Synthesis of two-dimensional materials through electrochemical exfolation for energy storage

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Presented iin 2025, Departamento de Química de Materiales, Instituto de ciencia y Tecnología del Carbono (INCAR-CSIC).

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Objectives and novelty

The rapid growth in the demand for renewable energy has underscored the importance of developing energy storage devices with high energy density, stability, and low cost, which are essential for meeting future energy and environmental demands. Conventional materials such as activated carbons, metal oxides or conducting polymers face intrinsic limitations in terms of energy density, cycling stability, or cost-effectiveness. In this context, two-dimensional (2D) materials, such as graphene and transition metal dichalcogenides (TMDs), have sparked strong interest owing to their high surface area, tunable electronic structure and chemical versatility.

However, the widespread implementation of these materials is still hindered by the lack of scalable and environmentally friendly synthesis methods. Classical approaches for producing graphene and TMDs, such as chemical oxidation–reduction, mechanical exfoliation or chemical vapor deposition, either involve hazardous reagents, require sophisticated infrastructure or are not suitable for large-scale production. Similarly, liquid-phase exfoliation strategies typically rely on ultrasonication in organic solvents, which raises concerns regarding reproducibility, cost and sustainability.

This work aims to obtain 2D materials, particularly graphene and TMDs, via electrochemical exfoliation for use in electrochemical energy storage devices (supercapacitors, hybrid aqueous zinc-ion capacitors and lithium storage). Specifically, anodic exfoliation has enabled the rapid and straightforward production of oxidized graphene with good structural quality and extensive aromatic domains, making it an ideal precursor for porous graphene with uniformly distributed nanometric pores. This is reflected in its good electrochemical performance as a supercapacitor electrode. Anodic exfoliation also allows control over the population and type of oxygen functional groups in the resulting graphenes through appropriate choice of electrolyte, enhancing properties such as wettability and charge storage capacity for hybrid zinc-ion storage devices. In addition, cathodic exfoliation in aqueous electrolyte has facilitated access to metallic TMD nanostructures (NbSe2, NbS2, and VSe2) with morphological control (nanorolls and nanosheets), which directly affects the behavior of these materials as electrodes for lithium storage.

Results

In the realm of graphene, one of the main contributions of this thesis was the investigation of a novel strategy based on anodic exfoliation of graphite to obtain highly oxidized graphene, which represents a very attractive alternative due to its simplicity and speed in comparison to conventional methods for obtaining highly oxidized graphene (such as graphene oxide prepared by the Hummers method). At the same time, and different to the case of such conventional methods, the anodic route affords oxidized graphene of a relatively good structural quality, characterized by dense and small oxidized domains, where the oxygen functional groups are concentrated, interspersed with relatively extensive aromatic domains. This makes the present anodic oxidized graphene an ideal precursor for the generation of holey graphene, where the hole (pores) generated through selective attack of the oxidized domains present small and uniform dimensions (a few nanometers), and also exhibit a uniform spatial distribution across the nanosheet.

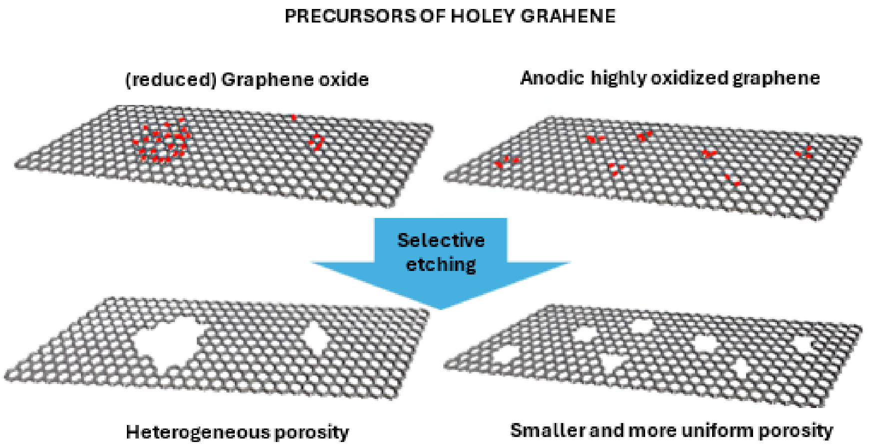

Figure 1. Schematic representation of the preparation of holey graphene from structurally and chemically different precursors.

