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Carbon nanosheets derived from soluble pitch molecules and their applications in organic transistors

Jae-Seon Lee [a,b], Han-Ik Joh [a], Tae-Wook Kim [c,*], Sungho Lee [a,b,*]

[a] Carbon Convergence Materials Research Center, Korea Institute of Science and Technology, San 101, Eunha-ri, Bongdong-eup, Wanju-gun, Jeollabuk-do 565-905, Republic of Korea
[b] Department of Nano-Material Engineering, University of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea
[c] Soft Innovative Materials Research Center, Korea Institute of Science and Technology, San 101, Eunha-ri, Bongdong-eup, Wanju-gun, Jeollabuk-do 565-905, Republic of Korea

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ABSTRACT

We report a synthesis method for carbon nanosheets (CNSs) using pitch prepared by reforming a commercially available naphtha cracking bottom oil, which is often used as a carbon fiber precursor. The pitch solution is spin-coated on a silicon wafer without using a catalyst support. After stabilization and carbonization, the CNSs as thin as 2 nm show an electrical conductivity of approximately 30,000 S/m. Although the CNSs do not have a well-developed graphitic structure, as observed using Raman spectroscopy and transmission electron microscopy, they are conductive enough for use as electrodes in an organic thin film transistor.

1. Introduction

Carbon material with graphitic structure is one of the constantly studied topics for centuries and the discovery of carbon allotropes such as fullerenes, carbon nanotubes and graphene has ignited interest in the study of carbon material. Especially, graphene, a type of carbonaceous material consisting of a one-atom-thick planar sheet of sp^2-bonded carbon atoms [1–4], have attracted a lot of attention from researchers due to its extraordinary properties such as high electron mobility, superior strength, large surface to volume ratio and impermeability of gas. Graphene with the peculiar properties is expected to be used in numerous potential applications such as electronic devices, composite filling, gas barrier, and energy storage. Therefore, various synthetic methods for practical studies and applications of graphene have been reported: mechanical exfoliation [1,2], chemical exfoliation [3,4], and chemical vapor deposition (CVD) [1,2,5].

The technique of a mechanical exfoliation of highly oriented pyrolytic graphite (HOPG) is a well-known way to produce pure graphene exhibiting the highest quality, but it is also observed that this technique is not suitable for mass production and a large scale growth of graphene [1,2,6]. Chemical exfoliation from bulk graphite is appropriate for bulk production of graphene, but is still not a suitable for method to synthesize large scale graphene [3,4]. Also, properties of graphene made by this synthetic method exhibit lower values than intrinsic properties of graphene due to many defects and functional groups introduced during a redox process although chemically exfoliated graphene can be used for various applications through proper treatments like heat treatment reducing defects or doping for increasing electrical or catalytic properties [6–8]. CVD growth using carbon sources on metal used as catalyst layer is affordable for synthesis of graphene with high quality and large scale. Therefore, CVD growth has been

* Corresponding authors. Address: Carbon Convergence Materials Research Center, Korea Institute of Science and Technology, San 101, Eunha-ri, Bongdong-eup, Wanju-gun, Jeollabuk-do 565-905, Republic of Korea. Tel.: +82 63 219 8136; fax: +82 63 219 8249 (T-W. Kim), tel.: +82 63 219 8134; fax: +82 63 219 8269 (S. Lee).
E-mail addresses: twkim@kist.re.kr (T.-W. Kim), sunghol@kist.re.kr (S. Lee).

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considered as a proper method for synthesis of graphene to be used in electronic devices [1,2,5]. CVD growth of graphene requires low vacuum and two post-processing for removing metal layer and transferring to a target substrate. However, artifacts during two post-processing such as defects, wrinkles and impurities may occur on graphene, which lessen original properties [9].

In this study, we report a new approach for producing pitch-derived carbon nanosheets (CNSs) synthesized on a silicon wafer directly without using any catalytic supports at atmospheric pressure, which reduced process steps such as catalyst removal and nanosheets transfer. Pitches which have been prepared as by-products of naphtha cracking or coking utilizing the thermal or catalytic polymerization of petroleum residual oil or of coal tar are some of the cheapest precursors for producing carbon fibers (CFs) contained polynuclear aromatic hydrocarbon molecules with a small number of aliphatic side chains [10–12]. For fiber manufacturing, after stabilization, which leads to infusible pitch fibers, a heat treatment is applied to carbonize the fibers. In carbonization up to 1000 °C, most of the gases, such as H_2, N_2, CO, CO_2, and CH_4, are generated and removed from the fibers [13,14]. A further increase in temperature results in more-ordered structures, and with a heat treatment above 2100 °C, significantly developed graphene layers were observed [15]. Therefore, recently carbon fibers (CFs) have been used to prepare graphene-related materials [16,17]. Polyacrylonitrile-based CFs, which contain graphene layers with turbostratic structures, were used to extract graphene using microwave radiation [16]. And also graphene quantum dots with a size distribution of 1–4 nm were extracted from pitch-based CFs including graphene layers through chemical oxidation [17].

