MoS$_2$ nanoparticle precipitation in turbulent micromixers

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HIGHLIGHTS

► The wet chemical synthesis of MoS$_2$ nanoparticles has been performed in a micromixer.
► The NP size was controlled by varying the chemical and fluid-dynamic parameters.
► Loosely agglomerated nanoparticles with a mean size of 60 nm have been obtained.
► By controlling the reactant flow rate it was possible to cut by half the NP dimension.

ARTICLE INFO

ABSTRACT

Molybdenum sulfide nanoparticles (NP) have been successfully obtained, for lubricant applications, by means of a wet chemical synthesis in an aqueous solution employing ammonium molybdate, citric acid and ammonium sulfide as the reactants. Mo:citrate molar ratio and pH were optimized to control the phase and morphology of the final products. The production of MoS$_2$ NP has then been performed in a micromixer, which has the feature of matching high degrees of reactant mixing, induced by the turbulent vorticous flow inside the precipitation chamber, and low residence times, which allow to suitably control the NP size. Remarkable MoS$_2$ concentrations were obtained (around 20 wt.%), still being nanosized although loosely agglomerated, which lead to exceptional productivities per unit of reactor volume.

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1. Introduction

Fluid lubricants are used in almost every field of human technological activity and their purpose is multi-fold: they reduce frictional resistance, protect the contacting surfaces of engines against wear, remove wear debris, reduce heat and contribute to cooling, improve fuel economy and improve emissions.

Advanced nanomaterials have shown some promise because of their contribution to reducing friction and enhancing protection against wear [1–3]. When incorporated in full lubricant formulations in a stable way, and if their performance benefits can be sustained under those circumstances, they offer the possibility of some performance breakthroughs which have not witnessed since the development of the now ubiquitous anti-wear additives, Zinc Dialkyl Dithiophosphates (ZDDP's), about 70 years ago. These developments can contribute to a substantial energy saving, reduce equipment maintenance and lengthen the life of the machines. In the case of engine oil (crankcase) applications, these nanomaterials can help increase the durability and performance of exhaust-treatments and reduce harmful emissions: in fact, exhaust catalysts tend to become poisoned by the Sulfur and Phosphorous that are present in conventional lubricant additives.

Transition metal dichalcogenides, with the generic formula MX$_2$ (M = W, Mo; X = S, Se), whose synthesis was first demonstrated at the Weizmann institute by Tenne and co-workers [4–6], seem to be very promising materials to be dispersed as nanoparticles in the oil matrix. They involve a reaction between MO$_3$ and H$_2$S, in reducing atmosphere at high temperatures, and the corresponding sulfide (WS$_2$ or MoS$_2$) is obtained. Many other synthetic routes have also been followed to obtain these kinds of nano-structured materials [7–16].

The specific lubrication mechanism ascribed to these metal sulfides, often called inorganic fullerenes due to their peculiar structure of spherical concentric layers, is currently debated; however, several studies clearly indicate that an exfoliation process of these layers, and the consequent liberation of nanosheets directly inside the surface contact area, is the prevalent lubricating mechanism for these systems [17,18]. It was also hypothesized that these nanoparticles behave as nano-ball bearings, due to their spherical shape, ultra-hardness and nano-size. In fact, also amorphous nanoparticles demonstrated to induce a considerable friction reduction when employed as lubricant additives. Investigations involving direct visualization of the nanoparticle behavior in the contact area, over a broad pressure range, were attempted by combining Transmission Electron Microscope (TEM) and Atomic Force Microscopy (AFM) [19].

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The present study focuses on the synthesis of MoS_2 nanoparticles which have to be incorporated in engine lubricant oils. A wet synthesis technique has been devised. This technique is based on the preparation of an aqueous solution of citric acid and ammonium molybdate to form a complex of molybdenum(IV) with citric acid, to which a suitable amount of ammonium sulfide was added to obtain MoS_2. This technique resorts to a simple and scalable process, and involves low-cost reagents, instead of other more complex reaction methods. This synthesis route is extremely versatile since it could potentially be employed to produce particles directly in the hosting oil via micro-emulsion reactor systems, which are currently under development within our research group [20,21], in order to overcome the problem of dry particle dispersion in oil.

