Electrochemistry Communications 43 (2014) 87–90

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Direct voltammetry of colloidal graphene oxides

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ARTICLE INFO

Article history:
Received 20 December 2013
Received in revised form 7 March 2014
Accepted 20 March 2014
Available online 29 March 2014

Keywords:
Colloidal graphene
Graphene oxide
Cyclic voltammetry

ABSTRACT

The direct voltammetry of aqueous colloidal graphene oxide (GO) solutions is presented in this fundamental study. Since its inception, the majority of GO electrochemistry has been centred on the use of solid-state modified electrodes whereas the voltammetry of solution-based GO species is not well known. Overall, pH and GO particle size are found to be important aspects that influence the observed results, and voltammetric profiles of nano-sized GO under acidic condition bear the closest similarities to electrode surface-modified GO. Greater knowledge of colloidal GO electrochemistry potentially allows for its future development in electrochemical sensing applications.

1. Introduction

Graphene-related materials such as graphene oxide (GO) have garnered much attention in the field of analytical electrochemistry [1–5]. This significant interest can be attributed to the use of GOs either as labels [1–3], or for enhancement of analytical signals [4,5] in electrochemical and biological sensing applications. Many such approaches rely on the characteristic electroactivity of GO itself, arising from inherent oxygen functionalities that are abundant in GO [6,7]. The large majority of electrochemical research on graphene materials involves solid-state modification of electrodes, using common techniques such as drop-casting [8] and carbon paste electrodes [9,10]. To the best of our knowledge however, there is a scarcity of reports on direct electrochemistry of free GOs in solution.

The first reported use of cyclic voltammetry (CV) in colloidal GO solutions was by Liu et al., where a thin layer of reduced GO can be deposited onto glassy carbon as a result of the cycled potential [11]. The aim of employing the CV technique in their seminal work and also in other studies that followed was only to achieve deposition of a reduced-graphene film on the electrode surface for a variety of sensing purposes [11–13]. It was also previously reported that one can detect soot nanoparticles (~5 nm) directly from their colloidal solutions by cyclic voltammetry [14]. The aim of this work is thus to study the voltammetry of the colloidal GO itself, arising from the redox activity of inherent oxygen-containing groups including epoxyls, carbonyls and quinonyls [6,7,15,16]. Therefore, the foremost difference in purpose from earlier CV studies is not to achieve deposition of a graphene film but to exploit the electroactive nature of colloidal GOs for future use in analytical electrochemical sensing.

In addition to the inherent reduction of oxygen functionalities in all GOs, we have also recently reported on the *chemically reversible* electrochemistry of GOs [16] specifically produced through the permanganate oxidation methods of Hummers [17] and Tour [18]. An important implication we identified for future research is that electrochemically-reduced GO can continue to exhibit distinctive electroactive behaviour [7,16], in contrast to the traditionally held notion that their reductions are irreversible [19,20]. As such, a secondary goal is to ascertain if such unique electrochemistry may also be observed when GOs exist freely in solution, in comparison to our prior study utilising electrode surface modification. Towards these objectives, we perform a systematic investigation into the experimental conditions that support measurements directly in colloidal solutions.

2. Experimental

2.1. Materials and experimental procedures

Both high purity vein graphite and stacked graphite nanofibres were used for the production of graphite oxide. Vein graphite was obtained from Sri Lanka, while synthetic graphite nanofibres (50 × 50 nm dimensions) were purchased from Strem Chemicals (Newburyport, USA). The oxidation of graphite to graphite oxide was performed using the Hummers oxidation method as previously reported in the literature [16,17]. All other chemicals were obtained from Sigma-Aldrich and of analytical grade. Glassy carbon (GC) electrodes (CH Instruments, USA) of 3 mm diameter were used as the working electrode, while a platinum electrode served as the auxiliary electrode. An Ag/AgCl electrode (1 M KCl) was used as the reference. Colloidal GO solutions at concentrations of 0.1 and 1.0 mg mL^{-1} were prepared by ultrasonication of solid graphite oxides in 50 mM phosphate-buffered saline (PBS) at various pHs for 1

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http://dx.doi.org/10.1016/j.elecom.2014.03.021
1388-2481/

h to obtain the colloidal graphene oxide solutions. Variations in the pH of the final colloidal solutions were found to be negligible (typically less than 0.2 pH units) compared to the initial pH of the buffer. Deionised water with a resistivity of 18.2 MΩ cm was used throughout for the preparation of solutions. Scanning electron micrographs of the GO materials on screen-printed carbon electrodes (Zensor SE-100; eDAQ, Australia) were obtained with a JEOL 7600F field-emission scanning electron microscope (JEOL, Japan).

