

Hyper Branched Graphene for Solar Cell Applications

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Abstract- Graphene, a synergistic and excellent material for the researchers working in material science, has an exclusive two-dimensional nanostructure as well as possess outstanding mechanical, optical and electronic properties. Graphene has established a good material in organic solar cells. In this present work, we synthesized hyper branched graphene from hypercross-linked polymers through Friedel-Crafts alkylation route. The hypercross-linked polymers and graphene materials were characterized by the transmission electron microscopy; diffuse reflectance UV visible spectroscopy and X-ray diffraction techniques.

Keywords- Graphene, Friedel-Crafts alkylation, hyper-branched graphene, solar cells, dehydrogenation

1. Introduction

Now-a-days, the world is facing a major crisis with regards to the pollution of the earth and shortage of sustainable, safe and environmental friendly energy resources. Several concerns arise due to the utilization of non-renewable energy resources from carbon based fuels, shortage of available energy sources, and other factors related to health and environmental issues such as air pollution, carbon dioxide emission and green house effects. Therefore, efforts in lowering energy consumption and protecting the environment have gradually motivated all the researchers in the world to explore the alternative energy sources [1].

Among the renewable energy resources, solar cells or photovoltaic are considered to be very promising candidate for the researchers around the globe. It has the following advantages, (i) it is present in abundance, (ii) they have no moving parts and hence require little maintenance and work quite satisfactorily without any focusing device, (iii) it does not cause any environmental pollution like the fossil fuels and nuclear power and (iv) solar cells last a longer time and have low running costs.

Graphene, synthesized from the raw graphite, is a great boon to mankind for potential applications in versatile technological fields such as sensors, supercapacitors, transparent conductive films, solar cells [2, 3], and gas storage media. Graphene possess extremely good electrical conductivity [4, 5], high optical transmittance [6], outstanding flexibility and stability [7, 8], and high surface area. This makes it a perfect candidate material for creating organic solar devices.

There have been ample reports available of synthesizing graphene semiconductors, compared to all the above multistep methods our recent single step method appears simple, and best suited to commercial production. Conversion of our semiconducting materials which are actually 3D semiconducting graphene sheets, into 3D conducting graphene sheets involves mere heating without a catalyst. Recently we have published some papers of hyper cross-linked conjugated quinonoid chromophores for sorption of CO₂, volatile organic carbons and NO_x [9, 10]. They were synthesized by hyper cross-linking of mono, bi and tri nuclear aromatic monomers with dimethoxy methane, 1, 3, 5-trioxane and paraformaldehyde in the presence of FeCl₃. They are all wide as well as narrow bandgap 3D semiconducting graphene balls absorbing light from 200 to below 1200 nm. Their bandgap characteristic is due to nano structures of graphene having fewer quinonoid content as well as sheets carrying quinonoid islands separated by -CH₂- bridges as shown below. So, in graphene there must be either large number of -CH₂- bridges or large number of ring carbons without bridges in order to have semiconducting characteristics. In this context, our method of synthesizing semiconducting graphene appears to be better than any other methods reported so far. The as-synthesized polymer is semiconducting, and when it was thermally treated (annealed) at 700 or 900 °C, it becomes conducting.

2. Experimental

2.1. Materials

Pyrene is obtained from Sigma-Aldrich, USA. Dimethoxy methane, paraformaldehyde and trioxane were purchased from Daejung Chemicals, South Korea.

2.2. Formation of graphene

Graphene was prepared by two step method. First, pyrene was subjected into Friedel-Crafts reaction in the presence of ferric chloride catalyst. A brief experimental procedure is given below. 1.0 g of pyrene was taken in a two neck round bottom flask with guard tube and condenser. 20 mL of 1, 2-dichloroethane and dimethoxy methane was added into that as solvent and cross-linker respectively. Then FeCl₃ was added in the reaction mixture to induce the reaction. The temperature was set at 80 °C for 24 h. The resultant product was filtered and dried at over for 12 h. The final product

named as hypercross-linked polymers (HCPs) of pyrene. Secondly, the synthesized hypercross-linked polymer was subjected into thermal dehydrogenation under helium atmosphere at 600 °C. The material derived from above process is graphene. The schematic representation of reaction protocol is represented in Fig. 1.

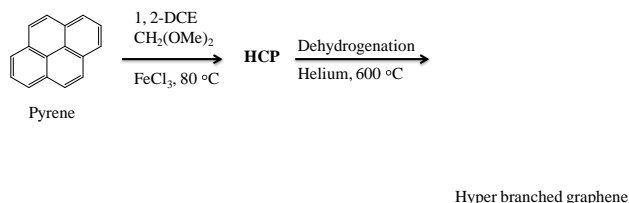


Fig. 1. Schematic representation of formation of grapheme

3. Results and Discussion

3.1. Transmission Electron Microscopy

The TEM images of the as-synthesized and annealed polymers, shown in Fig. 2, established micropores, and surrounding the micropores are the graphene sheets. As the micropore size is invariably same throughout, their origin is not due to gap formed when graphene sheets are filed, but due to the pore present in the graphene sheet.

