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DIAMOND-LIKE CARBON: A VERSATILE MATERIAL FOR DEVELOPING INNOVATIVE SMART TEXTILES APPLICATIONS. A SHORT REVIEW

DANIELA CASCHERA [a] *, ROBERTA GRAZIA TORO [a], BARBARA CORTESE [b], FULVIO FEDERICI [a], DOMENICO LOMBARDO [c] AND PIETRO CALANDRA [a]

ABSTRACT. Smart textiles are *fabrics* that have been developed or modified with *new technologies* providing *added value* to the wearer. The emerging smart textile technologies have to take into account the aesthetics and comfort of the textiles, using at the same time a simple and intuitive technology interface. Diamond-Like Carbon (DLC), is an amorphous carbons allotrope, containing a mixture of sp^2 and sp^3 -hybridized carbon atoms. This is a well-known material for mechanical and industrial applications, but it is recently receiving much attention for its innovative utilization in the design and construction of smart and multifunctional textile-based systems through the proper functionalization and modification of the surface of the cellulosic substrates. Allowing the simultaneous inclusion of other nanostructured materials with the ultimate formation of a complex nanocomposite-based structure, adds value and novel properties to the material, making DLC an optimal candidate for smart self-cleaning properties. The latest developments, strategies and materials, are herein addressed. Future perspectives, using the approach of complex systems physics, for developing new and ecological applications in nanotechnologies as well as the development of micro and nano techniques for fiber treatment are highlighted.

1. Introduction

In recent decades, there has been a notable increase in the market for non-apparel fabrics, which, thanks specially to the application of nanotechnologies, has increased the development of specific sectors of the textile industry, most of them are necessarily interdisciplinary. Promising recent developments in material processing, device design and system configuration enable the scientific and industrial community to concentrate efforts on the realization of smart textiles (Schneegass and Amft 2017). The combination of implementable properties of the fabrics such as strength, together with intrinsic flexibility and toughness of the fibers themselves, linked with the possibility of nanotechnology to add innovative properties, can allow the development of new engineering areas of the textile industry (Cortese *et al.* 2013; Yetisen *et al.* 2016; Asif and Hasan 2018). In this view, the textiles of the future will improve people's everyday lives and benefit the industry, the health

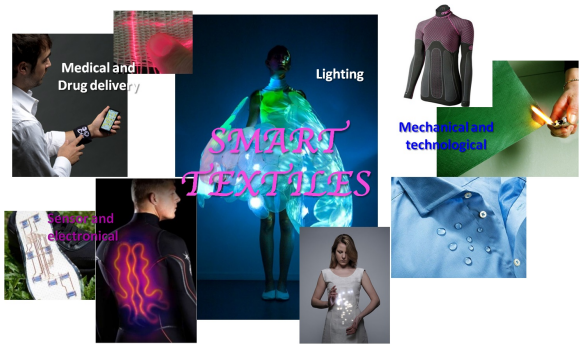

FIGURE 1. Evidence of some possible high technological applications fields for new appealing smart textiles.

care sector and the environment. In Figure 1, some possible application fields of the new smart textiles have been indicated.

The challenge of combining specific chemical and physical properties to generate complex nanostructure-based systems with novel characteristics for applications in nanotechnology is very appealing (Calandra *et al.* 2015a; Caschera *et al.* 2018). In this perspective, carbon and its variety of allotropic forms represent a very attractive class of materials. Carbon Nanotubes (CNTs), Graphene and Diamond-like Carbon (DLC) are well known as advanced materials for applications in several industrial fields as electronic and optoelectronic materials (Loh *et al.* 2010), protective coatings (Faraldi *et al.* 2014b; Toro *et al.* 2016), materials for solar cells (Calandra *et al.* 2010d). Important results involving carbon derivates are also achieved in biotechnological fields: as example, attempts to use modified CNT with gold nanoparticles with the aim to fabricate new hybrid nano-biosensors are reported (Calò *et al.* 2010; Curulli *et al.* 2010). Nevertheless, some peculiar properties of carbon-based materials make them very promising candidates for next-generation smart textiles and wearable devices (Di *et al.* 2016; Karim *et al.* 2017; Salavagione *et al.* 2018). In this short review, our attention will be in particular focused on Diamond-Like Carbon (DLC), an amorphous carbons allotrope, containing a mixture of sp^2 and sp^3 and its innovative utilization, in synergy with other nanostructured materials, in the design and construction of smart and multifunctional textile-based systems through the proper functionalization and modification of the surface properties of the cellulosic substrates. Finally, some perspectives through the approach of complex systems physics will be presented suggesting methods to functionalize DLC-based materials in order to develop systems with new emerging properties.

