Hanane Akram*, Cecilia Mateos-Pedrero, Esteban Gallegos-Suarez, Tarik Chafik, Antonio Guerrero-Ruiz and Inmaculada Rodríguez-Ramos

Effect of surfactant concentration on the morphology of Mo<sub>x</sub>S<sub>y</sub> nanoparticles prepared by a solvothermal route

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Abstract: The preparation of Mo<sub>x</sub>S<sub>y</sub> nanoparticles with different morphologies via a surfactant-assisted one-pot solvothermal route was reported. The concentration of surfactant was studied to evaluate its effects on the morphology and the size of the as obtained nanoparticles. The final products were comprehensively characterized using XRD, TEM, HRTEM, IR, TGA and XPS. It was found that at low surfactant concentration, MoS<sub>2</sub> spherical shapes were obtained whereas tubular morphologies are formed at higher concentration. This issue has been discussed based on various relevant experimental data.

Keywords: MoS<sub>2</sub>; nanospheres; nanotubes; solvothermal synthesis; surfactant.

1 Introduction

Molybdenum disulphide (MoS<sub>2</sub>) is the most studied dichalcogenide material regarding its catalytic performances and lubricants properties [1–5] due to its sandwich interlayer structure formed by stacking of the (S-Mo-S) layers in the direction [001]. These layers are loosely bounded by van der Waals forces, which accounts for easy cleavage of layers in the [001] direction [6]. As a useful semiconductor, molybdenum disulfide generally crystallizes with a hexagonal lamellar structure (S-Mo-S) with sulfur layers located between Mo atoms [7] accordingly. MoS<sub>2</sub> has received considerable attention thanks to related exceptional properties [8]. Thus, number of MoS<sub>2</sub> preparation methods have been reported to permit obtaining various morphologies including nanowires, nanotubes [9–11], microscale spherical [12], fullerene-like [13], hollow nanospheres [14]. These methods included gas-phase reactions [15], sulfidation of oxide [16], thermal decomposition of precursors [17], sonochemical process [18], hydrothermal and solvothermal methods [10, 19] etc. Note that special conditions and complex apparatus were involved without allowing the control of the size and the morphology of the resulting nanoparticles. This challenging issue has been addressed by adding surfactants to the synthesis reaction depending on the targeted shapes [7]. Nicole Berntsen et al. have prepared nanostructured MoS<sub>2</sub> by using solvothermal conditions without and with surfactant (CTAB) permitting to obtain MoS<sub>2</sub> string-like morphology with developed surface area [20]. Also, Zhuangzhi Wu et al. have successfully synthesized MoS<sub>2</sub> nanospheres with an average diameter of 100 nm using polyethylene glycol surfactant-assisted route [21]. The latter promotes the formation of nanospheres through binding effect, which prevents also MoS<sub>2</sub> crystallization of, yielding to layer stacking decrease and textural stabilization.

The aim of the present work is to study the effect of surfactant on the synthesis and the control of morphology and size of MoS<sub>y</sub> nanomaterials. The adopted surfactant-assisted solvothermal route developed in the present work to fabricate MoS<sub>y</sub> nanomaterials at lower temperature (180°C) for 24 h. We chose a cationic surfactant, (CTAB (C<sub>16</sub>H<sub>33</sub>N(CH<sub>3</sub>)<sub>3</sub>Br)), widely used for these
The obtained results were compared with our previous works [11, 14] reporting successful preparation of different MoS₂ morphologies (hollow nanospheres, nanotubes) only by optimizing experimental conditions and electrolyte concentration. The present article highlights the role of surfactant and its concentration on the structure and morphology of the grown Mo₅S₇ nanomaterials.

