

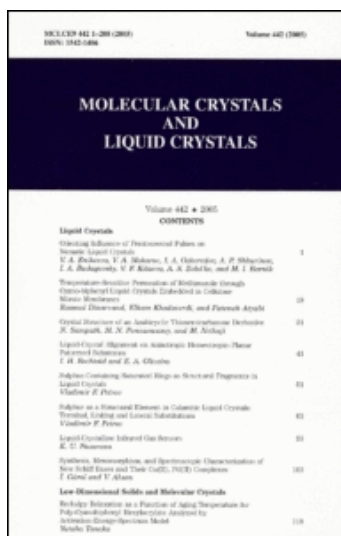
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# Deposition of Molybdenum Disulfide Thin Film on a Gold Surface

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*The restacking of molybdenum disulphide (MoS<sub>2</sub>) on a gold surface is reported. Thin films were obtained by spontaneous deposition from single-layer suspensions of the sulfide on a Quartz Crystal Microbalance gold electrode at room temperature. Quartz crystal frequency shift, contact angle, and Atomic Force Microscopy measurements indicates the films are constituted by islands in which the MoS<sub>2</sub> layers are arranged with their basal planes oriented perpendicularly to the gold surface. Cyclic voltammetry studies indicate that lithium can be inserted/extracted in the Au/MoS<sub>2</sub> electrode. The effect on the electrochemical behavior of the MoS<sub>2</sub> film of both electrode surface morphology and presence of water in the medium are discussed.*

**Keywords** Atomic force microscopy; cyclic voltammetry; films; molybdenum disulfide; quartz crystal microbalance

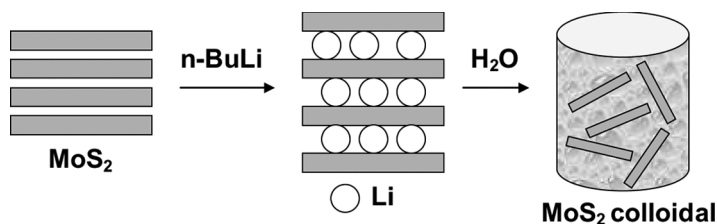
## 1. Introduction

Molybdenum disulfide (MoS<sub>2</sub>) is a stable and versatile member of the family of layered dichalcogenides. Because of its availability and low cost, MoS<sub>2</sub> find many practical applications, among them, as solid lubricant [1], electrode material for batteries [2], and catalyst for hydrosulfurization (HDS) in the petroleum industry [3]. The use MoS<sub>2</sub> as a possible a catalyst for biomimetic hydrogen evolution has been also proposed [4]. Catalytic properties of MoS<sub>2</sub> are however mainly centred in the edges of the layers since the basal plane would be catalytically inactive [5].

Although the pristine MoS<sub>2</sub> is in general inert to the insertion of chemical species in its interlayer spaces, lithium atoms can be incorporated into this layered sulphide upon treatment with strong reducing agents such as n-buthyllithium (n-BuLi) [6,7]

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**Scheme 1.** Exfoliation of Molybdenum disulfide in water.

thus leading to LiMoS<sub>2</sub>. The oxidation of the product with water according to the following reaction



results in a colloidal suspension of single layers of the material (Scheme 1) [8,9]. These layers can be either recovered as a restacked sulphide or by precipitation after adding a wide variety of guest species – for instance discrete molecules, polymers, metal cluster, or dyes [10–14] – which remain intercalated in the interlayer spaces of the MoS<sub>2</sub>. The remarkable ability of exfoliated MoS<sub>2</sub> to encapsulate such a large diversity of chemical species, which converts this chemistry in a promising source of materials for a number of applications including water treatment, hazardous waste removal and the development of new forms of HDS catalysts [15], has encourage much interest in investigating the properties of the exfoliated and restacked forms of this sulphide [16–19].

Manufacturing of high-quality thin films potentially useful as materials has deserved much attention during the last years [20]. Particularly interesting is the deposition of atomic and molecular layers of semiconductors with thicknesses in the range of the angstroms or nanometers which are expected to display chemical and physical properties much different from those observed in the bulk [21]. Therefore there is interest in investigating the formation of molecular films of MoS<sub>2</sub> as a way to the development of new materials [22]. Thin films of MoS<sub>2</sub> have been prepared by a variety of methods, for instance, by chemical bath deposition [23], pulse electrochemical deposition [24], pulsed laser evaporation [25], sputtering [26], chemical vapour deposition (CVD) [27], using organic compounds by AACVD (aerosol assisted CVD) [28], spin coating [29] and sulfidation treatments with H<sub>2</sub>S or gas mixture containing H<sub>2</sub>S while depositing films of Mo [30] and MoO<sub>3</sub> [31].

