



Electrochemical investigation of chemical vapour deposition monolayer and bilayer graphene on the microscale[☆]



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ABSTRACT

A micromanipulator combined with a microinjection system was employed to inject micro-droplets of aqueous solutions containing redox-active species on selected areas of graphene. Chronoamperometric and voltammetric measurements were performed in order to investigate the diffusion regime established within the micro-droplets. The heterogeneous electron transfer rate for two model redox couples, $\text{Fe}(\text{CN})_6^{3-}$ and IrCl_6^{2-} were estimated on various regions of chemical vapour deposited monolayer and turbostratic bilayer graphene on the basis of the voltammetric responses. New insights are thus obtained into the electron transfer properties of graphene, which is of primary importance for its exploitation as an electrode material.

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1. Introduction

Since graphene was prepared for the first time by mechanical exfoliation of graphite in 2004 [1], many studies have been carried out to characterize the physical properties of this new material [2–5]. Although the mechanical exfoliation of graphite is still the best methodology to achieve single crystal monolayers of high quality, it is a time consuming approach and it is not compatible with the fabrication of large (i.e. greater than 1 mm diameter) samples. However, graphene can be produced in bulk quantities and good quality by chemical vapour deposition (CVD) on metallic substrates, using precursor gases such as methane or other hydrocarbons. The first attempts to prepare graphene by CVD used nickel substrates [6,7], but growth seemed to be limited by the small grain size of the metal and by the high solubility of carbon in nickel. Furthermore, graphene grown on nickel is usually characterized by the presence of multilayers at grain boundaries [8]. More recently,

monolayer graphene of better quality was achieved by CVD on copper substrates [8,9], copper being a better choice with respect to nickel because of the low solubility of carbon and the capability to grow very large grains when annealed. Inconveniently, when graphene is deposited on metals it may be difficult to distinguish its electrochemical behaviour from the substrate underneath, because extended vacancies or grain boundaries may be present, exposing metallic areas to the electrolyte. However, different methodologies to transfer graphene to insulating substrates have been developed during the past few years [8,9] and this progress has opened the way to a more systematic study of the electrochemical behaviour of CVD graphene [10].

Understanding the electron transfer properties of graphene is of primary importance for its exploitation as an electrode material, and ultimately for applications of graphene in supercapacitors or as a transparent electrode for solar cells. It also has important consequences for conventional graphite electrodes, as there is some controversy over the electrochemical behaviour of carbon: graphene provides a model system to develop the fundamental science. A report from 2011 investigates the ruthenium hexamine redox system on commercially available CVD graphene grown on nickel: the reaction was found to be quasi-reversible using cyclic voltammetry, where the entire (macroscopic) exposed area of the CVD sample was probed simultaneously [11]. The authors

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attributed the favourable electron transfer kinetics to the presence of intrinsic defects within the film and, in particular, to the role played by the presence of “graphitic islands”, which would dominate the electrochemical behaviour in the case of these commercial CVD samples as they consisted of a mosaic of monolayer, bilayer and thicker materials. The first attempts to study the electron transfer kinetics of CVD graphene transferred onto insulating substrates (oxide covered silicon wafers) were reported by Li et al. [12]. The standard heterogeneous electron transfer rate for the oxidation of ferrocenemethanol was estimated to be more than 10-fold higher for CVD graphene films than for the basal planes of bulk graphite. In this case, the authors suggested that enhanced kinetics were a consequence of intrinsic corrugations of the monolayer graphene, which are not present on atomically flat surfaces of bulk graphite. More recently, the same group of researchers used a scanning electrochemical microscope (SECM) to investigate how the heterogeneous electron transfer rate of CVD graphene films changed with the presence of defects and for different redox couples [13]. The findings suggested that ferrocenemethanol is less sensitive than ferricyanide to the presence of defects on CVD graphene, consistent with previous work on highly oriented pyrolytic graphite (HOPG) [14,15]. Further, it was found that the edges of artificially created defects, such as holes drilled using a glass tip, showed better kinetics than those found for undamaged CVD graphene. Finally, the authors proposed that different types of defect may lead to different kinetics. The heterogeneous electron transfer rate of CVD graphene transferred onto insulating substrates has also been investigated using the technique of scanning electrochemical cell microscopy (SECCM) [16]. In this case, CVD graphene was grown on Ni and transferred, through use of a polymer film, to an oxide-covered silicon wafer. The sample contained a mosaic of different layer thicknesses, with grain sizes on the order of a few microns. The use of SECCM allowed the micron-scale mapping of the oxidation current for a ferrocene-derivative (ferrocenylmethyl trimethylammonium) across the surface of the samples and correlation with the morphology of the graphene surface. Specifically, the authors stated that the heterogeneous electron transfer rate at graphene electrodes increased with the number of graphene layers.

