



# Synthesis of and characterization of freestanding, high-hierarchically structured graphene-nanodiamond films



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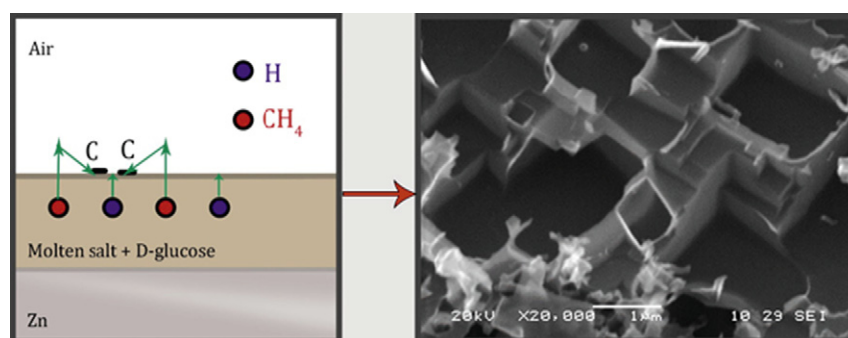
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## HIGHLIGHTS

- Synthesis of freestanding high-hierarchically structured nanodiamond/graphene films.
- Interaction of D-glucose with molten zinc under molten alkali chlorides
- Atomic hydrogen chemically induced graphene transition to the nanodiamond.
- Film is non-isomorphic: smooth on one side and highly evolved on the other side.
- A ratio of carbon atoms of sp<sup>2</sup> and sp<sup>3</sup> hybridization of 1:1

## GRAPHICAL ABSTRACT



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## ABSTRACT

A novel carbon structure is synthesised during the interaction of solid organic precursors as D-glucose with a molten metallic zinc catalyst under a layer of molten alkali chlorides at air atmosphere. Scanning electronic microscopy studies show that the formed pure carbon film is non-isomorphic and smooth on one side, but highly evolved, with square steps, on the other. The Raman spectrum of the smooth side resembles that of multilayer graphene. The Raman spectrum of the developed side shows a typical sharp and narrow diamond peak at 1332 cm<sup>-1</sup> along with graphene peaks. XPS data show that the most of the carbon atoms are at diamond sites. According to the results of an Auger spectroscopy investigation, obtained carbon film is composed of carbon atoms of sp<sup>2</sup> and sp<sup>3</sup> hybridisation in a ratio of 1:1. From the average graphene cluster size of 5 nm and average diamond crystal diameter of 2–7 nm, it may be concluded that the formation of graphene-nanodiamond films in this system is thermodynamically possible at this temperature range without application of increased pressure. Chemically induced transition to the nanodiamond structure occurs in graphene layers due to presence of large quantities of atomic hydrogen in the molten salt media.

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## 1. Introduction

The different allotrope modifications of carbon are very attractive materials for numerous applications in electronics and energy devices. Nowadays hundreds of papers are devoted to the synthesis of graphene

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and graphene composites with oxides and other carbon materials such as carbon nanotubes and porous carbon [1–3]. In general, these graphene-oxide and graphene carbon composites exhibit a variety of new properties not inherent in the initial materials. Thus, graphene formed on a diamond film shows anisotropic electrical properties: the diamond side remains an electrical insulator while the graphene side of the film has conductive attributes [4]. Such films are therefore promising for application in chemical power sources [5–7].

Fundamental research into the possibility of mutual phase transitions between nanodiamond and graphene is of great importance. One of the promising lines of research in this direction is the possible formation of graphene on a diamond film surface during treatment by highly energetic methods, such as plasma or laser beam machining [8–12]. Data from Raman spectroscopy confirm the formation of graphene during high-dose irradiation of diamond films and subsequent annealing on the surface of CVD-fabricated diamond films. In other research, in which two-sided films of diamond-graphene (or graphite) were obtained, Raman spectra were reported having, on the one hand, cubic diamond and line broadening features associated with nanodiamond and, on the other, lines pertaining to the graphite spectrum. In addition, computer simulations also show the possibility of graphene formation on the (100) and (111) diamond planes [13,14]. Thus, the existence of non-isomorphous diamond-graphene films exhibiting a variety of uncommon properties was demonstrated [15].

A different approach to the synthesis of novel carbon materials, e.g., porous films, was presented. Here, the main idea consists in the formation of porous carbon films having a highly developed surface through the thermal decomposition of some organic products as soybeans [16], potato [17], eggplants [18] and even shiitake mushroom [19]. In some cases, chemical processing (by alkaline solutions, for example) took place with the subsequent semi-product heated at temperatures from 200 °C to 1100 °C. In [20], molten salt synthesis with the application of zinc chloride as a reactive media was proposed. In all these cases, the distinctive feature is that the porous carbon structures obtained have a very large specific surface but are rather thick, contain a lot of amorphous carbon and their structure is not regularised.