2. Diamond-like carbon: an attractive material

Diamond-like carbon (DLC) is an amorphous carbon-based material; its structure is characterized by the presence of both sp^2 and sp^3 carbon atoms, and a certain amount of hydrogen (Robertson 2002). Thanks to their unique properties, DLC-based materials have attracted great attention in several industrial and technological fields (Figure 2). High hardness, low friction coefficient, high thermal stability, optical transparency, excellent abrasion resistance, wide band gap, high resistivity, high dielectric strength, and good

FIGURE 2. Illustration of several industrial applications for DLC coatings, thans to their unique properties.

thermal conductivity permit DLC film to be an ideal choice as a thin protective coating (Grill 1999; Viswanathan *et al.* 2018). Moreover, its low water permeability, chemical inertness to any solvent and good resistance against acids (even strong acid mixtures), alkalis or organic mixtures render DLC coatings suitable for nanoscale-based applications even in extreme environmental conditions (Sharma *et al.* 2008; Faraldi *et al.* 2014a; Faraldi *et al.* 2016).

DLC properties are strongly affected by the relative population of sp^2 and sp^3 hybridizations of the carbon atoms involved. Since the carbon sp^2/sp^3 ratio can be varied by opportunely tuning the deposition process parameter and either the deposition technique itself, it is possible to impart to the DLC layer the required properties just changing opportunely the way in which the coatings are realized. DLC films can be produced by a wide range of deposition methods, both chemical and physical, such as ion beam deposition (Puzikov and Semenov 1991)sputtering (Hong-mei *et al.* 2011), pulsed laser ablation (Voevodin *et al.* 1997), plasma technologies (Tither *et al.* 1997). In particular, Plasma Enhanced Chemical Vapor Deposition (PECVD) method is a very promising and versatile process to produce DLC (Viana *et al.* 2010; Caschera *et al.* 2011b), since it allows the carbon film growth also at low temperatures of the substrate and provides ion bombardment of the surface which gives the advantage of increasing adhesion of the film onto the substrate thus enhancing film quality. The mild operating conditions and the specificity of this technique offer a clean technology solution to modify the fiber surface without changing the bulk characteristics of textile. This is achieved by plasma activation and/or thin coating deposition (Karahan and Ozdogan 2008; Zille *et al.* 2014; Kan and Lam 2018). Moreover, plasma treatment can be considered a green technology because it is essentially a "solvent free" method, so it could replace effectively many traditional wet chemistry-based finishing processes, with a great environmental and energy saving effort. For all these reasons plasma processing is attractive for textile industry.

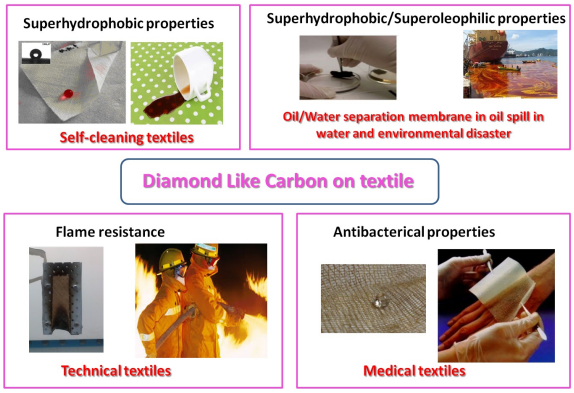

FIGURE 3. Possible innovative application for DLC modified textiles.

3. Innovative Applications of DLC cotton systems

Water repellency or absorbency depends upon the chemical composition and the topographical morphology of a surface. Considering that the degree to which a surface repels or absorbs a liquid is a dominant characteristic influencing many of surface's applications, it is easy to understand that controlling the wettability behavior of the surfaces through the micro/nano structuring of low surface energy materials is the key for developing attractive potential textiles in many applications as water proof and self-cleaning apparel or with better adsorption capacity and bioactive properties. Plasma process provides a facile way to realize a hierarchal rough DLC coating on cotton surfaces, modifying the hydrophilic surface properties of textiles, and inducing specific new properties to the DLC modified textiles (Figure 3).

