Systematic study of the correlation between surface chemistry, conductivity and electrocatalytic properties of graphene oxide nanosheets

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ABSTRACT

A main advantage of graphene oxide (GO) over other materials is the high tunability of its surface functional groups and of its electric conductivity. However, the complex chemical composition of GO renders difficult to unravel the correlation between structural and electric properties. Here, we use a combination of electron spectroscopy and electrochemistry to correlate the surface chemistry of GO to its electrical conductivity and electrocatalytic properties with respect to two molecules of high biological interest: β-nicotinamide adenine dinucleotide (NADH) and vitamin C. We demonstrate that the electrocatalytic properties of the material are due to hydroxyl, carbonyl and carboxyl groups residues that, even if already present on pristine GO, become electroactive only upon GO reduction.

The results of this study demonstrate the advantages in the use of GO in amperometric biosensing and in enzymatic biofuel cells: it allows the oxidation of the target molecules at low potential values, with a sensitivity >15 times higher with respect to standard, carbon-based electrode materials.

Finally, we demonstrate that the right amount of chemical groups to achieve such high performance can be obtained also by direct electrochemical exfoliation of bulk graphite, without passing through GO production, thus rendering this approach suitable for cheap, large-scale applications.

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1. Introduction

Graphene is one of the materials most studied nowadays for its numerous potential applications, including energy storage and sensing [1—5]. Outstanding performance of this nanosized material comes from its peculiar physico-chemical properties, such as high surface area (>2600 m²/g for single-layer graphene), excellent thermal and electric conductivity and high mechanical strength.

Large-scale production methods of graphene are currently used also at industrial level [6]. However, they usually yield a mixture of graphene multilayers, with a variable amount of monolayers. The only method to achieve quantitative exfoliation of graphite down to single layers is by chemical oxidation, which yields graphene oxide (GO) solutions mostly composed of monolayers of carbon nanosheets [7,8]. The stability of GO suspensions is due to the high number of oxidized residues on the carbon surface; they favour the stability of GO in different solvents, water included, but render the material poorly conductive [9,10]. Due to its highly defective nature, GO has long been the underdog of the graphene family. However, this prejudice is now being challenged and GO is used for many interesting potential applications.

GO can be reduced by thermal, chemical and electrochemical procedures, in order to partially remove the oxidized functional groups and to re-establish sp² structure of the material. The material obtained is generally referred to as 'reduced graphene oxide' (RGO). Among the different methods used to such a purpose, the electrochemical approach allows fine tuning of the reduction level of the material, finally conditioning the surface chemistry and degree of interaction between adjacent graphene foils [11—13]. Correspondingly, the electrical conductivity of GO may be tuned from insulating

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to highly conductive [8,14], and the surface chemistry from highly hydrophilic to hydrophobic character [15]. Electrochemical methods can be also used for controlled functionalization of graphene nanosheets [16] as well for production of graphene-based electrodes [16] or of composite foams [17]. In recent years, electrochemical procedures have also demonstrated to constitute suitable tools for mass production of graphene from graphite [7,18] at industrial level.

Although it is well established that the elimination of oxidized functionalities improves the conductivity of the material [11], it was recently found that the residual oxidized groups, not removed by the reducing process, play a key role in the electrocatalytic properties of GO, as an example in favouring the electrochemical oxidation of gallic acid [13]. Electrochemical techniques are thus ideal to study both conductivity and electrocatalytic performance of GO at different degrees of reduction.

Even if several published works tried to study in detail the actual role played by the different functional groups on carbon nanosheets in the electrocatalytic performance of graphene, a clear explanation is still missing. The scenario is complicated by the lack of a definition of the chemical structure of the specific graphene used in many papers and by the possible presence of residual heavy metal ions coming from the synthetic procedure, that can themselves induce electrocatalytic processes [19].

In this work we deposited GO nanosheets on commercial screen-printed electrodes (SPE), typically used for electrochemistry. The GO was then reduced to various degrees by applying an electrochemical potential, in order to study the role of the different oxygen functional groups present on the nanosheets in the electrocatalytic properties of the material, at the basis of its actual application. For such a purpose, two particular chemical species of biological interest were used as the benchmarks: nicotinamide adenine dinucleotide (NADH) and ascorbic acid (AA), also known as vitamin C. As such, they constitute quite interesting benchmarks to test the electrocatalytic performance of the material, due to overvoltages affecting their electrochemical oxidation at bare surfaces [20,21]. From an applicative point of view, they constitute two important chemical species that require to be detected in many biological frames by rapid and simple analytical systems. In particular, AA is one of the most important vitamins present in many biological and food matrices, whereas $NADH/NAD^+$ redox couple constitutes the cofactor of many oxido-reductase enzymes. The possible occurrence of electrocatalytic process in charge of this latter species may lead to quite efficient amperometric biosensors for a wide number of chemical species constituting the substrate of a defined enzyme [20] and to enzymatic biofuel cells [22–24].

