

material (e.g. natural graphite powder) in an oxidizing liquid medium (e.g. a mixture of sulfuric acid, nitric acid, and potassium permanganate) in a reaction vessel at a desired temperature for a period of time (typically from 0.5 to 96 hours, depending upon the nature of the starting material and the type of oxidizing agent used). As previously described above, the resulting graphite oxide particles may then be subjected to thermal exfoliation or ultrasonic wave-induced exfoliation to produce isolated GO sheets. These GO sheets can then be converted into various graphene materials by substituting —OH groups with other chemical groups (e.g. —Br, NH_2 , etc.).

[0105] Fluorinated graphene or graphene fluoride is herein used as an example of the halogenated graphene material group. There are two different approaches that have been followed to produce fluorinated graphene: (1) fluorination of pre-synthesized graphene: This approach entails treating graphene prepared by mechanical exfoliation or by CVD growth with fluorinating agent such as XeF_2 , or F-based plasmas; (2) Exfoliation of multilayered graphite fluorides: Both mechanical exfoliation and liquid phase exfoliation of graphite fluoride can be readily accomplished.

[0106] Interaction of F_2 with graphite at high temperature leads to covalent graphite fluorides $(\text{CF})_n$ or $(\text{C}_2\text{F})_n$, while at low temperatures graphite intercalation compounds (GIC) C_xF ($2 \leq x \leq 24$) form. In $(\text{CF})_n$ carbon atoms are sp^3 -hybridized and thus the fluorocarbon layers are corrugated consisting of trans-linked cyclohexane chairs. In $(\text{C}_2\text{F})_n$ only half of the C atoms are fluorinated and every pair of the adjacent carbon sheets are linked together by covalent C—C bonds. Systematic studies on the fluorination reaction showed that the resulting F/C ratio is largely dependent on the fluorination temperature, the partial pressure of the fluorine in the fluorinating gas, and physical characteristics of the graphite precursor, including the degree of graphitization, particle size, and specific surface area. In addition to fluorine (F_2), other fluorinating agents may be used, although most of the available literature involves fluorination with F_2 gas, sometimes in presence of fluorides.

[0107] For exfoliating a layered precursor material to the state of individual layers or few-layers, it is necessary to overcome the attractive forces between adjacent layers and to further stabilize the layers. This may be achieved by either covalent modification of the graphene surface by functional groups or by non-covalent modification using specific solvents, surfactants, polymers, or donor-acceptor aromatic molecules. The process of liquid phase exfoliation includes ultra-sonic treatment of a graphite fluoride in a liquid medium.

[0108] The nitrogenation of graphene can be conducted by exposing a graphene material, such as graphene oxide, to ammonia at high temperatures (200-400° C.). Nitrogenated graphene could also be formed at lower temperatures by a hydrothermal method; e.g. by sealing GO and ammonia in an autoclave and then increased the temperature to 150-250° C. Other methods to synthesize nitrogen doped graphene include nitrogen plasma treatment on graphene, arc-discharge between graphite electrodes in the presence of ammonia, ammonolysis of graphene oxide under CVD conditions, and hydrothermal treatment of graphene oxide and urea at different temperatures.

[0109] The aforementioned features are further described and explained in detail as follows: As illustrated in FIG. 2(B), a graphite particle (e.g. **100**) is typically composed of

multiple graphite crystallites or grains. A graphite crystallite is made up of layer planes of hexagonal networks of carbon atoms. These layer planes of hexagonally arranged carbon atoms are substantially flat and are oriented or ordered so as to be substantially parallel and equidistant to one another in a particular crystallite. These layers of hexagonal-structured carbon atoms, commonly referred to as graphene layers or basal planes, are weakly bonded together in their thickness direction (crystallographic c-axis direction) by weak van der Waals forces and groups of these graphene layers are arranged in crystallites. The graphite crystallite structure is usually characterized in terms of two axes or directions: the c-axis direction and the a-axis (or b-axis) direction. The c-axis is the direction perpendicular to the basal planes. The a- or b-axes are the directions parallel to the basal planes (perpendicular to the c-axis direction).

[0110] Due to the weak van der Waals forces holding the parallel graphene layers, natural graphite can be treated so that the spacing between the graphene layers can be appreciably opened up so as to provide a marked expansion in the c-axis direction, and thus form an expanded graphite structure in which the laminar character of the carbon layers is substantially retained. The process for manufacturing flexible graphite is well-known in the art. In general, flakes of natural graphite (e.g. **100** in FIG. 2(B)) are intercalated in an acid solution to produce graphite intercalation compounds (GICs, **102**). The GICs are washed, dried, and then exfoliated by exposure to a high temperature for a short period of time. This causes the flakes to expand or exfoliate in the c-axis direction of the graphite up to 80-300 times of their original dimensions. The exfoliated graphite flakes are vermiciform in appearance and, hence, are commonly referred to as graphite worms **104**. These worms of graphite flakes which have been greatly expanded can be formed without the use of a binder into cohesive or integrated sheets of expanded graphite, e.g. webs, papers, strips, tapes, foils, mats or the like (typically referred to as “flexible graphite” **106**) having a typical density of about 0.04-2.0 g/cm³ for most applications.

[0111] Acids, such as sulfuric acid, are not the only type of intercalating agent (intercalant) that penetrate into spaces between graphene planes to obtain GICs. Many other types of intercalating agents, such as alkali metals (Li, K, Na, Cs, and their alloys or eutectics), can be used to intercalate graphite to stage 1, stage 2, stage 3, etc. Stage n implies one intercalant layer for every n graphene planes. For instance, a stage-1 potassium-intercalated GIC means there is one layer of K for every graphene plane; or, one can find one layer of K atoms inserted between two adjacent graphene planes in a G/K/G/K/G/KG . . . sequence, where G is a graphene plane and K is a potassium atom plane. A stage-2 GIC will have a sequence of GG/K/GG/K/GG/K/GG . . . and a stage-3 GIC will have a sequence of GGG/K/GGG/K/GGG . . . etc. These GICs can then be brought in contact with water or water-alcohol mixture to produce exfoliated graphite and/or separated/isolated graphene sheets.

[0112] Exfoliated graphite worms may be subjected to high-intensity mechanical shearing/separation treatments using a high-intensity air jet mill, high-intensity ball mill, or ultrasonic device to produce separated nano graphene platelets (NGPs) with all the graphene platelets thinner than 100 nm, mostly thinner than 10 nm, and, in many cases, being single-layer graphene (also illustrated as **112** in FIG. 2(B)). An NGP is composed of a graphene sheet or a plurality of