In the present work we describe for the first time the spontaneous restaking of MoS<sub>2</sub> from its aqueous single layer suspension on a gold surface of a Quartz Crystal Microbalance electrode at room temperature. Deposited MoS<sub>2</sub>, which according to quartz crystal frequency shifts, contact angle, and atomic force microscopy (AFM) measurements is found to form islands interacting with the gold substrate by the edges of the layers remaining the basal planes perpendicular to the surface, is able to undergo electrochemical lithium intercalation.

## 2. Experimental

A colloidal, single layer, aqueous suspension  $3 \cdot 10^{-4}$  M of MoS<sub>2</sub> was prepared by rapid hydrolysis of Li<sub>x</sub>MoS<sub>2</sub> ( $x \geq 1$ ). The Li<sub>x</sub>MoS<sub>2</sub> ( $x \geq 1$ ) was prepared by reaction

of MoS<sub>2</sub> powder <2 μm (Aldrich) in 1.6 M hexane solution of *n*-butyl lithium (Merck) for 48 h. under argon at 55–60°C, centrifuged, washed with *n*-hexane, and dried under vacuum [6–10].

The deposition was performed by immersing a polished gold electrode (5-MHz Cr/Au) of a Quartz Crystal Microbalance (RCQM MASTEX Inc.) in the MoS<sub>2</sub> single-layer aqueous suspension at 25°C. Before each measure quartz crystal electrodes were cleaned by immersion (5 min) in Piranha solution, rinsed in pure water (5 MOhm), and dried in extra pure (99.999%) nitrogen gas flow.

Contact angles were measured with deionized water in a goniometer (Pocket Goniometer Model P2 Fibro System AB). Reported contact angles are average values from 3–4 drops placed on different parts of the surface. Results were analyzed with the PocketGoniometer<sup>®</sup> Program version 1.7.4.0 [32]. Measurement deviations were always within 2°.

Atomic force microscopy (AFM) was used to examine the surface morphology of the film. AFM images were obtained at the air, using multimode scanning probe microscope Nanoscope IIIa equipment (Digital Instrument, Santa Barbara, CA) in the tapping mode.

Cyclic voltammetric studies of MoS<sub>2</sub> films supported on a quartz crystal gold electrode were performed using the film as working electrode and a piece of metallic lithium acting as both counter and reference electrode. As supported electrolyte a 0.1 M LiClO<sub>4</sub> solution in 1: 1 ethylene carbonate/propylene carbonate was used. Measurements were performed at 25°C over a potential range of 1.5–3.0 V vs. Li/Li<sup>+</sup> at scan rates of 1 mV/s using an Autolab Potentiostat Galvanostat 12 (Eco Chemie, B. V, Utrech, The Netherlands).

### 3. Results and Discussion

The affinity of gold for species containing sulfur in low oxidation states is well known. Particularly the interaction with thiols which is often used for the functionalization of gold surfaces has been studied extensively [33–36]. On the basis of these

