Chemical Vapour Deposition of Graphene Derived from Waste Engine Oil—Influence of Vaporization Temperature

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Abstract

This article presents waste engine oil (WEO) as a carbon precursor and the effect of precursor temperature on the growth of graphene synthesized via thermal chemical vapor deposition method. Thermogravimetric analysis of waste engine oil revealed the vaporization phase at below 350°C and the cracking phase at higher than 350°C. Under the flowing argon atmosphere, WEO was vaporized with different precursor temperatures of room temperature (RT), 250, 300, 350, 400, and 450°C. The XRD results indicate that graphitic reflection peak of (002) is observed from all the samples except from the sample prepared at RT as there is no carbon species vaporizes. The maximum absorption peak for graphene from 300°C is red-shifted (249nm) attributes to the of π→π* transition of aromatic C-C bonds revealed better sp^2 conjugation in the graphene layer. In addition, a strong UV absorption peak observed in the graphene layer proved the enhancement in photonic properties. Hence, the graphene layer prepared with 300°C precursor temperature can be a promising material for optoelectronic technology.

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1. Introduction

The unique properties of graphene have induced attraction in scientific society all over the world. Its outstanding electrical, optical, and mechanical properties such as extraordinary thermal conductivity, high surface area, and high mechanical strength has drawn much attention due to its potential to improve performances in numerous materials. Amid the various uses envisioned for graphene, graphene could be applied as solar cells, humidity sensor, bioelectronic device, highly conductive, transparent electrodes and chemical sensors [1-7].

Due to their wide applications, the development of large-scale synthesis methods is necessary. In thermal chemical vapor deposition (TCVD) method, the carbon precursor for the growth of graphene may be in the form of gas, liquid, or solid [8-10]. Most importantly, it required the precursor to be in gas form to reach the surface of the metal catalyst. Therefore, precursor temperature plays an important role for the growth of graphene. The precursor needs to be vaporized slightly above its vaporization temperature to prevent it from returning to its original form and deposited onto the hot quartz tube instead of the metal catalyst [11].

Around the world, massive amounts of used oil such as waste cooking oil, hydraulic oil, and waste engine oil are produced abundantly. Every year, approximately 24 million metric tons of untreated waste engine oil is released into the environment endangering health and life [12]. Herein, waste engine oil (WEO) is introduced as a carbon precursor to produce graphene via TCVD method. TCVD method by far delivers the best quality graphene that may be used at the industrial setting. It would be beneficial by converting contaminated matters into valuable resources for a sustainable option.

2. Materials and methods

The carbon precursor, waste engine oil (WEO) was collected from the local Perodua vehicle service centre as raw material. The oil was used for 20, 000 km mileage. The WEO undergoes a pre-treatment process prior to the experiment being started which involves filtration to remove unnecessary foreign elements. Nickel substrate of 20 mm thickness was used as a metal catalyst for the growth of the graphene layer. The substrate undergoes pre-treatment before the synthesis process. The synthesis of the graphene layer was done using thermal chemical vapour deposition which was equipped with double furnaces under the flowing atmosphere of Argon gas as in **Fig. 1**. The carbon precursor, WEO, was placed in Furnace 1 for the vaporization process, meanwhile the nickel substrate which acted as metal catalyst was placed in Furnace 2 for the synthesizing process of graphene layer. Some amount of WEO was vaporized at different vaporization temperatures of RT, 250, 300, 350, 400, and 450°C in Furnace 1 and the graphene layer was synthesized at an optimum synthesis temperature of 1000°C in Furnace 2. Characterization is one of the most crucial aspects of studying matter. In this study, thermal properties of waste engine oil were investigated through thermogravimetric analysis. The optical and structural properties of the graphene layer were studied via ultraviolet-visible spectrometer and X-ray diffraction. In TGA analysis, a solid sample is constantly weighted while heated in an inert gas ambience. The mass changes of the sample are recorded. In this study, Pyris1of Pelkin Elmer was used to study the thermal properties of waste engine oil. Absorption spectra were recorded on a Cary 5000 UV-Vis-NIR spectrophotometer of the Varian model. Meanwhile, PANalytical X'Pert PRO was used to study the phase identification of crystalline structures of the samples obtained from the experiment. The Cu kα radiation (1.54056Å) was use for the measurement. The data were analysed by using software X'Pert Highscore Plus.