2.2. Electrochemical measurements

Electrochemical analysis was made using an Autolab PGSTAT 101 electrochemical analyser (Eco Chemie, Utrecht, The Netherlands). GC electrodes were renewed prior to each measurement by polishing with a 0.05 μm alumina particle slurry on a polishing pad followed by washing with copious amounts of deionised water. Voltammetry was then performed directly in the colloidal GO solutions using the standard

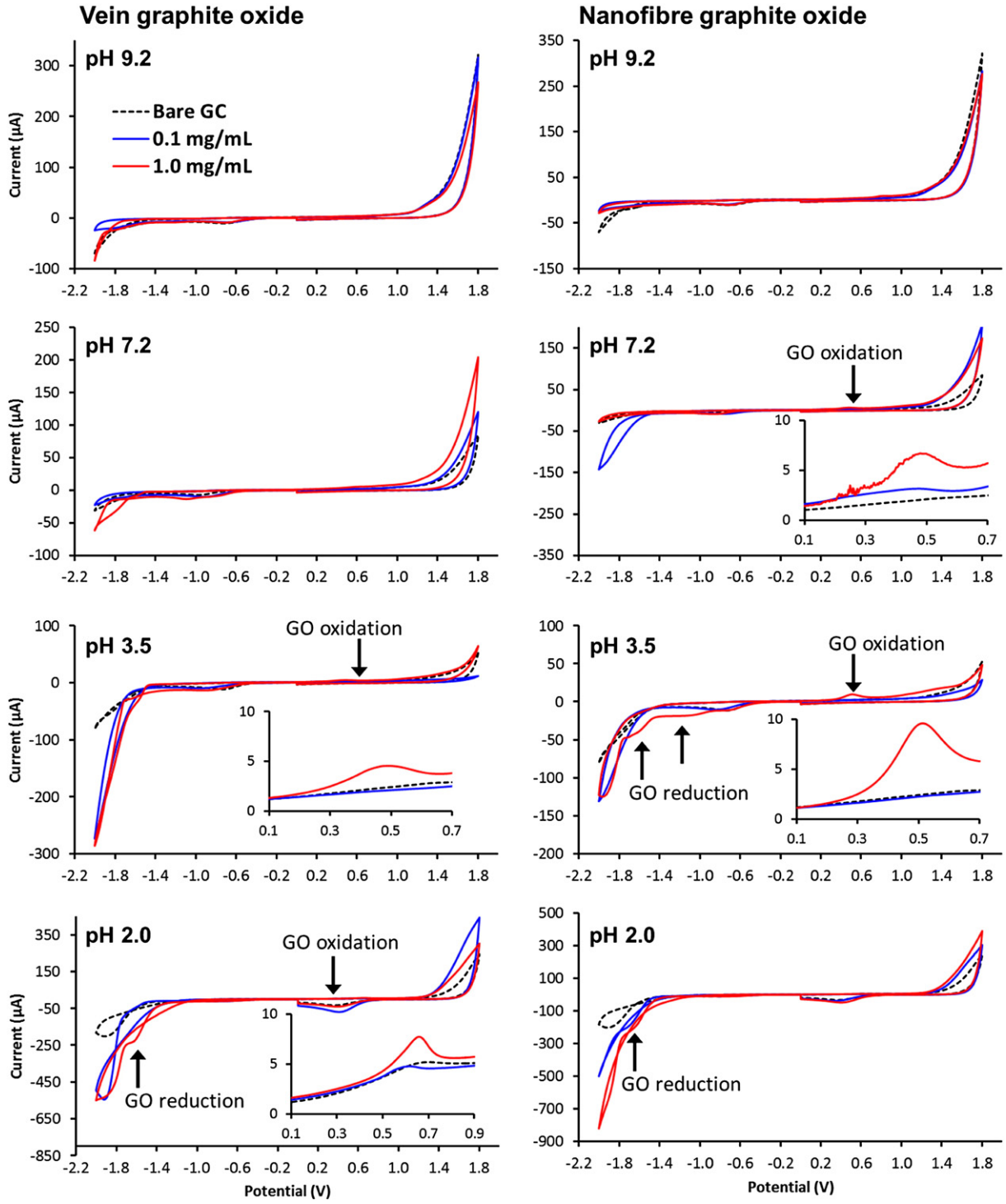

Fig. 1. Cyclic voltammograms of colloidal GO solutions at various pHs, at the concentrations of 0.1 and 1.0 mg mL^{-1}. Colloidal GOs are obtained based on the Hummers oxidation route from both natural vein graphite (left panel) and synthetic graphite nanofibre (right panel) sources. Inset diagrams of oxidation peaks are also shown whenever observed. Conditions: quiescent 50 mM PBS solution, starting potential from 0.0 V scanned towards cathodic direction, $\nu = 100$ mV s^{-1}.