Electrochemical exfoliation of MoS_2 crystal for hydrogen electrogeneration

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Abstract

Transition metal dichalcogenides (TMDs) have recently emerged within the group of 2D materials due to their electrical, catalytic and optical properties significantly enhanced and useful when down-sized to single layer. In particular, MoS_2 has attracted much attention due to its semiconducting nature with a useful band gap when present as single layer, the enhanced photoluminescence, but also importantly the excellent catalytic properties towards the electrochemical hydrogen evolution. We present here the preparation of thin layers MoS_2 nanosheets with enhanced catalytic properties towards the hydrogen evolution reaction by means of an easy and fast electrochemical top-down exfoliation procedure in aqueous solution from a naturally occurring MoS_2 crystal. After structural and chemical characterization with STEM, AFM, XPS and Raman spectroscopy we performed electrochemical investigations to test catalytic properties in acidic solution for the electrogeneration of hydrogen and compare it to MoS_2 nanosheets obtained through the widely employed chemical Li intercalation/exfoliation. Electrochemically exfoliated MoS_2 shows lower Tafel slope than its counterpart obtained with chemical exfoliation.

Keywords: Molybdenum sulfide, exfoliation, layered compound, electrochemistry, hydrogen evolution reaction.

1. Introduction

After the discovery of the attractive properties of graphene, useful in several different applications such as electronics,[1] catalysis,[2] electrochemistry,[3] energy storage and conversion,[4-5] mechanical hardener,[6] corrosion protection,[7] etc., other 2D materials have attracted much attention due to other extraordinary properties[8-9] rising especially when reducing the thickness of the material to single layer, and which can complement with those of graphene.[10-13] For example semiconducting materials with a direct bandgap could be more appropriate for optoelectronic applications than the zero-bandgap graphene.[14-16] Other materials possess excellent catalytic properties towards water splitting and other organic reactions and which are not attributable to graphene.[17] Particularly attractive for the above properties is MoS_2 which belongs to the transition metal dichalcogenide compounds and represents the most widely investigated.[18-19] With a direct bandgap of 1.8 eV is a semiconductor potentially useful in several electronic applications and also solar power conversion.[20-21] In addition, it demonstrated excellent catalytic properties for the electrogeneration of hydrogen due to the binding enthalpy with H close to zero, similar to Pt.[22] Methods for the fabrication of single or few layer MoS_2 sheets are available and similarly to graphene can be categorized into two main approaches: top-down and bottom-up. Taking into consideration only those which are potentially scalable for industrial production, we find the chemical and liquid exfoliation of a bulk MoS_2 crystal as main top-down methods and the chemical vapor deposition from elemental precursors as the main bottom-up synthetic procedure. Sonication-assisted liquid exfoliation of bulk MoS_2 is simple but requires large amounts of organic solvents, long process time and suffers from low yields.[23] Intercalation/exfoliation with Li-based organic solvents is certainly more efficient with large

amount of single or few-layer thick nanosheets obtained. [24] However, it makes use of dangerous Li-based compounds which require strict and controlled environments to be used safely. Chemical vapor deposition produces MoS_2 with excellent electronic properties but requires expensive instrumentations and highly technical skills.[25-26]

Another procedure which demonstrated excellent results in terms of quality of the exfoliated material, high yields, simple operations and lower environmental impact is represented by the electrochemical-assisted exfoliation. Extremely powerful when applied for the exfoliation of graphite to obtain graphene,[27-28] is recently being considered also for the exfoliation of other layered materials such as Bi_2Se_3, Bi_2Te_3,[29] black phosphorous[30] and MoS_2,[31-32] showing potentiality as universal procedure for fast and efficient top-down method.

Here we present an easy electrochemical procedure to exfoliate naturally occurring MoS_2 crystals in aqueous solution avoiding therefore lengthy operations with dangerous organic solvents used during Li-assisted exfoliation both chemical[24] and electrochemical.[32] The produced material has then been tested for hydrogen evolution reaction (HER) demonstrating similar performance than the chemically exfoliated counterpart.

