CVD nanocrystalline multilayer graphene coated 3D-printed alumina lattices

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ABSTRACT

3D printing technologies have expanded the possibilities of fabricating new composite materials with tailored properties, which depend on both the materials selected and the structural design at multiple length scales. Here, a catalyst-free CVD method has been used to produce hybrid materials based on 3D printed α-Al2O3 substrates decorated by either nanocrystalline graphene or nanocrystalline graphitic films of tunable number of layers. Graphene-based coatings of variable thickness and crystallinity have been controlled by the alteration of the parameters of CVD processing, performed under CH4/H2 flux. Transmission electron microscopy has confirmed the effective growth of nanocrystalline graphene layers on the scaffolds due to the penetration of CVD gases into the open pores. The fully-connected and highly conductive 3D pathways have displayed a room temperature electrical conductivity in the range of 101–102 S m−1. Furthermore, the thermal conductivity has also increased by 50% for the specimen decorated with a 20 nm thick graphitic coating as compared to a bare 3D ceramic scaffold. The developed structures open up new possibilities for expanding the field of application of graphene/ceramic composites for conditions requiring dielectric substrates of various shapes coated with conductive films or graphene-based catalytic supports with good structural stability.

1. Introduction

The development of graphene-added composites is a successful approach to a wide variety of novel cost-efficient materials for many emerging applications owing to the exceptional electrical, thermal, and mechanical properties of graphene [1]. Even with a small amount of graphene-based fillers, the composites can be tailored for functionality far beyond those of the corresponding monolithic materials. In the case of ceramic matrix composites, this approach has been used to fabricate toughened and strengthened materials with improved electrical conductivity and wear resistance [2]. These composites are often used as supports with improved catalytic efficiency, electrodes, electromagnetic interference (EMI) shields, piezoelectric nanogenerators, products made of reinforced concrete, and novel platforms for biosensors and tissue engineering [3].

Chemical vapor deposition (CVD) using a metallic substrate (Cu, Ni, Co, Pt or Ir) as catalyst [4] is one of the mainstream methods for attaining large-area graphene sheets of controlled thickness and reduced number of defects. The catalytic growth on transition metals takes place via absorption, surface segregation, and/or precipitation of carbon atoms at both low and high temperatures. Therefore, the process is strongly influenced by the substrate characteristics, such as the crystal orientation, carbon solubility, and surface roughness; moreover, depending on the targeted application, the as-grown graphene film can also be transferred to other supports. The CVD growth of graphene on ceramic supports is a less common approach. Recently, a simple time-effective procedure of the catalyst-free direct deposition of carbon nanostructures on porous alumina has been demonstrated by the application of a hot-wall single-step CVD process as detailed in Ref. [5]. Formerly, thin homogeneous conductive graphene films have been successfully deposited directly on dielectric substrates or powders for the fabrication of electronic devices [6], and bulk composites and hybrids [7,8]. In general, the non-catalytic method proceeds due to spontaneous dehydration of the carbon precursor on various ceramic...
substances in the presence of surface defects [9]. Although this approach is less desirable in terms of carbon defects, the transfer-free procedure greatly simplifies the technological process. Fanton et al. [10] pioneered the growth of mono- and bi-layer graphene films on sapphire at temperatures above 1400 °C and, subsequently, more accessible poly-crystalline substrates have been used as well, such as silicon nitride (Si3N4), γ-aluminum oxide (γ-Al2O3) and β-tricalcium phosphate (β-TCP) [11–14].

