Comparative study of different types of graphenes as electrocatalysts for ascorbic acid

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A comparative study regarding the electrocatalytic activity of graphene oxide (GO), chemically-reduced graphene oxide (cGO) and graphene produced by direct liquid exfoliation (dG) is presented. Sensors were developed by modifying glassy carbon (GC) electrodes with GO, cGO and dG and ascorbic acid was used as a pilot analyte. GC GO electrodes offer substantially lower oxidation overpotential, up to 350 mV, compared with GC/cGO, GC/dG and unmodified GC electrodes. In addition, the different carbon-to-oxygen atomic ratios in GO, as it occurs depending on the synthetic route, were found to have a remarkable effect on the performance of the sensors. Reduction of GO was achieved by immersing the modified electrodes into a stirred solution of NaBH4 for 10 min at room temperature. This process was used alternatively of the time consuming and laborious process of hydrazine, and its effectiveness was confirmed by cyclic voltammetry and electrochemical impedance spectroscopy. Analytical utility of the sensors is demonstrated.

1. Introduction

Carbon materials have been widely used in electroanalytical chemistry due to their low cost, wide potential window, relatively inert electrochemistry and electrocatalytic activity for a variety of redox reactions. Graphene, a one-atom-thick sp2-bonded carbon 2-D sheet, has recently attracted the scientific interest, due to its fascinating physical properties [1–5]. It is considered as the basic building block for carbon-based materials of all other dimensionalities, as it can be stacked into 3-D graphite, wrapped up into 0-D fullerenes and rolled into 1-D carbon nanotubes, which have been, so far, utilized in electrochemical sensors. In the latter application, electrode modification is accomplished from dispersive graphene materials, which include monolayer and few-layer graphenes.

Graphene has been used to fabricate electrochemical sensors for ascorbic acid [6], β-NADH [6,7], H2O2 [7], hydrazine [8], and chemical-warfare agent [9], as well as biosensors [10]. In all the aforementioned works, graphite oxide was primarily prepared by oxidizing powdered graphite [11] and then, after reduction by means of electrochemical or chemical routes, reduced graphene oxide or graphene (fully reduced form), were used as electrocatalysts for specific applications. Reduction of graphene oxide to reduced graphene oxide is a common step that is performed in order to increase the conductivity of the catalyst. Indeed, reduced graphene oxide exhibits resistance from 100 kΩ to a few MΩ that is approximately four orders of magnitude lower than non-reduced (pristine) graphene oxide [12]. However, results presented in this work show that, sensors based on graphene oxide (GO) offer substantial lower oxidation overpotential compared with sensors based on chemically-reduced graphene oxide (cGO) or pure graphene sheets (dG), towards ascorbic acid (AA). An additional finding of great electrocatalytic interest is that the sensitivity of GO-based sensors is greatly affected by the carbon-to-oxygen (C/O) atomic ratio in GO, as it occurs depending on the synthetic route. Graphene oxide catalysts, designated as (GO1) and (GO3) were prepared from the same starting carbon material after single and triple acid treatment, respectively.

2. Experimental

Graphite oxide was synthesized using a modified Staudenmaier’s method [13,14]. In a typical synthesis, 10 g of powdered graphite (purum, powder <0.2 mm, Fluka) were added to a mixture of 400 mL of 95–97% H3SO4 (Riedel-de Haén) and 200 mL of 65% HNO3 (Fluka), while cooling in an ice-water bath. 200 g of powdered KClO3 (Fluka) were added to the mixture in small portions under continuous stirring and cooling. The reaction was quenched after 18 h by pouring the mixture into distilled water and the oxidation product was washed until the pH reached 6.0, and finally dried at room temperature. According to elemental analysis data, the C/O atomic ratio of the resulting product (graphite oxide, 1) is 2.6. The above procedure was repeated three times and graphite oxide, 3 with a C/O atomic ratio of 2.2 was synthesized.

Stable suspensions of 1.0 mg mL−1 GO1 and GO3 were prepared by mixing the appropriate amount of the catalysts in double distilled...
water (DDW). After vigorous stirring for 1 h, suspensions were sonicated (50 W) for 2 h. dG suspension (0.1 mg mL\(^{-1}\)) was prepared by liquid-phase exfoliation of graphite (purum, powder ≤0.2 mm, Fluka) using pyridine solvent, as reported elsewhere [15].

Prior to the modification, glassy carbon (GC) electrodes (Ij Cambria) were polished with aluminum oxide (0.01 μm), rinsed thoroughly with DDW, sonicated for 1 min in DDW, rinsed with DDW and dried under Ar. Modification of the GC electrodes was achieved by dropping 10 μL of GO1, GO3 or dG suspensions over the active surface and left the solvent to evaporate overnight. Chemical reduction of GO films was achieved by immersing the modified electrodes into a 1.0 mg mL\(^{-1}\) NaBH\(_4\) solution for 10 min under continuous stirring at room temperature.

All electrochemical measurements were performed with the electrochemical analyzer PGSTAT12/FRA2 (Metrohm Autolab), using a three-electrode electrochemical cell. Modified or bare GC electrodes were used as working electrodes and a platinum wire served as the auxiliary electrode. The reference electrode was a Ag/AgCl/3 M KCl (Ij Cambria) electrode and all potentials reported hereafter refer to the potential of this electrode. EIS spectra were recorded over the frequency range of 10\(^{-1}\) to 10\(^5\) Hz, using a single sinusoidal excitation signal (10 mV rms), superimposed on +190 mV.

