Electrochimica Acta 172 (2015) 28–36

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Doping of cathodically polarized glassy carbon by natural graphite. A simple procedure for overlaying different carbons with electrochemically modifiable graphene layers

Viatcheslav Jouikov [a], Jacques Simonet [b,*]

[a] UMR 6226, CPM, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France
[b] Laboratoire MaSCE, UMR 6226, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

A R T I C L E I N F O

Article history:
Received 30 October 2014
Received in revised form 2 March 2015
Accepted 3 March 2015
Available online 16 March 2015

Key words:
Graphite
Exfoliation
Graphene surfaces
Modified carbon electrodes

A B S T R A C T

The reduction of graphite (at ca. −2 V vs. Ag/AgCl, in DMF containing tetraalkylammonium salts) deposited onto smooth glassy carbon leads to intense graphite exfoliation that can be monitored through voltammetric scans or by fixed-potential electrolyses ($E < -1.8$ V). These simple and extremely efficient processes result in very stable modified carbon surfaces exhibiting simple and astonishingly reproducible voltammetric responses (both in nature and intensity). The reduction peaks assigned to the cathodic doping of deposited graphene layers are found to be proportional to the scan rate. The modification of these graphene-like surface structures in two types or reactions: with a series of organic electrophiles (in the reaction with doped graphene that acts as a poly-nucleophile) or with *in situ* generated benzyl-type radicals was successfully achieved and compared with the results obtained on smooth carbon surfaces. Striking examples with additions of hexylferrocene, benzylic derivatives of anthraquinone, anthracene and perylene, and of *para*-substituted benzyls ($R = NO_2$, I, Br, F) certainly underline the interest for these new materials.

1. Introduction

Glassy carbon (GC) is widely used as a convenient electrode material for electroanalyses and electrolyses, especially within the cathodic domain [1,2], often at potentials more cathodic than −1.8 V in organic aprotic polar solvents. The use of such materials (as rods, plates, micro-electrodes, etc) permitted to develop a large panel of analyses and electro-organic reactions [3]. However, recent studies reported that at $E < -1.7$ V GC is no longer inert due to the presence of ribbons or other inclusions of graphite-like structures [4–6]. Cathodic charging (accompanied by insertion of organic or inorganic cations) of these C_{sp2}-inclusions has been exploited in many nucleophilic reactions of CG with a large palette of electrophilic reagents [7,8] and it quite certainly accounts for a high reactivity of carbons in general, in particular towards free radicals commonly used for decorating such materials.

Obviously, it has to be recalled that the use of polar organic solvents enables the cathodic charge of varieties of graphites [9], especially of highly oriented pyrolytic graphite (HOPG), specifically leading to well-defined insertion forms $[C_n^-, TAA^+]$ through concomitant insertion of electrons and tetraalkylammonium salts (TAAX). Stoichiometry of these salts depends on many factors, principally on the applied potential and on the amount of electricity consumed relative to the amount of material. Constant-potential reduction and first evidences for exfoliation of natural graphite by bulky ammonium salts have been reported back in 77' [9]. Such electrochemically prepared "graphite salts", akin to {TAA-amalgams} and naturally sensitive to the contact with oxygen, have to be considered both as a novel class of reducing agents and as new poly-nucleophilic materials (highly reactive towards organic reagents thus allowing the modification of graphites and carbons [10,11]). Primordial point in modification of glassy carbon is therefore to consider this material as containing large amounts of graphite nano-particles allowing, under cathodic charge, the creation of poly-nucleophilic centers [7,8,12].

Recently, interest for graphene both in chemistry and physics knew a huge development [13]. In particular, many ingenious approaches for making graphene planes where proposed: the recent literature is rich in organic methods (total syntheses) [14], other methods rely on the processes of solution-based, chemical [15] and electrochemical exfoliation [16,17]. Original method [18] based on graphite exfoliation in ionic liquids deserves being

---

[*] Corresponding author.
E-mail address: jacques.simonet@univ-rennes1.fr (J. Simonet).

http://dx.doi.org/10.1016/j.electacta.2015.03.027
0013-4686/

mentioned. Thus, – among the other processes – the electrochemical method based on artificial disaggregating graphite via its exfoliation may appear quite valuable. Let us recall that presently, the common approach to obtain graphenes via electrochemistry remains the reduction of graphene oxide [19]. Additionally, the attempts to modify commercially available graphenes chemically and electrochemically were recently undertaken. Let us quote the 3D {graphene-GC} electrodes modified with redox units [8,20] for the use in catalysis. When using fluidized bed processes, graphene suspensions could permit huge electrochemical functionalization. In particular (but not limited to), carboxylation of graphenes was realised at high level (reaching one carboxylate function per 100 carbons) [21].

