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CVD nano-coating of carbon composites for space materials atomic oxygen shielding

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Abstract

The present work analyzes the possibility to employ carbon nanostructures as a basic material to prevent the erosion effects of atomic oxygen suffered by the carbon fiber reinforced polymeric material used in low earth orbit space environment. The application of thin protecting coatings to base materials is a widely used method for preventing the atomic oxygen induced erosion, and thus degradation. The generic purpose is to integrate carbon nanostructures onto carbon composites surface in order to develop the basic substrate of advanced nanocomposite for atomic oxygen protection. The final goal is the characterization of carbon nanostructures-reinforced carbon composites by means of on-ground atomic oxygen simulation facility, with the future objective to assess and optimize the process of carbon-multiscale advanced composites production. With such an aim, a wide investigation on the methane chemical vapor deposition (CVD) over catalyzed carbon fiber-based substrates has been carried out. The as grown nanostructures have been analyzed in terms of morphology, as well as regarding the main features of the resulting growth (yield, purity, homogeneity, coating uniformity, etc.) and the influence of the deposition route operating parameters (catalyst typology, gas flowing rate, growth time/temperature, etc.). A high degree of reproducibility in terms of the relationship between the carbon deposit type/yield and the main process variables (catalyst and protocol) has been thus obtained. Finally, atomic oxygen ground tests have been conducted in order to evaluate the coating process effectiveness. The on-ground test in atomic oxygen environment, with respect to the performances of the reference carbon composites (in terms of total mass loss and atomic oxygen rate of erosion), showed a worsening for the disordered carbon deposit, while an intriguing improvement was achieved by the high-yield carbon nano-filaments deposition.

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1. Introduction

In recent years, the emphasis in space research has been shifting from space exploration to commercialization of space. In order to utilize space for commercial purposes it is necessary to understand the low earth orbit (LEO) space environment where most of the activities will be carried out. LEO environment includes hazards such as atomic oxygen (AO), ultraviolet (UV) radiation, ionizing radiation (electrons, protons), high vacuum, plasma, micrometeoroids and debris, as well as severe temperature cycles. Studies on LEO environment are mainly focused towards understanding the AO effect on spacecraft materials. AO doesn't exist naturally for very long on the surface of Earth, as it is very reactive. But in space, where there is plenty of UV radiation, oxygen molecules are more easily broken apart to create AO. The atmosphere in LEO is comprised of about 96% atomic oxygen. In the early days of NASA's space shuttle missions, the presence of AO caused problems. In the first few shuttle flights, materials looked frosty because they were actually being eroded and textured: AO reacts with organic materials on spacecraft exteriors, gradually damaging them. When a spacecraft travesl in LEO (where crewed vehicles and the International Space Station fly), AO formed from the residual atmosphere can react with spacecraft surfaces, causing damage to the vehicle. When the solar arrays were designed for the Space Station, there was a concern that the solar array blankets, which are made of polymers, would quickly erode due to atomic oxygen as specified by Leger (1982, 1983) Leger et al. (1983), Hedin (1987), Peters et al.(1983), Park (1983), Whitaker (1983), Visentine (1988), Allegri et al. (2003), and Bitetti et al. (2004).

Polymers are widely used in space vehicles and systems as structural materials, thermal blankets, thermal control coatings, conformal coatings, adhesives, lubricants, etc. Exposure of polymers and composites to the space environment may result in different detrimental effects via modification of their chemical, electrical, thermal, optical and mechanical properties as well as surface erosion. The major degradation effects in polymers are due to exposure to AO, vacuum UV or synergistic effects, as reported by D'Avanzo et al. (2001), Allegri et al. (2003), and Coluzzi (2008). The exposure may result in different damaging effects by modification of the polymer's chemical, electrical, thermal, optical, mechanical and surface properties. In hydrocarbon containing polymers the main AO effect is erosion via chemical reactions and release of volatile reaction products associated with mass loss as specified in Mileti et al. (2009). Metal and metal oxide coatings appear to provide good protection to polymer composite materials from degrading effects of AO impact. Metal matrix and ceramic matrix composites prepared under optimum conditions appear to be alternative materials for polymer composite materials in LEO spacecraft application. Modified resins with AO resistant materials appear to survive long-term in the LEO environment. The application of a thin protective coating to base materials is one of the most commonly used methods to prevent AO degradation. The effectiveness of a coating depends on its continuity, porosity, degree of adhesion and durability in the environment. In addition to the technicalities of forming an effective barrier, such factors as cost, convenience of application and ease of repair are important considerations in the selection of a coating for a particular application. Though these coatings are efficient in protecting polymer composites, their application on composites imposes severe constraints. Their thermal expansion coefficients differ markedly from those of polymer composite substrates. As a result, cracks may develop in the coatings due to thermal cycling and AO can penetrate through them to the substrate.

