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Scanning electrochemical microscopy for the analysis and patterning of graphene materials: A review

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ABSTRACT

Graphene and related materials have recently emerged as outstanding materials due to a range of properties such as high mechanical strength, high electron mobility, thermal conductivity, etc. Due to their high surface area and conductivity, graphene materials have also been used for electrochemical applications such as supercapacitors, batteries, sensors, etc. Therefore, the characterization of the electroactivity of graphene materials is necessary and different electrochemical techniques such as cyclic voltammetry and electrochemical impedance spectroscopy have been widely used for this purpose. Scanning electrochemical microscopy has appeared as a unique technique that can be used to test electron transfer kinetics, electroactivity and conductivity of these materials. Even patterns can be created on graphene materials by this technique. This review aims to compile the different works performed with graphene materials and scanning electrochemical microscopy technique and provide new perspectives into the analysis of graphene materials using this technique.

Contents

1. Introduction

Since the isolation of graphene in 2004 by A.K. Geim and K.S. Novoselov [1], the number of graphene research and publications has risen dramatically. Its isolation and the groundbreaking experiments they performed with this material led to Geim and Novoselov being awarded the Nobel Prize in Physics 2010 [2]. Graphene has outstanding properties such as high electron mobility ($2.5 \times 10^5\ cm^2\ V^{-1}\ s^{-1}$), high thermal conductivity (above $3000\ W\ m\ K^{-1}$), mechanical properties (Young's Modulus (1 TPa), intrinsic strength (130 GPa), easy chemical functionalization, impermeability to gases, ability to sustain high electric current

Abbreviations: AFM, atomic force microscopy; BSA, bovine serum albumin; CV, cyclic voltammetry; CVD, chemical vapor deposition; EDOT, 3,4-ethylenedioxythiophene; EIS, electrochemical impedance spectroscopy; ERGO, electrochemically reduced graphene oxide; FeHCF, iron (III) hexacyanoferrate (II); FETs, field effect transistors; G, graphene; GO, graphene oxide; NP, nanoparticle; Pani, polyaniline; PDMS, polydimethylsiloxane; PEDOT, poly(3,4-ethylenedioxythiophene); PES, polyester; PMMA, poly(methyl methacrylate); PPy, polypyrrole; RGO, reduced graphene oxide; SECM, scanning electrochemical microscopy.

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densities, optical transparency, etc. [3]. Different applications have been pointed out in the bibliography for G materials such as: photonics and optoelectronics, flexible electronics, spintronics, sensors, energy generation and storage, biomedical applications, composite materials, to name but some [3,4]. The European Union is devoting a substantial budget (1000 million €) to graphene research with the Graphene Flagship under the Horizon 2020 programme. The aim of this research programme is "to take graphene and related layered materials from the realm of fundamental science to industrial and societal applications in the space of ten years".

The electrical conductivity and high surface area of 2630 $m^2 g^{-1}$ (theoretical value) [3] makes graphene an ideal material for electrochemical applications such as supercapacitors [5,6], batteries [6], sensors and biosensors [7,8], among others. Electrochemical properties of graphene and its electrochemical characterization has been covered in different reviews [9–12]. The techniques used for the characterization of graphene materials include CV and EIS. SECM is emerging as a unique technique that can be used for this purpose [13]. However, no review has been devoted to the characterization of G materials by this technique until now. The present review aims to fill the existing gap and provide a compilation of the work performed with SECM and G materials. This technique has been used to create patterns on graphene materials, studying electron transfer kinetics, conductivity, etc.

SECM is one of the scanning probe microscopies in which a microelectrode, as a working electrode, is positioned at an accurate distance above the substrate to obtain an appropriate response. A typical electrochemical cell consists of a microelectrode, a counter electrode and a reference electrode in a solution containing an electrolyte and the electroactive species. When a potential, sufficiently positive/negative is applied to the microelectrode, the oxidation/reduction of the electroactive species occurs at a diffusion-controlled rate on the surface of the microelectrode, and an anodic/cathodic current passes through the microelectrode. This current, $i_{T,\infty}$, attains the steady-state quite quickly and its value depends on the electroactive species concentration, C, and its diffusion coefficient, D, according to the Eq. (1):