At present, highly porous graphene and graphene hybrid cellular materials are of increasing interest due to their high surface area, electrical conductivity and low density [15–17]. Therefore, the catalyst-free CVD growth of graphene directly on porous ceramic substrates appears as a highly promising route to create novel graphene-containing hybrids with a unique set of properties. Accordingly, graphene has been grown on aluminum nitride (AlN) and Al2O3 porous substrates with micrometer-scale graphitic layers for thermal applications [18], and on Si3N4 and Al2O3 for microwave absorption purposes [19,20]. However, efforts toward synthesizing 3D highly porous graphene/ceramic hybrid materials have been scarce. Zhou et al. [21] reported the CVD of few-layer graphene films on porous anodic Al2O3 templates and Al2O3 foams made by the replica method, demonstrating the formation of Al–O–C and Al–C covalent bonds by carbothermic reduction on the substrate surface, which favored the nucleation and segregation of the graphene layers. Their graphene-coated foams showed a sheet resistance of 20 Ω-sq⁻¹ and faster thermal transport than the uncoated sample. More recently, Wang et al. [22] used a graphene foam, grown by CVD on Ni foam, as a porous support for chemical vapor infiltration with silicon-boron carbonitride to produce EMI shielding hybrid materials. Foams, however, present a limit in the freedom to produce architectures with intricate geometries customized for a special use, which can be fulfilled with the additive manufacturing (AM) approach.

Today, AM technologies are transforming the perspectives of advanced materials fabrication, as they present multiple advantages for the design of devices and supports with complex shapes, reducing the time and cost of production. Besides, in the case of cellular materials, AM offers great opportunities in the production of highly porous patterned monoliths with hierarchical porosity, from the micro- and meso-scale porosity of the struts, defined by the ink characteristics and sintering process, to the macro-scale pattern, which is computer controlled through the design of the scaffold parameters, in contrast to foams. These AM architectures can enhance, for instance, the process intensification, as mass and thermal transfer would increase due to the open channels [23]. As results, they could be employed in a broad range of applications, among them, structural design, thermal management, tissue engineering, catalysis and energy storage. In recent years, efforts have been made to develop, by different AM methods, 3D printed graphene-based cellular materials, which in a major way include 3D pure graphene and polymer-based composite architectures and, to a lesser extent, 3D graphene/ceramic composite scaffolds [24,25]. In addition, there is a small subgroup consisting in coating 3D printed graphene scaffolds with metallic or ceramic films to improve their structural and/or functional properties [26–28]. The opposite approach would involve the graphene coating of 3D printed cellular supports, which, to the best of our knowledge, has not been tackled hitherto. The success of this challenging approach would be advantageous for combining a stronger support with a graphene surface of improved catalytic response and appealing electrical and thermal functionalities, as some studies performed on porous substrates or foams have previously demonstrated [18–22]. Therefore, the aim of the present work is to develop for the first time catalyst-free CVD graphene growth on highly porous 3D printed patterned alumina scaffolds. These ceramic supports were selected because combine the easy and low-cost processing of printable inks and low sintering temperatures [29] with the highest industrial applicability based on its excellent mechanical, thermal and chemical resistances, being one of the most utilized materials for the development of catalyst supports and adsorbents. In addition, a thorough study of different CVD graphene growing parameters has been carried out to give deep insights for the optimization of the electrical and thermal properties of 3D graphene-alumina hybrid architectures.

2. Materials and methods

2.1. 3D printing of highly porous α-Al2O3 scaffolds

Highly porous α-Al2O3 cuboid scaffolds of 6.0 × 6.0 × 4.0 mm³ were additive manufactured, as described in a previous work [29]. Briefly, boehmite-based aqueous inks were prepared by blade and planetary centrifugal mixing boehmite powders (Dispal 11N-80, Sasol, TX, USA) with a proportion of solids to ultrapure water of 52:48 (wt.%). The 3D structures were printed into a layer-by-layer sequence by direct ink writing (DIW) using a robocasting system (A3200, 3-D Inks LLC, Tulsa, OK, USA) with a nozzle diameter of 330 μm, and following a grid pattern with separation between rods of 0.72 mm in the X-Y plane, and 0.46 mm between the n and n+2 layer in the Z direction, building consecutive orthogonal layers. Subsequently, the as-printed scaffolds underwent a thermal treatment at 1300 °C for 2 h in air to remove the water content and promote the full transformation from boehmite to the α-Al2O3 phase, maintaining the high porosity of the ceramic skeleton (~82% of total porosity in the boehmite scaffold versus ~80% total porosity in α-Al2O3 scaffold). Densities and porosities of the α-Al2O3 scaffolds were estimated according to equations described in the Supplementary information. In essence, geometrical density ρgeo and total porosity ρtotal were assessed from the weight and dimensions of the scaffolds, the density of the ceramic skeleton ρskeleton and porosity of the rods ρrod were calculated using the Archimedes’ method and considering a theoretical density value for α-Al2O3 of 3.98 g cm⁻³. The porosity at macro-scale associated to the patterned channels ρmacro was determined from ρtotal, ρrod and the volume fraction of rods in the whole structure; whereas the open porosity of the skeleton ρskeleton was estimated from the apparent density ρapp, and close porosity of the rods ρskeleton.

