***In situ* generation of 3D graphene-like networks from cellulose nanofibres in sintered ceramics**

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Establishing a 3D electrically percolating network in an insulating matrix is key to numerous engineering and functional applications. To this end, using hydrophobic carbon nanofillers is tempting, but still results in suboptimal performance due to processing challenges. Here, we demonstrate how natural cellulose nanofibres can be *in situ* transformed into graphene-like sheets connected to a 3D network enhancing both the transport and the mechanical properties of sintered engineering ceramics. The network architecture also permits the decoupling of electrical and thermal conductivities, which represents a major obstacle in attaining efficient thermoelectric materials. We foresee that our transferable methodology can pave the way for the use of natural nanofibres to unravel the full potential of 3D graphene-like networks to accelerate development in fields like energy and telecommunications.

Introduction

3-Dimensional (3D) percolating networks are ubiquitous in nature and technology like neural networks ensuring the communication of electrical signals¹ or as macroscopic carbon architectures for sensing, healthcare and energy applications.^{2,65} Similar percolating networks in dielectric ceramic matrices can be established by adding small amounts of carbon nanofillers that provide electrical conductivity while preserving or even improving mechanical properties.⁶⁶ On the other hand, phonon barriers constituted by electro-conducting carbon nanotubes and other nanoscale materials can greatly reduce their thermal conductivity,⁹ which could improve thermoelectric materials.¹⁰ However, a major challenge represents the reliable and effective embedding of fine carbon nanofillers in ceramic matrices^{11,12} and therefore, unconventional but facile approaches for the creation of percolating 3D networks are still sought. To date electro-conductive fillers like nanostructured carbon allotropes, *i.e.* carbon nanotubes, graphene, and reduced graphene oxide, are incorporated into ceramic matrices by mixing and blending processes,^{13,14} but the homogeneous dispersion of these carbon nanofillers in a ceramic matrix remains an issue attributed to their hydrophobic nature and concomitant colloidal instability in hydrophilic media.^{13,15} As a result, electrical and mechanical properties deteriorate or have to be compensated by increasing the amount of the filler (>10%).

Here, we report an alternative methodology for the generation of embedded 3D conducting networks in conjunction with the use of natural nanofillers that are of high current research interest.^{16,18} Wood-derived cellulose nanofibres (CNF) are flexible, semi-crystalline fibrils displaying an I crystal structure. They are of approximately 3 nm thickness and exhibit extraordinary mechanical strength, optical transparency, and chemical versatility.^{19,20} It has also been shown that CNF can be a versatile precursor for a variety of highly conducting carbon nanostructures produced by pyrolysis.^{21,22} Nonetheless, it has never been reported before that CNF could serve concomitantly as a mechanical and electrical reinforcement agent in sintered ceramics.

In the work presented, we demonstrate that CNF can be *in situ* converted during a spark plasma sintering (SPS) process into 3-dimensionally connected graphene-like sheets to effectively enhance the electrical and mechanical properties of engineering ceramics. The 2D graphene-like nanostructures were produced in dielectric alumina (Al₂O₃) and ion conducting

3 mol% yttria-stabilised zirconia (YSZ) to showcase the process. The generated few-layer graphene (FLG) network not only enhanced the permittivity of the composite ceramic materials, which is relevant for telecommunication devices, but also decoupled thermal and electrical conductivities, which is of fundamental importance for engineering efficient thermoelectric materials. Lastly, we demonstrated that the FLG-ceramics were also suited for electro-discharge machining, a post-sinter shaping process for complex shapes.

