TOPICAL REVIEW

Deposition of graphene and related nanomaterials by dynamic spray-gun method: a new route to implement nanomaterials in real applications

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Abstract

The dynamic spray-gun deposition method was developed in 2006 to fabricate field effect transistors based on random arrays of carbon nanotubes (CNTs) field effect transistors for gas sensing applications. Thanks to this deposition method, we were able to fabricate hundreds of operational devices in a reproducible way that were integrated in electronic chips. Following this first implementation, we decided to widen the application of the deposition technique to the field of Energy and specifically to the fabrication of supercapacitors. In this context, we demonstrated in 2012 the fabrication of nanostructured electrodes for supercapacitors, using mixtures of graphene/graphite and CNTs increasing the device capacitance and the power delivered of a factor 2.5 compared to CNT based electrochemical-double-layer-capacitors. Indeed, with high quality graphene we could reach a value of around 100 W Kg\(^{-1}\). This value is extremely promising also considering that it has been obtained with an industrially suitable technique. This dynamic spray-gun deposition has been also exploited for the fabrication of resistance based random access memories, making use of thin layers of graphene oxide and of oxidized carbon nanofibers. In the first case, 5000 cycles of ‘write’ and ‘read’ phases were demonstrated. These results pave the way for the fabrication of very low cost memories that can be embedded in smart-cards, patches for health monitoring (e.g. diabetes), ID cards, RFID tags and more generally smart packaging. Finally we are also working on the utilization of this technique for the fabrication of layers for electro-magnetic interference shielding application. Thanks to a new machine with four nozzles, developed within the frame of the Graphene Flagship project, we are able to deposit four different nanomaterials at the same time or alternatively on a large surface (30 cm × 30 cm) creating specific nano-structuration and therefore ad hoc architectures allowing the smart absorption of specific frequencies (e.g. X-band). All these applications demonstrate the extreme versatility of this technique that constitutes a real breakthrough for exploiting the nanomaterials characteristics in real devices, using an industrial suitable fabrication method that can be implemented using roll-to-roll technique.

Introduction

The discovery and the availability of nanomaterials and of their extraordinary physical/chemical properties have deeply changed the way we deal with material science. Indeed the properties of materials can be different at the
nanoscale for two fundamental reasons. Firstly, considering that nanomaterials have potentially a larger surface area compared to the same mass of macro-material, this makes this new class of materials more chemically reactive, and affect their strength or their electrical properties. We can mention, for example, graphene [1] also called the ‘wonderful material’ that has a huge electric conductivity, electronic mobility, an impressive thermal conductivity and mechanical strength. Secondly, quantum effects can begin to dominate the behavior of matter at the nanoscale influencing in a dramatic way the optical, electrical and magnetic behavior of materials. One example is given by the exotic properties of 2D materials. We can mention 2D topological insulators such as stanene [2], or valleytronics using MoS₂ or other transition metal dichalcogenides [3]. Therefore, thanks to nanomaterials we can imagine to dramatically improve the performance of devices having a strong impact in our everyday life, reducing their dimensions and increasing the level of integration, while adding more functionalities and reducing the energy consumption. However, a big issue was rapidly pointed out: how to implement the properties of nanomaterials in a suitable and reproducible way, in order to make a real impact on the performances of ‘macro-devices’. Indeed, since the beginning, research teams have been focusing their efforts mainly on the study of the nano-objects by themselves, neglecting the potential issues related to their integration in real devices and systems. Our approach has been pragmatic and we have decided to take into account from the very beginning the fabrication method. The objective was to succeed in creating, designing and fabricating devices that can move from the dream realm to reality and therefore to real products. In this contribution, we discuss the development of a new deposition method for nanomaterials, based on the dynamic spray of suspensions of nanomaterials in specific solvents on large surface areas, with the possibility of implementation through roll-to-roll method. We show how we have conceived the fabrication method in parallel with the study of the nanomaterials properties and how these two aspects are both essential and can lead to effective innovations for devices in different fields of applications. We focus our contribution on four main applications: (i) gas sensors using carbon nanotubes field effect transistors (CNTFETs), (ii) supercapacitors based on mixtures of carbon nanotubes (CNTs), carbon nanofibers (CNFs) and graphene, (iii) non-volatile resistance random access memories (ReRAM) making use of graphene oxide and oxidized carbon nanofibers (ox-CNFS) and finally (iv) electromagnetic interference (EMI) shielding layers based on graphene related materials. All those four applications have been implemented using the dynamic spray-gun deposition technique. We also show how this technique has evolved moving from a hand-operated technique for small surface areas to a totally automatic technique with potential for roll-to-roll fabrication. This contribution demonstrates how basic research on nanomaterials can promote real advancements in terms of technological developments and leading to devices that can be integrated in existing systems if the fabrication issues are taking into account from the beginning. Thanks to this fabrication method we will to achieve a nano-structuration of the materials deposited using a technique of fabrication, industrially suitable and potentially low-cost. This is an important breakthrough in the field of fabrication techniques that can also be implemented for a large panel of applications with very large markets (see figure 1).

