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Chemistry and Mechanism of One-Step Formation of Graphene from Agrowaste

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Abstract: The one-step synthesis of high-quality graphene derivatives via CVD process has gained considerable importance nowadays for high-performance electronics and sensors. However, the use of harsh chemicals, high temperature, sensitivity, and the problem of separation of graphene from the substrate, motivated the one-step synthesis of graphene from a non-graphitic precursor, bypassing the use of graphite. In this paper, we have reported for the first time, the synthesis of graphene nanosheets from sugarcane bagasse at the normal atmospheric condition in a single step, avoiding the formation of GO. Here, the pyrolysis of sugarcane bagasse was carried out in the temperature range of 250-450^o C in the presence of sodium hydroxide. The results suggested that even the low temperature (250–450^o C) facilitated the development of graphitic planes via condensation and aromatization of the glucose monomers present in the precursor. The XRD pattern showed 2θ at around 25^o in each case, which confirmed the formation of graphene instead of GO. The FESEM, TEM, and EDX analysis proved the formation of few-layer nanosheets of graphene from carbon-rich waste precursors in a single step.

Keywords: Sugarcane bagasse; NaOH; pyrolysis; few layer graphene.

1. Introduction

During the last decade, graphene oxide (GO) and reduced graphene oxide (r-GO) were reported from graphite powders involving a two-step process [1-3]. Simultaneously, a new strategy to prepare GO and r-GO was also adopted using non-graphitic biomass and agro-waste materials, avoiding the graphite precursor [4-10]. Very recently, the direct synthesis of graphene derivatives has gained considerable importance, bypassing the formation of GO [11]. Despite several shortcomings such as specialized equipment, harsh chemicals, a large amount of energy requirements, etc. numerous reports were available on CVD as the most researched method of mass production of graphene especially, for high-tech electronics and sensors applications [12-18]. However, its sensitivity towards the change of parameters and the separation of graphene from the substrate without affecting the properties of the material or damaging the structure of the graphene is highly challenging. In addition, the commercial and economical production of graphene may prevent this method from becoming the preferred method of synthesis of graphene in the future.

In view of these observations and in continuation of our research work on a two-step synthesis of graphene, a one-step process has been reported for the first time in the synthesis of graphene from a non-graphitic agro-waste, which has been untouched till now [19]. Here, the pyrolysis of sugarcane bagasse was carried out at three different temperatures viz. 250^o C, 350° C, and 450° C in the presence of sodium hydroxide. The effect of temperature and time was studied for the formation of graphene, and the mechanism has been explained. The results suggested that the in-situ use of sodium hydroxide hindered the attack of oxygen during pyrolysis. The mechanism confirmed the participation of glucose monomers in the aromatization and condensation process, leading to the formation of nanosheets of graphene in a single step.

2. Materials and Methods

Sugarcane bagasse was collected from a local market. P-XRD pattern was recorded by Bruker D8 advance diffractometer in the 2θ range of 5 – 60°. FE-SEM, along with EDX images, were observed by using Sigma-300, Carl Zeiss, HRTEM images were collected using a Jeol JEM-2100 microscope at an acceleration voltage of 200 kV.

Bagasse sample was cut into small pieces, washed thoroughly with deionized water several times for removing dust, dried in sunlight for 2 to 3 days, and finally dried in the oven for 24 hours. The finely grinded powder after drying was mixed with sodium hydroxide in a 1:1 ratio and subjected to pyrolysis at different temperatures viz. 250° C, 350° C, and 450° C. The obtained shiny black colored powder products were washed with 2M nitric acid and deionized water thoroughly for removing the unwanted products, then filtered and dried overnight.

3. Results and Discussion

In recent years, graphene and its derivatives have been gained considerable attention towards glucose-sensing due to high surface area, which can serve as a superior platform for fabricating new composites in glucose sensing[20-30]. The main aim was to prepare the graphene from non-graphitic agro-waste material in a single step instead of functionalized graphene (GO) without using any inert atmosphere. Moreover, the purpose of using NaOH was just to prevent the formation of GO. The strong reducing nature of NaOH, which might have resulted in graphene during a long heating time, due to the absence of an inert atmosphere. Hence, when the 1:1 ratio of sugarcane bagasse and sodium hydroxide was pyrolyzed at various temperatures, black colored crystalline products were obtained in each case. In the XRD pattern (Figure 1), it was observed that when the sugarcane bagasse was pyrolyzed at 250° C for 2 hrs, a peak was observed at 2θ of 27.4°. In the case of heating at 350° C for 2 hrs, a more intense peak was obtained (Figure 1b) at 2θ of 25.6°. Figure 1c showed a significant decrease in the peak intensity at around 2θ of 24.9°. The results showed that on heating at 250° C for 2 hrs, both graphene nanosheets and nanoparticles were formed, indicating that the glucose monomers were not getting sufficient time for aromatization and condensation. The heat-treatment at 450° C for 1hr, although resulted in the formation of nanosheets, was found to be broken due to high temperature. In contrast to 250° C and 450° C, the pyrolysis at 350° C for 2 hrs resulted in the formation of graphene nanosheets only, which confirmed that this temperature and the retention time was essentially required for the condensation and aromatization of glucose monomers and finally to the development of graphitic planes. Moreover, the formation of 002 planes in all the temperatures confirmed that sodium hydroxide prevented the formation of GO at normal atmospheric conditions during pyrolysis.