3.1. Self-cleaning properties. One of the ways surfaces can effectively self-clean is by repelling water so that contaminant floating on water cannot stick. This is the basis of the so called "Lotus Effect" exhibited by the leaves of *Nelumbo nucifera* or "lotus flower", characterized by ultra-hydrophobic properties (i.e. when rain falls on lotus leaves, spherically-shaped water droplets are formed with high contact angles on the leaves surface; the rain droplets promptly roll off the leaves, collecting dirt and particles of dust along their way). This strong superhydrophobicity, due to a precise combination of the chemical structure of the surface and the hierarchical micro roughness, has, in recent years, stimulated much research effort worldwide for developing self-cleaning surfaces based on lotus effect with very high static water contact angles greater than 160° and a low roll-off angle (Marmur 2004; Patankar 2004; Cheng *et al.* 2006; Cortese *et al.* 2008; Nishimoto and Bhushan 2013), which can be suitable for a variety of applications ranging from self-cleaning window glasses, exterior paints for buildings and navigation of ships, utensils, roof tiles, textiles, solar panels, and applications requiring a reduction of drag in fluid flow (Abidi *et al.* 2009; Chae Jung and Bhushan 2009; Midtdal and Jelle 2013; Yao and He 2013). The creation of clothes that can clean themselves ("self-cleaning clothes") has been a hot-topic for several decades and carbon based materials have been deeply investigated as possible functionalization to

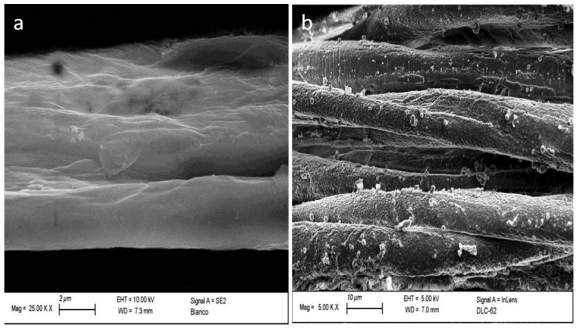

FIGURE 4. SEM images of a) cotton pristine and b) DLC on cotton.

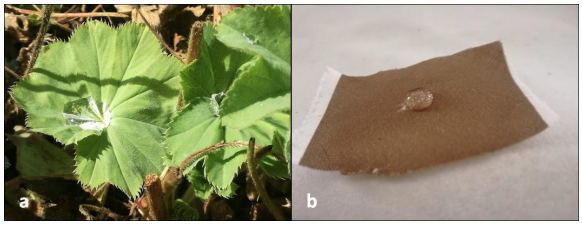

FIGURE 5. Lotus effect a) a drop of water retained on a leaf; b) the "lotus effect" on a DLC-modified textile.

develop water repellant textiles, with superior properties (Liu *et al.* 2007; Anandan *et al.* 2013; Karimi *et al.* 2014; Tissera *et al.* 2015). Very recently, Plasma-Enhanced Chemical Vapor Deposition (PECVD) of DLC has been employed in the fabrication of water repellent cotton textile, inducing nanoscale roughness on cotton and lowering its surface energy. The two-step plasma process, (Caschera *et al.* 2013) consisting of a plasma pretreatment in different gas reactive atmospheres and a subsequent DLC thin layer deposition, results in a superhydrophobic system with water contact angle as high as 146°C. Different pretreatments in plasma (in Ar, H_2 or O_2 gas flow) carried out prior to effective DLC deposition, have been evaluated to introduce specific hierarchical morphology to the cotton surface, but also to enhance film adhesion (Caschera *et al.* 2011a, 2014). Figure 4 shows the effect on the cotton morphology of the application of this dual plasma treatment: before plasma process, the cotton surface appears smooth and homogeneous, with a surface roughness of about 19.3 nm.; after plasma treatment and DLC deposition, the cotton morphology showed a close packed microclustered surface, with arrays of large cauliflower-like structures of different dimensions and a roughness increase up to 52.7 nm.

The Lotus Effect for these as-optimized DLC coated cotton samples is shown in Figure 5, and their self cleaning properties were also verified covering them with particles of dust and then forcing the water droplets to pass on surface: this simple experiment showed that as the water drops rolled off the surface, they easily removed the dirt on the cotton fabric (Figure 6).

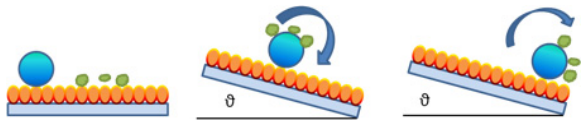

FIGURE 6. Schematization of the DLC coating self cleaning mechanism, according to which a water drop can roll off to the modified superhydrophobic surface, removing the dirt present on the surface.