We demonstrate here CNSs with graphitic structure randomly stacked using cheap pitch based precursors coated on a silicon wafer. To investigate the feasibility of using our CNSs as an electrode, we fabricated pentacene-based organic thin film transistors (OTFTs) without using a transfer process, which is necessary for CVD grown graphene films when applying them to electronic devices.

2. Experimental

2.1. Materials

Naphtha cracking bottom (NCB) oil (SK Co., Korea) was reformed using a reforming reactor to obtain pitch. The NCB oil was stirred with a nitrogen flow rate of 4 l/min at 390 °C for 3 h. The softening point of the resulting pitch was found to be 190 °C using the Mettler Toledo FP-83, which was controlled by the FP-90 universal control system according to ASTM D3104-99.

2.2. Preparation of CNSs

Dimethylformamide (DMF, Aldrich) solutions of the pitch were prepared by dissolving 10 g of pitch in 100 g of DMF, and the insoluble components were removed by filtration. The DMF was evaporated to obtain pitch solids, and the pitch was dissolved in DMF to produce 1, 3, and 5 wt% solutions. The resulting solutions were spin-coated on silicon wafers with 100 nm thick SiO_2 layers to produce thin films with thicknesses of 12.2 ± 0.7 – 62.8 ± 2.4 nm (see Supporting Information, Fig. S2). These thin films were stabilized at 300 °C for 2 h under an air atmosphere in a tubular oven. The stabilized films were heat-treated at 1200 °C under a gas mixture of H_2 and Ar to carbonize them.

2.3. Characterization of CNSs

The molecular weight distribution of the pitch was observed by a matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF, Voyager-DE STR Biospectrometry Workstation, Applied Biosystems Inc.). The broad molecular weight peak at ~320 was observed (see Fig. S1). The surface morphology was examined using atomic force microscopy (AFM, Digital Instruments Nanoscope IIIA, Veeco) in tapping mode with silicon tips having a resonance frequency of 260 kHz. The chemical components of the CNSs were investigated using X-ray photoelectron spectroscopy (XPS, AXIS-NOVA, Kratos Inc., USA). Raman spectroscopy was performed using a Lab-RAM HR system (Horiba Jobin Yvon, France) with a 16 mW and 514.54 nm laser. All spectra were obtained for a spectral range of 800–3500 cm^{-1}. The surface resistivity was measured using a resistivity meter (FPP-RS8, Dasol Eng., Korea). The optical properties of CNSs transferred onto a glass substrate were characterized using a UV/Visible spectrometer (V 670, Jasco). To investigate the structure of the CNSs using transmission electron microscopy (TEM, JEM2200FS, USA), CNSs were transferred onto a Formvar/carbon film-supported copper grid.

2.4. Preparation of OTFTs

OTFTs with pitch-derived CNS electrodes were directly fabricated on a 100 nm thick SiO_2 layer on a heavily doped Si substrate. The CNS patterning process for both source and drain electrodes was performed using a well-known dry and wet etch sequence. First, a 50 nm thick Ni layer was evaporated through a shadow mask onto CNSs. Second, the unprotected area of the CNSs was completely removed by an oxygen plasma at 100 mTorr and 100 W for 5 min. Third, the Ni mask patterns were etched away by dipping the CNSs into a $FeCl_3$ solution. Last, a pentacene active layer (~50 nm) was deposited using a thermal evaporation method through a shadow mask onto the patterned CNS electrodes. The fabricated pentacene-based OTFTs had widths of 1000 μm and channel lengths of 250 μm. All electrical characterizations were performed using a HP4145B semiconductor parameter analyzer in a nitrogen-filled glove box system.

3. Results and discussion

3.1. Properties of CNSs

Pitch, prepared from the thermal reformation of a commercially available naphtha cracking bottom oil, was used