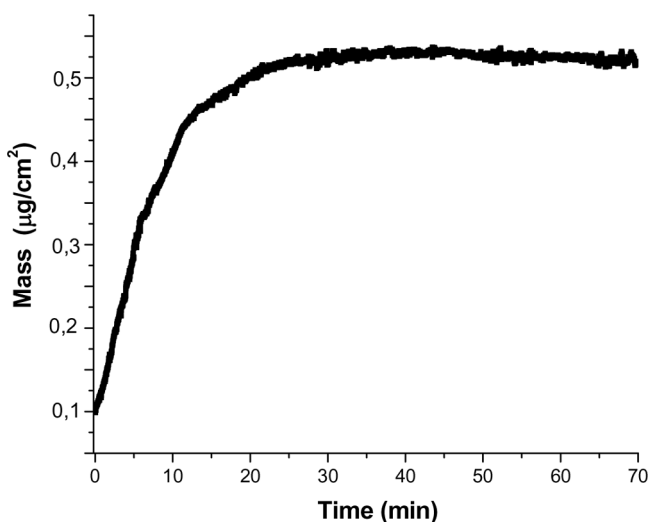
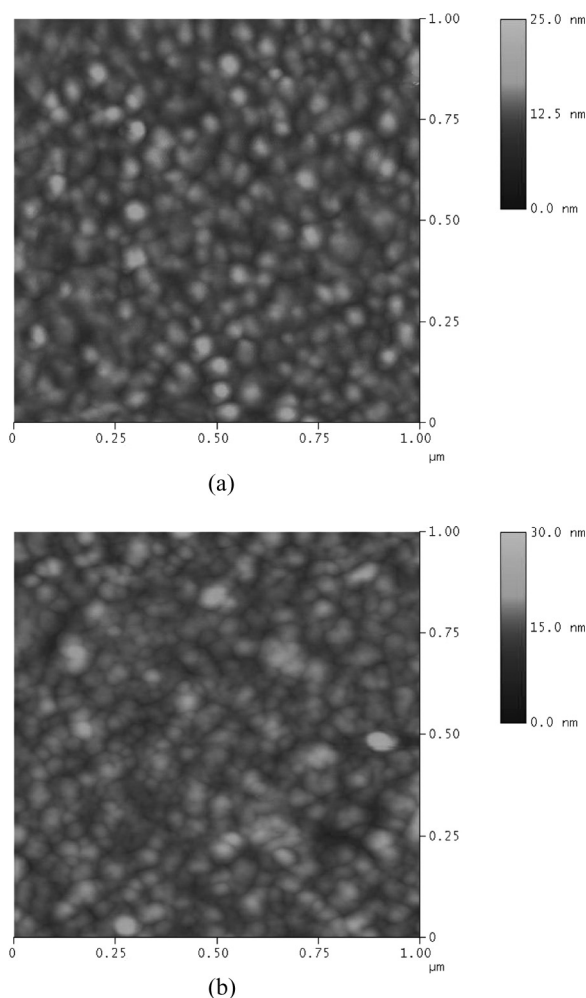


Figure 1. Deposition of MoS<sub>2</sub> into a Quartz Crystal Microbalance gold electrode.

experiments we monitored the spontaneous deposition of MoS<sub>2</sub> monolayers on a gold surface electrode by recording the quartz crystal frequency shifts.

The preparation of suspended MoS<sub>2</sub> single layers implies firstly the interaction of pristine MoS<sub>2</sub> with butyllithium leading to the intercalation of lithium between the sulfide slabs. Then the intercalated material is put into contact with water and lithium is oxidized, hydrogen is produced and the sulfide slabs are exfoliated, becoming the single layers dispersed in water as illustrated in Scheme 1.

In Figure 1 is shown the variation of the quartz crystal (5-MHz QCM-Cr/Au) resonance frequency produced by the spontaneous deposition of MoS<sub>2</sub> on the electrode. As observed, after approximately 70 minutes the equilibrium is achieved. Resulting frequency shift corresponds to an average deposition of  $5.6 \cdot 10^{-1} \mu\text{g}/\text{cm}^2$ . Calculations using a simple molecular model indicate that in a planar MoS<sub>2</sub> sheet, each molybdenum atom generates a superficial area of  $8.6 \text{ \AA}^2$  on each face of the lamina. According to that, such an amount of deposited mass on the electrode is nearly equivalent to the formation of a film constituted by single MoS<sub>2</sub> layer [37].

