

## A Study on MoS<sub>2</sub> Thin Films Electrochemically Deposited in Ethylene Glycol at 165°C

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The electrosynthesis of nanoparticle thin films of MoS<sub>2</sub> from solutions of (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> in ethylene glycol at 165°C, is described. The as-deposited MoS<sub>2</sub> thin films (~150 nm thick) were X-ray amorphous and exhibited featureless optical absorption spectra over the 1-3.5 eV spectral range. High resolution transmission electron microscopy (HRTEM) revealed the presence of single or double (0002) plane-sized 2H-MoS<sub>2</sub> thin nanoplatelets (~2-3 nm) embedded in an amorphous matrix. Annealing the as-deposited samples under Ar for 1 h at 550°C, resolved a broad and weak-intensity peak in the respective X-ray spectra, identified as the (0002) Bragg peak of the bulk 2H-MoS<sub>2</sub> polytype, as well as some spectral features in the optical absorption spectra. HRTEM images disclose generation of a variety of nanostructures, consisting of 2-5 2H-MoS<sub>2</sub> (0002) planes stacks (some bent) together with few polyhedral nanostructures with triangular or rectangular projections. An appraisal of the factors influencing the reaction mechanism of the various MoS<sub>2</sub> nanostructures formation is proposed.

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Semiconductor layered transition metal dichalcogenides MX<sub>2</sub> (M for Mo or W; X for S or Se) are particularly interesting materials since they possess fascinating structures and exhibit related potential industrial applications, ranging from photomaterials for solar cells, optical filters, and detectors, to catalysis and lubricants.

Thin films of MoS<sub>2</sub> have been prepared by a variety of electrochemical methods, which primarily govern size, shape, and orientation of the resulting material.<sup>1-5</sup> Of particular interest are those materials composed of nanoparticles. Because of their layered structure, these materials, when reduced to nanometer sizes, are intrinsically unstable in the planar form and under certain conditions, can crystallize into unusual polyhedral (fullerene-like) topologies.<sup>6-8</sup> As both size and shape of particles may influence changes in their respective complex electronic band structures and related charge transport properties, new physics occurs when one or more dimensions of the semiconductor crystallite material are reduced to a size comparable to bulk electron delocalization length. Thus, size and shape are additional parameters available for designing materials and controlling their behavior.

We have shown recently<sup>9</sup> that the electrosynthesis of MoS<sub>2</sub> nanoparticles of 1-8 (0002) plane (0.6 nm apart) sizes, in thin film form, is possible by cathodic reduction of MoS<sub>4</sub><sup>2-</sup> in ethylene glycol at room temperature. This surprising finding that quantum sized, platelike nanocrystallites of MoS<sub>2</sub> were formed within these films produced electrochemically in an organic medium, suggested further fundamental and preparative perspectives to this area of study. Since synthesis in ethylene glycol solutions can be performed at temperatures up to the boiling point (195°C under ambient pressure), we investigated the electrochemical synthesis of MoS<sub>2</sub> thin films at 165°C to find possible effects of the electrodeposition temperature on the size or morphology of the particles. The microstructural and optical properties of the films, as prepared and annealed at 550°C under an argon atmosphere, were studied.

### Experimental

The electrochemical deposition was performed at 165°C in ethylene glycol, under potentiostatic conditions, by a standard three-electrode setup, with a calomel electrode as the reference, a platinum wire as the counter electrode, and an F-doped SnO<sub>2</sub>, 10 Ω/cm<sup>2</sup> conductive glass (1 × 5 cm<sup>2</sup>) as the cathode. The conductive glass was previously cleaned with trichloroethylene and acetone, rinsed with water, and dried in an Ar flow before MoS<sub>2</sub> deposition.

The electrodeposition apparatus was custom built. The software allowed precise and reproducible control of current, voltage, and

temperature. The deposition solution consisted of 0.005 M (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> mixed in 0.1 M KCl (supporting electrolyte) and 0.57 M NH<sub>4</sub>Cl (as proton donor).<sup>9</sup> Reagents were of analytical grade. Ethylene glycol was used as purchased, without further distillation. In a typical run, deposition occurred at 165°C, at a constant current density (~0.5 mA·cm<sup>-2</sup>), a potential maintained at -0.4 V (homogeneous layers), and a charge of 0.07 C·cm<sup>-2</sup> passed during 100 s, which resulted in a layer ~150 nm thick, brown, smooth, and well adherent to the electrode. At thicknesses exceeding 1500 nm, (longer deposition times), layers peeled off the substrate. Subsequent annealing of the as-deposited thin film was at 550°C, for 1 h under an Ar atmosphere.