### Table 1: CTAB/Mo molar ratio used for the syntheses A, B, C and D.

<table>
<thead>
<tr>
<th>Syntheses</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB/Mo molar ratio</td>
<td>1.5</td>
<td>2</td>
<td>2.5</td>
<td>3</td>
</tr>
<tr>
<td>CTAB added to the reaction synthesis (g)</td>
<td>0.437</td>
<td>0.583</td>
<td>0.728</td>
<td>0.874</td>
</tr>
</tbody>
</table>

### Materials and methods

#### 2.1 Preparation method

The Mo₅S₇ nanoparticles were synthesized using a solvothermal method. All the reagents were used without further purification. The studied samples were prepared with four different CTAB amounts calculated with respect to the CTAB/Mo molar ratio (Table 1) using a batch reactor of 180 ml wherein is introduced 0.1412 g ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O), 0.0513 g elemental sulphur, 1.15 g lithium hydroxide monohydrate (LiOH·H₂O), 0.0615 g ammonium carbonate (NH₄)₂CO₃, 8 ml hydrazine monohydrate (N₂H₄·H₂O), and the appropriate CTAB amount for each reaction in a Teflon lined stainless steel autoclave. The syntheses are labeled A, B, C and D. Then, ethylenediamine (solvent) was used to fill the autoclave up to 80% of its total volume (180 ml). The autoclave was kept at 180°C during 24 h then cool down to room temperature. Finally, the black

![Figure 1: X-ray diffraction patterns of samples A, B, C and D, CTAB bulk and MoS₂-2H.](image-url)
product is recovered by centrifugation and washed several times with acetone and distilled water, the resulting powders were dried under vacuum at 60°C for 3 h.

2.2 Characterization

The crystalline structure and phase purity of the samples were studied by X-ray diffraction (XRD), using a Xpert Pro X-ray diffractometer with Ni-filtered Cu/Kα radiation (λ = 0.01544 nm) operating at 45 kV and 40 mA. For each sample, Bragg’s angles between 4° and 90° were scanned at a rate of 0.04 deg/sec.

TEM, HRTEM and STEM/EDX analyses were performed using a JEOL JEM-2100F field emission gun electron microscope operated at 200 kV and equipped with an energy-dispersive X-ray spectrometer. The TEM specimens were prepared by dispersing a small material amount in ethanol and placing one drop of the suspension on a lacey carbon film coated copper grid (3.0 mm, 200 mesh, Aname manufacturer) and allowing the solvent to evaporate.

Fourier transform infrared spectroscopy (FT-IR) Varian 600-IR spectrometer equipped with a mercury-cadmium-telluride detector was used at a spectral resolution of 4 cm⁻¹. The spectra were recorded with sample powder (3% wt.) thoroughly ground and mixed with KBr and pressed into disks.

Thermogravimetry analysis was determined with a micro-balance MK2-MC5 equipped with a Multicard III Controller made by C.I. Electronics. The sample was heated from room temperature up to 600°C with a heating rate of 5°C/min under He flow of 50 cm³/min. The weight of sample was continuously monitored as a function of temperature.

XPS measurements were performed using an Omicron spectrometer equipped with an EA125 hemispherical electron multichannel analyzer and Mg Kα X-ray source at radiation energy of 1253.6 eV. The pressure in the analysis chamber was kept below 10⁻⁹ Pa. The spectra of the samples were registered at 150 W and pass energy of 40 eV and the binding energy was referenced to the C 1s line at 284.6 eV. The error in determination of electron binding energies and the line widths did not exceed 0.2 eV.

Figure 2: TEM image of the spherical particles obtained from sample A.
3 Results and discussion

