

Carbon quantum dots/graphene hybrids with broad photoresponsivity – BANDPASS

L. Monica Veca^{1*}, Anamaria Terec², Crina Socaci³, Cristina Banciu⁴

¹National Institute for Research and Development in Microtechnologies – IMT Bucharest, 126 A Erou Iancu Nicolae, 077190, Bucharest, Romania; ²Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, 1 M. Kogalniceanu, 400084, Cluj-Napoca, Roumania; ³National Institute of Research and Development for Isotopic and Molecular Technologies, Donath 67-103, RO-400293 Cluj-Napoca, Romania; ⁴National Institute for Research and Development in Electrical Engineering ICPE-CA, 313 Splaiul Unirii, 030138, Bucharest, Romania.

*Corresponding author: monica.veca@imt.ro;

ABSTRACT

Flexible photodetectors of graphene-derivatives and carbon quantum dots hybrid thin-films with controlled composition and photodetection properties are developed employing a solution-processed approach. The hybrid films, fabricated on polymer, showed reliable and good photoswitching characteristics under the white light of 40 mW/cm² incident power at low bias voltage. An essential role in promoting the enhancement in the photodetection having been ascribed to the efficient charge transfer processes at the interface of carbon quantum dots/graphene hybrids. Future possible extensions of the project include integration in wearable medical devices for real-time health monitoring.

Keywords: flexible photodetector; carbon quantum dots; graphene-derivatives.

1. INTRODUCTION

- In this miniaturization era, the realization of ultra-thin and flexible photodetectors is particularly challenging for the conventional semiconductor technology, due to the brittle nature of the materials used and low absorption at nano-scale thickness. So, our aim was to develop flexible carbon-based photodetectors (PDs) with detection window broader than Si-based photodetectors (with sensitivity ranging from UV to NIR region of the electromagnetic spectrum at room temperature) and responsivity comparable with the current technology based on flexible, semiconducting materials. In order to advance the development of flexible, broadband PDs we considered engineering the graphene surface by hybridization of single-layer graphene (SLG) or its derivatives (graphene foam and reduced graphene oxide) with light-sensitizing materials such as carbon-quantum dots (CQD). This economical, multicolor PD system showing responsivity at room temperature offers the advantage of scalable PD arrays fabrication.
- The advantages that our CQD/graphene hybrids present come from their easy processability (use of solution-processed materials), high and

tuneable photo-responsivities, biocompatibility and eco-friendliness, to name only some of their features. Their responsivity covers UV-Vis region and we are extending them currently to near IR domain.

- Our obtained data go beyond the current state-of-the-art, as we have proven a strong correlation between the different degrees of reduction of graphene oxide on the final responsivity of the PD device, along with a variation upon use of undoped/N-doped graphene. All our findings highlight the influence of the extent of CQD-graphene interaction on good charge transfer and photocurrent enhancement.

2. STATE OF THE ART

Thin silicon has been used to provide flexibility in PDs with good responsivity and detection across the visible range of the electromagnetic spectrum, but it does not sustain cyclic fatigue. In addition, Si-based PD have reduced detection outside the 400 – 1000 nm domain (absorption edge of Si at 1100 nm, high reflection coefficient, and shallow penetration depth of UV light in silicon) [1].

Several initiatives were undertaken to develop flexible photodetectors, the majority exploring new low dimensional nanomaterials and their hybridized structures, among which 2D layered materials and solution processed films were the first to be considered due to their favourable properties for photodetection [2,3].

Advancements in flexible PD, with respect to responsivity and operating bandwidth were achieved in graphene-inorganic quantum dots hybrid structures. The majority of these devices exhibit a decrease in responsivity with increasing the incident power due to the quick saturation of the available states for photoexcitation [4]. In addition, semiconducting quantum dots (SQD) (e.g. PbS, CdSe) require high temperatures synthesis, needs a careful control of the particle size in order to control their band gap, uses hazardous elements and several steps for ligand exchange in order to be integrated into the final device [5].

The realization of broad band flexible PDs has been hindered in SLG due to their low absorption. To solve this low PD responsivity barrier, two main approaches have been endeavoured, the substrate engineering approach and graphene modification. The first relies on graphene transfer on pre-stretched substrates and the latter, on the graphene surface functionalization or hybridization. They all hold great promises but neither has exceeded the stage of the proof of concept. Moreover, the CQDs have some advantages over the inorganic quantum dots, like low toxicity, facile and economical synthetic protocols. As such, construction of mainly-carbon PDs receives increased attention [4].

3. BREAKTHROUGH CHARACTER OF THE PROJECT

The potential of the CQD to complement and replace the current PD based on semiconducting quantum dots materials offers the promise to develop wideband, flexible and wearable photodetectors which do not require different material systems to cover the same spectral range of detection.