The latter issues drive the aerospace research toward the development of novel light composite materials, like the so called polymer nanocomposites. Polymer nanocomposites are composites with a polymer matrix and a filler with at least one dimension less than 100 nanometers. Current interest in nanocomposites has been generated and maintained because nanoparticle-filled polymers exhibit unique combinations of properties not achievable with traditional composites. These combinations of properties can be achieved because of the small size of the fillers, the large surface area the fillers provide, and in many cases the unique properties of the fillers themselves. In many cases these large changes in the material properties require small to modest nanofiller loadings. Unlike traditional micron-filled composites, these novel fillers often alter the properties of the entire polymer matrix while, at the same time, imparting new functionality because of their chemical composition and nano-scale size as specified by Swallow (1973), Demarrio et al. (1985), Banks et al. (1988), Meshishnek et al. (1988), Koontz et al. (1990), Steckel et al. (1992), Packirisamy et al. (1995), Visentine et al. (1998), Gouzman et al. (2001), and Micheli et al. (2010).

The present work is joined in such framework, by the purpose to integrate the carbon nanostructures (CNs) within carbon fiber (CF) materials in order to develop the basic substrate of advanced carbon-based nanocomposite for AO

protection. The nanostructures grown on CFs was achieved by an extensive test plan carried out by chemical vapor deposition (CVD) method, and it is believed to be used to create multiscale hybrid CNs/CFs composites where individual CFs, which are several microns in diameter, are surrounded by nanofilaments. Final goal of the present work is thus the characterization of CNs-reinforced CFs in AO-enriched environment, with the future further objective (starting from the experimental results, i.e. whereas some positive hints are discovered) to assess and optimize the process of carbon multiscale-reinforced composite material. This latter should eventually represent an ideal candidate as material for AO and, in general, space environment protection application, by providing high performances, lightweight and low cost technology simultaneously.

Nomenclature

AO	atomic oxygen
CF	carbon fiber
CNs	carbon nanostructures
CVD	chemical vapor deposition
LEO	low earth orbit
SEM	scanning electron microscope
UV	ultraviolet

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2. Materials and method

2.1 CVD set-up

CVD growth methods are highly promising for scale-up of carbon nanostructures-based materials: enable controlled nanofilaments growth represents a novel approach to ordered nanowire structures that can be addressed and utilized. The aim of researchers working on this field is finding the right 'formula' to obtain a more and more controlled and ordered growth by CVD route. Gaining an understanding of the chemistry involved in the catalyst and nanofilaments growth process is critical to enable materials scale-up by CVD: the choice of many of the parameters in CVD requires to be rationalized in order to optimize the material growth. The experimental activity carried out for the present work is included in this sphere. Thanks to the experimental equipment available at DIAEE SASLab - CVD apparatus for the carbon nanostructures synthesis (see Fig.1) and scanning electron microscope (SEM) for their morphological analysis - the methane catalytic CVD process was investigated by performing several syntheses with different experimental conditions, including growth temperature, time, gas-flowing, catalyst etc. and by analyzing at scanning electron microscopy the as-grown (i.e. without any purification treatment) samples produced. In this work methane was used as carbon source, while iron-, nickel- and cobalt-based materials were used as catalyst on the support material (i.e. the substrate) placed on a steel bar to carry the samples in/out the quartz tube furnace. A standard commercial bidirectional medium modulus carbon fiber fabric has been employed. A lot of possibilities can be explored in the experimental set-up; in particular, for each gas injected in the CVD chamber the values of residence time, operating temperature and flux rate can be balanced in a quasi-continuous way, thus giving rise to a virtually endless number of parameters combination. After preliminary test, three process features have been chosen as growth parameters and analyzed by discrete variations. Two catalysts types have been identified to be the most effective, both of them based on iron nitrate solution, one enriched with metal nanoparticles. The deposition process occurred in two different protocols, only one providing for the catalyst reduction step. Three methane flowing values have been set in the range 500-900ml/min, while argon and (when present) hydrogen flux were kept fixed.