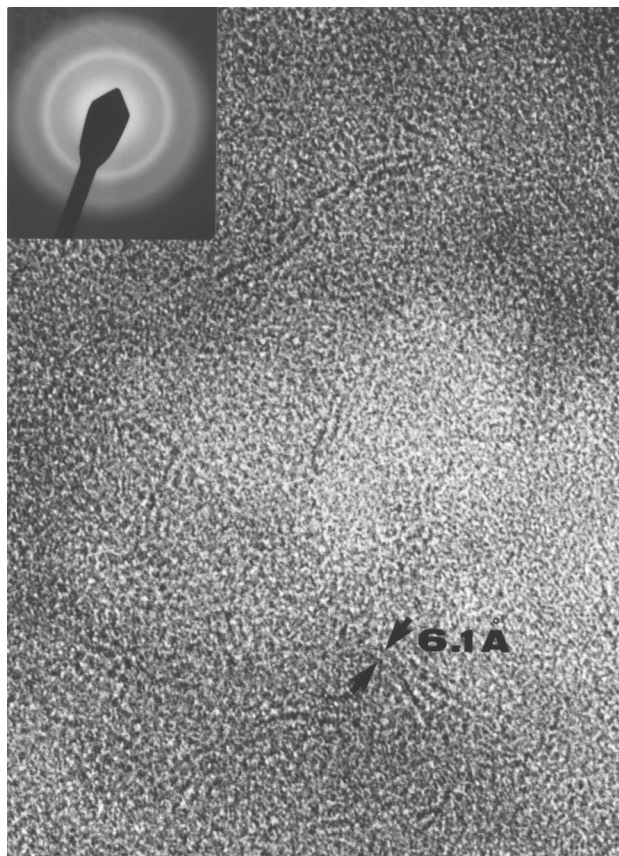
The thickness of the as-deposited and annealed MoS<sub>2</sub> thin films was measured with a TENCOR P-1 long-scan profiler (Tencor Instruments). Electron probe microanalysis (EPMA) was carried out with a Camebax apparatus. X-ray diffraction (XRD) spectra of the deposited films were recorded with a Philips PW 1710 powder X-ray diffractometer using Cu Kα radiation. The optical properties of the films were investigated in transmission using a Cary 2400 spectrophotometer. A substrate of the same glass, having identical thickness, was used as a reference. Optical absorption densities of the films were calculated from transmission spectra measured in the 1-3.5 eV photon energy range, without correction for reflection losses. High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAD), were carried out to provide detailed examination of the structure of the MoS<sub>2</sub> thin films. Carbon-coated copper grids were used for examination in a JEOL-JEM 4000EX HRTEM. All micrographs were taken at 400 kV at approximate Scherzer defocus.

### Results

As-deposited MoS<sub>2</sub> films were ~150 nm thick and exhibited a typical brown color. The EPMA analysis indicated an atomic ratio S/Mo of 1.9. The films were X-ray amorphous: no Bragg peak typical of MoS<sub>2</sub> could be observed in their XRD spectra. HRTEM of the films (Fig. 1) disclosed the typical image of an amorphous material, embodying some single or double fringes (observed under optimum defocus conditions) which indicated the presence of crystalline single or double (0002) plane-sized 2H-MoS<sub>2</sub> thin "nanoplatelets". On tilting the film, the lattice fringes in some regions disappeared and new fringes emerged at different positions, indicating that the single-plane nanocrystallites at these different positions newly satisfied the Bragg diffraction conditions, suggesting their random distribution within the film. As shown in Fig. 1, the size of the crystalline domains was rather small (2-3 nm in this case). The electron diffraction results (see inset in Fig. 1) confirmed that the material was

