Nitrogen-carbon graphite-like semiconductor synthesized from uric acid

Roberto C. Dante [a, *], Pedro Chamorro-Posada [b], José Vázquez-Cabo [c],
Óscar Rubiños-López [c], Francisco M. Sánchez-Árevalo [d], Lázaro Huerta [d],
Pablo Martín-Ramos [e], Luis Lartundo-Rojas [f], Carlos F. Ávila-Vega [g],
Edgar D. Rivera-Tapia [h], Cristian A. Fajardo-Pruna [i], Álvaro J. Ávila-Vega [j],
Omar Solorza-Feria [k]

[a] Research, Development & Innovation, 2Dto3D S.r.l.s. Via Revalanca 5, 12036, San Firmino, Revello, CN, Italy
[b] Dpto. de Teoría de la Señal y Comunicaciones e IT, Universidad de Valladolid, ETSI Telecomunicación, Paseo Belén 15, 47011, Valladolid, Spain
[c] Dpto. de Teoría de la Señal y Comunicaciones, Universidad de Vigo, ETSI Telecomunicación, Lagoas Marcosende s/n, Vigo, Spain
[d] Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apdo. Postal 70-360, Cd. Universitaria, Mexico City, 04510, Mexico
[e] EPS, Instituto Universitario de Ciencias Ambientales de Aragón (IUCA), Universidad de Zaragoza, Carretera de Cuarte s/n, 22071, Huesca, Spain
[f] Instituto Politécnico Nacional, Centro de Nanociencias y Micro y Nanotecnologías de Nanociencias, UPALM, Zacatenco, Mexico City, 07738, Mexico
[g] Departamento de Ingeniería Civil y Ambiental, Escuela Politécnica, Escuela Politécnica Nacional (EPN), Ladrón de Guevara E11 - 253, Quito, Ecuador
[h] Newcastle University, School of Mechanical Engineering, Newcastle upon Tyne, NE1 7RU, UK
[i] Escuela Politécnica Nacional, Departamento de Formación Básica, Ladrón de Guevara E11-253, Quito, Ecuador
[j] Instituto Nacional de Eficiencia Energética y Energías Renovables (INER), Iñaquito N3537 y Juan Pablo Saenz, Quito, Ecuador
[k] Departamento de Química, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional (CINVESTAV-IPN), Av. IPN 2508, Col. San Pedro Zacatenco, Apdo. Postal 14-740, Mexico D.F., 07360, Mexico

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ABSTRACT

A new carbon-nitrogen organic semiconductor has been synthesized by pyrolysis of uric acid. This layered carbon-nitrogen material contains imidazole-, pyridine (naphthyridine)- and graphitic-like nitrogen, as evinced by infrared and X-ray photoelectron spectroscopies. Quantum chemistry calculations support that it would consist of a 2D polymeric material held together by hydrogen bonds. Layers are stacked with an interplanar distance between 3.30 and 3.36 Å, as in graphite and coke. Terahertz spectroscopy shows a behavior similar to that of amorphous carbons, such as coke, with non-interacting layers. This material features substantial differences from polymeric carbon nitride, with some characteristics closer to those of nitrogen-doped graphene, in spite of its higher nitrogen content. The direct optical band gap, dependent on the polycondensation temperature, ranges from 2.10 to 2.32 eV. Although in general the degree of crystallinity is low, in the material synthesized at 600 °C some spots with a certain degree of crystallinity can be found.

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1. Introduction

The piece of work presented herein on the products obtained from the pyrolysis of uric acid (UA) started with the objective to find an alternative pathway for the synthesis of polymeric carbon nitride (g-C_3N_4), an organic semiconductor that is receiving substantial attention due to its versatility and many potential applications [1–15]. However, the chosen precursor yielded a material with a lower nitrogen content (N to C atomic ratio ~0.6) than that of g-C_3N_4 (N to C atomic ratio of 1.33) and different polymer structure and electronic properties.

This novel carbon-nitrogen material would also belong to the class of organic semiconductors, which combine the electronic advantages of semiconducting materials with the chemical (and mechanical) benefits of organic compounds. Therefore, the ability to absorb light and conduct electricity is coupled with a structure with a flexible backbone that can easily be modified by chemical synthesis (however, the control of modifications would depend on

several factors).

The new synthesized material can be regarded as a graphitic material with imidazole-, pyridine (naphthyridine)- and graphitic-like nitrogen. Nonetheless, whereas the concentration of nitrogen in the either nitrogen-doped or defective graphite is around 2 or 3 at% (N to C atomic ratio of *ca.* 0.03), the nitrogen content in this new material is much higher (~33 at%), forcing to a less randomized distribution of defects. For example, the recently synthesized C_2N exhibited a very organized 2D structure. C_2N, in combination with g-C_3N_4, offers a potential way to improve the efficiencies of both photoabsorption and electron–hole separation of g-C_3N_4 without involving any transition metals. Fechler et al. synthesized nitrogen rich graphitic materials starting from various types of quinones and urea as precursors, showing that the amount of nitrogen in the final materials depended on reaction temperature [16–19].

Another extensively nitrogen-doped (mesoporous) carbon was synthesized by Goel et al. from melamine and formaldehyde. They obtained an interesting cross-linked structure by nanocasting that would mainly be ascribed to a certain type of melamine-formaldehyde resin with a high content of bridging oxygen atoms [20]. On the contrary, the material under study has a very low content of oxygen. Organic semiconductors of the indolocarbazole family have similar nitrogen-containing basic units and tend to have a π-π stacking and band gaps between 2.50 and 2.90 eV, depending on the side chains and the oligomer type [21–23]. Their degree of crystallinity has been shown to depend largely on the side chains and oligomer length, copolymers, as well as on the deposition method [21,22]. When they are part of large polymers, they tend to be more amorphous and the diffraction peaks become much broader and can be considerably shifted [23]. An example of these basic semiconductors is shown in Fig. 1, where R can be a side chain.

