Preparation of bidimensional materials for energy storage and environmental applications

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Objectives and novelty

In recent years, nanomaterials and more specifically two-dimensional (2D) materials have been attracting great interest due to the change in physicochemical properties from their bulk forms and the possibility of their selective modulation. Thus, 2D materials feature a wide variety of applications such as electrochemical energy storage, biomedicine, (opto) electronics, (electro)catalysis, or (bio)sensors, among others. Despite all the research efforts, there are still limitations in the preparation and modification methods of 2D materials regarding the control of both structural quality and final properties. In this context, the present doctoral thesis has mainly focused on:

(1) Optimization of top-down methodologies for the preparation of MoS_2 and $MoSe_2$ 2D nanosheets. For this purpose, sonication-assisted liquid phase exfoliation (LPE) in organic medium and an optimized cathodic electrochemical exfoliation (CEE) in both aqueous and organic medium were employed.

(2) Investigation of molecular functionalization and chalcogen vacancies generation strategies in 2D TMDs. An electrolytic methodology for covalent molecular functionalization of MoS_2 nanosheets during CEE was implemented, as well as a reductive treatment at temperature for the generation of chalcogen vacancies (S and Se, respectively) in MoS_2 and $MoSe_2$ nanosheets obtained via LPE.

(3) Applications of 2D nanosheets as catalysts for the degradation of water pollutant species and as electrodes for Li-ion electrochemical storage. The intrinsic catalytic activity of MoS_2 and $MoSe_2$ 2D nanosheets obtained by LPE (with and without chalcogen vacancy generation) was compared, and the catalytic potential of functionalized MoS_2 nanosheets was studied, respectively, towards the reduction of nitroarenes and organic dyes is aqueous medium. The performance of MoS_2 nanosheets prepared via LPE and cathodic EE in organic medium as anodes for lithium electrochemical devices was investigated.

Results

A CEE strategy in organic medium has been developed to exfoliate thin MoS_2 nanosheets for their implementation as electroactive material for anodes in lithium storage devices. While previous studies have been focused in tetraalkylammonium salts, this study explored trimethylalkylammonium salts as electrolyte for the first time. After optimizing the exfoliation experimental conditions, an electrolyte based on the hexyltrimethylammonium cation ($HTMA^+$) was chosen, as it yielded a higher degree of exfoliation, prevented the well-known 2H-1T phase transition and led to thinner MoS_2 nanosheets related to other tested electrolytes.

The performance of MoS_2 nanosheets obtained by CEE (ee-MoS_2) was compared with those obtained by LPE (lpe-MoS_2) as anodes for lithium storage devices. The smaller thickness of ee-MoS_2 nanosheets (which decreases their electrical resistance and shortens the Li diffusion paths) and their greater flexibility resulted in better electrochemical performance as an anode for Li storage compared to lpe-MoS_2, in terms of obtained gravimetric capacity during discharge, capacity retention with increasing current density (rate capability) and long-term cyclability.

Beyond energy storage, 2D TMDs also display promising applications in the field of catalysis as an alternative for noble metal-based catalysts due to their relative earth-abundance, cost-effectiveness and suitable catalytic activity towards several reactions of interest, such as hydrogen and oxygen evolution reaction, CO_2, N_2 and, more recently, several nitroarenes reduction reaction. Nonetheless, catalytic performance of 2D nanosheets is strongly dependent on their colloidal stability in the corresponding medium and, despite potential intrinsic advantages of CEE, no electrochemical functionalization method has been reported yet. To that purpose, an electrochemical functionalization method of MoS_2 nanosheets was optimized towards enhanced hydrophilicity for their use as a catalyst for the reduction of nitroarenes and organic dyes, relevant in water decontamination and in the synthesis of certain pharmaceuticals.