To come back to exfoliation, first evidence grounding the development of an electrochemical method of splitting graphitic materials by TAA^+ cations under specific conditions was reported by one of us more than 37 years ago [9]. Based on this finding, the present contribution develops an original method permitting a quasi total disaggregation of graphene layers in the graphite deposits fixed onto a solid conducting support. This work, further developing our preliminary observations [20], uses carbon as main substrate but most of solid conductors are also good candidates to be overlaid with graphene according to the method described here. As explained in details hereafter, it allows a facile and reliable obtaining of modified glassy carbon interface covered with very thin graphene layers. Different TAAX salts were tested and compared in this process. Facile electrochemical exfoliation of graphite, realised by its reduction at about $-2.0\,V$, certainly represents a fascinating method for *in situ* generating thin graphene layers at electrified solid substrates. Moreover, it can be extended to a large panel of solid conductors and metals (gold, silver, rhodium, copper, platinum and palladium).

For the first time, grafting of redox-active chemical functions to such graphene overlays using electro-generated benzylic radicals was successfully achieved. Other processes exploiting the capability of deposited graphene layers to be charged ($E < -2\,V$) and doped to form poly-nucleophilic species were considered. The examples of modification of graphene with redox groups and aromatics are brought along this contribution. Finally, this method permits chemical modifications of any solid conductor preliminary electrochemically overlaid with graphene. For us, this issue is very important. We illustrate, at the end of this contribution, large possibilities offered by of this new approach for surface modification.

2. Experimental section

Voltammetric measurements and coulometry were performed at a PAR 273 potentiostat using three-electrode cells separated with a fritted glass. Other electrochemical instrumentation has been previously reported [7]. The reported potentials are given related to aqueous $Ag/AgCl/KCl_{(sat)}$. The measurements were carried out in 0.1 M solutions of tetraalkylammonium salts (TAAX), primarily tetrafluoroborates, with various cations: tetramethylammonium (TMA^+), tetraethylammonium (TEA^+), tetra-*n*-butylammonium (TBA^+), and tetra-*n*-octylammonium (TOA^+) in upper grade dimethylformamide (DMF). The experiments described in this work did not need special treatment of electrolytic solutions when fresh DMF solutions are employed.

Used as supports for graphite deposition, GC disk electrodes had geometric area of 1 and 7 mm^2. All carbon samples were from Tokai Carbon C° (GC Rod) and from Carbone Lorraine (carbon vitreous VD 1500). Larger GC plates (Carbone Lorraine) were employed for making flat electrodes with surface area of 1–3 cm^2.

Before modification by deposition of natural graphite, GC samples were carefully polished first with a coarse (Struers 500) and then with a finer (Struers 1200) silicon carbide polishing paper. Next, natural Ceylon graphite or highly oriented pyrolytic graphite (HOPG), both preliminary partly exfoliated by the electrolytic method quoted in the preliminary works [9,20], were disposed on a planar carbon surface. Graphite was mixed with acetone in order to obtain a paste easily deposited onto carbon. Once acetone dried off, the electrode was firmly rubbed at a glassy cardboard in a polishing manner until the surface obtained a shiny aspect of carbon. Short sonication may help to eliminate residual graphite flakes. Final process for the exfoliation of thus prepared deposit is detailed in 3.1. On may note that different recipes are quite equivalent as checked by cyclic

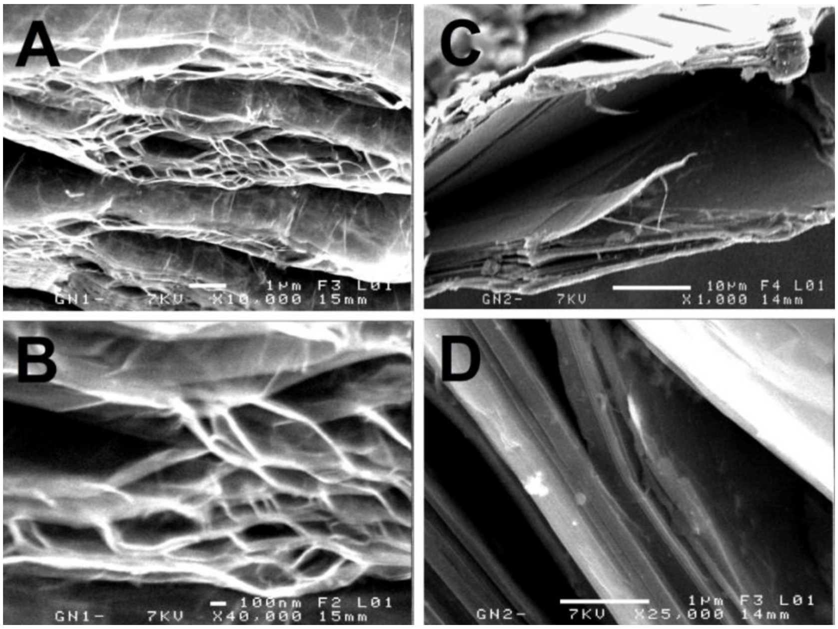

Fig. 1. SEM imaging of flakes (A and B) of natural Ceylon graphite partially exfoliated in DMF/$TMABF_4$ (at a mercury pool, see text). For comparison, images (C) and (D) display graphite samples not subjected to pre-exfoliation.