Graphitic carbon subnitride: Synthesis, structure, electron and proton transport, photoluminescence and thermoelectric properties

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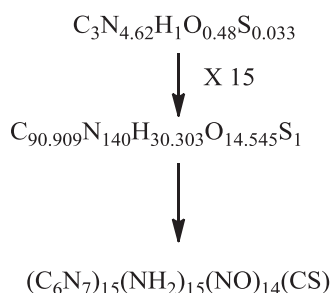[b] Technical Centre of NAS of Ukraine, Pokrovska Str. 13, Kyiv 04070, Ukraine
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HIGHLIGHTS

- We synthesised graphitic carbon subnitride with N-cross-linking between planes.
- It had an antiferromagnetic structure with strong photoluminescence/thermoelectric.
- Its specific inner injected proton conductivity was $10^{-7} \div 10^{-5}$ S/cm at 20−400 °C.
- Its specific electric conductivity was $10^{-7} \div 10^{-6}$ S/cm following spin wave formation.

GRAPHICAL ABSTRACT

$$C_3N_{4.62}H_1O_{0.48}S_{0.033}$$

$$\downarrow \quad X\ 15$$

$$C_{90.909}N_{140}H_{30.303}O_{14.545}S_1$$

$$\downarrow$$

$$(C_6N_7)_{15}(NH_2)_{15}(NO)_{14}(CS)$$

ARTICLE INFO

ABSTRACT

We have synthesised graphitic carbon subnitride by using pyrolysis of cheap ammonium thiocyanate. We've attempted to understand the structure and properties of CN-derivatives. It has been ascertained that graphitic carbon subnitride is the heptazine adduct with N-cross-linking between graphitic planes. It had gone antiferromagnetic structure with strong visible and UV photoluminescence and pronounced thermoelectric properties. Its measured specific inner electric conductivity is $10^{-7}\dots10^{-6}$ S/cm within the temperature's range 20−400 °C. The specific injected proton conductivity is $10^{-7}\dots10^{-5}$ S/cm and couldn't be separated from the electron component. Both types of its conductivity depend on the relative humidity, even at 300…400 °C. A possible mechanism for this effect has been discussed. As a whole, the electromagnetic conductivity of carbon subnitride is defined by the electron component following spin wave formation. So, carbon subnitride derivatives show themselves as promising materials for spin waveguide applications including proton-exchanged specimens. Generation of an inner potential makes it possible to consider these compounds as showing prospects for power sources and thermoelectric devices.

1. Background

Graphitic carbon nitride (g-C_3N_4) and its derivatives are the most promising materials for different applications including

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optoelectronics, mainly because of its chemical and physical hardness [1—5] as well as a metal-free catalyst [6]. It is insoluble in a large class of solvents, such as water, ethanol, toluene, and diethyl ether and is non-volatile up to 600 °C [7,8]. Carbon nitride based materials can display different structural phases [9], and their related properties [10,11]. Actually, several synthesis methods were employed in the production of graphitic carbon nitride materials, namely: phase and chemical vapour deposition (PVD and CVD), solvothermal method, solid-state reaction and thermal nitridation [12]. In general, the synthesis requires nitrogen-rich sources like cyanamide, dicyandiamide [13—15], and its ionic liquids [16], urea [14,17], melamine [18] or thiocyanates [19,20]. Jürgens et al. [21] postulated the mechanism of precursors' condensation: at temperatures slightly higher than 300 °C condensation with ammonia liberation provides the formation of the 2,5,8-triamino-tri-s-triazine (also called as heptazine or melem, or carbon subnitride) and its derivatives. The subsequent linking mechanism of heptazine units determines the melon or polymeric carbon nitride. Despite the universally recognised growth mechanism of thermally synthesised graphitic carbon nitride materials, their structure is still debated and their determination represents a challenge for the correct prediction of physical and chemical properties [22—27]. CN-nanofibers or nanolayers were prepared by mechanical grinding [28] or hydrolyzing [29] of bulk CN-derivatives. Nevertheless, high-yield synthesis methods testify the scalability of the graphitic carbon subnitrides to mass production for optoelectronics [30]. Dissolution of carbon nitride [31] and its application as proton conductors [32] and electrochemiluminescent sensor [27] were reported. It will be interesting to know can we use carbon subnitride as proton-exchanged waveguides for photonic applications. So, this study is devoted to ascertaining the structure of carbon subnitride obtained from cheap raw ammonium thiocyanate, and the measurement of electron and proton transport through the bulk synthesised samples.

