

Preparation of Graphene with Few Layers and Large Scalability

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Abstract—Graphene nano-sheets were prepared via modified chemical exfoliation route and utilizing graphite as starting material. The employed preparation route ensured simplicity, short preparation time, room temperature preparation, and low cost. The graphite was first purified chemically, and then exfoliated via ultra-sonication assisted chemical treatment to produce exfoliated graphite (EG). This process was followed by thermal irradiation that leads to the formation of graphene after centrifugation process. Atomic force microscope (AFM), scanning electron microscope (SEM) and Raman spectroscopy were used to characterize the prepared graphene sheets. It was shown that the prepared graphene has trend to form hexagonal shaped sheets with wrinkled morphology. The resultant thickness of few layers graphene stacks is about (3.34 nm) with large sheet diameter of about (97.44 nm).

Keywords: Ceramic nanomaterials, Graphene, Chemical route.

I. Introduction

Graphene is a two dimensional one atom thick planar sheet of bonded carbon atoms, densely packed in a honeycomb structure [1, 2]. Graphene has generated in recent years a significant attention from the research community, due to its outstanding physical properties and enormous potentials in practical uses, which span the fields of nanoelectronics, composite materials, energy storage, and molecular sensors [3].

Recent efforts have focused on methods for the development of larger scale production of graphene. Basically, there are two different approaches to preparing graphene; the first is based on that the graphene can be detached from an already existing graphite crystal, the so-called exfoliation methods. The second approach is based on that the graphene layers can be grown directly on a substrate surface [4, 5].

Chemical exfoliation is widely considered as a promising approach for large-scale production of graphene sheets (GSs) [6]. Chemical exfoliation is preceded by weakening the Van der Waals cohesive force upon insertion of reactants in the inter-layer space. Subsequently the loosened layer stacking is disrupted when the intercalate decomposition produces a high gas pressure. As a consequence, the sp^2 lattice is partially degraded into a sp^2 - sp^3 sheet that possesses less π - π stacking stability [7].

Chemical exfoliation can be performed in suspension and hence up scalability is straightforward and it could offer a route to large-scale graphene production [7]. This technique offers several significant advantages since it utilizes inexpensive and readily available graphite flakes, do not require methods of transferring the graphene from the growth substrate, and can employ existing technologies for scale up to large volume processing [8].

However, the (GSs) obtained by this method usually suffer from poor quality mainly due to the introduction of oxygen-containing functional groups during synthetic process, which consequently prevents their further applications, especially as electrically conductive composites and nanodevices. As a result, a post-treatment process, such as reduction of (GSs) by chemical method or thermal annealing, is required to remove the oxygen-containing groups. However, some structural defects such as vacancies and topological defects simultaneously produced during the removal of functional groups. Moreover, some (GSs) inevitably agglomerated during the post reduction process, resulting in an increase of the number of layers [6]. In fact, these defects are virtually impossible to remove completely; even after annealing at 1100°C [9].

II. Materials and methods

The starting materials were graphite (90%, LYRA, Germany), hydrochloric acid (HCl) (35.4%, Gainland chemical Co., UK), hydrogen peroxide (H_2O_2) (30%, Sigma-Aldrich, Germany), sulfuric acid (H_2SO_4) (98%, Himedia, India), water.

The first step in the preparation of graphene sheets (GSs) is the purification of graphite via chemical means using hydrochloric acid assisted by ultrasonication process. After purification step, the chemical exfoliation of 5g of the purified graphite is performed utilizing hydrogen peroxide and sulphuric acid as intercalators. The mixture was stirred via magnetic stirrer for 1hr and then ultrasonicated for another 1hr. Then, filtration of the produced material was carried out through cellulosic nitrate paper. The product is washed and filtered three times with deionized water.

The produced graphene is kept at 60°C for 3hr and then a further drying is performed via 20s irradiation in a

microwave oven. As a final step, the produced graphene is mixed with 50ml of deionized water and ultrasonicated for 1hr, then, subjected to centrifugation process. The reason for centrifuging was to remove big and thick flakes while the small flakes remains in the outer space of the liquid. The graphene sheets (GSs) is collected via vacuum filtration through cellulosic nitrate paper and air-drying.

III. Results and Discussions

As the sulphuric acid was used as intercalation agent via chemical exfoliation process, the outer layers will be highly oxidized graphene sheets with larger proportions of oxygen functionalities. The ultrasonication process provides a chance for detaching of the inner layers that is rich in oxygen functionalities. In addition, the centrifuging places that oxygen rich graphene at the outer space that could be separate at the centrifugation stage. Subsequent purification resulted in homogeneous black dispersion of graphene.

Figure (1) shows the AFM image of the prepared graphene by chemical exfoliation route. This figure represents the effective transformation ability of the cheap, available graphite to expensive and noble graphene. From this figure it can be observed that the hexagonal lattice of graphene structure with thickness of about 3.34 nm; which meaning few layer graphene and its granularity accumulation chart indicated in figure (2), that the average sheet diameter is (97.44 nm).

Two main bands G and D can be clearly seen from Raman spectrum as indicated in figure (3). These the appearance of these bands is the strongest confirmation of the graphene formation. The G band of graphene broadened and D band is strong while the intensity of D band of the prepared graphene is high and this could be attributed to two main reasons, the first is due to high proportion of defects of edge and ripples within the prepared sheets. While, the second reason is the significant decrease of the layer thickness according to the decrease of the size of the in plane sp^2 domain during the oxidation and ultrasonication exfoliation stage through [10].

