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## Power Electronic Devices and Components



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# Unleashing the power: Superior properties of fluorographene-derived materials for energy storage applications

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ARTICLE INFO

Keywords: Fluorographene Graphite fluoride Supercapacitors Li-ion batteries Li-S batteries Graphene derivatives

### ABSTRACT

Fluorographene exhibits a rich chemistry and a wide range of applications in energy storage devices. This review, which is based on our lab results acquired in the last decade, explores the synthesis, properties, and performance of fluorographene-based materials in supercapacitors and batteries. Fluorographene can be prepared through mechanical or chemical delamination of graphite fluoride, allowing for scalable synthesis and further chemical processing. The chemical versatility of fluorographene enables a wide portfolio of chemical reactions, leading to a new class of graphene derivatives. Graphene acid, a product of fluorographene chemistry, exhibits excellent specific capacitance, cycling stability, and rate capability. Hybridizing graphene acid with metal-organic frameworks can achieve even higher energy and power densities. Furthermore, nitrogen-doped graphene derived from fluorographene demonstrates remarkable capacitive behavior, making it an efficient electrode material for supercapacitors. Additionally, fluorographene-based materials, such as graphene acid, graphene-sulfur hybrids, and graphene-based anodes, have exhibited outstanding performance in lithium-in and lithium-sulfur batteries. The scalable synthesis, high performance, and versatility of fluorographene-derived for practical energy storage applications. The unique properties and wide range of chemistries offered by fluorographene chemistry open new possibilities for improving advanced energy storage devices.

#### Introduction

Graphene derivatives have shown great potential as favorable substances for energy storage purposes, particularly in the realm of supercapacitors and materials utilized in battery electrodes. However, the direct preparation of graphene derivatives from graphene is hindered by the high chemical inertness of graphene. This calls for alternative pathways leading to graphene derivatives. One possible solution is the utilization of fluorographene chemistry, which can be carried out under mild and controllable conditions (Chronopoulos et al., 2017). Furthermore, the chemistry of fluorographene benefits from a readily available pristine material, graphite fluoride. This material is available in tons on the market as an industrial lubricant and primary battery electrode material. So far, various graphene derivatives have been prepared using fluorographene chemistry. These derivatives dispose various promising properties, which can be utilized in sensing, imaging, single-atom catalysis, and energy storage devices, including supercapacitors and batteries.

### Fluorographene

Fluorographene, which was discovered in 2010, can be prepared i) up-down by mechanical or chemical delamination of graphite fluoride and ii) bottom-up by fluorination of graphene. Particularly the chemical

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https://doi.org/10.1016/j.pedc.2024.100058

Received 17 August 2023; Received in revised form 6 January 2024; Accepted 17 January 2024 Available online 18 January 2024

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**Fig. 1.** Schematic depiction of fluorographene production by graphite fluoride exfoliation (a) and its reactivity offering variously functionalized graphene derivatives (b). Numbers in brackets refer to the literature as listed in the references.

exfoliation is suitable for upscaling fluorographene synthesis and further chemical processing (Fig. 1a). As a perfluorinated hydrocarbon labeled as a two-dimensional Teflon counterpart (Nair et al., 2010), it was considered unreactive due to the strength of the carbon-fluorine bond, which is regarded as one of the strongest single chemical bonds. The C-F bonds on tertiary carbon atoms, which make the backbone of fluorographene, are considered an Achilles heel of fluorocarbons. In addition, real fluorographene samples contain radical defects (Medved et al., 2018), which are strong electrophiles and trigger a rich chemistry of fluorographene, leading to a broad portfolio of surface functionalized graphenes (Matochová et al., 2018).

As depicted in Fig. 1b, fluorographene can undergo a wide portfolio of chemical reactions primarily based on defect-induced nucleophilic substitution (Matochová et al., 2018; Bakandritsos et al., 2017; Tuček et al., 2017; Tantis et al., 2021; Urbanová et al., 2015; Whitener et al., 2015; Vermisoglou et al., 2019; Vermisoglou et al., 2021; Zhao et al., 2019). Fluorographene reacts with Grignard reagents (Chronopoulos et al., 2017a; Mazánek et al., 2017) and chemicals formed during Friedel-Crafts (Lai et al., 2018), Suzuki-Miyaura (Huang et al., 2021), Sonogashira (Chronopoulos et al., 2019), and Bingel-Hirsch-type reactions (Bakandritsos et al., 2018). The nitrogen doping of graphene lattice can also be achieved by fluorographene chemistry due to the healing of introduced vacancies with nitrogen species (Zoppellaro et al., 2019; Zaoralová et al., 2020; Šedajová et al., 2022). In addition, fluorine atoms in partially fluorinated graphene may promote cycloaddition reactions. This was initially observed with dichlorocarbene inducing cyclopropanation on fluorographene (Lazar et al., 2015), followed by the Diels-Alder reaction for s-cis-dienes binding to the graphene surface (Barès et al., 2019). One (Chronopoulos et al., 2020) or two-step (Barès et al., 2019) double functionalization of fluorographene was also successfully achieved. Fluorographene chemistry always includes two channels, one causing fluorographene defluorination toward sp<sup>2</sup> carbons and the other leading to fluorine replacement by another functional group (Matochová et al., 2018). Therefore, the as-prepared graphene derivatives are conductive (due to an established network of conjugated sp<sup>2</sup> carbons) and homogeneously surface-functionalized graphenes on both sides, reaching degrees of functionalization from a

few up to dozens of percent. This unique, scalable, and well-controllable chemistry represents a vivid strategy for achieving chemically well-defined graphenes. From the industrial point of view, it must be emphasized that the synthesis and the resulting graphene derivatives are well reproducible (Sedajová et al., 2020), and some of them are already marketed (see graphene-derivatives.com).