However, since MoS_2 precipitation is a fast process, it results that the rate and extension of mixing is determining for the process outcome: because of their ability to achieve the high mixing efficiencies necessary in the precipitation process, passive micro-mixers are currently being investigated for this application. The term micro-device strictly refers to systems with characteristic length-scales that are in the range of micrometers. Small dimensions lead to behaviors strictly controlled by molecular phenomena [22], allowing rapid diffusive mixing with time-scales ranging from tens to hundreds of milliseconds [23]. Very interesting is also the recent investigation of large micro-mixers (with characteristics length-scales ranging from hundreds of micrometers to a few millimeters) in which some flow instability is allowed to develop resulting, under extreme operating conditions, in turbulent flow and turbulent mixing [24]. These devices present the main advantages of passive micromixers, such as more controlled process conditions, better and faster homogenization of the feed streams, short mean residence time and narrow residence time distribution, combined with other additional advantages, such as limited power consumption (when compared with traditional micro-fluidic systems) and ease of scalability for process intensification.

This work focuses on a multi-inlet vortex reactor, which is constituted of a round mixing chamber, where reaction occurs, and four injectors arranged in directions allowing vortex turbulent flow to develop. Very effective mixing can be reached due to the collision and redirection of the injected flows. As the injected flows have a swirling manner instead of impingement, the reactor does not require equal inlet momenta [25], which confers a great flexibility of this device in case one of the reactants is predominant in terms of amount to be fed.

In this work, the use of such Vortex-shaped micromixers has successfully been employed to synthesize MoS_2 nanoparticles, in continuous mode, and with the possibility to tune the particle sizes according to the fluid-dynamics inside the reactor.

2. Experimental procedure

The synthesis of the nanosized MoS_2 powders was carried out by employing ammonium molybdate tetrahydrate $(NH_4)_6Mo_7O_{24}\cdot4H_2O$, citric acid $C_6H_8O_7$ and ammonium sulfide $(NH_4)_2S$ as the reactants, all of which were supplied by Sigma Aldrich. An aqueous solution was prepared by dissolving at 90 °C suitable amounts of ammonium molybdate and citric acid in order to achieve a Mo:citrate molar ratio of 1:1. The quantity of citric acid employed in the synthesis was considered as a significant parameter and it was varied to four times the stoichiometric value. After the complete dissolution of the reactants, the solution was cooled and a suitable quantity of 20 wt.% solution of ammonium sulfide in water was added drop-by-drop. The solution changed from clear to dark red, and finally to black. The solution was subsequently centrifuged at 4000 rpm for 1 h, and the obtained precipitates were washed in distilled water and then dried at 80 °C for 12 h.

This procedure was identified as "batch procedure" and allowed to select optimal operating conditions (pH, reactant mole ratios, etc.), but remained a low productivity method to achieve NP, and no control of the nucleation, growth and agglomeration rate could be achieved in the beaker.

Therefore, the so-called Vortex micro-mixer was employed for this process: the geometry we employed for our tests was characterized by four square or circular inlets (as in Fig. 1). The circular channel geometry was chosen because it allowed better cleaning procedures and avoided solid accumulation: each inlet channel is 1 mm in diameter, and the reaction chamber (highlighted in red in Fig. 1b) is of 4 mm in diameter and 1 mm in height. Therefore the channels and the chamber are characterized by the same height and no cross flow area reduction is induced to the flow which enters the chamber. The product is discharged in a 2 mm diameter duct, perpendicular to inlet radial flows.

The described Vortex micro-mixer was employed for the synthesis of MoS_2 nanoparticles. The four inlets were connected by means of PP pipes to four 20 ml PP syringes. The syringes were filled in pairs with the Mo–citrate solution and the ammonium sulfide solution, respectively (Fig. 2). The syringes were placed and fixed on a KD Scientific KDS220 infusion syringe pump. The outlet solution, which contains the nanoparticles, was collected in a beaker and maintained in agitation until the infusion was complete and the solution was ready to be centrifuged.