The SEM images showed the formation of nanosheets (Figures 2a, 3a, b, and 4a) at all three temperatures. The elemental composition of the energy-dispersive X-ray spectroscopy

(EDX) analysis exhibited the signals of carbon and oxygen (Figure 2b, 3c, and 4b) and confirmed that sodium hydroxide successfully prevented the formation of GO.

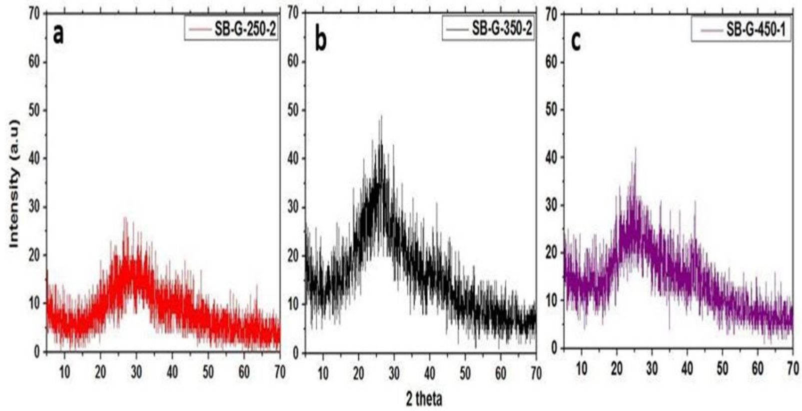

Figure 1. XRD patterns of graphene at various temperatures viz. 250º C(a), 350º C (b) and 450º C (**c**).

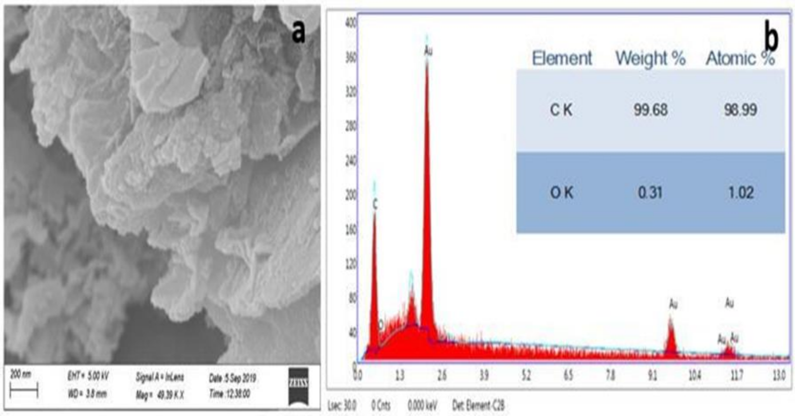

Figure 2. SEM image (a) and EDX of graphene (b) at 250º C temperature.

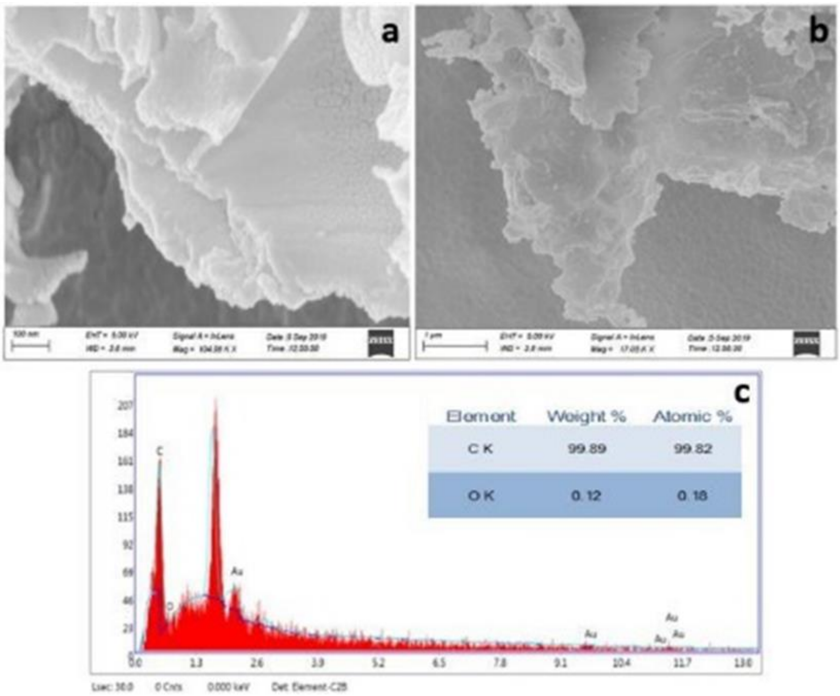

Figure 3. SEM images (a), (b) and EDX of graphene (c) at 350º C temperature.