3. Results and discussion

In graphene sheets, electron transport, mostly, takes place on the edges of them, while electron transfer processes from the plane of a graphene sheet is almost zero [4]. The oxygen-containing (hydroxyl, carboxyl, and epoxy) groups have a great influence on their electrochemical and electrocatalytic properties; however, there is a controversy over whether this influence enhances or inhibits the heterogeneous electron transfer rates [4]. The influence of the initial oxygen content as well as the influence of the chemical reduction on the electrocatalytic properties of GO1 and GO3 was examined.

3.1. Performance towards hexacyanoferrate (II)/(III) redox couple

CVs obtained for both materials, before (Fig. 1A) and after (Fig. 1B) their chemical reduction, reveal that the material with the lowest oxygen content, that is GO1, promotes, in both cases, the electrocatalysis of the reversible, outer-sphere redox couple. The recorded peak currents were greater for GO1 and crGO1 compared with those recorded for GO3 and crGO3, respectively, even though the observed differences are noticeable, mostly, in the non-reduced materials-based electrodes. This behavior can be attributed to the fact that reduction process leads to the same, negligible oxygen content (<3–4% by weight) [16] in both reduced materials. Recorded CVs reveal also that chemical reduction has a positive impact on the electrocatalytic properties of both materials. Reduced GO-based electrodes exhibit a well-defined pair of peaks, while in the case of non-reduced GO-based electrodes the intensity of the faradic currents is significantly lower. The effectiveness of the reduction process was also supported by the Nyquist plots presented in Fig. 1C. At GC/GO1 electrodes, \(R_{ct}\) values were increased from 40 Ω (\(R_{ct}\) value that observed at bare GC electrodes) to 878 Ω, while after chemical reduction, the (almost) deoxygenated surfaces exhibited significant lower \(R_{ct}\) values of 77 Ω. Lowering of the observed \(R_{ct}\) values can be attributed to the loss of the majority of the surface negative charges, as a consequence of the lower O\(_2\) content, [16] and to the improved electrical conductivity of the crGO1 films due to the restoration of a graphitic network of sp\(^2\) bonds [2–5].

3.2. Performance towards ascorbic acid

On the other hand, CVs obtained using GC/GO1 electrodes (Fig. 2A) show that the modification of the GC electrodes with (non-reduced) graphene oxide results in a significant decrease of the oxidation overpotential of AA, up to 350 mV, compared with the corresponding values observed for bare GC and GC/crGO1 electrodes (Fig. 2A, B). GC/GO3 electrodes (Fig. 2A) exhibit a similar behavior; however, the intensity of the electrocatalytic current is significantly lower. The oxygen-containing species present on the graphene oxide sheets, which are generated during acid treatment, seems to act as a regulator of the observed electrocatalytic behavior. Oxidation of AA is an inner-sphere, non-reversible reaction and the electron transfer kinetics is sensitive to the electrode surface properties [17,18]. Heterogeneous charge transfer for the oxidation of the endiol groups arises from a proton-coupled electron transfer mechanism [4]. Presumably, the oxygen-containing groups withdraw two protons from the endiol.
The influence of the C/O ratio upon the electrochemical behavior of graphene is more clearly depicted when the same electrocatalytic experiments towards AA were performed after GO1 and GO3 catalysts being chemically-reduced. As it is shown at the CVs (Fig. 2B) recorded for GC/rGO1 and GC/rGO3 electrodes the electrocatalytic properties of the reduced graphene oxides become less favorable, as AA is oxidized at such high overpotential as in the case of the unmodified GC electrodes. Similar results were also, obtained at GC electrodes being modified with dG catalyst (Fig. 2B), which was used as a control material in order to exclude reasons associated with a possible negative effect of the reduction process to the catalyst or to the electrode or to both of them. dG is an almost defectless material, which bears no oxygen-containing groups as it was prepared through π–π stacking from the solvent molecules to the carbon layers.

Finally, the response of the GC/GO1 sensors was tested over the concentration range 0.1–10 mM AA. As shown in Fig. 3, good linearity was achieved \( (r^2 = 0.996) \), while the sensors exhibited excellent working stability for over 50 runs.

4. Conclusions

The C/O atomic ratio at graphene oxide, chemically-reduced graphene oxide and pure graphene sheet-based catalysts appears to be a critical parameter affecting their electrochemical characteristics and electrocatalytic potency.

Towards an outer-sphere reversible redox couple as hexacyanoferrate (II)/(III), rGO- and dG-based electrodes exhibit a higher catalytic activity compared with that observed at GO-based electrodes. For both non-reduced and reduced materials, the catalyst with the lowest oxygen content (GO1), exhibits the highest catalytic activity.

Towards an inner-sphere non-reversible reducing analyte as AA, rGO- and dG-based electrodes exhibit a slightly higher catalytic activity, however, no benefit regarding the decrease of the required oxidation overpotential was observed. On the other hand, GO-based electrodes offer a substantial decrease of the oxidation overpotential up to 350 mV. Indeed, the catalyst with the lowest oxygen content (GO1) exhibits sufficiently high catalytic currents as well, and thereby fulfills the criteria for use in the fabrication of chemical sensors for AA.

References