The utilization of fluorographene chemistry as a tailored way to prepare novel graphene-based materials aligns with Regulation of Hazardous Substances (RoHS) directives (RoHS Directive - European Commission, 2022) if any of the used chemicals in the entire chemical process, including precursors, are not restricted under RoHS. The process is also more environmentally friendly compared with other processes, leading to graphene doping or functionalization. Operating mainly under mild conditions and low temperatures (<150 °C) (Zaoralová et al., 2020), the synthetic protocols involve low energy consumption and prevent the generation of hazardous gases. Moreover, most synthetic protocols are metal-free and devoid of heavy metal contaminants (Chronopoulos et al., 2017b; Hrubý et al., 2022a); their adaptability allows for the use of non-toxic solvents or facilitates the utilization of high-toxicity solvents with a possibility for closed-loop systems for recycling. The reproducibility of these materials also underscores the reliability of the fluorographene chemistry and offers considerable potential for scale-up productions (Bakandritsos et al., 2017; Šedajová et al., 2020; Obraztsov et al., 2022). For the subsequent use of these materials in electronic devices, significant efforts have been made to replace toxic and flammable electrolytes in batteries and supercapacitors and avoid using heavy and critical elements (Vermisoglou et al., 2021; Zaoralová et al., 2020; Titirici, 2021; Cavers et al., 2022). The end products resulting from fluorographene chemistry, comprised of naturally abundant elements, emerge as promising contenders due to their outstanding performance and as a significant stride towards a complete dedication to sustainable practices. It is worth noting, however, that a comprehensive Life Cycle Assessment (LCA) of fluorographene chemistry, which thoroughly evaluates the environmental impacts of products and processes across their entire life cycle, has not been published to date.

Fluorographene is a wide electronic gap semiconductor with a



**Fig. 2.** (a) GCD profiles depicting the behavior of GCEs modified with fluorographene subjected to hydrogen treatment at 450 °C for varying durations. (b) Exploration of the relationship between specific capacitance and time of fluorographene treatment. (c) GCD profiles illustrating the response of the FG-20H sample to current densities. (d) Investigation into the impact of current density on the FG-20H specific capacitance. The contour plot (e) revealing the interplay between specific capacitance, fluorographene treatment time, and diverse current densities. (f) Assessment of FG-20H life-time stability within a three-electrode setup. The experiments were realized using a 1 M Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte. Reproduced from the reference (Petr et al., 2019), The Royal Society of Chemistry, copyright 2019.

predicted electronic band gap of 7.1 eV (Dubecký et al., 2020) and an experimentally determined optical band gap of 5.75 eV (Hrubý et al., 2022b), which corresponds to the predicted value of 5.92 eV (Karlický & Otyepka, 2014) for the perfect structure of fluorographene. The electronic band gap is the energy difference between the top of the valence band and the bottom of the conduction band. The optical band gap, on the other hand, corresponds to the lowest energy dipole-allowed transition observable in absorption spectra. The optical band gap usually has lower energy than the electronic band gap due to the electrostatic binding between the excited electron and hole, forming an exciton. Fluorographene displays a high exciton binding energy of 1.9 eV (Karlický & Otyepka, 2014). It should be noted that defects in the fluorographene structure cause a formation of mid-gap states responsible for

absorptions at significantly lower energies and fluorographene fluorescence (Hrubý et al., 2022b). Such optoelectronic properties of fluorographene may be tunable, making it applicable in short-wavelength optical applications, power electronics, and high-temperature electronics (Morkoç et al., 1994).

Graphite fluoride, i.e., fluorographene pristine material, is used as electrode material in lithium primary batteries (Nakajima, 2013). Exfoliated graphite fluoride and fluorographene materials have been investigated as cathode materials for lithium batteries (Sun et al., 2014; Wang et al., 2019) and sodium primary batteries (Li et al., 2023). Alongside battery research, supercapacitors are intensively explored energy storage devices. In this field, fluorographene nanosheets have been identified as a potential supercapacitor electrode material (Lv



**Fig. 3.** (a) Galvanostatic charge–discharge (GCD) behavior of graphene acid (GA) within a dual-electrode arrangement, investigated over a broad spectrum of current densities. (b) Analysis of the specific capacitance as it reacts to escalating current density increments. (c) Examination of the robustness of GA performance under varying current densities, assessing its rate stability. (d) Assessment of the long-time stability of GA over a span of 60,000 cycles; inset illustrates the initial and final ten cycles at a potential range of 1 V (measured in -0.35-0.65 V range). (e) Evaluation of the operational efficiency of two supercapacitor cells, each utilizing GA, explored both in serial or parallel configurations. (f) Testing of two supercapacitor cells integrated with GA and connected in series demonstrated through an LED experiment. All experiments were performed utilizing a 1 M H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte. Reproduced from reference (Sedajová et al., 2020), MDPI, copyright 2020.

et al., 2019). However, the insulating properties of fluorographene hinder its direct application as supercapacitor electrode material. Therefore, the chemical derivatization of fluorographene towards higher  $sp^2$  carbon content makes it a more efficient supercapacitor electrode material (Bakandritsos et al., 2019).

