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Full Length Article

Spectroelectrochemical analysis of HOPG surface controlled modification

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ABSTRACT

In situ Raman spectroscopy is used to characterize the changes induced by electrochemical oxidation and silver electrodeposition at the step-edge and terrace sites of highly-oriented pyrolytic graphite (HOPG) surfaces. Ag crystallites are observed to become preferentially deposited onto previously oxidized step edges, thereby leading to an enhancement of the Raman active modes of the HOPG surface. Ex situ Raman spectra recorded after HOPG oxidation exhibit clear differences for both terrace and step-edge areas of the surface. An increase of D and Dí band intensity and two well-defined D-band contributions, D_1 (at 1324 cm^{-1}) and D_2 (at 1344 cm^{-1}), are the main features observed after oxidation. This effect can be correlated with the presence of step-edge sites on the surface, and are found to be strongly dependent on the pH of the solution used in the surface electrochemical oxidation experiments.

1. Introduction

The study of the physicochemical properties of graphite is essential for understanding the properties of new carbon forms, such as graphene, fullerenes, and carbon nanotubes [1]. Recently, a noticeable increase has been observed in the number of technological developments based on aggregates of few graphite layers or graphene sheets, in which edge defects and surface imperfections play an important role [2–4]. The investigation of surface defects is, therefore, of particular relevance to the development of graphite-based nanostructures for device applications.

The surface properties of highly oriented pyrolytic graphite (HOPG) electrodes have been widely studied, mainly by the McCreery and Unwin research groups [5–8]. HOPG is a well-defined model system with an extremely uniform surface, free of metal impurities and pores. Even though electrochemical oxidation in aqueous media leads to modification of surface microstructure and reactivity, HOPG is extensively used as an electrode for the study of several electrochemical reactions [9–11]. It is also well-known that HOPG oxidation occurs most favorably on the edge of steps [7,8,12–14]. There is extensive literature indicating that the electrochemical oxidation of HOPG generates an increase in the number of oxygenated surface groups [15–17]. Pittman and coworkers demonstrated that the rise in surface oxygenated functional groups was mainly due to an increase in carboxyl (COOH) or ester (COOR) groups [18]. The need for understanding the nature of the processes by which different oxygenated functional groups are locally generated on the graphite surface, besides of their potential applications are important incentives to continue the study of these systems.

The surface chemical properties and the quantity and distribution of surface oxygenated groups play a particularly important role in the reactivity of carbon-based materials such as graphene flakes and carbon nanotubes [12,13,19]. In that sense, Fisher and coworkers have conducted experiments of Raman magnifications of carbon surfaces employing metal particles synthesized by microwave plasma chemical vapor deposition [20,21]. The study of carbon stability in the cycling of lithium batteries is a clear example of how the presence of such groups produces changes in the electronic structure of graphite and promotes the activation of heterogeneous electron transfer at the edge plane [8,22]. Additionally, some authors have found that anodic oxidation of HOPG electrodes leads to the breakdown of the graphitic microstructure and increases the step-edge density [23,24]. In recent work, the electrochemical behavior of HOPG in the presence of a redox probe has been monitored at high spatial resolution, revealing modifications on the materials surface, which have been ultimately related to changes of its local electronic and microscopic structure [25].

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Among the different methods used for surface characterization, Raman spectroscopy has been shown to provide specific information on the microstructure and properties of carbon related materials [26–29]. Raman scattering measurements are non-destructive experiments with enough sensitivity to detect different states of carbon atom hybridization at the graphite surface. The first-order dispersive modes of HOPG surfaces can be detected in the spectral region from 1000 to 1700 cm^{-1}, whereas Raman signals at approximately 1580 cm^{-1} (G band), 1324–1344 cm^{-1} (D band), and 1621 cm^{-1} (Dí band), are the main bands that should be analyzed for a proper characterization of these systems [29]. The G and D/D' bands are related to sp^2 carbon vibrations in the aromatic ring and disorder modes at the edge zone of microcrystalline sheets, respectively. In the second-order spectral region, combination and overtone bands provide complete spectral information. Furthermore, frequency values and intensity ratios of typical (or new) bands at the graphite surface have an important role in the characterization of the material surface structure [1,2,5].

Activation of metal surfaces for surface enhancement of Raman spectroscopy (SERS) has been extensively implemented as a means of enhancing Raman signals at HOPG surfaces [30–34]. Besides, coupling of these spectroscopic methods to an optical microscope has facilitated the recording of recording spectra from sites on the surface, at high sensitivity and resolution. An approach based on simultaneous combining in situ Raman spectroscopy and electrochemical measurements can also be used to gather direct information about the electrode/electrolyte solution interface [35–37].

In this paper, changes in the Raman spectra corresponding to different areas on the HOPG surface, such as those with high density of step edges (**SE**) or terraces (**T**), induced by selective electrochemical oxidation, are investigated by ex situ and in situ experiments. Oxygenated functional groups electrochemically generated at the surface are detected by the spectral differences observed between oxidized step-edge (**SEox**) and oxidized terrace (**Tox**) zones. The anodic oxidation of **SE** areas increases the susceptibility of defect sites towards silver electrochemical nucleation, and the **SE** ability to catalyze electron transfer to Ag^+ ions during the formation of silver SERS-active crystallites. This selective nucleation enables the highly sensitive detection of specific vibrational modes of the **SE** area. The most significant features, which have been found to be strongly dependent on the solution pH and electrode potential, correspond to the presence of two clearly defined contributions for the D band (1324 and 1344 cm^{-1}), and the Dí band (1621 cm^{-1}) close to the G band.