GO films have been used as such or after *in situ* electrochemical pre-treatment at fixed negative potentials. Such a pre-treatment leads to formation of RGO films with increasing electrical conductivity, related to a decreasing number of hydrophilic oxygen groups on its surface. The electrochemical and electrocatalytic performance of graphene films was correlated to the functional groups present at the material surface, measured by X-ray photoelectron spectroscopy (XPS). To understand the effect of oxygen-based functional groups on the performance of graphene, we also chemically modified the graphite electrode surface by electrochemical oxidation/activation of the surface [25] and subsequent deposition of hydroquinone (HQ) and catechol (CT) molecules.

The tunable electrochemical reduction of GO allows the obtainment of the right amount of defects to foster the electrocatalytic oxidation of both NADH and AA at low potential values.

The right surface chemistry and the good electrocatalytic performance can be achieved also skipping completely GO preparation-reduction steps, by direct use of electrochemically exfoliated graphene oxide (EGO). This material, directly obtained by

electrochemical oxidation and exfoliation of bulk graphite, is more suitable than GO for large scale industrial applications because it can be obtained at low cost and high speed, without using the harsh chemical or solvents necessary for the production of GO or of graphene [7,16,17,26].

2. Experimental section

2.1. Chemicals

All reagents were of analytical grade and supplied by Sigma-Aldrich.

GO was prepared from graphite flakes (Sigma Aldrich, 99% pure, <150 μm) using a modified Hummer's method, as described in Ref. [27]. The GO water suspension produced was then subjected to dialysis to remove residual metal ions and acids. The amount of residual Mn, which is the most abundant metal introduced in the synthetic process, resulted lower than 2.7 ppm, as determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, XSeries II Thermo Fisher Scientific). The purified GO dispersion was sonicated for about 1.5 h, and unexfoliated GO was removed by centrifugation (3000 rpm, 5 min). The concentration of the resulting GO aqueous suspension was 4.0 g L^{-1}.

A stable suspension of EGO in DMF was prepared from graphite flakes (Sigma Aldrich, 99% pure, <150 μm) according to the method previously reported in Ref. [26]; the use of the same commercial graphite stock for EGO and GO production allows a correct comparison between the performance of the different materials. Due to the low stability of SPEs in DMF, EGO was transferred into an isopropyl alcohol (IPA) solution.

In order to allow a direct comparison between EGO and GO modified electrodes, both materials were deposited on the electrodes from a 0.5 g L^{-1} solution in IPA with a loading of 0.020 ± 0.002 mg cm^{-2}.

2.2. Instruments

All electrochemical measurements were performed using a computerized Autolab PGSTAT 30 (Ecochemie, Utrecht, The Netherlands). SPEs were acquired from DropSens (Llanera, Asturias, Spain) and consisted of a 4 mm diameter graphite working electrode, a graphite auxiliary electrode and an Ag pseudo-reference electrode.

The XPS measurements were performed on each deposit with a Phoibos 100 hemispherical energy analyzer (Specs), using Mg Kα excitation source (XR-50, Specs) (photon energy = 1253.6 eV). The X-ray power was 250 W. The base pressure in the analysis chamber during analysis was 2×10^{-10} mbar.

The morphology of the working electrode surfaces was investigated by a Nova NanoSEM 450 scanning electron microscope (SEM, FEI Company) working in high vacuum conditions, equipped with an Energy Dispersive Spectrometer (EDS, Bruker QUANTAX-200).

Raman spectra of modified electrode surfaces have been registered with a Laser DXR (532 nm laser wavelength at 1 mW laser power).

Change in work function among the different electrode coatings was measured using two experimental techniques such as macroscopic Kelvin Probe (KP) and Kelvin Probe Force Microscopy (KPFM) performed under ambient conditions.

Macroscopic KP measurements [28] were performed using 2 mm diameter gold tip amplifier (Ambient Kelvin Probe Package KP020 from KP Technology Ltd, UK). The technique provides a voltage resolution of about 5 mV. Calibration of the probe was performed comparing two reference surfaces: aged gold thin film