2. Experimental

2.1 Materials and apparatus

MoS_2 crystals were obtained from the Sçrumsaasen mine, Spikkestad, Drammen, Norway. *N*,*N*-dimethylformamide, (DMF) and potassium sulfate were purchased from Sigma–Aldrich, Singapore. Glassy carbon (GC) with a diameter of 3 mm was obtained from CH Instruments, USA. Scanning Transmission Electron Microscopy (STEM) images were obtained by using Jeol 7600F SEM (Jeol, Japan) operating at 30 kV. X-ray photoelectron

spectroscopy (XPS) was performed with a monochromatic Mg X-ray radiation source and a Phoibos 100 spectrometer (SPECS, Germany). Raman spectroscopy analysis was performed using a confocal micro-Raman LabRam HR instrument (Horiba Scientific, Japan) in backscattering geometry with a CCD detector, a 633 nm HeNe laser and a 100x objective mounted on a Olympus optical microscope.

2.2 Electrochemical exfoliation of MoS_2

Small crystal flakes with size of about 1 cm in length were connected to the power supply trough copper tape ensuring isolation of the copper from the solution. A Pt foil was used as counter electrode and placed in solution at a distance of about 2 cm from the MoS_2 flake. Aqueous K_2SO_4 0.5 M solution was employed as electrolyte during the exfoliation procedure. An initial voltage of 2 V was applied between the electrodes with the MoS_2 set as anode for 5 min. Then the voltage was raised to +10 V during which a little material release was observed from the MoS_2 anode during only 5 min. Further exfoliation was observed only upon switching of electrode polarity alternating +10 V and -10 V during 5 min intervals. This was carried out for a total period of 1 h during which a significant amount of yellowish material was released from the MoS_2 crystal. Collection and washing of the exfoliated material was done by centrifugation in ultrapure water before drying in a vacuum oven at 40° C for two days.

2.3 Chemical exfoliation of MoS_2

A suspension of 3 g of MoS_2 bulk powder in 20 ml of 1.6 M *n*-buthyllithium in hexane has been stirred for 72 h at 25 °C under argon atmosphere. The Li-intercalated material has then been separated by suction filtration under argon atmosphere and the intercalated compound was washed several times with hexane (dried over Na). The separated MoS_2 with intercalated

Li was placed in water (100 ml) and repeatedly centrifuged (18 000 g). Obtained material was dried in vacuum oven at 50 °C for 48 hours prior the further use.

2.4 Electrochemical characterizations

Electrochemical experiments were performed at room temperature by using a three-electrode configuration on a Autolab PGSTAT101 electrochemical analyzer (Methrom Autolab B. V., The Netherlands) connected to a personal computer and controlled by NOVA software Version 1.9 (Methrom Autolab B. V.). A platinum electrode (Autolab) served as an auxiliary electrode, while an Ag/AgCl electrode (CH Instruments, USA) served as a reference electrode. The exfoliated materials were drop casted onto a previously polished working electrode (GC) from 1 mg/mL water dispersions. Polarization curves for HER were recorded in 0.5 M H_2SO_4 solution at scan rate of 5 mV/s. All potentials are considered versus the relative hydrogen electrode (RHE) using the conversion relation: $E_{(RHE)} = E_{(Ag/AgCl)} + 0.059pH + E^o_{(Ag/AgCl)}$. Electrochemical active surface area (ECSA) of GC electrode modified with chemical and electrochemical exfoliated MoS_2, was estimated using Randles-Sevcik equation upon measuring cyclic voltammetric responses at different scan rates for the probe $[Fe(CN)_6]^{4-}$ in aqueous solution. An ECSA of 32.6 and 38.4 cm^2 resulted for BuLi exfoliated and electrochemical exfoliated MoS_2, respectively.

3. Results and Discussion

MoS_2 is naturally occurring as the mineral molybdenite available in large amounts in several locations such as Norway, North America and Australia.[33] Natural crystals are generally of good quality and can be used as starting material for the top-down preparation of single or few layer thick MoS_2 sheets. We used here natural crystals as starting material for the

electrochemical exfoliation (Figure 1B). Figure 1A illustrates the schematic of the experimental setup used. As explained in detail in the experimental section, alternating anodic and cathodic potentials of 10 V to the working MoS_2 electrode in 5 min intervals generated the release in solution of yellowish material consisting of thin MoS_2 nanosheets (Figure 1C). The material can be redispersed in water after washing steps obtaining a stable homogeneous dispersion (Figure 1D).

