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Glassy carbon electrodes doped by surface graphite nano-flakes Multi-step redox transitions functionalization

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ABSTRACT

A simple mechanical deposition of soft graphite (natural from Ceylon or highly oriented pyrolytic graphite, HOPG) onto properly polished glassy carbon surfaces permits, after sonication, their profound and stable modification by coverage with graphite nano-particles (NP size ≤ 100 nm). Those electrode surfaces (tested in organic polar solvents containing tetraalkylammonium salts, TAA^+X^-) disclosed unsuspected features in cyclic voltammetry: the appearance of several redox steps whose potentials as well as shape and relative size are reproducible and stable. These features were found to be specific of each TAA^+ cation. The stability of those layers was studied as a function of the cation bulkiness (from tetramethyl- to tetraoctylammonium) and the expected consequences of the exfoliation of the deposited material. Redox doping of NPs at these versatile surfaces permits redox catalysis of the reduction of alkyl halides RX via the concomitant generation of free alkyl radicals allowing chemical functionalization of these NPs.

1. Introduction

The interest for all kinds of carbon remains high in electrochemistry. For long, the use of glassy carbons (GC) as electrodes has been general [1] and often preferred to metals due to a larger hydrogen overvoltage. Those electrode materials, supposed to be non reactive towards the products issued from electrode reaction, could be considered as an almost ideal material, especially in the field of the cathodic scission of carbon–halogen bonds [2]. The addition of free aryl [3] and alkyl radicals [4] onto glassy carbon permitted one to (re)consider that GC was finally a composite material embedding graphite and fullerenes nano-particles that endow GC with its chemical reactivity.

The intensive research on graphene recently reactivated interest for graphite [5] already developed in electrochemistry, not only for energy storage (lithium batteries) [6] but also for elaborating new reducing materials by the potentially controlled ion insertion, especially using tetraalkylammonium salts TAA^+X^- that permit one to reach very negative potentials (<-3 V vs. Ag/AgCl) in aprotic polar solvents. This way, the mechanism of ion insertion was demonstrated and the level of filling of pores was found to be strictly dependent on the potential of polarization of graphite [7]. The conditions of the process leading to almost total exfoliation of graphite by TTA^+ cations have been described [8]. The direct formation of a single graphene plan from a well mastered exfoliation was tentatively achieved [9,10].

We wish now to explore another way in graphite electrochemistry by means of a simple mechanical deposition of graphite onto smooth GC. The proposed method permits the formation of quite thin films, giving very reproducible responses in electrochemistry and stable (also under prolonged sonication) at least with TAA^+ of small radii (tetramethyl- and tetraethylammonium ions). The cathodic reduction of graphitic films leads to successive series of well reproducible redox steps whose feature is specific to each TAA^+. The amounts of electricity concerned in the successive charge processes are quite small and very reproducible. The concentration of the dispersed charge with different electrodes roughly corresponds to 10^{-9} to 5×10^{-9} mol cm^{-2} if the basic area of the substrate GC is taken into account. The building of such surfaces that exhibits a succession of reduction steps between -1.7 V and -2.3 V vs. Ag/AgClsat allows one to achieve surface redox catalysis (for example, indirect reduction of alkyl and aryl halides RX and ArX) and the subsequent grafting of free radicals R• generated at the doped graphite interface. On the contrary, bulky cations such as tetra-*n*-hexyl and tetra-*n*-octylammonium may lead, after few scans, to simplified redox responses, which is possibly due to strong and efficient (almost total?) graphite exfoliation processes under different conditions of formation of the graphene layers.

2. Experimental section

Voltammetry was essentially carried out in 0.1 M solutions of tetraalkylammonium salts (TAAX) such as tetramethylammonium ($TMABF_4$), tetraethylammonium ($TEABF_4$), tetra-*n*-butylammonium ($TBABF_4$), tetrafluoroborates, tetra-*n*-hexylammonium iodide (THAI), and tetra-*n*-octylammonium chloride (TOACl) in reagent grade dimethylformamide (DMF). Experiments described in this work needed no special treatment of electrolytic solutions.

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Potentials are referred to the aqueous Ag/AgCl/KCl$_{(sat)}$. Voltammetric and coulometric measurements were performed using three-electrode cells separated with a fritted glass. The electrochemical instrumentation has been previously reported [4].

Glassy carbon (GC) electrodes used as substrates for graphite deposition had a geometric area of 7 mm^2. All carbon samples were purchased from Tokai Carbon Co (code: GC Rod).

Prior to being modified by deposition of graphite, the electrodes were carefully polished, first with silicon carbide paper (Struers 500) and then with Norton polishing paper (type 02). Then, natural graphite (from Ceylon) or highly oriented pyrolytic graphite (HOPG) disposed on a planar surface (glassy cardboard, polished agate, or vitreous plate of carbon) was rubbed onto the electrodes until shiny carbon surfaces were obtained. Then, the electrodes were sonicated for 5 min in water and rinsed three times with acetone.