CNTFETs gas sensors

In 2004, within the frame of the Nanocarb lab at Thales Research and Technology (joint lab between Ecole Polytechnique and Thales), we decided to develop a new concept of CNTFETs for gas sensing applications. The first research paper on CNTFETs used as gas sensors, was published by Kong et al from Stanford in 2000 [4]. In this pioneering study, the transistor channel was constituted by a single single-walled-carbon-nanotube (SWCNT). The CNTFET was exposed to air, NH₃ and NO₂ and its transfer characteristics (i.e. the variation of the current between drain and source as a function of the gate bias) were observed to change as a function of the type of gas. The interaction of gases with the CNT was interpreted as strictly connected to charge transfers leading to doping effects. However, some years later it was highlighted by different studies that the main effect, for channels shorter than 100 µm, was mainly on the work function of the metal contacts, which was shifted by the adsorption of the gas molecules [5–9]. This was the main reason for the change of the transfer characteristics (drain–source current as function of the gate voltage) of the CNTFETs. A lot of other works in the field followed, exploiting the same transistor configuration. The main common issue of all these contributions was to correctly built-up the contact between the CNT and the drain and source electrodes. This issue had already affected the development of CNTFETs for logic gates by IBM at the end of the 90ies [10–14] considering the difficulties to achieve ohmic-type contacts. In our case, we focused our efforts on CNTFETs fabricated using random mats of percolating SWCNTs. Indeed it had been demonstrated by previous studies, that exploiting the percolation of a layer of SWCNTs with larger concentration of semiconducting specimens compared to metallic ones, it was possible to obtain an overall semiconducting electrical behavior [15, 16], and therefore to use these mats as transistor channels. Moreover, as demonstrated by Furher et al in 2000 [17], the percolating chains linking the electrodes are composed only by semiconducting SWCNTs. Actually, Furher and co-workers evaluated the
resistance of the contact between two metallic SWCNTs (MM), two semiconducting (SS) and of one semiconducting and one metallic one (SM). Experimentally they found a resistance of SM contacts twofold compared to SS or MM because the moving charges experienced tunneling between the two SWCNTs, as in case of SS and MM, but also a Schottky barrier linked to their different electronic character. Considering that statistically the concentration of metallic SWCNTs is largely lower than the concentration of semiconducting ones (respectively 33% and 66% for standard CNTs production), the consequence is that only semiconducting chains bear the current between the two contacts. The main advantages of exploiting SWCNT-based mats compared to single CNT FETs, are therefore:

- The potential to collectively fabricate arrays of transistors.
- The dramatic cost reduction in fabricating the devices considering also the implementation on large surfaces.
- The electrical characteristics of the contacts are the results of the average of the effect of several SWCNTs on the metal electrodes. Thanks to this averaging effect, the final performances are more reproducible and do not depend anymore on the characteristics of each single SWCNT/metal contact as before.

In this context in 2006, we conceived and set-up a new fabrication technology based on dynamic spray-gun deposition of the nanomaterials on 2" substrates, with pre-patterned electrodes, to fabricate arrays of hundreds of CNTFETs exploiting SWCNTs mats as channels for gas sensing application. To achieve uniform depositions, a new process and a new facility needed to be developed. Figure 2 picture shows the set-up of the first deposition machine.