## Derivatized fluorographene as supercapacitor electrode material

Higher efficiency of derivatized fluorographene in supercapacitors was demonstrated on partially isothermally reduced fluorographene at 450 °C, which was prepared in a reducing atmosphere of hydrogen. The final composition, i.e., carbon  $sp^2/sp^3$  ratio, of the partially reduced fluorographene was fine-tuned by thermal treatment time. Among the set of prepared and tested samples, the highest performance was achieved with the fluorographene sample after 20-hour thermal treatment (FG-20H sample, Fig. 2a and b). The optimized material demonstrated very high specific capacitance values of 539 F/g (Fig. 2c–e) at 0.25 A/g current density. In a three-electrode setup (Fig. 2f), it also exhibited high cycling durability, retaining 100 % of its specific capacitance after 1500 cycles and maintaining 96.7 % of its specific capacitance after enduring 30,000 cycles in a two-electrode configuration (Petr et al., 2019).

Graphene acid is a well-described, standardized, and already available product of fluorographene chemistry on the market. The graphene acid is produced through a two-step synthesis via a cyanographene intermediate. It bears  $\sim 12$  % of carboxyl groups covalently grafted on

both surface sides homogeneously (Bakandritsos et al., 2017). It is a conductive (~25 S/m), perfectly water-dispersible, and nontoxic material, making it an excellent candidate for supercapacitor electrodes. This has been demonstrated by assembling a two-electrode symmetric capacitor cell from an aqueous suspension of graphene acid and aqueous 1 M H<sub>2</sub>SO<sub>4</sub> as an electrolyte (Sedajová et al., 2020). Such a system manifested only a slow decline in specific capacitance with the rising current density after scanning its GCD responses across a wide range of current densities (Fig. 3a and b). This behavior was also stable over several cycles with varying current densities as a part of the rate test (Fig. 3c). Further experiments at 3 A/g concluded that graphene acid demonstrated a capacitance of ~100 F/g and high stability of specific capacitance (> 95 %) after 60,000 GCD cycles in a two-electrode setup (Fig. 3d) (Šedajová et al., 2020; Heng Cheong et al., 2019). Meeting the energy or power requirements for practice, the supercapacitors were connected in parallel or in series, respectively, to extend both voltage window and capacitance performance (Fig. 3e and f).

Combining graphene acid with a metal-organic framework (MOF) materials further enhances its performance (Jayaramulu et al., 2021). When graphene acid is hybridized with amine-terminated MOF, the resulting hybrid material serves as an efficient charge storage nanomaterial, exhibiting a capacitance of 650 F/g. This hybrid system works well as the positive electrode in an asymmetric capacitor, paired with a  $Ti_3C_2T_x$  MXene opposing electrode and 1 M Na<sub>2</sub>SO<sub>4</sub> as the electrolyte. Such a system demonstrates an impressive energy density of 73 Wh/kg



**Fig. 4.** The electrochemical behavior of the  $GA@UiO-66-NH_2/Ti_3C_2T_x$  asymmetric supercapacitor was subjected to evaluation using a 1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte. The analysis included: (a) GCD profiles recorded under diverse current densities. (b) Exploration of the relationship of specific capacitance vs. current density. (c) A comparison of the device's performance through a Ragone plot against other asymmetric systems. (d) Assessment of life-time stability through a 10,000-cycle examination at 5.2 A/g and Coulombic efficiency assessment. The figure was reproduced from the ref. (Jayaramulu et al., 2021), John Wiley and Sons, copyright 2021.

and a power density of 16 kW/kg (Jayaramulu et al., 2021). These values are close to those of commercial devices like nickel-metal hydride and lead-acid batteries. Even after undergoing 10,000 cycles at an intermediate loading level, the device keeps 88 % of capacitance (Fig. 4).

Nitrogen-doped graphenes obtained by reducing fluorographene using nitrogen-containing compounds represent another fascinating class of materials highly suited for supercapacitor electrodes (Zoppellaro et al., 2019; Zaoralová et al., 2020; Šedajová et al., 2022). Among them, GN3 (prepared by the reaction of fluorographene with sodium azide) stands out as a nitrogen-doped graphene with exceptionally high levels of nitrogen (~16 %) and containing diamond-like bonds. Compared with graphite, it has a higher density of 2.8 g/mL (Sedajová et al., 2022). This unique material exhibits unprecedented capacitive behavior. When utilized as active material in a symmetric capacitor, paired with an ionic liquid electrolyte (1-ethyl-3-methylimidazolium tetrafluoroborate, EMIM-BF4, and 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) in a 9:1 ratio), it displays remarkable volumetric energy density (200 Wh/L) and power density (52 kW/L) while maintaining excellent cycling stability (Fig. 5). Since such values are record among the high-performance supercapacitor materials (Fig. 6), commercialization of the nitrogen-doped graphene (labeled as SC-GN3) is under development with the support of the EIC Transition project (trans2Dchem.com) funded by the European Union. The qualification of the initial prototypes, featuring both wound (cylindrical) and pouch geometries, is scheduled for 2024.

