Fluorescence from graphene nanoribbons of well-defined structure

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ABSTRACT

Graphene nanoribbons synthesized by the bottom-up approach with optical energy gaps in the visible are investigated by means of optical spectroscopy. The optical absorption and fluorescence spectra of two graphene nanoribbons with different structures are reported as well as the life-time of the excited states. The possibility of the formation of excimer states in stacks of individual graphene nanoribbons is discussed in order to interpret the broad and highly Stokes-shifted luminescence lines observed on both structures. Finally, combined atomic force microscopy and confocal fluorescence measurements have been performed on small aggregates, showing the ability of graphene nanoribbons to emit light in the solid state. These observations open interesting perspectives for the use of graphene nanoribbons as near-infrared emitters.

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1. Introduction

In the last decade, research on graphene has been extensively developed. It is now well established that graphene shows unique physical properties, as represented by the exceptionally high charge-carrier mobility. It demonstrates promises for a wealth of applications such as electrode for energy storage applications, for composites, sensing or electronics [1]. However, graphene is a zero-bandgap semiconductor. Therefore, a lot of studies have been carried out to develop graphene-like semiconductors with large bandgaps. In this context, graphene nanoribbons (GNRs) are promising materials that enable applications in carbon electronics and optoelectronics [2–4]. Indeed, these nano-objects have strong assets such as the tunability of most of their properties by controlling the width and edges structure [3,5,6]. For example, the engineering of the edges provides a control on a wide variety of properties: gap energy, electronic band structure, optical selection rules, magnetic order, etc … [3,7–9] For instance, zigzag edged GNRs are predicted to possess a magnetic localized edge state with

negligible bandgaps, whereas the addition of a benzo-fused edge (see Fig. 1(a)) leads to the disappearance of the edge state and the opening of a ~2.25 eV bandgap [3].

Harnessing the great potential of these objects is only possible through a precise control of their structure. In the last decade, most of the synthesis methods of GNRs have been based on "top-down" approaches [10,11]. These processes, which often rely on lithographic or oxidative routes, are not suitable to produce GNRs with small widths (<10 nm) and lead to uncontrolled edge structures. In the perspective of reaching a fine control of the GNR geometry, the bottom-up chemical synthesis of long GNRs with defined structures represents a major breakthrough [12–16]. It opens the possibility to obtain a variety of desired structures by correctly designing specific precursors and the assembly route. Recently, significant progresses have been made in the GNRs synthesis. For instance, armchair edge GNRs with various widths, "cove"-type edge GNRs, and even zigzag edge GNRs showing the theoretically predicted localized states have been achieved [13,15]. The electronic properties of the GNRs have been intensively studied e.g., by scanning tunneling spectroscopy, angle-resolved photoelectron spectroscopy, high-resolution electron energy loss spectroscopy, and fabrication of field-effect transistor devices [17–19]. In contrast, there is an obvious lack of knowledge about their optical

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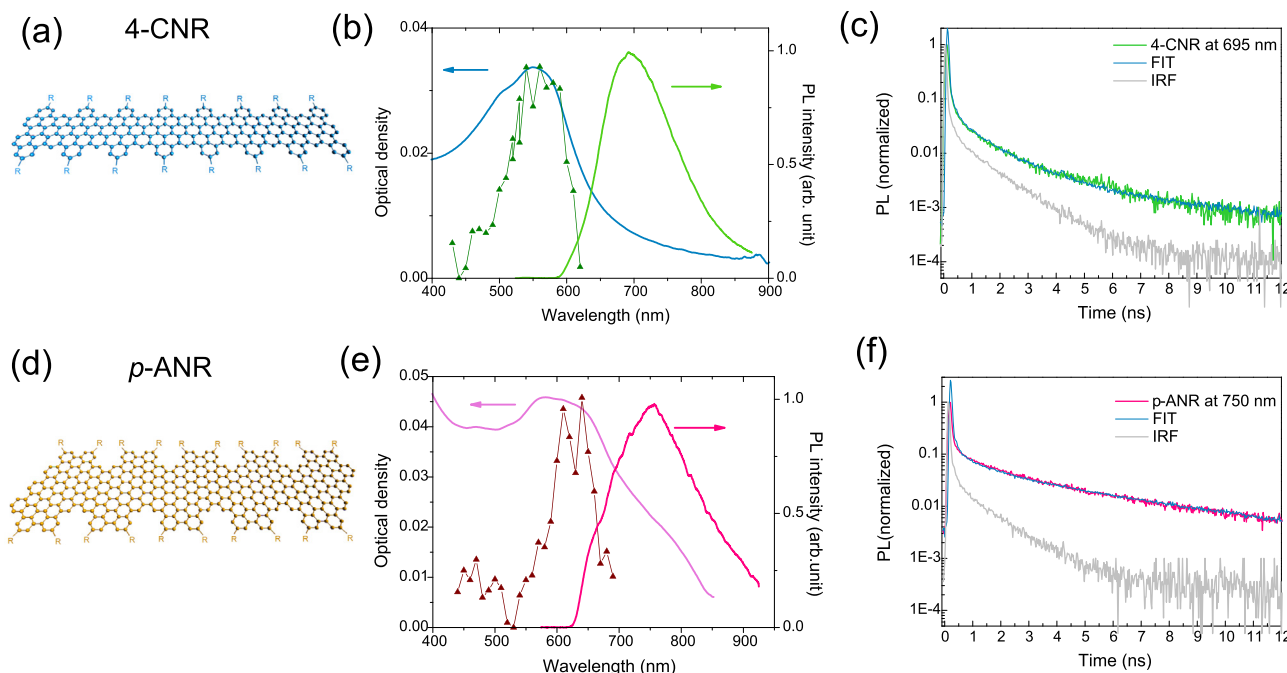 E-mail address: jean-sebastien.lauret@lac.u-psud.fr (J.S. Lauret).