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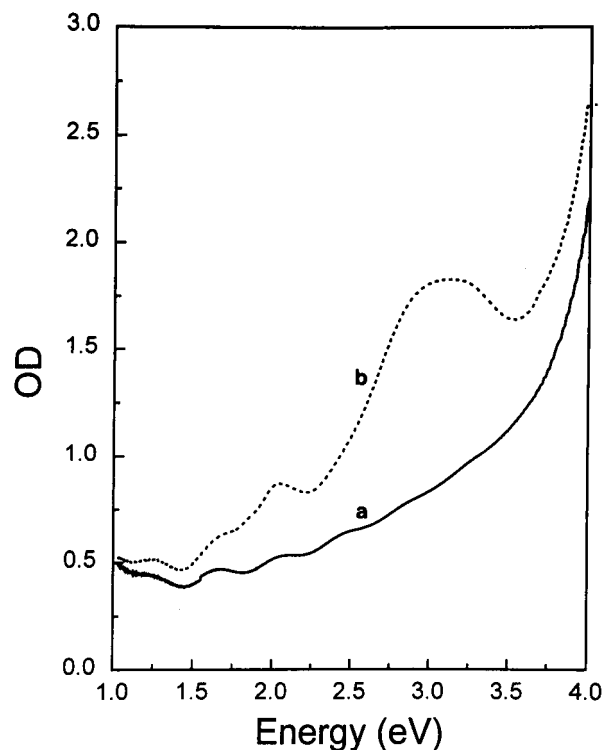
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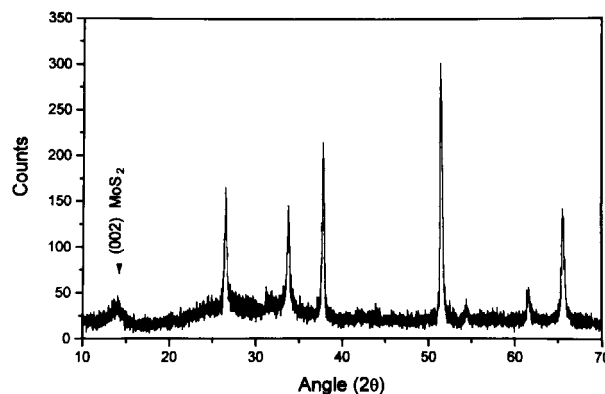
**Figure 1.** HRTEM image and the corresponding SAD pattern (inset) of the as-deposited MoS<sub>2</sub> thin film (~150 nm thick), synthesized from ethylene glycol on conducting glass at a potential of -0.4 V and 165°C, showing lattice images of 2H-MoS<sub>2</sub> nanosize platelets (~2-3 nm) within an amorphous matrix.

2H-MoS<sub>2</sub>. The films showed a gradual increase in optical density toward increasing photon energy (Fig. 2, curve a). The absorption threshold at ~3.5 eV was attributed to the conductive glass.

Annealing the as-deposited film in Ar at 550°C for 1 h led to significant changes in the films. The thickness of the film was reduced by 30-50%, probably due to an increase in density and compactness of the films, or some material loss by evaporation.<sup>3</sup> The color changed from brown to a reflecting metallic appearance. A broad, weak-intensity peak appearing around 14° (2θ) in the X-ray spectra (Fig. 3) was identified as the (0002) Bragg peak of the 2H-MoS<sub>2</sub> poly-type (bulk phase). The optical absorption spectrum (Fig. 2, curve b) exhibited now several spectral features. The absorption threshold at ~1.7 eV, is associated with a direct transition (at the K point of the Brillouin zone).<sup>10,11</sup> The broad peak on the high energy side of this threshold corresponds to the A and B excitonic transitions which are not well resolved in energy. The threshold at 2.5 eV is due to a direct transition (from deep in the valence band to the conduction band). The broad peak at the high energy side is associated with the C and D excitonic transitions. The third absorption threshold corresponds to the glass absorption. The energy position of the various observed absorption features are not altered with respect to that of the bulk 2H-MoS<sub>2</sub>.<sup>10</sup> The HRTEM image (Fig. 4) now exhibited a network of bent, tangled, interlocking structures consisting of two to five 2H-MoS<sub>2</sub> (0002) planes, occasionally enclosing voids or joined with a common crystal plane and exhibiting bifurcation in two directions. Additionally, some particles showed dislocation-like or stacking fault structures. The main change was the occurrence, albeit of a small number, of heavily bent stacks comprising three or four 2H-MoS<sub>2</sub> (0002) planes, which defined rectangular or triangular nanoparticles. The HRTEM image of a typical MoS<sub>2</sub> nanoparti-



**Figure 2.** Room temperature optical absorption spectra of the MoS<sub>2</sub> thin film synthesized at 165°C in ethylene glycol: curves (a) and (b) correspond to the as-deposited sample, and annealed in Ar for 1 h at 550°C sample, respectively.