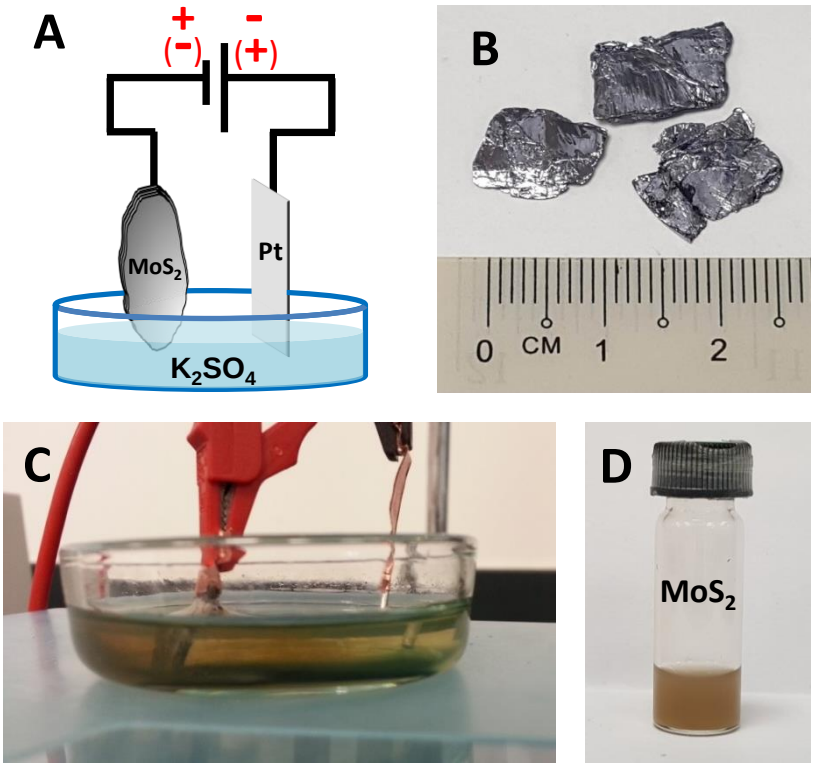

Fig. 1 A) Schematic of the electrochemical setup for the exfoliation of natural MoS_2 crystals. B) Photographs of MoS_2 crystals. C) Snapshot taken during the exfoliation process (after 20 min). D) Electrochemical exfoliated MoS_2 dispersion in ultrapure water at 1 mg/mL concentration.

Analysis performed using scanning transmission electron microscopy (STEM) revealed that the electrochemical exfoliation process produced sub-micrometer sized MoS_2 sheets as illustrated in Figure 2. This differs from the chemical exfoliation through Li intercalation

which can generate larger sheets (see Figure S1 of Supporting Information). While the small size could represent a limiting characteristic for optoelectronic applications, it may be advantageous for catalysis since a larger edge surface is exposed and available and which is the most active particularly for hydrogen evolution reaction (HER).[34-35]

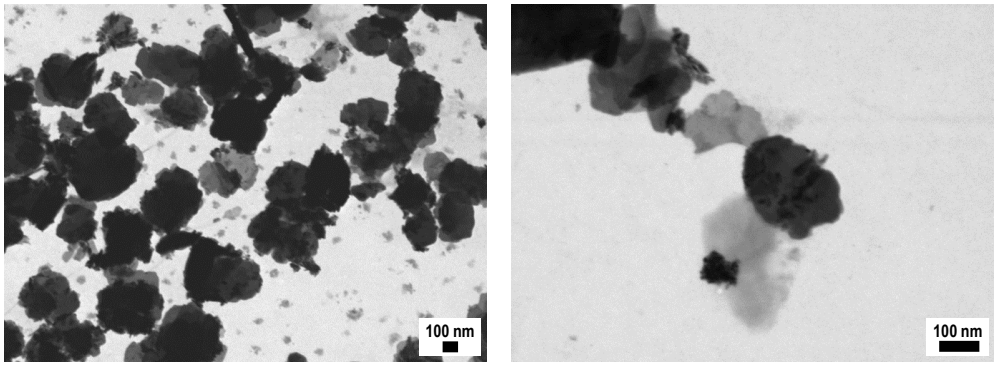

Fig. 2 STEM images of electrochemical exfoliated MoS_2 at different magnifications.

