



Short communication

The silver–graphene electrode. Building, stability, and catalytic efficiency

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ABSTRACT

The cathodic polarization of smooth silver surfaces covered with natural graphite in dimethylformamide or acetonitrile containing tetraalkylammonium salts induces a spectacular exfoliation process followed by the release of almost all deposited graphite particles; the ablation goes practically to the last (few) layer(s) of graphene in immediate contact with Ag. Another efficient method to form such interesting interfaces consists in the deposit of graphite micro-flakes (pre-exfoliated at a mercury pool at -2 V) by rubbing them onto small size Ag electrodes. The as-prepared silver/graphite surfaces are stable and exhibit reproducible voltammetric responses related to the reduction (doping) of remaining graphene layers. Their nature and intensities (not related to diffusion and quasi perfectly proportional to the scan rate) essentially depend on the size of the concerned TAA⁺ cations. Total amounts of electricity involved in reduction/oxidation are quite stable and can be assigned to the doping of remaining graphene layers attached to Ag. The average coverage based on TAA⁺ mono-layer formation was estimated to be $< 10^{-9}$ mol cm⁻². Chemical modifications of these carbon layers and first experiments concerning catalytic properties assigned both to graphene and Ag are presented.

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1. Introduction

Glassy carbon (GC) is typically used as a convenient and popular electrode material well appropriate to the cathodic domain [1], especially at $E < -1.8$ V in polar organic aprotic solvents. However, GC remains a complex material, depending on the mode of its manufacturing and presents the particularity to contain micro-inclusions (*i.e.*, specks of graphite and fullerene-like formations [2,3]). On the other hand, despite their low hydrogen over-voltage, platinum, gold, and palladium electrodes [4] are quite convenient and useful in many applications, in particular for electrocatalysis. In a recent past, smooth silver electrodes displayed interesting possibilities in the field of catalytic scission of carbon–halogen bonds [5,6]. Interestingly, silver cathodes were applied for de-pollution even in aqueous media [7,8]. Last findings and uses of new heterogeneous electrodes based on silver, copper and palladium alloys were also recently published [9–11].

Herein, we report a new model of electrode that allies silver and graphene both with their specific catalytic capabilities. As recalled above, silver presents a general capacity for activating the scission of carbon–halogen bonds while graphene—as was recently shown within a wide range of potentials is maybe better than a wide interval of potentials—combines the possibilities of trapping free radicals by its large unsaturated network and enabling, beyond its charging potential

(< -1.7 V), S_N2 reactions with electrophilic organic species. Preparation of this composite electrode, its characteristics and its reacting capacities are described together with preliminary experiments on catalysis and grafting of redox groups to highlight a few potentialities of this promising material.

2. Experimental section

Electrochemical analyses were performed in 0.1 M solutions of tetraalkylammonium salts (TAAX) such as tetramethylammonium (TMABF₄), tetraethylammonium (TEABF₄), tetra-*n*-butylammonium (TBABF₄), and tetra-*n*-octylammonium tetrafluoroborate (TOABF₄), dissolved in upper grade dimethylformamide (DMF). Measurements were performed using a regular three-electrode cell with a porous glass frit separating the working and auxiliary compartments. All potentials are referred to an aqueous Ag/AgCl/KCl_(sat). The electrochemical instrumentation has been previously reported [9]. Silver electrodes made of Ag wire (\varnothing 1 mm²) sealed in a Pyrex tube, were carefully polished first with coarse (Struers 500) and then with finer (Struers 1200) silicon carbide polishing paper. Prior to being deposited onto the smooth Ag surface, natural graphite (from Ceylon) was partly exfoliated by electrolytic method [12]. Pre-conditioned graphite was wetted with acetone to form a slurry prior to the deposition onto Ag. Alternatively, micro-flakes of graphite can be deposited on Ag using a small rubber eraser, which enables also a nice and reproducible deposit. Characterization of the as-produced layers was performed by SEM using a JEOL JSM–7600F microscope.

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3. Results

First, graphite was pre-electrolyzed in DMF at a mercury pool at -2.1 V with a passed charge of 12 C per gram of carbon. This electrochemical conditioning produces a soft material very convenient for an easy coverage of silver surfaces. A moderate swelling of graphite can be checked by SEM investigation (Fig. 1A). Comparison of this material with non-treated graphite shows this pre-conditioning to be very advantageous since an almost total exfoliation is sought for the final modification of silver. Slurry of this “expanded” material was then deposited onto the Ag surfaces. After drying, electrode were electrified by means of voltammetric scans or fixed potential electrolyses ($E < -1.8$ V). Note that the deposit of graphite flakes can be also achieved by a precise contact of a rubber eraser and the electrode (Fig. 1D). Macroscopically, such electrochemical treatments induced the exfoliation of graphite and the subsequent release of almost all carbon deposit. Recurrent scans in DMF/TMABF₄ allowed visualizing the whole process (Fig. 1B). After a huge reversible step in the first scan, a progressive decay of the current occurs until merging of fine reduction steps (Fig. 1C). Basically, the deposits prepared according to these two procedures show quite reproducible voltammograms upon a large number of recurrent scans. For example, TEA⁺-based salts (triflate, BF₄⁻ and ClO₄⁻) exhibit specific voltammetric responses for which no noticeable decay of current is observed during repetitive cycles (Fig. 2A). For $E > -2.2$ V, three reversible charge processes are observed and each cathodic step has a corresponding anodic discharge step. The currents are proportional to the scan rate at least up to 1 V s⁻¹ (Fig. 2B). Similar features are observed with THA⁺ and TOA⁺ although only one step is seen (Fig. 2C). Very thin layers of graphite deposited on Ag were then formatted in DMF using different TAA⁺ salts. As the cation radii increase, the charge intensities of the peaks observed between -1.7 and -2.2 V (at a given scan rate) slightly decay while cathodic charging steps (for $E > -2.2$ V) progressively drift to more negative potentials. In moving from TMA⁺ to TBA⁺, total charges (calculated for apparent surface area 0.8 mm²) decline from 2.5×10^{-3} to 2.0×10^{-3} C cm⁻². For very bulky salts like tetra-*n*-hexyl-ammonium and tetra-*n*-octyl-ammonium, the charge value is even smaller, 1.6×10^{-3} C cm⁻². The nature of the counter anion was shown to have a minor influence.

