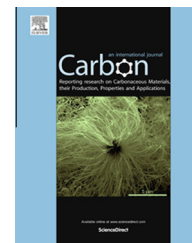


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Formation of graphene aqueous suspensions using fluorinated surfactant-assisted ultrasonication of pristine graphite



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ABSTRACT

The present study describes some physical and kinetic details concerning a method for obtaining highly concentrated aqueous suspensions of few-layered graphene platelets via direct fluorinated surfactant-assisted ultrasonic exfoliation of pristine graphite. Process kinetics and qualitative properties of the product were studied using laser diffractometry, X-ray diffraction, transmission electron microscopy, electron diffraction, and Raman spectroscopy. The advantages of the described process are the ease of scalability, environmental friendliness, and high yield of few-layered graphene particles which makes it attractive for use in a wide area of applications.

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1. Introduction

A variety of techniques for obtaining graphene particles can be found in the literature [1–4], of which those involving suspensions of graphitic materials in ionic liquids [5], organic solvents [3,4,6,7] or water in the presence of surfactants [3,4,8–10] are considered to be of substantial interest.

The most prominent advantage of this set of techniques is the possibility to organize facile easily scalable technology [2–10]. Graphene particles suspensions thus formed consist primarily of few-layered (mostly single- to tri-layered for best methods [5–7,11]) graphene platelets (FLGP) and are of great importance for such processes as subsequent chemical functionalization, mixing with polymers, obtaining of thin films, surface coating, and impregnation of porous materials

[4,6–11]. In fact, most of the recently reported nanocomposites were fabricated using suspensions of graphene particles in polymers, organic solvents or water [12–14].

It was shown [12–14] that even tiny amounts of graphene particles (10^{-3} – 10^{-1} mass%) lead to significant increase in strength, Young’s modulus and electrical conductivity of nanocomposites. Moreover, graphene particles suspensions can be directly used for biosensing [15], as cooling agents of increased heat conductivity [16], and also applied for supercondensators, gas sensors, hydrogen fuel cells and photovoltaic devices [12–14]. Recent studies suggest that graphene particles can be used as effective functional aerogels (for example, with superhydrophobic properties [17]).

In order to obtain suspensions of graphene particles, oxidized graphite (the so-called graphite oxide (GO)) – a product

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of treatment of pristine graphite with different agents, e.g. potassium hydroxide [8] or sulfuric acid [18,19], is normally used as a precursor. Due to its partial intercalation and oxidation, GO contains particles with increased interlayer distances and distorted layer structure which alleviates graphite exfoliation process [2–4]. This method has serious disadvantages, such as consumption of significant quantities of acidulous and toxic reagents and the need for their subsequent removal and utilization [2–4]. Moreover, oxidation process leads to the formation of intralayer defects that tend to change the properties of graphene particles, e.g. drastically reduce their conductivity (transformation into dielectric is not uncommon [18,20–22]). These defects cannot be completely removed using traditional hydrazine-assisted reduction or heat shock treatment at about 1000 °C in hydrogen or inert atmosphere (or plasma) [22]. This phenomenon can lead to the loss of advantages expected from graphene suspensions in many applications (e.g. fabrication of electrically conductive composites [12–14]). Another promising graphite compound capable of being transformed into single- and few-layered 2D-particles is graphite fluoride – conventional product widely used in fuel cell and battery industry; graphene fluoride obtained in the presence of fluorinated surfactant possessed intriguing optical properties [23]; unfortunately, it is an insulator as well.

Significantly fewer studies are devoted to pristine graphite or highly-oriented pyrolytic graphite direct exfoliation in either different organic solvents [4,7,24–26] or water [4,27–34], although it is well established that these processes are also possible. Using such solvents as N-methyl-2-pyrrolidone, stable FLGP suspensions with concentrations of up to 25–30 mg/ml were obtained [25]. FLGPs fabricated this way contain fewer defects than those obtained from GO or reduced GO [35]. Ecological and economic reasons suggest that exfoliation of pristine graphite, world's resources of which are very vast, in water appears to be the most prospective mass production route for graphene precursors and graphene-based materials [3,4]. The interest in aqueous suspensions of graphene particles is steadily increasing mainly due to the need for development of green technologies [30,36,37]. Organic reagents-free suspensions containing large (500–2000 nm) FLGPs with minimal defects concentrations are needed as a source material for fabrication of medical biosensors [15] and prospective electronic devices based on quantum dots principles [12–14].

