



Short communication

Electrochemical activity and metal deposition using few-layer graphene and carbon nanotubes assembled at the liquid–liquid interface



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ABSTRACT

A simple route to assemble liquid exfoliated few-layer graphene (GR) and single wall carbon nanotubes (SWCNTs) at the interface between two immiscible electrolytic solutions (ITIES) is reported. The electrochemical reactivity of these interface-assembled low dimensional carbon films was probed by model redox species. The ITIES is also shown to be an ideal substrate for the generation of metal nanoparticles on such conducting nano-carbon supports: this approach is exemplified using the electro-deposition of palladium nanoparticles on the free-standing GR and SWCNT layers.

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1. Introduction

The interface between two immiscible electrolyte solutions (ITIES) can be electrically polarised to generate electrochemical potential gradients that are capable of promoting ion and electron transfer across the molecular boundary [1]. In addition, electrostatically stabilised nanostructures can be reversibly assembled and constructed *in situ* at polarisable liquid–liquid interfaces [2], such as complex catalytic centres and supports [3], photoactive oxides [4,5] and metallic nanostructures [6–9]. Recent studies have demonstrated the catalytic activity displayed by particles assembled at the ITIES towards hydrogen evolution and oxygen reduction, in the presence of lipophilic electron donor species [3]. Multi wall carbon nanotubes (MWCNTs) have been used as supports for some of the catalysts, such as molybdenum carbide (Mo_2C), at organic–water interfaces [10]. An imidazolium functionalised single wall carbon nanotube (SWCNT) layer was self-assembled at the chloroform–water interface due to its unique wettability and an attempt to measure the properties of this layer by scanning electrochemical microscopy was reported [11]. Conventional, *i.e.* non-polarised, liquid–liquid interfaces have been used to form layers of carbon nanomaterials, such as CNTs, and adsorbed films composed of few-layer graphene flakes or reduced graphene-oxide (rGO) flakes to prepare transparent carbon-coated electrode materials [12–16].

In this communication we report a process for the controlled assembly of exfoliated few-layer graphene (GR) or SWCNT layers at the ITIES and a study of the electroactivity of these free-standing carbon films. Noble metal (palladium) nanoparticles (Pd NPs) were deposited on

either the GR or the SWCNT film, using *in situ* electro-deposition at the organic–water interface.

2. Material and methods

Lithium chloride (LiCl, 99.99%); potassium hexacyanoferrate (III) ($\text{K}_3\text{Fe}(\text{CN})_6$, 99 + %); potassium hexacyanoferrate (II) trihydrate ($\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, $\geq 98.5\%$); 1,1'-dimethylferrocene (DMFc, 97%); ammonium tetrachloropalladate ($(\text{NH}_4)_2\text{PdCl}_4$, 99.995%); and the organic solvent 1,2-dichloroethane (DCE, $\geq 99.8\%$) were used as received. The organic phase electrolyte bis(triphenylphosphorylidene) tetrakis(4-chlorophenyl)borate (BTTPATPBCl) was prepared as described elsewhere [5] from potassium tetrakis(4-chlorophenyl)borate (KTPBCl, $\geq 98.0\%$) and bis(triphenylphosphorylidene)ammonium chloride (BTTPACl, 97%), all chemicals were purchased from Sigma-Aldrich. De-ionized water ($18.2 \text{ M}\Omega \text{ cm}$ resistivity), purified by a "PURELAB" Ultra-filtration unit (Elga Process Water), was used for solution preparation.

Cyclic voltammetry experiments were performed using a four-electrode configuration with an Autolab PGSTAT100 potentiostat (Metrohm-Autolab). Homemade Ag/AgCl reference electrodes (REs) were directly immersed in the chloride containing aqueous phase [8]. The cell used for the liquid–liquid electrochemical measurements had a working area of 0.74 cm^2 and a total solution volume of 2.5 mL (Fig. 1C). The potential scale was normalized in every case using the tetraphenylarsonium tetraphenylborate (TATB) extra-thermodynamic assumption [17]. UV–vis spectroscopic measurements were carried out using a UV–vis absorption spectrometer (DH-2000-BAL, Ocean Optics) and USB2000 interface (Mircopack GmbH). A Clifton Ultrasonic Bath (Nickel Electro Ltd.), operating at 30–40 kHz, was used to prepare the SWCNT (Elicarb®, Thomas Swan & Co. Ltd.) dispersion in organic