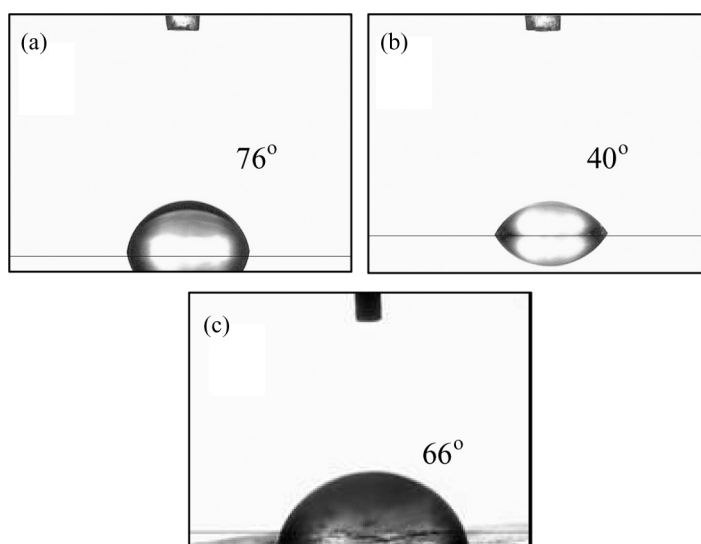


**Figure 2.** AFM images of (a) gold surface; (b) MoS<sub>2</sub> thin film on gold surface.

**Table 1.** Analysis of AFM images of QCM gold electrode clean and covered by a MoS<sub>2</sub> thin film

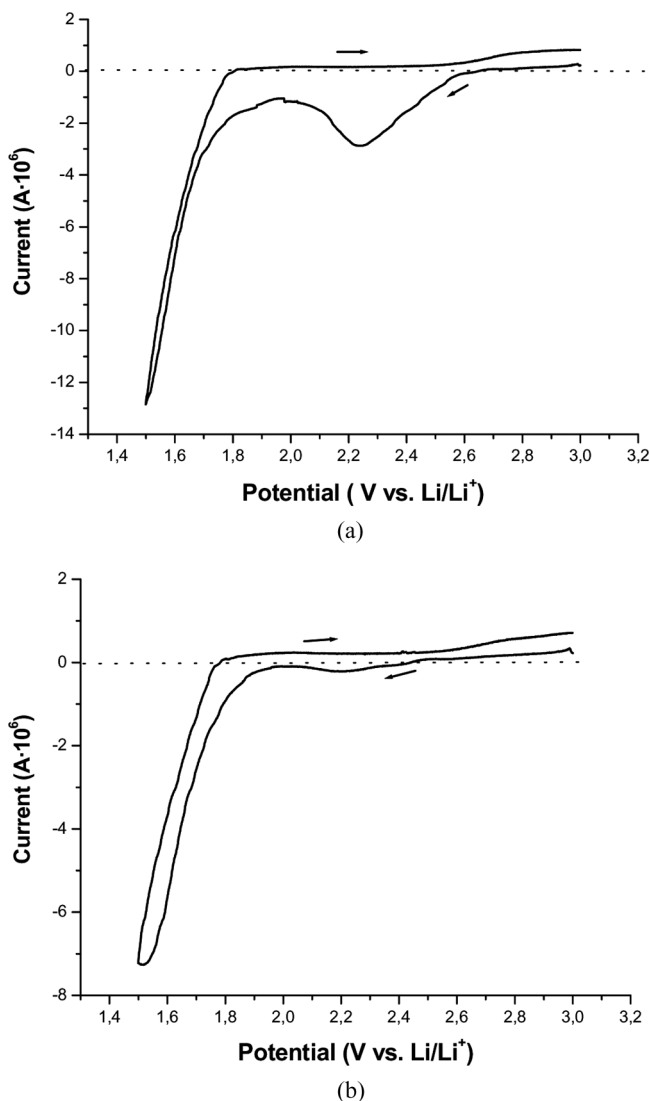
	Au	Au–MoS <sub>2</sub>
Roughness/nm	1.171	1.416
Diameter size/nm	83.985	45.899
Depth/nm	6.971	9.736

The homogeneity, texture, and nature of the MoS<sub>2</sub> film were examined by Atomic Force Microscopy. In Figure 2 are compared the AFM images of both pristine gold and Au/MoS<sub>2</sub> electrode surfaces. Quite homogenous surfaces formed by ellipsoidal aggregations are observed. The difference in brightness of the grains and the roughness of the surfaces permits to identify those areas on the Au/MoS<sub>2</sub> electrode which are more extensively covered by the sulfide. An analysis of these AFM images is reported in Table 1. A clear diminution of average grain diameter, from 83.985 nm in the Au into 45.899 nm in the Au–MoS<sub>2</sub> electrode, is observed. Deposited MoS<sub>2</sub> appears to be rather homogeneously distributed on the electrode but forming relatively narrow islands. Since for an orientation of the MoS<sub>2</sub> basal planes parallel to the gold surface a smoother, staggered morphology would be expected, we think than an orientation of the laminas perpendicular to the electrode surface is more reasonable. Edge-bonded MoS<sub>2</sub> cluster have been obtained in a series of supports, among them, on glass and quartz [38], NaCl (by the use a high quality substrate (single crystal) [39], Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> [40]. Considering that gold has a well known tendency to bond sulfur species, particularly with thiols and disulfide [33–36], and the similitude of these species with the dangling sulfur bonds at the edges of MoS<sub>2</sub> clusters, proposed orientation makes sense.