3.2. Raman Spectroscopy

The Raman spectrum of the as-synthesized pyrene polymer is shown in Fig. 3(a). Due to luminescence of nano graphene structures the characteristic vibrations of $-CH_2-$ bridges and aromatic rings and their $-CH-$ bending vibrations are obscured. The sheets are built with nano graphene layers with varying sizes and bandgaps, and their bandgap excitation by the intense laser radiation results in fluorescence covering the entire spectrum. As a result, the D and G bands between 1300 and 1600 cm^{-1} is largely blocked, and so, they appear as small protuberances. The Raman spectrum of the thermally treated pyrene is shown in Fig. 3(b). It shows the characteristic D and G vibrations of graphene between 1000 and 1800 cm^{-1} . The D band is much intense due to bridges and unsubstituted ring carbons. The undehydrogenated $-CH_2-$ groups are also the defects in the graphene nano sheets. It also accounts for the weak 2D band just above 2300 cm^{-1} . So, thermal treatment enlarges the dimension of the graphene nano structures by dehydrogenating the bridges, and as a result the fluorescence is also completely lost.

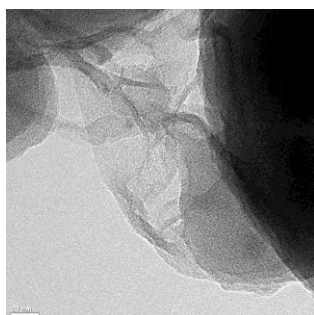


Fig. 2. TEM image of thermally treated pyrene

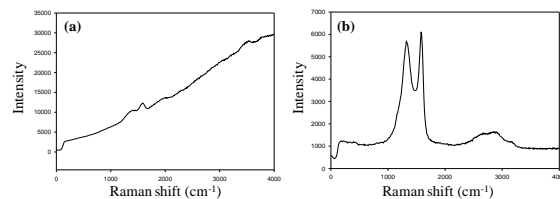


Fig. 3. Raman spectra of (a) pyrene and (b) treated pyrene

3.3. DRS UV Visible Spectroscopy

The DRS UV Vis spectra of as-synthesized polymer and the heat treated polymer are shown in Fig. 4. Both the spectra exhibit a broad semiconductor like light absorption. The broad maximum of the annealed polymer is shifted to longer wavelength than that of the as-synthesized polymer. It evidences dehydrogenation of the cross-links and extending of conjugation in graphene sheets. As graphene of large dimension does not absorb light, the annealed polymer spheres must carry graphene and semiconductor graphene sheets together.

3.4. X-Ray Diffraction Studies

The X-ray diffraction spectra of the as-synthesized and the annealed polymers are shown in Fig. 5. Both are not showing the patterns of graphite, so, in the graphene sheets the large or nano graphene structures are not associating to the level of graphite. The broad reflections around 25.2° theta are due to condensed graphene layers.

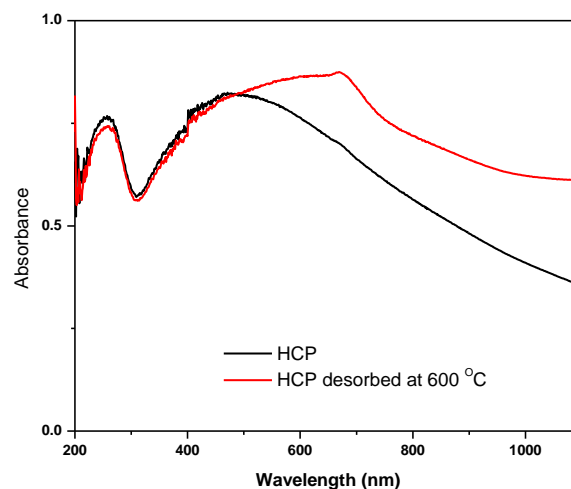


Fig. 4. DRS UV-Visible spectra of pyrene and treated pyrene

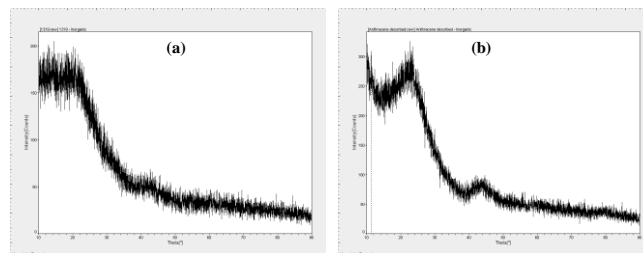


Fig. 5. XRD pattern of (a) pyrene and (b) treated pyrene

4. Conclusions

Finally, we conclude that hypercross-linked polymers successfully synthesized through Friedel-Crafts reaction. After the dehydrogenation of HCPs yield graphene sheets. The formation of graphene structure was confirmed by X-ray diffraction studies, transmission electron microscopy, DRS UV-Visible spectroscopy and Raman spectroscopy analyzes. Due to the high surface area and porous nature, these materials are potential candidate in solar cell devices and supercapacitors. Our future work is to fabricate the solar cell and study the performance evaluation of the prepared material.

Acknowledgements

The authors gratefully acknowledge the financial support from Hanseo University and grants from Korea CCS R&D Centre, funded by the Ministry of Education, Science and Technology of the Korean Government. Correspondence should be addressed to Dr. Hyun Tae Jang (htjang@hanseo.ac.kr).

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Received: Month xx, 20xx