The products were characterized by X-ray diffraction (X'Pert Philips, range 2θ: 10–70°, radiation CuKα, $\lambda = 1,54056$ Å) and by X-ray fluorescence (Rigaku ZSX100E). The particle size distribution (PSD) of the produced nanoparticles was measured by dynamic light scattering (DLS) with Malvern Nano ZS90 providing reliable information in the size range from 1 to 6000 nm; the PSD was then used to determine the mean particle size (d_{mean}). The microstructural characterization was performed through a field emission scanning electron microscopy (Leo Supra 40) equipped with an EDS probe. The samples were prepared for electron microscopy observations by suspending a small quantity of nanoparticles in isopropanol, through ultrasonic mixing for 30 min, and subsequently by placing a drop of the dispersion on a copper grid coated with a layer of amorphous carbon.

3. Results and discussion

The "batch procedure" allowed to optimize the synthesis parameters and to transfer these to the "Vortex procedure". The role of citric acid was considered crucial, due to its reducing and complexing behavior. On the other hand, the chemistry of molybdenum and molybdenum compounds is quite complex and it is very difficult to provide exact and reliable reactions [26]. The ammonium molybdate is supposed to decompose, in an acid environment, into molybdenum trioxide and its hydrated forms, also referred to molybdic acid. The citric acid can react with both molybdic acid and molybdenum trioxide. In the first case, some various Mo–citrate complexes are formed, the composition of which is not defined and for this reason it is difficult to draw up univocal chemical reactions. In the second case, the citric acid reduces the Mo (VI) to a lower (IV) valence state, in the form of molybdenum dioxide. This compound reacts with the ammonium sulfide with the final formation of molybdenum disulfide.

Following this reaction scheme, the content of citric acid was carefully considered and Mo:citrate molar ratios from 1:1 to 1:4 were employed.

In all cases, the synthesized nanoparticles were very amorphous, without any significant difference in the phase obtained by varying the citrate content. Fig. 3 shows the XRD pattern for the Mo:citrate molar ratio 1:2. As can be noted, only a very broad
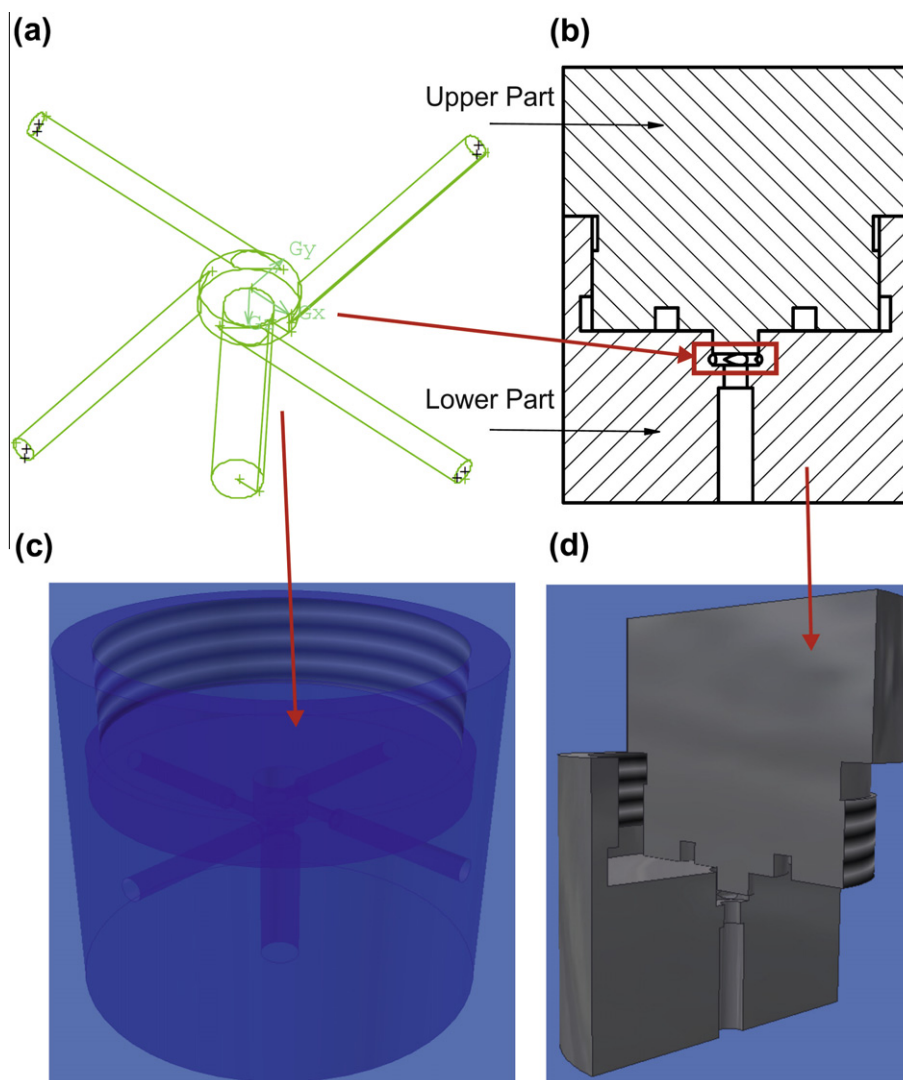
Fig. 1. Vortex micromixer geometry: (a) reaction chamber; (b–d) quotes and rendering of the whole apparatus.