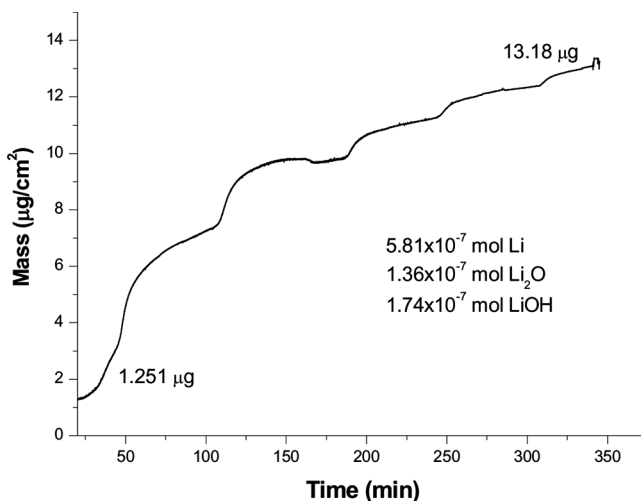
**Figure 3.** Water drop contact angle on (a) gold surface; (b) MoS<sub>2</sub> deposited on gold surface; and (c) MoS<sub>2</sub> van der Waals surface.

The water contact angle measurements reported in Figure 3, measured in different sectors of the surface, also agrees with the description above. Observed value of about  $40^\circ$  is clearly lower than that of the uncovered Au electrode ( $76^\circ$ ) as well as of that of MoS<sub>2</sub> van der Waals surface ( $66^\circ$ ) as measured on a MoS<sub>2</sub> pressed sample, where the sulfide basal planes are preferentially arranged perpendicularly to the direction of applied pressure [41].

The arrangement of the MoS<sub>2</sub> on the gold surface discussed above – islands of the sulfide surrounded by uncovered substrate surface – appears to be also responsible of observed electrochemical lithium deposition on the electrode. This fact together with the conditions under which these experiments were performed,



**Figure 4.** Cyclic voltammogram showing the reduction and oxidation of lithium in a Au/MoS<sub>2</sub> electrode at a scan rate of 1 mV/s. (a) First cycle; (b) Third cycle.



**Figure 5.** Irreversible increment of mass in the Au/MoS<sub>2</sub> electrode during five voltammetric cycles. Deposition of Li<sub>2</sub>O/LiOH is produced by the reduction of water (solvent).

particularly the low but significant water content in both the restacked MoS<sub>2</sub> and the supporting electrolyte, makes it necessary to consider two important factors, namely the electrochemical reduction of water and the lithium deposition on gold which occur within the potential window necessary for the experiment. In order to gain further information to understand the influence of these effects, a series of cyclic voltammetry (CV) experiments using both electrodes, pristine gold and Au–MoS<sub>2</sub>, while monitoring charge and mass changes occurring in the process were performed.

As observed in the Figure 4a illustrating the first CV cycle in the Au/MoS<sub>2</sub> electrode, the behavior of the electrode in the initial cycles is mainly dominated by the reduction of water which induces the irreversible deposition of LiOH (or Li<sub>2</sub>O) on the electrode producing an increment of mass, Figure 5. Meanwhile in latter cycles (Fig. 4b), when no or few water is available, the predominance of lithium reduction/oxidation processes is observed. In the MoS<sub>2</sub> electrode which displays an initial equilibrium potential of about 3 V vs. Li/Li<sup>+</sup>, the amount of lithium reduced was equivalent to that oxidized in the same cycle. This feature which is directly observed in latter cycles may be also detected in the formers when the amount of charge corresponding to the reduction of water is discounted. As observed in Table 2 in which a

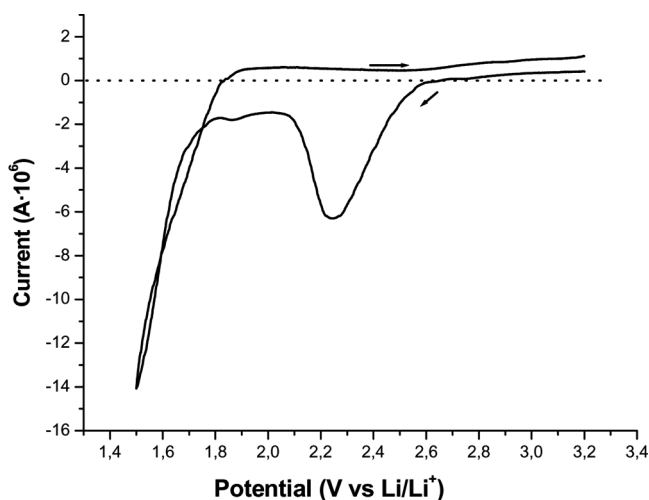
**Table 2.** Cyclic voltammetry of Au/MoS<sub>2</sub> electrode. Charge process and Lithium deposition

