Fast electron transfer kinetics on novel interconnected nanospheres of graphene layers electrodes

A.C. Peterlevitz a, P.W. May b, R.L. Harniman b, J.A. Jones b, H.J. Ceragioli a, H. Zanin a,b,*

a Carbon Sci-Tech Labs, Universidade Estadual de Campinas, Campinas 13 083-832, Brazil
b School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom

A R T I C L E   I N F O

Article history:
Received 27 April 2016
Received in revised form 26 August 2016
Accepted 21 September 2016
Available online 22 September 2016

Keywords:
Sensor
Electrochemistry
Graphene
Layers
Thin film

A B S T R A C T

A novel thin solid film of interconnected carbon nanospheres (ICNS) has been developed and characterized as electrode. The thin film is composed of interconnected carbon nanospheres with average crystallite size of ~5 nm and lamellar graphene layers separated by an interplanar spacing of ~0.32 nm. An electrode was prepared in a one-step process by depositing ICNS onto a niobium substrate by hot filament chemical vapour deposition. To prepare an electrode, solvent-refined oil without additives was annealed up to 530 °C under ~2700 Pa of a gas mixture containing ethanol, methanol, water, and boron trifluoride. The resulting ICNS film was characterized by scanning and transmission electron microscopy, plus Raman, Fourier transform infrared and energy dispersive spectroscopies. The contact angle between deionized water and the ICNS surface was zero - the water droplet instantaneously spread over the sample surface indicating a hydrophilic surface. The film behaviour as an electrochemical electrode was studied by cyclic voltammetry and electrochemical impedance spectroscopy. ICNS layers exhibited a large potential window, low uncompensated resistance, as well as low charge-transfer impedance in the presence of ferrocene-methanol or ferrocyanide as redox probes. These useful properties make ICNS electrodes very promising for future applications in electrocatalysis and (bio)sensors.

1. Introduction

Carbon is a very attractive material for electrochemical applications due to its different allotropes (fullerenes, nanotubes, graphene and diamond) of dimensionality from 0D to 3D [1,2]. Carbon materials can be prepared in various microtextures from powders to freestanding fibres, foams, amorphous, crystals and composites [3,4]. As an electrode material, carbon surface shows fairly low charge transfer impedance and high chemical stability in strongly acidic or basic solutions with material, carbon surface shows fairly low charge transfer impedance.

Among these various sp2 carbon nanostructures, carbon nanospheres (CNSs) have been investigated as an electrode material. These spheres are hydrophilic and exhibit fast electron transfer in the presence of ferrocene-methanol or ferrocyanide as redox probes, which evidence their applicability as electrochemical sensors.

2. Experimental

2.1. ICNS film growth

The thin films of ICNSs were deposited on niobium disks (diameter 25 mm and thickness 2 mm) by hot filament chemical vapour deposition (HFCVD). Prior to the deposition, the substrates were polished and cleaned in an ethanol bath under sonication. After drying the samples, a drop of concentrated hydrocarbon oil (Vitre 100 oil manufactured and sold commercially by Shell) was placed on the top surface where it spread out uniformly. The sample was then placed into a reactor chamber, which was then evacuated to a base pressure of 0.03 Pa. A gas mixture of 85 sccm of hydrogen, 15 sccm of nitrogen...
and 10 sccm of the vapour from an ethanol:methanol:water (40:80:64) solution was introduced into the chamber via suitable mass flow controllers. Hydrogen gas was bubbled through this mixture carrying it into the chamber. The chamber pressure was maintained at 2600–2800 Pa throughout the deposition run. For thin film formation, a tungsten filament was position 5 mm above the sample and resistively heated up to 2000 °C measured by a pyrometer. Radiative heat from the filament heated the sample at a rate of 50 °C/min for 10 min to a temperature of ~530 °C, and this temperature was maintained for a further 30 min, after which the filament was progressively cooled down in a pure hydrogen atmosphere for 10 min. The substrate temperature was measured using a thermocouple embedded in the back side of substrate.