As shown in figure 1 (the scheme and the real set-up), the system was composed by a spray-gun with a specific nozzle that can move along Z and X axis while the chuck (with the hotplate) could move on Y axis. Thanks to that we were able to cover completely the surface of the substrate (clamped on the hotplate thanks to a vacuum pump) knowing the Gaussian distribution of the cone related to the material sprayed on the surface and so calculating the best pitch between the scan lines (the movement of the spray-gun) executed by the machine. The spray-gun was a 780S dispense valve by Nordson that uses nitrogen to atomize and spray the suspension. The nozzle could have dimensions varying between 0.4 and 1.7 mm as a function of the nanomaterials sprayed. The drops, with dimension < 100 μm, reached the substrate that was heated at a temperature larger than the boiling point of the solvent, avoiding the so-called ‘coffee-ring effect’ [18, 19]. Indeed, the dispersed nanomaterials in a specific solvent tend to move to the borders of the droplets, when they are deposited by spray,
if the solvent dries at ambient temperature. This is related to the capillary flow induced by the differential evaporation rates across the drop (see figure 3): liquid evaporating from the edge is replenished by liquid from the interior.

For this reason, after drying completely, a pattern of concentric rings is observed. As a consequence, the final deposition is not uniform and not reproducible. To avoid this phenomenon, the substrate was heated (thanks to a hotplate) to a temperature that allows instantaneous vaporization of the drops upon contact, thus avoiding the migration of nanomaterials to the borders of the drops. Thanks to that, the nanomaterials are stuck at the point where they have impacted the substrate. In order to obtain stable suspensions to be sprayed, we employed N-methyl-pyrrolidone (NMP) \[20, 21\]. In case of utilization of NMP, the substrate temperature was set to 220 °C considering that the boiling point of NMP is 202 °C. Indeed, we need around 20 °C more to compensate the fact that during the spray, the substrate temperature is reduced. Moreover, the substrate temperature had to be precisely adjusted, not too high, to prevent droplets vaporization before reaching the substrate, which would reduce dramatically the final yield of the overall deposition. Here, the yield is defined as the ratio between the weight of the nanomaterials in the suspension and the weight of the nanomaterials effectively deposited on the substrate. In case of gas sensors, the SWCNTs used were supplied by SouthWest NanoTechnologies, and were CoMoCat SG65 [22] composed by 90% of semiconducting SWCNTs. Co, Mo and Cat stand respectively for Cobalt, Molybdenum and Cat for Catalysts [23]. We decided to use these SWCNTs considering that these were, in 2004, the only products that could be purchased with this high concentration of semiconducting SWCNTs, without any additional purification steps and at a reasonable price (around 500$ for 1gr). SWCNT bundles and residual impurities (e.g. catalyst particles) were eliminated from the original SWCNT suspension. This was accomplished by sonication using a probe to ‘break’ the bundles (1 h), followed by centrifugation (two phases of 10 min at 3000 rpm) and careful recuperation of the supernatant part of the suspension.

This deposition method, patented \[24, 25\], allowed fabricating wafers of CNTFETs with reproducible performances and with on/off current ratios of at least three orders of magnitude \[26\]. In order to perform a selective sensing we decided to fabricate an array of sensors composed by different metals as source and drain.
contacts (see patent [27]). Actually, considering that the detection is based on the effect of gases on the Fermi level between the metal contacts and CNTs, and that each metal has a different work function, a particular gas changes in a very specific way the transfer characteristics of the CNTFETs as a function of the nature of the metal contact. Thanks to that, we are able to achieve an electronic fingerprinting of the gas after exposure to the array of CNTFETs. In figure 4, the response of an array composed by CNTFETs with four different metals (Au, Pd, Ti, Pt) as contacts is shown after exposure to NO₂ and NH₃. We chose these metals because of their different work functions.

We decided to perform the first tests using NO₂ and NH₃ because they have two opposite chemical affinities and they were the most common gases used by all the groups working in the field. In the first case, NO₂ is defined
as an ‘electron-donating’ gas and for NH$_3$ as an ‘electron-accepting’ gas [14, 28]. This is related to the fact that in the first case, the current ($I_{DS}$), after gas exposure, tends to rise and in the second case to decrease. Thanks to the satisfying performance obtained in terms of detection level and recovery time, an array of transistors was integrated on a final gas sensing chip (see figure 5). The data obtained during the measurements were recorded by a specific data treatment module in order to perform a selective detection reducing the false alarm rate and to avoid the interferences of the environment on the final response. The sensor response data processing was based on a principal component analysis (PCA) [29]. This multivariate technique represents the data table (i.e. the characteristics of all the transistors simultaneously recorded when exposed to the gas to be detected) in a set of new orthogonal variables called principal components. The components are classified by their amount of information they contain, the first one being the most informative. PCA allows identifying which combination of the transistor responses contains the most informative value, i.e. contribute to the selectivity. The success of the exploitation of the dynamic spray-gun deposition method in this gas sensing activity motivated our team to implement its application in other fields, such as the fabrication of energy storage devices and more specifically supercapacitors.