peak with very low intensity can be individuated (see Fig. 3a), which corresponds to (0 0 2) in accordance to the 2H–MoS$_2$ JCPDS card 37-1492. The nanoparticles were treated at 900 °C for 1 h in Ar atmosphere in order to increase their crystallinity. As a consequence, other MoS$_2$ peaks appeared in the XRD pattern, as illustrated in Fig. 3b.

A microstructural characterization of the nanoparticles obtained with different Mo:citrate molar ratios was carried out, in order to investigate a possible influence of the citric acid content on the morphological properties. The sample obtained with the Mo:citrate molar ratio of 1:1 showed a high degree of agglomeration and a mean size of the primary particles of about 80 nm, as shown in Fig. 4a. On the other hand, when the quantity of citric acid introduced was doubled, the MoS$_2$ nanoparticles were softly agglomerated, with an average particle size of about 50 nm (see Fig. 4b). This result demonstrated that the citric acid played an important role not only in the reduction of the Mo valence state, but also in the final morphology of the powders. From these microstructural results, it can be supposed that the citric acid acted as a template to achieve softly agglomerated powders, with a decreased size of the primary particles compared to a smaller amount of citric acid. A further addition of citric acid with an Mo:citrate molar ratio of 1:4 did not give rise to any significant change in the morphology of the nanopowders. The detailed morphological results of this "batch procedure" optimization are given in some recent works by the authors [27].

The PSD characterization of the nanoparticles obtained by the "batch procedure" is illustrated in Fig. 5. As can be noticed, the powders showed a bimodal distribution: nearly half of the agglomerates has a dimension of hundreds of nanometers, while the remaining part has big sizes, between 2 and 4 μm. The mean diameter was calculated and the value was 1.53 μm.

A 1:3 Mo:citrate molar ratio was chosen in order to optimize the MoS$_2$ synthesis through the Vortex reactor. A suitable dilution of the ammonium sulfide solution was used in order to keep the Mo:S molar ratio stoichiometric.

The first step of the study regarded the characterization of the MoS$_2$ nanoparticles after the synthesis, centrifugation and drying operations (named hereafter "before washing") and after the washing step of the same nanoparticles (identified as "after washing"). The inlet flow rate was kept constant to 10 ml/min for each inlet channel.