2.2. Characterization and electrochemical studies

ICNS samples were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy, energy dispersive spectroscopy (EDS), contact angle (CA) and electrochemical tests. SEM and TEM were performed with a JEOL6330 operated at 10 kV and JEOL2011 operated at 200 kV, respectively. Raman spectra were recorded at room temperature using a Renishaw microprobe, employing UV (325 nm), green (514 nm) and near infrared (785 nm) laser excitation. Surface chemical electrodes and oil were investigated by Fourier transform infrared attenuated total reflection spectroscopy (ATR-FTIR: Spectrum Spotlight-400, Perkin-Elmer). The semi-quantitative analysis of chemical elements was performed by EDS measurements using an Inca Penta FET ×3 Oxford Instruments. A Krüss Easy-Drop system employing the sessile-drop method was used to evaluate the wettability of electrodes by measuring the CA of the ICNS layers with high-purity deionized water drops.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were recorded with an Autolab PGSTAT30 potentiostat. The electrochemical responses of ICNS films grown on niobium were compared with those from a niobium disk substrate using Ar-saturated aqueous electrolyte solutions containing KNO₃, C₁₁H₁₂FeO or K₄Fe(CN)₆ as the supporting electrolyte and redox probe, respectively. The geometrical surface area of the working electrode was defined by using chemically inert adhesive 3 M Teflon tape to mask off some of the film, leaving a 3-mm-diameter open hole of fixed area (0.071 cm²). The electrical contact was made on the top of the electrode using a crocodile clip covered by parafilm wrap. Ag/AgCl (in saturated KCl) and a pure platinum mesh were employed as reference and counter electrodes, respectively. All chemicals and supporting electrodes were purchased from Sigma Aldrich.

3. Results and discussion

3.1. Structural characterization of the ICNS layer

Fig. 2(a–c) shows electron and atomic force micrographs of the ICNS films revealing (a) interconnected quasi-spherical structures covering the whole niobium substrate; and details of (b) the topography of the sample and (c–f) the particle shape and sizes and the layered structures filling the nanospheres. Particle diameters ranged from 2.5 to 10 nm with interplanar spacing 0.32 ± 0.02 nm.

Fig. 3(a–d) shows Raman spectra from ICNS films obtained from (b) UV, 325 nm, (c) green, 514 nm and (d) near IR, 785 nm excitation wavelengths. Fig. 3(a) shows all spectra overlapped and Fig. 3(b–d) each spectrum deconvoluted. In the first-order of all Raman spectra the two main peaks are known as the D- and G-bands, assigned to sp² carbon structures. In Fig. 3 (a) the D-band centre position has shifted from 1360 to 1347 cm⁻¹ as excitation wavelength was changed from 785 to 514.5 nm, respectively. The D band is associated with a double resonance process involving a phonon and a defect, commonly observed in disordered nanoscale carbon phases [19]. This is consistent with the
SEM images showing large amounts of edges and boundaries present in the film.

The G-peak is centred at 1600 cm$^{-1}$ and does not shift with the excitation wavelength, suggesting the presence of a crystalline carbon phase. The G-band stems from in-plane vibrations and has $E_{2g}$ symmetry corresponding to stretching vibrations in the basal plane ($sp^2$ domains) of single-crystal graphene or nanocrystalline graphite.

We have observed that the ratio of the area under the D and G peaks ($A_D/A_G$) increases as the excitation laser energy ($E_L$) increases. The $A_D/A_G$ ratio is useful to calculate the average crystallite size ($L$) using Eq. (1) [20], where $E_L$ is the laser excitation energy in eV:

$$L (\text{nm}) = \frac{560}{E_L^4} \left(\frac{A_D}{A_G}\right)^{-1}$$

For $E_L = 2.41$ eV (excitation by 514 nm, Fig. 3(c)), our sample has $A_D/A_G = 3.5$ and thus a crystallite size $\approx 4.8$ nm, which is consistent with the TEM observations (Fig. 2(c)).

Deconvolution of the Raman spectra of ICNS films measured using 325, 514 and 785 nm excitation are shown in detail in Figs. 3(b) to (d), which exhibit features associated with the $sp^2$ and $sp^3$ carbon sites and carbon and oxygen bonds. In the first-order of all Raman spectra, besides the D- and G-bands already discussed, the feature at 1218–1273 cm$^{-1}$ has its origin in a double resonance process on graphene phonon dispersion curves [21]. From the presence of the latter mode and D- and G-band analyses, we can infer the predominance of $sp^2$ carbon in the film. The small peak at around 1060 cm$^{-1}$ (T-peak) reveals a slight content of $sp^3$ carbon [22], which only could be detected by UV excitation (Fig. 3(b)). The band centred at around 1489 cm$^{-1}$ appears on all Raman spectra and is evidence of oxygen functional groups bonded to carbon on ICNSs [23]. In summary, Raman analyses indicate mainly the presence of highly crystalline carbon, such as graphene, together with oxygen groups attached to the surface.

