



Electrochemical properties and long-term stability of molybdenum disulfide and platinum counter electrodes for solar cells: A comparative study

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ABSTRACT

The electrocatalytic properties of few-layer thick MoS₂ films, grown on Mo foils by soft sulfurization, are explored in two different redox shuttles, i.e. S²⁻/S_n²⁻ and I⁻/I₃⁻. The dependence of the MoS₂ catalytic activity on cycling in the polysulfide electrolyte is explored for the first time. MoS₂ exhibits an unprecedented self-improving behavior with increasing cycling, in addition to extraordinary stability against corrosion under soaking conditions for up to two months. On the contrary, Pt-based nanostructured catalysts present appreciable deactivation under the same conditions. Pristine and pretreated MoS₂ films in a polysulfide electrolyte under successive cycling are evaluated as counter electrodes in DSSCs and the effect of the number of cycles is examined. The DSSC with the pretreated MoS₂/Mo foil CE yields a 35% and a 20% increment of the efficiency and the short circuit current density respectively, compared to an untreated CE. Besides, the role of the surface roughness of Mo foil in the catalytic activity and stability of the MoS₂ films has been examined. The current results show that tailoring the morphology of nanometer-thick MoS₂ films - grown by sulfurization of Mo foils - can lead to enhanced electrocatalytic properties compared to Pt-based nanostructured films.

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1. Introduction

Dye sensitized solar cells (DSSC) and quantum dot sensitized solar cells (QDSSC) belong to the third generation of photovoltaics and share several common features. They differ primarily in the agent for light absorption and the redox shuttle used for the regeneration of the dye molecules or the quantum dots (QD), respectively. Both devices use a counter electrode (CE) for the collection of electrons from the external circuit and for the reduction of oxidized species (such as I₃⁻ ions and S_n²⁻ ions), produced by the regeneration of dye molecules and quantum dots during operation of the solar cell, respectively [1]. Therefore, an efficient CE must exhibit sufficiently good catalytic properties towards the redox couple and electrical conductivity for fast electron transfer.

For example, the charge transfer resistance should preferably be lower than 0.5 Ω/cm² [2], while chemical and mechanical stability are also important issues, since corrosion (or poisoning), irreversible adsorption of different species, such as I₂, I₃⁻ and I⁻ into a nonelectroactive state [3] and detachment from the substrate of even a small quantity can lead to catalytic deactivation, affecting both the current density and the fill factor of the devices. Besides, as in most cases transparency is not a prerequisite, CEs with high reflectivity can be used [4].

Pt based CEs have been applied in photoelectrochemical cells in combination with electrolytes containing the iodide/triiodide (I⁻/I₃⁻) redox couple – even before the breakthrough in DSSCs – due to their high catalytic activity towards the reduction of triiodide ions [5]. Despite their merits, Pt based CEs present certain disadvantages, such as high cost, especially in the case where a conductive glass substrate (FTO) is also used, partial detachment from the substrate, and change in their electrocatalytic properties due to adsorption of iodide species, including iodine, not only in the case of polycrystalline Pt, but also in the case of Pt nanoparticles

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(4–6 nm in size) [3]. That leads in some cases to the formation of PtL_4 [1,6–8]. Besides, a change in the valence state of Pt has also been observed [9]. To avoid corrosion of metal contacts and light absorption caused by the I^-/I_3^- redox couple, other redox shuttles such as the thiolate/disulfide (T^-/T_2) [10,11] and Co (II/III) [12,13], have been applied in DSSCs, where Pt based CEs have exhibited moderate performance. In QDSSC the predominant $\text{S}^{2-}/\text{S}_n^{2-}$ redox couple is used, instead of I^-/I_3^- , since the last one causes photo-corrosion to the QDs [14,15]. In this case, the main drawback of Pt is the strong chemisorption of $\text{S}^{2-}/\text{S}_n^{2-}$ redox couple that leads to reduced catalytic activity [16].

Given the above context, it is obvious the imperative need to substitute the Pt based CEs, to improve the conversion efficiency and the stability of solar cells operation or at least reduce the cost of CEs, without sacrificing to a large extent these two parameters. In this direction, other materials such as carbon based materials, conductive polymers, transition metal compounds and hybrid nanomaterials have been investigated, (see the relevant recent reviews [16–19]). Among them, 2D crystals, such as transition metal chalcogenides (TMDCs) have attracted a great interest, due to the advantages they present, e.g. low cost and good catalytic activity towards various redox shuttles, even when few-layers of the material are used [15,20].

MoS_2 belongs to the TMDCs family of layered crystals. Only recently it has been explored as CE in DSSCs, exhibiting catalytic properties comparable to that of Pt based CEs and reaching, at best, the efficiency of a DSSC with a Pt based CE [20–29]. Hybrids of MoS_2 and carbon-based materials (graphene, carbon nanotubes, etc.) result usually in efficiencies better than that of the Pt based CE [30–38]. While for the MoS_2 based hybrids the CE stability has been examined in the vast majority [30–32,36,37] only few such studies have been reported so far for neat MoS_2 CEs [20,23]. Therefore, whether neat MoS_2 can surpass Pt as a catalyst for CE in DSSCs, still remains an open question.