Further size evaluation was carried out by means of atomic force microscopy (AFM). As it can be seen in Figure S2 of Supporting Information the electrochemically exfoliated MoS_2 nanosheets possess a lateral size between 100-200 nm and thickness mostly in the range 10-15 nm corresponding to 15-20 layers.

Raman spectroscopy has been used to investigate structural characteristics of MoS_2 nanosheets obtained with electrochemical exfoliation. [36] A comparison was made with the chemical exfoliated material. Raman spectra were recorded focusing the excitation laser onto isolated particles avoiding to the best of our abilities the contribution from bulk particles also present. A representative picture of the sample taken with the optical microscope prior Raman measurement is shown in figure S3 of supporting information. It can be seen in Figure 3 that both materials show two prominent bands at about 380 cm^{-1} and 405 cm^{-1} which correspond to the in-plane E_{2g} and out-of-plane A_{1g} vibration modes, respectively. [37] No

significant difference could be observed in the Raman spectra for the two materials demonstrating that from a structural point of view the electrochemical exfoliation can produce MoS_2 nanosheets with comparable quality than the widely employed chemical exfoliation.

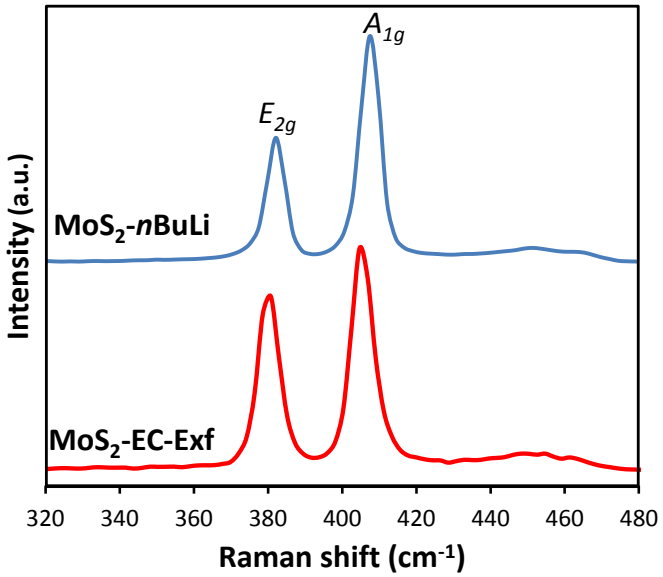

Fig. 3 Raman spectra recorded for chemical exfoliated MoS_2 (top) and electrochemical exfoliated MoS_2 (bottom).

The XPS analysis, useful to verify the chemical composition of the material, revealed the presence of a significant amount of oxidized species. From the high-resolution Mo 3d spectrum of the electrochemical exfoliated MoS_2 it can be seen that bands appears at binding energy of 232 and 236 eV which correspond to $Mo^{VI}\ 3d_{5/2}$ and $Mo^{VI}\ 3d_{3/2}$, respectively (Figure 4B). $Mo^{IV}\ 3d_{5/2}$ and $Mo^{IV}\ 3d_{3/2}$ signals are visible in the spectrum of the *n*-BuLi exfoliated MoS_2 at binding energy of 229 and 232 eV (Figure 4A). The significant shifting of the Mo 3d signals to higher binding energies demonstrates that Mo oxides were generated during the exfoliation. Figure S4 of supporting information presents the survey spectra of the materials where the evidently the oxygen signal is of higher intensity for the electrochemical

