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Electrocatalytic behahiour of cobalt tetraamino-phthalocyanine in the presence of a composite of reduced graphene nanosheets and of multi-walled carbon nanotubes

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ABSTRACT

A composite of multi-walled carbon nanotubes (MWCNT) with reduced graphene nanosheets (rGNS-2) was developed in order to minimize the restacking of the latter. The composite was used to modify a glassy carbon electrode (GCE). GCE was further modified with cobalt tetraamino phthalocyanine (CoTAPc). The modified electrode is represented as rGNS-2-MWCNT-CoTAPc-GCE. X-ray photoelectron spectroscopy, transmission electron microscopy, scanning electrochemical microscopy and Raman spectroscopy were used to explore into surface functionalities, morphology and topography of the nanocomposite. The rGNS-2-MWCNT-CoTAPc-GCE had a low limit of detection of 3.32×10^{-8} M towards the detection of paraguat as a test analyte. A mechanism for paraquat detection using an rGNS-2-MWCNT-CoTAPc-GCE is also proposed in this work.

1. Introduction

Reduced graphene nanosheets (rGNS) have recently drawn increasing attention as novel nanocarbon materials due to their outstanding electronic, thermal, mechanical and chemical properties, high surface area and broad electrochemical window [1–12]. However graphene sheets can undergo π-stacking through van der Vaal's interactions [13,14], thereby reducing the available active surface area for applications such as in electrocatalysis. A possible route to harness such outstanding properties of graphene nanosheets for practical applications is to make nanocomposites by incorporating some nanomaterials into the graphene sheets, which will inhibit the agglomeration and improve the electrode conductivity [15]. Graphene nanosheets–polystyrene nanocomposites have been reported and were found to display high electrical conductivity and good tensile strength [16,17]. Carbon black nanoparticles were used as spacers for graphene nanosheets and the electrochemical performances of hybrid materials were found to be superior compared to pure graphene material [15]. Carbon nanotubes (CNTs) and fullerenes (C60) were incorporated into graphene nanosheets for enhancement of storage capacity in lithium batteries [10]. GNS-Pt electrocatalyst composites have shown unusually high activity towards methanol oxidation relative to Pt-carbon black catalyst [18]. GNS-Al_2O_3 composites have also been reported to have better electrical conductivity than individual GNS [19]. In this work we envisage the design of a smart platform for fabrication of a composite electrocatalyst containing MWCNT and reduced graphene nanosheets. The multiwalled carbon nanotubes (MWCNT) - rGNS nanocomposites are further decorated with cobalt tetraamino phthalocyanine (CoTAPc) because of its well-known electrocatalytic behaviour towards detection of herbicides [20–22]. We use a herbicide, paraquat (N, N'-dimethyl-4,4′-bipyridilium dichloride), Fig. 1, as a test molecule, to demonstrate the effect of the presence of MWCNT and reduced graphene nanosheet on the electrocatalytic performance of CoTAPc.

2. Experimental

2.1. Materials

Graphene oxide nanosheets (GONS), $NaBH_4$, multiwalled carbon nanotubes, alumina, polycrystalline diamond suspensions (3F μm, 1F μm, 0.25 μm), dimethylformide (DMF), paraquat, amitrole, diuron, urea and atrazine were from Sigma Aldrich, 98% H_2SO_4 was obtained from B & M Scientific. Aqueous solutions of paraquat in pH 4 buffer were prepared using millipore water from Milli-Q Water Systems (Millipore Corp. Bedford, MA, USA) and cobalt tetraamino phthalocyanine (CoTAPc) was synthesized according to a reported methods [23].

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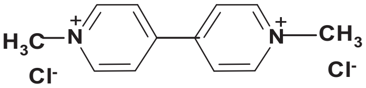

Fig. 1. The structure of PQ.

2.2. *Equipment and Material characterizations*

A Princeton Applied Research potentiostat/galvanostat Model 263A was used for all cyclic voltammetry (CV) and square wave voltammetry (SWV) studies. A three electrode electrochemical cell comprising of a glassy carbon electrode (GCE) (geometric area = 0.071 cm^2) as the working electrode, Ag|AgCl (3 M KCl) as reference electrode, and a platinum wire as the counter electrode was employed. Electrochemical Impedance spectroscopy (EIS) studies were performed between 0.1 Hz and 10 kHz, using a 5 mV rms sinusoidal modulation, using an Autolab Potentiostat PGSTAT30 equipped with GPES software version 4.9. A nonlinear least squares (NNLS) method based on the EQUIVCRT programme was used for automatic fitting of the obtained EIS data.

Scanning electrochemical microscopy (SECM) experiments were carried out with the Uniscan Instruments SCV 370, employing a three electrode cell with platinum SECM micro-tip, a platinum wire counter electrode, and a Ag|AgCl reference electrode. X-ray photoelectron spectroscopy (XPS) was done with a Kratos Axis Ultra DLD, using an Al (monochromatic) anode, equipped with charge neutralizer and the operating pressure kept below 5×10^{-9} torr. For wide/survey XPS scans, the following parameters were used: emission current was kept at 5 mA and the Al anode voltage at 15 kV. The resolution used to acquire wide/survey scans was at 160 eV pass energy using a hybrid lens in the slot mode. The centre used for the scans was at 520 eV and the width at 1205 eV, with steps at 1 eV and dwell times at 300 ms. For the high resolution scans, the resolution was changed to 40 eV pass energy in the slot mode. Curve fitting was performed using a Gaussian-Lorentzian peak shape after performing a linear background correction. Transmission electron microscope (TEM) micrographs for the nanoparticles were obtained using a Zeiss Libra 120 TEM operating at 80 kV. Raman spectra were obtained using a Bruker Vertex 70-Ram II Raman spectrometer (equipped with a 1064 nm Nd: YAG laser and liquid nitrogen cooled germanium detector).