#### Fluorographene-derived materials as Li battery electrodes

The effectiveness of materials derived from fluorographene has also been demonstrated in lithium batteries as efficient electrode materials. In the case of graphene acid, its carboxylic groups can reversibly bind lithium ions, making it a promising high-energy anode. Experiments have revealed that the graphene acid anode exhibits exceptional charge transport, Li intercalation properties, and redox activity at the singlelayer level while maintaining the electrode stability (Fig. 7). This behavior surpasses all previously reported organic anodes, incorporating commercial graphene and nanoplatelets of graphene (Fig. 8) (Obraztsov et al., 2022). With a practical capacity of 800 mAh/g (0.05 A/g) and a rate capability of 174 mAh/g (2.0 A/g), the graphene acid anodes demonstrate their true potential in advanced lithium-ion batteries.

The chemistry of fluorographene also enables the covalent conjugation of graphene with polysulfide chains, resulting in the development of polysulfide covalently-interlinked graphene (GPS). This remarkable material exhibits exceptional potential as a Li-sulfur battery cathode nanomaterial due to its outstanding characteristics. The GPS cathode depicts a high full-cathode-mass capacity and rate ability, coupled with excellent cycling stability, effectively addressing the challenges associated with the shuttling effect (Tantis et al., 2021). Cathodes composed of 90 % GPS, 5 % conductive additive, and 5 % binder were evaluated against metallic lithium in a Li bis(trifluoromethanesulfonyl)imide (LiTFSI) electrolyte dissolved in dioxolane and tetraethylene glycol dimethyl ether (DOL:TTE) mixture. The CD process of this Li-S system exhibited excellent reversibility (Fig. 9a), demonstrating two discharge plateaus with capacities of 418 mAh/g and 1254 mAh/g using a specific 0.1 C current (Fig. 9b). The electrochemical profiles during galvanostatic charge/discharge were maintained over 50 cycles at a specific current of 0.1 C (Fig. 9c), highlighting the high electrochemical reversibility of the GPS cathode. The GPS material exhibited exceptional stability at high and low specific currents, retaining initial capacities above 470 mAh/g even after 500 cycles at 1 C current (Fig. 9d). Moreover, the GPS cathode achieved capacities of 485 mAh/g at 1 C and 290 mAh/g at 2 C (Fig. 9e). Compared to noncovalent graphene-sulfur (GS) derivatives, the GPS cathode outperformed them, exhibiting superior stability compared to other sulfur-based materials investigated for lithium-sulfur batteries. The stability of GPS over GS is further evidenced by the absence of elemental sulfur in the separator after 250 cycles. In contrast, sulfur was observed in the GS sample after only 45



**Fig. 5.** Electrochemical analysis of a symmetrical supercapacitor configuration utilizing GN3 electrodes. (a) Cyclic voltammograms in EMIM-BF<sub>4</sub> and TTE (9:1) electrolyte. (b) GCD curves recorded at different current densities. (c) Energy density and power density of GN3 electrodes. (d) Comparative study pitting the GN3 cell against symmetrical cells constructed with commercially available high surface area carbon materials (2 A/g), and (e) parameters of the devices. (f) Demonstration of life-time stability for GN3 under 20 A/g current density. The figure was reproduced from the ref. (Sedajová et al., 2022), The Royal Society of Chemistry, copyright 2021.



**Fig. 6.** (a) Compared to electrodes crafted from commercial 2000  $m^2/g$  active carbon and notable counterparts sourced from literature, handpicked for their promising attributes, GN3 electrodes achieve higher energy and power density output. These analogs include holey graphene (holey G) (Sun et al., 2014), dense MEGO (compressed, microwave expanded, and activated reduced graphene oxide) (Wang et al., 2019), tri-doped carbon (Li et al., 2023), densified G (capillary densified graphene) (Lv et al., 2019), ultrathick graphene (Bakandritsos et al., 2019), 1T-MoS<sub>2</sub> (Petr et al., 2019), and EGM-GO (exfoliated graphene-mediated graphene oxide) (Heng Cheong et al., 2019). (b) When considering a GN3 mass loading of 10 mg/cm, the specific capacitance in a symmetric cell reaches 99 % of the recorded capacitance from a mass loading of 1 mg/cm. GN3 electrode coin cells on aluminum foils, both prior (c) and after assemblage (d). The constructed cell successfully powered a 4 V LED. The figure was reproduced from the ref. (Šedajová et al., 2022), The Royal Society of Chemistry, copyright 2021.