2.2. Graphene coatings

The graphene coating of the ceramic scaffolds was done by a catalyst-free one-step CVD method based on the surface epitaxy mechanism, described in detail elsewhere [5]. In this process, the α-Al2O3 scaffolds...
were placed inside a tube furnace at 1000 °C for 10 min in air and, afterwards, an N₂ flux of 1000 sccm was purged for 10 min. Next, CH₄ and H₂ were simultaneously introduced using different flux rate settings and times—varying H₂:CH₄ ratio (R) between 0 and 10—(Table 1). All CVD treatments finished by cooling the specimens down to room temperature in an N₂ flux of 4000 sccm (the cooling procedure shifts the sample from the hot zone in the center of the furnace to the pipe outlet, which has room temperature, in 20 s. Cooling is completed in 1 min).

T1 and T6 treatments (see Table 1) were selected to observe the effect of using a pure CH₄ flux and large H₂ flux, respectively; T2 and T3 changed H₂ flux rate while maintaining the CH₄ fixed and, finally, T4 and T5 changed the deposition time keeping fixed the settings of CH₄ and H₂ fluxes at R = 0.5. The final carbon content, which directly reflects coating thickness, was estimated from the weight of the scaffolds after 10 min at 1000 °C in air inside the CVD chamber (WDry) and the weight immediately after each CVD process (Wcoated).

### 2.3. Microstructural characterisation

Field emission scanning electron microscopy (FESEM Hitachi S-4700, Japan) and transmission electron microscopy (TEM, JEOL 2100F, JEOL JEM 3000F, Tokio, Japan) were employed to observe the microstructure of the rod surface, the graphene film thickness and its distribution around the ceramic grains. Electron-energy-loss spectroscopy (EELS) of C-K edge was also performed. For TEM, the scaffolds were gently crushed with an agate mortar, and the acetone-dispersed particles were drop cast on TEM copper grids. Confocal Raman spectroscopy (532 nm excitation wavelength, Alpha 300a WITec confocal microscope, Germany) was used to analyse the quality of the graphene films by scanning areas of 15 × 15 μm² and 100 × 100 points per image on the surface of the rods. Single Raman spectra of 0.06 s and 20 accumulations were also acquired across the interior of a fractured scaffold to study the homogeneity of the graphene coating. The average spectra of the scanned surfaces were deconvoluted by fitting bands to Voigt peaks in the 1000-2000 cm⁻¹ region and used to calculate the intensity ratios (integrated areas or peak heights) between the distinct bands associated with graphene domains (D, D', G and 2D). In this way, I_D/I_G and I_D'/I_G would give a general notion of the amount and type of defects; while I_2D'/I_G is associated with the graphene thickness (few-layer, multilayer, loss of stacking order). The full width at half maximum (FWHM) allowed also making comparisons of the degree of crystallinity achieved with the different treatments.

### 2.4. Surface hydrophobicity

The effect of graphene coating on the interaction of 3D printed porous support with water was observed by depositing a 7 μl water drop on the scaffolds top layer and acquiring an optical image to measure the apparent contact angle.

### 2.5. Electrical and thermal characterization

Electrical conductivity of the coated scaffolds was determined by the four-probe method (Agilent E3646A power supply and Agilent 34401A and 33461 multimeters, Agilent Technologies, USA), applying silver paint (Electrolube, ERSCP03B) to the samples in opposite X-Z faces that served as outer electrodes to control the applied current. Two parallel lines were also internally painted, surrounding the samples, which were used as inner electrodes for the voltage measurement. Current-voltage curves were plotted to obtain the resistance R of the portion of the samples between the inner electrodes and their conductivity σ was, then, assessed by the following equation:

\[
\sigma = \frac{L}{RS}
\]

where L is the distance between the inner silver-painted lines and S is the total area of sample’s X-Z plane. One sample per CVD treatment was measured.