2.3. *Preparation of graphene nanosheets*

2.3.1. *Reduced graphene nanosheets*

Graphene oxide nanosheets (0.1 g) were dispersed in 100 ml Milli pore water through ultrasonication. $NaBH_4$ (0.57 g, 15 mmol) was added to reduce the graphene oxide sheets, followed by heating at 70 °C for 3 h. The black solid product obtained by filtration over a fritted glass funnel, was washed with copious amount of water (5×50 ml), and dried in an oven at 70 °C. The resulting sample is designated rGNS-1. A portion of rGNS-1 was further treated with 98% H_2SO_4 and the product was collected and designated rGNS-2. The H_2SO_4 was employed to eliminate the aliphatic functionality and dehydrate the remaining hydroxyl functionalities to form alkenes that resemble graphitic sp^2 carbon network [24].

2.3.2. *Preparation of MWCNT intercalated reduced graphene nanosheets*

A mixtute of rGNS-2 and MWCNT (9:1 by mass) was added to 200 ml millipore water and sonicated for 5 h to obtain the rGNS-2-MWCNT suspension. The solid was filtered and washed several times with Millipore water, absolute ethanol, and dried in an oven at 70 °C. The resulting sample is designated rGNS-2-MWCNT in this work.

2.4. *Electrochemical studies*

The GCE was polished on a Buehler-felt pad using alumina (10 μm), 3F μm, 1F μm and 0.25 μm polycrystalline diamond suspensions, washed with millipore water, sonicated for 5 min in millipore water and rinsed again with millipore water before each use. For CV, SWV and SECM studies, a 10 mg sample of each of GONS, rGNS-1, rGNS-2 or rGNS-MWCNT was separately added to 1 ml of DMF and then subjected to ultrasonication for 10 h to promote even dispersion. The suspensions (5 μL) of each were placed on glassy carbon electrode surface and dried. The resulting electrodes are designated as GONS-GCE, rGNS-1-GCE, rGNS-2-GCE or rGNS-MWCNT-GCE. For the preparation of rGNS-2-MWCNT-CoTAPc-GCE, 1 mg CoTAPc was dissolved in 1 ml DMF and a drop (5 μL) of it was added on top of rGNS-MWCNT layer followed by drying. The mass ratio of the rGNS-2-MWCNT to CoTAPc was a 10:1. Experiments were also performed on CoTAPc (represented as CoTAPc-GCE), CoTAPc drop-dried on MWCNT (represented as CoTAPc-MWCNT-GCE) and CoTAPc drop-dried on rGNS-2 (represented as rGNS-2-CoTAPc-GCE) for comparative purposes. Square wave voltammetry was used for selectivity studies using rGNS-2-MWCNT-CoTAPc-GCE and 30 μM (in 0.1 KCl) of the analytes. All solutions were purged with argon gas for 15 min to drive out oxygen before each cyclic voltammetry analysis, and the atmosphere of argon was maintained throughout the period of analysis.

3. Results

3.1. *Characterisation of GONS, rGNS-1, rGNS-2 and rGNS-MWCNT.*

Reduction of GONS results in large changes in the microstructure and properties of GONS. Visual characteristics, Raman spectroscopy and XPS were important tools employed in this work to elucidate the extent of GONS reduction.

3.1.1. *Visual characterisation*

A clear indication of reduction was the formation of a charcoal black suspension (of rGNS-2) from the original brilliant-brown suspension (of GONS) as shown in Fig. 2A. This behaviour is thought to emanate from an increase in the hydrophobicity of the rGNS due to a decrease in sheet surface polar functionalities [1].

The difference in the extent of reduction using $NaBH_4$ (rGNS-1) or $NaBH_4$ followed H_2SO_4 (rGNS-2) is shown by the resultant suspension i.e. a transparent brown-black suspension for rGNS-1 and a charcoal-black suspension for rGNS-2, Fig. 2A. $NaBH_4$ has moderate efficiency in removing oxygen functionalities relative to concentrated sulphuric acid (98%). It has been reported that acid treatment dehydrates the remaining tertiary alcohols to form alkenes that adds to the sp^2 of the graphitic structure [24]. There was no observable colour change when MWCNT were added to rGNS-2, Fig. 2A. Furthermore, the increase in electrical conductivity due to improved charge carrier concentration and mobility enhances incident light reflection. This gives the rGNS their metallic lustrous appearance as shown in Fig. 2B.

3.1.2. *Raman Studies.*

Carbon materials are known to show some characteristic Raman peaks which are centered around 1500 cm^{-1} (G, tangential mode; *sp*^{2}) and 1270 cm^{-1} (D, disorder band; *sp*^{3}) [25–27]. The D:G (*sp*^{3}:*sp*^{2}) ratio is generally considered as a quality parameter to determine the extent of functionalization of the carbon nanomaterials. This is because the G-band is not affected by defects, whereas the D-band is enhanced by the presence of sp^3 defects in the sp^2 lattice [25]. D:G ratio gives information on establishment of sp^2 hybridization and deoxygenation. The D-band for rGNS-1 (0.00158)