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Highlights

- A carbon/ AlF_3 nanocomposite was produced by a novel combustion synthesis route.
- The combustion product is composed of cubic α - AlF_3 nanoparticles dispersed in a porous carbon foam matrix.
- The combustion method represents a fast and scalable alternative to wet chemical procedures.

Novel combustion synthesis of carbon foam-aluminum fluoride nanocomposite materials

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Abstract

The facile, rapid and bulk production of composite materials consisting of carbon nanostructures doped with metal-based compounds has been a significant challenge for various research areas where such types of materials can be applied, including catalysis, energy storage and water purification. In this work, a carbon foam-aluminum fluoride composite (C-AlF₃) was developed by adopting a combustion synthesis approach, which is an attractive alternative to wet chemical methods usually employed for such purposes. The flame ignition and combustion of a solid-state mixture comprising a fluoropolymer and nano-sized Al powder leads to the formation of a porous carbon foam network doped with dispersed cubic-like AlF₃ nanoparticles (100 to 500 nm in size), as observed by high-resolution microscopy methods. Selective area electron diffraction and X-ray diffraction studies revealed a rhombohedral α -AlF₃ crystal structure for these embedded particles, while micro-Raman spectroscopy indicated typical carbonaceous features for the foamy matrix. The C-AlF₃ composite also showed a combination of micro-, meso- and macro-porous characteristics (i.e. pore sizes in the nanometer scale) based on the analysis of N₂ sorption data collected at 77 K. The findings of this study provide useful insights for further research on carbon-based nanocomposite materials prepared via direct combustion synthesis routes.

Keywords: nanocomposite; porous material; carbon foam; aluminum fluoride; combustion synthesis

1. Introduction

Significant research efforts have been devoted over the last decade towards the facile, rapid, high-yield and low-cost development of composites consisting of carbon nanostructures (e.g. activated carbons, nanotubes, graphene etc.) and other compounds, such as metallic- and/or inorganic-based nano-sized particles, clusters or thin films [1-5]. Such composite materials may exhibit a combination of properties favorable for rapidly expanding and materials-oriented research areas, including gas sensing [6], carbon dioxide conversion [7], hydrogen storage [8], electrochemical energy storage [9], water treatment [10] and capacitive desalination [11]. Their promising performance in such applications is attributed not only to the individual characteristics of the host carbonaceous support and the hosted/embedded substance, but also to the potential synergy between the two. Even though a large number of carbon-based composite structures has been presented in the literature, only limited attention has been given to the development of carbon-metal fluoride systems. Metal/inorganic fluorides such as aluminum fluoride (AlF_3) have been widely used as catalysts for the production of olefins in petrochemical processes [12,13], as additives for the production of aluminum in electrolytic cells [14,15], as well as ingredients for the production of fluoride glasses for mid-infrared optical applications [16,17]. In recent years, nano-sized AlF_3 has also attracted significant attention in the technology of rechargeable lithium-ion batteries by acting as a useful additive to enhance their electrochemical performance [18-21]. The most common laboratory-scale method of preparing AlF_3 involves the wet chemical treatment of Al or Al-based substances with hydrofluoric acid (HF) [22]. On the other hand, amorphous carbon foams with tuned porosity, specific areas, pore volumes and surface chemistries are frequently produced using a variety of procedures, such as physical or chemical blowing of carbon precursors, template carbonization, compression of exfoliated graphite, and assembly of graphene nanosheets [23-26]. Such porous carbonaceous structures act as effective matrices/substrates for the deposition of catalytically

active nanoparticles, which are, in most cases, introduced onto the carbon surface in a subsequent stage (upon synthesis), combining wet chemical and thermal reduction processes [1].

In this work, a carbon foam-aluminum fluoride composite material (denoted hereafter as C-AlF₃) was developed on the basis of a rapid, reproducible, scalable, and wet-free synthesis method that involves the combustion of a commercially available fluoropolymer (THV) mixed with nano-sized aluminum (nAl) powder. The use of nAl promotes significantly the reaction rates due to the larger available specific area of the nano-sized particles compared to their micro-scale counterparts [27]. Solid mixtures of Al and fluoropolymers can react rapidly and form AlF₃ while releasing large amounts of heat upon combustion [28]. Characteristically, the fluorination reaction of Al that leads to the formation of AlF₃ can release up to ~56 kJ per g of Al powder, while other Al-based compounds, such as alumina (Al₂O₃), exhibit about half of this energy release (up to ~31 kJ) [29]. Recent work has been reported on the production of such nanostructured solid mixtures, composed of Al and PFTE (polytetrafluoroethylene), for energetic applications by ball milling procedures, but the product species and morphology have not been investigated [30]. Surface morphology, elemental composition, structure and porosity of the reaction product were investigated by scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) combined with selected area electron diffraction (SAED), X-ray diffraction (XRD), micro-Raman spectroscopy, as well as N₂ adsorption and desorption measurements at 77 K. The synthesis approach of fabricating composite nanostructures through combustion of solid-state reactants offers an attractive alternative to complicated, multi-step and time-consuming physical and/or chemical synthesis procedures.