The external graphene layer is supposedly the only reactive layer as can be concluded from a quasi absence of diffusion of TAA⁺ cations through the graphene stacks during short time lapses (a few tens of seconds maximum) of voltammetric experiments. Then, the reduction

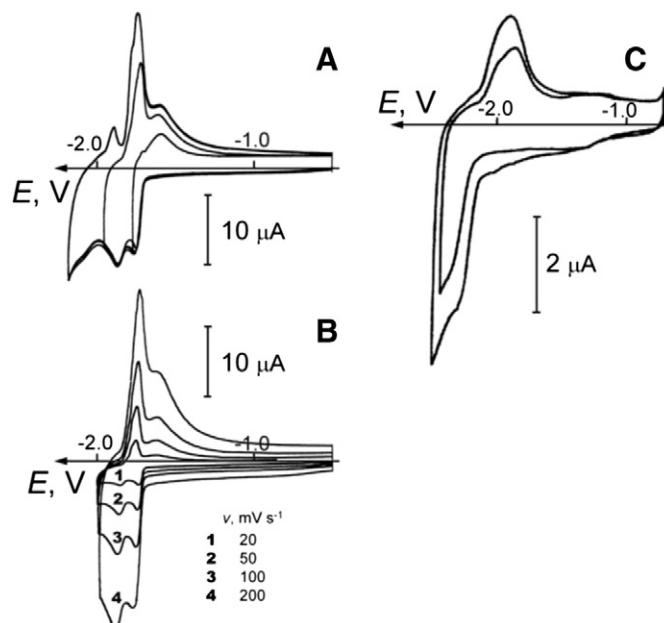


Fig. 2. Voltammetry of an Ag-graphene electrode. (A) In DMF/TEABF₄, $v = 100$ mV s⁻¹. Reverse scans after first, second and third steps. (B) Voltammograms at different scan rates. (C) Behavior of the same surface measured in DMF using tetra-*n*-hexylammonium iodide (THAI) at 0.1 M ($v = 50$ mV s⁻¹).

peaks with each TAA⁺ salt ($E < -1.8$ V) could be perceived as reflecting the formation of different graphene poly-anions assimilated to surface modifications, at least for a given potential. Therefore, each cathodic (or anodic) peak should correspond to a given coverage level. The position of TAA⁺ ions would be seen as statistically distributed, as a sort of soft-grafting without fixed locations on the graphene network. Then, assimilating cathodic peaks to the successive reduction steps could permit to quantify the coverage levels of TAA⁺ ions. It is easy to find, at least for the first steps (assuming one-electron transfer at each step), the coverage level and to rely it to the bulkiness of the corresponding cation as far as ion mono-layers are concerned. Thus, the values for TMA⁺ and TEA⁺ were found to be 5×10^{-9} and 8×10^{-9} mol cm⁻², respectively. These rather high values could be due to high roughness of the graphene layer, to the edge effect and possibility to some diffusion through the graphene

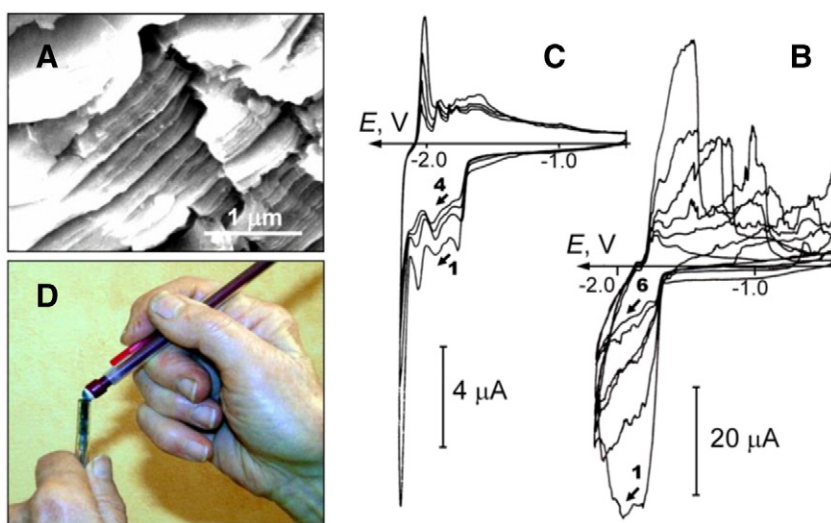


Fig. 1. Electrochemical preparation of an Ag-graphene electrode by progressive exfoliation under the conditions of cyclic voltammetry. (A) SEM image of pre-exfoliated graphite deposited onto silver (0.8 mm²). (B) Corresponding CVs of this electrode measured in DMF/TMABF₄, first six scans ($v = 50$ mV s⁻¹). (C) Final four scans obviously different from the first one displayed in B. (D) Deposition of graphite on Ag electrode with a rubber eraser (see experimental section).

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