Using TRIM-SRIM code simulations to determine defect density produced in HOPG irradiated with high energy heavy ions.

***L.H. Avanzi[1], V.A.P. Aguiar[2], K.M. Costa[1], T.O. Santarelli[1], N.H. Medina[2], J.R.B. Oliveira[2], F. Cappuzzello[3,4], F. Iazzi[5,6], V. Capirossi[5,6], F. Pinna[5,6], M. Cavallaro[4] and M.A. Guazzelli[1] for the NUMEN collaboration**

[1]Centro Universitário da FEI, São Bernardo do Campo, São Paulo, Brazil
[2]Instituto de Física da Universidade de São Paulo, São Paulo, Brazil
[3]Dipartimento di Fisica e Astronomia "Ettore Majorana", Università di Catania, Catania, Italy
[4]Istituto Nazionale di Fisica Nucleare–Laboratori Nazionali del Sud, Catania, Italy
[5]Istituto Nazionale di Fisica Nucleare–Sezione di Torino, Turin, Italy
[6]Dipartimento Scienza Applicata e Tecnologia, Politecnico di Torino, Torino, Italy

[*]lhavanci@fei.edu.br

Abstract. This work is part of the NUMEN Project (NUclear Matrix Elements for Neutrinoless double beta decay), which, among other goals, aims to measure cross-section of double charge exchange reactions (DCE). In the experiments to be carried out at the Laboratori Nazionali del Sud, in Catania, Italy, a target deposited on a carefully chosen backing (substrate) will be irradiated with a high energy ion beam and, importantly, neither the target nor the substrate will be allowed to overheat as this would affect their structures and its properties, which are special for the experiment. Within this context, highly oriented pyrolytic graphite (HOPG) was chosen as a substrate for the deposition of target elements that will be irradiated by ions such as ^{12}C, ^{18}O and ^{20}Ne, with energies ranging from 15 MeV/u to 60 MeV/u. HOPG is considered a semimetal structured in layers, being composed of a stack of graphene sheets with a small and very subtle disorientation (less than 1°), which makes it to approach to a single crystal. With its specific flat hexagonal molecular structure, consisting only of carbon atoms, HOPG has good thermal conductivity in these sheets, making it an excellent candidate as a heat sink. However, for the HOPG to act with thermal energy dissipation functionality during the experiments proposed by the NUMEN project, it is necessary to verify whether possible changes caused by exposure to the radiation beam have a direct or indirect influence on its mechanical and thermal properties. Regarding the thermal conductivity, vacancies produced during irradiation is one of the factors that considerably decrease such property. As the production of vacancies during irradiation is one of the factors that considerably decrease thermal conductivity, in this work it was used the SRIM/TRIM code simulations to investigate the mechanisms of vacancy production in the target plus HOPG backing system. In the simulations, it was considered different types and doses of incident ion beams as well as different target thickness. From the results it was possible to estimated how long a target-HOPG system can be irradiated before the HOPG high heat conductivity property is lost.

1. Introduction

With one of the main aims being to better understand the nature and behaviour of subatomic particles named neutrinos, the NUMEN Project will carry out several experiments involving a system of a thin film target deposited on a substrate where, it is hoped, will result in the occurrence of double charge exchange reactions (DCE) which are analogous to the so-called double beta decay. Neutrinoless double beta decay ($0\nu\beta\beta$), if confirmed, would indicate that the neutrino is a Majorana fermion (equal to its own antiparticle). However, besides on the $0\nu\beta\beta$ decay partial half-life, the effective neutrino mass depends also on nuclear transition matrix elements, presently known only theoretically. The experimental access to the analogous DCE nuclear matrix elements of the same initial to final nuclear state transitions is the main objective of the NUMEN project [1,2,3].

The definition of the materials that should be used as targets, its specifications and properties, on which substrate they will be deposited and how the large amount of heat produced in nuclear reactions will be dissipated are the determining points of this research. Finally, after defining the backing for the nuclear reaction target, it is necessary to know for how long the composite target (reaction element + heat dissipating backing) can be irradiated uninterruptedly. One of the problems is that the large amount of heat produced during irradiation can melt the target material, mainly of low melting point elements, making it impossible to study the reaction product. Some of the proposals for the material that has the functionality required for this composite target involve the use of highly oriented pyrolytic graphite (HOPG) as a backing (substrate) for the thin film targets deposition. As a material formed by a stacking sheet of graphene, HOPG has excellent thermal properties in the plane of carbon atoms, which, it is hoped, will aid in the removal of heat and prevent target melting. However, this excellent thermal conductivity of HOPG depends mainly on the perfection of its crystalline structure, which will be lost with the large number of defects produced by irradiations. As the crystalline structure of HOPG deteriorates, its thermal conductivity will decrease and, at the limit, may approach that of amorphous carbon. Before that happens, it will be necessary to replace the target.