**Fig. 7.** Electrochemical evaluation of graphene acid in a half-cell versus lithium includes the following tests: (a) Assessment of rate capability; (b) The 10th CD curve extracted from the test described in (a). (c) Analysis of cycling performance at 0.2 A/g following a single cycle at 0.05 A/g at a temperature of  $24 \pm 2$  °C. (d) A comparative study between GA and anodes composed of graphene and nanoplatelets of graphene (0.05 A/g, 5th cycle), conducted under the same conditions. Open symbols describe lithiation in panels (a) and (c), while full symbols indicate delithiation. The figure was reproduced from the ref. (Obraztsov et al., 2022), John Wiley and Sons, copyright 2021.



**Fig. 8.** Comparing the performance of GA with various organic materials includes PTp-COOH [44], humic acid [45], G/c-PMMA [46], 2,6-Naph(COOLi)<sub>2</sub> [47], Li<sub>2</sub>(SND), Li<sub>2</sub>(SNB) [48], as well as electrodes utilizing commercial graphene (both monolayer and nanoplatelets). Capacities are normalized to the overall electrode material mass and pertain to the stable capacity during the current rate assessments. The figure was reproduced from the ref. (Obraztsov et al., 2022), from the John Wiley and Sons, copyright 2021.

cycles (Fig. 9f). The lasagna-like structure of GPS prevented the sulfur shuttling effect, which typically stands behind a low cyclability of Li-S batteries (LSBs).

## **Conclusions and perspectives**

Fluorographene chemistry offers an industrially scalable process that leads to a new class of densely homogeneous and surface-functionalized graphenes. These materials exhibit immense versatility for a broad range of energy storage applications, containing, for instance, supercapacitors and batteries. Among supercapacitor electrodes, GN3 stands out with its exceptional energy and power densities, making it an up-and-coming candidate for the transition of graphene supercapacitor devices into real-world applications soon. On the other hand, graphene acid, the most versatile among fluorographene-derived materials, exhibits excellent capacitive behavior in a simple system of aqueous sulfuric acid electrolytes, offering a cost-effective and eco-friendly alternative. The capacitive abilities of graphene acid can be further enhanced through hybridization with metal-organic frameworks (MOFs), opening up new routes for improved energy storage performance. Additionally, graphene acid exhibits remarkable potential as a high-energy content anode in organic lithium batteries, thanks to its reversible reaction with lithium ions, leading to significant performance enhancements. Lastly, owing to its interlinked graphene superstructure character, GPS material may serve as an unprecedent cathode material in Li-S batteries, overcoming the sulfur shuttling effect and retaining high capacity over time. Overall, the tested fluorographene-derived materials have proven to be highly efficient electrode materials for applications related to energy storage. Given the elegance of fluorographene chemistry, we anticipate the emergence of more fluorographene-derived materials, expanding the possibilities in energy storage devices and further pushing their efficiency limits.

## CRediT authorship contribution statement

Vítězslav Hrubý: Visualization, Writing – original draft, Writing – review & editing. Veronika Šedajová: Conceptualization, Investigation, Writing – original draft, Writing – review & editing. Petr Jakubec: Supervision, Visualization, Writing – original draft, Writing – review & editing. Aristides Bakandritsos: Conceptualization, Writing – original draft. Radek Zbořil: Conceptualization, Writing – original draft. Michal Otyepka: Conceptualization, Funding acquisition, Supervision, Writing – original draft, Writing – review & editing.



**Fig. 9.** Assessing the electrochemical effectiveness of the GPS electrode vs. Li within a 1 M LiTFSI solution using DOL:TTE (1:1) electrolyte involves the following analyses: (a) Cyclic voltammograms. (b) Presentation of CD profiles. (c,d) Evaluation of cycling stability. (e) Study of rate capability at a range of rates spanning from 0.2 to 2 C. (f) Depiction of images showing the glass fiber separator after cycling for both the GPS and GS cathodes (1672 mA/g = 1 C). The illustrated specific capacities are based on the mass of S content. The figure was reproduced from the ref. (Tantis et al., 2021), John Wiley and Sons, copyright 2021.

#### 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.

## Data availability

No data was used for the research described in the article.

## Acknowledgments

The work was supported by ERC (2Dchem ID:683024), ERC PoC (UP2Dchem ID:899245 and FunGraB ID:101069293), and EIC Transition (Trans2Dchem ID:101057616) grants. We also acknowledge support from the ERDF/ESF project TECHSCALE (no. CZ.02.01.01/00/22\_008/0004587) and the financial support of the European Union under the REFRESH – Research Excellence For REgion Sustainability and High-tech Industries project number CZ.10.03.01/00/22\_003/000048 via the Operational Programme Just Transition. This review also relates to the presentation given by Michal Otyepka at the 4th PCNS Passive Components Networking Symposium conference held from September 11th to 14th, 2023, in Sønderborg, Denmark.