The thermal conductivity, resistivity and Seebeck coefficient of selected coated scaffolds were simultaneously measured using the thermal transport puck of physical property measurement system (PPMS, Quantum Design, San Diego, CA, USA). For this purpose, a high thermal conductivity silver epoxy resin was used to cover two opposite sides of the lattice structures (X-Y planes), followed by the attachment
of two copper probes. The measurements were carried out in a two probe configuration from 10 K to 400 K. The direction of measurement (Z-axis) was orthogonal to the one used for electrical conductivity by the four probe method due to the best placement of the sample in the PPMS.

3. Results and discussion

Fig. 1 collects a representative example of a 3D printed cellular α-Al₂O₃ cuboid support sintered at 1300 °C (Fig. 1a), a detailed view of the printed patterned grid in the X–Y plane (Fig. 1b), and the microstructure of the rods showing pore sizes in the range from mesoporosity to ~200 nm, the latter estimated from FESEM observations (Fig. 1c). The 3D α-Al₂O₃ structures presented the following density and porosity parameters: ρgeo = 0.84 ± 0.04 g cm⁻³, πtotal = 79 ± 1.0%, π3D = 56 ± 2.8%, πrod = 52 ± 4.6% and πopen = 21 ± 3.3%. As result, multi-scale porosity (meso-, macro-) in the whole scaffold was developed. Besides, the rod microstructure clearly evidenced α-Al₂O₃ grain growth from boehmite dehydration process and neck formation between grains, conferring a moderate mechanical strength (compressive strength (σc) ~20 MPa and elastic modulus ~450 MPa [29]). This result is significant in terms of supporting a graphene phase since pure graphene-based architectures are characterized by a lower strength, for instance, pure, GNP [16] and rGO [30] scaffolds showed σc of 0.84 MPa and 2.2 MPa respectively, which could make them too weak for some applications.

Micro-Raman spectroscopy was employed to investigate the film grown on the 3D α-Al₂O₃ supports (Fig. 2). In this way, the G band intensity map of T3 sample surface (Fig. 2a), here used as illustrative example, reproduced the ceramic substrate microstructure (Fig. 1c). When Raman spectra is collected 1 μm inside the rod, the areas associated with pores presented an increased G band signal (marked regions in Fig. 2b). Therefore, the multi-scale porosity allowed the nucleation of carbonaceous films in the external exposed surfaces of the scaffolds and also in their inner channels. Raman intensity maps for D/G (Fig. 2c) and 2D/G (Fig. 2d) showed an even distribution of the achieved film thickness on the surface with some areas exhibiting higher concentrations of defects.

The effect of the different CVD parameters on the Raman signal is summarized in Fig. 2e and f and Table 2. For a practical purpose, G band was fitted first as a single peak, allowing easy comparison of I_D/I_G in integrated area ratio (see the complete data of D and G bands fittings in the Supplementary information). All treatments led, in general, to coating films with a relatively broad D and G bands at ~1353 cm⁻¹ and ~1600 cm⁻¹.
cm$^{-1}$ average positions, respectively, and area ratios ($I_{2D}/I_O$) ranging from 1.3 to 4.6. Most of the films also showed the presence of the 2D band ($\sim$2690 cm$^{-1}$), with diverse $I_{2D}/I_G$ peak height ratios (0.16–1.2) that clearly reflected the variety of thicknesses and crystallinity grades. Raman spectra presented intense D band relative to G peak, which has been observed in nanocrystalline graphene films grown on different ceramic substrates [7,31–33]. The position of G band in the analyzed spectra exhibited a blue shift that increases with $I_{2D}/I_G$ ratio, and is associated with compressive strain induced by thermal expansion/contraction of carbon and alumina substrate [34,35]. The domain size ($La$), according to expression $La$ (nm) = (2.4x10$^{-10}$)$I_d^2$(I$_{2D}$/I$_O$)$^{-1}$ from Cançado et al. [36], is plotted against the $H_2$CH$_4$ ratio in Fig. 2F. From these Raman spectroscopy results, it can be stated that employing methane as sole gas source for the CVD treatment (T1, R = 0) generated a thick carbon film (18.3 wt% carbon) with the highest lattice disorder and smallest crystallites ($I_{2D}/I_G = 4.6$, $La = 4.2$ nm); whereas, a large proportion of $H_2$ to CH$_4$ (T6, R = 10) produced unevenly coated scaffolds, evidenced by the occurrence of some areas maintaining the white color of the alumina substrate (see Fig. S4). Both types of samples were discarded due to their defective nature and subsequent electrical characterization was solely performed on T2 to T5 samples.