Fig. 4 contrasts the ATR-FTIR spectra from the ICNS film with that from the hydrocarbon oil, which was used as precursor. From the spectrum we can observe the carbon-carbon and carbon-oxygen bonds. The band around 1532 cm$^{-1}$ is attributed to the C–C graphitic structure of carbon nanospheres, while the C–C bonds of the aromatic nuclei appear at both ~700 and 1200 cm$^{-1}$ [24,25]. The peaks centred at ~1250 and 1466 cm$^{-1}$ are assigned to C–O and C–H (of carboxylic groups), respectively [26,27]. The band at ~1660 cm$^{-1}$ is assigned to the C=O stretching mode in quinone groups, and the band at ~1730 cm$^{-1}$ is indicative of the C=O in carboxylic groups (COOH) [26], which is consistent with Raman analyses and EDS results (spectra not shown).

**Fig. 3.** (a) Overlapped Raman spectra of the ICNS layer measured at different excitation wavelengths (UV) 325 nm, (green) 514 nm and (near IR) 785 nm. Deconvoluted Raman spectra obtained from (b) 325 nm, (c) 514 nm and (d) 785 nm excitation wavelengths. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Fig. 4.** ATR-FTIR spectra of ICNS layers and the hydrocarbon oil (Vitrea 100) used for sample preparation.
3.2. Electrochemical properties of ICNS films

Cyclic voltamograms (CVs) of ICNS film electrodes are displayed in Fig. 5 showing (a) 0.1 M KNO₃ electrolyte solution scanned at 100 mV s⁻¹ and (b) 0.1 M KNO₃ electrolyte plus 0.5 mM ferrocene-methanol and (c) 0.1 M potassium nitrate plus 0.5 mM ferrocyanide, taken at different scan rates (10, 25, 50 75 and 100 mV s⁻¹).

From EDS, we semi-quantified the atomic composition of the CNS film as ~86% carbon with the balance being oxygen. The main oxygen source is the solvent used for hydrocarbon oil refining and the alcohol (methanol and ethanol) vapours used during growth. These oxygen functional groups revealed by FTIR have polar characteristics and can interact strongly with water. The contact angle between deionized water and the ICNS surfaces is zero, where the water droplet instantaneously spreads over the sample surface, indicating an extreme hydrophilic surface. Also from FTIR spectra the band at 1030 cm⁻¹ represents C–N bond stretching vibrations, and is found only on ICNS samples [28], where the main source is the nitrogen gas used during growth. The band that ranges from −2250–2390 cm⁻¹ is assigned to uncompensated CO₂ (g) from the air in the spectrometer. Both peaks centred at 1380 and 2920 cm⁻¹ are assigned as bending and stretching vibrations of C–H. The intense bands at 3400 cm⁻¹ indicate stretching vibrations of isolated surface —OH moieties and/or —OH in carboxyl groups in absorbed water [29]. From FTIR spectra we can conclude the oxygen functional groups are attached to the carbon in the ICNS film, changing the surface wettability of the sample. Hydrophilic carbon materials are desirable for charge transfer across an electrode/electrolyte interface.

4. Conclusions

We have presented a novel class of carbon nanospheres with diameters ranging from 2.5 to 10 nm and an interplanar spacing...
0.32 ± 0.02 nm. We believe that interplanar spacing is slightly lower than graphite due to internal stress of spherical configuration. However, this is a complex topic. For instance, literature showed that the spacing values of DWCNTs and MWCNTs vary from 0.27 up to 0.42 nm [33]. The most common values are in the range of 0.32–0.35 nm and do not strongly depend on the synthesis method. In particular, it was indicated that the stability of a CNT depends only on the interlayer spacing, which reaches an energy minimum when the mean interlayer separation is 0.34. In our case, the interplanar spacings are very similar ranging from 0.30 to 0.34 nm, suggesting that electrostatic interactions between partially charged atomic centres, which exist in our sample and are probably absent in graphite. These interconnected conducting spheres have a low production cost and show fast charge-transfer rate in the presence of ferrocene-methanol or ferrocyanide as a redox probes. The thin films are fairly well adherent to the substrate. The capacitance is about 21 μF/cm² which is similar to that of HOPG (5 μF/cm²). The difference observed is probably due to the substrate roughness. These useful properties make ICNS electrodes very promising for future electrochemical applications as sensitive electrodes.

Acknowledgements

We gratefully acknowledge the University of Bristol School of Chemistry electron microscopy unit for TEM and the British Council, Brazilian agencies Fapesp (2014/02163-7) and the Royal Society for Newton Travel fund N11/40181 for financial support. Peakforce atomic force microscopy was carried out in the Chemical Imaging Facility, University of Bristol with equipment funded by EPSRC under “Atoms to Applications” Grant ref. (EP/K035746/1).

References