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IMPROVED CHEMICAL SYNTHESIS OF GRAPHENE USING A SAFER SOLVOTHERMAL ROUTE

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Graphene has been synthesized using thermal decomposition of ethyl alcohol in a medium pressure autoclave. The synthesis was carried out in the presence of strong alkaline solution at a temperature of $\sim 230^\circ$C and pressure of 60 bar. The as-synthesized graphene has been characterized using atomic force microscopy (AFM) and high-resolution transmission electron microscopy (HRTEM). AFM analysis on various graphene sheets shows the presence of monolayer ($n = 1$) to trilayer ($n = 3$) graphene sheets with thickness of ~ 1.168 nm. HRTEM studies confirm the high quality of graphene obtained after purification of as-synthesized product. Use of chemically nonexplosive material for synthesis and reduced reaction time along with the absence of post-pyrolysis process make it a commercially viable process for bulk production of graphene.

Keywords: Graphene; chemical synthesis; HRTEM; AFM; bulk production.

1. Introduction

Graphene is a single atomic layer thick thin sheet of ideally sp^2 bonded carbon atoms that are densely packed in a honeycomb crystal lattice. The question about the existence of single monolayer crystals came to halt with the invent of graphene single layer.[1] The electronic structure was found to evolve with the number of layers approaching the 3D limit of graphite at 10 layers.[2] Extremely large surface to volume ratio and high conductivity provided by graphene powder can lead to improvements in the efficiency of batteries, taking over from the carbon nanofibers used in modern batteries. Miniaturized nanoelectronic components, solid-state gas sensors, spin valve and superconducting field effect transistors, hysteretic magnetoresistance, and substantial bipolar supercurrents are major potential applications.[3] Experiments on epitaxial graphene monolayers on silicon carbide[4] have provided the first demonstration of the spectrum of massless Dirac particles in graphene.

Graphene was first experimentally realized by mechanical exfoliation of graphite using scotch tape.[1] But micromechanical exfoliation yields small samples of graphenes useful only for fundamental study. Another method of epitaxial growth is to heat silicon carbide to high temperatures ($> 1100^\circ$C) to reduce it to graphene[5] The size of graphene crystal is dependent upon the size of the SiC substrate used. High-quality sheets of few layer graphene exceeding 1 cm^2 in area have been synthesized via chemical vapor deposition (CVD) on thin nickel layers.[6] Graphene-type carbon materials have been produced by substrate-free chemical vapor deposition (CVD),[7] radio-frequency plasma-enhanced CVD,[8] and aerosol pyrolysis. Ruoff *et al.*[9] have recently reviewed the chemical methods for the production of graphene.

Recently gram-scale production of graphene has been reported by reduction of ethanol using sodium metal, followed by pyrolysis of the ethoxide product, and washing with water to remove sodium salts.[10] Use and handling of sodium metal in their report make the process complicated and require precautionary measures and expert handling. Here, we report on a large-scale chemical synthesis of graphene sheets by a relatively safer and easier method using an autoclave.

2. Experimental Details

Graphene synthesis was carried out in a medium pressure autoclave with stainless steel chamber. In a typical reaction, 80 ml of ethyl alcohol was mixed with the solution of 4.3 gm of $NaBH_4$ and 15 ml of 10 M NaOH solution. Reaction was carried out with and without addition of sodium dodecyl sulphate (SDS). Amount of SDS added was 2 w% of ethyl alcohol, i.e., 1.26 gm was added to the solution. Reaction was carried out for 20 h at 230°C. The pressure in the reaction vessel was noted around 60 bar. The reaction product obtained was filtered with water and alcohol repeatedly to reach a pH value 7. This product was dried for 10 h in hot oven at 60°C. The measured weight of the product was ~ 125 mg. As-produced graphene contained impurities like amorphous carbon, graphite, fullerene, and some fraction of iron. Iron impurity in the sample was introduced from the stainless steel reaction chamber (vessel) used for the synthesis. The as-synthesized product was purified through refluxing with 3 mol HNO_3. During the reaction, $KMnO_4$ solution was added slowly through dropping funnel. This reaction was carried over oil bath at constant temperature of 150°C for 5 h. The product obtained was continuously washed with water and dried.