2.2 AO facility

The atomic oxygen simulator available at DIEE SASLab (AOS) is a small vacuum chamber in which an OS-Prey RF plasma source (supplied by Oxford Scientific Instruments - SPECS) which provides a neutral oxygen plasma is

installed in order to simulate the atomic oxygen effect on the space materials in LEO. This advanced device is depicted in Fig.2. The chamber is 52cm length and has an inner diameter of 16cm. A scroll XDS5 Varian Turbo V-550 is employed to reach ultra-high vacuum conditions (minimum pressure achievable: 10^{-5} Pa). The device working is based on the dissociation of the molecular oxygen flowing within the chamber (and controlled by high precision flowmeters) by means of the energy from the radio frequency source (13.56MHz). Such procedure gives rise to an oxygen-based beam constituted by 99% of neutral species (by about 60% of monoatomic O and 40% of molecular O2), at a fluence of 1.5×10^{20} n.s./cm^2, and a remaining 1% of O+ ions with energy 5÷25 eV and fluence 6.7×10^{15} atoms/cm^2 (value based on the witness sample erosion of Kapton HN, a material of known in-space erosion yield, as suggested by ASTM E2089). The working pressure is in the order of 10^{-4} Pa. The apparatus is able to carry out twelve tests simultaneously (three blank test included). For the weight measurements the experimental apparatus is equipped by a high precision micro-balance (Mettler-Toledo, sensitivity 0.002 mg).
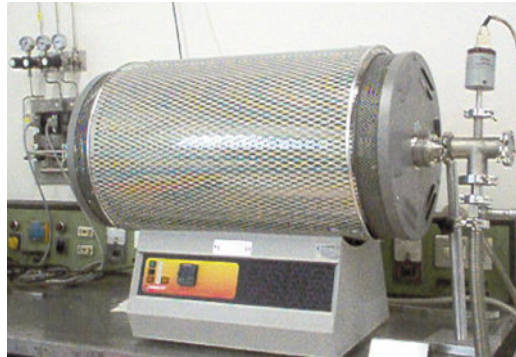

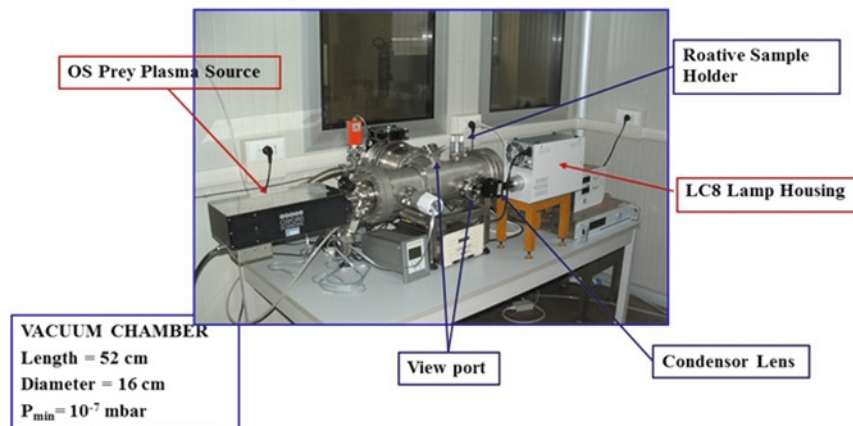Fig. 1. CVD apparatus used at DIAEE SASLab for the synthesis of carbon nanostructures.