2. Materials and methods

2.1 Combustion synthesis method

The C-AlF₃ composite was directly produced using THV (3M™ Dyneon™ 221AZ fluoropolymer) and nAl powder (Novacentrix; 80 nm average particle diameter; 76% active content) as precursors, followed by ignition and self-propagating combustion of their mixture. THV has the empirical formula C_{2.29}F_{4.33}H_{0.25}, comprises of three different monomers, i.e. tetrafluoroethylene (C₂F₄), hexafluoropropylene (C₃F₆) and vinylidene fluoride (C₂H₂F₂), and possesses a melting point of 115 °C. Molten THV is very viscous and it has a very low melt flow index. In a typical synthesis procedure, 900 mg of THV was placed in a stainless steel bowl and was heated to 160 °C using a hot plate. In a following step, 100 mg of nAl was poured on the molten THV. The mixture was then pressed and folded in half repeatedly by hand for 30 min to make sure the particles were well distributed within the viscous THV matrix. The THV-nAl mixture (total mass of 1 g) was solidified upon cooling down to room temperature. Small pieces were cut using a blade and then ignited using a butane torch within a fume hood. Once ignited, the mixture started burning at an average rate of 0.2 mm/s and the combustion reaction formed a “foam snake”. The final product was collected as a black powder and was studied without further processing (i.e. in the as-prepared condition). Fig. 1 shows digital photos of the solidified THV-nAl mixture before and during combustion.

Fig. 1 – Digital photos showing (a) the mixed THV-nAl solid sample and (b) the formation of the foam product phase during combustion.

2.2 Characterization methods

SEM images at different magnifications were collected using an FEI Quanta 200 microscope using acceleration voltages between 10 and 20 kV and a working distance of 10 mm. The studied sample was sputter-coated with a gold (Au) layer (estimated thickness of 1-2 nm) under an argon atmosphere using a Quorum Technologies SC7640 sputter coater to inhibit charging effects during imaging as well as to support the powder onto the sample holder and avoid particle movements. The same sample was also micro-analyzed using an EDVAC Genesis X-ray analysis probe mounted on the SEM instrument using an acceleration voltage of 20 kV to obtain EDX spectral patterns for various sites of its surface.

High-resolution TEM images were collected using an FEI Titan Environmental microscope operated at 300 kV acceleration voltage. The powder sample was diluted in acetone at 1 wt.% and mixed via ultrasonication until a homogeneous solution was obtained. TEM copper grids were then dipped into the as-prepared solution to form a thin film of ~200 nm. SAED patterns were also collected for the same sample and subsequently analyzed to determine the produced crystalline phases. The aperture size was 200 μm and the probed area had a radius of ~2 μm . The results of this analysis were also verified with diffraction pattern simulations performed in the CrysTBox software [31]. Fractal dimension analysis of SEM and TEM images was carried out via box-counting algorithms on grey-scale rasters using the MATLAB software for image processing [32].

X-ray diffractograms were recorded by a Bruker-AXS D8 Advance diffractometer equipped with Cu K α radiation (wavelength λ ~1.54 Å) using voltage and current values of 40 kV and 40 mA, respectively. These measurements were performed in Bragg-Brentano geometry using a continuous scan speed mode between the diffraction angles (2θ) of 10 and 60°, a 0.01° step width and a 0.5°/min scan speed.

Micro-Raman spectroscopic investigations were performed by excitation with a solid-state laser emitting at 514.5 nm on an inVia Reflex Renishaw spectrometer. The laser beam was focused on spots of 4.5 μm in diameter with an objective lens having $\times 20$ magnification and 0.14 numerical aperture. The Raman signal averages on sample areas of 20 μm^2 with a power density of 0.02 mW/ μm^2 that was determined as a safety threshold against laser heating and thermally induced spectral changes. In order to achieve a high-quality quantitative analysis, the recorded Raman spectrum was peak fitted with mixed Lorentzian-Gaussian components.