2. Methods

2.1. Synthesis of carbon subnitride

We synthesised molecular carbon subnitride by using the pyrolysis of NH_4SCN. In a typical synthesis process, a quartz tube, 32 mm in inner diameter and 170 mm in length, was used as the reaction chamber. Fine powder of ammonium thiocyanate (Sigma-Aldrich) was charged as the precursor. The synthesis was carried out at the temperatures from about 420 to 500 °C for 3 h in the atmosphere of He under the autogenous pressure due to the pyrolysis of the precursor. The quartz reactor was cooled to the ambient temperature naturally. Then the floccular powders were collected and washed with acetone, ethanol, and distilled water repeatedly to remove the residual reactants and byproducts. Finally, samples were dried in a hot air flow.

2.2. Characterization of carbon subnitride

The compositions of the samples were examined using the CH-N elemental analysis through the Pregl-Dumas technique. The sulphur content was determined by titration with barium perchlorate in acetone-water medium to the Nitchromazo endpoint. The structural analysis of the products was carried out using powder X-ray diffractometry with Rigaku MiniFlex 600 operating with Cu K_α radiation. The Fourier transform infrared (FTIR) analysis was performed using vacuum Fourier spectrometer Bruker Vertex 70 V. The FTIR spectra (diffuse reflectance) were recorded at T = 300 K using A 528-P/Q (Pike Technologies) diffuse reflectance accessory. The FTIR signals were excited by the globar. The spectra

were plotted as Kubelka-Munk transformed spectrum (absorbance). The structural (vibrational and radiative recombination) properties, as well as the defect-impurity state of hydrogenated g-C_3N_4 powders, were characterised using micro-Raman scattering and photoluminescence (PL) spectroscopy. The μ-RS and PL spectra were measured at T = 300 K using the triple spectrometer HORIBA Jobin-Yvon T64000 equipped with a confocal microscope UV-Visible-NIR Olympus BX4 for micro-Raman and PL sampling. As an excitation tools for Raman scattering and photoluminescence, the 2.54 eV (488 nm) line from Ar-Kr laser, 3.82 eV (325 nm) from He-Cd laser, as well as 1.58 eV (785 nm) line from the diode, pumped solid state laser were used. The scanning electron microscopy (SEM) images were taken using JSM − 6490LV JEOL microscope working at 20.0 kV.

2.3. Proper electronic conductivity and injected proton conductivity of carbon subnitride

Study of the proper electronic and injected proton conductivity of the synthesised samples was performed at the elevated temperatures by using the installation shown in Fig. 1a. The main element of the installation is the reactor (1), a quartz cylinder with the height of 100 mm and inner diameter 18 mm. Carbon subnitride (2) was centred inside the reactor between two electrodes (4). The operation area of the sample was 0.489 cm^2; its mass was 0.025 g. The value of the current in the external circuit corresponded to the current through the semiconductor material. A constant voltage to electrodes (4) was applied from an external B5-50 power unit (5). Voltage control was performed using the voltmeter (6), and the current control in the external circuit was made by an ammeter (7). Autonomous heating the reactor was carried out using an electric furnace (3). The temperature was controlled by the thermocouple (4) joined to the potentiometer (5). Conductivity measurements were performed within the temperature range 25…420 °C with imposing the voltage 0.1−1.0 V.

Our developed technique allowed the separation of protonic and electronic components of the total conductivity. The electronic component of the total conductivity was separated by usage of the
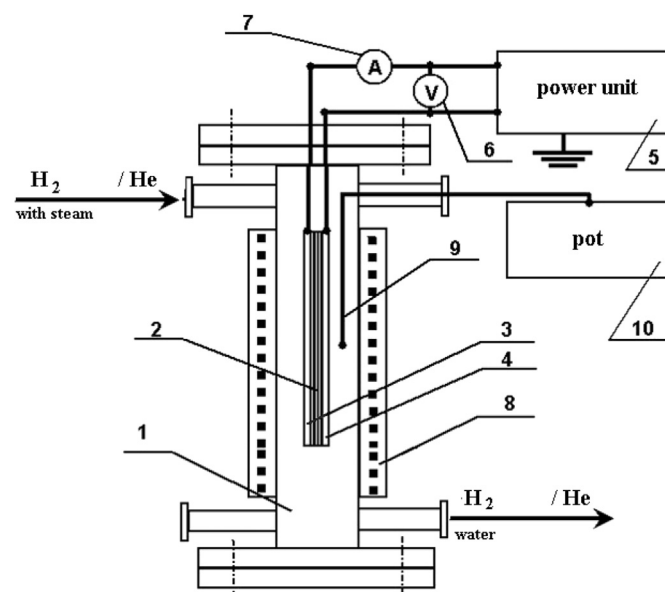

Fig. 1. Laboratory installation for measuring the injected proton conductivity: 1 — reactor; 2 — studied material; 3 and 4 — electrodes; 5 — power supply; 6 — voltmeter; 7 — ammeter; 8 — electric furnace; 9 — thermocouple; 10 — pot.