Fig. 2. AO apparatus developed at DIAEE SASLab.

3. Results and discussion

3.1 CVD growth of CNs onto CFs

Hereafter the parameters details are reported:

Catalyst 1) "standard" : Fe(NO$_3$)$_3$-9H$_2$O dissolved in 2-propanol (isopropylic alcohol)

Catalyst 2) "nano-assisted" : $Fe(NO_3)_3$-$9H_2O$, mixed with nanoparticles of nickel (Ni) and cobalt (Co), dissolved in 2-propanol (isopropylic alcohol)

Protocol A) "methane" : $Ar \rightarrow T2 = 900°$ C, CH_4 $\Delta t = 30$'
Protocol B) "hydrogen" : $Ar \rightarrow T1 = 700°$ C, (H_2+Ar) $\Delta t1 = 30$', $Ar \rightarrow T2 = 900°$ C, CH_4 $\Delta t2 = 30$'

Ar   flux   1000 ml/min;
H_2 flux   350 ml/min
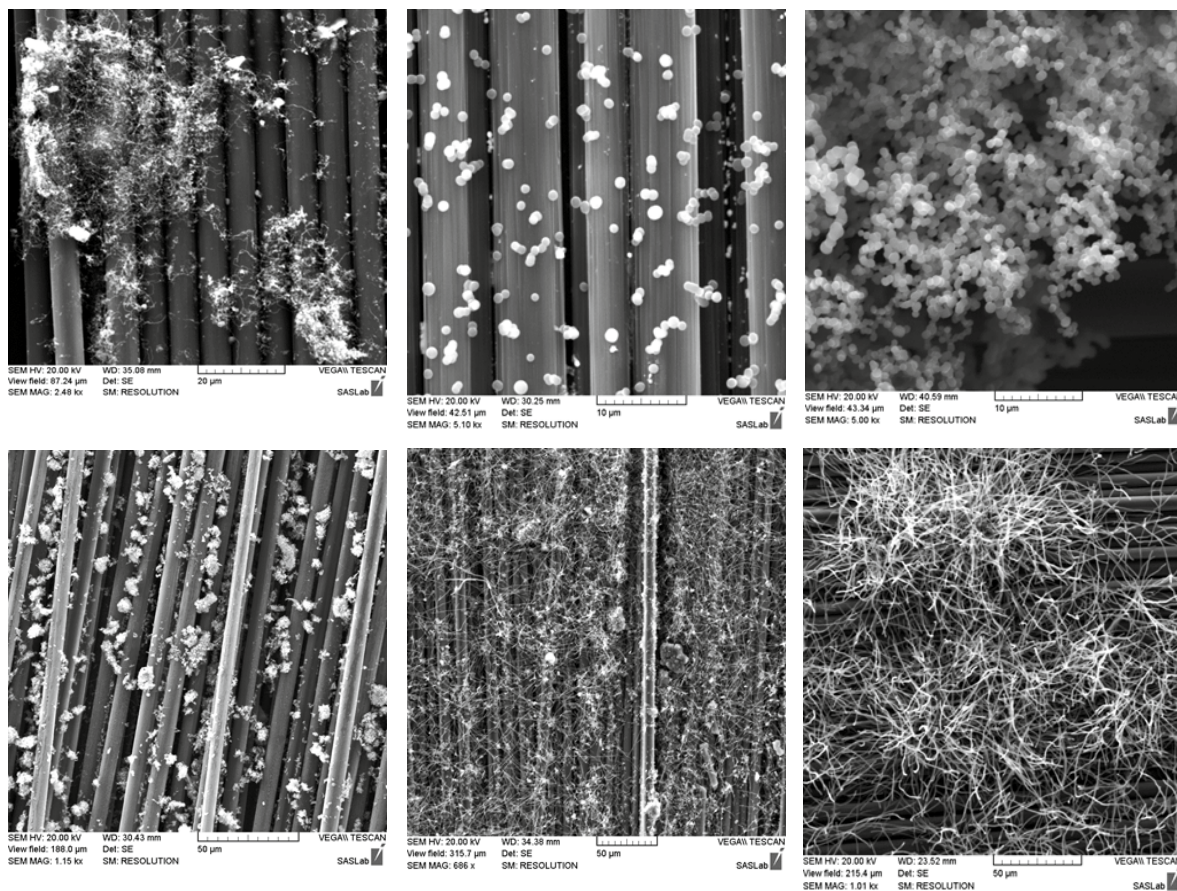CH_4 flux   500 ml/min ("low") - 700 ml/min ("medium") - 900 ml/min ("high")