Results and discussion

[Fig. 1a](#) shows an AFM micrograph of TEMPO-mediated oxidized CNF revealing a fibril thickness of 3 nm and a length of 400–1000 nm. The fibrils display the typical kinks that impart the flexibility to CNF. Dispersing CNF hydrogels in aqueous slurries of YSZ and Al_2O_3 powders rendered the respective ceramic suspensions with a CNF content ranging from 0.5 to 4 wt%. Additional attrition milling results in homogeneous and colloidally stable CNF/ceramic slurries without particle segregation or de-mixing phenomena ([Fig. S1](#)), which can be attributed to the hydrophilic nature of CNF.²⁰ Freeze-dried CNF/ceramic composite powders contained non-aggregated, individual cellulose nanofibres as exemplified for 2%CNF-YSZ and 3%CNF- Al_2O_3 ([Fig. 1b](#) and [Fig. S2](#)). These compositions were also used in the microstructural and mechanical characterization of the green and sintered nanocomposite ceramics since both compositions are in the regime of electrical percolation (*cf.* [Fig. S8](#) and discussion below). Significant mechanical reinforcement brought about by the CNF could be clearly demonstrated since cold isostatic pressing (CIP) at 250 MPa of these powders renders highly compacted green bodies that displayed very high flexural strength of 17 and 15 MPa for 2%CNF-YSZ and 3%CNF- Al_2O_3 , respectively ([Table S1](#)). These values are an order of magnitude larger as compared to dry-pressed green bodies containing polymeric binders²¹ and thus, these CNF/ceramic composites are suitable for green machining, which is an industrially important pre-sintering rapid prototype shaping technique ([Fig. 1c](#)).²² SPS sintering of the 2%CNF-YSZ and 3%CNF- Al_2O_3 green bodies at 1250 °C and at 1350 °C, respectively, yielded black coloured, dense nanocomposite ceramics ([Fig. 1d](#) and [Table S1](#)).

Fig. 1 Microstructure of green and SPS-sintered CNF/YSZ ceramics. (a) Atomic force microscopy (AFM) micrograph of individual cellulose nanofibres deposited on an APTES-modified mica substrate. The magnified inset image underlines the 1D morphology of CNF, which is transformed into a 2D carbon phase during SPS sintering as observable in e. (b) SEM micrograph of freeze-dried 2%CNF-YSZ powder. (c) Photograph of a machined 2%CNF-YSZ green body. (d) Photograph of 2%CNF-YSZ before and after SPS sintering showing a white to black colour change. (e) BF STEM image of SPS sintered 2%CNF-YSZ. (f) Electron energy loss spectroscopy (EELS) mapping across a grain boundary in 2%CNF-YSZ using the carbon (C) and the zirconium (Zr) signals, respectively. The scale bars in c and d refer to 1 cm, respectively.

Energy dispersive X-ray spectroscopy (EDX) mapping (Fig. S3^A) and bright and dark field STEM images (Fig. 2a) of the sintered composites revealed a continuous carbon phase, which is uniformly distributed within the material at the macroscopic and microscopic levels, respectively. At the nanoscale level, STEM imaging (Fig. 1e) and quantitative EELS mapping (Fig. 1f) demonstrate that the carbon phase is concentrated as an intergranular film forming a 263 nm thick grain boundary (GB) layer completely surrounding the grains (Fig. 2b). These observations suggest that the 1-dimensional cellulose nanofibres are transformed into a 2-dimensional carbon film during SPS sintering (*cf.* Fig. 1a and e). In fact, there is clear evidence from HRTEM analysis that this carbon film has a layered microstructure in both

ceramic nanocomposites (Fig. S4[†]). Fig. 2c shows graphitic layers with an interlayer distance of 3.4 Å matching the *c*-axis lattice constant of graphite or the distance between stacked graphene layers.²⁵ The observed films consist of 6610 layers typical of few-layered graphene (FLG).²⁶ Graphitic carbon was also confirmed by core level C 1s X-ray photoelectron spectroscopy (XPS) (Fig. S5[†]) and in Raman spectra (Fig. 2d). The latter are characterized by the D and G bands at 1350 and 1595 cm⁻¹, respectively, as well as the 2D band at 2704 cm⁻¹. While the G band is attributed to the in-plane C6C vibrations of sp² hybridised carbon atoms, the 2D band originates from second-order phonon processes sensitive to the stacking order of graphene layers.²⁶

