

Editorial

# Optical and Electronic Properties of Carbon-Based Nanomaterials and Composites

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Dear Colleagues,

We are delighted to have served as guest Editors for the Special Issue “Optical and Electronic Properties of Carbon-Based Nanomaterials and Composites” recently published in *C*, and we thank all the colleagues who have participated to the project with such enthusiasm. This volume focuses on different physical and chemical aspects of nanodimensional carbon materials, and includes a collection of experimental works, theoretical first-principle studies and review articles. The collected manuscripts address several aspects of the electronic properties and photophysics of carbon dots (CDs) and graphene (Gr), but also include some interesting results on other types of carbon-based nanomaterials and composites covering a wide variety of topics from synthesis to applications and modeling. Actually, nanomaterials obtained from carbon, ranging from two-dimensional graphene to zero-dimensional carbon dots, going through one-dimensional carbon nanotubes, carbon chains and diamond-like carbon, have all attracted widespread interest from physics to material science, medicine, engineering and beyond.

Beginning with 0D materials, the synthesis of graphene quantum dots (GQD) from waste products was demonstrated, starting from antibiotics (oxacillin) and ethylenediamine (EDA) obtaining GQDs with excellent optical properties by a thermal procedure in an autoclave [1]. In another work [2], the thermally induced decomposition of organic precursors was used to synthesize nitrogen-rich CDs (N-CDs) with an inner core constituted of a  $\beta$ -C<sub>3</sub>N<sub>4</sub> crystalline structure embedded in a surface shell with a variety of polar functional groups. This study also showed that the presence of charged surface groups related to nitrogen and oxygen onto the N-CD's surface is relevant for the colloidal stability of CDs, shedding light on the electrostatic repulsion mechanism that allows for the remarkable colloidal stability of N-CDs dispersions. The comparison of commercial aqueous solution of “carbon quantum dots” and of laboratory produced CDs was the main topic addressed in ref. [3], revealing that the careful analysis of contaminations is critical for the correct attribution of CDs optical features, to avoid any effect of contaminating fluorescent dyes [3]. In this respect, the problems arising from the apparent proliferation of “carbon-deficient or even largely carbon-less carbon quantum dots” in the literature, was accurately discussed [3]. Another paper in the issue addressed the interplay of surface charge of CDs and environment, through the study of the interaction between CDs and halogens ions of different atomic number [4]. The authors showed that negatively charged ions cause an emission quenching effect due to intersystem crossing to triplet states. The quenching is mostly static, arising from the binding of halogen ions on suitable surface sites at C-dots, whereas collisional quenching only occurs at very high iodide concentrations. First-principles studies of optical and chemical properties of  $\beta$ -C<sub>3</sub>N<sub>4</sub> structures from bulk to nanoclusters were reported in [5]. A connection between the electronic

and optical properties of this nanomaterial to their surface states is demonstrated with overwhelming effects for nanoclusters, and a high reactivity of the surface is evidenced for all the 0D to 3D systems with bandgap modifications. In a review article, the origin of fluorescence emission of carbonaceous nanoparticles was discussed in detail at the fundamental level [6]. In particular, the paper provides a critical analysis of the photophysical behavior of C-based nanoparticles based on the well-developed physical theory of molecular excitons and a model is proposed to interpret the optical response of CDs by resonance electronic interactions among the chromophore elements within these nanoparticles. The other review paper of CDs proposed a critical analysis of the models reported in the literature to interpret the optical properties of CDs [7]. In particular, the paper deeply considered the interplay between core and surface properties in CDs, highlighting the need to better clarify these mechanisms to fully exploit the potential of these nanodimensional systems for optoelectronic applications.

Frontier 1D linear carbon chains produced by carbon plasma ion-stimulated condensation were studied both theoretically, by density functional theory, and experimentally in a temperature range up to 400 °C [8]. The reported results showed that a combination of substrate structure and terminal group type of the carbon chain influences the work function of the material, a property exploitable both for the electronic and sensing applications of these systems. A review of the properties of this novel material was reported in [9] summarizing the theoretical predictions of its unique properties and a comparison with available experimental data.

2D carbon nanomaterials were addressed in the review article on the preparation of single and multilayer graphene (Gr) by ethanol vapor, where the authors showed the advantages and criticalities of this preparation route as contrasted to the more standard preparation from methane [10]. A concise summary of the state of the art on the growth of graphene on Cu by ethanol-CVD, focusing on both continuous films and isolated single-crystal grains, is reported, evidencing that reduction of the growth process duration can be obtained. Another review paper on the electronic and structural properties of single layer Gr and their investigation through spectroscopic techniques illustrated the potential of these experimental approaches, and how the properties of Gr can be engineered through thermal doping [11]. As an application, epitaxial single layer Gr on 4H-SiC by thermal decomposition was proposed as a platform which can be used for Hg sensing [12]. The results showed the complexity of the reduction reaction of  $\text{Hg}^{2+}$  at Gr with kinetics of the Hg species at the Gr/SiC surface in part governed by the three-dimensional instantaneous nucleation mechanism. Experimental data were also compared to Density Functional Theory (DFT) calculations evidencing weak dispersive force interaction between Hg and Gr and the need to increase the concentration of interaction sites to improve sensitivity. The application of Gr in microelectronics and the related problems of device preparation were addressed in [13]. In particular, the need to grow high quality dielectrics on epitaxial Gr on SiC and on CVD Gr was investigated, and the recent advances in the atomic layer deposition (ALD) of high-k materials was reviewed. In detail, the “in-situ” seed-layer approach and the recent reports on seed-layer-free ALD growth of  $\text{Al}_2\text{O}_3$  were discussed, showing the role played by Gr interaction with the underlying substrates. Finally, the Gr oxide (GO) derivative was exploited to obtain an implantable patch of electrospun poly(caprolactone), covered with GO [14]. The study of the release of anti-inflammatory and antibiotic model molecules, also driven by near-infrared stimuli, shows that the functionalization of electrospun polymeric patches with GO can be employed to prepare smart nanocomposite patches for the treatment of burns and skin conditions.

Going to “extended” C systems, the role of amorphous hydrogenated carbon (a-C:H) in reinforcing the promising biodegradable polymer polyhydroxybutyrate (PHB), was discussed in [15]. It was shown that stable layers of a-C:H up to 450 nm can be deposited on PHB with customizable properties dependent on the thickness and growth plasma, and correlated to the  $\text{sp}^2/\text{sp}^3$  ratio within a-C:H. In addition, a study of Ag-bombarded amorphous carbon films (Ag:a-C) to obtain composites was reported in [16]. The work highlights that the Ag nanoparticle aggregation/size modifies the overall optical response of the nanocomposite causing a blue shift of the surface plasmon resonance wavelength and the tuning of the optical response of the material exploitable for optical coatings

and solar applications. As a further example of carbon-based hybrid systems, the review work [17] discussed porphyrinoid–fullerene systems, where the fullerene acts as electron acceptor and the porphyrinoid as electron donor. The photophysics of these systems was investigated in detail, showing that “supramolecular hybrids comprising porphyrinoids and fullerene moieties display plenty of imperative as well as desirable features” that could be exploited in solar energy conversion.

We hope that this overall collection of frontiers contributions will reach the widest auditorium of materials science researchers working in the field of carbon-related materials.

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