The as-prepared materials were first characterized by XRD. Figure 1 displays XRD patterns of the products obtained according to the aforementioned four different syntheses in addition to those corresponding to crystalline 2H-MoS$_2$ and the bulk CTAB for shake of comparison. It is shown the presence of two phases, corresponding, respectively, to a crystalline phase identified by the intense peaks, and a second one recognized by broad peaks (Figure 1A–D) typical for nanostructured phase [7, 22]. The intense peaks are, probably, due to the presence of some CTAB amount, absorbed on the sample surface. Thus, it seems that under the used experimental conditions, the formation of crystalline MoS$_2$ phase is far from complete, because of the required synthesis or calcinations temperatures higher than 700°C [8]. On the other hand, the comparison of the intense peaks positions observed in the diffraction patterns of the four samples with the XRD patterns of the bulk CTAB illustrate an excellent similarity. In fact, the complete decomposition of the used surfactant needs temperature around 230°C which is higher than that used for the solvothermal synthesis (180°C). This might be the reason for the remaining intact surfactant, found absorbed on the nanoparticles surface even after excessive washing with water and acetone [20]. However, the broad peak of low intensity observed around $2\theta = 12^\circ$ in the XRD patterns of the four synthesized materials, can be reasonably ascribed to the (002) plane of MoS$_2$-2H. These features are indicative of the amorphous nature of the obtained materials and indicate the low stacking as well as the highly disordered packing of their MoS$_2$ layers [23, 24].

Furthermore, Transmission electron micrographs of the prepared samples are displayed in Figures 2–5. It is observed

Figure 3: TEM image of amorphous clusters obtained from sample B.
for the sample obtained from synthesis A a non-uniformity in shape and size of the formed particles as well as the presence of small aggregates of spherical particles and some nanospheres of poor dispersion in size in addition to amorphous clusters. In the case of sample B, TEM images reveal the presence of some amorphous clusters and hollow tubular structures having a wall formed of several layers, their size distribution is ranging from 10 to 15 nm, while their length varies from 40 to 80 nm. However, for sample C, it is observed the formation of nanotubes with a filled structure indicating the development of highly developed morphology as compared with samples A and B. The observed tubes have a diameter distribution ranging between 500 and 800 nm and a length extending to a few microns, in addition to the presence of spheres with diameter around 0.6 microns (Figure 4). Of interest, the obtained nanotubes represent 50% with respect to the total morphologies observed by TEM for this sample, an interesting value as compared to result reported in literature (not exceeding 30%) [25]. These nanotubes have also been studied by HRTEM to observe their layer structure. During the analysis by HRTEM, the tubular structures begin to degrade (Figure 6). The filled structure is destroyed, until the disappearance of their tubular shape, probably as a result of the high energy of the electron beam (200 kV). Furthermore, the TEM images of the particles obtained by the synthesis D allows to observe the presence of highly aggregated and very poorly dispersed tubular cluster (Figure 5). These clusters have cracks in the ends indicating their instability.

The amount of CTAB used in reaction seems to play an important role in determining the obtained morphology. With a moderate surfactant concentration, tubular structures, with a relatively high percentage, are obtained (synthesis C), however with low or high concentrations, only
amorphous clusters are observed. Moreover, subsequent EDX analysis of the obtained nanotubes reveals the presence, in addition to molybdenum and sulfur, of several other chemical elements (C, O, Na) thus proving the contamination of the samples structure and confirming the results obtained by XRD (Supplementary Information S.1). These impurities are due, probably, to the surfactant used during the solvothermal syntheses. The atomic S/M ratio is equal to 2.5.

According to the structural characterization of the samples prepared by the solvothermal syntheses assisted by CTAB, we identified the relationship between the amount of surfactant and the nature of the formed morphologies, thus confirming the observations reported in the literature [6, 26]. Furthermore, the synthesized materials exhibit non-homogeneity in their chemical composition and crystallinity (confirmed by XRD and EDX results) probably due to the intrinsic nature of CTAB which is difficult to remove by reiterative washing with water and acetone [20, 27]. However, and for a deeper study of these materials, nanotubes obtained from synthesis C were selected to be characterized by IR, TGA and XPS.

The IR spectra of the nanotubes and bulk CTAB are compared in Figure 7. We can observe, easily, the similarity between the two infrared spectra, which is probably due to the presence of CTAB particles absorbed on the surface of the MoS$_2$ material [28], a result in good agreement with those obtained by XRD and EDX. However, for sample C (Figure 7B), a band at 484 cm$^{-1}$ assigned to the Mo-S stretching mode of vibrations is observed, as well as the band at 530 cm$^{-1}$ scribed to bridging S$_2^2$ species [11]. The recorded IR spectrum indicate also the presence of IR band at 646 cm$^{-1}$ corresponding to sulphate groups, commonly present in amorphous or well dispersed MoS$_2$. 