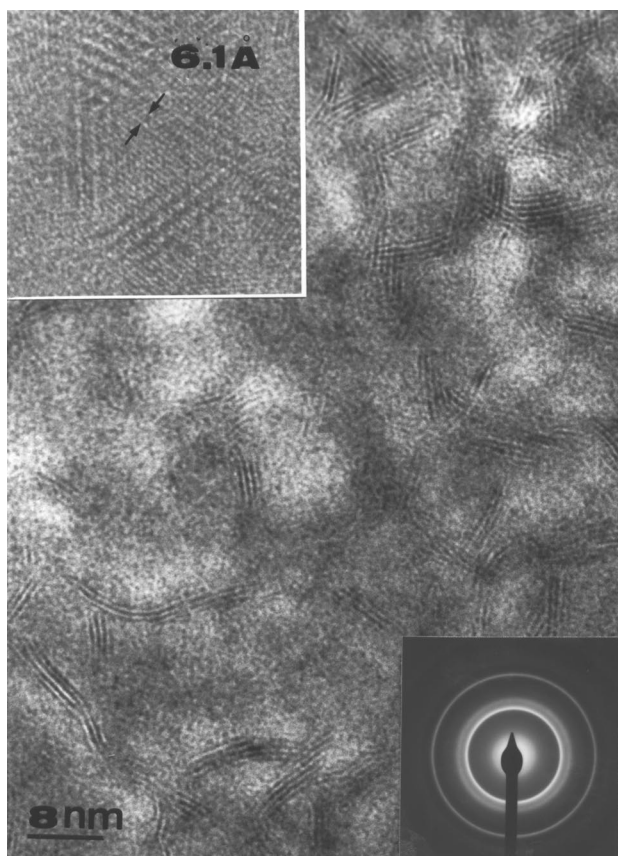


**Figure 3.** XRD spectrum of the annealed (1 h, 550°C, Ar) MoS<sub>2</sub> thin film sample, synthesized in ethylene glycol at 165°C. MoS<sub>2</sub> exhibits only the (0002) Bragg peak. Unlabeled peaks correspond to the substrate.

cle (~10 nm) with a triangular projection is shown in the inset of Fig. 4. As the particle shown stemmed from a larger cluster, lattice fringes from other particles are visible. Apparently, all these features nucleated within the amorphous matrix. The spacing between layers was ~6 Å, in good agreement with the layer spacing in bulk hexagonal 2H-MoS<sub>2</sub> poly-type (6.15 Å). In the present study, we did not obtain any information regarding the detailed structures and closure of these polyhedra, and further HRTEM studies with the tilting strategy should be performed to elucidate the closure. The SAD pattern (inset in Fig. 4) corresponds well to 2H-MoS<sub>2</sub> crystalline material of too small dimensions to give rise to detectable XRD patterns.

#### Discussion

The findings of the present study demonstrated that the films as deposited in ethylene glycol at 165°C were X-ray amorphous, and



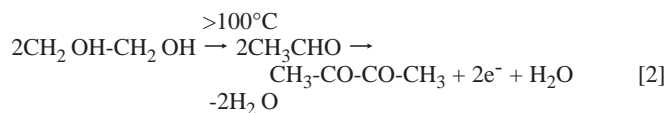
**Figure 4.** HRTEM image and the corresponding SAD pattern (inset) of the annealed (1 h, 550°C, Ar) MoS<sub>2</sub> thin film sample, synthesized at 165°C in ethylene glycol, showing bent (0002) irregularly shaped lattice planes, some exhibiting dislocation-like structures. A nanoparticle with a triangular projection is shown at higher magnification in inset.

