Influence of the precursor alcohol on the adsorptive properties of graphene foams elaborated by a solvothermal-based process

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A B S T R A C T

Besides the well-known research concerning graphene, great attention has more recently been paid to three-dimensional graphene structures, motivated by the combination of the properties of graphene and the development of porosity and large specific surface areas. The most current methods of obtaining for this kind of structure start from graphite oxide, which can be thermally treated or assembled in liquid-phase. This work is focused on a little-known and bottom-up method of elaboration, which consists in a solvothermal reaction between metallic sodium and an alcohol, followed by a thermal treatment. The as-obtained graphene foams exhibit very large specific surface areas. More specifically, the length of the carbon chain of the precursor alcohol employed for the solvothermal reaction is found to have a strong influence on the adsorptive properties of the foams, especially on their pore size distribution. The mechanism of formation of such porous structures is discussed through the exploration of the compounds of the carbon-sodium-oxygen system.

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1. Introduction

Graphene is now a well-known material for the scientific world. Numerous studies of its properties report a particular electronic structure [1,2], outstanding electronic [3] and thermal [4] transport properties, great mechanical resistance [5], quasi-transparency [6] and impermeability [7]. These properties pave the way for a wide range of potential application domains, as for example electronics [8,9], energy [10], composite materials [11], biology and medicine [12]. Several major methods of elaboration of graphene and graphene-based materials have been developed: mechanical cleavage of graphite [2], liquid-phase exfoliation of graphite [13], graphite oxide [14] or graphite intercalation compounds [15], or supported growth on metal surfaces [16] or silicon carbide [17]. Each of these methods lead to the obtaining of graphene samples which are different in several fronts: structural quality, purity, presentation (deposited on a substrate, powdery, dispersed in liquid-phase), cost. The elaboration of large quantities of graphene materials with controlled features remains difficult, but the first commercial releases of graphene-based devices are expected in the coming years [18].

More recently, besides the research concerning the preparation of bidimensional graphene samples, more and more studies focus on three-dimensional graphene structures, as crumpled graphene sheets or graphene foams [19—21]. This kind of structure, composed of graphene sheets interconnected in a three-dimensional network, combines a part of the properties of graphene with a high specific surface area. Indeed, the theoretical specific surface area of a graphene layer is 2630 m^2 g^{-1} [22], which is very elevated for a carbon material, but in practice, aggregation of the graphene sheets or deposition on a substrate limit the accessible surface of the material [19,20]. The elaboration of a graphene-based porous structure is particularly interesting in several domains as energy (lithium-ion batteries [23,24], supercapacitors [25—31], fuel cells [32]), catalysis [33] or medicine [34,35].

3D graphene samples can be obtained by thermal reduction of graphite oxide [36,37], or graphene oxide aqueous suspensions [32,35]. Folds and tortuosity, generated by structural defects, dangling bonds or oxygen groups [37,38], prevent the aggregation of the sheets: the BET specific surface area of such samples can reach 1000 m^2 g^{-1} [36]. Porosity in graphene can be created by chemical activation with potassium hydroxide: the as-obtained

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material presents a BET specific surface area higher than 3000 m^2 g^{-1} (higher than the theoretical value because of the use of the BET model) while preserving a good structural quality [39]. Liquid-phase assembly, from graphene oxide gels for example, is also a current method for the elaboration of three-dimensional graphene samples [27,28]. Templated methods from graphene oxide suspensions have been reported too [40].

As the majority of the methods of elaboration of three-dimensional graphene foams starts from graphene oxide, we chose to focus on a solvothermal-based process, an uncommon and bottom-up technique first reported in 2009 [41]. It consists in a solvothermal reaction between sodium and an alcohol, followed by a thermal treatment and a washing step. The sodium alkoxide obtained after the solvothermal reaction is supposed to entrap alcohol molecules during its formation, and its rapid heating would lead to the creation of a porous graphene foam structure from the presence of the alcohol [41,42]. The most of the thermal treatment step consists in a very rapid combustion under air [41,43–45], eventually followed by a second treatment under inert atmosphere to improve the structural quality of the materials [46–48]. The reported BET specific surface areas of graphene foams obtained by a solvothermal-based process vary from around 500 m^2 g^{-1} [42] to around 1500 m^2 g^{-1} [46]. They show promising results in various energy domains, as supercapacitors [42], lithium-ion batteries [43,49] and fuel cells [46,47].

In this work, we perform a pyrolysis under a nitrogen flow (heating rate around 20 °C.min^{-1}), which is a one-step treatment where the experimental conditions and then, the properties of the foams, are well controlled. The influence of the conditions of pyrolysis and the optimal temperature and time was studied in a previous work [50]: here we focus on the influence of the precursor alcohol, which was found to have a drastic influence on the porosity of the graphene foams. Ethanol is the most widely used alcohol, some authors chose different ones as methanol [44] or propanol [42] but without interesting on the effects of change. We present here the influence of the length of the carbon chain of the precursor alcohol by comparing the results obtained with methanol, ethanol and butan-1-ol.

