Recycling of Graphite Waste into High Quality Graphene Products

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ABSTRACT

Graphite is a stack of carbon layers where carbon atoms form hexagons in a honeycomb structure. Graphene on the other hand is a single atom thick layer which offers unique physical, chemical and biological properties compared to graphite. Recycling graphite waste and converting it into graphene may offer many economic, environmental and health benefits, and may also be used in many applications. Graphite has been used widely in iron-steel, chemical, and nuclear industries for electrical, mechanical and other applications (e.g., metallurgy, pencil, coatings, lubricants and paint). Especially, most of the anode materials of batteries for car, truck and other vehicles and electronic devices are made of graphite. After two to four years of life-time, these anode materials are either landfilled or sent to an incineration furnace. The major goal of this study is to produce recycled graphene from graphite waste. The objectives of this study are to recycle graphite from batteries and other sources, exfoliate it using surfactants and electrochemical methods, and investigate the effects of exfoliated graphene. In this study, graphite-based batteries were collected from local waste collection companies and the used graphite was manually removed from the batteries. After washing and cleaning processes, The graphite rods obtained are exfoliated to single layers using an electrochemical exfoliation process.

Keywords: waste graphite, recycling, graphene, electrochemical exfoliation.

1 INTRODUCTION

Graphene has been of significant interest in recent years due to its variety of applications [1–6]. Graphene is defined as a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice [7]. Along with its unique structure, graphene displays a range of unusual properties [8]: most significantly the thermal conductivity and mechanical stiffness values are much better than the original values for graphite; the strength may be comparable to that of carbon nanotubes; and individual graphene is found to have excellent electronic transport properties. These properties hold a great promise for applications in fields like nanoelectronics, sensors, transistors [9], batteries, as well as conducting polymer composites [8]. Many studies have therefore been directed toward developing techniques to create single layer graphene, which can in general be classified into three different routes: namely (i) mechanical peeling, (ii) epitaxial graphene growth and (iii) solution-based reduction of graphene oxide. Mechanical peeling using the so called ‘‘Scotch tape” [1] can repeatedly produce single graphene sheets of up to 10 µm in planar size. The Graphene produced by this method can only be used to study the fundamental properties of graphene. The epitaxial graphene sheets were prepared by treatment of silicon carbide wafers at high temperatures. The graphene produced in this technique consists of several layers and their overall quality depends highly on the type of substrate materials [10,11]. The above methods were not consistent in producing high quality graphene, and can only produce very small quantities of graphene, being unable to meet the demands for mass production. The solution-based route has emerged as a promising approach to produce graphene in large quantities [12–14]. In this technique, graphite oxide (GO) is used as a medium to obtain stable graphene dispersion in a solvent: graphite oxide (GO) is a product from oxidation of graphite [15], which maintains the original layered structure of graphite. The electrochemical method [16] can also give a very high yield of mono layer graphene.

The graphite used in batteries and other sources is just dumped and not recycled into any other useful products and also the waste is an environmental hazard. So the process to convert the waste graphite into graphene products can be very helpful in the production of high quality graphene products and can open the world towards more research into the properties of graphene in different forms. Also, the process of recycling will be very economical and following the electrochemical method for exfoliation of graphite will yield good quality graphene products. Recycling of graphite to produce graphene can be very useful and economical.

The produced graphene can be added at 0.5, 1, 2 and 4wt% (weight percent) into cement, sand and gravel

mixtures to make nanocomposite concretes. By applying the compression test we can determine the properties of nanocomposite concretes. The use of graphene in increasing the strength of concrete can be very useful in the field of contruction. Graphene based nanocomposites can revolutionize the contruction world.

2 EXPERIMENTAL MEASUREMENTS

2.1 Recycling Process

Dead Batteries were collected from various sources and were used to extract the graphite electrode from them. The batteries were carefully dismantled, and the dry graphite rods were carefully removed from batteries. The graphite electrodes/rods were then moved to a sealed container to prevent it from oxidation.

2.2 Materials Used

Recycled graphite electrodes, Sodium Hydroxide (NaOH), Paraffin wax, Nickel foam electrodes, deionized water, Ethanol (C_2H_5OH), Petroleum ether, N-methyl-2-pyrrolidone (NMP), Ammonium Nitrate (NH_4NO_3) and Urea ($CO\text{-}(NH_2)_2$).

2.3 Equipment

DC controlled voltage supply (0-12V), Vaccum filtration setup, Porous filter membranes, Ultrasonic bath and Centrifuge.

2.3 Graphite to Graphene products (Electro chemical Exfoliation process)

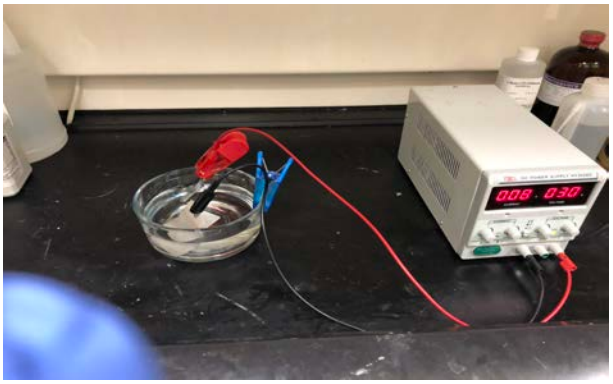


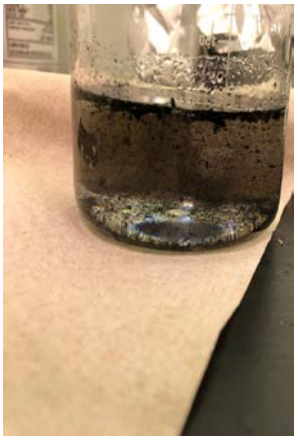
Figure 1: Electrochemical exfoliation process.