#### References

Bakandritsos, A., Chronopoulos, D. D., Jakubec, P., Pykal, M., Čépe, K., Steriotis, T., Kalytchuk, S., Petr, M., Zbořil, R., & Otyepka, M. (2018). High-performance supercapacitors based on a Zwitterionic network of covalently functionalized graphene with iron tetraaminophthalocyanine. Advanced Functional Materials, 28, Article 1801111. https://doi.org/10.1002/adfm.201801111

- Bakandritsos, A., Jakubec, P., Pykal, M., & Otyepka, M. (2019). Covalently functionalized graphene as a supercapacitor electrode material. *FlatChem*, 13, 25–33. https://doi.org/10.1016/j.flatc.2018.12.004
- Bakandritsos, A., Pykal, M., Błoński, P., Jakubec, P., Chronopoulos, D. D., Poláková, K., Georgakilas, V., Čépe, K., Tomanec, O., Ranc, V., Bourlinos, A. B., Zbořil, R., & Otyepka, M. (2017). Cyanographene and graphene acid: Emerging derivatives enabling high-yield and selective functionalization of graphene. ACS Nano, 11, 2982–2991. https://doi.org/10.1021/acsnano.6b08449
- Barès, H., Bakandritsos, A., Medved, M., Ugolotti, J., Jakubec, P., Tomanec, O., Kalytchuk, S., Zbořil, R., & Otyepka, M. (2019). Bimodal role of fluoroine atoms in fluorographene chemistry opens a simple way toward double functionalization of graphene. *Carbon*, 145, 251–258. https://doi.org/10.1016/j.carbon.2019.01.059
- Cavers, H., Molaiyan, P., Abdollahifar, M., Lassi, U., & Kwade, A. (2022). Perspectives on improving the safety and sustainability of high voltage lithium-ion batteries through the electrolyte and separator region. Advanced Energy Materials, 12, Article 2200147. https://doi.org/10.1002/aenm.202200147
- Chronopoulos, D. D., Bakandritsos, A., Lazar, P., Pykal, M., Čépe, K., Zbořil, R., & Otyepka, M. (2017). High-yield alkylation and arylation of graphene via grignard reaction with fluorographene. *Chemistry of Materials : A Publication of the American Chemical Society*, 29, 926–930. https://doi.org/10.1021/acs.chemmater.6b05040
- Chronopoulos, D. D., Bakandritsos, A., Pykal, M., Zbořil, R., & Otyepka, M. (2017). Chemistry, properties, and applications of fluorographene. *Applied Materials Today*, 9, 60–70. https://doi.org/10.1016/j.apmt.2017.05.004
- Chronopoulos, D. D., Medved', M., Błoński, P., Nováček, Z., Jakubec, P., Tomanec, O., Bakandritsos, A., Novotná, V., Zbořil, R., & Otyepka, M. (2019). Alkynylation of graphene via the Sonogashira C–C cross-coupling reaction on fluorographene. *Chemical Communications*, 55, 1088–1091. https://doi.org/10.1039/C8CC08492K
- Chronopoulos, D. D., Medveď, M., Potsi, G., Tomanec, O., Scheibe, M., & Otyepka, M. (2020). Tunable one-step double functionalization of graphene based on fluorographene chemistry. *Chem. Commun.*, 56, 1936–1939. https://doi.org/ 10.1039/C9CC09514D
- Dubecký, M., Karlický, F., Minárik, S., & Mitas, L. (2020). Fundamental gap of fluorographene by many-body GW and fixed-node diffusion Monte Carlo methods. *The Journal of Chemical Physics*, 153, Article 184706. https://doi.org/10.1063/ 5.0030952
- Heng Cheong, Y., Nasir, M. Z. M., Bakandritsos, A., Pykal, M., Jakubec, P., Zbořil, R., Otyepka, M., & Pumera, M. (2019). Cyanographene and graphene acid: The functional group of graphene derivative determines the application in electrochemical sensing and capacitors. *ChemElectroChem*, 6, 229–234. https://doi. org/10.1002/celc.201800675

