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# Supramolecular functionalization of graphene related materials for heat transfer applications and devices

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# Summary

The thermal management in flexible electronic devices requires new materials able to dissipate heat to guarantee for the required lifetime and continuously increasing performance of modern electronic devices.

In recent years, Graphene, which is an allotrope of carbon in form of two- hexagonal lattice in which one atom forms each vertex, has generated a great interest for its unique mechanical, electrical and thermal proprieties. Despite this material is mainly used for electronic and optoelectronic applications, because the production cost is still relatively too high, graphene related materials (GRM) have being exploited are being increasingly exploited.

In fact, graphene research projects around the world are still growing due to the great impact of graphene results and applications. In Europe it has reached its peak in research funding since the European Commission decided to support the Graphene flagship which is the European largest research initiative, tasked with taking graphene from laboratories into the market with 1 billion budget over ten years. The Graphene flagship project includes more than 150 European industrials and academic partners and it involve 16 Work Packages covering almost all areas of graphene from fundamental science to scientific research for industrial applications from health to environment and electronics.

A strong interest in the use of these materials is found in heat management application where both increasingly efficient materials and mechanical characteristics such as flexibility are required. For some years now, in fact, heat spreader GRM based have been developing with thermal conductivity characteristics superior to the most commercially used metals (copper and aluminum) and, at the same time, they have lower density with a consequent greater lightness considering an equal geometry.

Although at microscopic level, the single graphene surface shows thermal conductivity values in the order of miles  $\text{Wm}^{-1}\text{K}^{-1}$ , the relative macroscopic artefacts (such as foils or self-supporting membranes) show values much lower than the ideal case caused by defects that may be chemical or physical. The first ones are given by the presence of functional groups or atomic species that interacting with covalent bonds change the hybridization of carbon and therefore interrupt the aromaticity of the material that is the most responsible for the heat transfer. Physical defects, instead, are related to the quality of the material, so not only to the presence of vacancies but also to the surface area, surface/volume ratio, edges, number of layers. Moreover, the quality of the thermal contact between structures and the porosity of the material must also be considered in the manufacture of macrostructures.

Post-treatments are widely used such as thermal annealing, to regenerate  $sp^2$ -hybridization of the graphene plane but, on the other hand, they take place at very high temperatures, increasing the production considerably. Therefore new methods of synthesis are being explored.

Although studies of molecular dynamics and the functional theory of density have theoretically demonstrated the efficacy of molecular junctions, only in recent times, these researches have been developing on graphene materials where the functionalization at the edges, which covalently links several structures, improves heat transfer. An alternative method for the GRM functionalization, that does not introduce chemical defects and preserves the aromatic network, exploits  $\pi$ - $\pi$  stacking between the surface and the polycyclic aromatic compounds.

In this thesis, both approaches have been used to connect GRM structures aiming at decreasing the thermal resistance at the interface and extending the surface through which heat can be transmitted. The first method exploits the functionalization of graphene-related materials at the edges with bi-functional molecules of different lengths derived from maleic anhydride, in order to investigate the thermal conductivity of these structures connected to themselves with molecular bridges. The Diels Alder reaction has been exploited and Raman spectroscopy characterizations and thermo gravimetric analysis confirmed the functionalization of GnP that was used as raw material for the production of films. The second approach, instead, exploits the supramolecular interactions between graphene related materials and bispyrene-based compounds spaced by aliphatic chains with different lengths. The specifically synthesized bispyrene molecules have the terminal pyrene groups that act as an anchor group to link different GnP during the fabrication process, which has been studied by spectroscopic characterizations (UV-Vis and photoluminescence on dispersion).

Using these functionalized GRMs, the nanopapers have been manufactured using a gravimetric filtration process and tested as heat spreaders. Through light flash analysis, the thermal diffusivity (that expresses the rate of heat spread) has been studied and considering the nanopapers as porous materials, different models were applied to investigate the relationship between porosity and thermal conductivity of the materials that has been experimentally demonstrated.

By simulating the heating of an electronic component into a device and how it should be cooled, the behaviour of nanopapers for cooling a hot spot was compared with both copper and aluminium heat spreaders. Moreover, from the analysis of thermal gradients and the application of classical mathematical models of finned surfaces it has been possible to understand how the rough surface of nanopapers may affect the heat exchange coefficient with the surround obtaining more performing heat spreader than metallic ones.