The dry graphite rods were cleaned and made free from any impurities and then subjected to the electro chemical exfoliation process to produce graphene products.

As shown in Figure 1, the graphite rod was used as a working electrode and Nickel foam was used as a counter electrode and subjected to electrolysis at 3-9V in a 10M NaOH electrolyte. The Graphite rod was coated with paraffin exposing only the bottom part to have a controlled exfoliation process. A DC power supply of 3-9V is applied to the electrodes at room temperature. The electrolysis is performed until the graphite rod completely depletes. Once the electrolysis is done, the product, Black precipitate, is collected using vaccum filtration and then the product is washed with deionized water, Ethanol and petroleum ether in order to remove the impurities and paraffin.

Figure 2: Graphene precipitate collected after vaccum filtration.

The washed product precipitate as shown in Figure 2 is then dispersed in 100mL NMP solution (Figure 3(a)). The solution is treated with ultrasound for 30 min and a homogeneous graphene dispersion is obtained as seen in Figure 3(b). The graphene suspension is then centrifuged to remove the thicker graphene.



(a)

(b)

Figure 3: Graphene suspension in NMP solution.

The grephene dispersion was vaccum filtered using a micro filter. The filter adhered with graphene was then transferred to a beaker filled with deionized water and due to

the hydrophobic property of graphene it peels off from the filter and floats on top of the water surface while the filter sinks to the bottom. The thin graphene film formed on the surface is then carefully collected on a glass membrane. Finally the colleted film is subjected to heat trarment and dried in vaccum. To obtain less sheet resistant films, the dispered graphene is mixed with urea or ammonium nitrate and then vaccum filtered to finally obtain graphene films treated with urea or ammonium nitrate. These films are subjected to heat treatment and annealed under the same conditions.

3 RESULTS AND DISCUSSION

3.1 Recycling of the Waste Graphite

The graphite waste which is usually sent to a incernation furnance as a waste was succesfully recycled and used to produce a useful graphene product. The Graphene product obtained by this process is economical when compared to other graphene production techniques.

Figure 4: Graphite waste.

3.2 Exfoliation Process

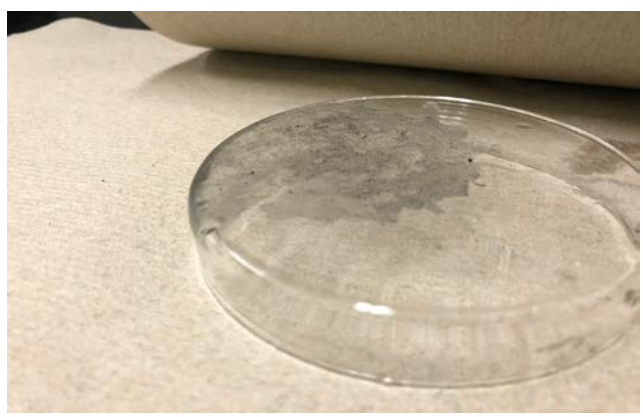
Figure 4 shows the graphite rod after the electrolysis process. The individual graphene layers peel off from the graphite rod during the electro chemical exfoliation process. This layer by layer exfoliation is a result of paraffin coating as it only exposes the bottom layer of the graphite rod. After the exfoliation, the graphite rod is depleted and shortened significantly.

3.2 Graphene Film

Figures 5(a) and 5(b) and 5(c) show the formation of thin graphene film on top of the water surface and on the glass membrane respectively.

(a)

(b)



(c)

Figure 5: Graphene thin film.

The precipitate after the electrolysis contain thick layers of graphene with impurities and after it has been treated with ethanol and ether, the impurities are washed away but the graphene is still multilayered and thick. This thicker graphene is then prepared as a graphene dispersion in NMP solution and subjected to ultra sound and centrifuged at high speeds to obtain more thinner graphene. The graphene is then obtained in the form of a uniformly distributed graphene dispersion. The graphene dispersion itself can be used as a liquid graphene in a large number of products to improve their strength and properties. To obtain a thin film, we subject the graphne dispersion to vaccum filtration and collect the graphene film on top of the water surface. The graphene film due to its hydrophobic property floats on top of water and thus can be easily collected on a glass membrane and then dried by the heat treatment process. This dried film of graphene can be subjected to different charecterization techniques to obtain the exact properties and advantages of the graphene films obtained by this process.

4 CONCLUSIONS

Graphite waste was successfully recycled and converted into high quality graphene sheets via electrochemical exfoliation method. The paraffin coating was helpful in preventing the excessive expansion and stops it from premature peeling of the graphene layers from graphite. Under proper conditions and by maintaining proper distance between the electrodes, good quality of graphene sheets can be obtained. The graphene film is obtained after the vaccum filtration and heat treatment processes. This process is very economical and can be used for producing graphene with a high yield.

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