In this study, we used the SRIM/TRIM program (Transport of ions in matter) [4,5] to simulate as detailed as possible real irradiation conditions and determine how the density of defects in the HOPG crystal lattice reduces its ability to act as a heat sink. In the TRIM simulations, parameters such as target type and thickness and incident ion beam energy can be changed to match the values used in the NUMEN experiments. The TRIM simulations results shown the number of vacancies produced by the incident ions and by recoils. The incident ion flux can be calculated from the beam current and the fluence is related to the irradiation time. With all these parameters it is possible to estimate the lifespan of a target, that is, how long it can be irradiated before the HOPG crystal structure deteriorates and turns into amorphous carbon, losing its functionality as a heat sink.

1.1. Production and dissipation of heat in the target-backing system

During the NUMEN experiments, thin targets will be irradiated with high-intensity ion beams. In this aspect, the main issues to be addressed arise from the thickness of the target, which affects the energy resolution of the detection of the desired reaction product, and the dissipation of the heat produced in the target by beam energy loss. The proposed solution is that each target is made by deposition of 140-550 $\mu g/cm^2$ of isotopes of interest on top of a HOPG substrate, whose importance lies in supporting the films used as targets, quickly transferring heat to a refrigeration system conveniently designed and coupled to the HOPG [6]. Between the target and the HOPG substrate there may be an intermediate layer (buffer layer). The heat production is related to the very intense heavy ions beams, which will be used in the next NUMEN experiments. The use of ^{18}O and ^{20}Ne beams with intensity up to 13 and 17 μA, respectively, with energies ranging from 15 MeV/u to 60 MeV/u is expected. The focal point of the beam on the target will have dimensions close to 0.03 cm^2, causing the power density deposited on the target to be greater than 10^5 W/cm^3 for the lowest beam energy [3]. Table 1 provides information on some of the selected isotopes.

Table 1. Power deposited by a 13 μA (^{18}O) beam on ^{116}Sn and by 17 μA (^{20}Ne) beam on ^{130}Te target (adapted from ref. [3]).

Target (beam)	**Surface density** (μg/cm^2)	**Deposited power** (W)				**Melting point** (K)
		15 MeV/u	30 MeV/u	45 MeV/u	60 MeV/u	
^{116}Sn (^{18}O)	219	0.46	0.27	0.20	0.16	505
^{130}Te (^{20}Ne)	250	0.67	0.40	0.29	0.24	722.6

This amount of energy could cause the target material to melt. To prevent such damage, in addition to the refrigeration system [6], the use of HOPG is of fundamental importance in heat dissipation.

1.2. HOPG, other allotropic forms of carbon and their thermal conductivity

HOPG, considered a semimetal, is a material composed entirely of carbon atoms, being formed by a stacking of several graphene layers with a slight disorientation between them (less than 1º in the samples used in NUMEN). This disorientation depends on what manufacturers call a "grid". HOPG has a hexagonal crystal structure, in the basal planes the carbon atoms are covalently bonded, and the interlayer bond is weak and must arise from dispersion or Van der Waals-type interaction. Its peculiar structure makes it highly anisotropic, but because its high orientation, its behaviour approaches that of a single crystal. In Figure 1 the X-ray diffractogram of a typical HOPG sample used in NUMEN is shown. In the diffractogram, only reflections produced by planes parallel to a single direction are observed.