**Application to the energy field: supercapacitors based on mixtures of graphene and CNTs**

The versatility of the deposition technique by dynamic spray motivated us to exploit it for the fabrication of supercapacitors also called electrochemical-double-layer-capacitors (EDLC). One of the first papers showing that spray could be used to fabricate this kind of devices was published by Kaempgen et al in 2009 [30]. In this case, Kaempgen and co-workers fabricated thin film supercapacitors with sprayed networks of SWCNTs, which were in water suspension with a specific surfactant, serving both as electrodes and charge collectors. Specifically, with a static spray-gun, the stable suspension was deposited onto polyethylene-terephthalate (PET) substrates placed on a hotplate. During spraying, the water was evaporated and the SWCNTs formed an entangled random network on the PET without any other treatment. The mass of the SWCNTs coated on each substrate was determined by weighing the PET before and after the deposition. All SWCNT films typically had a sheet resistance of $\sim 40-50 \, \Omega \, \text{m}^{-2}$ and a thickness of $\sim 0.6 \, \mu\text{m}$. This thickness was extremely small considering that in commercial supercapacitors the thickness is of the order of $\sim 100 \, \mu\text{m}$. Even though these devices were not yet optimized, mainly in terms of the electrical conductivity and thickness of the CNT films, their performance already spanned the typical range of conventional supercapacitor devices for all electrolytes used. This was achieved thanks to the increased effective surface in the thin films, maximizing the efficiency of the supercapacitors, compared to the thick activated carbon electrodes in regular devices. Moreover, the simplified architecture had the potential to promote a new class of light, flexible and printable charge storage devices. In 2011, Cheng et al [31] demonstrated the interest of using mixtures of graphene and CNTs to fabricate nanostructured electrodes; they managed to increase the overall surface area to store charges, and so the density
of energy, using the CNTs as spacers, thus preventing the restacking of the graphene flakes (and the concomitant loss of effective surface). At the same time, this mixture also allows creating a mesoporous distribution inside the electrode that could raise the value of the delivered power. In fact, the term ‘mesoporous’ is used to highlight a pore distribution with sizes that can vary between 2 and 50 nm. A mesoporous distribution constitutes a favorable pore network that fits the charge dimensions and therefore can improve the circulation of the ions inside the electrodes. As a result, a very fast charge and discharge of the device can be achieved. In 2012, exploiting our dynamic spray-gun deposition technique, we decided to fabricate mixtures of partially exfoliated graphite and multi-walled-carbon-nanotubes (MWCNTs) \[32\]. Graphite (ref 332461) and MWGNT (ref 724769-25G) powders were purchased from Sigma Aldrich. Both powders were dispersed in NMP at concentrations of 0.5 mg ml\(^{-1}\). MWCNT-based solutions were sonicated for 10 min at high power (Vibra-cell 75185 by Sonics, 130 W). In order to prevent the destruction of the partially exfoliated graphite flakes, we sonicated them during 18 h in a low power sonic bath (Branson 1510E-MT bath sonicator, 70 W). No centrifugation was performed after dispersion, whether CNT or graphite suspensions were concerned. The graphite and CNT suspensions were then mixed in 5 different volume ratios (0%, 25%, 50%, 75% and 100%) to obtain different proportions. In this way we wanted to identify the best compromise to achieve the more effective electrode in term of specific capacitance and power. Both dispersions had the same nanomaterial concentration (0.5 mg ml\(^{-1}\)). The 5 final mixtures were further sonicated for 18 h in the low power sonic bath to improve the entanglement of the nanomaterials. The final stable suspensions were then gun-sprayed on graphite collectors (graphite foil, EYGS182307, Panasonic) at a constant distance of \(\sim 15\) cm from the surface. In their paper, Cheng et al obtained the electrodes by fabricating bucky papers through complex filtration steps. This technique clearly cannot be scaled-up and it is mainly used for lab samples fabrication. In our case, the main advantage is that we could perform the uniform deposition on relatively large surface electrodes (15 cm \(\times\) 15 cm). The results of these first tries were very promising in terms of power density (\(\sim 40\) kW Kg\(^{-1}\)) thanks to the nanostructuration that we were able to achieve with our deposition technique (see figure 6).