The XRD analysis did not show any significant difference between the phase formed. As in the case of the sample obtained by the batch procedure, the MoS$_2$ nanoparticles were very amorphous and only the (0 0 2) peak was identified (see Fig. 6).
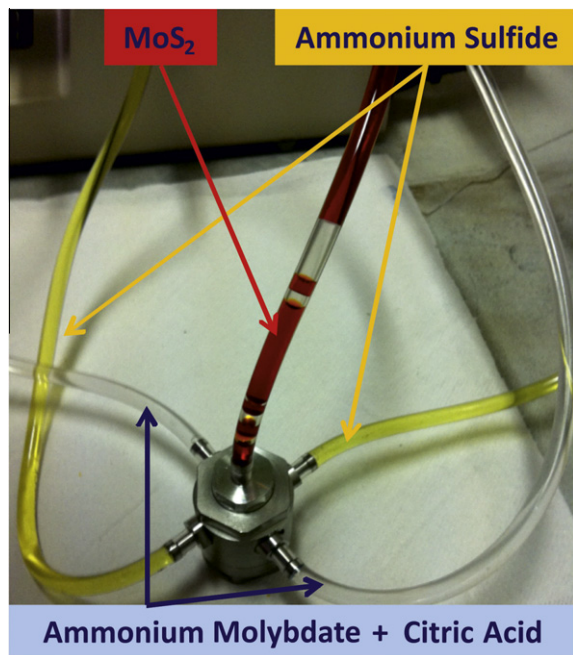
Fig. 2. Picture of the MoS$_2$ nanoparticle synthesis with the Vortex micromixer.
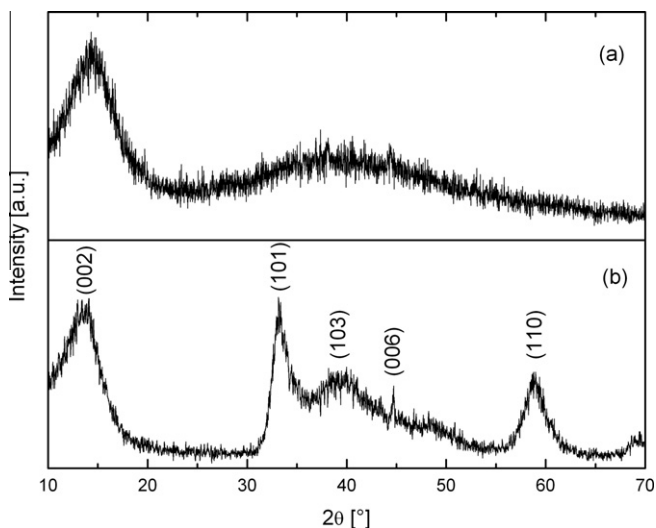

Fig. 3. XRD patterns of the MoS$_2$ nanoparticles obtained by the "batch procedure" (a) with Mo:citrate molar ratio 1:2 and (b) heat treated at 900 °C for 1 h.

Fig. 4. FESEM micrographs of the MoS$_2$ nanoparticles obtained by the "batch procedure" with Mo:citrate molar ratios (a) 1:1 and (b) 1:2.

Fig. 5. PSD distributive (solid) and cumulative (dash) curves of the MoS$_2$ nanoparticles obtained by the "batch procedure" with Mo:citrate molar ratio 1:2.

The microstructural characterization showed some differences in the samples between before and after washing, as illustrated in Figs. 7 and 8. The sample before washing showed two kinds of primary particle morphologies, as can be appreciated in Fig. 7b. Some agglomerates are formed by perfectly spherical particles, sized hundreds of nanometers, while some others contain very small nanoparticles, with shape approaching spheres and average dimension of about 50 nm. Both agglomerates are uniformly distributed and have dimension of some microns. The EDS analysis did not show any particular difference between the two morphologies in terms of element composition.