Fig. 2 Microstructure and formation of intergranular FLG films. (a) STEM bright field (BF) and dark field (DF) images of SPS sintered 2%CNF-YSZ. The contrast at the ceramic grain boundaries (GBs) in the BF and DF mode is indicative of a continuous intergranular carbon network. (b) DF STEM image of Al₂O₃ grains and the surrounding GB phase in 3%CNF-Al₂O₃. Color EELS maps that use the signals of the C K₁ edge, Al L_{2,3} edge, and O K₁ edge, respectively, show that the GB consists of a carbon-containing phase, while Al and O are confined in the bulk of the grains. (c) BF STEM image of a few-layered graphene (FLG) film between Al₂O₃ grains in 3%CNF-Al₂O₃. An atomic

plane distance of 3.4 Å is indicated. (d) Raman spectra of SPS sintered 2%CNF-YSZ (i) and 3%CNF-Al₂O₃ (ii). * = O₂(g) and N₂(g). (e) TEM image of SPS sintered 3%CNF-Al₂O₃ highlighting a Y junction of the intergranular FLG films that fuse together.

The unimodal shape and width (FWHM = 70 cm⁻¹) of the recorded band suggest a multi-layered graphene phase, which is in agreement with the HRTEM observations. Nonetheless, the presence of a pronounced D band (intensity ratio $I_D/I_G \approx 0.9$) in the spectra also indicates that the FLG contains defects possibly arising from graphitic crystal edges, point defects, and sp³hybridized carbon atoms.²⁶ It should be noted, however, that cellulose is usually considered as a non-graphitisable carbon source, but cellulose of high crystallinity and purity like cellulose nanofibres may indeed show capability for graphitisation.²⁷ The cellulose nanofibres used in this work displayed a crystallinity index of 61% and a crystallite size of 1.9 nm typical of CNF from eucalyptus.²⁸ Interestingly, the distance between the glucopyranose planes in cellulose I is 3.8 Å (0.5 *a* of the cellulose I unit cell),²⁹ which is close to the interlayer distance of graphite (*i.e.* 3.35 Å). This circumstance possibly favours the generation of high quality graphitic multilayers from crystalline cellulose³⁰ even though a full understanding of the exact mechanism is still challenging.²⁷ Nevertheless, supporting this assumption, we could demonstrate a clear effect of CNF *versus* glucose on the electrical properties of sintered YSZ nanocomposites. With dissolved glucose as the carbon source the resulting material displayed a 75% reduced electrical conductivity (*vide infra*) when compared to the equivalent 2% CNF-YSZ material. This result suggests that the intrinsic crystalline arrangement of the glucopyranose units in CNF as opposed to the randomly distributed glucose molecules indeed seems to favour the formation of a percolating network. A schematic illustration of the conversion of the CNFópowder nanocomposite into the FLGóceramic nanocomposite during SPS sintering is presented in [Fig. 3](#) also showing the lattices of cellulose I and graphene.

Fig. 3 Schematic illustration of the conversion of the CNF/powder nanocomposite into a FLG/ceramic nanocomposite. The lattices of cellulose I and graphene are included

Interestingly, the FLG films follow the contour of the grains (Fig. 2e and S4a) suggesting a high ability of bending and wrapping similar to individual graphene sheets.³³ This specific behaviour and the resultant morphology is inherited from the flexible cellulose nanofibres that wrapped around the grains in the nanocomposite green body (*cf.* Fig. 1b). During SPS sintering the CNF network transformed into thin graphene-like sheets maintaining the 3D topology and connectivity of the original network (Fig. 2e). This process evokes certain similarities to the high temperature covalent fusion of carbon nanotubes³² or graphene sheets²³ forming interconnected 3D networks.⁴ Indeed, the high electrical conductivity (*cf.* Fig. S8) of the FLG-ceramics suggests that the cellulose-derived FLG sheets are bonded together reaching the percolation threshold. A δ Y δ junction of three FLG films can be observed in Fig. 2e. On the other hand, the high defect concentration inferred from the intense Raman D band could be associated with vacancies and interstitials generated at the junction of the FLG sheets.^{32,33} Also, the finite size effects in FLG due to their confinement between grains in the ceramic matrix as well as a lack of long ranged crystallinity coherence of the grown FLG cannot be ruled out as the cause of the large intensity of the D peak.³⁴

An estimation of the carbon content in the ceramics from the XPS spectra (Fig. S6) yielded values below 1 wt%, which was corroborated by elemental analysis. However, these measurements were ambiguous due to the low carbon content and possible carbon re-adsorption during the XPS analysis. It is also important to note that the carbon diffused neither into the Al₂O₃ nor the YSZ grains, as observed in the corresponding EELS maps (Fig.