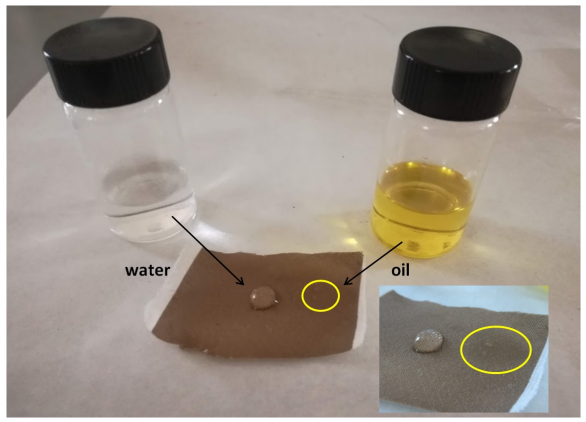

FIGURE 7. Superhydrophobic/superoleophilic properties of DLC-modified cotton textile. The water drop was retained on the surface, while the oil water was rapidly absorbed (inset).

4. Oil water separation

The possibility to design next-generation materials for oil–water separation suggests attractive potential applications in industrial oily wastewater treatments and oil spill cleanup. In this field, in particular, carbon based materials have attracted great interest in the last years, since their use to opportunely modify textile, membrane or sponge can improve the capacity in separation oil to water (Huang *et al.* 2012; Ge *et al.* 2014; Hsieh *et al.* 2016). Cortese *et al.* (2014) prepared a PECVD DLC-coated cotton textile with superhydrophobic/superoleophilic properties (Figure 7) and demonstrated for the first time the possibility to employ it as a membrane for filtration: during the gravity-driven oil–water separation experiment, they observed that the oil quickly passed through the DLC textile because of the superoleophilicity and superhydrophobicity of the functionalized textile, while all of the water was retained above the membranes due to the superhydrophobicity and low water adhesion of the DLC-coated fabric.

Moreover, effective selective (>99%) separation of water from a broad variety of oils and organic solvents such as vegetable oil, gasoline, diesel, and even crude oil was also demonstrated without the need for external power. No auxiliary treatments were required for the collection of oil, and effective absorption capacities approaching 55 to 94 times of the DLC coated cotton's weight were obtained.

The same authors have also tested DLC coatings on cotton as substrates for the hydrothermal growth of zinc oxide (ZnO) nanorods (Palamà *et al.* 2015). ZnO was chosen because of its excellent stability, environmental friendliness and low cost (Sun *et al.* 2013, 2014; Kan and Lam 2018). Furthermore, ZnO nanostructures exhibit reversible wettability by simply altering external stimuli such as UV light illumination (Palamà *et al.* 2014). In particular, they realized for the first time a new organic/inorganic coating for oil–water separation applications characterized by a tunable wettability, with underwater superoleophobicity, and self-cleaning ability. They demonstrated that the peculiar morphology of the ZnO nanorods grown on DLC coating favors the formation of a plastron of air trapped on the surface itself that can switch from underwater superoleophilicity to underwater superoleophobicity. Furthermore, ZnO/DLC coatings on cotton exhibited excellent stable reversibility in their wettability properties: when the fabric was irradiated by UV light, the surface hydrophilicity was greatly improved and resulted in a contact angle of 0°C while the original hydrophobicity was gradually recovered after placing the UV irradiated sample in the dark. Recovery of the pre-UV hydrophobicity state can be accelerated by applying vacuum during the dark storage process.

5. Flame retardant

Most of the commonly used flame-retardant strategies for textiles are based on the employment of highly toxic and endocrine disruptive halogen, formaldehyde, nitrogen, and organic-phosphorous compounds. To this regard many efforts are made to develop eco-friendly flame retardant products for cellulosic material, with the aim to satisfy social expectations. Furthermore, the treatment processes developed to produce flame resistant fabrics often do not meet all the requirements with respect to flame retardancy, toxicity and environmental compatibility preserving at the same time the vital intrinsic textile properties. In recent years carbon based materials have drawn more attention from both scientists and engineers also as flame retardant addictive for textiles, due to their excellent fire retardant effect (Beyer 2002; Higginbotham *et al.* 2009; Huang *et al.* 2012, 2014a). Very recently, plasma deposition of DLC thin films has been proposed as an efficient, eco-friendly and cost effective process that can impart the required high-performance property of flame retardancy to cotton fibers while still preserving its natural properties (Caschera *et al.* 2015). In the same work, it has been proved that DLC nano-coatings can successfully impart to cotton textiles the desired new functionality: the burning test for DLC coated cotton indicated a resistance to flame propagation almost twice with respect to the pristine cotton. DLC coating seemed to act as a dehydrating agent, thus enhancing the cotton resistance to the thermal degradation process. Moreover, the burning time of H_2 pre-treated DLC coated cotton fabrics showed a remarkable increase confirming the beneficial influence of plasma pre-treatments on the Flame Retardant properties of the DLC coating. In this case, the favorable combination of the DLC with a particular hierarchical morphology and nanostructure induced by H2 plasma pre-treatment was particularly effective in contrasting the thermal degradation process both increasing the starting temperature and lowering the final one. Moreover, formation of flammable volatiles (higher% of residual char), as shown in Figure 8 can increase the efficiency of the flame retardancy property.

