Diamond & Related Materials 83 (2018) 75–79

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Anomalous resistivity of heavily nitrogen doped graphitic carbon

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ARTICLE INFO

Keywords:
Carbon nitride
Graphite
Electrical properties characterization
Impurity characterization
Electrical conductivity

ABSTRACT

The C-N samples were synthesized at 500 °C from melamine and four kinds of pitch. At 50–100 mass % of pitch all samples were single phase nitrogen solid solutions in graphitic carbon. Maximal detected concentration of 22.4 mass % N correspond to solid solution with formula $C_{100}H_{26.8}N_{26.3}O_{3.1}$. According to infrared spectroscopy the N atoms chaotically substitute carbon. The electric resistivity of samples with 22.4 mass % N was 1.3–67 Ω ∗ m, which is 100–1000 times lower than resistivity of corresponding graphitic carbon without doping (430–6700 Ω ∗ m). The resistivity of graphitic C_3N_4 is about 10^{11} Ω∗m.

1. Introduction

Nitrogen doped carbon materials represent an exciting challenge to both fundamental and applied research. Its two formal components, carbon and C_3N_4, are already well explored in different forms revealing outstanding physical properties. The promising approach for tuning and controlling the electronic properties of graphite is doping with heteroatoms, similar to that elaborated for the silicon-based technology. A nitrogen atom contains one additional electron and when replacing a carbon atom in the graphite lattice, novel electronic properties can be envisaged. Producing of intermediate C-N compounds cannot be done via convenient ceramic way by heat treatment of carbon and C_3N_4 mixture since decomposition of carbon nitride starts at 500–600 °C [1], much earlier than any significant reaction with carbon.

The examples of nitrogen doped carbon materials are much more rare than those of carbon and C_3N_4 alone but their electrical and chemical properties make it a promising material for production of supercapacitors, batteries and fuel cells [2–16], anodes for H_2O_2 production [11,12], selective adsorbents [17], and sensors [18–21].

Nitrogen doped carbons have been prepared in different ways, but most of them were obtained as amorphous materials with relatively low N content of 1–15 mass % as summarized in reviews [2,13]. The production methods include laser or magnetron sputtering [13,22,23], CVD [13,24], treatment of carbon materials by nitrogen-rich molecules [5,7,9,11,13,15,17,25], thermolysis of polymer [4,8,13,14,16,26], ionic liquids [12,13], aminosugar [27], terephthalonitrile [28], ethylenediamine tetraacetic acid disodium magnesium salt [10] or gaseous pyridine and pyrrole [18,29–32].

Synthesis of bulk C_3N_4 is usually performed by thermolysis of various precursors like melamine, urea, thiourea, dicyanamide at 450–600 °C [1]. Melamine usually provides more pure and better crystallized product with higher yield. On the other hand, there is a well known method of production of graphite comprised by slow thermolysis of coal tar or petroleum pitches at 500–1000 °C [33]. Nonetheless, methods of bulk production of nitrogen doped graphite from pitch and melamine have not been explored in detail.

The aim of present work is a systematic investigation of phase composition and specific resistivity of materials prepared by thermolysis of melamine mixed with one of four kinds of pitch.

2. Materials and methods

Reagent grade melamine and four kinds of pitch were used in the synthesis: medium temperature coal tar pitch (MidT Pitch), high temperature coal tar pitch (HiT Pitch), petroleum pitch (Oil Pitch) and shale tar pitch (Shale Pitch). Softening temperatures are 67–83, 135–150, 85–95 and 75–100 °C correspondingly. Portions of 0, 1, … 10 g of pitch were added respectively to 10, 9, … 0 g of melamine, then

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https://doi.org/10.1016/j.diamond.2018.01.026
Received 23 December 2017; Received in revised form 19 January 2018; Accepted 29 January 2018

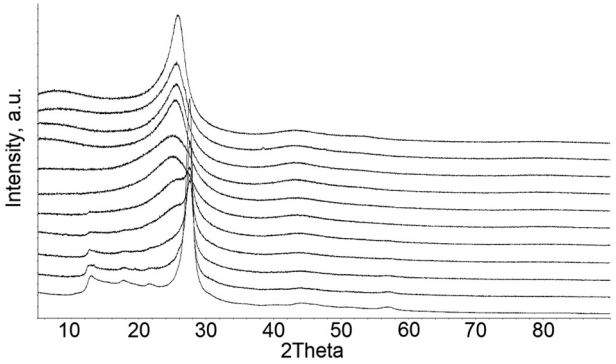

Fig. 1. The PXRD patterns of medium temperature coal tar pitch – melamine samples after exposure to 500 °C. From top to bottom: 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 0 mass % pitch/(pitch + melamine).

samples were ground and thermolysed with no air access. The mixtures were heated in glass vessels to 500 °C during 500 h and held for 100 h at this temperature. Another series of samples was prepared in the same way and additionally heated from 500 to 950 °C within 8 h.

The X-ray diffraction was performed on a powder diffractometer Rigaku Ultima IV (Cu K_α radiation). Infrared (IR) spectra were collected with FTIR-spectrometer Shimadzu IRAffinity-1S. Investigation of the morphology of the samples was done using a scanning electron microscope Jeol JSM-7001F. The X-ray fluorescence analysis was performed with energy dispersive X-ray (EDX) spectrometer Oxford INCA X-max 80 installed on this microscope. C, N, H content was determined with Perkin Elmer 2400 Series II CHN analyzer. Resistivity was measured by two point method on a compacted powder samples.