2b and S7, respectively). For instance, the quantification of the GB layer composition in 2%CNF-YSZ suggests that 87% is carbon and 13% is zirconium, while oxygen is not encountered in this layer (Fig. S7).

The graphene-like carbon acts as an electro-conductive nanofiller and both alumina- and YSZ-based composites show extremely increased electrical conductivity in the range of 400 S m^{-1} for 4%CNF- Al_2O_3 and 250 S m^{-1} for 3%CNF-YSZ. The percolation threshold for carbon-based electrical conductivity is as low as 1 and 0.5 wt% CNF, respectively, (Fig. S8), which is on par or even below the typical values obtained for graphene or carbon nanotube reinforced ceramics.^{11,35} Our results are significant because the conductivity values encountered would usually require considerably higher amounts of nanofiller (1610%), which, however, negatively affect the microstructural homogeneity and downgrades the mechanical properties.

Fig. 4 displays the significant changes in the dielectric and charge transport properties of the sintered composites. The conductivity (σ) vs. frequency (f) data for x CNF-YSZ are shown in Fig. 4a together with the equivalent circuit fits. The values extracted from the fits at different temperatures (T s) were plotted on the Arrhenius axes (Fig. 4b), which shows the pronounced transition from the well-known ionic oxygen vacancy conduction in pure YSZ³⁶ to mixed ionic/electronic conduction (MIEC) in 0.5%CNF-YSZ with dominating ionic contributions. The signs of ionic conduction are also clearly visible in the complex impedance plots of Z'' vs. Z' (Fig. 4c) and in the dielectric permittivity ϵ' vs. f (Fig. 4c inset). In the former, the low- f -interface (IF) pike is a hallmark feature of ionic conductivity, whereas in the latter the massive linear increase in dielectric permittivity at the low f -end is associated with ionic conductivity too.³⁷ The GB and bulk activation energies for the ionic contributions were similar in the 0%CNF-YSZ and 0.5%CNF-YSZ samples (0.961.0 eV), and the absolute conductivity values were unaffected by the CNF in the grain interior bulk regions. The latter is a clear confirmation of the findings from compositional analyses that the CNF derived carbon does not diffuse into bulk areas. On the other hand, the ionic conductivity in the GB areas is lower in the presence of CNF, because graphitised GB layers may block some ionic pathways. Although the ionic conductivity is dominant in 0.5%CNF-YSZ, the electronic contribution is visible at high f in the plots of σ vs. f by an unusual upturn (Fig. 4a). The electronic contributions become dominating at CNF concentrations of $\times 1$ wt%. MIEC is indicated in the presence of CNF, and the composites of higher and percolating CNF concentrations may be highly relevant for application as an electrode material in SOFCs.

Fig. 4 Transport properties of the sintered nanocomposite ceramics: impedance spectroscopy data (open symbols) were fitted to a standard equivalent circuit model (black solid squares) containing 1 or 2 standard RQ elements of an ideal resistor (R) and parallel non-ideal capacitor (Q). The RQ elements were connected in series to represent GB and bulk contributions.³⁷ (a) Conductivity σ vs. frequency f plots of $x\text{CNF-YSZ}$. The 0.5%CNF-YSZ curve shows a high- f upturn, modelled by an additional series resistor. (b) Plots of σ vs. $1000/T$ plots for $x\text{CNF-YSZ}$ showing good linearity. The σ values were obtained from circuit fits, and the activation energies for GB (solid symbols) and bulk (open symbols) conduction were derived from the corresponding Arrhenius plots.