The N_2 adsorption/desorption isotherm was recorded at 77 K by a Quantachrome Autosorb-1 MP volumetric gas sorption analyzer using a liquid N_2 bath and ultra-pure (99.999 %) N_2 gas. Prior to these measurements, a sample of ~ 50 mg was degassed under vacuum (10^{-6} mbar) at 250 $^\circ\text{C}$ overnight with the aim of removing any physisorbed species remaining on the material's surface. The total specific area was calculated using the multi-point Brunauer-Emmet-Teller (BET) method in the relative pressure region (P/P_0) between 0.05 and 0.12 of the N_2 adsorption data, following the BET consistency criteria of the International Standard Organization (ISO 9277:2010) [33]. The micropore specific area and volume values (i.e. for pore widths below 2 nm) were estimated using the Carbon Black statistical thickness equation (also known as t-plot method) [34]. A detailed pore size distribution (PSD) analysis was carried out by applying the Quenched Solid Density Functional Theory (QSDFT) kernel for slit/cylinder-like shape pores in the recorded N_2 desorption data [35].

3 Results and discussion

3.1 Surface morphology and elemental composition

[Fig. 2](#) shows SEM images in a sequence of increasing magnification revealing the hierarchical structure of the as-prepared CF-AlF₃ nanocomposite. [Fig. 2a](#) evidences a foam-like morphology generated from the interconnection of carbon-based particles linked in a way that forms an open network with a series of micron- and nano-scale spaces and voids ([Figs. 2b and 2c](#)). Characteristic cubic- and/or cuboid-like shaped particles can be clearly observed at higher magnifications in many locations within the foamy structure of the powder material ([Figs. 2d-f](#)). These dispersed particles possess sharp edges and exhibit a characteristic size in the range of 100 to 550 nm, with an average particle size of ~240 nm as estimated from a statistical analysis of different high-magnification SEM images ([Fig. S1](#)).

The aforementioned morphology was also investigated in more detail using high-resolution TEM analysis ([Fig. 2g and 2h](#)). Specifically, [Fig. 2g](#) shows clearly two of these particles having cuboid-like shapes with side lengths between ~250 and ~550 nm, similar to the values previously mentioned in the SEM analysis, while [Fig. 2h](#) displays the amorphous carbonaceous foam which appears to exhibit a porous shell-like structure. The morphology of the starting THV-nAl mixture prior combustion is also shown in [Fig. S2](#) for comparison. The equivalent TEM image highlights agglomerates of spherical nAl particles, with sub-micrometer dimensions, dispersed within the THV polymer matrix. The individual nAl particles exhibit diameters below 100 nm, in good agreement with the technical specifications of the nAl powder presented in [section 2.1](#) (i.e. 80 nm average size).

Fig. 2 – SEM images of the as-prepared C-AlF₃ composite at different magnifications showing (a), (b), (c) the hierarchical details of the open carbon foam structure and (d), (e), (f) the embedded α -AlF₃ nanoparticles and high-resolution TEM images of the (g) α -AlF₃ crystals and (h) amorphous carbonaceous foam.

Table 1 illustrates the fractal dimension parameters (f) for the SEM and TEM images of Fig. 2, through capacity, information, correlation and probability-based image processing algorithms [36]. By moving to lower dimensions, the f values show clearly a continuous finite, bimodal self-similarity, transitioning from a Brownian branching network for the amorphous carbon foam to an Apollonian globular pack of α -AlF₃ crystal nanoparticles, thus indicating multiple types of surface area contributors within the composite structure [37].

Table 1 – Fractal dimension parameters (f) of the SEM and TEM images shown in Fig. 2.

	Fig. 2a 500 μ m	Fig. 2b 100 μ m	Fig. 2c 10 μ m	Fig. 2d 5 μ m	Fig. 2e 1 μ m	Fig. 2f 500 nm	Fig. 2g 100 nm	Fig. 2h 20 nm	Average
Capacity	2.71	2.63	2.51	2.57	2.50	2.30	2.27	2.59	2.51
Information	2.64	2.52	2.39	2.47	2.38	2.13	2.15	2.58	2.41
Correlation	2.36	2.26	2.16	2.22	2.18	2.02	2.11	2.57	2.23
Probability	2.47	2.37	2.39	2.36	2.26	2.23	2.29	2.66	2.38