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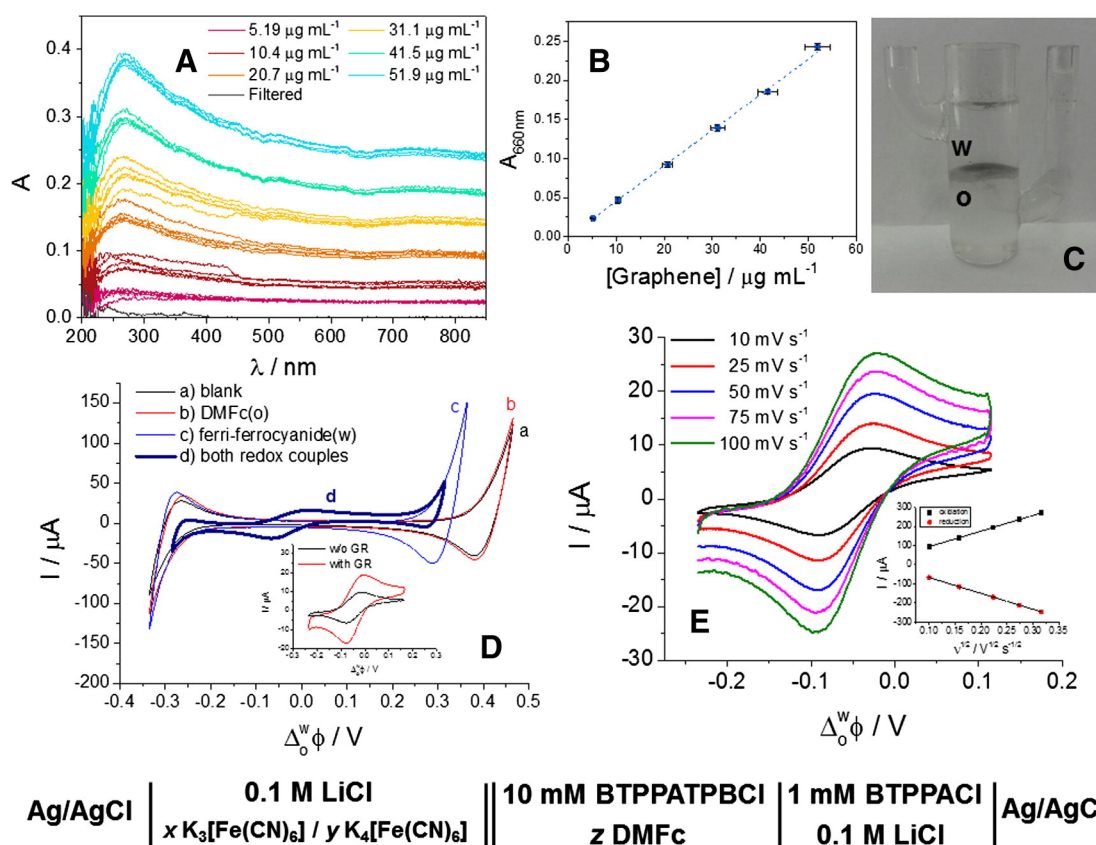


Fig. 1. UV–vis spectra (A) of GR dispersions at different concentrations and the filtered solution, the calibration curve (B) of the measured absorbance vs. the concentration of GR. Photograph of the cell (C) with the aqueous (w) and the organic (o) phases. Voltammetric responses of the redox couples at the DCE water interface in the absence (D) and in the presence of GR film (E). The CVs of interfacial DMFc oxidation in the absence and presence of the GR thin layer ($8.41 \mu\text{g cm}^{-2}$) at the interface are shown in the inset of D. Scan rates: 50 mV s^{-1} (D) and $10\text{--}100 \text{ mV s}^{-1}$ (E). The magnitude of the peak current is plotted against the square root of scan rate in the inset of E. The cell composition for the voltammetric measurements is also given in Fig. 1. The DMFc concentration, z , is $100 \mu\text{M}$ in DCE, and the ferricyanide and ferrocyanide concentration, x and y , are 0.1 M and 0.01 M , respectively, in water.

