Novel method for graphene synthesis using PVC through electron beam irradiation

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1. Introduction

Graphene is an ideal two-dimensional material backboned with sp2-hybridized carbon atoms and draws significant interest due to its superior electrical properties represented by its high carrier mobility and its remarkable structure stability [1,2]. Based on these excellent characteristics, graphene is assessed as a material with unlimited potential for practical uses [2]. Since its first isolation by mechanical exfoliation [3], various techniques have been developed for the synthesis of graphene, such as epitaxial growth from silicon carbide [4], chemical reduction of graphene oxide [5], and chemical vapor deposition(CVD) on transition metal substrates [1,6-7].

However, mechanical exfoliation and epitaxial growth on silicon carbide have limitation for synthesis the large area graphene due to its quality, shape and size. While large scale and high quality graphene can be synthesized by CVD process [8], thus the CVD process has become a dominant method in graphene production. Nevertheless, in the case of CVD, there is also disadvantages that there are a risk of explosion by using a combustible gas at a high temperature around 1000℃ and it needs complicated process such as preparation, growth, cooling, and transference [1]. Therefore, a relatively safe synthesis method is required compared to the existing production process.

Miller, A.A. reported that the structure of PVC (Polyvinyl chloride) film was changed when irradiated at high energy electron beam [9]. During irradiation process, C-Cl bond in PVC was broken and carbon radical was produced due to high energy beam. Then, long chain of hydrocarbon was created by bonding the carbon radicals together.

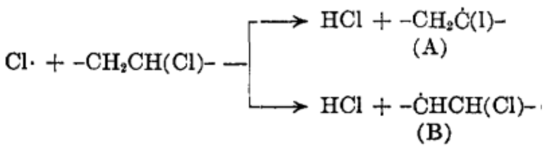

Fig. 1. Structural change of PVC during electron beam irradiation

In radiation process, break and creation of chain are called scission and crosslinking. After irradiation, polyene and aromatic ring, which are the foundation of graphene, could be created through scission and crosslinking of polymer by radiation. Thus, graphene can be made by controlling the degree of polyenes and aromatic rings with controlling the amount of electron beam [10]. However, this process is hard to use at industries because of its high energy. Herein we report that graphene like-carbon is created in PVC and PVDC through low energy electron beam irradiation. Irradiation process doesn't require many process & chemicals in synthesis of graphene, but it is more safety than other synthesis method because it is performed at room temperature. The 50keV electron beam device manufactured by our laboratory is used and the generation of graphene like-carbon is confirmed through the Raman spectrum.

2. Methods

2.1. Sample preparation

In the considered experiments, spin coated PVC solution and 15 μm PVC film(Goodfellow) were prepared. In case of PVC solution, PVC solution mixed with 0.5, 1.0, 1.5st% of PVC and DMF (Dimethylformamide) was mixed uniformly through sonication process. SiO_2/Si substrate was also prepared in order to drop the solution. SiO_2/Si substrate was cut by 1x1cm^2, then it was sonicated in an ethanol solution for 10 minutes to remove impurities. Even after, impurities and dust in substrate were removed using N_2 gas air gun. After that, the PVC solution was formed into a film on the substrate by spin coating process at 2000 rpm. In cased of PVC film, 99.6%, 0.1mm titanium (Goodfellow) substrate was used to fix the PVC film in vacuum. Titanium substrate was cut by 2x2cm^2, then it was sonicated in an ethanol solution for 10 minutes to remove impurities. Even after, impurities and dust in substrate were removed using N_2 gas air gun. PVC film is also washed by ethyl alcohol solution and dried by N_2 gas gun. The ethyl alcohol solution was dropped about 2-3 drops to serve as an adhesive between the titanium substrate and PVC film, then PVC film was completely adhered to the titanium substrate so as not to bubble. After that, remained ethyl alcohol was vaporized by using dryer, finally, nitrogen gas was blown out by air gun to remove impurities.