In the present work the electrochemical behaviour of CVD graphene transferred onto oxide covered silicon wafers was directly performed in droplets of electrolyte deposited on selected areas of the films. This technique provides a viable and less expensive alternative to the use of SECM or SECCM, although it does not provide the same high spatial resolution. Droplets of aqueous solutions containing redox-active species, were deposited using a microinjection system onto the surface of CVD graphene monolayers, CVD graphene turbostratic bilayers and, as a comparison, onto platinum foils. Electrochemical measurements were performed in a three-electrode configuration, using the area of the specimen beneath the droplet as a working electrode. The findings indicate that the relationship between electrochemical activity and number of graphene monolayers is, in fact, a complex one, with contrasting behaviour being observed for the couples investigated herein.

2. Experimental

2.1. Sample preparation and characterization

Monolayer graphene films were grown on copper foils by CVD, as described elsewhere [8,9]. The copper foil was inserted in a 4 in. diameter quartz tube and kept at a pressure of 200 mTorr, with a hydrogen gas flow of 20 standard cubic centimetres per minute (sccm). The temperature was gradually raised to 1000 °C and, once the final temperature was reached, the copper foils were annealed

for 30 min, in order to increase the average grain size from a few to several hundred micrometers and to completely remove the native oxide. Successively, the precursor gas, a mixture of hydrogen and methane at flow rates of 20 and 40 sccm respectively, was introduced into the chamber and the pressure maintained at 600 mTorr for 30 min. The samples were rapidly cooled to room temperature in a hydrogen atmosphere at a pressure of 200 mTorr. The achieved monolayer graphene films were transferred onto Si/SiO₂ substrates using a methodology described elsewhere [8,9]. Bilayer graphene films were obtained by stacking a second monolayer graphene film over the first one. A Witec spectrometer (100× objective, ~0.6 mW power) at an excitation wavelength of 633 nm was used to characterize the monolayer and bilayer graphene films after transfer. At least three different spectra were collected for each sample, in at least three different sites.

2.2. Electrochemical measurements

Voltammetric and chronoamperometric measurements were performed in a three electrode cell configuration using an Ivium CompactStat or an AUTOLAB 302N potentiostat. A silver wire covered by a silver chloride coating was employed as reference electrode and a platinum wire was used as the counter electrode. Monolayer and bilayer graphene samples were connected to the potentiostat via silver paint, which was used to connect to a copper wire. A flame cleaned platinum foil (Advent Research Materials Ltd., 0.125 mm thickness, 99.99% purity) was used as a comparison for the electrochemical measurements. The reference and counter electrodes were immersed in a pipette prepared from a borosilicate capillary (1 mm outer diameter, 0.58 mm inner diameter), using a micropipette puller (Sutter P-97 Flaming/Brown Micropipette Puller). The borosilicate pipette was backfilled with the electrolyte and connected to a microinjector (PV820 Pneumatic PicoPump, WPI) which was controlled by a motorized manipulator (Siskiyou MX7630). Prior to each measurement, a droplet of electrolyte was deposited onto the sample surface using an injection pressure between 135 and 275 kPa for about 10–50 ms. In order to counteract the tendency of the droplet to retract due to the capillary action induced by the pipette, a hold pressure in the range 2–10 kPa was applied and kept constant during the measurements. Droplet diameters ranged between 20 and 200 μm. A high concentration of supporting electrolyte (6 M LiCl) was employed in order to avoid the evaporation of the droplets, which were stable for days after deposition. The K₃Fe(CN)₆ and the (NH₄)₂IrCl₆ (5 mM concentration in both case) were selected as the redox active species and used for all the electrochemical measurements described in the present work. For the electrolyte solutions the salts were purchased from Sigma–Aldrich and used as received. Water was obtained from an ELGA PureLab-Ultra purifier (minimum resistance 18.2 MΩ cm). Voltammetric responses were collected at scan rates between 100 and 350 mV s⁻¹; current transients were measured by stepping the applied potential from +0.9 V to +0.2 V in the case of K₃Fe(CN)₆ and from +1.1 V to +0.6 V for the (NH₄)₂IrCl₆ every 20 s for five cycles on platinum foil.

3. Results and discussion

3.1. Sample characterization

Raman spectra for monolayer and bilayer graphene are reported in Fig. 1. D, G and 2D peaks, typical of CVD graphene, were evident for both monolayer and bilayer graphene. A Lorentz function was employed to fit the peaks, which were found to be centred at approximately 1350 cm⁻¹, 1590 cm⁻¹ and 2700 cm⁻¹ respectively. The Full Width at Half Maximum (FWHM) of the 2D peak can be

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