3. Results and discussion

According to powder X-Ray diffraction (PXRD) data, after 500 °C samples prepared with 50–100 mass % pitch form graphite based N solid solutions (Fig. 1) [33]. Sample prepared with 100 mass % melamine form pure C_3N_4 [1]. Samples prepared with 10–40 mass % pitch form graphite based solid solution mixed with C_3N_4 phase. Optical microscopy of samples reveals black carbon mass in samples prepared with 50–100 mass % pitch and light-yellow flakes of C_3N_4 in black mass in the samples prepared with 10–40 mass % pitch (Fig. S1), in agreement with PXRD results. Morphology of the samples after 500 °C heat treatment revealed gradual change from loose packed C_3N_4 flakes through macroporous solid solution to dense layered graphite (Fig. 2).

Layered graphitic morphology indicates formation of pitch mesophase on heating (Fig. 2c). Diffractograms containing overlapping peaks of two phases were deconvoluted into individual peaks. The (002) C_3N_4 peak position [1] is identical for all two-phase samples and stands at 27.53–27.58°2θ coinciding with peak of pure C_3N_4 (Fig. S2a). The (002) graphite peak position [33] remains in the narrow interval of 25.2–25.9°2θ for all solid solutions regardless of pitch content and pitch type (Fig. S2a). It means that interplanar distance of nitrogen doped graphite remains independent on N concentration. The (002) graphite peak FWHM increases linearly with pitch content from 4.7 to 7.6°2θ (Fig. S2b). According to Scherrer equation the correspondent crystallite size L_c of N-doped graphite drops down from 1.1 to 0.7 nm with N content growth. The FWHM of C_3N_4 does not change with sample composition. Heating to 950 °C turn all graphite peak position to smaller angle that correspond to expansion of interplanar distance (Fig. S2a). Simultaneously the FWHM of all graphite peaks after 950 °C become larger, indicating more disordered structure (Fig. S2b).

The IR spectra has distinct change at 50 mass % pitch (Fig. 3).The specific C_3N_4 IR breathing mode peak at 806.25 cm^{-1} [1] is absent in spectra of N-doped graphite samples. The other series of samples prepared with different pitches has very similar PXRD, SEM and IR

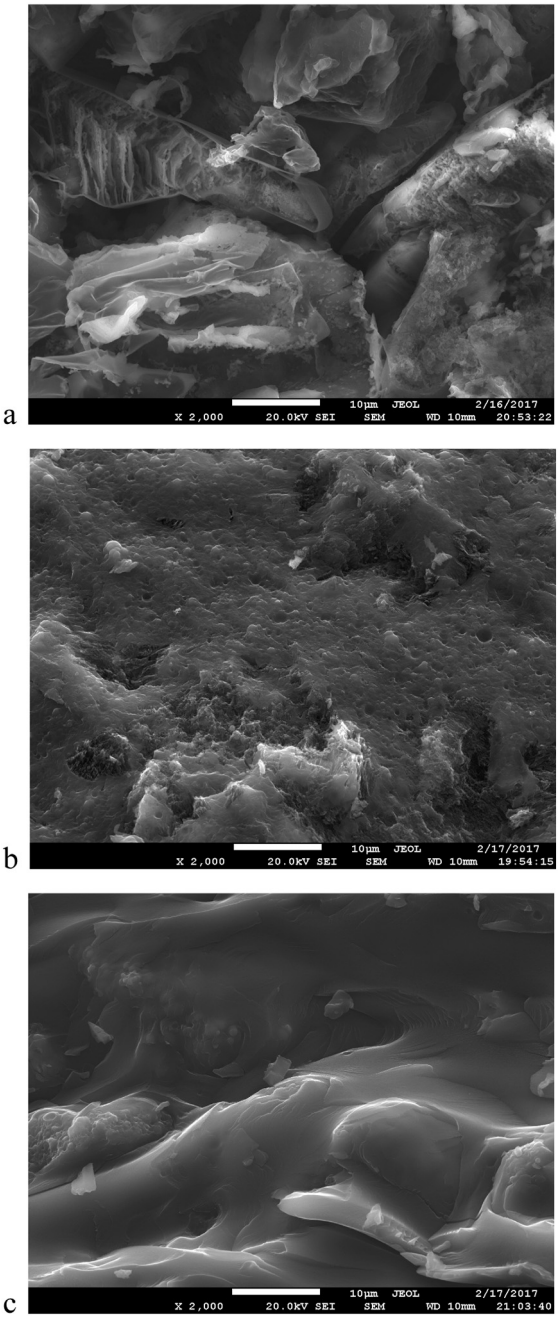

Fig. 2. Fresh cracked surface SEM images of samples with 0 (a), 70 (b) and 100% (c) of medium temperature coal tar pitch.

patterns.

To determine influence of nitrogen on local structure of homogeneous graphitic samples with 50–100 mass % of pitch after exposure to 500 °C it also were investigated by Raman spectroscopy at a wavelength of the excitation laser 632.8 nm. To register Raman spectra there were used the iHR 320 spectrometer Labram attached to a microscope Olimpus BX41 in 180° geometry. Microscope objective × 50 was used to focus the laser beam on area of approximately 5 μm in diameter. Obtained Raman spectra of Shale Pitch and MidT Pitch based samples (Fig. S4) were deconvoluted into two Gaussian curves to find the position and intensities of the graphitic G and disordered carbon D peaks.

The positions of the D and G peaks maxima are in the range 1334–1347 and 1574–1589 cm^{-1} for the Shale Pitch samples and 1331–1338 and 1570–1589 cm^{-1} for MidT Pitch samples, respectively, that are typical for similar materials [33–36].