These structural features translate into graphenes with improved electrochemical performance when used as active materials in supercapacitors, showing higher charge storage capacity and energy density compared to similar materials derived from standard, Hummers-based graphene oxide.

The anodic exfoliation route to graphene has not only allowed modulating the oxidation degree of the resulting nanosheets, but it has also enabled some control over the populations of oxygen functional groups present in these graphenes. Specifically, it has been shown that the type and relative amount of these groups can be tuned through appropriate choice of the aqueous electrolyte used for anodic exfoliation. In particular, this ability has afforded graphenes with increased amounts of carboxyl groups, which in turn was shown to improve such properties as the wettability, and led to higher charge storage capacities when these graphenes were used as cathode material in aqueous zinc-ion hybrid capacitors. Further to this, the performance of electrodes based on this type of graphene has been enhanced by incorporating redox-active molecules, such as flavin mononucleotide, and coating zinc electrodes with carboxyl-enriched graphene has been proven to improve their cyclability and stability by preventing dendrite formation, a factor that limits the applicability of batteries and capacitors using metallic zinc as the anode.

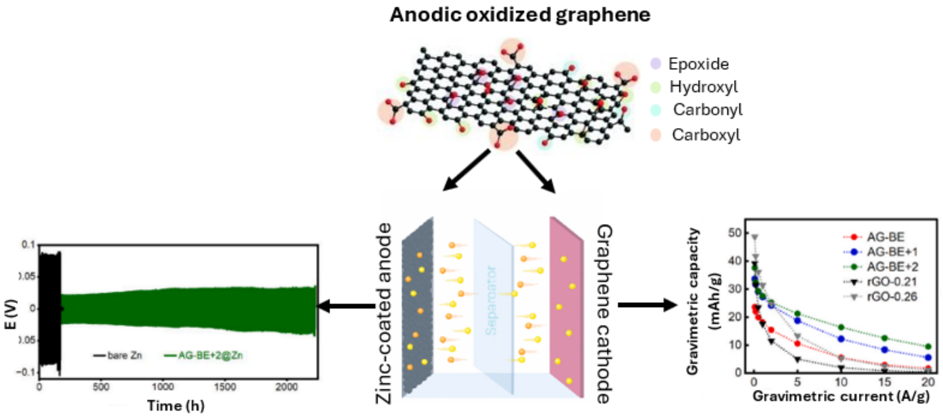

Figure 2. Schematic representation of the diverse applications of modular graphene obtained through anodic electrochemical exfoliation.

Finally, cathodic exfoliation in an aqueous medium has been investigated as an efficient method for obtaining 2D nanosheets of metallic TMDs, mainly $NbSe_2$, but also NbS_2 and VSe_2, also with control over the material's final morphology (e.g., nanoroll vs. nanosheet). Such morphological control has led to TMD-based electrodes with different behaviors in electrochemical lithium storage. Specifically, electrodes based on $NbSe_2$ nanorolls exhibit a higher storage capacity than that of nanosheets, attributable to the less compact packing of the electrode with the former, which facilitates a better electrolyte access. Moreover, it was shown that the mechanism of cathodic exfoliation developed here for these TMDs is entirely different from that occurring in common electrochemical (cathodic or anodic) exfoliation processes of layered materials.

Conclusions

This thesis has demonstrated the potential of electrochemical exfoliation as a versatile, scalable, and environmentally friendly strategy for the synthesis of relevant two-dimensional materials, i.e., graphene and metallic TMDs, tailored for energy storage applications.

For graphene, anodic exfoliation enables the production of highly oxidized materials with preserved structural quality, combining oxidized domains and extended aromatic regions. This makes them ideal precursors for holey graphene with nanometer-sized pores, leading to enhanced supercapacitor performance. The anodic route also allows control over oxygenated functional groups through electrolyte selection, with carboxyl enrichment improving wettability and charge storage in zinc-ion hybrid capacitors. Performance is further boosted by redox-active molecules and by coating zinc anodes with carboxyl-rich graphene, which suppresses dendrites and enhances stability.

In parallel, cathodic exfoliation in aqueous media provides metallic TMDs with tunable morphologies that strongly affect lithium storage behavior. The results also reveal a distinct exfoliation mechanism for metallic TMDs compared to other layered materials.

References

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