Specifically, the electrochemical functionalization treatment led to acetic acid-derivatized MoS_2 nanosheets displaying improved colloidal stability in water related to non-derivatized ones. External supply of electrons (from cathodic potential or chemical electron donor) enables functionalization, and the presence of S vacancies in the basal plane of the nanosheets enables the anchoring of organic functional groups. The functionalized MoS_2 nanosheets showed significantly higher catalytic activity than other MoS_2-based catalysts (1T or 2H phase) previously reported. A relationship between the order of reduction reaction and the net electric charge of the substrate molecules was found. The functionalized nanosheets maintained good catalytic efficiency at realistic concentrations of nitroarenes and in binary and ternary mixtures of such reactants. In addition, to facilitate their handling and reuse, the nanosheets could be immobilized on a polymeric support.

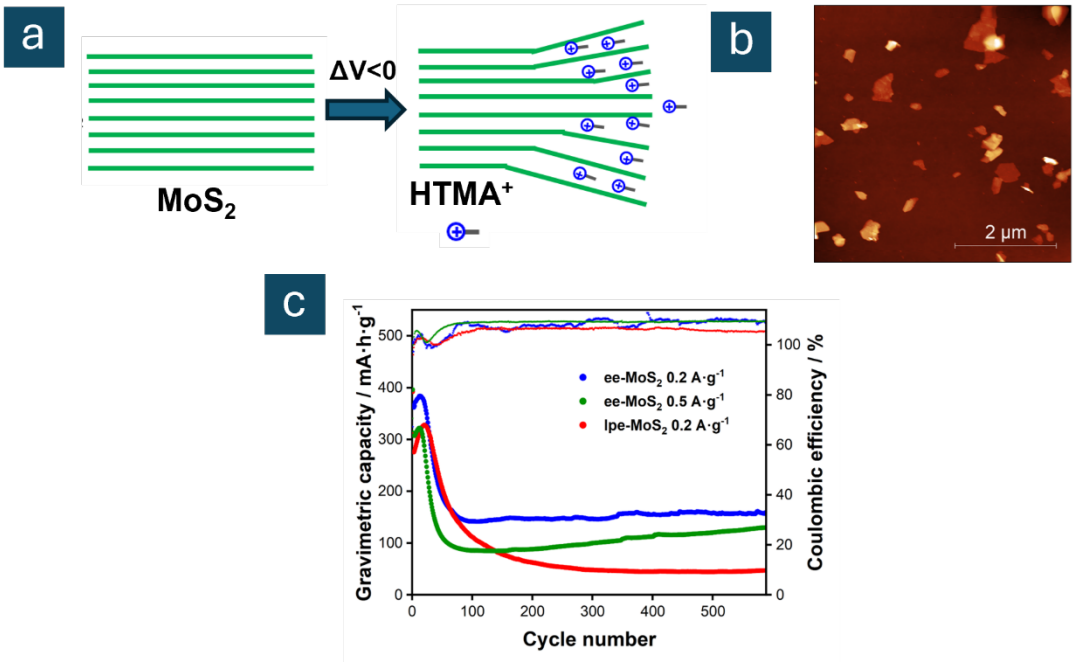
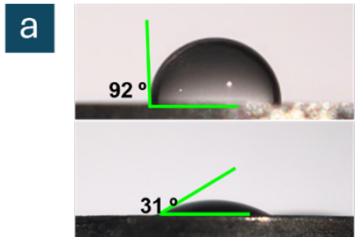


Figure 1. a) Scheme of the electrochemical intercalation mechanism during CEE with HTMA+-based electrolyte. b) Digital image obtained by atomic force microscopy of ee-MoS_2 2D nanosheets. c) Gravimetric capacity for long-term cyclability (larger circles) and coulombic efficiency (smaller circles) for ee-MoS_2 and lpe-MoS_2 nanosheets at different current densities for lithium-ion storage.



b

Substrate	Catalytic activity (h^{-1})
4-nitrophenol	63
2-nitrophenol	340
4-nitroaniline	180
2-nitroaniline	90
nitrobenzene	78
methyl orange	71
methylene blue	44

Figure 2. a) Contact angle with a water droplet of the non-functionalized (92º) and functionalized (31º) nanosheets. b) Catalytic activity values of the functionalized MoS_2 nanosheets with the studied substrates.