3. Results and Discussions

Thermogravimetric analysis is a method frequently used to evaluate the thermal stability of a wide variety of materials by measuring mass loss as a function of temperature, time, and heating rate. This TGA test involves a weight change as the waste engine oil was heated gradually under atmospheric nitrogen. The thermal stability of the oil is assessed using thermogravimetric analysis under the increase of sample temperature from 25 to 600°C at the rate of 10.00°C/min. As can be seen from **Fig. 2**, the thermogravimetric analysis revealed thermal degradation of waste engine oil. It shows the weight loss and decomposition of waste engine oil samples with the corresponding temperatures. The forming and

breakage of physical and chemical bonds at high temperatures resulted in the changes in weight of the oil sample [13]. From Fig. 2, the weight percentage of waste engine oil decreased abruptly for about 90% at the temperature of 250°C, but in comparison, fresh engine oil has reduced to 90% of weight at the temperature of 340°C [14]. Generally, oil derivatives vaporize and degrade thermally below 340-350°C, leaving no carbonaceous residue. Following the vaporization phase, there came a phase known as cracking reaction. Above 350°C, the thermal cracking process of free-radical chain reactions took place where greater energy needed for the process to complete [15-17]. It is observed that at 450°C and above, mass loss of the waste engine oil is ~100% which conveys there are completely no solids that exist above the temperature. XRD analysis was done to study the crystal structure of the graphene synthesized from waste engine oil. The XRD patterns of graphene layers synthesized at different vaporization temperatures of RT, 250, 300, 350, 400, and 450°C are shown in **Fig. 3**.

The (002) diffraction peak of the graphene layer at about $2\theta = 26°$ corresponds to pristine graphite [18]. Differently, the significant peak of graphene oxide is at (002) where $2\theta = 17.2°$ corresponds to the addition of oxygen functional groups in the non-uniform crystal structure of graphite oxide [19]. No peaks observed at room temperature (RT) because there was no carbonaceous element vaporizing from WEO at RT which resulted in typical amorphous solid pattern. In contrast, the graphene layer obtained from precursor temperatures of 250 to 450°C showed (002) peaks indicating good crystallinity of the sample [20]. A remarkable decrease in the peak intensity of the graphene layer synthesized from WEO at $2\theta = 26.4°$ as compared to graphite peak was observed in the samples. The (002) peak of the graphene layer at 250°C is higher compared to the other sample and may correlate with low vapor pressure at lower temperature which causes the change in graphene quality [21-22]. The broad, non-sharp peaks indicate graphene is formed with precursor temperatures of 300-450°C instead of graphite despite the presence of the graphitic peaks. The XRD result confirms the structural crystallinity of the synthesized graphene. From the UV-vis spectra obtained, it is proved that the precursor temperature is one of the major factors for the growth of graphene. It controls the rate and quantity of carbon atoms dispersed on Ni substrate and the development of graphene formed. **Fig. 4** shows the UV-Vis spectra obtained for graphene layers prepared with different precursor temperatures from room temperature (RT) to 450°C with the increment of 50°C. The spectra of the sample with precursor temperatures of 250-450°C exhibit a maximum absorption peak at the UV region of approximately 248 nm. However, in contrast, the maximum absorption peak for the sample prepared at RT appears at the visible region. The presence of a peak at ~248 nm is due to the excitation of π electrons of the graphitic structure [23]. The formation of $\pi \rightarrow \pi^*$ transition of aromatic C-C bonds indicates the relative abundance of C-C in the samples. The amount of aromatic C-C present in graphene can be indicated from absorbance; therefore, graphene synthesized with vaporization temperature of 250°C contains a relatively higher number of aromatic C-C groups than the other precursor temperatures. In TCVD method, prior to reaching the metal catalyst's surface, the utilised precursor must be gaseous.

In order to decompose hydrocarbon to obtain active carbon atoms from the precursor, appropriate working temperatures as attained from TGA analysis are relatively required [24]. This is in agreement with the XRD result where graphene with 250°C precursor temperature is having the sharpest peak of (002). The degree of conjugation can be studied from the absorption wavelength; where the higher wavelength values indicate lower energy of light required to excite the electrons for a highly conjugated system. From **Fig. 4**, the maximum absorption peak of the sample with precursor temperature of 250°C appears at the wavelength of 246 nm and red-shifted to 249 and 250 nm with precursor temperatures of 300 and 350°C respectively.