The specific combination of imidazolic, pyridinic, and graphitic nitrogen of the materials synthesized with UA is actually determined by the decomposition pathway of the crystalline UA and can be regarded as one of the upper limits of nitrogen-doped graphite (graphene) materials, such as those reported by Fechler, Zussblatt, Rothe, Schlögl, Willinger, Chmelka and Antonietti [19] and Mahmood Mahmood, Lee, Jung, Shin, Jeon, Jung, Choi, Seo, Bae, Sohn, Park, Oh, Shin and Baek [17].

2. Experimental

2.1. Materials

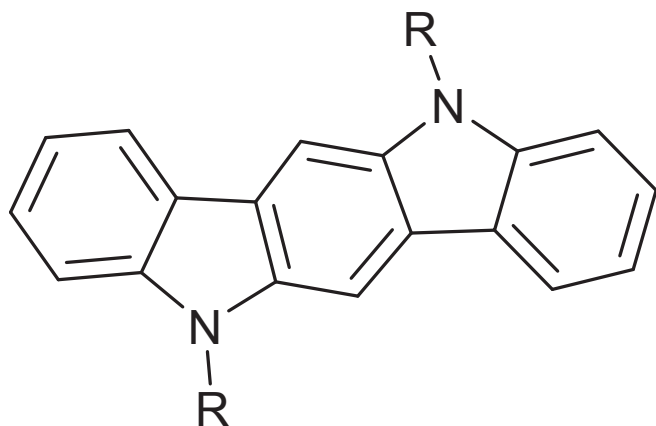Uric acid was supplied by Aesar and melamine was supplied by Sigma-Aldrich with purities higher than 99% (the chemical formulas are displayed in Fig. 2). A mixture of 95 wt% of uric acid and 5 wt% of melamine was prepared and milled in an agate mortar for 5 min (both materials are solids). Portions of 5 g of the blend were treated at different temperatures and times in air: 450 °C for 15 min, 550 °C for 15 min, 600 °C for 15 and 30 min. Samples were identified as CN450, CN550, CN600-1, and CN600-2, respectively. The (weight) reaction yields were 74.33%, 67.87%, 44.89%, and 34.36%, respectively, corresponding to different decomposition advancements and to the formation of nitrogen-rich powder products. The products exhibited different colors, ranging from brown (CN450) to intense black (CN600-2).

2.2. Analytical methods

FT-IR spectroscopy: The infrared spectra were acquired by means of a Agilent Carey 630 Fourier Transform-Infrared (FT-IR) spectrometer (Agilent Technologies, Santa Clara, CA, USA). The IR spectra were obtained directly from the solid materials by attenuated total reflectance (ATR).

X-ray diffraction measurements: The X-ray diffraction patterns were obtained with a Rigaku ULTIMA-IV Bragg-Brentano powder diffractometer (Rigaki Corp., Tokyo, Japan) with Cu Kα radiation. Glass capillaries were used for sample mounting. The measurements always lasted for 1 h, and crystalline silicon was used as a standard.

TEM characterization: Samples were studied by transmission electron microscopy (TEM) with a JEM-2010F and a JEM-1010 (JEOL, Akishima, Tokyo, Japan) in order to observe the particles morphology at lower magnifications and to find structural information complementary to the X-ray diffraction data. The samples' preparation consisted in dispersing the materials into 2-butanol, treating them in an ultrasonic bath for 30 min, and then depositing a micro-droplet (2.5 μL) of the suspended fraction on a Cu grid. Once the 2-butanol evaporated, the grids were ready for observation.

Thermal analysis: The thermal stability and decomposition rate of the products was evaluated by thermogravimetric analysis using a SETSYS Evolution 1750 TGA-DTA/DSC (SETARAM Instrumentation, Caluire-et-Cuire, France) with a nitrogen flow rate of 30 mL/min and a temperature increment rate of 10 °C/min up to 900 °C.

UV–vis spectroscopy: UV–Vis diffuse reflectance spectra were measured using a Perkin Elmer Lambda 35 UV–Vis spectrophotometer (Perkin Elmer Inc., Waltham, MA, USA). A Spectralon® blank was used as reference. The reflectance data were transformed to absorbance data applying the Kubelka-Munk method (Equation (1)):

$$F(R) = \frac{(1-R)^2}{2R} \tag{1}$$

where R is the reflectance and $F(R)$ is the Kubelka-Munk (K-M) function. The band gap was estimated through a Tauc plot [24,25].

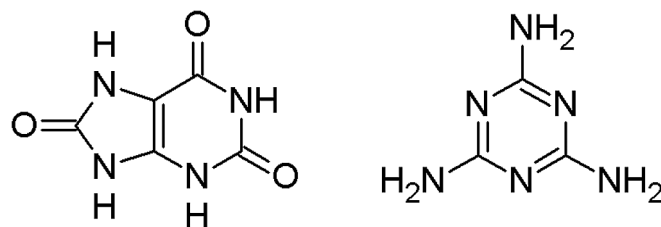*TeraHertz-time domain spectroscopy measurements*: The

Fig. 1. Chemical structure of based oligomers, R is a side chain [22].

Fig. 2. Chemical structures of uric acid (*left*) and melamine (*right*).