In figure 6, the cross-section of supercapacitors electrode is shown. The intercalation of the CNTs between the layers of graphene/graphite can clearly be observed. The most interesting results (see figure 7) showed that when we use mixtures of 75% of Graphene/Graphite and 25% of CNTs we get the best performance in terms of power delivered which is around 2.5 times larger than the case of electrodes fabricated using only CNTs (see the value for 0% of Graphene/Graphite concentration in figure 7). This seemed to be the best concentration that allows achieving the best pore distribution. Similar results were obtained using carbon nanodiamonds with high graphitic quality at the place of CNTs. However this kind of material is more difficult to purchase compared to SWCNTs. This was the first time that EDLC where fabricated using this deposition technique exploiting graphene related materials.

These preliminary results were dramatically improved in 2017 using mixtures of high quality exfoliated few layer graphene (supplied by the Italian Institute of Technology in Genoa, Italy) and SWCNTs \[33\]. The few layer graphene flakes were produced by liquid phase exfoliation after mixing 20 g of graphite (Sigma-Aldrich, flakes) with 1 l of NMP (Sigma-Aldrich, purity 99%). The exfoliation was performed by bath sonicator (VWR) for 6 h and then ultracentrifuged at \(\sim 12300\) g (10k RPM in a Beckman Coulter Optima™ XE-90 with a SW32Ti rotor) for 30 min at 15 \(^{\circ}\)C, to exploit sedimentation-based separation. The supernatant was then collected by pipetting, obtaining a SLG/FLG flakes-based dispersion. Concerning the SWCNTs, the powder (BuckyUSA, BU-203,
purity 95% in weight, length 0.5–5 μm, diameter 0.7–2.5 nm) was used as received (without any purification step). SWCNTs were dispersed in NMP at a concentration of 0.5 mg ml⁻¹ by soninating the dispersion for 10 min at high power (0.625 W ml⁻¹, Vibra-cell 75185 by Sonics). The two suspensions were mixed together and sprayed on a graphite based collector. The devices were assembled using 2 cm² area electrodes and a common aqueous electrolyte (3M LiNO₃) to build a coin cell. This architecture allows us to effectively balance the supercapacitors performance achieving gravimetric capacitance, specific energy and power of 104 F g⁻¹, 20.8 Wh kg⁻¹, and 92.3 W kg⁻¹, respectively.

In figure 8, we can see that the supercapacitor cells were cycled up to 5000 cycles without any strong deviation after the first 2000. These results, based on industrially scalable materials production and deposition method, represent a real breakthrough compared to state-of-the-art lab-scale devices. Since 2017, at Thales Research and Technology, we have worked on the development of a new machine with two nozzles (see figure 9). Thanks to that we have been able to fabricate finely tuned multilayered structures to improve the EDLC performances creating a more adapted mesoporous distribution. Indeed, with this new machine, it is possible to alternate the deposition of two different spray-guns, fabricating multi-layered structures in a more deterministic way. Considering that the samples for EDLC fabrication are largely thicker (tens/hundredths of μm) than the layers needed for gas sensors applications (some nms), using the one nozzle machine, we have faced some problems concerning the clogging of the spray-gun. In the set-up of the new machine we decided to integrate a circulation system (see figure 9) in the spray-guns to avoid this issue and also to keep the suspensions always in movement, to prevent sedimentation.