In the past 10–15 years, numerous investigations of producing carbon coatings or nanomaterials, including nanotubes, in molten salt media [21,22] have been published. Molten salts are used as a medium for electrolytic production of a number of active metals, coatings, powders, thermal and chemical-thermal treatment of metallic materials due to their inherently valuable technological properties: high thermal and electrical conductivity, low viscosity, high diffusion coefficients and absence of hydrogenation. The wide operating temperature interval expands the possibility of forming products of a certain phase composition and the desired morphology, which can not or cannot be obtained by traditional, e.g., hydrochemical methods.

The basic methods for synthesis of carbon of different structures are electrolysis of carbon (graphite) electrodes in molten salts, particularly lithium chloride [23,24]. Alternatively, cathode reduction of carbonate ions or carbon dioxide in molten chlorides or fluorides of alkali metals can be used [25–29]. A route for producing diamond nanocrystals in molten salt media is reported in [30].  $\text{Li}_2\text{CO}_3$ -containing carbon nanostructures synthesised in molten LiCl were transformed into nanodiamonds by simple heating at atmospheric pressure, comprising far less severe conditions than those produced in conventional processes.

Over the last few years, our group has been studying the interaction of molten metals with inorganic carbon-containing precursors in a molten metal environment. As a result of this interaction, a number of metal carbon composite materials, such as lead-graphene composite [31] and aluminium-graphene composite [32,33], were synthesised. For the first time, cubic diamonds were also synthesised in an aluminium matrix at atmospheric pressure [34].

The present work is a continuation of this cycle of studies, in which the interaction of organic precursors, including glucose, is investigated

with molten zinc under a layer of molten alkali metal halides. One of the products of interaction was the carbon films that formed on the surface of the melt, their morphology and structure became an unexpected discovery for us, since, in a one-stage synthesis, it was possible to obtain a hybrid carbon structure, the description of which was not found in the literature.

The aim of the present study is the creation of a new method for synthesising high-hierarchically structured bilateral *freestanding diamond/graphene films* from the chemical interaction of solid organic precursors with molten alkali halogenides under air atmosphere.

## 2. Experimental

The chemical interaction of solid organic precursors of different types – hydrocarbons (stearin, paraffin), carboxylic acids (tartaric acid, oxalic acid) and carbohydrates (sucrose, glucose) with liquid metal catalyst (zinc) in molten halides of alkali metals was investigated. The main results presented in this work concern the synthesis using D-glucose precursor. The chlorides of alkali metals, such as lithium, sodium, potassium, caesium, as well as additive fluorides of ammonium, potassium, sodium and aluminium having a melting point below 700 °C used for the salt mixtures.

The schema for the synthesis process is presented in Fig. 1a. The pre-melted salts were extensively clustered and mixed with a quantity of solid organic substance not >10% by weight and then placed on weighted amount of zinc granules in alumina crucible. Most of experiments conducted at temperatures of 700 °C and 750 °C. The duration of the experiments varied from 0.5 to 2 h depending on the carbon precursor amount and type. Following the high-temperature procedure, the salt melt and molten zinc was poured into a cold crucible. After the salt mixture had solidified, it was dissolved in distilled water and the carbon powder was carefully and thoroughly washed from the salts (Fig. 1 b, c). The solution process was shown in the accompanying video. The by-product zinc oxide nanopowders and nanorods were found in the solution bulk.

During the experiment, abundant light black films were observed floating on the water surface following the dissolution of the salts, forming large agglomerates that could be easily dissociated into separate flocks after drying-out. The black carbon powder filtered from the salt solution and washed with dilute sulphuric acid and then a large volume of distilled water in order to remove residual zinc oxide powder.

The carbon flocks were studied by scanning and transmission electron microscopy, as well as by energy-dispersive X-ray spectroscopy using Tescan, JEOL 5900LV and Zeiss Sigma VP scanning electron microscopes, an Auriga CrossBeam Workstation (Carl Zeiss NTS, Germany), equipped with an Inca Energy 350 X-MAX EDS spectrometer (Oxford instruments, UK) and a JEOL 2010 transmission electron microscope.

Raman spectra were collected using a Renishaw U 1000 Raman spectrometer connected to a Leica DML microscope equipped with lenses of 50× and 100× magnifications. An  $\text{Ar}^+$  laser (1160 Physics model) with a wavelength of 514.5 nm and power of 20 mW was used as the excitation source. The diameter of the laser spot was about 1 μm; the acquisition time was set to 20 or 30 s. The depth of the Raman signal depended on the transparency of investigated material and was <1 μm for black flakes.

Powder X-ray diffraction (PXRD) in Bragg–Brentano mode was used for phase purity control and the determination of crystal lattice parameters in the obtained samples. The diffraction patterns were collected at room temperature in the  $2\theta$  range 10 to 90° with the help of a PANalytical X'pert Pro diffractometer using  $\text{CuK}\alpha$ -radiation and Ni filter at the Ural Federal University (Ekaterinburg).

Photoelectron spectroscopy and Auger electron spectroscopy as well as differential scanning calorimetry were performed using a K-Alpha XPS X-ray photoelectron spectrometer (Thermo Fisher Scientific, UK) and an STA 449C Jupiter® thermal analyser (NETZSCH, Germany),

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