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Carbon nanosheets by the graphenization of ungraphitizable isotropic pitch molecules

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ABSTRACT

We report a tremendous structural evolution of carbon nanosheets (CNSs) through the graphenization of isotropic pitches prepared by reforming commercially available naphtha cracking bottom oil. CNSs with thicknesses of 2–13 nm were prepared by spin-coating on quartz substrates directly without a catalytic material, followed by two successive thermal treatments consisting of stabilization at 270 °C in air and carbonization at up to 1200 °C in H_2/Ar. The development of well-ordered graphene layers around pebble-like structures with increasing carbonization temperature was observed in only the 13-nm thick CNSs by transmission electron microscopy, whereas thin CNSs did not reveal well-developed fringe growth. In addition, Raman, UV–vis, and X-ray photoelectron spectroscopies along with mass spectrometry unanimously showed clear evidence indicating that unusually well-developed crystalline structure was formed in the thick CNSs. It should be noted that isotropic pitches, which are intrinsically non-graphitizable carbon sources, evolved into highly ordered structures at a relatively low carbonization temperature (1200 °C). We believe that the graphenization of spin-coated films of pitch molecules resulted from the condensation of small pitch molecules and their self-assembled structure during carbonization under the anisotropic pressure induced by significant shrinkage in the vertical axis.

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1. Introduction

In carbon materials, graphitization enhances crystallinity and is therefore one of the key factors involved in improving their performances in various applications such as electrochemical capacitors, lithium-ion batteries, reinforced composites, structural materials, and hydrogen storage materials [1–4]. Graphitization with adequate precursors requires considerably high temperatures for the pyrolysis of the non-carbon organic materials. It is known that a graphitic structure containing stiff and straight graphitic layers stacked sequentially develops over 2000 °C and that a highly ordered graphitic structure develops near 3000 °C in an inert atmosphere [5].

Generally, the carbon materials that form an ordered graphitic structure through high-temperature treatments (HTT) are classified as graphitizable carbons (or soft carbons). In contrast, non-graphitizable carbon materials (or hard carbons) form disordered carbon structures, such as the turbostratic structure, through HTT, although short-range-ordered graphitic structures have been observed in small regions [6]. Therefore, graphitizable carbons derived from mesophase pitch are usually used to obtain ordered graphitic carbon materials [7]. For several decades, researchers have reported various methods for the facile synthesis of graphitic carbon materials to overcome the limitations of graphitization [8–10]. For instance, ordered graphitic structures can be developed in non-graphitizable carbons by using additional treatments such as adding catalytic materials (i.e., metal), applying strain, and pre-aligning molecules before HTT. These treatments also decrease the graphitizing temperature of non-graphitizable and graphitizable

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carbons [8–10].

Furthermore, these studies have led to a more comprehensive understanding of the graphitizing mechanism of carbon materials. Oberlin et al. have extensively studied the structural evolution of mesophase pitch-based carbon fibers as graphitizable carbons at temperatures up to 3000 °C [5]. They classified structural changes by four stages as a function of thermal treatment temperature. During stage 1 (up to 600 °C), the basic structural units (BSUs) of mesophase pitch fibers with columns of 2–3 fringes were observed by transmission electron microscopy (TEM). During stage 2 (600–1500 °C), the length of the BSUs did not change, but single BSUs piled up into distorted columns due to the release of heteroatoms (hydrogen and oxygen) ending at 800 °C. Single misoriented BSUs trapped between distorted columns were observed. These misoriented BSUs disappeared entirely in the next stage. In the transition stage from 1500 to 1900 °C, the distorted columns turned into stacks of distorted layers, leading to a fast increase in crystallite thickness. During stage 3 (1900–2100 °C), the wrinkles of the layers and the turbostratic structure disappeared. During stage 4, above 2100 °C, the three-dimensional order grew quickly as the graphitic layers became stiff and perfect.

These four steps can be considered as two processes. One is the carbonization that removes the heteroatoms (stages 1 and 2), and the other is the graphitization that develops the graphitic structure. From this point of view, stages 3 and 4 are unlikely to occur in non-graphitizable carbons due to their original structure. Isotropic pitch is known as a precursor of non-graphitizable carbon materials [11]. Normally, pitches are polymerized and thermally or catalytically condensed, using residuals of petroleum oil or coal tar or using by-products of naphtha cracking or coking. Pitches are a complex mixture containing aromatic hydrocarbons having more than three fused rings and aliphatic hydrocarbons with aliphatic side chains [12–14]. Pitches can be classified by their preparation method and structure: isotropic pitches and mesophase (or anisotropic) pitches. Mesophase pitches show a highly oriented molecular structure associated with external shear stress. In contrast, isotropic pitches show lower molecular orientation. Therefore, it should be noted that thermal treatment cannot lead to ordered graphitic structures from isotropic pitches.