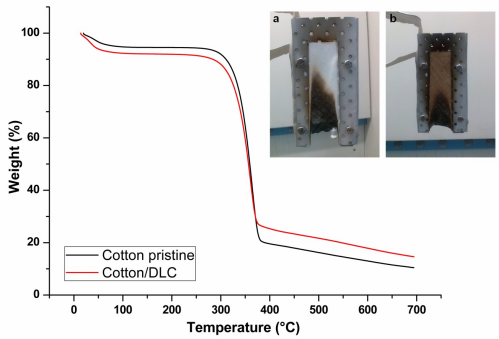

FIGURE 8. TG curves for cotton pristine and cotton modified with DLC coating, after a H_2 plasma pre-treatment of 60 min. In the inset, Optical images of the burning test results after 5 s for (a) pristine cotton and (b) cotton/DLC.

6. Biotechnological applications

Carbon-based nanomaterials are also actively investigated in several areas of biomedical engineering (Harrison and Atala 2007; Kumar Roy and Lee 2007; Cha *et al.* 2013). Considering its superior properties in terms of biocompatibility, chemical inertness, mechanical robustness, wear protection and corrosion resistance DLC coatings have been activately studied in the last decade as a versatile protective materials in a large variety of cardiovascualry, orthopedic, biosensor, and implantable medical devices (Love *et al.* 2013). Therefore, many studies have been focused on the antibacterial properties of DLC films deposited on many solid substrates (Schwarz *et al.* 2008). However there are only few reports on the use of DLC film for textile application (Zhou *et al.* 2008; Kitahara *et al.* 2010). In their work, Kitahara *et al.* (2010) evaluated the natural antibacterial properties of DLC coating on textile materials (cotton fibers) using Staphylococcus aureus (S. aureus) and Klebsiella pneumoniae (K. pneumoniae) as indicator of the experimental bacteria. The reported results evidenced that in the case of the textile material with DLC coating, no active bacteria were observed after incubation for 18 h in contrast with the original cotton textile where the number of cell colonies increased 100 times. These evidences confirmed that DLC coating can be considered effective to restrain the increase of active bacteria. A well accepted method to improve the selective resistance to bacteria of DLC films is given by the introduction of nobel metal or metal oxide nanoparticles, such as Silver and Copper, or Titanium Oxide (Schwarz *et al.* 2009; Stritzker 2011; Ban and Hasegawa 2012). From a structural point of view, the introduction of metal or metal oxide nanoparticles implies the increase of the graphite-like bonds in DLC matrix, as suggested by the increase of the intensity ratio of D and G Raman peak area and the shift of G and D bands towards higher wavenumbers (Selvakumar *et al.* 2014; Wachesk *et al.* 2016). Silver, for example, is an antiseptic metal and has been known since ancient times for its strong biocidal effect (Feng *et al.* 2000; Chen and Chiang 2008). It is well agreed that the Ag NPs are easily oxidized to Ag^+ ions when they interact with water molecules, hence the potential activity