The 0%CNF-YSZ (pure YSZ) is a purely ionic conductor, the 0.5%CNF-YSZ is an MIEC with dominating ionic, and the 1%CNF-YSZ is an MIEC with dominating electronic conduction. (c) Complex impedance plot Z'' vs. Z' and dielectric permittivity ϵ'' vs. f (inset) of 0.5%CNF-YSZ. The open symbols correspond to experimental data and full squares correspond to fits to the equivalent circuit model. (d) Activation energies $E_A(T)$ vs. T for x CNF-YSZ and x CNF- Al_2O_3 . $E_A(T)$ in the FLG grain boundary phase is T -dependent increasing from 0.5 to higher values in the range of 266 meV. (e) Schematic illustration of the FLG films at a triple junction between the ceramic grains. Here the case of YSZ is demonstrated; the equivalent features can be observed at the triple grain junctions in sintered CNF- Al_2O_3 nanocomposites. The electron (e^-) and ionic oxygen vacancy ($h_{\text{O}^{2-}}$) conduction mechanisms of YSZ are indicated. The activation energy, $E_A(T)$, for oxygen vacancy conduction in the YSZ bulk is 0.9 eV, while the $E_A(T)$ of electron conduction in the FLG grain boundary phase is T -dependent.

It should be further noted that the sintered 1%CNF-YSZ sample showed a semiconducting T -dependence of conductivity with a small charge transport gap of ~ 6.5 meV (Fig. 4b), whereas the 2%CNF-YSZ sample shows a metallic $\propto T^{-3/2}$ dependence, which, however, was shown to be extrinsic. The correct dc resistance was therefore determined by the 4-point van-der-Pauw measurements at various T . The resulting Arrhenius curves (Fig. S9A) show a certain degree of non-linearity, which indicates a T -dependent activation energy $E_A(T)$ (Fig. 4d) due to an opening charge transport gap upon heating (Fig. 4e). The E_A vs. T curves for sintered x CNF-YSZ and x CNF- Al_2O_3 in Fig. 4d are qualitatively similar indicating an opening gap as part of the equivalent charge transport mechanism, which therefore may well originate from the carbon layers instead of the very different charge transport in YSZ or Al_2O_3 . The temperature dependence of this small transport gap in the graphene-like 2D phase may originate from the crumpling of the carbon layers,³¹ in turn influenced by local stress fields resulting from a thermal expansion mismatch. The proposed ionic conduction and MIEC mechanisms in x CNF-YSZ are illustrated in Fig. 4e. In the case of x CNF- Al_2O_3 a transition from an insulating Al_2O_3 -type charge transport to semiconducting graphene-like conduction was observed (cf. Fig. S9A). Alternatively, variable-range hopping (VRH) models have been applied previously to explain non-linear Arrhenius plots.³² However, this approach may not be reasonable in systems with metallic and

delocalized or weakly localised electrons with a small gap since VRH is a localised electron hopping model based on fully localised electron tunnelling exhibiting larger transport gaps.³²

Another remarkable property of the CNF-YSZ ceramics is demonstrated by the plot of the electrical conductivity together with the thermal conductivity at 300 K vs. the CNF doping level (Fig. 5a). The electrical conductivity increases by 14 orders of magnitude, while the thermal conductivity increases only by 6%, comparing YSZ and 2%CNF-YSZ. Usually, the thermal and electrical conductivities are strongly coupled due to the thermal contribution of electron conduction.⁴⁰ A big challenge in applications like thermoelectrics is therefore the de-coupling of these two transport properties^{10,38,41} as demonstrated recently in metallic vanadium dioxide nanowires.⁴⁰ Here, we show electric and thermal de-coupling in macroscopic materials with immediate implications for the above-mentioned technological applications. The nanometric dimensions of the graphene network in the nanocomposite ceramics are likely to give rise to a high thermal interface or phonon resistance similar to carbon nanotube composites.³³

Fig. 5 Electronic and thermal conductivity, dielectric permittivity. (a) Electrical and thermal conductivity vs. CNF doping level in YSZ composites measured at 300 K. (b) Dielectric permittivity ϵ' vs. T of sintered $x\text{CNF-YSZ}$, where bulk and GB permittivity is indicated. The inset schemes indicate the dielectrically active areas (white colour) in terms of the ceramic grains for the bulk and the FLG layers for the GB contributions. Both contributions can be represented by thin (GB) or thick (bulk) capacitors connected

in series. The ϵ values were obtained from the equivalent circuit fits of dielectric spectra. (c) ϵ values at 1 K Hz and 300 K of sintered x CNF- Al_2O_3 as a function of the CNF content. The inset shows the ϵ vs. frequency.

