Structural and optical properties of carbon nitride polymorphs

CrossMark

Luigi Stagi, Daniele Chiriu, Carlo Maria Carbonaro, Riccardo Corpino, Pier Carlo Ricci *

Dipartimento di Fisica, Università di Cagliari, sp. N°8 Km 0.700, 09042 Monserrato, Cagliari, Italy

ABSTRACT

Graphitic carbon nitride (g-C_3N_4) is considered as one of the most promising photocatalysts for environmental improvement and energy storage. It presents a graphene – like 2D structure, composed of heptazine units connected by amino groups. Here we report multi-technique experimental data (XRD patterns, Raman, steady-time and time resolved Luminescence, Photoluminescence Excitation spectra, Reflectivity spectra) to analyze the relationship between structural and optical properties. We found that the low temperature phase of carbon nitride, namely Melem, presents the main optical features shifted towards higher energies with respect to the higher temperature phase, i.e. Liebig's melon structure or Polymeric Carbon Nitride (PCN). Time resolved luminescence in the ns-domain was therefore exploited to further analyze the kinetics of the excitons generated during optical excitation. Two decay trends were observed in both the structures, with decay time constants depending on sample structure and cell parameters: the faster component, with sub-nanosecond decay time, is related to the recombination from the σ* band whilst the slower decay time is assigned to recombinations within the single triamino-tri-s-triazine unit. The correlation between structural parameters and optical properties is discussed and a model on the optical levels is proposed.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Carbon nitrides based materials attracted researches' attention as promising heterogeneous metal-free catalyst for numerous environmental friendly applications [1,4]. Progressively, C_3N_4 materials have been exploited in the processes of CO_2 capture or control of pollutants [5], water splitting and energy storage devices. [1–11] Reviews on recent development on carbon nitride materials as photocatalysts for water splitting or, more in general for energy related uses are already available [11,12].

Recently, carbon nitride nanopowders were proposed as optically active materials in light emitting devices, extending their potential applications to optoelectronic field. [13,14].

Carbon nitride based systems can display different structural phases, and therefore related properties, the different phases being in general attainable by controlling the temperature and pressure conditions of synthesis [15–19]. Among the possible phases, graphitic carbon nitride (g-C_3N_4) is by far the most intriguing and fascinating compound for different applications, mainly because of its chemical and physical hardness [23]. Indeed, it is a semiconductor with band-gap at 2.7 eV, insoluble in a large class of solvent, such as water, ethanol, toluene, diethyl ether and THF [20] and non-volatile up to 600 °C [21,22]. Furthermore, high yield synthesis methods and elevate purity of the final

products testify the scalability of the graphitic structures to mass production, for example for depollution devices and solar energy storage [13]. Actually, several synthesis methods were employed in g-C_3N_4 production, such as phase and chemical vapor deposition (PVD and CVD), solvothermal method, solid-state reaction and thermal nitridation [22]. In general, the synthesis requires nitrogen rich sources like dicyandiamide, urea or melamine. Among these, melamine, the s-triazine based compound investigated in the present study, undergoes a condensation process with ammonia losses under thermal treatment [23,24] Jürgens et al. [25] postulated the mechanism of melamine condensation: at a temperature slightly higher than 300 °C the further condensation with ammonia liberation provides the so-called Melem structure or the 2,5,8-triamino-tri-s-triazine (heptazine); finally, the subsequent linking mechanism of heptazine units determines the Melon or Polymeric Carbon Nitride (PCN).

Despite the universally recognized growth mechanism of thermally synthesized g-C_3N_4, its structure is still debated and its determination represents a prominent problem for the correct prediction of physical and chemical properties [25–29]. Indeed, the presence of only few well-defined diffraction peaks in the XRD spectra of the samples annealed at temperature above 400 °C makes the structure analysis really hard, motivating a heuristic approaches. Moreover, the parameters of the synthesis procedure, like temperature, environmental condition, duration of the heat treatment, precursors and heating rate, strongly affect the features of the final compounds [30–32] while, unfortunately, it often happens that only the synthesis temperature is reported with few details on the effective structure obtained.

---

* Corresponding author.
  E-mail address: carlo.ricci@dsf.unica.it (P.C. Ricci).

The use of different characterization techniques improves the predictive process. In this regard, we report a detailed analysis of the vibrational and optical properties of g-C_3N_4 samples grown in controlled atmosphere at different temperature. The experimental results, with the support of DFT calculations, provide deep insights on the correlation between spectroscopic features and morphology and effective structure of the carbon nitride polymers.

2. Methods

2.1. Synthesis

A certain amount of melamine powders (Aldrich, 99%) was put in an alumina crucible, placed in a quartz tube accommodated in tubular furnace and treated at the temperature of 300 °C (Me300), 400 °C (Me400), 500 °C (PCN500) and 600 °C (PCN600), for 2 h at the rate of 5 °C/min under constant nitrogen flux (30 ml/min).

2.2. Experimental details

The samples prepared by thermal polycondensation of melamine were analyzed by Raman scattering measurements in back scattering geometry with excitation wavelength at 1064 nm generated by a Nd:YAG laser, to avoid luminescence contribution in the visible range. The system operates in Stokes region up to 2500 cm^{-1}. Accordingly, the experimental and theoretical data are investigated within the same spectral range. Measurements were performed in air at room temperature with a spectrometer BWTEK i-Raman Ex with a spectral resolution of 9 cm^{-1}. All the spectra were collected with low power excitation (below 5 mW) concentrated in a spot of 1 mm^2.