Fig. 3. Different growth of CNs onto CFs substrate.

An in-depth morphological study of the CVD-treated materials has been carried out by scanning electron microscopy analysis. In the SEM images of Fig. 3 the most striking features of the sample analyzed are reported, trying to provide a descriptive ensemble of the different characteristics and potentialities of the employed experimental processes. Quantitative details for the sample weight increasing after the deposition are given in the next section. The results of the process with catalyst 1 - protocol A with the maximum methane flux shownat macroscopic sight (low magnification view) a big amount growth. It was observed that the catalyst/protocol 1-A and 2-B combinations are the less effective, since the amorphous carbon is the dominant species grown, with not uniform substrate coating and low yield almost everywhere. The size of catalyst nucleation sites can be identified as the main reason of such behavior: the absence of hydrogen doesn't allow to the iron nitrate particles to be size-reduced, thus forbidding the required nanostructured growth in the case 1-A, whereas the formation of metal

hydrides due to nanoparticles interaction with hydrogen flow is likely the main effect that suppresses an ordered growth in the case 2-B. On the other hand, iron-based solution provides for a quite uniform formation of catalytic sites in hydrogen environment, allowing for a reliable synthesis of carbon nanosphere-based material in the case 1-B: the yield/uniformity increasing with methane flux lowering can be ascribed to a relatively slow rate of reaction, that can be upset by a too high methane input flow. Finally, the intrinsic nanostructure of catalyst makes the nanofilaments growth possible in the methane protocol (case 2-A): in this process the reaction is favored from the free energy point of view, as confirmed by the nanofibers yield and uniformity direct relationship to the precursor flow rate value.

Table 1. Test Conditions and calculation sequence.

Exposed AO fluence	Total Mass Loss (TML)
$\sim 1.5 \times 10^{20}$ atoms/cm^2	$\Delta M / M_i$
Fluence (F) = $\Delta M / (\rho \cdot A \cdot t \cdot E_y)$ $\rightarrow$	AO react coeff. (E_y)

Table 2. AO Test results.

SAMPLE TYPOLOGY	growth quality	weight increase (%)	TML (%)	AO reactivity coefficient (10^{-24} cm^3/atom)
naked CF	-	-	0.51	1.1
CF + carbon amorphous	low	0.08	0.56	1.2
	high	0.55	0.81	1.7
CF + carbon nanosphere	low	0.11	0.65	1.3
	high	0.50	0.52	1.1
CF + carbon nanofilaments	low	0.19	0.48	1.0
	high	0.63	0.39	0.8

3.2 AO test

All the samples have been positioned inside the AOS and conditioned for 48h at a pressure of 260mbar as required by ASTM E2089 for atomic oxygen tests. After such treatment the samples have been exposed to AO, till a final exposition of 1000 Equivalent Sun Hours (EHS) at an effective fluence of 1.5×10^{20} n.s./cm^2 (Tab.1). In Tab.2 the results of AO tests are reported, i.e. the erosion rate after the treatment, given in terms of volume eroded for impacting oxygen atom: this latter is evaluated starting from the percentage of weight decrease due to the AO erosion (TML), also reported. Of big interest, of course, is the comparison to the weight increases due to the material deposition after the vapor growth treatment: the mismatch between these two mass variations can be identified as the most reliable indicator of the present investigation, since the coating effectiveness against the AO effect has to be related to the naked substrate behavior. In the SEM images reported in Fig.4 some features of the morphological AO-induced phenomena are shown. The first result to highlight is the AO reactivity coefficient