Meanwhile, the maximum absorption peak for graphene from higher temperatures of 400 and 450°C is 248 nm. It is obvious that the sp^2 conjugation in the graphene layer with precursor temperatures of 300 and 350°C is better than the other sample. In addition, the enhancement of UV absorption in graphene with precursor temperature of 300°C made it potentially to improve the performance of many optoelectronic devices [25-26].
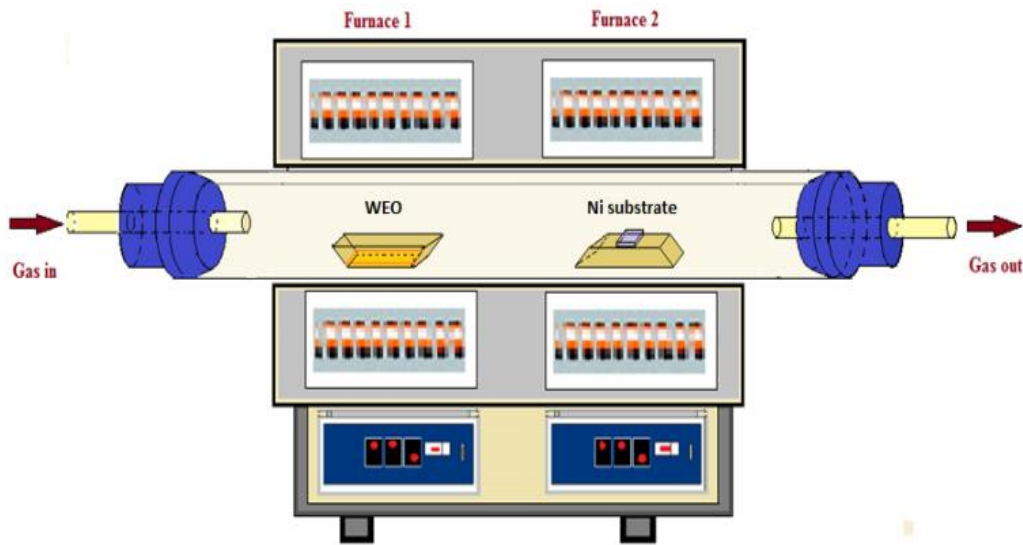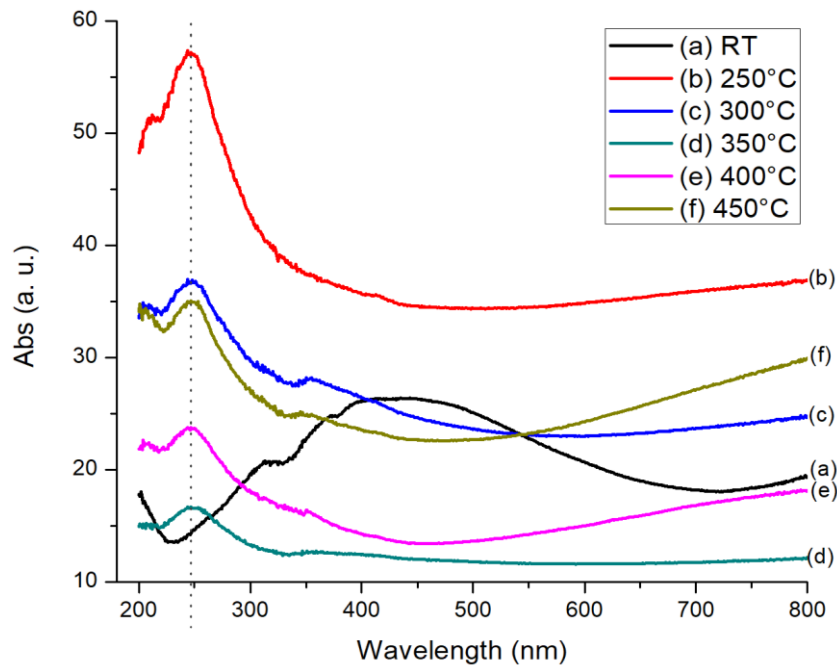