HRTEM showed that they contained locally single or double (0002) plane-sized 2H-MoS<sub>2</sub> platelets embedded in an amorphous matrix. These results are surprising if we recall the previous HRTEM images of as-deposited thin films of MoS<sub>2</sub> electrodeposited in ethylene glycol at 20°C,<sup>9</sup> which revealed a different morphology of crystalline, platelike shaped MoS<sub>2</sub> grains exhibiting 5-8 (0002) basal planes of individual hexagonal S-Mo-S sheets. However, the presence of a variety of nanostructures shaped by the curved MoS<sub>2</sub> shell structures or, although in lesser extent, of polyhedral nanostructures with triangular or rectangular projections, that were observed in the annealed films is intriguing, especially considering that they were electrochemically produced. The results may be accounted for by considering the following possible reaction mechanisms for the formation of these nanometer-size structures.

1. The electrodeposition of MoS<sub>2</sub> films was originally explained in terms of the reduction of tetrathiomolybdate to MoS<sub>2</sub>, corresponding to the reduction of Mo<sup>6+</sup> to Mo<sup>4+</sup> ions.<sup>1-4</sup> It involves electrons generated by the cathodic process



As the MoS<sub>2</sub> structures in nanoparticle forms were produced by electrosynthesis in ethylene glycol at high temperatures (165°C in our experiment), we investigated the process under the same conditions, except passing current and noted that deposition did occur, which led us to envisage a possible chemical mechanism in ethylene glycol solutions. We suggest that the primary reduction process may also involve a chemical redox reaction of ethylene glycol accompanying the conventional cathodic electron transfer (Eq. 1), in a manner which recalls the polyol mechanism



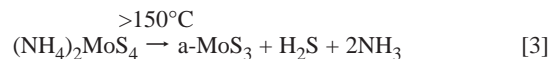
in which dehydration of ethylene glycol at temperatures above 100°C leads to the formation of diacetyl and to electron availability.<sup>12</sup>

The polyol method has been reported in the literature as a chemical way to prepare nanoscale particles of easily reducible oxides of Cu, Ag, Co, Ni, Cd, and Pb.<sup>12-16</sup> Various polyols such as ethylene glycol, diethylene glycol, or their mixtures, have been used both as solvent (owing to their rather high dielectric constant) and as reducing agent, under heating at an appropriate temperature. This temperature may reach the boiling point of the polyol in less easily reducible metal oxides.

In our previous work<sup>9</sup> we assumed that at room temperature (RT), the chemical (C) redox reaction by ethylene glycol, was very slow if any, whereas the electrochemical (EC) reduction reaction, although slower than at 165°C, generated flat and somewhat larger size particles, indicating that the lower RT limits nucleation and promotes particle growth. At high temperature (165°C), we assume that an abrupt nucleation of discrete MoS<sub>2</sub> upon the start of the electro-synthesis (EC)/chemical redox (C) polyol reaction in the hot reagent solution is achieved, and presumably, accounts for the resulting morphology.

2. The fact that the EC/C synthesis of MoS<sub>2</sub> was taking place in ethylene glycol at 165°C, implies that physical interaction of the solvent molecules from the solution within the semiconductor lattice or edge planes, cannot be avoided.<sup>17-19</sup> Indeed, the resulting morphology found in the present study suggests that the 2H-MoS<sub>2</sub> layered structure formed in ethylene glycol at 165°C is more susceptible to intercalation and exfoliation or edge passivation, which allowed a high degree of dispersity and prevented coalescence.

3. At the temperature of 165°C used in the present study, still another reaction of thermal decomposition of (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub><sup>20,21</sup>



may occur to a small extent, in the early stages, leading to locally confined, discontinuous nucleation of nanoscopic amorphous (a-MoS<sub>3</sub>) domains overlapping nuclei on the electrode. Admittedly, this effect should be less noticeable, if at all, at ambient temperatures. The occurrence of the nanometer-sized polyhedral objects observed in samples prepared at 165°C and annealed, and not in those prepared at RT, supports our hypothesis, which is discussed below. Additional experiments are in progress to fully elucidate this point. The apparent discrepancy with the EPMA analysis indicating an atomic ratio of 1.9 (*vide supra*) could be explained by the minute amounts of MoS<sub>3</sub> present in an inherently inhomogeneous sample. Based on the model proposed by Tenne *et al.*<sup>6-8,22,23</sup> for the formation of stable closed polyhedral inorganic fullerene structures in layered metal dichalcogenides (equivalent to the carbon system), we assume that the locally present (a-MoS<sub>3</sub>) (in samples prepared in ethylene glycol at 165°C), could crystallize, at 550°C when annealed, in the form of polyhedra via the exothermic ( $\Delta G = -6.2$  kcal/mol) chemical reaction