Top-surface and lateral views of a 3D printed $\alpha$-Al$_2$O$_3$ support and CVD-treated (T2 to T5) scaffolds are collected in Fig. 3. The samples can be clearly distinguished by their color, white color for the alumina support and a greyish color varying from light gray of T3 to darker and graphite-like color of T2 and T5, which is directly related to CVD graphene film thickness/carbon content in accordance with the information obtained by Raman spectroscopy and $I_{2D}/I_G$ ratios. As expected, a shorter deposition time (comparing T4 versus T5, both with R = 0.5) led to a thinner coating and lighter color, but most interesting is the effect of increasing $H_2$ flux rate varying R from 0 to 4 (T1, T2 and T3).

In the current CVD process, carbon radicals in close vicinity of the unsaturated aluminum sites and/or structural defects on the substrate surface create the necessary nucleation seeds for the development of sp$^3$ sheets. The thermal decomposition of methane itself produces hydrogen and carbon radicals together with intermediate compounds C$_n$H$_y$. The presence of additional hydrogen shifts the balance of the decomposition reactions capturing free carbon radicals and the formation of excessive amount of C$_n$H$_y$. Hydrogen interaction with the substrate influences the kinetic of CH$_4$ chemisorption, as $H_2$ and/or atomic H participate in the initial physical adsorption of CH$_4$, and create sites for sticking hydrocarbon and carbon radicals on the surface, eliminating hydrogen and passivating defects. Molecular $H_2$ gas then functions in different ways: i) $H_2$ is used as diluent gas in correlation with CH$_4$ to obtain various $H_2$ to CH$_4$ ratios, ii) it interacts with the substrate affecting the CH$_4$ chemisorption kinetics, and iii) it produces C-etching by bonding with loosely bonded C atoms to form CH$_3$ radicals, hence, playing an important role in the sp$^3$ to sp$^2$ transition [12,37,38]. $H_2$ can also passivate the surface defects and grain boundaries, thus, sealing some of the nucleation sites active for surface epitaxy, which results in larger sp$^2$ grains [39].

The absence of a tangible 2D peak and the highest measured $I_{2D}/I_G$ for the sample T1, where no $H_2$ flux was employed, provided evidence on a high level of out-of-plane grown sheets as well as high graphene layer count. Similarly, T5 showed the highest carbon content (20.7 wt%) with increased disorder when deposition extended in time.

The CVD procedures with CH$_4$H$_2$ ratios of 2:1 and 1:2 corresponding to samples T2 and T4 respectively produced films with similar Raman band characteristics. In these samples in particular a low $I_{2D}/I_G$ (~0.3) ratio was observed that further decreased by increasing the dwell time (T5, R = 0.5). In T5 a film with the highest carbon content (20.7 wt%) among the samples and with an incremented lattice disorder was observed. T3 treatment (R = 4) appears as the optimum CVD process, where the combination of settings (CH$_4$ and $H_2$ fluxes, gas ratio and process time) led to graphene coatings of higher quality, with high 2D peak intensity combined with relatively low $I_{2D}/I_G$ (1.8) and a narrow G band (Fig. 2E). These data reflected the growth of nanocrystalline few-layer graphene-like (FLG) films with $La \sim$11 nm. G band was subsequently split into G and D’ to elucidate the type of defects associated with the relation between D and D’ intensities ($I_{2D}/I_G$, Table 2, Table S2) [40]. For the samples with lower defects (T2, T3 and T4) realized from their lower $I_{2D}/I_G$ ratios, a predominance of boundary defects can be deciphered based on the averaged $I_{2D}/I_G$, value of ~4. Thereseence of this defect type can be explained by the growth mechanism of nucleation from several locations where surface defects are present on the $\alpha$-Al$_2$O$_3$ printed lattice, creating a nanocrystalline multilayer graphene (MLG) film. Thicker and most defective T1 and T5 samples presented $I_{2D}/I_G$ values of 1.1 and 1.8, respectively, which are related to out-of-plane bonded atoms [40].