Using this new machine, we have also worked on mixtures of graphene and CNFs. CNFs differ in relation to CNTs mainly on their structure, since for CNFs a cone angle between the graphite basal planes and the tube axis exists, which leads to the absence of the concentric structure that CNTs have. Due to this difference, CNFs appear to be compact sometime, in contrast with CNTs that have a hollow structure. The most important difference however, taking into account the spray-gun application, is their diameter difference; CNFs tend to be thicker, compared to CNTs. The following TEM images present the main structural alteration between CNTs and CNFs (figure 10).
Considering that CNTs and CNFs are used as sort of spacers between the graphene layers it is clear that using CNFs, with diameters between 50 and 100 nm we can optimize the porous distribution for ionic liquid utilization. Such electrolytes have been developed to fabricate supercapacitors that are able to withstand harsh environments, in a range of temperatures between $-40 \degree C$ and $+100 \degree C$ for avionics application. This is not possible using commercial aqueous electrolytes. There are no existing EDLCs able to satisfy these specifications up to now. One of the main characteristics of ionic liquids is the average larger size of ionic charge carriers. Moreover, viscosity of ionic liquids markedly increases at low temperature. As a consequence, to keep an acceptable value of the power delivered, we need to have a well interconnected network of pores, with a larger size compared to commercial aqueous electrolytes used in the previous works. Compared to the previous results the structures were fabricated in a more deterministic way, as mentioned above, alternating layers of graphene, in this specific case reduced graphene oxide (RGO) from Graphenea, and CNFs grown by the National Technological University of Athens with a length of around 10 $\mu m$ and diameter of around 100 nm. CNFs were synthesized through the thermal catalytic chemical vapor deposition method, by the supported catalyst approach. By this, tailored properties of the CNFs can be achieved, through the careful selection of the catalyst and the experimental conditions (temperature range, flow rate of the reaction gases, reaction atmosphere and duration, substrate, etc). In figure 11 a SEM image of the used CNFs is presented.

The results showed that the best result in terms of capacitance was obtained for a concentration of 90% of RGO (20 F g$^{-1}$, see figure 12) with a power delivered of 40 kW Kg$^{-1}$. This last value is at the state of the art for devices using ionic liquids and able to afford the interval of temperature mentioned above.

This last device was another representative example of the capacity to perform a nano-structuration exploiting our macro deposition technique avoiding complex and therefore non-industrially suitable processes that have no potential to be scaled-up.
Carbon-based non-volatile memories by spray-gun deposition

Another extremely promising application that can be implemented by dynamic spray-gun deposition method is the fabrication of low-cost graphite-based memories that might be integrated on flexible, plastic or paper based substrates [35]. Indeed in the international technology roadmap for semiconductors issued in 2011 [36–38], it was stated in the chapter concerning emerging research devices (i.e. ERD) and more specifically on memory devices, that ultrathin graphite layers were ‘interesting materials for macromolecular memories thanks to the potential fabrication costs that are considered as the primary driver for this type of memory, while extreme scaling is de-emphasized’. In fact, this kind of memories can be used for low-cost applications and integrated for example in ID cards, driver licenses, smart-cards or smart packaging in general. At the state of the art, there are no flexible, low-cost memories that have been integrated into existing systems. Therefore these memories will not be in competition with high performance ones such as magnetic random access memories that are used for new generation of computers but can open new market segments in flexible electronics where cheap, and also potentially disposable, memories are needed. Moreover considering that they are composed only by carbon and in an extremely low quantity, their impact on the environment is very low. In our case we wanted to fabricate metal–insulator–metal structures were the graphene-based materials were sandwiched between two contacts. This kind of structure is a resistance random access memory (Re-RAM) [39–41] where the resistance of the sandwiched material is changed applying a bias between the top and bottom contact. One of the first work showing the utilization of graphene-based mats for flexible non-volatile Re-RAM was published in 2010 by Jeong et al [42]. Thanks to its hydrophilic character, graphene oxide (GO) flakes were easily put in stable water suspensions and deposited on large surface using spin coating process. This team demonstrated the non-volatile effect on the resistance of a 70 nm thick layer of GO flakes in a layered structure composed by Al/GO/Al exploiting a classic cross-bar configuration. In this context, we can also mention the work of He et al in 2009.
where reliable and reproducible resistive switching behaviors were observed in GO thin films prepared by a vacuum filtration method [44], the common technique used to fabricate CNT-based bucky papers. The suggested physical principle at the origin of the switching effect was the absorption/desorption of oxygen-related groups on the GO sheets. The alignment of the oxygen vacancies creates conducting paths that reduces the resistance of the sandwiched layers. Another hypothesis concerns the oxidation of the top contact. Hong et al [45] performed a deep analysis of the switching mechanism for this kind of devices. They underlined that these structures had performance which were dependent on the origin of the top contacts. For example, in case of Au-based top electrodes that cannot be oxidized, there was no oxygen migration in contrast to Al electrodes. Thanks to that, we move from a high resistance state to a lower resistance state. These experiments underlined that GO was potentially useful for future non-volatile memory applications. In 2015, in a joint work with CEA (not published), we fabricated GO-based ReRAM using dynamic spray-gun deposition method. We achieved structures as show in figure 13 where the GO were sandwiched between two metal contacts, with a thickness of tens of nanometers.