Besides, nitroarene reduction reaction is an operation of interest in water remediation and pharmacological industry. Although MoS_2 is one of the most investigated members for this purpose, other TMDs remained unexplored, and such was the case with $MoSe_2$. Thus, intrinsic catalytic activities of 2D MoS_2 and $MoSe_2$ 2D nanosheets exfoliated by LPE towards reduction of nitroarenes were compared, with a superior catalytic performance of the latter. DFT studies allowed proposing a mechanism for the reduction reaction and provided an explanation for the selectivity shown by the different nitroaniline isomers to $MoSe_2$ nanosheets during catalysis. With aim to facilitate the practical implementation of $MoSe_2$ nanosheets, those were immobilized onto a polymeric support to facilitate their reuse during several catalytic cycles, displaying an appropriate catalytic activity retention.

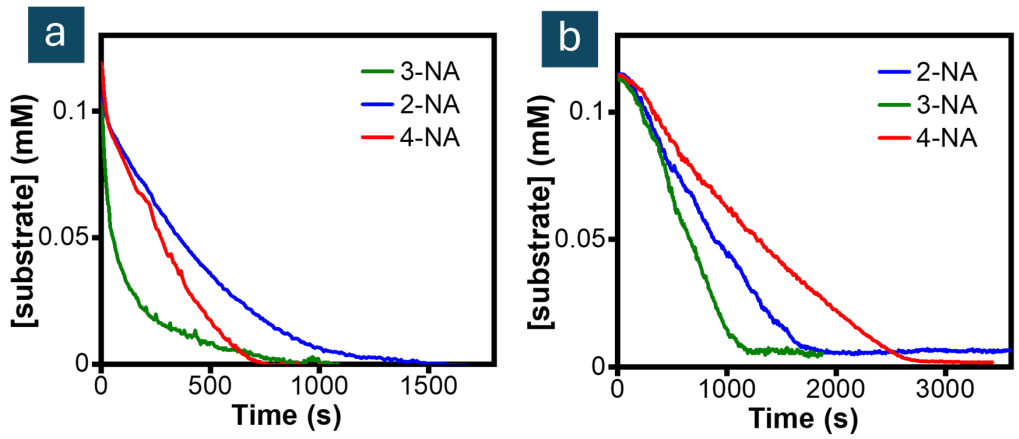


Figure 2. Kinetic profiles for the reduction reaction of several nitroaniline isomers in the presence of a) $MoSe_2$ and b) MoS_2 2D nanosheets as catalyst in aqueous solution.

Conclusions

It was verified that ee-MoS_2 nanosheets obtained by the CEE optimized methodology showed improved performance for Li-ion storage rather than LPE-MoS_2. An electrochemical functionalization method to enhance MoS_2 nanosheets colloidal stability towards their use as catalyst for nitroarene and organic dyes reduction was successfully developed. It was confirmed by both experimental and DFT calculations that $MoSe_2$ 2D nanosheets possess higher intrinsic catalytic activity than MoS_2 nanosheets for the reduction reaction of nitroarenes.

Related publications

[1] Martínez-Jodar A, Villar-Rodil S, Munuera JM, Castro-Muñiz A, Coleman JN, Raymundo-Piñeiro E, Paredes JI, Two-Dimensional MoS_2 Nanosheets Derived from Cathodic Exfoliation for Lithium Storage Applications, Nanomaterials, 2024, 14-932, 1-25.

[2] Martínez-Jódar A, Villar-Rodil S, Salvadó MA, Carrasco DF, Pertierra P, Recio JM, Paredes JI. Two-dimensional transition metal dichalcogenides beyond MoS_2 for the catalytic reduction of nitroarenes: $MoSe_2$ exhibits enhanced performance, Applied Catalysis B: Environmental, 2023, 339, 123174.

[3] García-Dalí S, Paredes JI, Villar-Rodil S, Martínez-Jódar A, Martínez-Alonso A, Tascón JMD, Molecular Functionalization of 2H-Phase MoS_2 Nanosheets via an Electrolytic Route for Enhanced Catalytic Performance, Applied Materials & Interfaces, 2021, 13, 33157-33171.

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