Figure 1: Deposition of graphene by thermal chemical vapour deposition method.
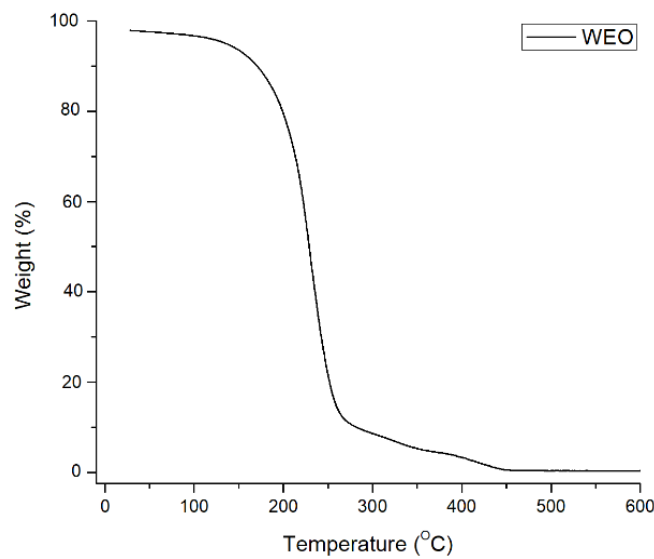
Figure 2: TGA of waste engine oil (WEO) at a scan rate of 10.00°C/min in nitrogen environment.
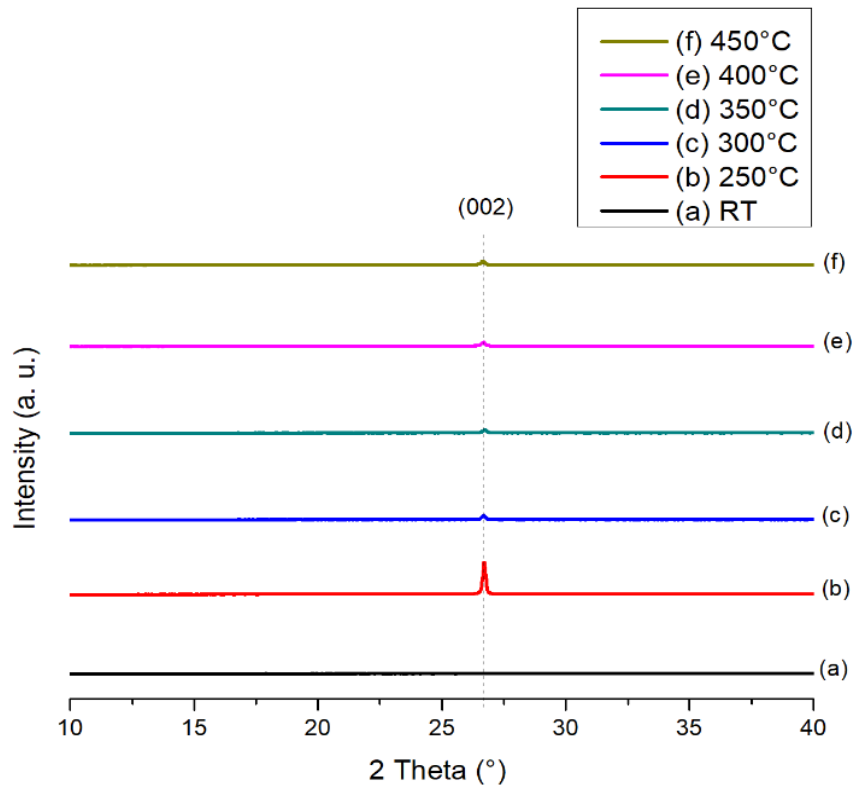
Figure 3: XRD pattern of graphene synthesized from waste engine oil vaporized at (a) RT, (b) 250, (c) 300, (d) 350, (e) 400, and (f) 450°C.

Figure 4: UV-VIS spectra of graphene at different precursor temperatures of (a) RT, (b) 250, (c) 300, (d) 350, (e) 400, and (f) 450°C.

4. Conclusions

In conclusion, the employment of suitable carbon precursors under the right circumstances can increase the graphene quality. Thermogravimetric analysis was used to study the thermal properties of the carbon precursor. Next, a series of graphene layers with different precursor temperatures were successfully fabricated by thermal vapor deposition method. The synthesized samples were further characterized by following methods such as XRD and UV-VIS absorption spectroscopy. The existence of (002) graphitic peak for the graphene prepared with 250-450°C precursor temperature confirms the structural crystallinity of the synthesized graphene. The graphene layer prepared with 300°C precursor temperature was found to exhibit the best properties compared to the others as the absorbance wavelength is red-shifted and the UV absorption is enhanced. Therefore, the present study demonstrates that the graphene synthesized with 300°C precursor temperature is a promising material for optoelectronic applications.

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