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Review

Electrochemical synthesis of molybdenum sulfide semiconductor

Akif Shikhan Aliyev [a], Mahmoud Elrouby [a,b,*], Samira Fikret Cafarova [a]

[a] Institute of chemical problems, National Academy of sciences of Azerbaijan, AZ 1143 Baku, Azerbaijan
[b] Chemistry Department, Faculty of Science, Sohag University, 82524 Sohag, Egypt

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ABSTRACT

The electrochemical deposition of MoS_2 from different media; aqueous, non-aqueous, molten salts and ionic liquids have been reviewed and discussed in this review. Electrochemical methods and substrates used for the electrodeposition of MoS_2 have been also discussed. All of the parameters affecting the electrodeposition process including temperature, pH and solution composition which lead to suitable shape of MoS_2 for using in different applications as photoelectrochemistry have been showed and discussed. The reaction mechanisms of the electrodeposition process of MoS_2 have been explored and discussed.

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1. Introduction

MoS_2 is one of an important IV–VI semiconductor type and diamagnetic, indirect bandgap semiconductor similar to silicon, with a band gap of 1.7 eV. MoS_2 with particle size in the range of 1–100 μm is a common dry lubricant. Few alternatives exist that confer high lubricity and stability at up to 350 °C in oxidizing environments [1,2].

When added to plastics, MoS_2 forms a composite with improved strength as well as reduced friction. Polymers that have been filled with MoS_2 include nylon (with the trade name Nylatron), Teflon, and Vespel. Self-lubricating composite coatings for high-temperature applications have

* Corresponding author at: Institute of chemical problems, National Academy of sciences of Azerbaijan, AZ 1143 Baku, Azerbaijan.
E-mail address: dr_mahmoudelrouby@hotmail.com (M. Elrouby).

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been developed consisting of molybdenum disulfide and titanium nitride by chemical vapor deposition.

MoS_2 is employed as a co-catalyst for desulfurization in Petrochemistry; e.g., hydro-desulfurization [3]. The effectiveness of the MoS_2 catalysts is enhanced by doping with small amounts of cobalt or nickel and the intimate mixture is supported on alumina. Such catalysts are generated in situ by treating molybdate/cobalt or nickel-impregnated alumina with H_2S or an equivalent reagent.

Nanotubes and buckyball-like molecules composed of MoS_2 exhibit unusual tribology and electronic properties [4]. MoS_2 has been investigated as a component of photoelectrochemical (e.g. for photocatalytic hydrogen production) applications and for microelectronics applications [5]. MoS_2 and other transition metal dichalcogenides form bulk crystals composed of two-dimensional layers stacked in the vertical direction. Such two-dimensional layers are similar in form to graphene and express diverse electronic and optical properties [6] that can differ from those in the bulk. Whereas bulk MoS_2 has an indirect band gap of 1.2 eV, single layers of MoS_2 have a direct 1.8 eV electronic bandgap [7] allowing the production of switchable transistors [5] and sensitive photodetectors [8]. The sulfur group on the surface of MoS_2 interacts with noble metals, including gold. The bond between MoS_2 and gold nanostructures was found to act as a highly coupled gate capacitor with a reduced carrier-transport thermal-barrier and increased thermal conductivity [9].

The main advantages of such semiconductors (MoS_2) is that they meet the requirements in order to function as a lubricant and efficient photoelectrode, (i) they exhibit intercrystalline slip and they adhere to the substrate well [10], and (ii) their inherently resistive nature to photocorrosion [11], because the photo transitions involve nonbonding d–d orbitals of Mo atoms [12].

The usual thin film preparation techniques, such as several methods already reported for preparation of MoS_2 thin layers, including scotch tape assisted micromechanical exfoliation [13,14], intercalation assisted exfoliation [15,16], solution exfoliation [17,18], physical vapor deposition [19,20], hydrothermal synthesis [21] and sulfurization of molybdenum oxides [22,23] are cost intensive and sometimes present special problems for the preparation of transition metal chalcogenides films.

Electrochemical deposition is an attractive method for preparation of thin films in commercial quantities because it uses relatively cheap equipment, enables the deposition in large area and easy control of growth parameters through applied potential, current, pH and temperature of the bath. Many researchers have studied the mechanism of an electrochemical deposition of MoS_2 from aqueous and little from non-aqueous solutions. A variety of electrodeposition techniques have been reported for the preparation of MoS_2 films, using anodic oxidation or cathodic reduction. Good results and observations were obtained and reported in this review.

2. Electrodeposition of MoS_2 thin films from aqueous solutions

It is known that, the electrodeposition potential of molybdenum is more negative than the electroreduction potential of hydrogen, so difficulties may be found for the cathodic electrodeposition of molybdenum chalcogenide films from aqueous solutions. Theoretically, the deposition of pure molybdenum by electrolytic reduction of molybdates in acidic aqueous solutions is possible according to the reaction equation as follows:

$$H_2MoO_{4(aq)} + 6H^+ + 6e^- \rightarrow Mo + 4H_2O \quad (1)$$

It should be noted that, the MoS_2 electrodeposition from solutions of molybdate and thiosulfate under various conditions of pH and temperature has some difficulties, which may be attributed to the big difference between the electrodeposition potential of Mo and the electroreduction of thiosulfate. But in other work it was reported that, thin films of molybdenum disulfide have been prepared by electrodeposition method under galvanostatic conditions for about ten minutes from an aqueous bath by using molybdenum trioxide dissolved in ammonia and sodium thiosulphate as Mo^+ ion and S^{-2} ion sources, respectively. The films deposited onto stainless steel and fluorine doped tin oxide (FTO) glass substrates were adherent to the substrate. The estimated deposition potentials for molybdenum disulfides is 1.32 V. X-ray diffraction studies show that films are polycrystalline in nature and orientation preferentially along the (116) plane. SEM shows films are continuous and uniform. Optical absorption gives bandgap energy of 1.7 eV [24].

Molybdenum sulfide thin films can be cathodically electrodeposited under potentiostatic conditions at a potential of −1.4 V vs. SCE from aqueous solutions of sodium tetrathiomolybdate Na_2MoS_4 anion on quartz substrate covered by a thin Ni–Cr layer. It was carried out by a two-electron reduction of tetrathiomolybdate ions (MoS_4^{2-}) as follows:

$$MoS_4^{2-} + 2e^- + 2H_2O \rightarrow MoS_2 + 2SH^- + 2OH^- \quad (2)$$

Annealing of these films in inert atmosphere at high-temperature in presence of sulfur resulted in the formation of highly-textured films of MoS_2 with the van der Waals planes parallel to the substrate and crystal size in the micrometer range. The annealed films are photoactive and their photoconductivity measurements reveal a direct band gap of about 1.71 eV [25]. But when the Mo and conductive glass were used as substrates, the electrodeposited annealed films have an optical spectrum characteristic of MoS_2, with a direct bandgap of 1.78 eV [26].

Polycrystalline thin films of MoS_2 are electrodeposited cathodically by using molybdic acid (H_2MoO_4) and sodium thiosulphate as initial solution on tin oxide (SnO_2) coated conducting glass substrates. The deposited films are characterized by various techniques includes the X-ray diffraction analysis, where the structure of the films is identified as hexagonal. From optical analysis, the bandgap value is calculated as 1.68 eV with indirect bandgap nature. From scanning electron micrographs, the surface appears to be comparatively granular with grains in irregularly shaped. From Mott–Schottky plots the films are found to be n-type semiconductor [27].