of Ag nanoparticles embedded in a carbon matrix mainly depends on their ability to release Ag^+ over time (Palomba *et al.* 2012). Juknius *et al.* (2016) have recently reported on a fabrication of a new antibacterial bandage by depositing a diamond-like carbon films with a variable content of silver nanoparticles (DLC:Ag) on synthetic silk tissue by means of DC-reactive unbalanced magnetron sputtering technique. In particular, they demonstrated that an additional O_2 plasma etching has a beneficial effects on the antibacterial properties of the deposited DLC:Ag layer: after 20-25 s of RF oxygen plasma etching, all the coatings with different silver content revealed the best antibacterial activity against S. aureus. The authors attributed these results to the duplex effects of O_2 plasma bombardment consisting of removing a thin layer of carbon from the DLC:Ag surface so as to expose more silver nanoparticles, and the oxidation of the exposed silver nanoparticles so as to increase the efficiency of Ag+ ions release to the aqueous media. An additional protective layer made of cellulose and gelatin with agar was found to promote an higher antimicrobial efficiency up to 50% respect to single DLC:Ag layer on silk textile, because it acts as an Ag+ ions accumulator layer thus favoring the fast Ag^+ ions migration into the surrounding medium. The high performance bandage prototype contains an amount of Ag nanoparticles of about 3.12 at %, that is well below the toxic level (up to 13.5 μg/mL) for organism cells and can kill more than 99.9% of all strains of bacteria after 320min, including methicillin-resistant Staphylococcus aureus. DLC coatings can be adherent on a vast range of biomaterials and no toxicity toward the tested living cells and no inflammatory response or loss of cell integrity have been reported so far (Cui and Li 2000). Furthermore, DLC has shown to have an excellent hemocompatibility, and a decreased tendency of thrombus formation, therefore it can be considered as an excellent and reliable coating for all the medical prostheses, as heart valves and stents. To this regard, Kocourek and his group (2008) studied the deposition, by pulsed laser deposition (PLD), of hydrogen-free amorphous DLC layers on artificial textile blood vessels. Artificial blood vessels possess tubes with inner diameter of several tenths of microns to several millimeters can be fabricated from polyethylene, polyurethane, textile, etc., and they can be considered the ideal vascular graft. In this study, the biocompatibility of the DLC coated vessels was tested in vivo using sheeps. Two sets of "harder" DLC coatings (sp^3 content 40 – 53 % of and thickness of 200 nm and 20 nm) and one set with "softer" coating (more "graphitic", layer thickness 150 nm) were tested. First of all, the adhesion of the DLC layers to the textile vessels was confirmed using ultrasonic bath with physiological serum. The coated and non-coated (used as a reference) prostheses were operated into arteria carotis of sheep on both sides. The immunohistological tests showed that the best results were achieved with the DLC coated prostheses thickness of 20 nm, with high content of sp^3 bonds (more "diamond").

7. Perspectives

In general, the design of novel materials with specific new appealing properties can be carried out by: 1) the synthesis of new molecules (synthetic chemistry); 2) the reduction of the materials size to the state of nanoparticles, nanowires, nanoplates; 3) the blending of known materials. This can be schematically shown in Figure 9:

It is worth of note, in this regard, that in material science, the smallest building blocks are always atoms and they need, in their first step, to be organized to form definite nanostructures

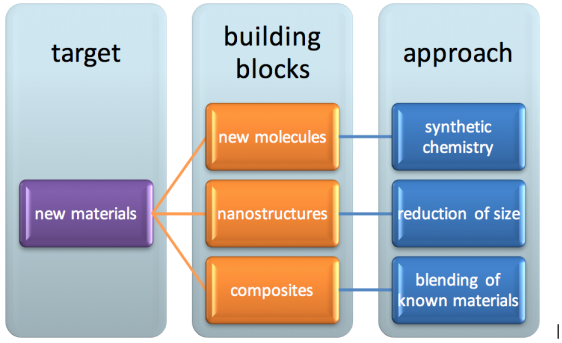

FIGURE 9. Scheme of the possible strategies used to build up new devices or materials in materials science.

which can be in turn arranged to form the macroscopic material. According to this, even the preparation itself of a nanostructured DLC film by plasma method can be seen as an example of the reduction of known materials to the sub-micrometer state, at least along one dimension. In this "self-assembly process"-like, which starts from the atomic length scale and ends up to the macro one, there is a complex pattern, so the experimental conditions can interfere with this bottom-up process of DLC preparation with different final results. As already pointed out, DLC has unique properties, all of these belonging to different categories: mechanical, chemical, surface and optical. The improvement of one or another of these properties requires specific interventions and/or the opportune insertion of other substances and permits to develop DLC-based materials with new functionalities. Just as mere examples, the plasma pre-treatment can influence the final coating morphology and its wetting properties, but the *addition* of nanoparticles can impart also anti-bacterial properties to the DLC film.

The relationship between the deposition process and the overall final result is not obvious, so some hints on physics of complex systems can now be of help. Complexity deals with the organization of units to form bigger entities whose properties cannot be traced back to the properties of its sub-units but, rather, to the interactions among these. This is true in any kind and material science cannot be an exception: elementary particles are somehow assembled to form atoms, which are assembled to form molecules, the molecules are assembled to form living cell or non-living materials and so on. The key point is that if a system was the bare collection of independent and non-interacting constituents, it would be just a "simple" assembly of its constituents: most of its characteristics could be predicted from the characteristics of its constituents. Instead, if the constituents are interacting the overall properties come also from the types and amount of the interactions among all the constituents. These properties are the so-called "emerging properties" and are usually of added-value in the piloted design of new materials with desired properties. The arising of emerging properties is strikingly the most immediate effect when different materials are put together. In the previous paragraphs, some very nice examples of novel properties shown by opportunely modified DLC coatings on textiles have been presented. The arising