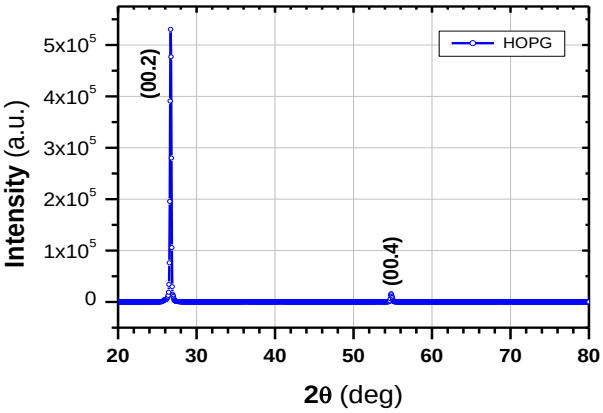

Figure 1. X-ray diffractogram (θ–2θ) showing only reflections of planes parallel to the sample surface. This result indicates a high ordering of atoms in the HOPG crystal lattice.

According to BALADIN [7], the thermal conductivity of different allotropic forms of carbon strongly depends on their crystalline structure and rapidly decreases as this crystalline perfection is lost. For diamond and for the basal plane of HOPG atoms (in-plane), this conductivity is approximately 2x10^3 W/mK; for polycrystalline graphite, this conductivity is approximately 100 W/mK; for HOPG cross-plane and for amorphous carbon, this value is less than 10 W/mK (all values at room temperature). As the crystalline perfection of HOPG goes from single crystal to polycrystal and then to amorphous, the thermal conductivity decreases by one order of magnitude at each transition (reference [7], Figures 1a and 1b).

One of the ways to decrease the perfection of the HOPG crystal lattice during the irradiations is the generation of several types of vacancies. As HOPG is formed by a stacking of several layers of graphene, and as it has not been possible so far to find data specifically referring to HOPG, we researched some works that deal with irradiation and vacancy generation in graphene and its corresponding decrease in thermal conductivity. In one of these works, MORTAZAVI and AHZI [8] report that with a defect concentration of only 0.25%, the thermal conductivity of graphene decreases by half and, with a defect concentration of 2%, there is a decrease of more than about 80% in the thermal conductivity of graphene (reference [8], Figure 8). This result, although it is for graphene, may indicate that something similar also may happens with HOPG and a small concentration of defects in the crystal lattice of HOPG will cause its thermal conductivity to be drastically reduced.

As the HOPG is the substrate for the films that will be irradiated (where the nuclear reactions of interest will take place), determining the decrease in its thermal conductivity as a function of defect concentration is important to establish how often the target-substrate systems should be replaced during the irradiations that will take place at NUMEN.

2. Methodology

To estimate the amount of vacancies created during irradiations, and to relate them to the HOPG thermal conductivity changes, the TRIM software and different ion beam target-substrate systems were used. The study sought to identify the effects caused by the interaction that an ion beam causes when crossing the entire thickness of the target and the HOPG used as a substrate. As the incident ion beam is formed by electrically charged particles passing through any material medium, they interact with the various atoms present in the medium. This interaction will be greater the longer the trajectory of the ion inside the material. TRIM is a Monte-Carlo simulation program embedded in the SRIM package [4,5], that calculates ion's energy loss, straggling, range, target's sputtering yield, vacancy formation and implanted ion distribution by means of binary collision calculations, considering Ziegler's ion-atom universal potential. It is a widely used program in the Ion Beam Analysis community and allows the study of any target composition, as long as correct target properties are input. With this code it is possible to evaluate the vacancy concentration created by beam impact on the target. In this study, this program was used to verify the energy transfer from the heavy-ion beam to the target and the number of vacancies arising from it, under different conditions, proposed to be carried out in the NUMEN project. In order to properly calculate target vacancies, a monolayer collision calculation option [5] was used.

3. Results and discussions

Simulations were carried out with real parameters that will be used during the irradiations that will take place at NUMEN experiments. The ion beams and their energies are shown in Table 2; the ion flux and irradiation time are presented in Table 3 and in Table 4 the target-substrate (backing) systems used in the simulations are shown. It is important to note that NUMEN experiments can last from 3 to 30 days and information about the maximum time that a target can be irradiated is of fundamental importance to define how many of them will be prepared and how often they should be replaced

Table 2 – Heavy ion beam parameters used in TRIM simulation

Ion Beam	**Energy** (MeV/nucleon)	**Total energy** (MeV)
^{20}Ne	13 – 30	260 – 600
^{18}O	16 – 60	288 – 1080
^{12}C	15 - 30	180 – 360

