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Electrochemical and photo-electrochemical properties of carbon spheres prepared via chemical vapor deposition

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ABSTRACT

A noncatalytic chemical vapor deposition method was used to prepare graphitized carbon spheres (CSs) from acetylene. The CSs (diameter of 115 ± 10 nm) with *n* type conductivity were found to be photo-electrochemically active with a diffuse reflectance spectrum band gap of 1.01 eV. The electrical conductivity followed an Arrhenius type law with an activation energy of 0.53 eV. From the capacitance measurements, the flat band potential ($V_{fb} = -0.75 V_{SCE}$) and the electron density ($N_D = 3.46 \times 10^{15}$ cm^{-3}) were determined.

1. Introduction

Nano and micro sized carbon materials have attracted particular interest due to their unique morphology, novel physico-chemical properties and their useful applications in many fields [1–4]. These materials are typically made of two dimensional (2D) monolayer sheets or flakes of sp^2 bonded carbon atoms. The fabrication of carbons with a particular morphology has led to their application in electrodes for batteries and fuel cells, adsorbents for water purification, and as catalyst supports [5–7]. Their use as electrodes for electrochemical energy storage is due to the good electrical conductivity.

More recently, spherical structured carbon materials called carbon spheres (CSs) have attracted considerable attention for their potential applications as catalyst supports and in drug delivery, lubricating materials, gas storage media, and lithium ion batteries [8,9]. Many different types of carbon spheres with different morphologies and sizes have been prepared through different processes using various carbon containing reagents as precursors [8–16].

The electrical conductivity of graphite is associated with carbon π bonds. The electron mobility occurs in the graphene planes and limited electron transfer occurs between graphene planes [17]. The electrical conductivity is influenced by the CS geometry and also by doping with non-C atoms. Similarly, conduction in carbon nanotubes (CNTs) is affected by tube curvature [18], the tube chirality and the tube diameter. Consequently, CNTs behave either as metallic conductors or semiconductors (SCs) [19–21]. However, little is known about the band gap of carbon spheres [22,23]. Carbon spheres have been shown to be made of graphene flakes. These flakes have curvature due to the presence of 5 (pentagon) and 7 (heptagon) membered rings. The collection of flakes generates the carbon spheres and the size of the spheres is determined by the number of flakes that agglomerate to make the sphere (Fig. 1) [24].

In the present work, the overall goal is to determine the energy diagram for carbon spheres (CSs) prepared by the chemical vapor deposition (CVD) method and also determine the physico-chemical properties of the CSs from their optical, electrical and photo-electrochemical characteristics.

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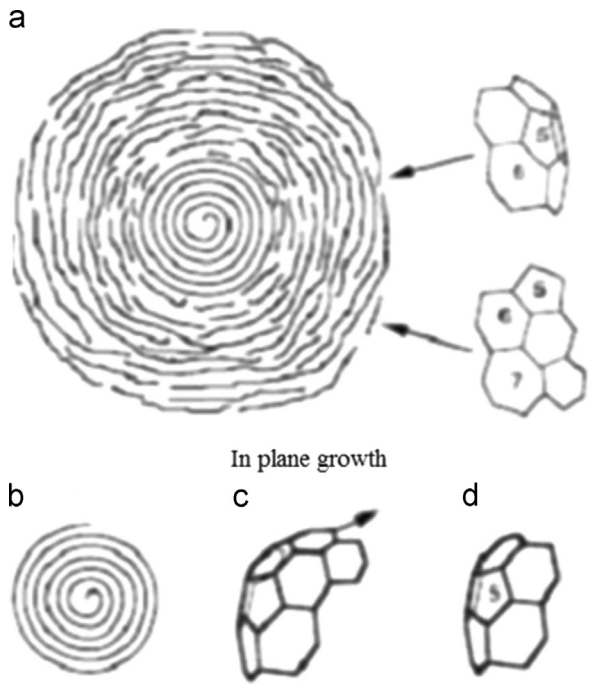

Fig. 1. (a) growth of a large carbon sphere, (b) formation of a spiral shell carbon particle proposed, (c) growth of a quasi-icosahedral shell and (d) nucleation of a pentagon [24].

