



# N-doped few-layered graphene-polyNi complex nanocomposite with excellent electrochromic properties



Marta Nunes<sup>a</sup>, Mariana Araújo<sup>a</sup>, Revathi Bacsa<sup>b</sup>, Roberta Viana Ferreira<sup>c</sup>,  
Eva Castillejos<sup>d</sup>, Phillipe Serp<sup>b</sup>, A. Robert Hillman<sup>e</sup>, Cristina Freire<sup>a,\*</sup>

<sup>a</sup> REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4169-007, Porto, Portugal

<sup>b</sup> Laboratoire de Chimie de Coordination UPR CNRS 8241, composante ENSIACET, Toulouse Université, 118 route Narbonne, 31077, Toulouse, France

<sup>c</sup> Departamento de Química, Universidade Federal de Minas Gerais, Campus Pampulha, 31270-901, Belo Horizonte, Minas Gerais, Brazil

<sup>d</sup> Grupo de Diseño Molecular de Catalizadores Heterogéneos, C/ Marie Curie, 2, Cantoblanco, Madrid, E-28049, Spain

<sup>e</sup> Department of Chemistry, University of Leicester, Leicester, LE1 7RH, United Kingdom

## ARTICLE INFO

### Article history:

Received 3 December 2016

Received in revised form

22 April 2017

Accepted 2 May 2017

Available online 3 May 2017

## ABSTRACT

A new nanocomposite was obtained through the incorporation of N-doped few-layered graphene (N-FLG) into films of the electroactive polymer poly[Ni(3-Mesalen)] (poly[1]). The nanocomposite, N-FLG@poly[1], prepared by *in situ* electropolymerization, showed similar electrochromic responses to pristine poly[1], but with more well-defined redox peaks and higher current intensities, in compliance with larger electroactive surface coverage. N-FLG incorporation did not affect the electronic structure of poly[1], but decreased in 12% the molar extinction coefficient of the charge transfer band between metal and oxidized ligand, which is a promising advantage since this band is related to polymer degradation.

The N-FLG@poly[1] showed multi-electrochromic behaviour (yellow in reduced state and green/russet in oxidized states) and revealed excellent improvement in electrochromic performance compared to original poly[1], specifically an increase of 71% in electrochemical stability (loss of 2.7% in charge after 10 000 switching cycles). Furthermore, nanocomposite formation decreased the switching time for oxidation (reduction)  $\tau = 9$  s (11 s) and improved the optical contrast ( $\Delta T = 35.9\%$ ; increase of 38%) and colouration efficiency ( $\eta = 108.9$  cm<sup>2</sup> C<sup>-1</sup>; increase of 12%), for a representative film of coverage  $\Gamma = 296$  nmol cm<sup>-2</sup>. The excellent electrochromic performance improvements are attributed to the alternative conducting pathways and to morphological modifications induced by N-FLG.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Electrochromic (EC) materials typically comprise redox-active species which exhibit significant, lasting and reversible changes in colour upon the injection or withdrawal of electrons [1]. The incorporation of these materials in EC devices has attracted a great deal of attention due to potential applications, such as in intelligent optical displays, rear-view mirrors (automotive industry) and energy-saving smart windows [2,3].

Among EC materials, conducting polymers (CPs) are very attractive, mainly due to their cost effectiveness, high optical contrast and multichromism [4,5]. Nonetheless, improvements in electrochemical stability, electrochromic contrast and switching

times remain priority requirements for their successful application [6]. In order to achieve these goals, composites of CPs with nanostructures have been prepared [7–9]; these new polymeric nanocomposites (PNCs), are functional hybrid materials that typically comprise a nanometric filler, and show considerable improved properties due to synergic effects between the components [10–12].

Due to its conjugated structure, excellent electron-transport properties and versatile chemistry, graphene (G) has emerged as one of the most attractive carbon nanomaterials to be combined with CPs. With a two-dimensional (2D) sp<sup>2</sup>-hybridized carbon structure in a single-atom-thick sheet, graphene shows interesting physicochemical properties, such as a large theoretical specific surface area, high carrier mobility at room temperature, good thermal conductivity, high Young's modulus and good optical transmittance [13–15]. Several graphene/PNCs have been prepared to optimize the properties and performances of polymers for

\* Corresponding author.