of novel properties when different substances are assembled together is of immediate realization in liquid systems due to the mobility of the species involved. For example, Kim and Honma (2005) observed an high proton conductivity exceeding 10^{-3}S cm^{-1} at high temperatures (above 100°C) by simply mixing benzimidazole and monododecyl phosphate acid, two well-known materials. This observation was explained in terms of two-dimensional proton-conducting pathways within the polar domains of highly ordered lamellar structures (Yamada and Honma 2004). Details on the origin of these effects were better pointed out in 2010 when it was shown that mixing two opportunely chosen liquids, especially amphiphiles, a noticeable local structure formation can be obtained (Calandra *et al.* 2010a,c). As for solid systems, as DLC films are, on the other hand, the arising of emerging properties is less immediate due to the compact structure in the solid jointly to restricted dynamics. This renders solids less prone than liquids to establish interactions with the surrounding medium excepted for the interfacial atoms. Nevertheless, some researchers succeeded in imparting DLC structure modification for improved performances. For example, DLC composite films modified with titanium alloy with enhanced tribological properties (Wang *et al.* 2015), due to surface effects, have been. Moreover, many others examples are present in literature about the inclusion of several metal atoms/nanostructures within the DLC structure: Cu incorporation in amorphous diamond like carbon composites gives efficient electron field emitting (Faruque Ahmed *et al.* 2017) and interesting optical properties (Zhou *et al.* 2016), skilled formation of copper/DLC composite films can be used for H_2S gas sensing (Bhadra *et al.* 2015), nano-gold/DLC composite thin films can improve nanomechanical properties (Paul *et al.* 2014). Nanostructured modified DLC coatings are usually produced by top-down techniques: sputtering method, for example, had demonstrated to be able to produce DLC structure with inclusion of several nanoparticles since the 90's (Butter *et al.* 1997; Lee *et al.* 1997). For the task of preparing nanocomposites involving DLC for added value applications, liquid systems and bottom-up methods could seem therefore not as promising, even if several examples can be found in the recent years, where nanocomposites-based DLC fabrication have been carried out in plasma process (Caschera *et al.* 2007, 2011b). However, to extend the scenario of possible ways to manage novel DLC-based nanostructures, we believe that it would be advisable that wet chemical methods would be re-adapted for their joint use in DLC modification, since they allow in principle a control of the process/material at a molecular level. In the field of smart textiles application, but not limited to this one, metal nanoparticles wet synthesis could be of support for furnishing nano-size metal structures to be included/supported in DLC coatings, fabricated with mild plasma conditions, which do not strongly modify the bulk properties of the textile substrate. In this context, particularly important could be the employment of liquid complex systems, since the comprehension of their structural features and dynamical processes is being expanding year after year. The exploitation of emerging properties arising thanks to the formation of local structures is a clear example of how, through low-cost and easy methods, new properties spanning from anomalous 1D diffusion (Calandra *et al.* 2013) to anti-Arrhenian behavior of proton conductivity (Calandra *et al.* 2015b) to even magnetically-induced birefringence (Pochylski *et al.* 2016). Surfactant-based liquid mixtures can be used to solubilize inorganic salts (Nicotera *et al.* 2014; Calandra *et al.* 2015b; Pochylski *et al.* 2016) through specific interactions. This can be potentially used to allow the preparation of colloidal nanostructures dispersed in exotic