Furthermore, the sintered CNF-ceramics showed striking improvements in the dielectric permittivity, which is relevant for miniaturising communication devices.^{6,42} High dielectric permittivity ϵ values of up to 10^4 were detected with increasing CNF, which represents giant increases of $250\times$ and $1000\times$ for x CNF-YSZ and x CNF- Al_2O_3 , respectively (Fig. 5b and c), similar to the ϵ values reported for graphene/ Al_2O_3 composites.⁶ Such a massive enhancement is not likely to be an intrinsic ceramic effect and, therefore, the alternative explanation of the formation of microscopic capacitors between the ceramic grains at the FLG GB areas may be favourable (Fig. 5b insets).^{6,43}

In addition to the reported improvements in the electrical and dielectric properties, the incorporation of CNF also improved the mechanical properties of both the dry-pressed green body (*vide supra*) and the sintered samples. For instance, the Vickers hardness H_v of the sintered 2%CNF-YSZ and 3%CNF- Al_2O_3 was 14.2 and 21.2 GPa, respectively, which is on par with pristine YSZ and several GPa higher than for pure coarse-grained alumina. On the other hand, the indentation toughness was 4.4 and 4.0 $\text{MPa m}^{0.5}$ (2%CNF-YSZ and 3%CNF- Al_2O_3 , respectively) (Table S1[†]), which is on par or slightly higher than the values of commercial benchmark ceramics and also nanocarbon reinforced composite ceramics.^{7,8,14,44} However, it has to be emphasised with respect to the latter, that especially graphene/ceramic nanocomposites are prone to the directional anisotropy of electrical *versus* mechanical properties as a result of the alignment of graphene flakes and hence, hampering the applicability of such materials,⁴⁵ which is not the case for the present CNF/ceramics system. The good mechanical properties of the sintered CNF/ceramics can be related to a microstructural refinement, where the FLG phase could successfully prevent the excessive grain growth during sintering by pinning the grain boundaries (Fig. S10 and S11[†]). An additional contribution stems from a toughening effect conveyed by the carbon phase. This effect was suggested from the fractographic analysis that demonstrated crack branching, bridging, and deflection (Fig. 6a). Occasionally, also carbonaceous layers were debonded from the ceramic matrix that bridged the crack (Fig. 6b). Both observations are common for fibre or sheet reinforced ceramics^{11,44,46} and can contribute to further increase the toughness as a result of reduced stress intensity at the crack tip. Therefore, it can also be assumed that the ex-cellulose FLG behaves like a sheet or fibre reinforcement. It is well-

known from natural biomineralised nanocomposite materials like nacre or bone that toughness is enhanced in a brittle material through the presence of nanometre thick and soft carbon-rich interfaces.⁴⁷

Fig. 6 Fracture behaviour and EDM application. (a) SEM micrograph of an arrested crack in sintered 2%CNF-YSZ after the Vickers indentation showing crack branching, bridging and deflection (white arrows) induced by the carbonaceous phase. (b) A close-up of (a) showing crack bridging of the FLG sheets debonded from the ceramic matrix. (c) Photograph of sintered 3%CNF- Al_2O_3 showing electro-discharge erosion pits and, (d) a close up of (c) made with a stereomicroscope.

Finally, the sintered CNF δ ceramics were tested for electro-discharge machining (EDM) as a technologically relevant subtractive manufacturing method for the complex shaping of dense and hard (sintered) materials. Fig. 6c and d show the erosion pits on the surface of 3%CNF- Al_2O_3 produced by die-sinking EDM. The volumetric material removal rate (MRR) was $0.33 \text{ mm}^3 \text{ min}^{-1}$ and the die-sink rate was 12.4 m min^{-1} . Even though this MRR was about 50% lower at the given pulse duration and current as compared to using conventional TiN or TiC fillers⁴⁸ it should be remarked that these higher MRRs were typically achieved at approximately 30–40 vol% filler content. In addition, the MRR should also be grain-size dependent, whereas in our case finely grain-sized samples will result in a slower EDM process. On the whole these results show that CNF incorporation represents a versatile

alternative to fabricate EDM suitable materials with a considerably lower second phase content (1 wt% vs. 50 wt%) as compared to conventional EDM materials⁴⁹ and are competitive with multiwall carbon nanotubes as EDM fillers.⁵⁰

