



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



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ABSTRACT

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 laminar 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 trioxide. 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.

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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 good performance over a wide range of temperatures [5,6,7]. Carbon nanotubes [8,9], carbon nanofibres [10,11], carbon trees [12], fullerenes [13], the C_n family [14], carbon onions [15,16] and carbon spheres [17] have all been investigated as an electrode material.

Among these various sp^2 carbon nanostructures, carbon nanospheres (CNSs) have attracted much attention because of their applications in electronic devices, catalysis, adsorbents and as anode materials in lithium-ion batteries [18–25]. To date, most of these carbon nanospheres are hollow carbon structures composed of stacked hexagonal graphene sheets linked as rings. By incorporating pentagons the flat

structures eliminate all dangling bonds, enabling them to curl up to form a ball [16,17]. Fullerene, C_n cage, onion-like carbon nanospheres have shells with radial graphene-like layers differing in their interplanar spacing, particle size and the numbers of both carbon atoms and shells (Fig. 1).

In this work we present a novel film of interconnected carbon nanospheres (ICNSs), which is composed of approximately a dozen laminar graphene layers. 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 prepared 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 (Vitrea 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

[☆] In memory of Prof Vitor Baranauskas.

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Fig. 1. Schematic representation of carbon nanospheres.

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 positioned 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 KNO_3 , $\text{C}_{11}\text{H}_{12}\text{FeO}$ or $\text{K}_4\text{Fe}(\text{CN})_6$ 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 cm^2). 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 $0.32 \pm 0.02 \text{ nm}$.

Fig. 3(a–d) shows Raman spectra from ICNS film 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 sp^2 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

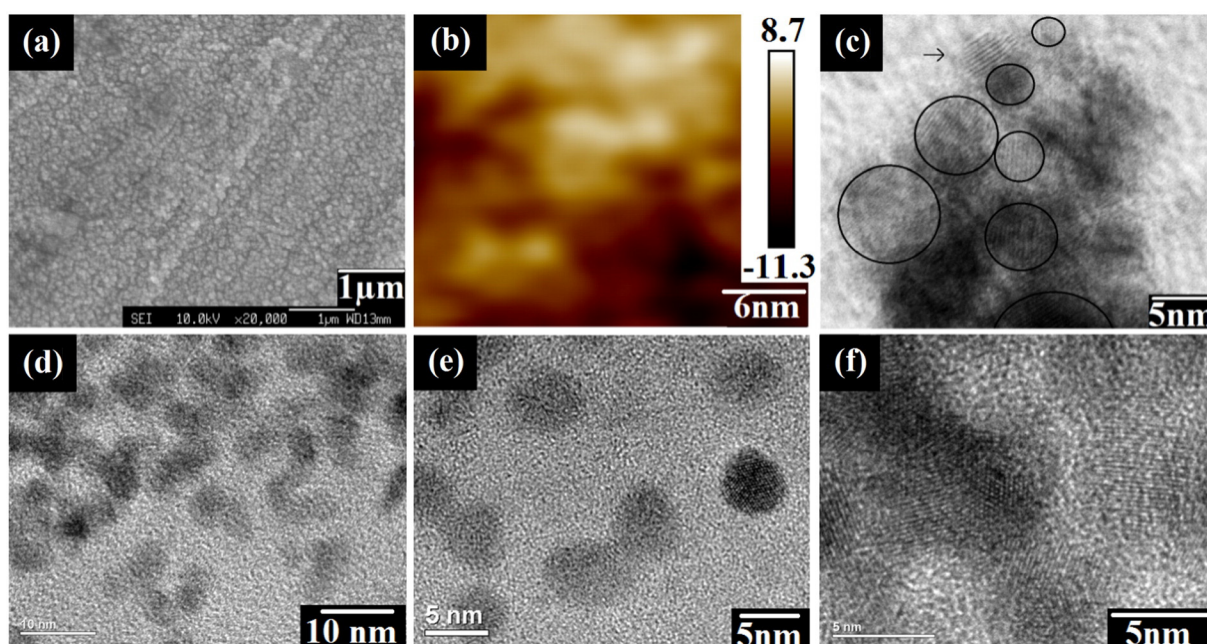


Fig. 2. (a) Scanning electron, (b) atomic force and (c–f) transmission electron microscope images of ICNS morphology prepared on a niobium substrate.

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