# LIGHT HARVESTING PROPERTIES OF GRAPHENE OXIDE NANORIBBONS ON SILICON

**S. Del Gobbo**[a],**P. Castrucci**[a*] ,**M. Scarselli**[a]

[a] Dipartimento di Fisica dellÕUniversit di Roma Tor Vergata
Via Della Ricerca Scientifica 1, 00133 Rome, Italy
[b] Department of Chemical and Materials Engineering, Chang Gung University
Kwei-Shan, Tao-Yuan 333
[a*]Corresponding author: *paola.castrucci@roma2.infn.it*

**Introduction:** In the last years most of the attention is moving from quasi-1D nanostructures (CNT) to quasi-2D nanostructure (graphene and graphenic structures) [1]. This is due in particular to the development of techniques to produce it, which accounts mechanical exfoliation of highly oriented pyrolitic graphite (HOPG) [2], catalytic chemical deposition of hydrocarbons on metals [3,4] and finally chemical unzipping of carbon nanotubes [5] which usually yields graphene nanoribbons (GNR). These techniques have open new fields of investigation which range from nano-electronics [6] to novel photovoltaic [7]. In this work we study the GNRs produced as reported in [5] in order to exploit them as transparent electrode in photovoltaic devices forming Schottky-type nano-junctions with silicon.

**Experimental:**Graphenic nanoribbons studied in this work were produced starting from multiwall carbon nanotubes (MWCNT) which were unzipped with a procedure based on acid catalytic oxidation by potassium permanganate ($KMnO_4$) [5]. The carboxylic groups terminating the graphene sheets produced during the oxidation were not reduced in a following step as in [5]. Therefore, the GNRs contain many carboxylic groups even on the surface and the former GNR are more properly named GONR (graphene oxide nanoribbon). The morphology of GONRs produced through this method was characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Two typical TEM images of a carbon nanoribbons specimen are shown in Fig. 1.

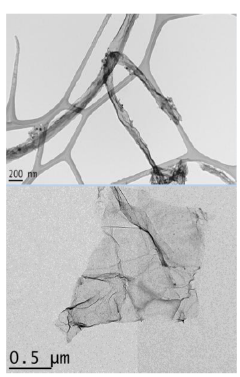


Figure 1: TEM image of long unzipped MWCNTs (upper picture). Sheet-like carbon nanoribbon coming from MWCNT (lower picture).

The photovoltaic devices were realized depositing by airbrush a thin layer of GONR (or MWCNT) on a 10 mm x 5 mm patterned $SiO_2$ silicon slices ($\rho$=1-10 $\Omega$/cm) and contacting with silver paint the GONR (or MWCNT) film and the bare backside of Si. The patterned $SiO_2$/Si substrates were prepared by wet etching a 3 mm wide window of bare Si between the two 300 nm thick $SiO_2$ steps and etching completely the $SiO_2$ on the backside. The GONR and MWCNT films are deposited on the substrates airbrushing a suspension of GONR or MWCNT in 1,2-dichlorobenzene. The film thickness is established by the deposition time while it is monitored measuring the sheet resistance and the transmission of the same film simultaneously deposited on a quartz slide.

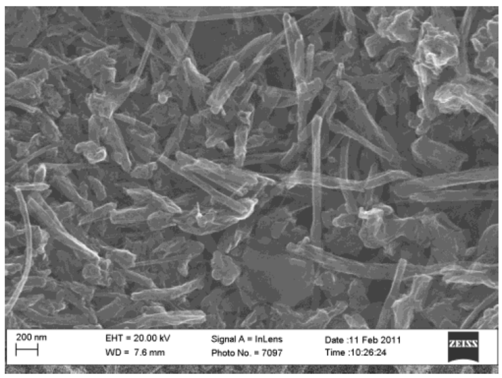


Figure 2: High magnification SEM image of GONRs deposited by airbrush on Si/$SiO_2$ substrate

The photovoltaic capabilities were studied in terms of quantum external efficiency (EQE) defined as the number of incident photons converted into photocurrent and measuring the current (I)-voltage (V) curves under dark and illumination conditions. The EQE and I-V measurements were performed experimentally similarly to what is reported in [8,9]. The EQE spectra are displayed in Fig. 3a while I-V curves are not shown here.

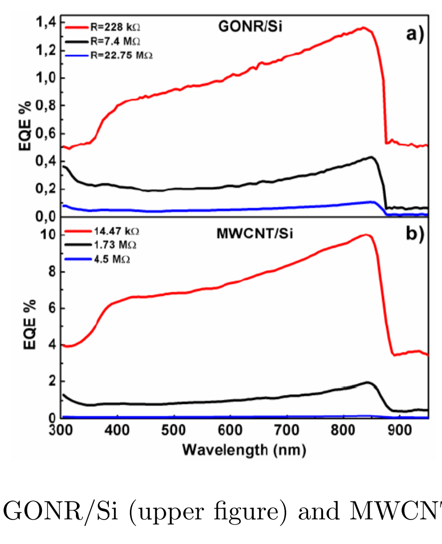


Figure 3: EQE spectra of GONR/Si (upper figure) and MWCNT/Si (lower figure) devices

**Results** TEM images of GONR are shown in Fig. 1. In one case (Fig.1, upper panel) it can be observed how the carbon nanotubes are not always completely unzipped but they partially retain their tubular shape. In the other case (Fig.1, lower panel), an extended wrinkled graphenic sheet can be seen. However, the large size of the object suggests that it is possibly made of several overlapped multilayer graphenic sheets coming from several unzipped MWCNTs and/or walls. The SEM pictures (Fig. 2) show that a thin and homogeneous layer of carbon nanostructures is deposited onto the patterned $SiO_2$/Si substrates allowing a good electrical contact between the carbon nanostructures and the Si underneath. The EQE measurements (Fig. 3a,b) show that the devices based on MWCNT/Si heterojunction are in general more efficient in respect to those based on GONR/Si heterojunction. As already reported in [9], the EQE increases with the film thickness thanks to the larger and larger number of MWCNT/Si nano-junctions but it starts to decrease when the film thickness reaches a threshold value when the film is too dense preventing the light to reach the Si underneath. However, even in the case of comparable film thicknesses between MWCNT and GONR, the EQE and ISC values are much larger for MWCNT-based devices. This can be explained with a not optimal contact between GONRs and Si as well as lower uniformity of the film in comparison with MWCNT/Si devices. Moreover, the high degree of GNRs oxidation, modifies the original electronic structure of graphene [9] giving rise to an unknown behavior in terms of photocurrent.

**Conclusions** Graphene oxide nanoribbons were successfully synthesized according to the procedure reported in [5]. TEM revealed the partially unzipped MWCNTs but also extended graphenic sheets, probably made up of several nanoribbons. The photovoltaic devices based on GONR/Si show worse performances if compared with MWCNT/Si devices. These results may be ascribed to the modified electronic properties of graphene oxide nanoribbons [10], but also to the poorer adhesion on Si of GONRs in respect to MWCNTs. An improvement of this procedure may allow us to have a better contact between GONR film and Si substrate and also a better uniformity of the film. Moreover, the electronic properties may be properly tuned increasing or decreasing the oxidation degrees of nanoribbons through the methods used in [5] and [11].

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