- Hrubý, V., Zaoralová, D., Medveď, M., Bakandritsos, A., Zbořil, R., & Otyepka, M. (2022). Emerging graphene derivatives as active 2D coordination platforms for single-atom catalysts. *Nanoscale*, 14, 13490–13499. https://doi.org/10.1039/D2NR03453K
- Hrubý, V., Zdražil, L., Dzíbelová, J., Šedajová, V., Bakandritsos, A., Lazar, P., & Otyepka, M. (2022). Unveiling the true band gap of fluorographene and its origins by teaming theory and experiment. *Applied Surface Science*, 587, Article 152839. https://doi.org/10.1016/i.apsusc.2022.152839
- Huang, F., Li, Y., Liu, X., Lai, W., Fan, K., Liu, X., & Wang, X. (2021). Suzuki–Miyaura reaction of C–F bonds in fluorographene. *Chemical Communications*, 57, 351–354. https://doi.org/10.1039/D0CC07651A
- Jayaramulu, K., Horn, M., Schneemann, A., Saini, H., Bakandritsos, A., Ranc, V., Petr, M., Stavila, V., Narayana, C., Scheibe, B., Kment, S., Otyepka, M., Motta, N., Dubal, D., Zbořil, R., & Fischer, R. A. (2021). Covalent graphene-MOF hybrids for highperformance asymmetric supercapacitors. Advanced Materials, 33, Article 2004560. https://doi.org/10.1002/adma.202004560
- Karlický, F., & Otyepka, M. (2014). Band gaps and optical spectra from single- and double-layer fluorographene to graphite fluoride: many-body effects and excitonic states: Band gaps and optical spectra from single- and double-layer fluorographene to graphite fluoride. Annalen Der Physik, 526, 408–414. https://doi.org/10.1002/ andp.201400095
- Lai, W., Liu, J., Luo, L., Wang, X., He, T., Fan, K., & Liu, X. (2018). The Friedel–Crafts reaction of fluorinated graphene for high-yield arylation of graphene. *Chemical Communications*, 54, 10168–10171. https://doi.org/10.1039/C8CC05762A
- Lazar, P., Chua, C. K., Holá, K., Zbořil, R., Otyepka, M., & Pumera, M. (2015). Dichlorocarbene-functionalized fluorographene: Synthesis and reaction mechanism. Small (Weinheim an der Bergstrasse, Germany), 11, 3790–3796. https://doi.org/ 10.1002/smll.201500364
- Li, Y.-Y., Liu, C., Chen, L., Wu, X.-Z., Zhou, P.-F., Shen, X.-Y., & Zhou, J. (2023). Multilayered fluorinated graphene cathode materials for lithium and sodium primary batteries. *Rare Metals*, 42, 940–953. https://doi.org/10.1007/s12598-022-02155-2
- Lv, J., Zeng, P., Abbas, S. C., Guan, X., Luo, P., Chen, D., & Wang, Y. (2019). Electrochemically scalable production of bilayer fluorographene nanosheets for solid-state supercapacitors. *Journal of Materials Chemistry A*, *7*, 16876–16882. https://doi.org/10.1039/C9TA04421C
- Matochová, D., Medved', M., Bakandritsos, A., Steklý, T., Zbořil, R., & Otyepka, M. (2018). 2D Chemistry: Chemical control of graphene derivatization. *The Journal of Physical Chemistry Letters*, 9, 3580–3585. https://doi.org/10.1021/acs. jpclett.8b01596
- Mazánek, V., Libánská, A., Šturala, J., Bouša, D., Sedmidubský, D., Pumera, M., Janoušek, Z., Plutnar, J., & Sofer, Z. (2017). Fluorographene modified by grignard reagents: A broad range of functional nanomaterials. *Chemistry – A European Journal*, 23, 1956–1964. https://doi.org/10.1002/chem.201604989
- Medveď, M., Zoppellaro, G., Ugolotti, J., Matochová, D., Lazar, P., Pospíšil, T., Bakandritsos, A., Tuček, J., Zbořil, R., & Otyepka, M. (2018). Reactivity of fluorographene is triggered by point defects: beyond the perfect 2D world. *Nanoscale*, 10, 4696–4707. https://doi.org/10.1039/C7NR09426D
- Morkoç, H., Strite, S., Gao, G. B., Lin, M. E., Sverdlov, B., & Burns, M. (1994). Largeband-gap SiC, III-V nitride, and II-VI ZnSe-based semiconductor device technologies. *Journal of Applied Physics*, 76, 1363–1398. https://doi.org/10.1063/1.358463
- Nair, R. R., Ren, W., Jalil, R., Riaz, I., Kravets, V. G., Britnell, L., Blake, P., Schedin, F., Mayorov, A. S., Yuan, S., Katsnelson, M. I., Cheng, H.-M., Strupinski, W., Bulusheva, L. G., Okotrub, A. V., Grigorieva, I. V., Grigorenko, A. N., Novoselov, K. S., & Geim, A. K. (2010). Fluorographene: A two-dimensional counterpart of teflon. *Small (Weinheim an der Bergstrasse, Germany), 6*, 2877–2884. https://doi.org/10.1002/smll.201001555
- Nakajima, T. (2013). Fluorine compounds as energy conversion materials. Journal of Fluorine Chemistry, 149, 104–111. https://doi.org/10.1016/j.jfluchem.2013.02.007 Obraztsov, I., Bakandritsos, A., Šedajová, V., Langer, R., Jakubec, P., Zoppellaro, G.,
- Obraztsov, I., Bakandritsos, A., Sedajova, V., Langer, R., Jakubec, P., Zoppellaro, G., Pykal, M., Presser, V., Otyepka, M., & Zböril, R. (2022). Graphene acid for lithiumion batteries—carboxylation boosts storage capacity in graphene. Advanced Energy Materials, 12, Article 2103010. https://doi.org/10.1002/aenm.202103010