2. Material and methods

2.1. Graphene foams elaboration

The elaboration of the graphene foams is completed as described elsewhere [50] by a solvothermal reaction between sodium and the precursor alcohol, followed by a pyrolysis under nitrogen flow at 850 °C during 4 h and a washing step. For the solvothermal reaction, anhydrous methanol, ethanol and butan-1-ol (hereafter named butanol) are purchased from Sigma Aldrich, used as received and introduced in equimolar quantity against sodium.

2.2. Characterization

Transmission electron microscopy (TEM) is performed with a Philips CM200 microscope running at 200 keV. For analysis, samples are dispersed in ethanol and deposited on a copper grid with a holey carbon film. X-ray diffraction (XRD) is carried out with a Bruker D8 Advance diffractometer (molybdenum radiation $\lambda Mo_{K\alpha 1} = 0.70930$ Å) in $\theta/2\theta$ configuration. Samples are placed in Lindemann glass capillary tubes (1.5 mm diameter). For the analysis of the sodium alkoxides, tubes are prepared in a glove bag under argon atmosphere to avoid the degradation of the solvothermal compounds. Thermal decomposition of sodium alkoxides is studied using thermogravimetric analysis coupled to mass spectrometry

(TGA-MS). Under argon atmosphere, 10 mg of sample are introduced in a platinum crucible and rapidly placed in the thermobalance (Setsys Evolutions 1750 Setaram) under a helium flow (20 mL min^{-1}), then heated from 20 °C to 600 °C with a heating rate of 20 °C.min^{-1} in order to reproduce the rate of pyrolysis. The gases released during the decomposition are analyzed with a coupled Pfeiffer GSD 310C Vacuum OmniStar mass spectrometer. For thermogravimetric analysis (TGA) of the final carbon materials, around 3 mg of sample are placed in a platinum crucible and analyzed with a Setsys 1750 Evolutions Setaram, under dry air on a range 20−1000 °C with a heating rate of 3 °C.min^{-1}. Raman spectroscopy is achieved with a Horiba Jobin-Yvon LabRAM HR800 spectrometer operating at $\lambda = 632.8$ nm. The analyzed spectral range is 850−1800 cm^{-1} (region of D, G and D′ bands). Samples are dispersed on ethanol and deposited on a glass slide. Adsorption isotherms (N$_2$, 77.3 K) are collected with a Micromeritics ASAP 2020 adsorption apparatus. Before analysis, samples are outgassed during 12 h at 400 °C. Specific surface areas are calculated using the BET [51] (completed with the Rouquerol correction [52]) and 2D-NLDFT [53] models, micropore volumes and pore size distributions are obtained using 2D-NLDFT model. 2D-NLDFT model is used in order to avoid the overestimation of the specific surface area by the BET model for microporous solids [54]. 2D-NLDFT calculations are carried out using SAIEUS software, with a corrugation parameter $\lambda = 4.375$ and an integration range from 0.36 to 50 nm.

3. Results

Sodium reacts with alcohols to form sodium alkoxides, following the reaction (with R the alkyl chain):

$$Na + R-OH \leftrightarrows R-ONa + ½ H_2 \tag{1}$$

X-ray diffractograms of the solvothermal compounds providing from the reactions with sodium and the three alcohols are presented Fig. 1.

For solvothermal reactions with methanol and ethanol, the as-obtained compounds are, as expected, sodium methoxide MeONa and sodium ethoxide EtONa. We did not find any crystal data concerning sodium butoxide BuONa, but the position and the evolution of the peaks of the diffractogram (c) tend to indicate the
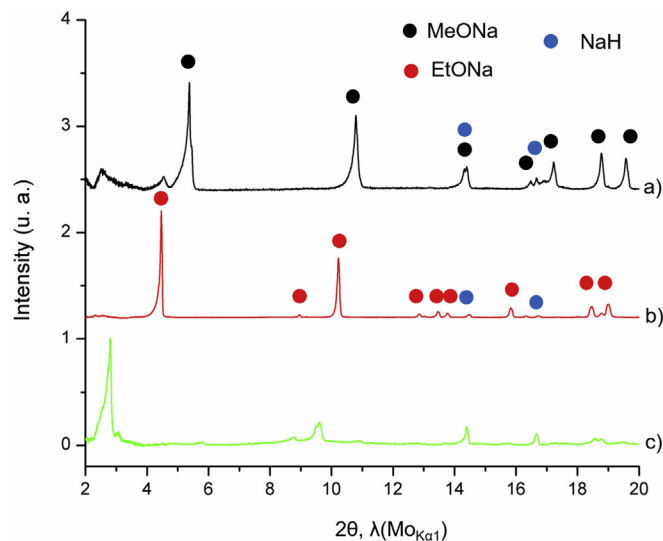

Fig. 1. X-ray diffractograms ($\lambda_{Mo} = 0.70930$ Å) of the samples obtained after solvothermal reactions of sodium with (a) methanol, (b) ethanol, (c) butanol. Indexation: sodium methoxide MeONa (PDF file n°00-019-1876), sodium ethoxide EtONa (PDF file n°00-031-1885), sodium hydride NaH (PDF file n°00-054-0409).