The structures obtained were cycled 100 times between ‘write’ and ‘delete’ phases showing also a very good ON stability during the ‘read’ phase (5000 cycles) as highlighted in figure 14. These results constitute the first example of graphene-based memories achieved using spray-gun deposition method.

Starting from these preliminary results, we have decided to implement the possibility to fabricate memory based on ox-CNFs, taking into account that CNFs are less expensive and that graphene was only the ‘carrier’ of the oxygen atoms. Considering that the final thickness of the insulator layer had to be around 50 nm we fabricated extremely diluted suspensions using ox-CNFs in de-ionized water. After defining specifications for

Figure 13. Graphene-based memories using graphene oxide layers. On the left-hand side, an overview of the device composed by 20 bottom contacts and 4 top contacts. The GO is sandwiched at the intersections creating MIM structures (work in collaboration with CEA, not published).

Figure 14. Top: persistence of the on state after 5000 cycles of reading. The switching time was of 1 ms. Bottom: switching characteristics after 100 cycles of ‘write’ and ‘delete’ (work in collaboration with CEA not published).
CNFs dimensions (diameters and length), the National Technical University of Athens (within the frame of the European H2020 NMP project MODCOMP [46]) provided ox-CNFs to prepare stable suspensions to be sprayed. CNFs were purified to remove any amorphous by-product and the metallic catalyst residues that could be at the origin of the formation of dendrites between the two electrodes and so of the short-circuit and pinning of the device [47]. Chemical functionalisation of their surface was carried out with a strong acid treatment. By this, oxidation of their surface was achieved, since oxygen groups were anchored (−COOH, −OH, =O).

Considering that the CNFs are oxidized, we could obtain extremely stable suspensions in water. This allowed us to develop a green-type process and to reduce the heating temperature of the hot plate, (that for NMP has to be larger than 202 °C), to around 100 °C. The suspensions were obtained using 10 mg of ox-CNfs in 500 ml of de-ionized water. We performed centrifugation during 20 min, in two phases, at 3000 rpm. We kept only the supernatant of the suspensions that was centrifuged. This step is very important to avoid utilization of thick CNF bundles, a critical parameter for the final fabrication of the memories. The supernatant was further diluted in 500 ml of de-ionized water and sonicated in a bath for 6 h, after what we performed the deposition on a 2″ silicon-based substrate that was preliminary metallized using a Ti/Pt layer. On top of the deposited CNF layer, we patterned 100 μm × 100 μm squares where we deposited AlCu/Au contacts. The active memory stack is depicted in figure 15.

The ox-CNfs are in contact with the inert bottom electrode of Pt and the easy to oxidize top electrode of AlCu. By applying a positive voltage between the bottom and top electrode, the oxygen atoms migrate from the ox-CNf layer to the AlCu electrode. By applying the opposite voltage, the oxidized AlCu electrode gives back the oxygen atoms to the CNF layer. This back and forth motion of the oxygen atoms leads to a hysteretic change of the current shown in figure 16.

These very promising results obtained on a hard substrate demonstrate that memories can be fabricated using CNFs and pave the way to the revolution of memories on flexible substrates (already fabricated and to be tested in the following months), which at the moment do not exist as commercial components in the market. This will allow widening the implementation of low-cost memories in large market applications as ID cards, smart cards, memories for health monitoring on specific patches (e.g. diabetes monitoring), ticketing, smart packaging.

Figure 15. Side and top views of the sample. (a) Cross-section of the structure (b) top-view of sample and detail of the top contact of MIM-type devices.

Figure 16. (a) Schematic side view of the two states of resistance of the memory stack (b) image of a cycle obtained by applying a voltage between the inert Pt electrode and the AlCu electrode. The hysteretic change of current results from the migration of oxygen atoms between the CNF layer and the AlCu metal.
Perspective for new applications (in progress): electromagnetic shielding