- Petr, M., Jakubec, P., Ranc, V., Šedajová, V., Langer, R., Medveď, M., Błoński, P., Kašlík, J., Kupka, V., Otyepka, M., & Zbořil, R. (2019). Thermally reduced fluorographenes as efficient electrode materials for supercapacitors. *Nanoscale*, 11, 21364–21375. https://doi.org/10.1039/C9NR07255A
- RoHS Directive European Commission, (2022). https://environment.ec.europa.eu/top ics/waste-and-recycling/rohs-directive\_en (accessed January 4, 2024).
- Šedajová, V., Bakandritsos, A., Błoński, P., Medveď, M., Langer, R., Zaoralová, D., Ugolotti, J., Dzíbelová, J., Jakubec, P., Kupka, V., & Otyepka, M. (2022). Nitrogen doped graphene with diamond-like bonds achieves unprecedented energy density at high power in a symmetric sustainable supercapacitor. *Energy & Environmental Science*, 15, 740–748. https://doi.org/10.1039/D1EE02234B
- Šedajová, V., Jakubec, P., Bakandritsos, A., Ranc, V., & Otyepka, M. (2020). New limits for stability of supercapacitor electrode material based on graphene derivative. *Nanomaterials*, 10, 1731. https://doi.org/10.3390/nano10091731
- Sun, C., Feng, Y., Li, Y., Qin, C., Zhang, Q., & Feng, W. (2014). Solvothermally exfoliated fluorographene for high-performance lithium primary batteries. *Nanoscale*, 6, 2634–2641. https://doi.org/10.1039/C3NR04609E
- Tantis, I., Bakandritsos, A., Zaoralová, D., Medveď, M., Jakubec, P., Havláková, J., Zboril, R., & Otyepka, M. (2021). Covalently interlinked graphene sheets with sulfurchains enable superior lithium-sulfur battery cathodes at full-mass level. Advanced Functional Materials, 31, Article 2101326. https://doi.org/10.1002/adfm.202101326
- Titirici, M.-M. (2021). Sustainable batteries—quo vadis? Advanced Energy Materials, 11, Article 2003700. https://doi.org/10.1002/aenm.202003700
- Tuček, J., Holá, K., Bourlinos, A. B., Błoński, P., Bakandritsos, A., Ugolotti, J., Dubecký, M., Karlický, F., Ranc, V., Čépe, K., Otyepka, M., & Zbořil, R. (2017). Room temperature organic magnets derived from sp3 functionalized graphene. *Nature Communications*, 8, 14525. https://doi.org/10.1038/ncomms14525
- Urbanová, V., Holá, K., Bourlinos, A. B., Čépe, K., Ambrosi, A., Loo, A. H., Pumera, M., Karlický, F., Otyepka, M., & Zbořil, R. (2015). Thiofluorographene–hydrophilic graphene derivative with semiconducting and genosensing properties. Advanced Materials, 27, 2305–2310. https://doi.org/10.1002/adma.201500094
- Vermisoglou, E. C., Jakubec, P., Bakandritsos, A., Kupka, V., Pykal, M., Šedajová, V., Vlček, J., Tomanec, O., Scheibe, M., Zbořil, R., & Otyepka, M. (2021). Graphene with covalently grafted amino acid as a route toward eco-friendly and sustainable supercapacitors. *ChemSusChem*, 14, 3904–3914. https://doi.org/10.1002/ cssc.202101039
- Vermisoglou, E. C., Jakubec, P., Bakandritsos, A., Pykal, M., Talande, S., Kupka, V., Zboril, R., & Otyepka, M. (2019). Chemical tuning of specific capacitance in functionalized fluorographene. *Chemistry of Materials : A Publication of the American Chemical Society, 31*, 4698–4709. https://doi.org/10.1021/acs.chemmater.9b00655
- Wang, L., Li, Y., Wang, S., Zhou, P., Zhao, Z., Li, X., Zhou, J., & Zhuo, S. (2019). Fluorinated Nanographite as a Cathode Material for Lithium Primary Batteries. *ChemElectroChem*, 6, 2201–2207. https://doi.org/10.1002/celc.201900194
- Whitener, K. E., Stine, R., Robinson, J. T., & Sheehan, P. E. (2015). Graphene as electrophile: Reactions of graphene fluoride. *Journal of Physical Chemistry C*, 119, 10507–10512. https://doi.org/10.1021/acs.jpcc.5b02730
- Zaoralová, D., Hrubý, V., Šedajová, V., Mach, R., Kupka, V., Ugolotti, J., Bakandritsos, A., Medved', M., & Otyepka, M. (2020). Tunable synthesis of nitrogen doped graphene from fluorographene under mild conditions. ACS Sustainable Chemistry & Engineering, 8, 4764–4772. https://doi.org/10.1021/acssuschemeng.9b07161
- Zhao, F.-G., Pan, B., Kong, Y.-T., Dong, L., Hu, C.-M., Sang, Y.-J., Zhou, X., Zuo, B., Dong, X., Li, B., & Li, W.-S. (2019). Nonmainstream out-plane fluoro- and aminocofunctionalized graphene for a striking electrocatalyst: Programming substitutive/ reductive defluorination toward graphite fluoride. Advanced Materials Interfaces, 6, Article 1801699. https://doi.org/10.1002/admi.201801699
- Zoppellaro, G., Bakandritsos, A., Tuček, J., Bloński, P., Susi, T., Lazar, P., Bad'ura, Z., Steklý, T., Opletalová, A., Otyepka, M., & Zbořil, R. (2019). Microwave energy drives "On–Off–On" spin-switch behavior in nitrogen-doped graphene. Advanced Materials, 31, Article 1902587. https://doi.org/10.1002/adma.201902587