exfoliated MoS2 compared to the chemical exfoliated. This is also confirmed by the shifting of the S 2p signal shown in Figure 4 appearing at binding energy of 168 eV for the electrochemically exfoliated MoS_2 (Figure 4B, right panel) versus 162 eV for the *n*-BuLi exfoliated material (Figure 4A, right panel). The presence of oxidized Mo species could affect the electrocatalytic properties of the materials and so tests were performed to study the ability of the electrochemical exfoliated MoS_2 to catalyze the hydrogen generation in acidic media and compared to that of the *n*-BuLi exfoliated counterpart. Both the materials seem to possess predominantly the characteristic of the semiconducting 2H polymorph of MoS_2. This could represent a disadvantage as the metallic phase 1T is notoriously a more performing catalyst for HER.

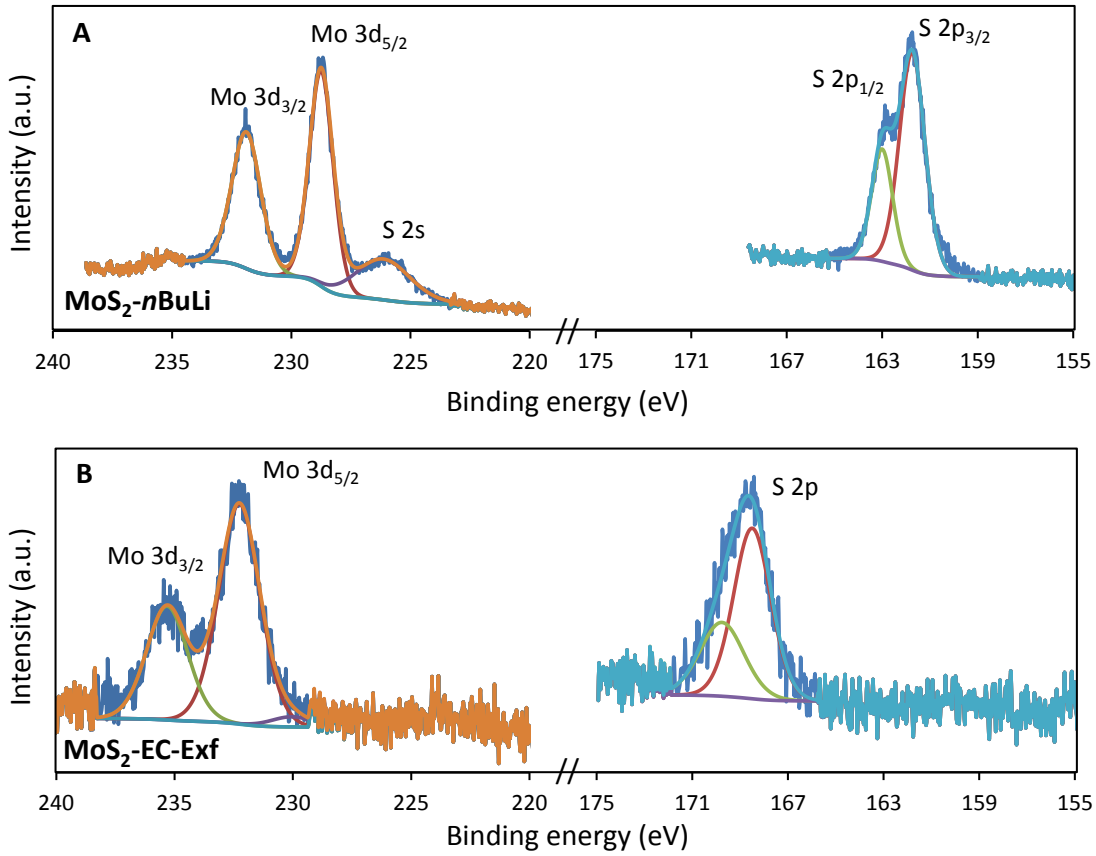

Fig. 4 High resolution Mo 3d and S 2p XPS spectra of A) chemical exfoliated MoS_2 and B) electrochemical exfoliated MoS_2.