solvent, to exfoliate the GR flakes from natural graphite powder (Branwell Graphite Ltd.) to give a suspension in DCE and to assemble the resultant dispersions of SWCNT and exfoliated GR at the liquid–liquid interface. Hydrophobic polyvinylidene fluoride (PVDF) membranes (EMD Millipore Durapore™, Fisher Scientific) were used to determine the mass of nanomaterial for the absorption coefficient determination (see below). DCE dispersions were prepared at an initial concentration of 2 mg mL^{-1} (SWCNT powder) and 1 mg mL^{-1} (graphite/GR), using a 30 min (SWCNT) or 2 h (graphite) bath sonication. Remaining non-dispersed particles were removed in both cases: the SWCNT dispersion was filtered through glass wool (Sigma–Aldrich) and the graphite dispersion was centrifuged for 45 min at 587 rpm; the remaining suspension ranges from 4 to 20 layers thick and is referred as a few-layer graphene sample. The absorption coefficient (α) was determined in both cases from the stable dispersions. A known volume of the dispersion was filtered through the pre-weighed $0.1 \mu\text{m}$ pore size PVDF membrane and, after drying, was weighed again to determine the mass and therefore calculate the concentration of either the SWCNT or GR in the dispersion. Several dilutions of dispersions were prepared from the remaining suspension that was not filtered through the membrane and their UV–vis spectra recorded. Scanning electron microscopy (SEM) characterisation and energy dispersive X-Ray spectroscopy (EDAX) elemental analysis (Philips XL30 ESEM–FEG, operated at 15.0 kV) were performed on the samples once transferred to a Si/SiO₂ wafer. Following deposition, the Pd NP-decorated SWCNT and GR layers were fished out using the Si/SiO₂ substrate, dried in air for 15 min, then washed in ethanol and isopropanol mixture (5 min) and then acetone (5 min), and finally blow-dried with nitrogen. The displayed errors are either standard deviations (arithmetic averages of multiple measured values) or absolute errors determined from the best fit errors.

3. Results and discussion

The absorption spectra of GR dispersions at various dilutions are depicted in Fig. 1A [18]. The absorbance values at 660 nm from five measurements were averaged and plotted versus the concentration of the GR dispersions (Fig. 2B). The absorption coefficient, α , was calculated from the slope of the calibration curve according to the Lambert–Beer law and found to be $2305 \pm 24 \text{ mL mg}^{-1} \text{ m}^{-1}$; this compares with a reported α value of $2460 \text{ mL mg}^{-1} \text{ m}^{-1}$ in a different organic solvent, *N*-methylpyrrolidone [18]. The liquid–liquid electrochemical cell was prepared by mixing an aliquot of dispersion with an equal volume of organic electrolyte solution, then adding an equal volume of aqueous phase on top of the organic phase. The cell was bath sonicated for 15 min to bring about assembly of the GR at the ITIES, as seen in Fig. 1C.

Two phase voltammetry was carried out between the aqueous and organic solvents (Fig. 1D); using just the supporting electrolytes ($0.1 \text{ M LiCl}_{(\text{w})}$ and $10 \text{ mM BTPPATPBCl}_{(\text{o})}$) the blank cyclic voltammogram (CV) was obtained (Fig. 1D-a), in which only the ion transport of the supporting electrolytes (Li^+ and Cl^-) can be observed. CVs when either the organic (DMFc(o), Fig. 1D-b) or the aqueous phase (ferri-ferrocyanide (w), Fig. 1D-c) redox-active species were present showed a similar shape. The only difference is that the potential window was narrower when the aqueous couple (Fig. 1D-c) was present, as K^+ transfer occurs at less positive potentials than Li^+ transfer [1]. In the presence of both redox couples, current features attributable to interfacial electron transfer (ET) were observed close to 0.0 V , consistent with either heterogeneous DMFc oxidation and re-reduction of DMFc^+ (Fig. 1D-d), according to Reaction 1 [19,20], or an analogous homogeneous process, coupled to ion transfer [21]. The concentration of DMFc, z , was much lower ($100 \mu\text{M}$, low enough to avoid the presence

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