The samples were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM). Powder XRD spectra were recorded using D8 Advanced tools Bruker in para-focusing geometry of the Bragg−Brentano optics using lock coupled scan mode. FTIR measurements were performed in the range 400−4000 cm^{-1} using Perkin−Elmer Spectrum one FTIR spectrometer. Morphology of graphene was studied using digital SEM (LEO 1430 VP) and high-resolution TEM (HRTEM) (JEOL 2010). The grids used for TEM studies were directly used for AFM measurements to find the number of layers. AFM images were recorded in contact mode using Nanoscope IVA from Vecco Instruments.

3. Results and Discussion

Figure 1 shows XRD pattern for as-prepared and purified graphene. Peaks corresponding to the lattice planes (002), (100), and (004) of graphitic materials are clearly observed. This indicates the formation of network of sp^2 like carbon structure. In the as-prepared samples, the (002), (100), and (004) oriented peaks related to graphitic carbon structure are shown.[11] Additional peaks marked with asterisk are due to the impurities present in the sample or filter paper. Extremely small amount of iron was found in the sample from energy-dispersive X-ray analysis. Iron is introduced basically from the reaction chamber which is made of stainless steel. After the purification process, the sample yield was small and the graphene tend to stick on the filter paper, which resulted in lower yield of purified product. As a first step, we have attempted to synthesize graphene without adding any surfactant. This resulted in a very low yield of graphene and the graphene sheets were bundled. With the addition of SDS during reaction, the product yield is drastically improved. The resulting morphology found in SEM is shown in Fig. 2. After the addition of SDS during

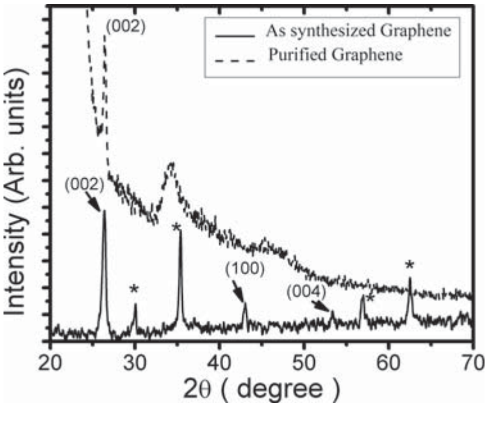

Fig. 1. XRD spectra of as-synthesized and purified graphene.

Fig. 2. SEM image of as-synthesized graphene sheets.

the reaction along with other reactants, well-separated graphene sheets were clearly observed. Since amorphous carbon is inherently present in as-grown samples, we went for purification of the as-prepared graphene by reflux reaction. Figure 3 shows the TEM image of the graphene obtained after purification. TEM images clearly show very high quality of graphene sheets. Major portion of the graphene sheets is flat except at the ends for some sheets, in which they are folded at edges observed as dark line like structures. FTIR study (not shown) on the as-prepared sample showed C−C stretching mode at 1644 cm^{-1} confirming the graphitic nature of the product.

To distinguish the product formed from graphite, AFM imaging was performed. The sectional analysis gives the height of the graphene sheet under view. Figure 4 shows the height difference between substrate and the graphene measured using an AFM. The measured height difference is equal to 1.168 nm. The interplanar spacing between layers of a crystallite graphite is 0.336 nm.[12] Thus, the graphene under view is a three-layered structure ($n = 3$). AFM images of various graphene sheets (not shown here) show the presence of monolayer ($n = 1$) to trilayer ($n = 3$) graphene sheets. AFM image and their analysis at various places in the sample confirm the presence of few-layer graphene structures.

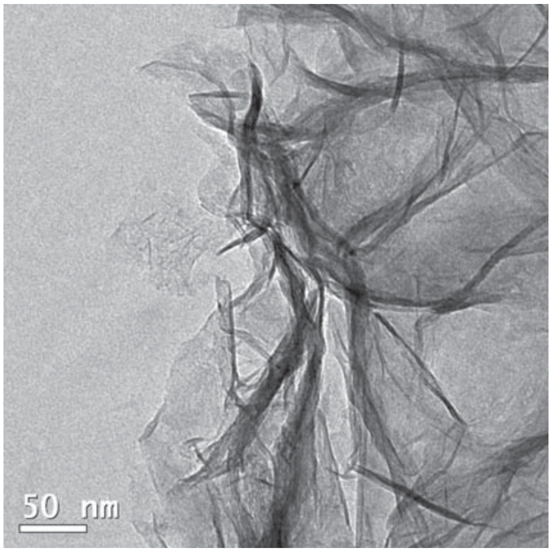

Fig. 3. TEM image of as-synthesized graphene showing large and separated sheets.