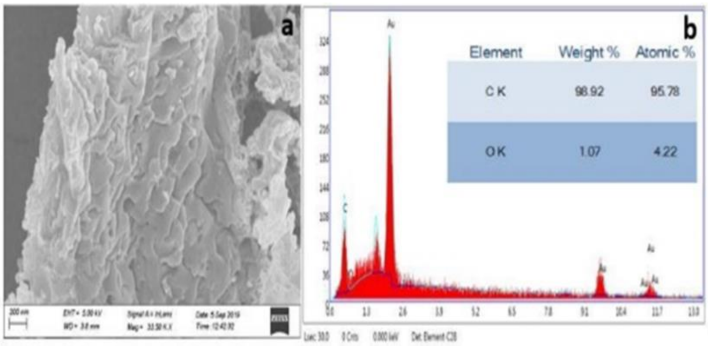

Figure 4. SEM images (a) and EDX of graphene (b) at 450^{o} C temperature.

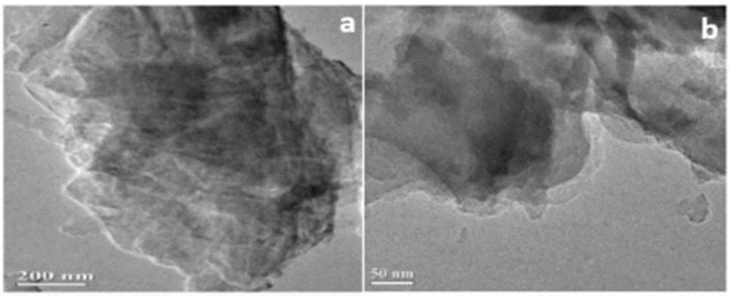

Figure 5. TEM images (a) and (b) at 350^{o} C temperature.

The mechanism has been presented in Figure 6, showing the chemistry behind the formation of graphene nanosheets. The carbon-rich bagasse primarily contains cellulose, which contains glycosidic bond and hydroxyl groups. When bagasse was pyrolyzed at the range of 250-450^{o} C, which led to the degradation of glucose monomers and these monomers, contain aldehydic and hydroxyl groups. It is well known that the formation of a cyclic hemiacetal structure can be possible when the hydroxyl group at the fifth carbon of glucose gets attached to the aldehydic group of the first carbon [31]. Since the resulting cyclic structure from glucose monomers resembles pyran, having six-membered heterocyclic rings, it might be possible that during heating at the range of 250-450^{o} C, a large number of glucose monomers joined together by glycosidic bonds. Further, the condensation and aromatization have occurred by dehydrogenation of existing cyclic rings to convert into the polyaromatic ring-like structures of graphitic planes.The powder XRD pattern confirmed the mechanism showing that sodium hydroxide was able to prevent the attack of oxygen during the pyrolysis of sugarcane bagasse, thereby preventing the formation of GO. The EDX analysis further confirmed the nonexistence of GO and involvement of OH groups of glucose monomers in the aromatization and condensation to form hexagonal polyaromatic rings, leading to the development of graphitic planes.

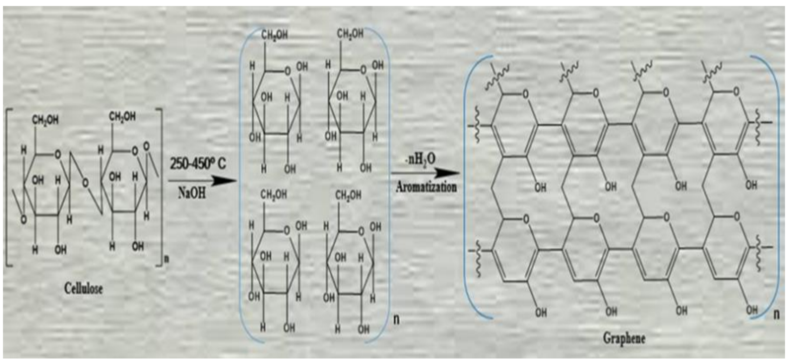

Figure 6. Mechanism of formation of graphene nanosheets at 250-350^{o} C.

4. Conclusions

A one-step approach has been reported for the formation of graphene nanosheets by pyrolysis of sugarcane bagasse at various temperatures viz. 250^o C, 350^o C, and 450^o C in the presence of sodium hydroxide at normal atmospheric conditions, bypassing the formation of GO. The XRD pattern showed an intense peak at around 2θ of 25.6^o at 350^o C temperature, which confirmed the formation of 002 planes of graphene. The SEM and TEM images further confirmed the formation of graphene nanosheets. The EDX analysis indicated that the sodium hydroxide was able to prevent the attack of oxygen during pyrolysis, thereby preventing the formation of GO. The results confirmed the chemistry of formation of graphene nanosheets in a single step, and the mechanism suggested that any hydrocarbon-rich agro-waste (cellulose-45-55%, hemicellulose-20-25%, and lignin-18-24%) can replace the graphite powder to prepare graphene nanosheets in an environmentally, ecofriendly and energetically favorable way without high temperature and hazardous chemicals.

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Conflicts of Interest

The authors declare no conflict of interest.

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