Raman spectroscopy was performed across the fracture surface of T3 scaffold (Fig. 4A) within the X direction (Fig. 4B), looking at the center of odd rods, and in the Z direction (Fig. 4C), through the layer-by-layer sequence at the rod surfaces. Raman data confirmed that the specimen was effectively coated not only on the surface of the 3D structure but also in the interior skeleton of the rods, creating a complete connected 3D network supported on the alumina grains. However, there are some differences in the Raman signature. In this way, the highest $I_{2D}/I_G$ and the lowest $I_{2D}/I_G$ values (Fig. 4D), i.e., the development of less defective nanocrystalline FLG coating, were attained at the external surface of the scaffold (top layer n°. 24 and I position); whereas Raman parameters at the interior were similar and showed lower values. A similar evolution is observed in radial direction from the surface to the center of the rods (Fig. 4E and F). This distinct coating performance can be associated with...
variations in the gas fluxes between the outer layers of the scaffolds as compared to the fluxes through the open channels (and inside rod porosity). Latter presumably leads to a slight pressure drop and different dilution rates of the CH$_4$. In fact, small band on the right side of 2D band, D$^+$D$'$ peak (~2930 cm$^{-1}$) that is a signature of C–H bonding [41] showed intensities in the range of 0.023–0.060 (normalized to D peak, see Table S4).

Despite the fact that wetting properties of graphene films are strongly influenced by the substrate and environmental parameters, showing contact angles in the range of 30$^\circ$ to 120$^\circ$ [42], it is well known that graphene coatings tend to produce more hydrophobic surfaces. In fact, this property has been exploited to develop graphene oxide oil filtration sponges and hydrophobic paints, which allows easy cleaning of surfaces [43,44]. Here, the observation of a water droplet deposited on the top layer of coated 3D printed supports (Fig. 5) indicated the high potential of the coatings to modify water adsorption by the cellular material. The highly porous α-Al$_2$O$_3$ 3D-support showed complete wetting with instant surface adsorption of the droplet. In contrast, the various graphene-based films obtained by individual CVD treatments increase surface energy between water and support surfaces impeding water spreading [45]. The apparent contact angles above 100$^\circ$ were shown to be similar to those measured for other 3D printed graphene-based honeycombs [46], except for the case of T6 top surface (T6B) for which selected CVD parameters produced an incomplete sample coating (less carbon was deposited compared to the opposite surface T6A).

Electrical conductivity ($\sigma$) of T2–T5 scaffolds was measured in order to determine the effect of film characteristics on this property. $I$–$V$ curves are plotted in Fig. 6, where less resistive specimens corresponded to those with the thicker film (T2 and T5) and, conversely, thinner coatings were more resistive (T3 and T4). This response is associated with the gradual change in the size and orientation of the graphene domains nucleating and growing along the surfaces of the scaffolds by the effect of treatment parameters. T2 and T5 provided more hydrocarbons to the growth process, controlled by relatively lower H$_2$ flux, and promoted the rapid formation of carbon films with increased
connectivity across the 3D structure. The $\sigma$ values, obtained assuming the 3D structures as a whole, are summarized in Table 3. Data varied from 60 S m$^{-1}$ (T4) to 1600 S m$^{-1}$ (T5), which presented the highest carbon content; while T3, containing a FLG film, reached a $\sigma$ value of 100 S m$^{-1}$ (considering only the surface occupied by rods section in the measuring direction $\sigma$ is ~4.5 times higher). Therefore, the further microstructural characterization and thermoelectric response will be focused on T3 and T5 scaffolds due to their large differences in film quality and electrical behavior.