chemical environment that can be used as suitable liquid precursors in plasma process. The synthesis of new liquid or solid precursors for chemical vapour deposition methods is a well known approach in inorganic film preparation (Lo Nigro *et al.* 2005; Fragalà *et al.* 2009; Lo Nigro *et al.* 2009), expecially for the synthesis of oxide materials for electronic field application (Losurdo *et al.* 2006). Liquid complex systems preparation methods can also be associated with the classical wet chemistry methods for nanoparticle synthesis by use of micellar/compartimentalizing systems (Pileni *et al.* 2008) even exploiting a fine control on the nanoparticle size and shape (Pileni and Tanori 1997) and their potential assembly in suprastructures (Pileni 1997). In addition to the structural effects, micellar systems also evidence a complex dynamic behavior due to combination of synergistic effects associated to the different type interactions in solution (Mallamace *et al.* 2001; Chen *et al.* 2002; Lombardo *et al.* 2004; Kiselev and Lombardo 2016). The versatility of the use of surfactants deserves to be pointed out because, thanks to dynamic processes of the molecules involved and the structural peculiarities of their assemblies (Calandra *et al.* 2015a), nanoparticles of water soluble salts (Calandra *et al.* 2009b; Calandra *et al.* 2013), organic molecules, also potentially polimerizable ones (Calandra *et al.* 2004a,b) and even locally chiral structures (Xia *et al.* 2011; Longo *et al.* 2015) and metal-semiconductor nanocomposites (Calandra *et al.* 2010d) can be prepared. Nanoparticles-containing micellar solutions could also be used to modify DLC-based textiles, in order to impart specific and novel surface properties and realize new smart complex systems. Our suggestion is therefore to succeed in coupling the local structure offered by novel fluids to the already existing properties of DLC via strong interactions between these two systems. The synergic exploitation of the properties of a solid and a liquid systems could be quite visionary but it is now well accepted that a certain degree of imagination is essential in added-value research (Calandra 2018). The directions we propose come after the observation of the recent evolution in nanotechnology. At the beginning of nanotechnology era in the early 90's (Malsch 1999), indeed, the main focus of researcher was to succeed in reducing the state of a material to the nano-size. After those years, more and more sophisticated protocols were set-up to control nanostructure size, shape, composition and properties. Now, generalizations of synthetic procedures are the main directions so that protocols of general applicability are established: sugar-based general methods (Panigrahi *et al.* 2004), biological synthesis of metallic nanoparticles (Thakkar *et al.* 2009) and green nanotechnologies using plants (Makarov *et al.* 2014) are examples of these trends. However, in this evolution some hybrid top-down/bottom-up methods have been set up. They are based on the synergic combination of a top-down approach (laser ablation, metal vaporization) and a bottom-up one (chemical synthesis, nanoparticle stabilisation) and simultaneously/synergically exploiting the merits of the two. Some examples have been given since year 2006 showing the feasibility of supplying top-down (metal vaporization) method with chemical self-assembly of stabilizing molecules (Longo *et al.* 2006) (soft absorption of surfactant) but in 2009-2010 this approach was applied using other different techniques (Sulaimankulova *et al.* 2009; Calandra *et al.* 2010d; Toro *et al.* 2015). Accordingly to this matter, our task is to coniugate different strategic methods to realize smart, complete and novel DLC-based systems on textiles. To achieve this aim, starting from the DLC film formation passing over a bottom-up steps from the atomic level to the micro-meter one in a "self-assembly process"-like, the functionalizations could be realized following different approaches: mixing the different components, directly

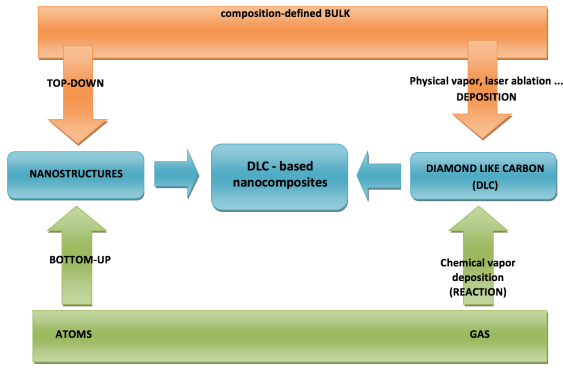

FIGURE 10. general strategies for nanostructure preparation (left side) and for DLC preparation (right side)

in the plasma process (as indicated according to "bottom strategy" in Figure 9), or using the new molecules offered by modern synthetic chemistry for surface functionalization of DLC-textile (according to "top strategy" in Figure 9). Both approaches, based on the synergic exploitation of the simultaneous presence of different species in the same complex system, can be considered a winning approach to impart novel properties, which deserves to be tailored for future directions and applications.

8. Conclusion

Diamond-Like Carbon (DLC) is an amorphous carbons allotrope that can give added value to smart textiles through the use of new technologies. Among the innovative properties that can be conferred to the textile by plasma DLC functionalization i) superhydrophobic properties ii) superhydrophobic superoleophilic property iii) flame resistance and iv) anti bacterical property have been explored in this short review. The simultaneous exploitation of the textile and DLC properties gives therefore novel properties which can be exploited for new applications. This can be seen in the framework of complex systems behaviour, whose treatment can help in rationalizing the observed phenomena and in furnishing interesting perspectives for future developments. In this ambit we have envisaged the parallel use of nanoparticles and surfactants to be included in the DLC/textile structure. Far from being a complete review of the problematics, for which many literature works are present, this contribution highlights the key aspects and furnishes interesting perspectives for future research directions.

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[a] CNR-ISMN
Via Salaria km. 29.300
Monterotondo Stazione (RM), Italy

[b] CNR- NANOTEC
c/o Università La Sapienza
P.zle A. Moro, Roma, Italy

[c] CNR-IPCF
Via Ferdinando Stagno d'Acontres, 31
Messina, Italy

* To whom correspondence should be addressed | email: daniela.caschera@ismn.cnr.it

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