Table 3 – Fluxes and irradiation time

Flux (ions/s)	**Time** (day)
10^{11}	5
10^{12}	30
10^{13}	3

Table 4 – Target plus HOPG parameters used in TRIM simulation

Layer	**Material**	**Thickness** (nm)
Target	**Sn** (Z = 50), **Ge** (Z = 32), **Te** (Z = 52)	≈ 300 – 800
Buffer layer	**Cr**, **Bi** or no buffer	≈ 10 – 40
Substrate	**HOPG**	≈ 2000 – 10000

The first simulations have shown that, for the beam energy range of interest for NUMEN, the vacancy density was constant throughout the target, allowing the simulation of thinner targets for better efficiency. Simulations were performed until error on total number of vacancies was better than 5%

(computational time between 36h – 48h / simulation). In Figure 2 the results for the number of vacancies (per ion and per depth in target) simulated for two different systems when irradiated with a 300 MeV ^{18}O: Sn+HOPG (Figure 2a) and Sn+Cr+HOPG (Figure 2b) are shown. In both simulations Sn layer has the same thickness and, in simulation presented in Figure 2b there is a Cr buffer layer between Sn and HOPG. These results show that the ion beam easily trespasses the entire target length, producing vacancies along its track. Another important result is that the number of vacancies produced in HOPG is the same in both cases, despite the Cr buffer layer (about 2.5×10^{-5} per angstrom per ion). Also, it is interesting to notice that the total HOPG target vacancies have a linear relationship with its thickness. The HOPG binding energy used is the one to produce a single vacancy.

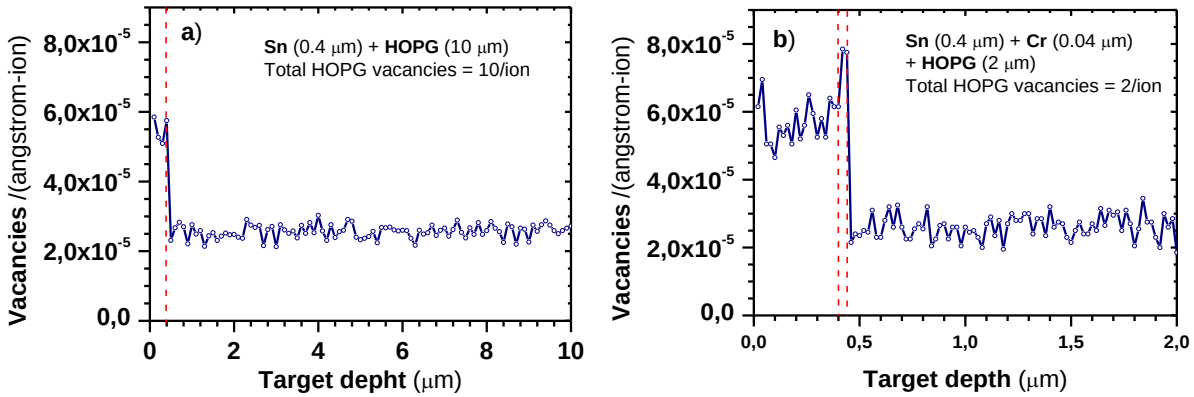

Figure 2. Graph of the number of vacancies (per ion and per angstrom in depth) produced by a 300 MeV ^{18}O beam. The simulated systems are **a)** Sn (0.4 μm) + HOPG (10 μm) and **b)** Sn (0.4 μm) Cr buffer layer (0.04 μm) + HOPG (10 μm). Other parameters used in simulations are density (g/cm^3) 7.3 (Sn), 7.18 (Cr) and 2.22 (HOPG); surface binding energy (eV): 3.12 (Sn), 4.12 (Cr) and 7.41 (HOPG); lattice binding energy (eV): 3.0 (Sn), 3.0 (Cr) and 3.0 (HOPG). Separations between target, buffer layer and substrate are indicated by dash lines.