Comparatively, the conductivity values achieved in the present work are similar to those obtained by graphene/$\alpha$-Al$_2$O$_3$ composites fabricated with other microstructures (see Table 3, bulk composites containing GNP or rGO platelets, and coated foams). Here, the CVD process presented the advantage of assuring connectivity of the polycrystalline graphene or graphitic network even at low carbon content [20,47,48], which may not be the case for composites parting from exfoliated pristine graphene sheets dispersed in a matrix. In the majority of bulk microstructures [49–52], GO has been the preferred material due to the high degree of exfoliation achieved in aqueous media, which reduces the percolation threshold in composites, e.g. three orders of magnitude higher conductivity has been achieved when using 1.3 wt% rGO than for similar content of graphene nanosheets (GNS) [49,51].

Table 3

<table>
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<th>Graphene Source</th>
<th>Carbon content (wt. %)</th>
<th>Structure Type</th>
<th>$\sigma$ (S m$^{-1}$)</th>
<th>Ref.</th>
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<td>[21]</td>
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Value for 3D samples considering whole geometry in the calculation.
CVD-G@γ-Al$_2$O$_3$: graphene growth on γ-Al$_2$O$_3$ fibers.
CVD-G@α-Al$_2$O$_3$: graphene growth on α-Al$_2$O$_3$ particles.
GNS: graphene nanosheets.
rGO: reduced graphene oxide.

Fig. 5. Variation of water contact angle compared to Al$_2$O$_3$ scaffold which instantly absorbs water drop. a) Optical image of droplet on the X-Y top surface of uncoated and CVD coated 3D-printed supports. For T6, an incompletely coated sample, images of the drop at bottom (T6A) and top (T6B) layers have been also included to remark differences, while the rest of the samples did not show such difference with the bottom layer. b) Apparent contact angles obtained from the images. (A colour version of this figure can be viewed online.)

Fig. 6. I–V curves of coated scaffolds after T2-T5 treatments. Resistivity was measured in Y direction. (A colour version of this figure can be viewed online.)
FESEM (Fig. 7a and b), but zoomed regions at the edges of the grains using TEM showed graphene films of less than 2 nm in thickness, which contained between 3 and 5 layers (Fig. 8a–c). In contrast, it was possible to identify by FESEM in T5 scaffolds both alumina grains with smoothed edges due to the coating and translucent sheets at some areas (Fig. 7c and d). TEM observations evidenced the formation of a thicker film (15–20 nm) that encapsulated alumina grains (Fig. 8d–f) and was exfoliated during TEM sample preparation (see free-standing graphene sheets marked with the arrow in Fig. 8d). Some individual uncrushed alumina grains exhibiting inner mesopores coated by graphene film were also identified (Fig. 8e). In accordance with Raman observations, T5 produced a more disordered structure, which was reflected in the

Fig. 7. FESEM micrographs at different magnifications of rods in fractured T3 (a and b) and T5 (c and d) scaffolds. (A colour version of this figure can be viewed online.)

Fig. 8. TEM micrographs of hybrid 3D graphene/α-Al₂O₃ T3 (a–c) and T5 (d–f) samples. FLG film deposited on alumina grains is observed in T3 and inset in c) is an augmented zone showing graphene planes piled up in c-axis direction. Thicker nanocrystalline graphite film in T5 (marked with yellow arrows) is clearly wrapping Al₂O₃ grains and inside pores. Inset in f) shows the FFT of graphene planes indicating misalignment/disorder during growth process. (A colour version of this figure can be viewed online.)
of the same samples (T2 and T5, Fig. S7) clearly evidenced $\pi^*$ (285 eV) and $\pi^+$ (292 eV) peaks of graphitic materials [53]. Graphene-based films grown on alumina substrates by a similar method have shown sp$^2$ bonding fraction in the range 60–70% [54]. Considering the results of Raman and TEM measurements a more precise description of the achieved films has been summarized in Table 4.