E-mail address: [acfreire@fc.up.pt](mailto:acfreire@fc.up.pt) (C. Freire).

several applications, such as in supercapacitors [16–18], fuel [19,20] and solar [21] cells, sensors [22,23], lithium-ion batteries [24] and in anticorrosion coatings [25]. For EC applications, some graphene/CPs nanocomposites with enhanced EC properties have also been reported, combining polyaniline (PANI) and pyrrole-derivatives with graphene [4,26], sulfonated-graphene [27], graphene oxide [28] or reduced graphene oxide [6], as counterparts. Ma *et al.* [1] reported the preparation of an electrochromic poly-schiff base functionalised with reduced graphene oxide.

More recently, the chemical doping of graphene with heteroatoms (nitrogen, boron and sulphur) has emerged as an important approach to tailor the electrical, morphological and chemical properties of pristine graphene. Nitrogen is the most commonly used dopant, mainly due to its similar atomic radius to carbon, which prevents significant lattice mismatch [29,30]. The main differences between nitrogen-doped graphene (N-G) and pristine graphene are (i) the spin density and charge distribution on the carbon atoms (influenced by the neighbour nitrogen dopants) and (ii) the open band gap, making N-G an n-type semiconductor [31], which is very useful for nanoelectronic applications. In the electrochromism field, the application of a N-G/TiO<sub>2</sub> nanocomposite, as an efficient electrode material to improve the EC properties of polythiophene-derivative EC polymer was reported [32].

This work reports the preparation of a novel PNC made from poly[Ni(3-Mesalen)] electroactive film, designated hereafter as poly[1], and nitrogen-doped few-layered graphene (N-FLG), and the evaluation of its EC performance. The study of the EC performance of the pristine poly[1], described elsewhere [33], revealed promising EC properties, with good electrochemical stability and interesting colour changes from yellow in neutral state to green and russet (reddish-brown) in oxidized states. The preparation of the nanocomposite between poly[1] and pristine graphene flakes (GF) [34] allowed a good improvement in the EC properties, leading to more favourable switching times and better optical modulation and electrochemical stability relatively to original poly[1]. The fundamental advance reported here is that a novel PNC, N-FLG@poly[1], prepared by *in situ* electropolymerization of poly[1] in the presence of N-FLG allowed the resulting nanocomposite to clearly surpass the conductive and electrochromic properties of both pristine poly[1] and the nanocomposite with GF; the implication is that N-doping of few-layered graphene, prepared by CVD using a literature adapted methodology, had a unique beneficial effect. To the best of our knowledge, this is the first study on PNCs from the group of Metal-salen type electroactive metallopolymers and nitrogen-doped graphene.

## 2. Experimental section

### 2.1. Materials and instrumentation

The complex *N,N'*-bis(3-methylsalicylideneimine) nickel(II), [Ni(3-Mesalen)], and the relevant *salen* ligand were prepared as described in the literature [35]. Acetonitrile and propylene carbonate (PC) (Romil, pro analysis grade) and LiClO<sub>4</sub> (Aldrich, 99%) were used as received. Ethylene and ammonia gases using in N-FLG preparation were obtained from Air Liquid, France. N-FLG was prepared by modifying our previously developed procedure for few layer graphene [36], as detailed in section 2.2.

X-ray photoelectron spectroscopy (XPS) measurements were performed at CEMUP (Porto, Portugal), in a Kratos AXIS Ultra HSA spectrometer with a monochromatic Al K $\alpha$  radiation (1486.7 eV), using the polymeric films or pellets of the nanomaterial (N-FLG). The raw XPS spectra were deconvoluted with the XPSPEAK 4.1 software, using a non-linear least squares fitting routine after a Shirley-type background subtraction. To correct for possible

deviations caused by sample charging, the C1s peak at 284.6 eV was taken as an internal standard. The surface atomic percentages were calculated from the corresponding peak areas, using sensitivity factors provided by the manufacturer.