Cycle	Charge/C · 10 <sup>3</sup>			Lithium deposition				
	Total	Reduction Lithium	Oxidation Water	Oxidation Lithium	Reduction mmol · 10 <sup>6</sup>	Oxidation mmol · 10 <sup>6</sup>	Reduction µg · 10 <sup>2</sup>	Oxidation µg · 10 <sup>2</sup>
1	4.38	0.50	3.88	0.45	5.18	4.70	3.63	3.29
2	2.65	0.50	2.15	0.49	5.18	5.13	3.63	3.59
3	2.18	0.50	1.68	0.47	5.18	4.95	3.63	3.47
4	1.70	0.50	1.20	0.59	5.18	6.19	3.63	4.33

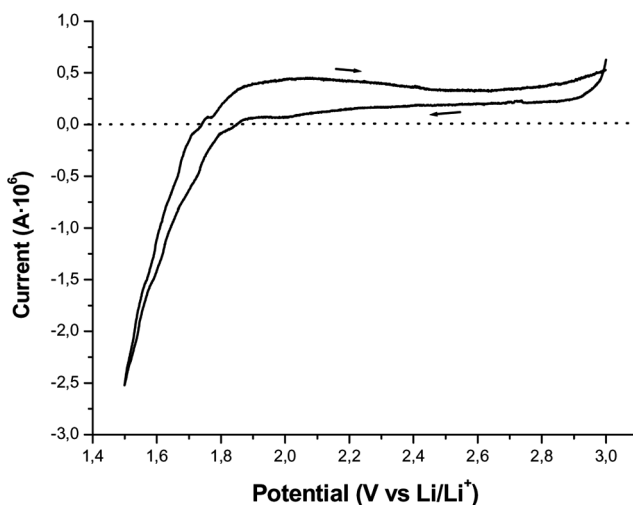


quantitative data from these experiments is reported, the amount of reduction and oxidation charge involved in the experiments performed with the Au/MoS<sub>2</sub> electrode is always approximately the same.

The gold electrode shows however a somewhat different behavior. The initial equilibrium potential of this electrode is about 3.2 V vs. Li/Li<sup>+</sup>. As observed in voltammograms reproduced in Figure 6a and 6b, the reduction of water also produces an irreversible deposition of LiOH/Li<sub>2</sub>O; however the integration of both reduction and oxidation current shows that in this electrode – under working conditions, namely environment, scanning rate, and potential window, similar to those for the



(a)



(b)

**Figure 6.** Cyclic voltammogram showing the reduction and oxidation of lithium in a gold electrode at a scan rate of 1 mV/s (a) First cycle; (b) Third cycle.

MoS<sub>2</sub> containing electrode – there is a clear tendency to the accumulation of reduced lithium in the electrode.

Although the charge symmetry and the potential observed in the charge/discharge processes in the Au/MoS<sub>2</sub> electrode, the analysis of the net amount of lithium involved in each cycle, approximately  $5 \cdot 10^{-4}$  C, reveals that it exceeds by far the capacity of molybdenum disulfide, about 1 mol lithium per mol MoS<sub>2</sub> ( $1.16 \cdot 10^{-4}$  C). Apparently in this electrode both, the expected intercalation of the metal into MoS<sub>2</sub> and the deposition of lithium on gold area not covered by the sulfide, are simultaneously occurring. That notwithstanding the oxidation behavior of lithium deposited on gold appears to be affected by the presence of the molybdenum disulfide which would avoid the accumulation observed in the gold electrode already described. Work to investigating such a feature that could be reflecting a kind of catalytic effect of molybdenum disulfide in such a kind of processes is still in progress.

#### 4. Conclusions

The immersion of a gold surface into a single layer suspension of MoS<sub>2</sub> at room temperature results in the spontaneous restacking of the disulfide on the substrate. The affinity between the sulfur dangling bonds at the MoS<sub>2</sub> layer edges and gold atoms, together with the tendency of the basal planes of the sulfide to stack by van der Waals interactions, results in the formation of cluster islands in which the basal planes are oriented perpendicularly to the substrate surface. The morphology of resulting films permits an electrochemical insertion of lithium that goes beyond the characteristic intercalation capacity of MoS<sub>2</sub> because of direct deposition of the alkali metal on the gold area between the sulfide clusters. Synergic effects, arising from the presence of MoS<sub>2</sub> on the electrode, appear to avoid the accumulation of lithium on gold thus permitting the total re-oxidation of inserted alkali metal.

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