2.2. Electron beam irradiation on polymer & Raman

In this paper, 50keV electron beam device produced in our lab was used. Each experimental condition is shown in the table 1. The PVC sample was fixedly placed in the electron beam irradiator, and then the inside of the irradiator was evacuated. At this time, the degree of vacuum was maintained at 10^{-6}torr by using a rotary pump and a turbo pump. Then, electron beam was irradiated to the PVC sample by controlling the current and the electron beam irradiation time in each experimental condition. After irradiation, synthesized graphene was characterized by a Raman spectrometer (514.5nm laser, ARAMIS, Horiba Jobin Yvon).

	1	2
Fluence($x10^{16}$#/cm^2)	1.788	10.7
Absorbed Dose (MGy)	5.791	34.748

Table 1. Experimental condition of each sample

3. Results and discussion

The raman spectra of the PVC without electron beam is shown at Fig.2.a, and those of spin-coated PVC irradiated with electron beam under each condition are shown at Fig.3. Raman spectra of spin-coated PVC shows a big, broad band at 1500-3500 cm^{-1}, and small peak at 1500-1600 cm^{-1} as a G peak region. It means the graphene-like carbon are synthesized in irradiated polymer. Also, the intensity of G peak increases as the absorbed dose increases. However, as the whole peak was broad, D peak and 2D peak couldn't be confirmed. The reason why these peaks couldn't be seen at Fig.2.b-c. was that the PVC particles didn't mix well in the solution such as Fig.3. and were united so that the chain reaction didn't occur actively during electron beam irradiation

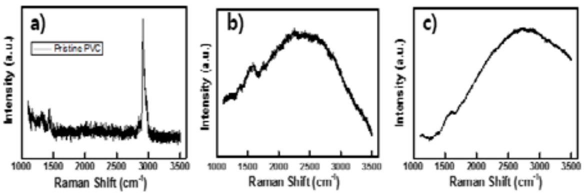

Fig. 2. Raman spectra of spin-coated PVC a) without electron beam irradiation and electron beam at b) first condition & c) second condtion

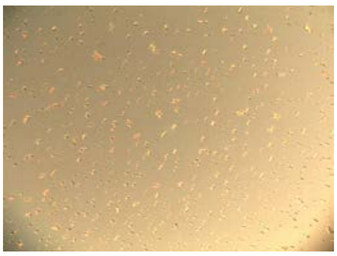

Figure 3. Optical image of spin-coated PVC

On the other hand, raman spectra of PVC film irradiated with electron beam at each condition (Fig.4.) shows more clear picks such as G,2D peak than that of spin-coated PVC. Especially, D peaks are also found in Raman values of defective graphitic materials, around 1300 cm^{-1}. It is confirmed that the generated material through electron beam irradiation become a graphitic material having defects.

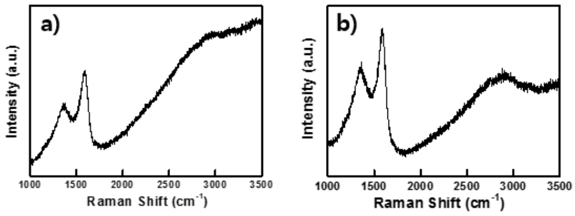

Fig. 4. Raman spectra of PVC film irradiated with electron beam at condition of a) sample 1 & b) sample 2

However, a few experiments at each condition were conducted in this paper. Thus, a lot of data of PVC with electron beam irradiation at various condition is required to synthesize the high quality graphene.

4. Conclusions

Graphene has been evaluated as a next generation material due to its superior electrical properties compared to conventional materials. However, conventional methods to synthesize graphene have many disadvantages in commercialization so a new method is required. We have presented a novel method to synthesize the graphene through electron beam irradiation on PVC film. Raman spectra of PVC film irradiated with electron beam shows that generated material in PVC film by electron beam has the characteristics of graphitic material having defects. Besides, the degree of graphite increases more as the electron beam dose increases. However, much data is required to optimize the experimental condition. To summarize, multi-layer graphene would be synthesized with electron beam as controlling the absorbed dose and more data should be required to optimize the condition of electron beam.

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