obtained for the blank, Fig.4(a) (the untreated carbon fiber) which is in good agreement with the results often reported in the literature. The results for the CVD-treated samples are presented for the ordered growth species (Fig. 4(b) (c) (i.e. carbon nanospheres and carbon nanofilaments). It was noticed that amorphous carbon is totally ineffective, mainly at higher deposition amount, thus establishing its intrinsic poor AO resistance capability compared to the carbon fiber, which results in any extent worsened (for both the weight increase and the AO protection lowering) by such kind of coating. The nanosphere-based coating doesn't seem to substantially improve the carbon fiber performances, the quantitative results indicating an AO resistance capability virtually analogous to that of the carbon fiber itself. Anyway the study of the high growth quality case suggests that such material could have not trivial properties by refining the coating process. The SEM images show that the grown material has been AO eroded almost everywhere, even if some protective clusters is still attached to the underlying fibers; the relatively low density of the nanosphere-based material could provide for a good compromise between weight increasing and resistance properties. Carbon nanofilaments high growth gives rise to the best results, by lowering the AO reactivity coefficient of the naked carbon fiber. From both the low and high growth quality cases the intrinsic carbon nanofilaments capability to withstand the AO erosion is discovered: in the case of higher yield the AO reactivity coefficient is remarkably reduced almost by 20%, thus attesting the expected structural resistance of such kind of nanostructures. These quantitative results are further supported by the observation of the erosion effects on the nanofilaments-reinforced samples: the SEM images show that the impinging AO flux has damaged the thick coating more by nanofibers bending rather than in terms of oxidative erosion (i.e. mass loss).