While carbon/graphene quantum dots are gradually finding their path to the photodetection's field, most of the reported studies so far revealed gate tuneable photo-responsivities lower than 1A/W, with even lower values in the case of photovoltaic driven PD. For the latter, graphene-based photodiode devices reported photo responsivities ranging from micro- to mA/W in a relatively broad wavelength range (Tab. 1).

Similar to the reported studies, our flexible two-terminal PD based on the CQD/reduced or doped graphene oxide films have shown photoresponsivities of 5.8 μ A/W with great improvement to the level of 0.25 mA/W at 5V and incident optical power of 40 mW/cm². The advantages of using these solution-processed

materials to make photodetectors offers ease of processing, compatibility with flexible substrates, as well as facile integration of Complementary Metal Oxide Semiconductor (CMOS) technology.

Tab. 1. Comparative presentation of performance parameters for several graphene, functionalised graphene and hybrid PDs

Type	Responsivity (mA/W)	λ range (nm)	Reference
GQD	2.1	254	6
GO/rGO	0.24 – 1.4	375 – 118.6 (μ m)	7
GO/Na ₂ SO ₄	17.5-95.8	455 – 980	8
GO	1x10 ⁻³ – 1	375 – 1610	9
rGO/ZnO	1x10 ⁻⁴ – 3x10 ⁻⁴	532 – 1064	10
rGO/CQD	0.25	White light	this work

From the scientific point of view, our results offer interesting aspects beyond the actual state-of-the-art, regarding the influence of the different degrees of oxidation/reduction of graphene oxide on the final responsivity of the PD device as well as valuable insights on the undoped/N-doped graphene comparison. The preliminary results are pointing towards the importance of the CQD – graphene interaction to favour/promote good charge transfer and generate photocurrent enhancement.

The spectral responsivity of the hybrids is expected to be across the UV-Vis with a great potential to reach the near IR domain. Further improvements are expected taking advantage of the photogating effect in our next three-terminal PD in corroboration with the 3D-like graphene structures which are going to increase the photoactive material loading and thus leading to an increase in the photoresponse to values as high as 10³-10⁴ A/W, similar to those recently reported in the literature [11,12].

4. PROJECT RESULTS

We have activated bare carbon nanoparticle and their passivation was achieved by reaction with amine terminated polymers either linear (polyethyleneglycol, PEG) (QY₃₅₀ = ~ 24 %), slightly branched (polypropyleneglycol, PPG) (QY₃₅₀ = ~ 4 %) or branched with extra nitrogen content (poly(N-isopropylacrylamide, NIPAM) (QY = 3.34%) Emission maxima for PEG and PPG appear at λ_{370} = 453 nm, λ_{350} = 440 nm and λ_{410} = 515 nm, respectively, while for NIPAM the later shifts to λ_{410} = 532 nm.

We prepared two types of graphene-based materials: graphene oxide with different oxidation/reduction degree and nitrogen-doped graphene. Reduced-graphene oxide (rGO) with various degrees of oxidation/reduction was obtained by thermal treatment of graphene oxide (GO) at different temperatures. The difference in the amount of

oxygen containing functional groups was proven by TGA analysis, FT-IR, XRD and XPS spectroscopy. In addition, combining graphene oxide (GO) and isomeric phenylenediamines by following two different preparation protocols – one hydrothermal and one thermal - at two different temperatures, yielded N-doped reduced-graphene oxide (rGO) with 7-10% nitrogen content. The as-prepared N-doped rGO present different structure, stacking layers and crystallinity depending on the used phenylenediamine and various O or N content correlated with the used temperature. The XPS spectra of N-doped rGO after hydrothermal vs. thermal treatments shows N-pyridinic : -pyrrolic : -graphitic ratios of 88:12 and 32:57:11 at%, respectively.

The 3D-graphene structures were synthesized from a gaseous mixture of methane, hydrogen and argon on nickel foam catalyst (porosity of 110 PPI and thickness lower than 2.5 mm), using thermal CVD method at atmospheric pressure in a horizontal furnace. The process was carried out at 1000°C, for various time. The freestanding 3D graphene foam (3D-GF) was obtained by etching the nickel foam in an aqueous solution of HCl (3 M) at 80°C for 10 h.

The graphene network has grown on the entire surface of the nickel foam substrate, replicating the interconnected 3D scaffold structure of the initial nickel foam substrate. The obtained graphene structures are porous, flexible, and light-weight. The Raman spectra of freestanding graphene networks obtained at different growing time reveals very low (ID/IG~0.1) ratio, indicating a high-quality graphene network with only few defects.