This loss of S from a-MoS<sub>3</sub> nanoparticles has previously been shown to trigger the nucleation of inorganic fullerene (IF) MoS<sub>2</sub> nanocrystallites even at ambient temperature.<sup>24</sup>

The absorption spectra of the MoS<sub>2</sub> thin films as deposited at 165°C are featureless, like those observed for the thin films deposited in ethylene glycol at room temperature,<sup>9</sup> and for colloidal MoS<sub>2</sub> particles.<sup>25,26</sup> In the last two cases, a blue shift of the spectra, relative to that of bulk MoS<sub>2</sub>, of about 0.3 to 0.7 eV, was observed. Such a shift is characteristic of quantized semiconductor particles. The smeared, blue-shifted absorption spectrum of these samples was

believed to originate from the relatively broad size distribution of the nanoparticles. Upon annealing at 550°C the thin film in this work, two broad ill-defined features appeared in the transmission spectrum. The low intensity and poor definition of the excitonic features, probably related to the poor degree of crystallinity of the films, did not allow us to determine if there was any energy shift caused by a quantization effect (blue shift),<sup>9,11</sup> or by the occurrence of the polyhedral nanostructures (red shift).<sup>27,28</sup> It will be possible to determine whether these effects are intrinsic to the nanoparticles when the synthesis is better controlled, and more uniform samples become available.

The few polyhedral nanostructures observed in the HRTEM images of films produced at 165°C and annealed at 550°C (see Fig. 4), resemble the closed polyhedra inorganic fullerene-like structures reported previously.<sup>24</sup> At the present stage, we were not able to decide whether the synthesis and annealing as in this work yielded closed nanoparticle structures. However, noticing the presence of such structures would point to their occurrences in these thin MoS<sub>2</sub> films electrochemically produced and could have some preparative value. Their barely observed occurrence raises the question of whether their formation is characteristic of the high temperature of both synthesis in ethylene glycol and annealing. We believe that the probability of the formation of polyhedral nanoparticles may be increased by raising the temperatures of reaction (which could rise to the ethylene glycol boiling point of 195°C at ambient pressure) and that of the annealing.

In conclusion, the results of the present study point to differences in the mechanism of formation of the MoS<sub>2</sub> nanoparticles by electro-synthesis in ethylene glycol or in an aqueous environment. We note that these polyhedral nanostructures are not present when the deposition is made from aqueous solutions. We imply that under the conditions of the electro-synthesis in ethylene glycol used in our investigation, more than a single mechanism may be involved in the network fabrication which leads to these structures. It is tentatively suggested that ethylene glycol may be an additional source of electrons for the reduction of MoS<sub>4</sub><sup>2-</sup> at 165°C (through the well-known polyol mechanism (Eq. 2)). We note that, while in aqueous solutions electrons are available only from the cathodic process (Eq. 1) in ethylene glycol and at 165°C, additional electrons could also become available from the polyol medium present in the reaction. It is emphasized, however, that at RT this reaction is very slow, if it occurs at all, and presumably has no effect. The influence of the chemical reduction reaction is particularly important in deposition at 165°C. However, the two processes are not independent since otherwise complete reduction of the precursor before electrodeposition of the film would take place. Furthermore, it is assumed that in the early stages of the synthesis at 165°C, the transformation of MoS<sub>4</sub><sup>2-</sup> → α-MoS<sub>3</sub> could occur, producing isolated, confined, nanometer-sized domains of α-MoS<sub>3</sub> which transform to MoS<sub>2</sub> via an exothermic reaction during subsequent annealing at 550°C.

The formation of nanometer-scale polyhedral MoS<sub>2</sub> particles via a mixed, chemical reduction in solution of tetrathiomolybdate (by ethylene glycol)/electroreduction mechanism, has been demonstrated. The consequent implications for a potential control of nanostructures production are presently envisaged.