The use of water-surfactant systems possesses several particularities due to large mixing enthalpy in graphite/water system [25]; moreover, when not containing any oxygroups, graphite surface is highly hydrophobic [24–26,28–30]. As a result, the process of exfoliation requires a lot of energy [3,4,7,9,25,30] and often does not allow obtaining of high concentrations of graphene particles [30,32]. Stabilizers successfully used to obtain high-quality FLGP suspensions in polar media include traditional surfactants [29,30,32], aromatic compounds [27,33], polymers noncovalently binding to graphene [32,34], bio-derived materials [32], and even layered silicates [38].

All these facts suggest the need to continue research on industrially scalable processes of graphene particles aqueous suspensions fabrication [4,36,37] while avoiding such steps as

intercalation or obtaining of GO; the search for easily removable surfactants and other additives increasing the effectiveness of exfoliation process is also of great importance. The aim of the present study was to investigate temporal aspects of the process of pristine graphite exfoliation in water under ultrasonic treatment, both in the presence of chosen surfactant and in its absence.

2. Experimental section

2.1. Sample preparation

GE pristine graphite supplied by JSC Zaval'evsk graphite combine was used as a precursor material. Graphite powder containing up to 10 mass% of mineral impurities was heat-treated at 2800 °C using an industrial graphitization furnace and subsequently heat-treated in Freon-12 atmosphere at 2200 °C (equipment and technology by LCC Grafi) in order to reduce mineral impurities content and thermally anneal some defects. The resulting mineral impurities content was less than 0.01 mass%, the maximal particle size being 200 μm.

Non-ionic fluorinated surfactant used was 1H,1H,11H-eycosofluor-1-decanole polyglycidyl ether (empirical formula $C_{26}H_{34}O_{11}F_{20}$) (Fig. 1a). The sample was synthesized and kindly supplied by late Dr. A.Y. Lyapunov (Semenov Institute of Chemical Physics, Moscow, Russia). Molecular structure of this surfactant contains hydrophobic fluorinated alkyl fragment (1H, 1H, 11H-eycosofluor-1-decyl) as well as hydrophilic fragment (primary and secondary free hydroxyls of oxypropylene chain). The presence of fluorinated fragment provides high surface activity of the surfactant in aqueous media even at concentrations as low as 0.001 mass% [39,40]. Its effectiveness in artificial graphite dispersion down to 1 μm was shown in the authors' previous study [41].

FLGP suspensions were obtained using Melfiz MEF-391 horn-type ultrasonicator (acoustic power 200 W) at 22.5 KHz frequency. Graphite powder (300 mg) was pre-suspended in water (50 ml) (initial graphite concentration thus being 6 mg/ml), after which 30 mg (0.6 mg/ml) of surfactant was introduced. Ultrasonication time varied from 10 min to 6 h. The resulting suspension is shown on Fig. 1b.

2.2. Characterization

Only suspensions of concentration 6 mg/ml (calculated as the ratio of the mass of precursor graphite to the volume of water)

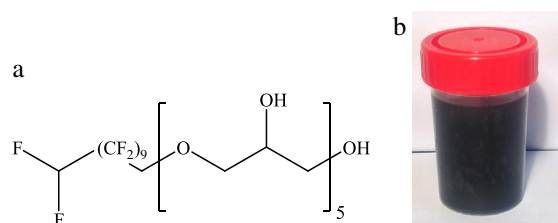


Fig. 1 – Structural formula of 1H,1H,11H-eycosofluor-1-decanole polyglycidyl ether (FAPGE) surfactant (a) and an image of the as-obtained suspension within 3 weeks after fabrication (b). (A color version of this figure can be viewed online.)

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