The synthesized materials were tested in the two-terminal photodetector configuration on the flexible substrate (PDMS). No photoresponsivity was observed in the case of rGOs, regardless of their oxidation degree, and an insignificant response was detected in the N-doped films. Instead, a clear response was revealed in both graphene derivatives-carbon quantum dots hybrid

films. The photoresponsivity of CQD in combination with the 3D-GF was undetectable, probably due to the highly conducting nature of the material. Tested freestanding GF of less than 8 layers (Raman estimation) obtained at 15 minutes deposition time had an electrical conductivity of ~12 S/cm.

With the fine tuning of the graphene derivatives oxidation/doping and their interaction with the CQD, the photoresponsivity of the graphene/CQD hybrids increases from 5.8 $\mu\text{A/W}$ to 0.25 mA/W at 5 V bias and 40 mW/cm^2 incident power density. The influence of the N-doping to the final device's response is shown in Fig. 1 and reveals an increase in the responsivity from 5.8 $\mu\text{A/W}$ to the 42 $\mu\text{A/W}$ under similar testing conditions. Furthermore, the intimate CQD/graphene interaction at the level of adequate charge transfer yielded photoresponsivities as high as 0.25 mA/W at an incident power density of 40 mW/cm^2 and a bias of 5V.

On the other hand, when the highly branched and high N-content CQD (NIPAM) were combined with the hydrothermally N-doped graphene oxide, more than fourfold increase in photoresponsivity was observed, from 0.02 mA/W in the case of linear PEG-CQD carbon dots to 0.09 mA/W in the case of NIPAM-CQD at an incident power density of 40 mW/cm^2 and a bias of 1V, with the responsivity reaching 1.25 mA/W at an incident power density of 70 mW/cm^2 and a bias of 5V. A data comparison is presented in Fig. 2.

It has been demonstrated the importance of the reduction/oxidation degree as well as of the doping level/type of bonds in the doped graphene derivatives materials to the photodetector performances. Ramification and nitrogen content of CQD, as well as CQD's interaction with the graphene material proved to be essential to the final photodetector responsivity.

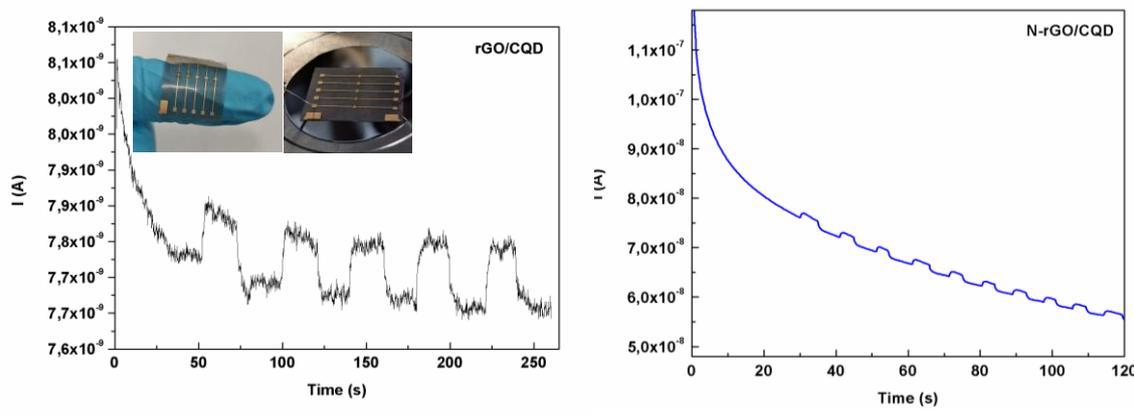


Fig. 1. Photoswitching behaviour of the PEG-CQD/reduced graphene oxide (left) and PEG-CQD/N-doped reduced graphene oxide (right) film photodetector under alternating ON/OFF cycles at 5 V bias and white light power density of 40 mW/cm^2 . Inset: photographs of the flexible graphene-based photodetector.