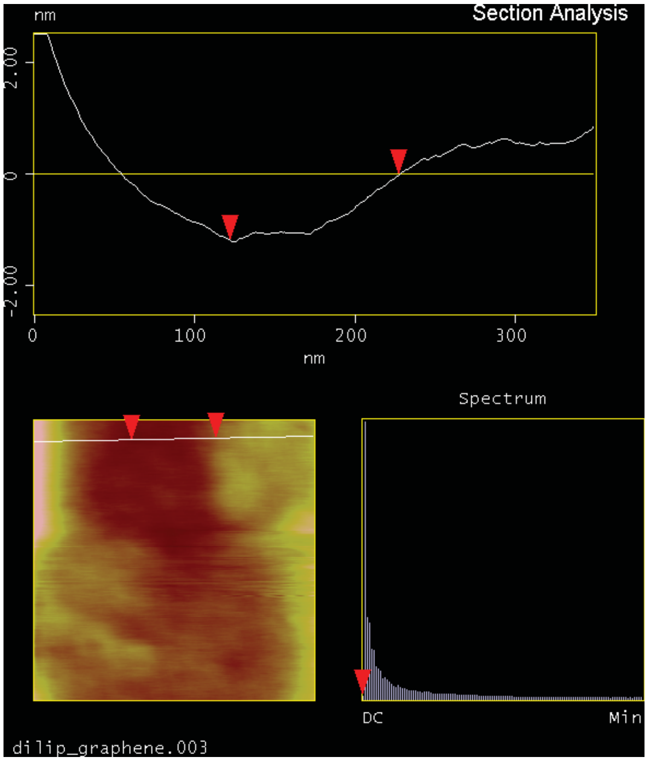

Fig. 4. AFM image and sectional analysis of as-synthesized graphene showing $n = 3$.

It has been reported that alcohol reacts directly with $NaBH_4$ to produce H_2, alkayl borates, and alkoxy borohydrides.[13] Therefore this reaction method was chosen for the possible chemical synthesis of graphene. It was found that NaOH aqueous solution with high concentration is essential for the formation of graphene. Addition of SDS during reaction further increased the product yield and well-dispersed graphene layers were formed. Reaction performed at lower temperature of 120°C shows very little product yield. There were no graphitic structures formed when the reaction were conducted in aqueous solution with low concentration of NaOH. We believe that high concentration of NaOH acts as a catalyst during the formation of graphene, which catalyzes reduction of ethyl alcohol with $NaBH_4$ under hydrothermal conditions.

The growth of well-separated graphene sheets in our experiment may be similar to the pressure-induced carbon condensation growth mechanism.[14] A high-density fluid phase, from which growth occurs, changes its compositions rapidly as carbon condenses, traversing a range of compositions during which different phenomena take place. This is likely to be responsible for the experimentally observed formation of graphene. This synthesis method has several advantages compared to other physical methods. First, the ethyl alcohol acts as a carbon source as well as the solvent, which decreases the cost of production and allows the reaction to be performed under mild conditions. As like other chemical methods of synthesis it is less expensive, simple, and has the potential for the industry-scalable production capacity. Our method avoids harsh reaction conditions involved in the earlier reports for synthesis of graphene carbon nanostructure. We have followed a method that is similar to the synthesis of multiwalled carbon nanotubes (MWCNT) using modified Wolf−Kishner reduction process.[15] We have used sodium borohydride as a reducing agent in place of sodium metal, and the reaction conditions are similar to the report of bulk synthesis methodology. We do not require any post-pyrolysis of produced product in the high-pressure reactor. In contrast to the reported method, our method essentially uses surfactant during the reaction to achieve improved yield and dispersion of graphene while growing.

4. Conclusions

We have demonstrated an improved method for bulk production of high-quality few-layer graphene using a medium pressure autoclave. Our method uses a mild catalyst sodium borohydride in place of sodium metal making this process better. Addition of surfactant during growth process shows improved morphology of graphene. Product yield increases upon addition of SDS during synthesis. This method is a safer and commercially viable process of bulk production of monolayer to few-layer graphene.

Acknowledgments

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