Conclusions

In summary, we report the use of natural nanofibres for the *in situ* generation of 3D percolating graphene-like networks embedded in engineering ceramics. The transformation of the cellulose nanofibres into a continuous, graphene-based architecture during sintering is the key to the remarkable electronic and dielectric properties of the microstructurally refined FLGóceramic composites, while at the same time the thermal conductivity is decoupled. Besides the transport properties, the incorporated cellulose nanofibres largely improve the mechanical properties and also enable the use of technologically important machining methods for electro-conductive ceramics. We envisage that our results can advance the processing science and technology to provide the improved hierarchical graphene composite materials needed for advanced applications in fields like energy and telecommunications.

Experimental

Materials

In the present work, commercially available α - Al_2O_3 (Taimicron TM-DAR, Taimei Chemicals Co., Ltd, Japan) and 3 mol% Y_2O_3 -stabilized ZrO_2 (YSZ; TZ-3Y-E, Tosoh, Japan) powders were used. Cellulose nanofibres, extracted from never-dried eucalyptus pulp, were provided by Prof. Mutje, University of Girona, Spain. In brief, an aqueous suspension of the pulp was subjected to a TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl)-mediated oxidation step to render carboxylated fibres (1.39 mmol g⁻¹ charge). The subsequent mechanical disintegration using a high-pressure homogenizer (Panda + 2000, GEA, Italy) renders fully defibrillated cellulose nanofibres. The mechanical treatment results in a highly viscous CNF dispersion with a concentration of about 1 wt% and a pH of 7. All other chemicals were purchased from Sigma-Aldrich.

Powder processing and sintering

Nanocomposite powder. Aqueous powder slurries (30 vol% solid loading) were prepared from citric-acid-stabilised γ - Al_2O_3 and YSZ nanoparticles, respectively, and adjusted to pH 8.5. The slurries were mixed with aqueous CNF gel to render CNF : nanoparticle ratios of 0.564 wt% (1.85610 vol%). The mixtures were attrition milled (3-millimetre-sized ZrO_2 milling balls) for 3 h following rapid freezing in liquid nitrogen and a freeze-drying step to obtain dry nanocomposite Al_2O_3 and YSZ powder. For comparison, a nanocomposite of YSZ containing 2 wt% of glucose was prepared by adding the corresponding amount of aqueous glucose solution to the YSZ powder slurry.

Green bodies. For the evaluation of the CNF reinforcement effect on green bodies the nanocomposite powders were cold isostatically pressed with 250 MPa. The green bodies were evaluated by green machining and by measuring flexural strength using a piston-on-three-balls setup.

Spark plasma sintering (SPS). For SPS sintering, 2 g of the nanocomposite powder was added into a 16 mm or 20 mm diameter graphite sintering die containing 0.5 mm thick graphite paper. The die was isolated with 5 mm thick graphite wool. The sintering was performed in an SPS furnace (SPS-615E, Dr SINTER; SPS Syntex Inc., Japan) under vacuum conditions. The heating rate was set to $100\text{ }^\circ\text{C min}^{-1}$, while the initial contact pressure was increased from 3 kN to a final pressure corresponding to 80 MPa in 1 minute during the most pronounced densification of the sample. The nanocomposite consolidated powders were sintered at a final temperature of $1250\text{ }^\circ\text{C}$ (YSZ containing samples) and at $1350\text{ }^\circ\text{C}$ (Al_2O_3 containing samples) with 5 minutes dwell time.

Characterization

Density. The densities of the SPS-sintered samples were determined using the Archimedes method, where deionized water was used as the immersion medium.

Microstructural analysis. The microstructure of the samples was characterised by field-emission scanning electron microscopy (FE-SEM; JEOL JSM 7600F) and focused ion beam SEM (FIB-SEM; Helios Nanolab 650, FEI, Hillsboro, USA). The average grain size was evaluated by measuring at least 100 grains from the SEM images of the fractured surfaces using the linear intercept method. No correction factor was used. The X-ray diffraction (XRD) patterns of sintered specimens were recorded using a PANalytical X'pert PRO MPD