It can be seen in Figure 5 that the electrochemical exfoliated MoS_2 presented catalytic properties similar to that of the chemically exfoliated MoS_2 with a slightly higher onset potential (η) of 0.31 V vs 0.2 V, respectively. However in terms of performance it can be noticed that the overpotential required to reach 10 mA/cm^2 current density is almost coincident at the value of -0.5 V (vs RHE). This is indication of a faster reaction process occurring at the electrochemically exfoliated MoS_2. It can be seen, in fact, that the corresponding Tafel plot (Figure 5B) presents a slope of 74 mV/dec which is lower than that obtained with the chemically exfoliated material (136 mV/dec). For comparison polarization curves and corresponding Tafel plots of bare glassy carbon (GC) electrode and Pt/C modified electrode are also shown in Figure 5. In general the performance of the electrochemical exfoliated MoS_2 is inferior to those reported previously and obtained via Li intercalation in organic solution.[32] This is likely due to the presence of oxides on the material surface as well as the predominant 2H semiconducting characteristics as evidenced by XPS measurements. In addition to the presence of oxides, other surface properties contribute to the resulting Tafel slope and overpotential, such as the presence of high-energy sites and adsorption energy as recently highlighted by Otyepková *et al*.[38]

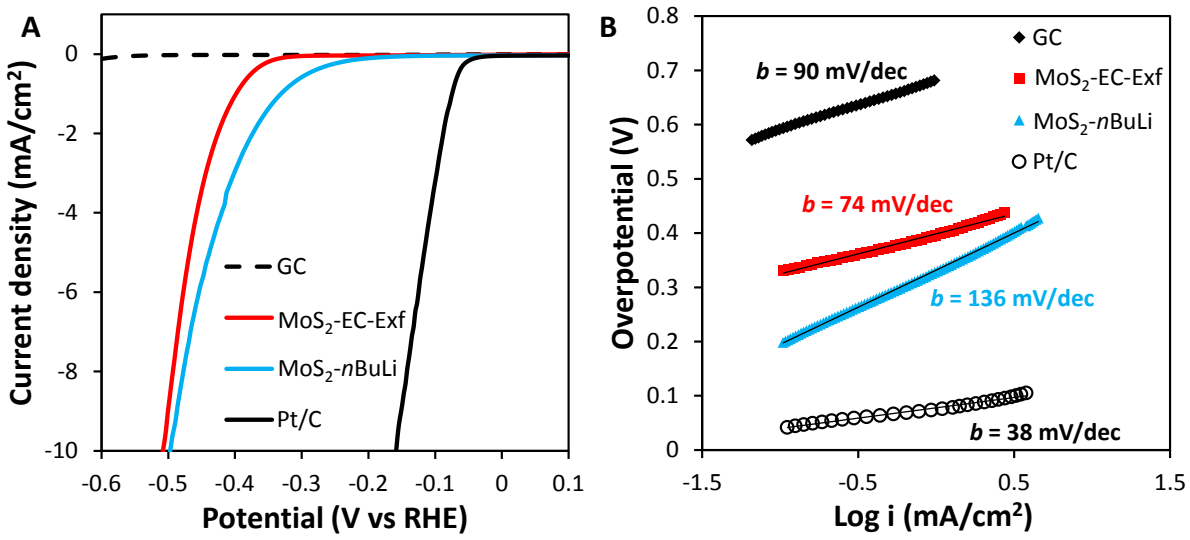

Fig. 5 A) Polarization curves and B) Corresponding Tafel plots for bare GC electrode (black) and electrode modified with electrochemical exfoliated MoS_2 (red), chemical exfoliated MoS_2 (blue) and Pt/C (black) in 0.5 M H_2SO_4 at scan rate of 5 mV/s.

4. Conclusions

We presented here a rapid and easy procedure for the preparation of thin MoS_2 nanosheets based on electrochemical process in aqueous solution. The application of alternative anodic and cathodic voltages to natural bulk crystal of MoS_2 used as electrode versus Pt counter electrode generates the release in solution of thin MoS_2 nanosheets. The material showed good structural and catalytic properties, similar to MoS_2 nanosheets obtained via the chemical Li intercalation/exfoliation which however requires lengthy procedures and the use of dangerous organic solvents. Electrochemical exfoliation in aqueous solution for the fabrication of thin MoS_2 sheets represents a valid alternative to the exfoliation in organic solvents not only for catalytic applications such as hydrogen evolution reaction, but also other application where the 2H semiconducting characteristics are preferred.