Figure 5: TEM image of tubular cluster obtained from sample D.
samples resulting from sample surface oxidation upon contact with air [29].

Figure 8 shows the thermogravimetric analysis of the nanomaterials, obtained from sample C, carried out under helium. The TGA curve exhibits a first weight loss of about 5.5% in the range of 25–160°C, attributed to the removal of residual solvent and the desorption of physisorbed water from the surface of the sample. Also, TGA curve shows another mass loss that occurs between 200 and 550°C, and corresponds to 17.1%. This weight loss can be attributed to the dehydroxylation of the sample, the removal of NH$_4^+$ cations resulting from the decomposition of (NH$_4$)$_2$CO$_3$ [30], as well as the decomposition of CTAB particles which are absorbed in the structure of MoS$_2$ tubes, and which can be eliminated at about 300°C [31].

Further XPS analysis of the MoS$_2$ solids prepared according to the C synthesis route are compiled in Table 2.
The binding energies (BE) of Mo 3d, S 2p and O 1s as well as the surface composition for the Mo₅Sy nanomaterials are shown. All binding energies were referenced to the C 1s peak of the adventitious carbon set at 284.6 eV.

Mo 3d spectra corresponding to the sample C reveals that the Mo 3d doublet presents a complex signal. The Mo 3d peak can be decomposed in four components located at 232.5, 235.7, 237.5 and 240.5 eV (Figure 9A). The BE of the first Mo 3d5/2 and Mo 3d3/2 components are in good agreement with the value reported for Mo in MoS₂ [32], while the other two components correspond to the Mo in Mo6⁺ in an oxidized state [33, 34]. On the other hand, The S 2p spectra of Mo₅Sy nanomaterials shows the presence of three S 2p3/2 components, the first one, located at 163.2 eV, is attributed to S²⁻ ions in MoS₂, whereas the second, observed at 168.7 eV, corresponds to elemental sulfur in itsSn form [35] while the third component corresponds to SO₄²⁻ originating, probably, from an air oxidation of the nanotubes surface, which confirms the non-homogeneity of the sample and the presence of impurities in the structure of the analyzed material (results already confirmed by XRD, EDX and FT-IR). The S/Mo ratio, determined from the relative amount of Mo (MoS₂) and S (MoS₂), is equal to 1.79, a value near to that of the commercial MoS₂ (Table 2).

In the light of the above described results, we notice the effect of increasing the mass of the surfactants on the formation of spherical or tubular structures. Obtaining these morphologies is the result of the self-aggregation of surfactant molecules in micelles, which play the role of template around which the inorganic species condense. This self-aggregation into micelles occurs only when their concentration exceeds the threshold of the critical micelle concentration (CMC) beyond which the surfactant molecules are organized to minimize the interactions between the hydrophobic and hydrophilic parts and reduce the solvent/surfactant interface [36]. In fact, this dual nature gives them both an attraction and repulsion for the solvent which induces the formation of these self-assemblies. Therefore, we assume that the synthesis assisted by surfactants of MoS₂ nanoparticles, with well-defined morphologies, is based on the ability of these surfactant...
molecules to the formation of micelles in the reaction medium. In consideration of the results mentioned in literature [37, 38] and in the present study, the synthesis mechanism is assumed to be as shown in Figure 10.

- The surfactant molecules in the neighborhood of the CMC spontaneously form spherical micelles.
- The MoS$_2$ germs begin to form during the synthesis reaction.
- Spherical micelles tend to approach to reduce the free energy, and thus form more stable elongated structures.
- These elongated micelles play the template role needed for the growth of MoS$_2$ germs giving rise to nanotubes formation.