3. Results

3.1. Morphology of graphitized carbon surfaces after a preliminary charge in TMA$^+$

After graphite deposition, the GC plates were sonicated, and then reduced at a fixed potential (−1.80 V, the beginning of the cathodic charge) in DMF containing 0.1 M TMABF$_4$. Fig. 1 exhibits two well different structures. In A, in the absence of a preliminary reduction process, the deposition of large graphene layers was observed. Contrariwise, after reduction of those layers, swelling and insertion of tetramethylammonium ions, graphene nano-structures appear, notably in images B and C. Large amounts of graphene flakes (average size ≈ 100 nm) are clearly seeable on the external surface. In some parts of the sample (image C), one may discover the presence of a porous layer, quite certainly very reactive to the insertion process in the course of successive reduction processes. In all cases, those SEM images display flat surfaces showing a quite homogenous and dense deposition of graphite nano-structures. These graphite deposits exhibit an electrochemical behavior very well different from that of the galvanostatic charge of HOPG crystals (Fig. 2, inset) that shows the progressive filling of graphite inter-planes by TMA$^+$ concomitantly with the potential decay of the sample. The reduction starts at −1.75 V and plateaus at −2.1 V and −2.4 V to mark stoichiometries corresponding to Me_4NC_{96} and Me_4NC_{24}. Similar features could be obtained with NBu_4^+, but exfoliation with the cations of bigger size made the results more questionable.

3.2. Intrinsic voltammetries of modified GC surfaces according to process A

Voltammetry of the surfaces modified by natural graphite is displayed in Fig. 2. The shape of responses of the NP in contact with the solutions of TEA$^+$ and TBA$^+$ in DMF does not depend on the number of scans and therefore it is proposed that the global redox reaction does not alter much NPs in the course of successive swelling/discharge cycles. The use of TBABF$_4$ as a salt leads to a very reproducible succession of reduction steps marked *a* to *f* (the largest *a*, *c*, *e*, and *f* steps have peak potentials equal to −1.76, −1.89, −2.02, and −2.22 V, respectively). By far the largest one (cathodic peak f) corresponds to a charge of 1×10^{-4} C. Those steps were shown to be diffusion-controlled, quite certainly owing to the diffusion rate of TAA$^+$ inside NPs during the charge process. The oxidation process does not display very sharp peaks; but on the contrary, a large global anodic process appears possibly reforming the status (*structure*) of the initial NP. Only two peaks emerge, *x* and *y*. The use of HOPG as a modifier of GC led to comparable results with two large cathodic peaks at −2.1 and −2.4 V.

Contrariwise, voltammetry of TEA$^+$ (displayed in Fig. 2) could correspond to a “classic” pattern of insertion, successive cathodic waves, and several anodic peaks *x*, *y*, and *z* (extremely reproducible) that emphasize the probable occurrence of an almost reversible redox process.

Lastly, the use of bulky TAA$^+$ offers a very intriguing alternative to the behavior described above, as displayed with TOACl (bottom of Fig. 2). It can be seen that the cathodic currents with TOA$^+$ are remarkably smaller,

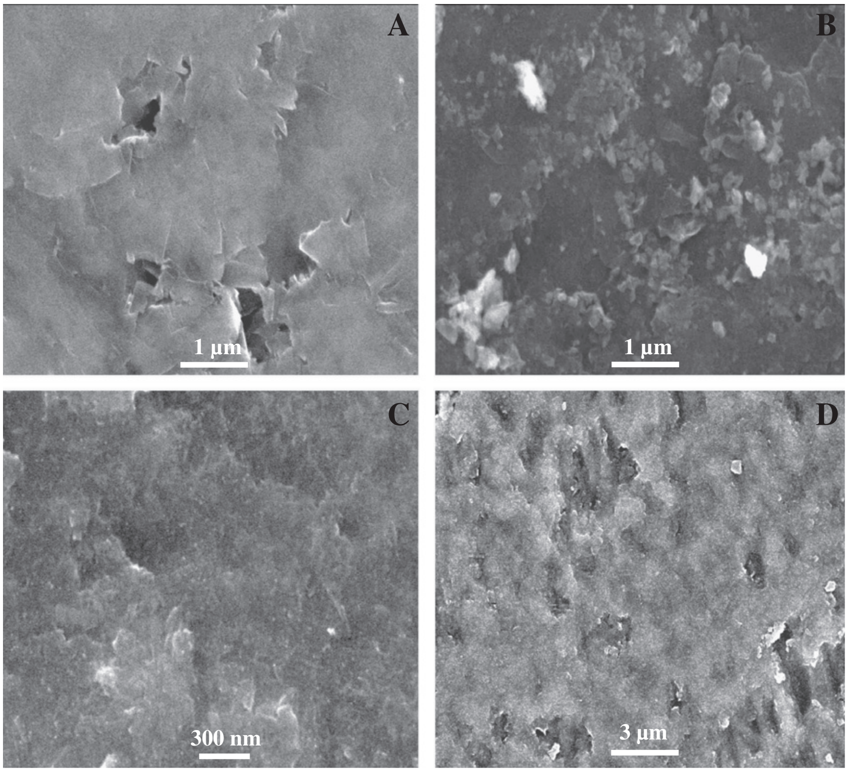

Fig. 1. Mechanical deposits of natural graphite nano-particles (see details on procedure in Section 3.1) onto polished glassy carbon sheet as substrate (image A) and then, after formatting by electro-reduction in DMF containing TMABF$_4$ at −1.75 V (different aspects of surface in B, C, and D). Total charge: 2×10^{-2} C cm^{-2}.