$$i_{T,\infty} = 4nFDaC \quad (1)$$

in which "n" is the number of electrons involved in the electrode reaction, F is the Faraday constant, D is the diffusion coefficient, C is the bulk concentration of the redox mediator and "a" is the radius of the microelectrode. The steady-state current results from the constant flux of electroactive species to the electrode surface driven by a hemispherical, diffusion layer around the microelectrode. In SECM, it is the perturbation of the tip current when the microelectrode tip is brought to within a few tip diameters of a surface, which constitutes the SECM response. When the tip is brought close to an insulating substrate, the steady-state current, i_T, will be smaller than $i_{T,\infty}$ because the insulating substrate partially hinders the diffusion of the electroactive species to the tip. The closer the tip is to the insulator surface, the smaller i_T is. This effect is termed "negative feedback". However, when the tip is close to a conductive substrate under a potential capable of oxidizing/reducing the electroactive species, a flux of electroactive species from the substrate in addition to the flux from the bulk solution occurs. In this case, $i_T > i_{T,\infty}$ as the distance tip/substrate decreases; this case is termed "positive feedback". Fig. 1 shows the different situations that can take place [14].

Both positive and negative feedback effects have been theoretically dealt with and it is possible to correlate experimental approach curves to analytical expressions to determine very accurately the position of the tip with respect to the substrate surface. Approach curves recorded over a conducting substrate provide an additional measurement of the effective radius of the microelectrode tip, while those recorded over insulators provide information about the effective RG (Rg/a) of the tip, where "Rg" is the radius of the insulating part of the microelectrode and "a" is the radius of the active electrode part.

A singular aspect that makes SECM different from other electrochemical techniques, is the possibility to study unbiased samples. In this case, the potential of an unbiased substrate is not controlled by the applied voltage. On the contrary, the substrate potential, depends on the separation distance, tip potential, and other experimental factors. The total substrate current, which is the sum of the mediator regeneration current flowing at the substrate portion facing the tip and the current produced by the opposite redox reaction occurring at the substrate periphery, must equal zero at any given moment. Thus, the substrate potential continuously adjusts over the course of the feedback experiment to keep the substrate current equal to zero. This makes the feedback response at an unbiased substrate extremely sensitive to the geometry of the tip/substrate arrangement.

The comparison between the experimental approach curves I_T ($i_T/i_{T,\infty}$) vs. L (d/a) and the analytical expressions according to the theoretical model makes it possible know the electrochemical nature of the substrate. The theoretical models can be more complicated than those two limiting cases described above, which are based on pure mass transport. For example, when the rate of the $Red \rightarrow Ox + 1e^-$ reaction on the substrate is governed by the

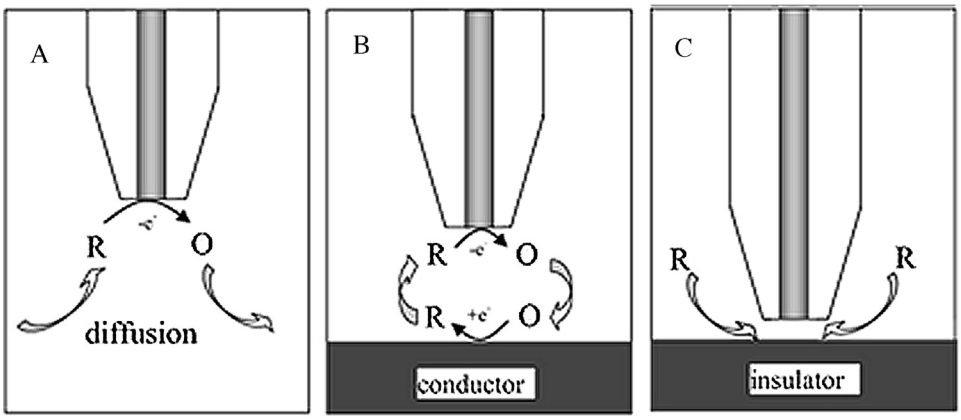

Fig. 1. Feedback mode of SECM operations. (A) the UME tip is far from the substrate. (B) positive feedback; species R is regenerated at the substrate. (C) Negative feedback: diffusion of R to the tip is hindered by the substrate.
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