Another potential application for the dynamic spray-gun deposition method is the fabrication of layered structures to achieve smart reflection or absorption of specific frequencies, performing what is commonly called electromagnetic interference shielding (EMI) [48]. As mentioned, two mechanisms of EMI coexist: one is based on reflection, the other on absorption. In the first case we want to achieve high conductivity layer thanks to spray gun deposition. Indeed, a solution to achieve high reflectivity is the use of metal for this application. The main issues are that metals are costly, they have high densities (and are heavy) with corrosion susceptibility. With spray-gun deposition of conducting nanomaterials, the weight would be decreased but it would also be possible to manufacture conformable surfaces exploiting mixing of nanomaterials with polymers [49–51]. In case of shielding exploiting absorption, it is necessary to have materials with electrical or magnetic dipoles. For this reason, in this case, materials with high dielectric constant (ZnO, SiO2, TiO2…) or high magnetic permeability (Ni, Co, Fe…) are exploited [52]. As quoted previously, these materials are heavy and their manufacturing is complex. Composites could replace them but with reduction in performance. One of the solutions that we will suggest to explore using deposition by spray-gun is to fabricate stacked alternating layers of dielectric and graphene. Thank to that, we want to exploit the Maxwell–Wagner–Sillars (MWS) phenomenon [53–55], i.e. polarization effects at the interface between the conductive materials (graphene sheets) and dielectric materials (e.g. polymers) to build device architectures able to trap the charges (see figure 17). We can mention the work of Li et al [56] where graphene sheets (GS)/polyacrylate (PA) composites favored the build-up of a segregated GS architecture stacked in the polymer matrix. This unique nanostructured GS architecture not only enhanced the electrical conductivity of composites, but also induced strong MWS polarization at the highly conductive GS/non-conductive PA interfaces. The EMI shielding effectiveness (SE) of these composites was enhanced with increasing the GS content, and the composite with 6 wt% GS loading exhibited a high EMI SE of ~66 dB over a frequency of 8.2–12.4 GHz, resulting from the pronounced conduction loss, dielectric relaxation, and multiscattering effects. Indeed thanks to graphene sheets we can increase the conductivity of the materials but also the absorption considering that graphene sheets have high aspect ratio, large interfaces, and high dielectric loss. Our approach in this field will be to be more deterministic in fabricating this kind of architectures on large surface with potential implementation for roll-to-roll fabrication (see figure 18).

Thanks to the new facility developed in the frame of the Graphene Flagship (see next paragraph for more details), we will be able to fabricate multi-layered structures. In this way we will be able to achieve, after design and modeling, structures with specific thickness and layers properties to tailor ad hoc absorption at specific frequencies, with the possibility of raising also the conductivity and the reflection using graphene based layers to achieve smart structures. This could be a real breakthrough for this field and open new horizons of innovation.

Conclusions and new developments: from small to larger surfaces

In this contribution we have highlighted the versatility and the large panel of applications of the dynamic spray-gun deposition especially for graphene and carbon based nanomaterials. This deposition technique allows exploiting the potential of these materials and to fabricate devices that can impact our everyday life. Recently, within the frame of the Graphene Flagship project in 2018 we have developed a new machine able to fabricate larger samples that can allow the scale-up of the fabrication technique to strike large markets. This machine is
composed by four nozzles able to spray on a 30 cm × 30 cm surface. This is the first and unique prototype of a new generation of machines that can be used in the future for a very large panel of applications changing the way in which the nanomaterials are effectively implemented in industrial applications.

This is the result of more than ten years of technological development that allows us moving from lab-type a small surface machine to completely automatic large surface compatible equipment (https://www.youtube.com/watch?v=XUysJ52LwXA). Thanks to this machine (see figure 18), which is the only existing prototype, we can imagine to spray layers of different nanomaterials and therefore to achieve the ‘lego view’ for utilization of 2D materials suggested by Nobel Prize Andrew Geim in 2013 [57] in a more realistic way, without complex processes for the precise positioning of several single layers of 2D materials. Indeed this is not suitable from an industrial point of view also considering that the final cost of the devices strongly depends on the capacity to scale-up the process and to reduce the fabrication time. In this optics in the Graphene Flagship consortium, the conception and set-up of a roll-to-roll machine to fabricate supercapacitors by spray is in progress and will be ultimate during the next year (2019). This will constitute a completely new way of producing supercapacitors that could be widened in the future for other applications already mentioned exploiting different kind of nanomaterials structuration on different kinds of substrates (e.g. paper, plastics etc…).

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References

[1] Geim A K and Novoselov K S 2007 Nat. Mater. 6 183–91
[2] Saxenas S, Chaudhary R P and Shukla S 2016 Sci. Rep. 6 31073
