 2D bands obviously appear in the Raman spectra at ~1572 cm⁻¹ and ~2700 cm⁻¹, respectively implying that there is graphene film on the surfaces. Figure 1 (h) shows the relations between soybean oil quantity and weight% of carbon and oxygen on the surface of the samples. This graph displays the weight% of oxygen reduces with increase in soybean oil quantity. Conversely, the weight% of carbon increases with increase in the soybean oil quantity. Generally, oxygen is an obstacle to graphene growth while carbon is a basic element of graphene structure therefore the low-oxygen and high-carbon environments are excellent condition for graphene growth on stainless-steel substrates. It is in a good agreement with Raman spectra in Figure 1 (g) which shows that the graphene can be grown on the samples annealed under soybean oil quantities of 20 ml and 25 ml.

Carbothermal reduction is the process for oxide reduction by annealing metal oxide at high temperature with reducing-agent carbon. The reducing-agent carbon may be gaseous CO and CO₂ in accordance with the following reactions [21]:

\[ \text{MO(s) + CO} \rightarrow \text{M(s) + CO}_2 \]
where M is metal. Stainless steel is iron-rich alloy, Liu et al. show a gas-phase equilibrium diagram of iron oxide which displays the temperature more than 600 K with large amount of gaseous carbon can reduce the iron oxide [22]. The reaction of reduction of iron oxide is displayed step by step as follows.

\[ 3\text{Fe}_2\text{O}_3 + \text{CO} = 2\text{Fe}_3\text{O}_4 + \text{CO}_2 \]
\[ \text{Fe}_3\text{O}_4 + \text{CO} = 3\text{FeO} + \text{CO}_2 \]
\[ \text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2 \]

In this experiment, the vapour of soybean oil is used as metal vapor with carbon for reduction of metal oxide on the stainless-steel surface at 900 °C. The results show that the oxides can be eliminated from the surface at high temperature if the quantity of soybean oil is much enough therefore annealing stainless steel at high temperature with enough soybean oil can grow graphene on its surface.

![Figure 1. FE-SEM images measured on the surface of the samples annealed at 900 °C for 30 minutes using soybean oil quantities of (a) 1 ml, (b) 5 ml, (c) 10 ml, (d) 15 ml, (e) 20 ml and (f) 25 ml as a carbon source. (g) Raman spectra of samples annealed at 900 °C for 30 minutes under the vapor of soybean oil quantities of 1-25 ml. (h) The relations between soybean oil quantity and weight% of carbon (blue) and oxygen (red).](image)

### 4. Conclusions

In this report, the growth of graphene on stainless steel by chemical vapor deposition using soybean oil as a carbon source was demonstrated. The annealing temperature and growth time were set at 900 °C and 30 minutes, respectively. In addition, the quantity of soybean oil was varied from 1 ml to 25 ml. We found that annealing stainless steel at high temperature (900 °C) with enough amount of carbon can
eliminate oxygen which is an obstacle to graphene growth on stainless-steel surface. In this research, we can grow graphene film on stainless steel by CVD using soybean oil quantities of 20 ml to 25 ml as a carbon source.

5. References
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