Fig. S3 presents a typical EDX spectrum of the as-prepared CF-AlF₃ material. The elements of carbon (C), oxygen (O), fluorine (F), aluminum (Al), and gold (Au) were detected. C, O, F and Al are part of the constituent phases of the initial mixing precursors (THV and nAl), whereas Au was used as the sputter-coating material prior to the SEM/EDX studies. The atomic percentages of these elements (excluding Au) are shown in the inset of Fig. S3 with the errors of the EDX quantification lying between 1 and 2 at.%. The dominant elements C and F (57.4 and 28.5 at.%, respectively) are complemented with lower proportions of Al and O (7.7 and 6.4 at.%, respectively). EDX elemental mapping of the surface is shown in Fig. S4, indicating that the locations where the cubic- and/or cuboid-like particles exist (i.e. regions 1 to 4) contain primarily Al and F. This suggests that these embedded nanoparticles are most probably AlF₃ crystals that were formed upon combustion of the THV-nAl mixture, whereas the calculated elemental fractions of Al and F also indicate that the latter is dominantly present within these crystals, nearly corresponding to the stoichiometric ratio of AlF₃ (1:3).

3.2 Combustion reaction and AlF_3 formation mechanism

The adiabatic reaction temperature and final product phases upon combustion were calculated using the NASA chemical equilibrium analysis (CEA) code at the composition of 10 wt.% nAl with an active content of 74 wt.% (the rest 26 wt.% being the oxide layer). Based on these findings, we are able to propose mechanisms related to the combustion reaction and AlF_3 formation, as described below. Once the solid THV-nAl mixture is ignited, the exothermic reactions between the decomposition products of THV, including HF, and nAl result in a combustion wave that rapidly travels across the sample to form a “foam snake” containing AlF_3 and carbon. Other calculated products are primarily gaseous CF_4 and CO and a small amount of HF. Although gaseous HF is hazardous, it can be recovered and re-used in synthesis of fluoropolymers in an industrial setting. For example, TFE (monomer for Teflon) is made using mixtures with HF reacted at temperatures up to 900 °C. The adiabatic reaction temperature is calculated at 1552 K, which is slightly above the sublimation temperature of AlF_3 (i.e. 1550 K). Therefore, once the AlF_3 sublimates, it reaches the cooler air and then condenses into the cube-like crystals of AlF_3 within the carbon matrix. The yield of the foamy product was also calculated at ~25 % by considering the mass change of the solidified THV-nAl mixture upon combustion (i.e. reduced by ~75 %).

3.3 Structural features

The SAED analysis of a single AlF_3 particle accompanied with a simulated diffraction pattern are both presented in Fig. 3. The interplanar spacings (d) calculated from the SAED patterns (Fig. 3a) were compared to literature to identify the reaction product phase. The analysis indicated that the cubic- and/or cuboid-like particles observed by the SEM and TEM are related to rhombohedral $\alpha\text{-AlF}_3$ crystals, which is thermodynamically the most stable polymorph out of the five well known AlF_3 phases [38]. In addition, the measured d values matched well with the ones of five crystallographic

planes, namely $(\bar{1} 1 \bar{2})$, $(\bar{1} 0 \bar{4})$, $(\bar{2} 2 \bar{4})$, $(\bar{2} 3 \bar{2})$, and $(\bar{3} 4 \bar{4})$, shown in the simulated diffraction pattern (Fig. 3b) provided by the CrysTBox software [31].

Fig. 3 – (a) SAED pattern of a single α -AlF₃ particle showing the spacings of five crystallographic planes and (b) simulated diffraction pattern showing a match with the experimental pattern for the zone axis $[4 2 \bar{1}]$.

The X-ray diffractogram of the as-prepared C-AlF₃ powder is presented in Fig. 4a. The dominant diffraction peak at $2\theta \sim 25.25^\circ$ clearly corresponds to the (012) reflection of the α -AlF₃ rhombohedral crystal phase, while additional but less intense peaks arising at $\sim 42.59^\circ$, $\sim 51.85^\circ$, $\sim 58.07^\circ$ and 59.06° also seem to describe α -AlF₃ reflections, in close agreement with the Joint Committee on Powder Diffraction Standards (JCPDS card no. 43-0435). This is also in agreement with the aforementioned SAED analysis as well as the primary observations for AlF₃ particle composition derived by the EDX analysis (see sections 3.1 and 3.2). Minor traces of metallic Al and Al₂O₃ were also detected as remnants of the combustion synthesis procedure. In any case, the available carbon fraction cannot be observed by XRD due to its amorphous nature, as observed by TEM (see section 3.1), and therefore micro-Raman spectroscopy was employed for this purpose. Carbon-based structures, such as