Another interesting result is the one presented in Figure 3, which shows the displacements produced by the ions in the beam together with those produced by the recoils of the target lattice. This result shows that, in the target, recoils produce more displacements than collisions with the ion beam itself. To evaluate the integrity of the HOPG post-irradiation, the vacancy density provided by simulations was used to determine the number of vacancies in the target's volume under beam interaction, consisting of a cylinder with an area equal to the beam spot size of 0.03 cm² and target thickness which is about 2.65 μm. The vacancy halo and beam spread inside the target were negligible. In Figure 3 the density of displacements found in the TRIM simulation for ^{20}Ne ions at 300 MeV is shown. In the thin target, the recoils play a major contribution to target's damage, but in the HOPG backing the cause of degradation can be assigned solely to incoming ions. Figure 4 shows in detail the formation of vacancies as a function of irradiation time, for three different fluxes, considering a ^{20}Ne beam at 270 MeV incident on Sn+HOPG. It is interesting to notice that by increasing the flux by one order of magnitude, the total vacancies also increase one order of magnitude. The parameters used in the simulations are written in the Figure caption.

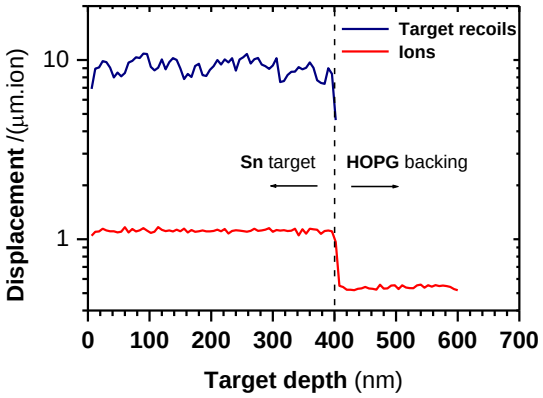

Figure 3. Density of displacements found for thin target and HOPG backing in the TRIM simulation for ^{20}Ne ions at 300 MeV. The conditions under which the simulation was performed are the same as those for the results shown in Figure 2.

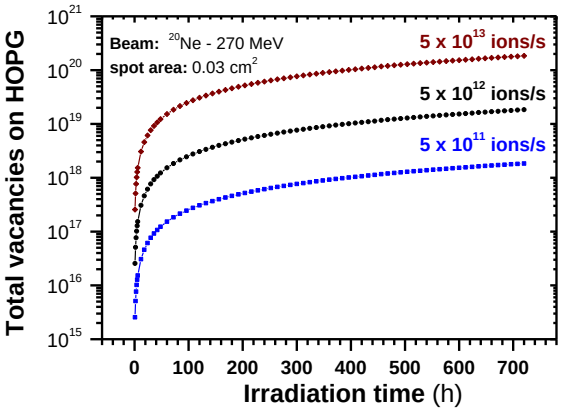

Figure 4. Graph of the total vacancies as a function of the irradiation time for three different fluxes, considering a ^{20}Ne beam at 270 MeV incident on Sn+HOPG (results obtained with the same parameters used in previous simulations).

In order to estimate the time up to defect concentration in HOPG reaches 0.25 %, the system Sn (0.4 μm) + HOPG (2.635 μm) was simulated considering irradiation with all ion beams used in NUMEN experiments considering the lowest and highest beam energies. The total number of vacancies in HOPG were compared to the number of atoms in the same region (under the volume irradiated by the ion beams), obtaining vacancy concentration, C. As C = vacancies/atoms, C = 1 means that, in average, every atom in that region has been displaced from its original position, transforming the HOPG into a crystallographically amorphous structure in that microvolume. As discussed before, in this case the thermal conductivity is the one for amorphous carbon, the HOPG has no longer the ability to act as a heat sink and the sample must be replaced. The vacancy number depends on the accumulated beam fluence for any planned experiment, therefore, depends upon particle flux and beam time.

The results obtained through these simulations, shown in Figure 5, indicate that, for a flux of 10^{11} ions/s, there is a degradation of 0.25% in about 240 hours, while for 10^{13} ions/s, the same percentage of vacancies may occur in about 2.4 hours, for ^{20}Ne beam.