Conflicts of Interest

The authors declare no competing financial interest.

Supporting Information.

STEM images of chemically exfoliated MoS_2 and XPS survey spectra of chemically and electrochemically exfoliated MoS_2.

Acknowledgment

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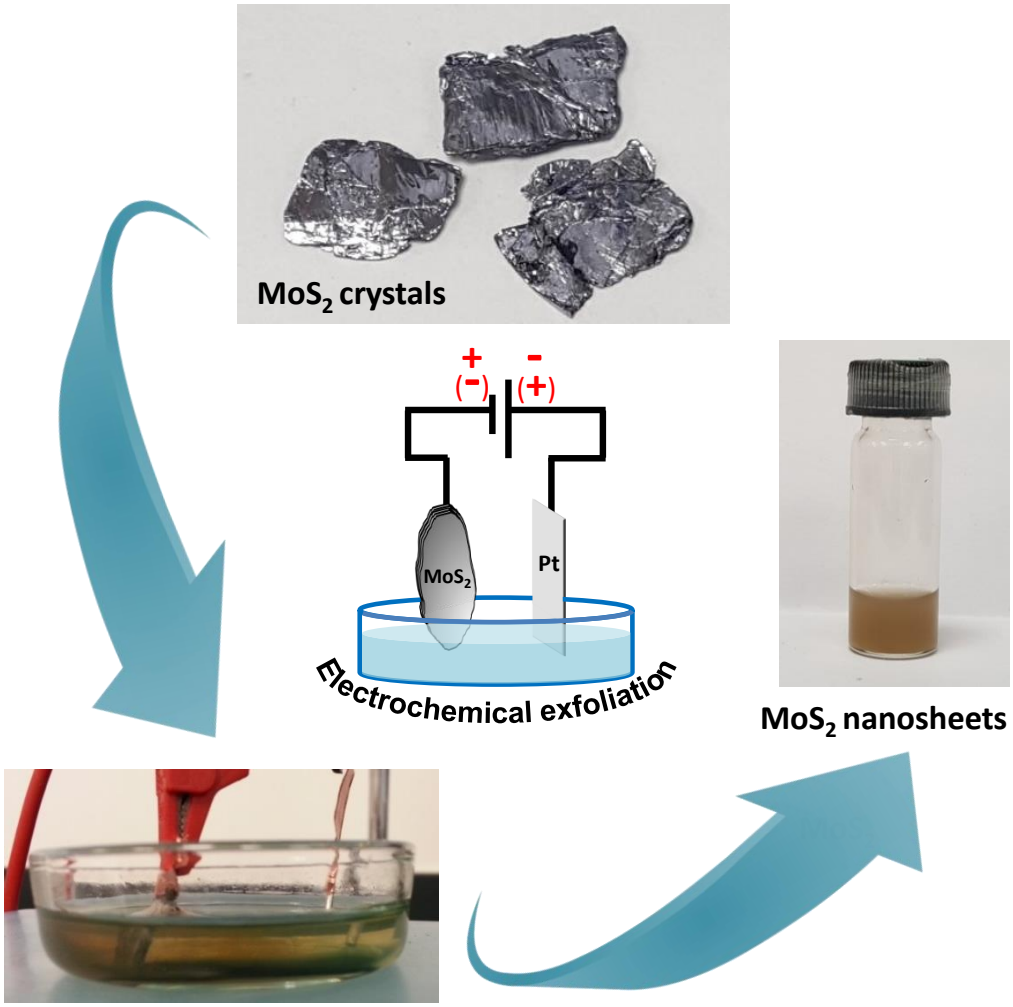

Fast and aqueous-based electrochemical exfoliation of natural bulk MoS_2 crystals has been used to produce MoS_2 nanosheets. These can be used for electrocatalytic hydrogen production or other electronic applications.