4. Conclusion and discussion

The present work represents a preliminary study of the possibilities to employ the carbon nanostructures as basic material to prevent the effects of erosion by atomic oxygen suffered by the carbon fiber-reinforced polymeric materials employed in the LEO environment. With such an aim, a wide investigation on the methane chemical vapor deposition over catalyzed carbon fiber-based substrates has been carried out. The as grown carbon nanostructures have been analyzed in terms of their morphology, as well as regarding the main features of the resulting growth (yield, purity, homogeneity, covering uniformity, etc.) and their relationship to the deposition route operating parameters (catalyst typology, gas flowing rate, growth time and temperature, etc.). Finally, fixed fluence atomic oxygen effect test has been conducted, in order to evaluate the effectiveness of the proposed carbon fiber coating route. Some remarkable results have been obtained. Firstly, an accurate definition of chemical vapor deposition parameters for the growth of carbon nanostructures onto the carbon fiber surface has been developed: a so high degree of reproducibility in terms of the relationship between the carbon deposit type/yield and the main process variables (catalyst and protocol) has been obtained. About the samples characterization in atomic oxygen environment, with respect to the performances of the reference carbon fiber (in terms of total mass loss and atomic oxygen rate of erosion), a worsening has been observed by the disordered carbon deposit, while an intriguing improvement was achieved by the high-yield carbon nanofilaments deposition. The future research activities provides for a more in depth analysis on the stricken out way. A further optimization of the chemical vapor deposition parameters to address the reliable full coverage of the carbon fiber surface by high purity nanofiber/nanotube deposition will be addressed. Atomic oxygen characterization at different fluxes will be carried out, in order to gain a better understanding of the relationship between the erosion rate and the deposition amount: such features will allow to achieve a better knowledge of the functionalities discovered between process parameters and deposition quality yield, as well as to provide the heuristic information needed for the implementation of the coating efficiency evaluation modeling, here preliminarily introduced. Finally, with the aim of an effective employment of the realized substrates for aerospace applications, the full integration of the coated carbon fiber within the polymeric matrix and the test of the as-realized multiscale reinforced composite material in atomic oxygen – or, even better – in space environment (including any other LEO regions hazard, as well as their synergistic effects) are planned be carried out.
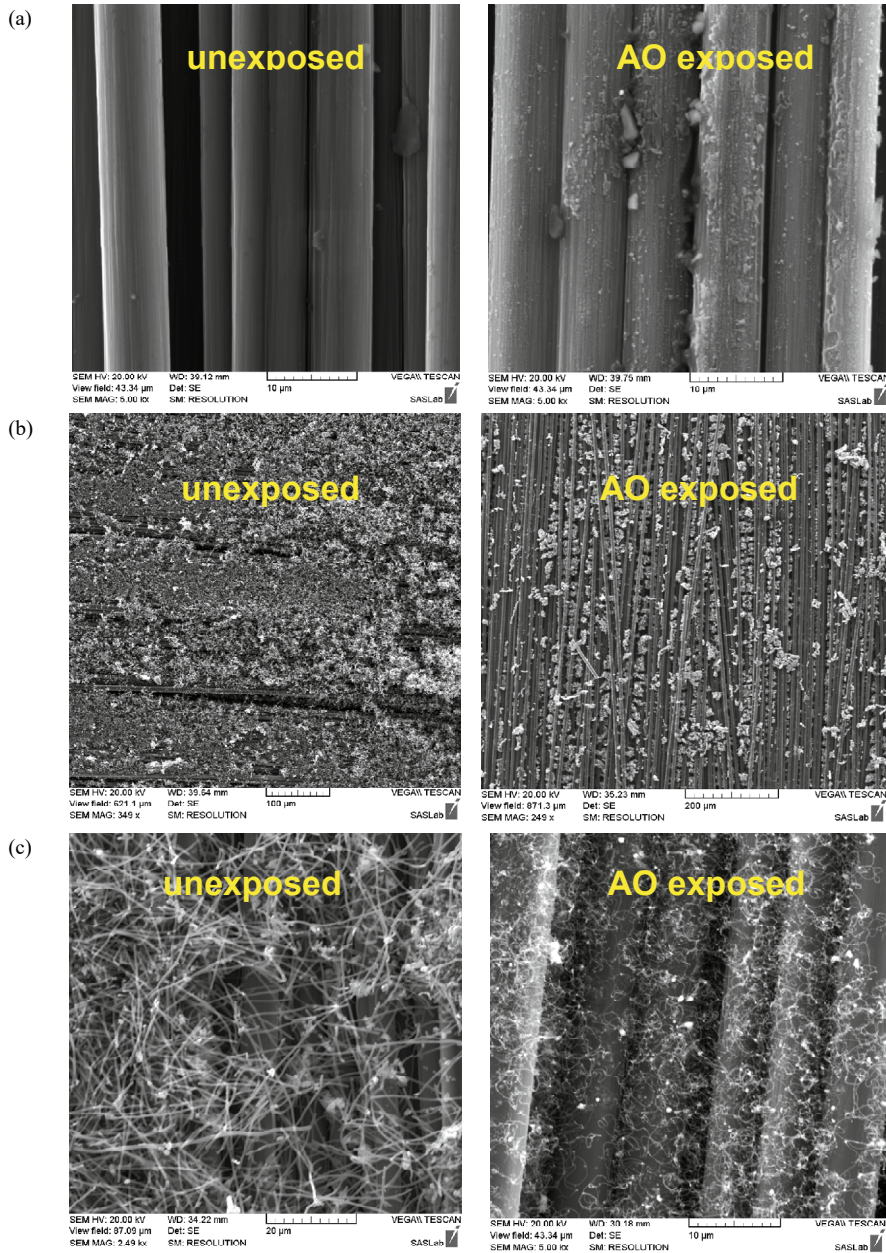
(a)

(b)

(c)

Fig. 4. AO test: SEM images before (left) and after (right) of AO exposition for Blank Carbon Fiber (a), Carbon Nanospheres (b), Carbon Nanofilaments (c).

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