diffractometer (PANalytical, Almelo, the Netherlands) equipped with a PIXcel detector and using a Cu-K_α radiation source. The measurements were carried out using fixed divergence (1°) and anti-scattering slits, a 10 mm mask, and a continuous scan mode in the 2θ range 20–100°. Transmission electron microscopy characterisation was performed on a scanning transmission electron microscope with atomic resolution (Jeol STEM ARM 200 CF) in the TEM and dark/bright-field scanning transmission electron microscopy (DF/BF STEM) modes. The particle size distribution of the nanocomposite powders was assessed with a laser particle-size analyser (LA-920, Horiba, Japan). Atomic force microscopy (AFM) of individual cellulose nanofibres deposited on the APTES-modified mica substrate was performed with a Cervantes instrument from Nanotec electrónica S.L. (Spain) equipped with Nanosensors PPP-FMR cantilevers with a spring constant of 1.5 N m⁻¹ and a resonance frequency of 75 kHz. Images were obtained under ambient conditions in a modulated amplitude mode.

Chemical analysis. The distribution of the carbon phase in the sintered ceramics was characterized by energy-dispersive X-ray spectroscopy (EDX) coupled to a (FEI NOVA Nano SEM 230) FE-SEM and by electron energy loss spectroscopy (EELS). The EDX maps were recorded with a Type SDD Apollo 10 EDAX detector and the data acquisition conditions were kept constant at a working distance of 6.5 mm, a spot size of 5.5, a landing energy of 5.0 keV, and an accumulation time of 500 s. The EELS spectra were collected in the STEM mode in scanned areas across the grain boundary; 24 mrad convergence and 60 mrad collection semi-angles were used. Low and core loss were acquired simultaneously using the Dual-EELS option of the system. The sample thickness where the EELS spectra were collected was between 30 and 50 nm. The chemical composition and the state of the carbon atoms were analysed by X-ray photoelectron spectroscopy (XPS) on a PHI-TFA XPS spectrometer (Physical Electronics), by elemental analysis (CHNS PerkinElmer 2400) and by Raman spectroscopy (EZ-RAMAN-N series, Enwave Optronics Inc., laser excitation was $\lambda = 532$ nm).

Electrical properties. The dielectric properties of the sintered composites were measured by alternating current (AC) impedance spectroscopy using a Novocontrol Alpha Analyser. Measurements were performed between $f = 1$ Hz–10 MHz with a 0.1 V applied AC voltage signal, over the T -range of 160 K–560 K (–113 °C to 287 °C) upon heating cycles in 20 K temperature increments. The data were taken under steady-state conditions after the selected T was stabilized for at least 10 minutes. Resistance as a function of magnetic field and temperature (2–300 K) was measured on 8×8 mm² square samples using the van der

Pauw configuration in a 9 T Quantum Design PPMS. Resistance measurements were taken in three configurations: two of them optimized for resistivity measurements along nominally orthogonal directions in the sample while the remaining configuration, with the current along the diagonal, maximized the Hall resistance.

Mechanical analysis. The biaxial flexural strength of the green and the SPS-sintered samples, where the latter were ground and polished on the tensile side (finished with 3 μ m diamond paste), were measured with a piston-on-three-balls setup, according to the ISO 6872 standard, on a universal testing machine (Quasar 50; Galdabini, Italy) at a loading rate of 1 mm min⁻¹. The hardness and indentation toughness of the samples were determined using a Vickers indentation hardness tester (Zwick GmbH & Co., Germany). The indents were made using a Vickers-type indenter by applying a 10 and 50 N load for 10 s for evaluating hardness and indentation toughness, respectively. The indentation toughness was then calculated directly from the crack lengths using the method of Niihara⁵¹ for Palmqvist cracks.

Electro-discharge machining. Electro-discharge machining (EDM) was performed on 2%CNF-YSZ and 3%CNF-Al₂O₃ samples by applying the die-sinking EDM principle on an IT Elektronika 200M-E machine (Slovenia). For the machining experiments, a rectangular (5.17 $\times$ 5.17 mm²) copper electrode was used. The duration of the machining was set to 20 min using the following machining parameters: discharge current $i_e = 2$ A, ignition voltage $u_i = 280$ V, discharge duration $t_e = 17$ μ s and pulse interval $t_o = 36$ μ s.

Conflicts of interest

There are no conflicts to declare.

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