The intensity ratio of the prepared graphene I_D/I_G is equal to (1.2) which indicates the establishment of the conjugated graphene-network and a small layer thickness as shown in AFM image figure (1).

Figure (4) displays scanning electron microscope (SEM) image of the chemically exfoliated graphene. This figure indicates the lateral structure of the prepared graphene. The thin structure morphology of graphene sheets can be observed in this figure. Also, it can be observed that the particles have a fluffy morphology, consisting of randomly aggregated, thin, and wrinkled sheets loosely associated with each other.

IV. Conclusions

A chemical exfoliation technique is used to obtain graphene sheets (GSs) from graphite after its purification process. In this work, the used materials for the both the purification and oxidation stages were available and inexpensive. The produced graphene characterized by its high quality and small thickness that make it is suitable for several applications.

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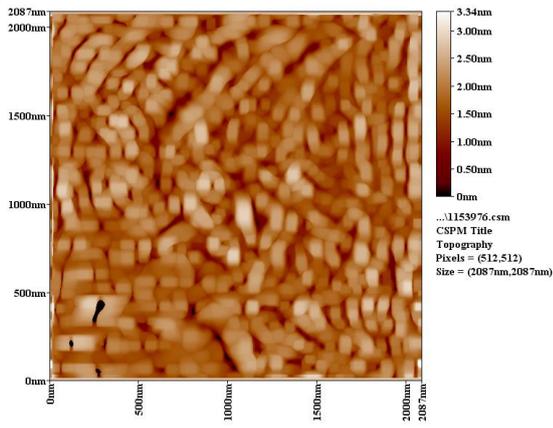


Figure (1): 2-D AFM image of chemically exfoliated graphene.

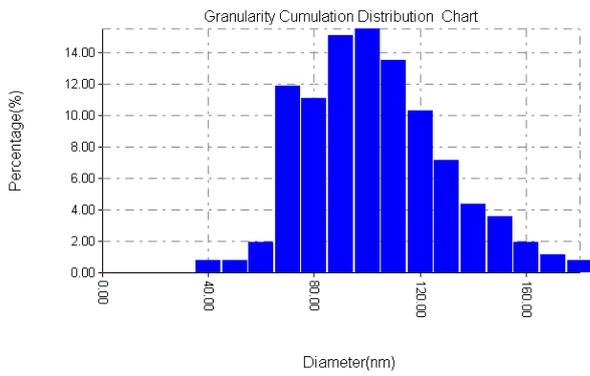


Figure (2): Granularity accumulation distribution chart of chemically exfoliated graphene.

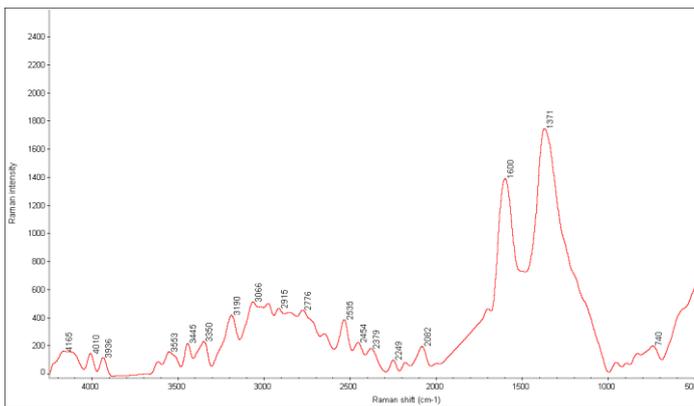


Figure (3): Raman spectroscopy of chemically exfoliated graphene.

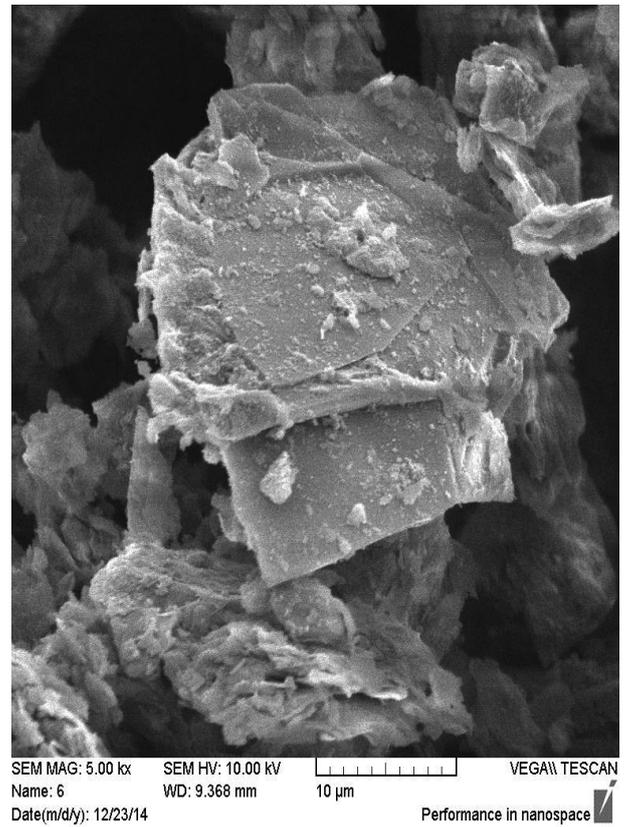


Figure (4): SEM image of chemically exfoliated graphene.