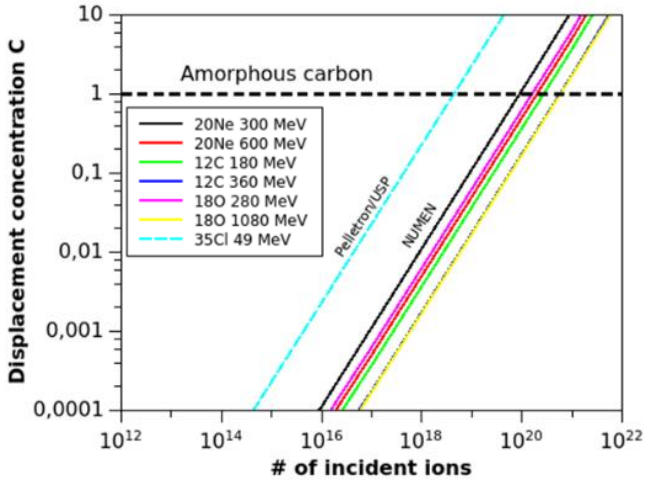

Figure 5. Displacement concentration C as a function of the ion beam fluence for different heavy-ion beams in 0,4 μm Sn + 2.635 μm HOPG thickness. C = 1 indicates that the HOPG crystalline structure became equal to that of amorphous carbon.

In Figure 5, the cyan line on the left represents the result for simulations performed with ^{35}Cl – 49 MeV beam. This ion beam will not be used in the NUMEN irradiations, but for the study of the damage, experiments with this ion beam are planned to take place at Pelletron accelerator of the Institute of Physics (IFUSP), Brazil. As, in this case, the ^{35}Cl ion has a lower energy compared to those used in NUMEN experiments, it will create a higher number of atom displacements and emulate NUMEN target degradation conditions. The simulation results for ^{35}Cl ions indicate that under these conditions, with a flux of 10^{13} ion/s, the limit of HOPG 0.25% defect concentration reached within about 24 hours.

4. Conclusion

In this work, the TRIM code was used to simulate the production of defects (vacancies and displacements) in target-substrate systems that will be used in the NUMEN project experiments. From these simulations, it was possible to observe that the ion beams easily cross the target-substrate (backing) set, producing defects along their entire trajectory. It was also possible to observe that, for the target, most of the atom displacements are produced by the recoil of atoms from the target itself, and not by collisions with the ion beams. Furthermore, it was possible to estimate the lifetime of a target-substrate system, based on the defect concentration increase produced in the HOPG crystal lattice and its consequent reduction in thermal conductivity. Depending on the ion flux that will be used in NUMEN experiments, the target lifetime may be only a few hours. Experimental tests are planned to confirm these predictions.

It is also important to emphasize that this study may improve the efficiency of NUMEN experiments and the results should generate technological advances related to the development of targets to be used where thermal conductivity is essential.

Acknowledgments
The authors acknowledge financial support from the funding agencies: INCT-FNA, CNPq (proc. n. 464898/2014-5, proc. n. 306353/2018-1, proc. n. 408800/2021-6) and Centro Universitário da FEI.

References

[1] Cappuzzello, F., Cavallaro, M., Agodi, C. et al. Heavy-ion double charge exchange reactions: A tool toward 0νββ nuclear matrix elements. *Eur. Phys. J.* A **51**, 145 (2015). https://doi.org/10.1140/epja/i2015-15145-5.
[2] Cappuzzello, F., Agodi, C., Cavallaro, M. et al. The NUMEN project: NUclear Matrix Elements for Neutrinoless double beta decay, *Eur. Phys. J.* A **54**: 72 (2018). https://doi.org/10.1140/epja/i2018-12509-3.
[3] Cappuzzello, F et al. The NUMEN Technical Design Report. *Int. J. Modern Physics* A **36** (30), 2130018 (2021). http://doi.org/10.1142/S0217751X21300180.
[4] Ziang, Z et al. Ultra-low threshold optically pumped random laser emission behaviour of highly oriented pyrolytic graphite. *Materials Letters* **115**, 261 (2014). https://doi.org/10.1016/j.matlet.2013.10.045.
[5] Ziegler, J. SRIM code. http://www.srim.org. Last access: January 17th, 2022.
[6] Pinna, F, et al. Project of Thin Targets for the NUMEN Experiment. *Journal of Physics: Conf. Series* **1056**, 012046 (2018). https://iopscience.iop.org/article/10.1088/1742-6596/1056/1/012046.
[7] Balandin, A. Thermal properties of graphene and nanostructured carbon materials. *Nature Mater* **10**, 569 (2011). https://doi.org/10.1038/nmat3064.
[8] Mortazavi, B. e Ahzi, S.: Thermal conductivity and tensile response of defective graphene: A molecular dynamics study. *Carbon* **63**, 460 (2013). https://doi.org/10.1016/j.carbon.2013.07.017.