Scanning Electron Microscopy/Energy-Dispersive X-Ray Spectroscopy (SEM/EDS) analyses were performed at CEMUP (Porto, Portugal), using a High Resolution (Schottky) Environmental Scanning Electron Microscope with X-Ray Microanalysis and Electron Backscattered Diffraction analysis (Quanta 400 FEG ESEM/EDAX Genesis X4M).

Transmission Electron Microscopy (TEM, JEOL 1400) was used to study the morphology of the N-FLG samples; Raman spectroscopy (HR 800 Jobin Yvon Horiba, micro spectrometer using the red line of an argon laser,  $\lambda = 639$  nm, as an excitation source) was used to study the structure of both FLG and N-FLG. Chemical analysis was carried out in STEM configuration (spot mode, probe diameter = 1 nm) using a Bruker EDAX spectrometer (provided with a Silicon Drift Detector with a resolution 127 eV).

Electrochemical studies were performed using an Autolab PGSTAT 30 potentiostat/galvanostat (EcoChimie B.V.), controlled by a GPES software. A three-electrode and separate compartment cell, enclosed in a grounded Faraday cage, was used with an Ag/AgCl (NaCl/1.0 mol dm<sup>-3</sup>) electrode (Metrohm ref. 6.0724.140) as the reference electrode, a Pt plate as the counter electrode and poly(ethylene terephthalate) (PET) coated with indium tin oxide (ITO) (ITO/PET) (Aldrich, resistivity of 60  $\Omega$  sq<sup>-1</sup>) as the working electrode. Coulometric measurements used a Pt disk working electrode (area 0.0314 cm<sup>2</sup>, BAS), previously polished with aluminium oxide of particle size 0.3  $\mu$ m (Buehler) on a microcloth polishing pad (Buehler), then washed with ultra-pure water (resistivity 18.2 M $\Omega$  cm at 25 °C, Millipore) and finally CH<sub>3</sub>CN.

The spectroelectrochemical studies were performed *in situ* using an Agilent 8453 spectrophotometer (with diode array detection) coupled to the potentiostat/galvanostat. The experimental set up consisted up a teflon cell with an Ag/AgCl (NaCl/3.0 mol dm<sup>-3</sup>) (Bio-Logic) reference electrode, a Pt grid counter electrode and an ITO/PET (typical area 0.785 cm<sup>2</sup>) as working electrode.

### 2.2. N-FLG preparation and characterization

N-FLG was prepared by CVD process, adapting a procedure reported elsewhere for the synthesis of few layer graphene (non-doped) [36]. Briefly, few layer graphene was produced by the catalytic chemical decomposition of a mixture of ethylene and hydrogen gas in a vertical fluidized bed reactor at 650 °C, in the presence of a cobalt ferrite spinel catalyst. Few layer graphene flakes were separated from the catalyst by dissolving the latter in 65% hydrochloric acid at 25 °C. Nitrogen doping was achieved by replacing pure ethylene by a mixture of ethylene and ammonia (90:10) under the same conditions. Both FLG and N-FLG powder was recovered after washing with 35% HCl at 25 °C. The nitrogen content was determined from both chemical analysis and XPS. The structure of the as-prepared N-FLG was confirmed from TEM and Raman spectroscopy.

### 2.3. Film preparation and electrochemical characterization

The N-FLG@poly[1] nanocomposite films were prepared by cyclic voltammetry (CV) from the corresponding monomer solution, 1.0 mmol dm<sup>-3</sup> [Ni(3-Mesalen)] complex in 0.1 mol dm<sup>-3</sup> LiClO<sub>4</sub>/CH<sub>3</sub>CN, containing 0.5 wt% (N-FLG/[Ni(3-Mesalen)] wt.%) of N-FLG. The potential of the working electrode (ITO/PET 3.0 cm<sup>2</sup>) was cycled between -0.2 and 1.3 V, at a scan rate  $v = 0.100$  V s<sup>-1</sup>, for 30 scans; other conditions are specified in the relevant text. Prior to electrodeposition, the starting solution was refluxed for 3 h, followed

Download English Version:

<https://daneshyari.com/en/article/5431622>

Download Persian Version:

<https://daneshyari.com/article/5431622>

[Daneshyari.com](https://daneshyari.com)