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Graphene oxide and graphene from low grade coal: Synthesis, characterization and applications

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ABSTRACT

Since 2004 and the awarding of the Nobel Prize for the discovery of graphene there has ensued a worldwide research effort to study and capitalize on the unique properties of graphene. A great deal of that research utilizes graphite as a starting material and strongly oxidizes it to produce graphene oxide. In this review an alternate way to produce graphene oxide that utilizes a less expensive carbon source and that requires less dangerous and environmentally impactful chemicals is reviewed. The carbon source is leonardite, which is a low grade lignite coal that occurs in many lignite deposits. Humic acid (HA) is the base extractable organic matter commonly found in soil. HA, extracted from leonardite, is highly oxidized and contains a number of oxygenated groups around the edges of the graphene like core. This material is very similar to graphene oxide (GO) produced by acid oxidation of graphite. This HA extract has been utilized as a starting material rather than graphite for producing GO and ultimately graphene. This paper reviews the characterization of this material as compared to GO, reduction and functionalization of the extract by several different chemical and thermal means, and reduction of the HA to graphene, and several applications of the reduced HA. This approach potentially provides a low cost source for reduced functionalized graphene nanosheets for large scale production.

1. Introduction

Ever since graphene was first isolated by Novosolov, Geim, and colleagues via mechanical exfoliation it has been of great interest to the scientific community [1]. This interest is due in large part to the remarkable properties of graphene including extremely high thermal conductivity [2], very high tensile modulus [3], and charge carrier mobilities exceeding 200,000 $cm^2 V^{-1} s^{-1}$ [4]. This has led to great interest in large scale production of graphene and there have been a number of methods proposed to do so [5]. Mechanical exfoliation is suitable for production at a laboratory scale but is not practical for large scale production. Other methods to produce graphene have been studied including electrochemical exfoliation [6,7], graphite exfoliation via intercalates [8,9], graphite solvation [10,11], arc discharge [12–14], unzipping carbon nanotubes [15–18], epitaxial growth [19,20], chemical vapor deposition [21–26], as well as other techniques [27–35]. The most commonly employed method for large scale preparation of graphene is the oxidation of graphite leading to exfoliation of individual sheets of graphene oxide followed by a reduction step, often based on Hummers method [36]. This alternative also has drawbacks including multiple steps and the use of reagents such as concentrated acids and hydrazine that are difficult to work with, present health hazards and disposal problems.

In soil science the base extractable organic matter is normally referred to as humic acid (HA). Leonardite can be extracted in a basic aqueous solution (pH of 10) with a very high yield in the range of 75% and then precipitated from solution by acidification to produce humic acid (HA) powder. HA is a readily available, low cost source of graphene oxide like sheets. A 2% dispersion of HA from leonardite has a very dark brown color. After chemical reduction, solutions of HA are black in color and evidence indicates that the sheets are highly conjugated graphene like analogues. In this review, HA derived from leonardite is characterized and compared to GO produced by the Hummer method, the HA is reduced by chemical and thermal means to graphene and compared to parallel reactions with GO. Several applications of the reduced HA will be reviewed. It appears that leonardite may provide an alternate inexpensive source for GO, functionalized GO and graphene.

2. Comparison of HA and GO morphologies

One of the critical characteristics of GO and graphene is the sheet like morphology that is one atom thick but can be microns in the other two directions. It is therefore important to first compare the morphology of HA and GO. This comparison has been done by Duraia et al. [38]. As shown in the SEM images of Fig. 1, HA nanoparticles can be compared with GO nanosheets. The HA particle appears to be more wrinkled or

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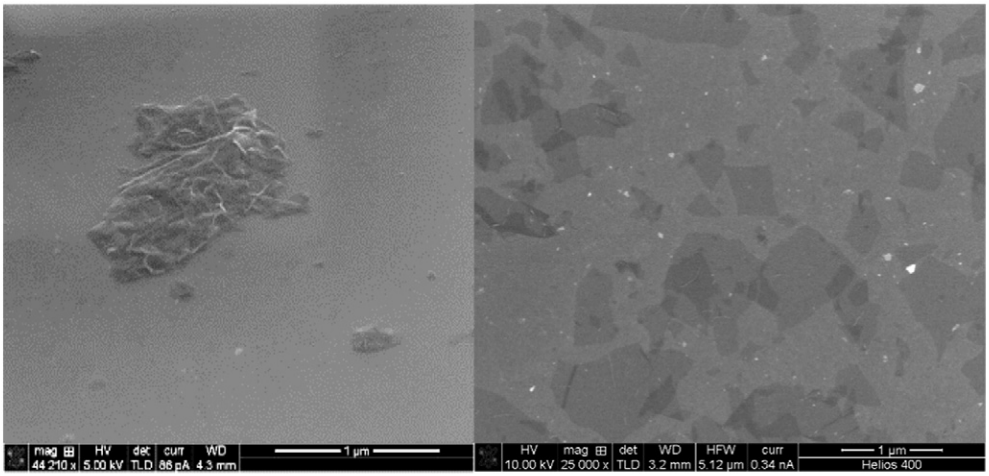

Fig. 1. Comparison of SEM photographs of HA particle derived from leonardite (left) and GO particles derived from graphite using the Hummer method.