2. Experimental section

All solutions were prepared with Millipore Milli-Q water and analytical grade reagents. The electrolytic solutions employed were 0.1 M $KClO_4$ (Carlo Erba) at different pH (3, 6, and 10), and 0.1 M $KClO_4$ (Carlo Erba) + 1.0 mM $AgClO_4$ (BDH Chemicals Ltd.), for anodic oxidation of HOPG and silver electrodeposition, respectively. $HClO_4$ (Carlo Erba) and KOH (Anhedra) were used to adjust the solution pH. Aqueous solutions were degassed using high purity N_2 (Indura S.A.) before their use in experiments.

HOPG (SPI Supplies, Brand Grade SPI-1) was cleaved with adhesive tape prior to each experiment in order to have a fresh surface. All electrochemical measurements were performed in a single compartment three electrode cell with access for the confocal microscope objective. The HOPG was placed at the bottom of the Teflon cell exposing an area of 0.43 cm^2. A platinum wire ring and a saturated calomel electrode (SCE) or Ag/Ag^+ (1.0 mM) were used as counter electrode and reference or quasi-reference electrode, respectively. The SCE was employed for anodic oxidation of HOPG surface, while the Ag/Ag^+ (1 mM) electrode was utilized for silver electrodeposition experiments. The potential range is indicated in the text and figures along with the reference electrode employed in each case. The difference between the two reference electrodes used is given as $E_{Ag/Ag^+} = -0.30$ V vs. SCE.

For the recording of Raman spectra, laser radiation was focused on two different regions on the HOPG surface: plain terrace (**T**) and high density of step-edge (**SE**) areas. Oxidation of the surface was carried out with a single potential pulse at +1.1 V_{SCE} during 5 s in $KClO_4$ solutions at different pH (3, 6, and 10), thereby generating **Tox** and **SEox** areas. The spectroscopic characterization of the HOPG surface before and after oxidation was performed by conducting ex situ Raman measurements in air and at room temperature. This arrangement was required to set adequate experimental conditions for the in situ study.

Electrochemical measurements were carried out using an Autolab (PGSTAT30 ECOCHEMIE) potentiostat/galvanostat or a CH Instruments Inc. 600E potentiostat/galvanostat for the oxidation before ex situ Raman or during in situ Raman analysis, respectively.

Raman spectra were acquired with a LABRAM-HR, Horiba Jobin-Yvon Raman microscope with a 100× objective lens (NA = 0.9). The 632.8 nm (He-Ne) wavelength was used for laser excitation, with 5 mW power in order to avoid laser induced heating. The illuminated area in all Raman experiments was 1.0 μm^2 with a spectral resolution of 1.5 cm^{-1}. The acquisition time was 10 s, taking the average of 10 spectra.

Ex situ SERS measurements were performed using samples electrochemically oxidized in solutions of different pH. These spectra were represented as normalized signal intensities (by integrated area), using the G band at 1580 cm^{-1} as reference.

In situ SERS spectra of **SE** areas, on which a 50× objective lens (NA = 0.45) was specifically focused, were recorded by applying simultaneously a complex potential-time program with a series of potential steps, in which the electrode surface was firstly oxidized and then silver crystallites were electrodeposited and electrodissolved. Measurements were conducted in aqueous 0.1 M $KClO_4$/1 mM $AgClO_4$ solution at pH 3, using a Teflon cell with an *ad hoc* design for the confocal microscope configuration. The study of electroforming of Ag nanoparticles at pH 6 and 10 could not been carried out, since silver is oxidized at pH values higher to 5.5 with dissolution of particles [38,39]. For this reason, the in situ SERS study with silver particles was only performed at pH 3. In situ spectra were normalized using as reference, the symmetric stretching mode of ClO_4^- ions (932 cm^{-1}), except where absolute values are specified. Raman intensity values presented in this article correspond to the band integral area after baseline corrections and fitting based on Lorentzian functions.

Scanning electron microscopy images were obtained using a Supra 40 (Zeiss Company) FE-SEM Σigma operating at 8 kV.

3. Results and discussion

3.1. Electrochemical oxidation of SE areas

The electrochemical oxidation of the HOPG surface was carried out by applying a potential pulse at 1.1 V_{SCE} during 5 s in 0.1 M $KClO_4$ solution at pH 3.0, 6.0, and 10.0. After anodic modification, cyclic voltammetry (CV) measurements were conducted in the corresponding electrolyte solutions. Fig. 1 shows the CV for HOPG at different pH, with the potential scan ranging between −0.1 and 0.7 V_{SCE}, and starting at 0.4 V_{SCE} and proceeding in the negative direction at 0.02 V s^{-1} scan rate. Noticeable changes in the onset potential for hydrogen evolution are observed for different pH values (not shown), and the formation of oxygen-containing groups on different surface sites at potential more positive than 0.1 V_{SCE}