functionalized graphene and graphene oxide materials [39-41], carbon nanotubes [42] as well as carbon foams [43-45], are routinely characterized for their structure using Raman spectroscopy. The micro-Raman spectrum recorded for the as-prepared C-AlF₃ composite is shown in Fig. 4b. Two very broad asymmetric bands are observed at Raman frequencies of 1365 and 1600 cm⁻¹, which correspond to the defect activated D band arising from the breathing vibrations of carbon atoms with sp³ hybridization and the graphitic G band due to the bond stretching of sp² carbon atoms in a two-dimensional hexagonal lattice, respectively. The spectrum at high frequency shows a very broad feature, which could be fitted with two very broad bands as well, at the frequencies of 2715 and 3010 cm⁻¹, corresponding to the 2D and D+G Raman overtones, respectively. The integrated intensity ratio of the D to G bands (A_D/A_G) is equal to 1.65 and the respective peak intensity ratio (I_D/I_G) is given as 0.77. These high ratios are indicative of extensive disorder in the structure, which corroborates the lacking graphitic peaks in the XRD patterns. Raman spectroscopy studies on carbon foam materials generally show the peaks of the D and G bands at about 1355 and 1588 cm⁻¹, respectively [43,44] (see marked vertical lines in Fig. 4b). In the case of the C-AlF₃ composite, the two bands are positively shifted and the G band peak reaches the frequency of 1600 cm⁻¹. The above observations in combination with the shape and width of the Raman bands indicate that the carbon foam structure is in stage 2 of the amorphization, which denotes the path from the nanocrystalline graphite to amorphous graphite according to Ferrari's classification [46], in the region where significant sp²-bonded rings still remain in the structure. There, the I_D/I_G ratio is proportional to L_a^2 in accordance to the semi-empirical equation $I_D/I_G = C \cdot L_a^2$, where L_a is the in-plane graphitic correlation length and C is a constant equal to 0.0055 Å⁻² under 514 nm excitation [46]. In this case, the equivalent L_a value was estimated at around 1.7 nm. In order to fully match the observed I_D/I_G ratios with the positive shifts of the Raman bands in

the Ferrari correlation graphs, significant compressive strain of the materials also has to be accounted for [47].

Fig. 4 – (a) X-ray diffractogram and (b) micro-Raman spectrum of the as-prepared C-AlF₃ composite; red and green spectra lines are fitting curves and spectral fitting components, respectively; vertical dashed lines mark the standard position of the D band (1355 cm⁻¹) and the G band (1588 cm⁻¹) [43,44].

3.4 Porosity and related properties

The N₂ adsorption/desorption isotherm recorded at 77 K is shown in Fig. 5a. The degassed C-AlF₃ composite demonstrates a type IV isotherm, as classified by the International Union of Pure and Applied Chemistry (IUPAC), which is characteristic of mesoporous materials (i.e. pore widths between 2 and 50 nm) [48]. The formation of a visible hysteresis loop between the adsorption and desorption curves at higher relative pressures ($P/P_0 > 0.5$) can be attributed to capillary condensation of N₂ gas within the mesopores. The shape of the loop is classified as an H3 type based on IUPAC [48]. However the desorption closing point is not connected with cavitation effects, which give a sharp step-down of the desorption branch at $P/P_0 \sim 0.4$ for N₂ at 77 K. Loops of this type are given by pore networks consisting of macropores (i.e. pores with widths greater than 50 nm) which are not completely filled with pore condensate. The fact that no point of saturation is reached up to the P/P_0 value of ~ 0.99 with the adsorption isotherm rising indefinitely in a vertical path is most likely attributed to N₂ condensation in macropores and/or multi-layer formation on the powder's external rough surface [34]. The specific area of the degassed C-AlF₃ composite was estimated at 50 m²/g using the multi-point BET method (Fig. S5a), while for comparison the equivalent value given by the QSDFT method was almost the same (i.e. 52 m²/g). A t-plot analysis of the data (see Fig. S5b) revealed the existence of quite limited microporosity (i.e. pore widths below 2 nm), with a micropore volume of 0.013 cm³/g and a micropore specific area of around 30 m²/g (representing 60 % of the total specific area). The PSD analysis on the basis of the QSDFT method (Fig. 5b) revealed that the existing pores across the surface should exhibit three size distribution maxima at ~ 1.2 , ~ 8.5 and ~ 14.5 nm, while the cumulative pore volume was

roughly estimated around $0.13 \text{ cm}^3/\text{g}$ for pores with widths less than 50 nm (see inset [Fig. 5b](#)). Based on the above, it seems that the as-prepared C-AlF₃ powder combines contributions of micro-, meso- and macro-porosity as well as external surface, in agreement with the SEM and TEM observations (see [section 3.1](#)).