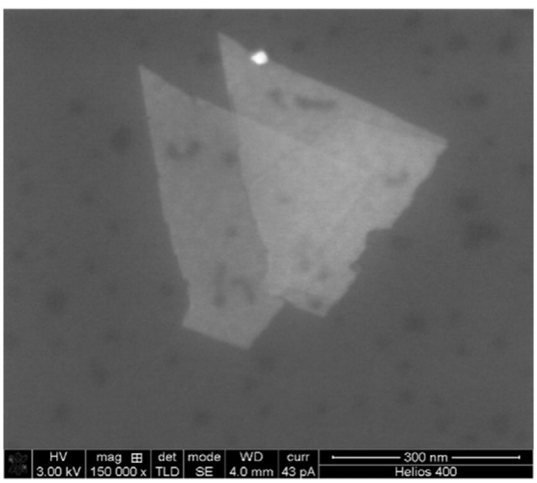

Fig. 2. SEM image of two HA particles that have appeared to cleave.

possibly composed of smaller particles than the GO particles. However, the HA particles appear to be quite sheet like and in the same size range as the GO particles. Fig. 2 contains an image of HA particles that appear to have cleaved and appear to be of atomic thickness. The next characteristic to measure is the thickness of the particles. Dispersions of HA were dried on silicon wafers and the thickness of the particles was measured. Fig. 3 contains the results of these measurements. As can be seen the particle appears to be of atomic layer thickness in the range of 0.4 nm. Morphologically the HA exhibits characteristics that are very similar to that seen in GO in particle size and thickness.

3. Carbon/oxygen ratios

One of the critical factors for graphene and GO is the carbon to oxygen ratio. The presence of oxygen in the structure creates defects that adversely affect the electrical, thermal and mechanical properties of the particles. The carbon and oxygen contents for GO and HA have been determined by EDS in the SEM while imaging the particles by Douglas [39]. The GO averaged 51.7% carbon and 48.3% oxygen while HA yielded values of 58.3% carbon and 41.2% oxygen. It appears that the HA is somewhat less oxidized as compared to the GO. Of course these ratios are heavily dependent on the details of GO oxidation, and there are many lower states of GO oxidation documented in the literature. It is very important to understand how much of the oxygen can be eliminated by chemical and thermal reduction of the two materials since this will result in restoration of some of the outstanding properties of graphene. A series of reduction experiments were executed with a number of common chemical reductants as well as thermal reduction with H_2, with subsequent measurement of carbon and oxygen contents [39]. The reductants included hydrazine, hydroxyl amine, sodium borohydride, sodium bisulfite, and benzyl alcohol. The treatments and abbreviations utilized in the graphics and discussion are listed below

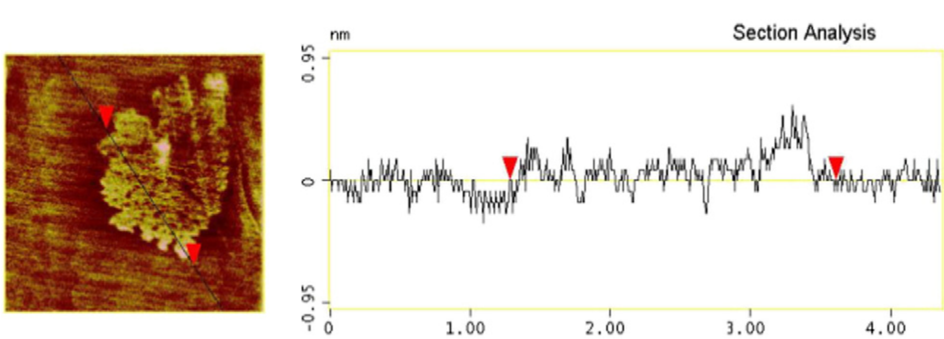

Fig. 3. AFM scan of a HA nanoparticle on a silicon wafer substrate indicating atomic layer thickness.