However, the elimination of surfactant from the obtained structure remains the most difficult step for the release and stabilization of formed morphologies. Typically, this removal is achieved by calcination of the obtained materials at relatively high temperatures (between 500 and 600°C) under flow of air or inert gas [39]. This finding may explain the presence of crystalline phase and impurities in the structure of prepared materials (identified by XRD and EDX) that were difficult to remove under lower drying temperature (60°C).

4 Conclusion

MoS$_2$ nanoparticles with different morphologies have been synthesized successfully using surfactant-assisted solvothermal route. The obtained structures depend, primarily, on the surfactant concentration. Comprehensive structural characterizations carried out show that at low surfactant concentration, small aggregates of spherical particles and some nanospheres of poor dispersion in size as well as amorphous clusters are observed, however, at moderate concentration, a mixture of nanotubes and nanospheres is formed. Nonetheless, at higher surfactant concentration, aggregated and very poorly dispersed tubular cluster with cracks in their ends are observed.

It should be pointed out that the obtained nanotubes represent 50% of the total morphologies observed by TEM, which represents an interesting value compared to those mentioned in literature. Nevertheless, non-homogeneity of the chemical composition and poor size and particle morphology dispersion was observed for all the synthesized materials. Therefore; the improvement and simplification of the surfactant-assisted solvothermal synthesis of MoS$_2$ become paramount, to provide MoS$_2$ nanomaterials with homogeneous composition and morphology, by studying the effect of the experimental conditions and the reaction kinetic on the formation of stables micelles and the interactions between surfactant and the used additives. Moreover, the removal of the organic template (that involves a calcination step either by air or under vacuum) has to be widely studied to ensure the subsequent elimination of the template without destruction of the formed nanostructure.

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References

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Bionotes

Hanane Akram

Hanane Akram received her PhD degree in Materials Science from the Faculty of Science and Technology (FST) of Tangier (Morocco) in 2012. Currently, she is a post-doctoral researcher at the Department of Chemical Engineering in FST. Her research fields are the synthesis, characterization and functionalization of nanomaterials and their stabilization in different environments (water and oil).

Cecilia Mateos-Pedrero

Cecilia Mateos-Pedrero Graduated in Chemistry, specialized in Inorganic Chemistry, from the University of Salamanca (Spain). She obtained her PhD from the Catholic University of Louvain (Belgium) in 2007. Her research interests lie in the area of heterogeneous catalysis (oxidation, reforming reactions), synthesis and characterization of supported metal catalytic materials and the development of H2-permselective inorganic membranes for H2 purification, fields in which she has published more than 25 papers.

Esteban Gallegos-Suarez

Esteban Gallegos-Suarez is a PhD student at the Instituto de Catálsis y Petroquímica (ICP-CSIC) and Universidad Nacional de Educación a Distancia (UNED), Madrid. His research field is...
heterogeneous catalysis based on carbon materials as catalyst supports applied for steam reforming and hydrogenolysis reactions. Furthermore, he is a specialist in the HRTEM technique for catalyst characterization.

Tarik Chafik

Tarik Chafik received his PhD in catalytic engineering processes from University of Lyon, France (1993). He was a post doc researcher at University of Patras (Greece) with Prof. Verykios, and subsequently at National Institute for Resources and Environment (Tsukuba Japan). He was also awarded as Fulbright visiting researcher at University California Berkeley (USA) with Prof A.T. Bell. His research activities focus on heterogeneous catalysis. Dr. Chafik currently works as group leader and full professor at the Faculty of Sciences and Technique of Tangier (Morocco). He is coordinator or member of several research projects and collaborations.

Antonio Guerrero-Ruiz

Antonio Guerrero-Ruiz is a Full Professor at the Department of Inorganic and Technical Chemistry of the UNED at Madrid (Spain), where he heads the Laboratory of Chemistry at Surfaces. His research activities are concentrated on the development of new heterogeneous catalyst materials. For this aim the preparation and characterization of, for example, metallic or bimetallic nanoparticles, functionalized carbon nanotubes, modified graphene composites has been accomplished. These materials are applied as catalysts or adsorbents for different technical processes.