Fig. 5 – (a) N_2 adsorption (full symbols) and desorption (empty symbols) isotherms recorded at 77 K for the degassed C- AlF_3 powder; the inset shows the adsorption behavior at $P/P_0 < 0.1$ and (b) differential and cumulative (inset) pore size distribution analysis of the degassed C- AlF_3 composite material using the QSDFT method for slit/cylinder-like shape pores in the N_2 desorption data.

3.5 Potential applications and future work

As briefly mentioned in the introduction, AlF_3 can be effectively used in the field of electrochemical energy storage and more specifically in the technology of Li-ion batteries. In this respect, AlF_3 can act as a promising cathode material [18], enhance the performance of graphite anodes [19] as well as improve the electrochemical cycling of Li-enriched nickel- manganese oxide electrodes [20]. Moreover, a coating layer of AlF_3 is proven to be very effective in suppressing the gas generation and swelling behavior of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) anodes in Li-ion batteries, thus allowing the improvement of their high-rate charge/discharge performance [21]. The carbon-based nature of the herein presented C- AlF_3 powder could allow the facile development of such functional components (e.g. electrodes, thin films or coatings) for the aforementioned applications by using binders, pressing or spark plasma sintering methods. Further research is necessary to control the size and dispersion of the AlF_3 nanoparticles within the porous network and to increase the available specific area of the carbonaceous foam by varying the initial Al particle size, mass fraction of Al/THV and combustion conditions. These can help overcome the limitations of the method, such as the cost and safety hazards of Al nanoparticles, while minimizing the release of gaseous HF from the reactions.

4 Conclusions

The current work demonstrates that carbon foam-aluminum fluoride (C- AlF_3) nanocomposite materials can be produced by employing a few-step and rapid combustion synthesis approach as an appealing alternative to well-established wet chemical procedures. Upon flame ignition and combustion of a solid-state mixture of THV fluoropolymer and nano-sized Al powder, a carbon foam-like porous structure doped with cubic- and/or cuboid-like AlF_3 nano-sized particles (i.e. from 100 up to 500 nm; ~240 nm in average) forms due to condensation of the sublimating AlF_3 . These embedded nanoparticles exhibit a rhombohedral α - AlF_3 crystal structure, the foamy matrix displays features of

disordered carbon-based materials, while the C-AlF₃ composite in total shows a combination of micro-, meso- and macro-porous characteristics with an available specific area of ~50 m²/g. The combustion synthesis method could have a significant impact on the design and development of composite material systems (e.g. carbon-metal, carbon-metal fluoride, etc.), while the structural optimization of the herein presented C-AlF₃ nanocomposite can potentially allow its usage in green energy-related applications such as electrochemical energy storage.

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Supplementary information associated with this article can be found in the online version.

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Supplementary Material

Fig. S1 – Particle size distribution histogram derived from a statistical analysis of 39 cubic nano-sized crystals from three different SEM images. The minimum and maximum particle sizes correspond to 100 and 550 nm, respectively, the average particle size is 240 nm, while the standard deviation is 96 nm.

Fig. S2 – High-magnification TEM image of the solid THV-nAl mixture dissolved in acetone and dried onto Cu grids. The clusters of Al nanoparticles are dispersed within the THV polymer matrix. The overall mass percent within the image is similar to the overall composition of the bulk composite.

Fig. S3 – (a) High-magnification SEM image showing the surface region investigated by EDX and (b) the respective EDX spectrum of the C-AlF₃ composite material; the inset table shows the atomic percentages of the detected elements (C, O, F and Al) excluding Au, which refers to the sputter-coating material used for improved conductivity for the SEM/EDX studies.

Fig. S4 – Elemental mapping of the C-AlF₃ microstructure using combined SEM/EDX. Left: SEM image with numbered regions (1 to 4) indicating nano-sized cubic AlF₃ crystals embedded within the surface; Right: corresponding elemental maps (C, O, F and Al) using EDX.

Fig. S5 – (a) Multi-point BET plot and (b) Carbon Black t-plot of the degassed C-AlF₃ sample showing a correlation coefficient of close-to-unity ($r \sim 1$).