In this study, we report an interesting structural evolution of graphene layers in isotropic pitch-based carbon nanosheets (CNSs), even though isotropic pitches are non-graphitizable carbon sources. We synthesized isotropic pitches from naphtha cracking bottom (NCB) oil Soluble isotropic pitches were spin-coated onto quartz substrates directly without using catalytic materials or applying external strains. Subsequent stabilization and carbonization up to 1200 °C produced CNSs with thicknesses of 2–13 nm. The structural evolution of the CNSs was systematically investigated using TEM, Raman, UV–vis, and X-ray photoelectron spectroscopies along with mass spectrometry. On the basis of the systematic characterization, the effects of thickness and the carbonization temperature on the structural evolution of the CNSs by graphenization were comprehensively studied. Moreover, the electrical properties and transmittance of the CNSs were evaluated to demonstrate their potential as transparent electrodes. This graphenization process of isotropic pitches on quartz substrates will be an important advance because of its simplicity and cost-effectiveness.

2. Experimental

2.1. Preparation of raw materials

The isotropic pitch used in this study was derived from NCB oil (SK Co., Korea) using a reforming reactor. The NCB oil was reformed under nitrogen flow (4 l/min) at 390 °C for 3 h. The resulting pitch was crushed into a fine powder using a mortar and pestle. The pitch powder (4 g) was added to 36 g of N,N-dimethylformamide (DMF, Aldrich) at 30 °C for 24 h. The resulting solution was filtered to separate the soluble portion from the insoluble portion, which has a relatively higher molecular weight than the soluble portion. The solid pitch was obtained by evaporating the DMF solvent from the soluble portion at 100 °C for several minutes.

2.2. Synthesis of CNSs

Four different concentrations, 1, 3, 5 and 7 wt%, of solidified soluble pitches in DMF solution were prepared to control the thickness of the CNSs. Quartz substrates were sonicated in a mixture of acetone and isopropyl alcohol for cleaning. The solutions with different concentrations were spin-coated on the quartz substrates at 4000 rpm for 90 s. The resulting thin films were pyrolyzed in two steps. First, stabilization was performed at 270 °C for 2 h under air in a convection oven. Then, the stabilized films were carbonized at 1200 °C under H_2/Ar. The samples spin-coated with 7 wt% pitch were thermally treated at 400, 600, 800 and 1000 °C under the same carbonization atmosphere. This allowed the effect of carbonizing temperature on the graphitic structure evolution to be investigated.

2.3. Characterization

2.3.1. Materials

The softening points of the reformed pitches were obtained using a FP-83 (Mettler Toledo, USA) with the FP-90 universal control system according to ASTM D3104-99. The molecular weight of the soluble isotropic pitch was measured by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF, Voyager-DE STR Biospectrometry Workstation, Applied Biosystems Inc.). Tetrahydrofuran (THF) and dithranol were used as a solvent and matrix, respectively.

2.3.2. Carbon nanosheets

Raman spectroscopy (Horiba, LabRAM HR UV–Visible–NIR) was performed to obtain information about the structural properties of the carbon materials using a laser excitation wavelength of 514.5 nm at a power of 16 mW. The spot size of the 100× objective incident laser was ~1 μm. All Raman spectra of CNSs on quartz were measured from 800 to 3500 cm^{-1} at room temperature. TEM (Tecnai G2 F20, FEI) was used to obtain high-resolution lattice structural information with an accelerating voltage of 200 kV. To examine a CNS by TEM, the following etching process was performed. First, CNSs were immerged in a buffer oxide etchant solution (BOE) to etch a SiO_2 layer between the CNSs and quartz. After 0.5–2 h (etching time depended on the CNS thickness), the floating CNSs were rinsed with deionized water for several hours. Finally, the CNSs were transferred onto a 200 mesh holey carbon-coated copper grid. Selective area electron diffraction (SAED) was employed to obtain crystallographic information about the CNSs. The surface morphologies and thicknesses of the CNSs were determined using atomic force microscopy in tapping mode (AFM, Veeco, SPM Dimension 3100 with Nanoscope IIIA controller). All matrix-free laser desorption/ionization mass spectrometry (LDI-MS) analyses of CNSs were performed with a Bruker Autoflex III (Bruker Daltonics, Germany) equipped with a Smartbeam laser (Nd:YAG, 355 nm, 120 μJ, 100 Hz, 50 μm spot diameter at target plate) in positive reflection mode. The accelerating voltage was 19 kV, and all spectra were obtained by averaging 500 laser shots with 100 μJ laser power unless otherwise indicated. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-alpha) was

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