The thermoelectric transport results of T3 and T5 scaffolds are plotted in Fig. 9 and data at 298 K are summarized in Table 5. The electrical resistivity measurements (Fig. 9a) obtained by a two probe configuration gave $\sigma$ values at 298 K (~50 S m$^{-1}$ for T3 and ~1130 S m$^{-1}$ for T5) lower than those calculated from I–V curves, where 4-probe method was used (100 and 1600 S m$^{-1}$, Table 3), due to the contribution of contact- and copper-wires resistances of the former. Note that the 4-probe method was applied through the Y direction whereas the 2-probe configuration was evaluated through the Z direction, which creates different paths of conduction that also affect the experimental resistance. The behavior of thermal conductivity ($\kappa$) of nanocrystalline FLG sample (T3) resembled that of uncoated Al$_2$O$_3$ scaffold, leading to a more defined $\kappa$ increment as the temperature decreased in the range 160–400 K associated with the behavior of crystalline materials where thermal conduction is controlled by phonons, whereas T5 exhibits a comparatively more constant behavior above 100 K due to the more continuous graphitic thick coating, giving values of 1.38 and 1.62 W m$^{-1}$K$^{-1}$ at room temperature. The $\kappa$ maximum values for T3 and T5 samples were achieved at 135 K (1.94 W m$^{-1}$K$^{-1}$) and 173 K (1.69 W m$^{-1}$K$^{-1}$), respectively. This small difference can be explained by the localization of Dirac fermions due to substrate-induced disorder potential in graphene grown on oxide substrates [55] leading to a strong temperature dependence of carrier promotion. T3 scaffold with FLG coating showed a well pronounced power law dependent electrical semiconducting transport at temperatures lower than 100 K (Fig. 9a). In contrast, the T5 scaffold with nanographite coating presented a semi-metallic transport up to 400 K. This observation helps to understand the stronger decay of $\kappa$ at temperatures higher than 100 K for T3 as compared to T5. To better visualize this effect, the Wiedemann-Franz law was employed to plot lattice ($\kappa_L$) and electronic ($\kappa_e$) contributions to $\kappa$ for both scaffolds (Fig. 10). In fact, $\kappa$ decay is mainly due to the lattice contribution. To clarify further, up to 100 K, mostly thermally enabled phonon modes facilitate the increases of $\kappa_L$. Above 100 K, the increasing thermal energy in the T3 scaffold passes the ionization energy of the localized electrons, thus, attributing to phonon-electron scattering phenomena that reduces the total thermal transport of this specimen. Furthermore, since Seebeck coefficient ($S$) is inversely proportional to carrier density [56], a lower carrier density and localization of charge in T3, that gives rise to hindered mobility and higher resistivity, also ensures higher S values (Fig. 9c).

The CVD-grown nanocrystalline graphene and nanocrystalline graphite films presented good adhesion to the Al$_2$O$_3$ grains, resisting the removal of particles by scratching (the film is stripped off together with the ceramic grains, Figs. S8 and S9); furthermore, no graphene/graphite-like residues were detected with the exfoliation test by adhesive tape’s peel off (Fig. S10) and the sonication of the samples. The adhesion energy of graphene grown on copper has been reported in the range of 0.72–12 J m$^{-2}$ using different techniques as the double cantilever beam configuration [57] or nanoscratch [58]. In the case of graphene grown on sapphire, a value of 1.4 J m$^{-2}$ has recently been
4. Conclusions

3D-printed α-Al₂O₃ supports with multi-scale porosity are fabricated by direct ink writing and, for the first time, successfully coated by a tailorable number of nanocrystalline graphene layers using a single-step catalyst-free CVD technique to develop cellular graphene/Al₂O₃ hybrids. A coating of 3–5 nanocrystalline graphene layers is deposited under the H₂:CH₄ precursor ratio of 4/1. The hybrid structures present a high electrical conductivity of 10⁶–10⁷ S m⁻¹ due to the continuous graphene/graphitic network on the surface of alumina lattice. The coating deposition also results in an increased thermal conductivity of up to ~50%, along with Seebeck coefficient values up to ~15 μV·K⁻¹. In addition, the modification of both internal and external surfaces of a highly porous Al₂O₃ substrate by the nanocrystalline graphene-based coating affects the water adsorption of the structure making it hydrophobic. The hybrids developed in this work can extend the application of intrinsically insulating materials to produce composites for conditions that require dielectric substrates of complex shapes coated with conductive films or graphene-based catalytic supports with good structural resistance.

CRediT authorship contribution statement


Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References