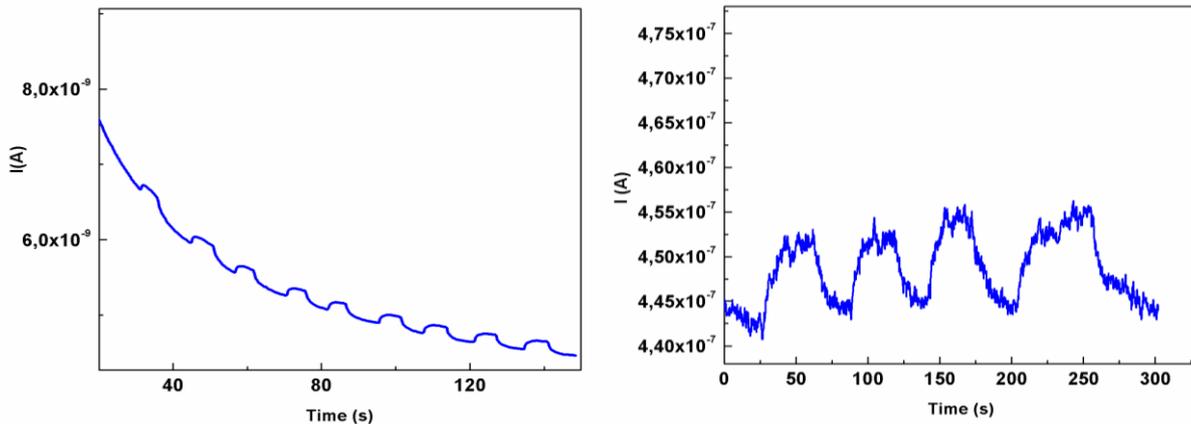


Fig. 2. Photoswitching behaviour of the PEG-CQD/hydrothermally doped graphene oxide (left) and NIPAM-CQD/hydrothermally doped graphene oxide (right) film photodetector under alternating ON/OFF cycles at 1 V bias and white light power density of 40 mW/cm².

5. FUTURE PROJECT VISION

5.1. Technology Scaling

In the ATTRACT Phase 2 we will start by bring the technology at the TRL level 4. As the materials we are employing are well suitable, a practical way to fabricate a large area of flexible devices with the micron-size resolution at high speed is to use printing techniques.

A considerable effort will have to be also made to integrate electronic and optoelectronic devices. To collaborate with an organization (SME) that can bring the optimized device to further development.

We are also considering to further enhancing the charge transfer efficiency between the carbon quantum dots and graphene derivatives to increase the responsivity and test their responsivity domain. This goal is feasible by adjusting the ratio between graphene and carbon dots; the preparation of doped graphene and carbon dots with improved optical and structural properties of the final PD; chemical modifications of 3D-graphene foams.

5.2. Project Synergies and Outreach

For ATTRACT Phase 1, our consortium consists of two Research Institutes and a University as partners. An industrial partner is needed for the second phase, for bringing our devices to the next technological levels. In this respect, we plan to adhere to regional/international Innovative clusters specialized in electronics, healthcare devices and services, energy fields, which could help us offer licensed technology. On the other hand, a cluster within ATTRACT Phase 1 grant holders is also envisaged, as we have contacted Prof. Maurizio Casalino from *REVEAL* ATTRACT Project. So, we could use our DOTS-graphene hybrids as absorptive

material the IR responsivity of Si-based photodetectors they produce and we believe that this would lead to an increasing in the performance of devices. Moreover, their industrial partner has also the ability to fabricate photonic devices in Silicon, but also, as an extension, on flexible PDMS that would be suitable for epidermal components, for example.

5.3. Technology application and demonstration cases

The future possible extensions of the project include integration in wearable medical devices for real-time health monitoring.

We are also expecting to find graphene-based PD in the next generation Epidermal Photoplethysmographic Sensor (used to detect blood volume changes in the microvascular bed of tissue), as well as in human E-Eye that can acquire the optical information through a photodetector array.

5.4. Technology commercialization

So far, we haven't taken any concrete steps towards commercialization of our technology. At the right moment we will try to identify and approach the local industry, pitch our technology to the angel investors groups and networks, or meet with venture capitalists. As an alternative, the scientific/industry conferences, and industrial brokerage sessions, are also considered.

5.5. Envisioned risks

The risks that the proposed project could present are of technical nature and solutions are accessible. For example, going to higher TRL, the validation of our products in the actual environment could be influenced by supplemental external stimuli; so, we envisaged appropriate inert coating/encapsulating for our products in these cases.

5.6. Liaison with Student Teams and Socio-Economic Study

We acknowledge the importance of transferring the knowledge behind our products and our products themselves to as many users as possible and we are aware there are applications yet unrevealed to our materials. Therefore, we are planning in involving young and early-stage researchers and MSc. Level students from various domains in our quest. Having as partner Babes-Bolyai University in our consortium, we have the personnel qualified for “translating” the materials of our technology to such teams. Moreover, we also propose the elaboration of several laboratory sessions (involving preparation of some of the basic parts of our materials) for Chemistry and Chemical Engineering MSc. students at BBU to ignite ideas inspired by our technology.

We are ready to contribute transparently to the expert-driven socio-economic study of the ATTRACT initiative and ecosystem by any means required by the study’s framework, including interviews and references to the impact of our technology.

6. ACKNOWLEDGEMENT

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