Fig. 1. Chemical structures of the 4-CNR (a) and p-ANR (d). Optical absorption spectra, photoluminescence and photoluminescence excitation spectra (triangles) of 4-CNR (b) and p-ANR (e) in SDS. Time-resolved photoluminescence decay of 4-CNR (c) and p-ANR (f). PLE spectra are recorded at the maximum of each PL line. (A colour version of this figure can be viewed online.)

properties. Optical absorption spectroscopy has been reported, showing the dependence of the gap on the width of the GNR [12,14,20−22]. The comparison between reflectivity measurements on GNRs grown on gold and *ab-initio* calculations recently highlighted the excitonic nature of the optical transitions, with exciton binding energy as high as 1.5−1.8 eV [23]. Likewise, pump/probe ultrafast transient absorption experiments demonstrated exciton-exciton annihilation and biexciton stimulated emission, with a bi-exciton binding energy of ~250 meV [24]. Nevertheless, the photoluminescence (PL) properties of GNRs have remained largely underexplored [22,25].

In this paper we report on a detailed study of the PL properties of two bottom-up-synthesized GNRs with defined structures, namely 4-CNR and p-ANR [14,22], following the name code used in Ref. [3]. Both GNRs show broad PL lines and a large Stokes shift. The PL line of p-ANR is red-shifted in comparison with that of 4-CNR due to a larger width of the ribbon leading to a lower degree of confinement. Multi-exponential decays are measured by means of time-resolved PL (TR-PL) experiments with life-time ranging from few ps to few ns. Finally, very small GNRs aggregates have been investigated simultaneously by confocal microscopy and atomic force microscopy, revealing their optical properties in the solid state.

2. Experimental

The suspensions of GNRs are made by tip-sonication (~1h30) in water with 2 wt% of sodium dodecyl sulfate. Same experiments with sodium cholate lead to comparable results (see optical absorption spectrum in ESI). Moreover, different duration and type of sonication (bath, tip) has been used without any reliable difference on the optical spectra. For the purpose of single object measurements, the suspension is drop-casted on the top of a coverslip and then rinsed several times to get rid of the excess of surfactant.

Optical absorption spectroscopy is performed on a PerkinElmer Lambda 950 spectrophotometer. In PL/PLE and TR-PL spectroscopy

experiments in suspension, the sample is excited with the white light of a supercontinuum laser (Fianium) filtered by a monochromator (Ropers Scientific SP2150i). The PL spectra are analyzed in a SP2500i (Roper Scientific) spectrometer equipped with a CCD camera (PIXIS 100 model: 7515-0002). Finally, time correlated single photon counting was used to perform the luminescence life-time measurements (TR-PL).

AFM images were recorded in tapping mode using an Asylum Research MFP-3D AFM. The AFM system is combined with an inverted confocal microscope allowing simultaneous AFM and PL imaging of the sample. The luminescence is excited by a Cobolt Mambo 100 594 nm laser and collected through the same oil immersion objective (×60, NA = 1.42). The luminescence is split from excitation laser using a dichroic mirror (Chroma ZT594rdc) and filtered using a longpass filter (Semrock BLP01-635R-25). The luminescence is then redirected rather on an avalanche photodiode in the single photon counting regime (PerkinElmer SPCM-AQR-13) or to a spectrograph (Ropers Scientific SP2150i).

3. Results and discussion

4-CNR and p-ANR were prepared adapting reported procedures, through the solution-mediated intramolecular oxidative cyclo-dehydrogenation, or "graphitization", of tailor-made poly-phenylene precursors [14,22,26]. Raman and FTIR spectra of both GNR samples were in agreement with our previous reports, which supported their GNR structures (see Fig. S7 and S8 in ESI) [14,22]. The first structure studied in this paper, 4-CNR, is described on Fig. 1(a). 4-CNR has a structure based on $N = 4$ zigzag edge GNRs with additional benzo-fused rings, where N stands for the number of carbon atoms across the nanoribbon [3]. It forms a "cove"-type edge configuration that leads to a semiconducting nanostructure with a visible gap [3]. Alkyl groups ($-C_{12}H_{25}$) are added on the edges in order to improve the dispersibility of GNRs. Fig. 1(b) displays the optical absorption spectrum of 4-CNR in suspension in water with 2 wt% of sodium dodecyl sulfate (SDS) (blue curve). An