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#### References

1. L. F. Schneemeyer and U. Cohen, *J. Electrochem. Soc.*, **130**, 1536 (1983).
2. H. J. Byker and A. E. Austin, *J. Electrochem. Soc.*, **128**, 381C (1981).
3. E. A. Ponomarev, M. Neumann-Spallart, G. Hodes, and C. Levy-Clement, *Thin Solid Films*, **280**, 86 (1996).
4. E. A. Ponomarev, R. Tenne, A. Katty, and C. Levy-Clement, *Sol. Energy Mater. Sol. Cells*, **52**, 125 (1998).
5. Y. Mastai, M. Homyonfer, A. Gedanken, and G. Hodes, *Adv. Mater.*, **11**, 1010 (1999).
6. R. Tenne, L. Margulis, M. Genut, and G. Hodes, *Nature*, **360**, 444 (1992).
7. L. Margulis, G. Salistra, R. Tenne, and M. Talianker, *Nature*, **365**, 113 (1993).
8. Y. Feldman, E. Wasserman, D. J. Strolovitz, and R. Tenne, *Science*, **267**, 222 (1995).
9. E. A. Ponomarev, A. Albu-Yaron, R. Tenne, and C. Levy-Clement, *J. Electrochem. Soc.*, **144**, L277 (1997).
10. R. Coehoorn, C. Haas, J. Dijkstra, C. J. F. Flipse, and R. A. de Groot, *Phys. Rev. B: Condens. Matter*, **35**, 6195, 6203 (1987).
11. J. P. Wilcoxon and G. A. Samara, *Phys. Rev., B: Condens. Matter*, **51**, 7299 (1995).
12. F. Fievet, J. P. Lagier, B. Blin, B. Beaudoin, and M. Figlarz, *Solid State Ionics*, **32/33**, 198 (1989).
13. F. Fievet, F. Fievet-Vincent, J-P. Lagier, B. Dumont, and M. Figlarz, *J. Mater. Chem.*, **3**, 627 (1993).
14. C. Duchamp-Sanguesa, R. Herrera-Urbina, and M. Figlarz, *Solid State Ionics*, **63-65**, 25 (1993).
15. L. K. Kurihara, G. M. Chow, and P. E. Schoen, *Nanostruct. Mater.*, **5**, 607 (1995).
16. A. Miyazaki, K. Takeshita, K. Aika, and Y. Nakano, *Chem. Lett.*, 361 (1998).
17. A. R. Beal, in *Physics and Chemistry of Materials with Layered Structures: Intercalated Layered Materials*, F. Levy, Editor, Redel, Dordrecht (1977).
18. W. M. R. Divigalpitiya, R. F. Frindt, and S. R. Morrison, *Science*, **246**, 369 (1989).
19. W. M. R. Divigalpitiya, S. R. Morrison, and R. F. Frindt, *Thin Solid Films*, **186**, 177 (1990).
20. D. M. Schleich and M. J. Martin, *J. Solid State Chem.*, **64**, 359 (1986).
21. D. Belanger, G. Laperrriere, and B. Marsan, *J. Electroanal. Chem.*, **347**, 165 (1993).
22. R. Tenne, *Adv. Mater.*, **7**, 965 (1995).
23. R. Tenne, M. Homyonfer, and Y. Feldman, *Chem. Mater.*, **10**, 3225 (1998).
24. L. Margulis, R. Tenne, and S. Iijima, *Microsc. Microanal. Microstruct.*, **7**, 87 (1996).
25. M. W. Peterson, M. T. Nenadovic, T. Rajh, R. Herak, O. I. Micic, J. B. Goral, and A. J. Nozik, *J. Phys. Chem.*, **92**, 1400 (1988).
26. M. Gutierrez and A. Henglein, *Ultrasonics*, **27**, 259 (1989).
27. G. L. Frey, S. Elani, M. Homyonfer, Y. Feldman, and R. Tenne, *Phys. Rev. B: Condens. Matter*, **57**, 6666 (1998).
28. G. L. Frey, R. Tenne, M. J. Matthews, M. S. Dresselhaus, and G. Dresselhaus, *J. Mater. Res.*, **13**, 2412 (1998).