As the catalytic activity of a material depends on the redox couple, the same material can show different behavior with different redox couples [39]. Notably, the catalytic properties of MoS_2 have been examined mainly for the I^-/I_3^- redox couple and only one study [21] explores the MoS_2 CE performance in combination with a different redox couple (T_2/T^-), where an improvement up to 40% in the efficiency was found compared to a Pt CE. Additionally, only in one study [40] a neat MoS_2 electrode has been used as a cathode in a QDSSC in conjunction with the $\text{S}^{2-}/\text{S}_n^{2-}$ redox couple, whereas MoS_2 composite electrodes have been used for the same purpose [41,42]. Efforts to improve the performance of MoS_2 electrodes have been undertaken in Ref. [29] and in Ref. [43] with the use of pulsed laser and microwave treatments, respectively. In the first case the improved performance was attributed to the enhanced crystallinity and the enhanced interconnection between the MoS_2 particles, while in the case of microwaves, the basal planes of MoS_2 crystal were cracked, revealing additional active edge sites. Nonetheless, in none of the aforementioned works the influence of successive cycling in the polysulfide electrolyte on the catalytic properties of the MoS_2 electrode was examined.

The above brief survey on the still unsettled issues of CE stability against various electrolytes in DSSCs and QDSSCs reveals that despite the sporadic studies there are still no systematic efforts undertaken to understand the role of various redox couples in the long-term stability of neat MoS_2 . Studies on hybrid material CEs, i.e. MoS_2 coupled with another nanostructure, do not enlighten the stability mechanism as no solid conclusions can be drawn about the role of each material. Therefore, in the current article we present a systematic investigation of a neat MoS_2 electrode, in comparison to Pt CEs, with two different redox couples and evaluate its catalytic properties and stability over ultra-long-term time periods and

hundreds of scans.

2. Experimental

2.1. Sulfurization of Mo foils

MoS_2 was prepared by sulfurization of Mo metal foils following the procedure described elsewhere [20]. Two kinds of molybdenum foils were used as substrates to perform the experiments, namely the high roughness (HR) and the low roughness (LR). The former was purchased from Alfa Aesar (99.95% purity, 0.05 mm thickness) and was used without any treatment while the other one is a polished polycrystalline molybdenum foil from MTI Corporation (99.9% purity, 0.5 mm thickness). Both were placed in a three-zone horizontal tube furnace for the growth of MoS_2 on the surface of Mo foils. Specimens were maintained at 800 °C, while an alumina boat loaded with high purity elemental sulfur was placed several centimeters upstream of the substrates. High purity Ar gas was used to purge the reaction tube for 1 h at a flow of 120 sccm before raising the temperature; the same gas flow was maintained during the growth process. The furnace was heated from ambient to 800 °C in about 20 min; it was kept at this temperature for 30 min so to achieve the desired MoS_2 film thickness and then it was turned off and left to cool down slowly before ceasing the gas purging [20].

2.2. Preparation of the Pt films

Platinum films were prepared by electrodeposition from an aqueous H_2PtCl_6 solution (0.002 M). A potentiostat–galvanostat (Autolab PGSTAT 204) and a three electrode configuration were used with a SnO_2 :F glass (FTO) serving as the working electrode, an Ag/AgCl electrode as the reference and a Pt wire as the counter electrode. The electrodeposition process was carried out at a constant current of 0.5 mA cm^{-2} for 200 s [1,6].

2.3. Characterization of materials

Electron microscopy images were recorded with the aid of a high-resolution field-emission scanning electron microscope (FE-SEM) instrument (Zeiss, SUPRA 35VP) operating at 15 kV. Raman spectra were accumulated with the 441.6 nm laser line as the excitation source emerging from a He–Cd laser (Kimon). The scattered light is analyzed by a LabRam HR800 (Jobin Yvon) micro-Raman spectrometer at a spectral resolution of about 2.0 cm^{-1} . A microscope objective with 50× magnification was used to focus the light onto a spot of about 3 μm in diameter. Low laser intensities were used (–0.37 mW on the sample) to avoid spectral changes due to heat-induced effects. The Raman shift was calibrated using the 520 cm^{-1} Raman band of crystalline Si.

Cyclic voltammetry (CV) was used to evaluate the electrochemical catalytic activity of the Pt/FTO and MoS_2/Mo electrodes for the two redox shuttles (iodide/triiodide and polysulfide ions). The compositions of the electrolytes, used for the CV experiments for I^-/I_3^- were 10 mM KI, 1 mM I_2 and 0.1 M LiClO_4 in propylene carbonate (PC) while an aqueous solution of 0.01 M S, 0.01 M Na_2S , 0.01 M NaOH was used for $\text{S}_n^{2-}/\text{S}^{2-}$. The same three-electrode setup was used, as for the electrodeposition, for CV experiments with the sweep rate varying between 5 and 100 mV/s. Diffusion coefficients and activation energies (E_a) were extracted from CV experiments. The latter was calculated from the slope of the graph $\ln j_p$ vs $1000/T$, where an Arrhenius behavior was observed, with j_p the measured peak current density [1]. No pretreatment or activation of the electrodes took place before the measurements.

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