X-ray diffraction patterns were recorded on a Seifert 3000 diffractometer with 2θ Bragg Brentano geometry with Cu, Kα wavelength. Low-angle diffraction patterns were recorded using a zero-background silicon sample holder.

Photoluminescence excitation (PLE) and steady state photoluminescence (SSPL) measurements were performed using the filtered light from a laser driven Xenon lamp (EQ-99-X) with a final bandwidth of about 1 nm.

Time-resolved photoluminescence (TRPL) measurements were performed through a streak camera (Hamamatsu C5680) coupled to grating spectrograph (Arc-Spectra-Pro 275i). Pulsed laser excitation source at λ_{exc} = 355 nm was provided by the third harmonic of Nd:YAG laser (Spectra Physics) with a pulse duration of 300 ps and repletion rate of 1 kHz. The laser spot was focused on a 500 μm spot with power 0.2 mW. PL measurements were obtained in different time range: temporal resolution was 100 ps in the 20 ns time range and lower than 40 ps in the 10 ns range and below.

Quantum yield measurements and reflectivity spectra were carried out were collected in the 350–950 nm range with a resolution < 2 nm by exciting the samples with a Xenon lamp and detecting the signal with an integration sphere (Hamamatsu Quantaurus C11347-11).

2.3. Calculation details

All the calculations were carried out using Gaussian 09 code [33]. According to Jiang et al., [34] Raman spectra calculations for the optimized structures were performed within density functional theory (DFT) with the Becke's 3 parameters and the Lee–Yang–Parr's nonlocal correlation functional (B3LYP) [34–36]. The basis sets for C, N, and H were 6-31G (d,p). Analysis of frequencies confirms that optimized structures are at minimum of potential surface and no imaginary frequencies are obtained. Calculated frequencies were compared to experimental data once scaled by 0.98, a factor due to the correction of the harmonic approximation.

3. Results

3.1. XRD results

Fig. 1 reports the XRD patterns of the heat treated melamine at the temperature of 300, 400, 500 and 600 °C, respectively, acquired in the Bragg angles range 10° ≤ 2θ ≤ 40°. Samples treated up to 400 °C (Me300 and ME400) present well-defined diffraction peaks while the graphitic structure is identified in the samples treated at higher temperature (PCN500 and PCN600) by only two main peaks, assigned to the periodic structural feature of the single sheets and to the graphite-like stacking, respectively [27].

In particular, the sample annealed at 300 °C shows a sequence of reflections assigned to the melamine crystalline phase [22]. Melamine crystal belongs to the monoclinic structure with $P2_1/c$ (no. 14) space group and lattice parameter a = 7.27 Å, b = 7.48 Å, c = 10.57 Å, α = β = 90° and γ = 112.3°.

According to Jürgens et al. [25], the sample Me400, grown at 400 °C, presents all the main peaks of the Melem phase. As Melamine, solid Melem presents monoclinic unit cell, belonging to space group $P2_1/c$ (no. 14). However, during the thermal process, melamine releases – NH_3, determining the new heptazine structure. It follows that the structure at 400 °C is mainly constituted by $C_6N_7(NH_2)_3$ units interconnected by hydrogen bridges, the single unit being formed by three annealed s-triazine rings, terminating by three N atoms in the positions 2, 5 and 8 of tri-s-triazine C_6N_7 block [26]. Melem unit cell is represented in Fig. 2.

Similarly to the case of trichloro-tri-s-triazine, the ring $C_6N_7(NH_2)_3$ is slightly distorted, composing two orientated layers alternating along c-axis with neighboring molecules forming an angle of about 40°. The interlayer distance is 327 pm, very close to the graphite one (334 pm).

The two broad reflection in the XRD pattern of the higher temperatures samples (PCN500 and PCN600) are at about 2θ = 13° and 27°.

To fully assign diffraction peaks and analyze the phases in the studied samples, the XRD patterns were refined by Rietveld method. The Liebig's melon structure, hereafter PCN (Polymeric carbon nitride), suggested for the first time by Tyborski and co-workers [26] and then confirmed by Fina et al. [27], was successfully applied to reproduce the XRD patterns of the samples synthetized at 500 °C (PCN500 sample) and 600 °C (PCN600). Accordingly, best-fit parameters are shown in Table S1 and fitting curves in Fig. S1.

The main peaks are located at 2θ = 27.3° and 2θ = 27.5° for the PCN500 and PCN600 samples respectively, and assigned to (001) reflection. [26,27] Based on these results, the corresponding interlayer distance results in d_s = 3.26 Å and d_s = 3.24 Å, that point out a decrease of the interlayer parameter as the annealing temperature increases
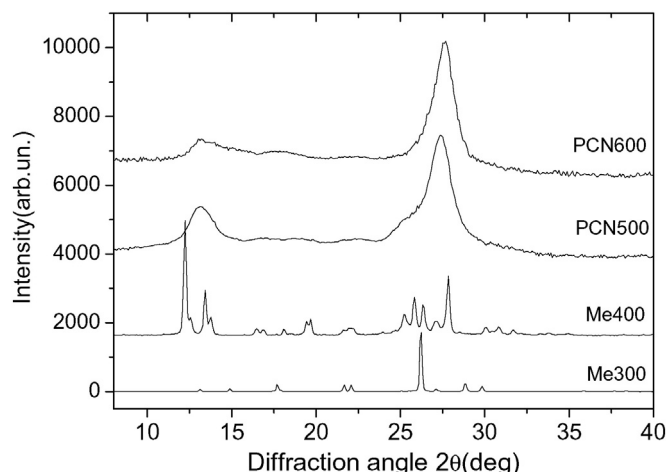

Fig. 1. XRD pattern of heat-treated melamine at various temperature.