2. Experimental section

2.1. Sample preparation

Carbon spheres (CSs) were prepared by a non-catalytic chemical vapor deposition (CVD) method using acetylene as the carbon source [25]. A tubular quartz reactor was placed horizontally in a furnace and the acetylene was pyrolyzed in the tube to generate the CSs. The temperature in the reactor was first increased to 900 °C in the presence of N_2 at a flow rate of 40 mL/min. Subsequently, acetylene was introduced into the reactor with a flow rate of 100 mL/min and held at 900 °C for 5 min. The yield of the reaction, defined as the ratio of the product (carbon deposit) produced to the amount of reactant used, was ca. 15%.

A sample for electrochemical and photo-electrochemical tests was prepared by thoroughly mixing CSs and paraffin oil in an agate mortar and pestle. The ratio of CSs to paraffin oil was 7/3 (weight/weight). The mixture was introduced into a glass tube ($d=2.0$ mm) in which a copper wire was embedded to ensure an electrical connection.

2.2. Characterizations techniques

X-ray diffraction (XRD) studies were performed with a Siemens D500 diffractometer using monochromatized Cu Kα radiation with 0.02° (2θ) steps and 1 s counting time in the range 10–80°. The Fourier transform infrared (FTIR) spectra were recorded with a Perkin-Elmer spectrometer over the range 4000–400 cm^{-1}, by mixing ~4 mg of powder with 100 mg of dried spectroscopic grade KBr which was pressed into a pellet. The diffuse reflectance spectrum was recorded with a Perkin-Elmer Lambda 9 spectrophotometer. Thermogravimetric analysis (TGA/DTG) was performed with a Perkin-Elmer STA6000 TGA using nitrogen or air as the purge gas at a heating rate of 10 °C/min and purge gas flow rate of 20 mL/min. The N_2 adsorption–desorption experiment was conducted using a Micromeritics TriStar surface area analyzer. Prior to the experiment, the sample was outgassed at 200 °C for 6 h. The BET surface area was obtained in a relative pressure range from 0.05 to 0.30. A transmission electron microscopy (TEM) study of the sample was carried out at 197 kV using a Philips CM200 TEM equipped with a LaB6 emitter, an Oxford ISIS EDX super ultrathin window detector and a Gatan Model 678 Imaging Filter (GIF).

The electrical conductivity data was measured at room temperature using the experimental setup shown in Fig. S1. The measurements were performed using 5 K-step measurements in the temperature range 300–500 K by the two-probe method using a GWINSTEK model GDM-8255 apparatus. The conductivity of the samples was measured as a function of temperature. Voltammetry measurements and electrochemical impedance spectroscopy (EIS) studies were carried out using a potentiostat/galvanostat PGZ301 (Radiometer). The electrochemical cell was assembled with a conventional three electrode system: a saturated calomel electrode (SCE) as reference electrode, a platinum wire counterelectrode (CE) and a prepared carbon paste as working electrode (WE). All electrochemical experiments were carried out at room temperature. The support electrolyte Na_2SO_4 (0.5 M, pH~6.8–7) was continually flushed with nitrogen. The light source consisted of a tungsten lamp (200 W) emitting in the range 400–800 nm. All tests were repeated three times.

3. Results and discussion

Fig. 2 shows a transmission electron microscopy (TEM) image of the CSs. The synthesized carbon spheres are obtained a good yield (ca. 15%) with a diameter of 115 ± 10 nm. The relative DTG curve exhibits one weight loss peak ca. 98%, located at 700 °C (Fig. S2). The results indicate that the carbon spheres are graphitic, and that they are stable up to about 700 °C, after which they begin to gradually lose weight in air [26]. The X-ray diffraction pattern of the CSs was recorded (Fig. S3). The strongest diffraction peaks at $2\theta=25.3°$ and 43°, indexed at (002) and (100), were ascribed to graphitic carbon [27]. The nitrogen adsorption–desorption isotherm and the pore size distribution for CSs are shown in Fig. S4. The isotherm for the CSs is type II with a pronounced H3 type hysteresis loops. The BET surface area is ~10 $m^2\ g^{-1}$ indicating that the spheres had little or no porosity. Fig. S4 inset shows the pore size distribution curve. The data obtained from the peak positions of the CS materials (122 and 160 nm) correspond to the void spaces between the spheres. The various results revealed that the CSs are perfectly round, pure, solid and do not contain any porosity.

The CS band gap was estimated from data based on the diffuse reflection spectral data [28]. The relation between the absorption coefficient (α) and the incident photon