The same sample washed with distilled water showed only one kind of agglomerate and primary particles. The size of the agglomerates significantly decreased and some of them can be considered aggregates due to the submicrometric dimension. The primary particl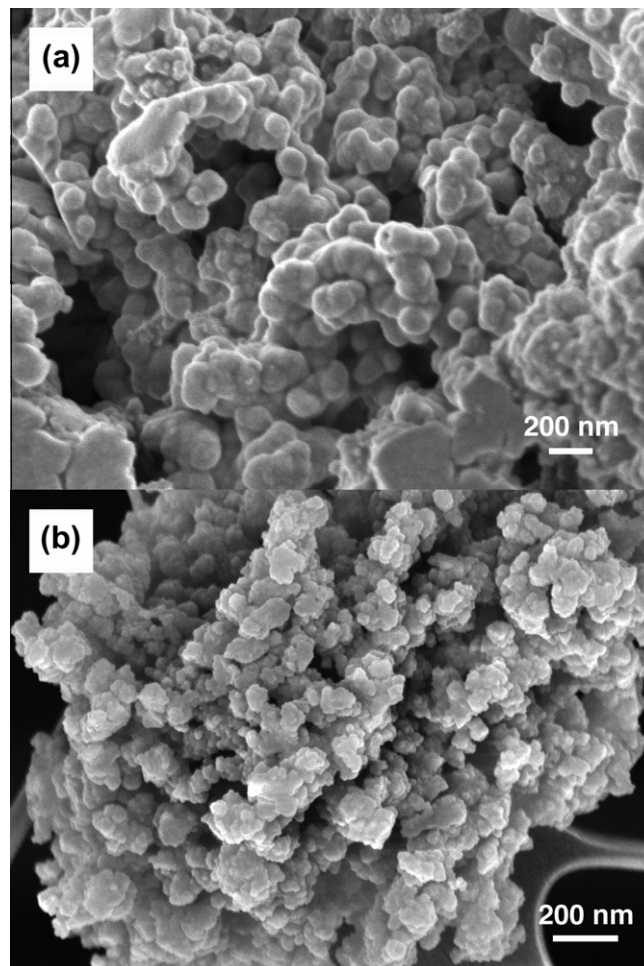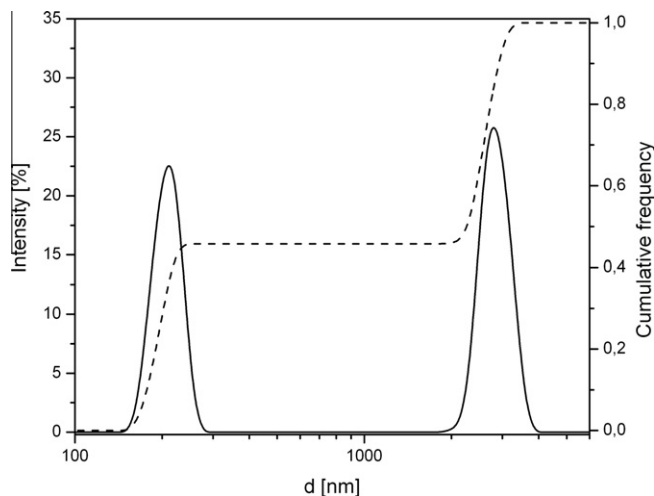es inside the agglomerates and aggregates resulted more dispersed and those spherical disappeared. The size of the primary particles was also decreased, with average value of about 40 nm (see Fig. 8b).

The PSD curves for the nanoparticles obtained before and after washing are reported in Fig. 9. As can be noticed, the PSD measure-
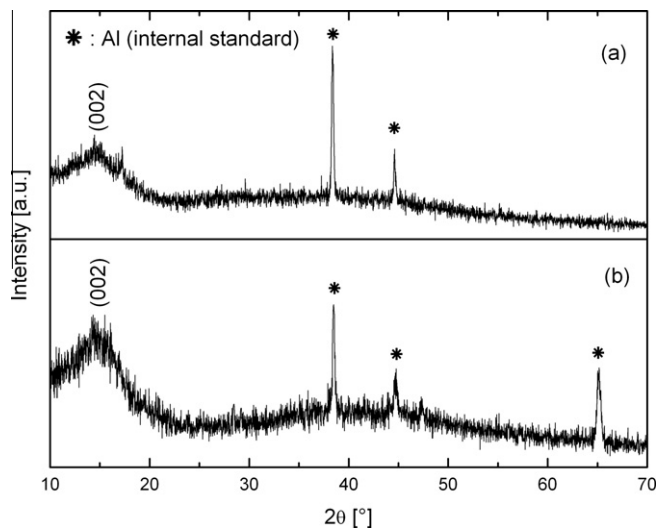
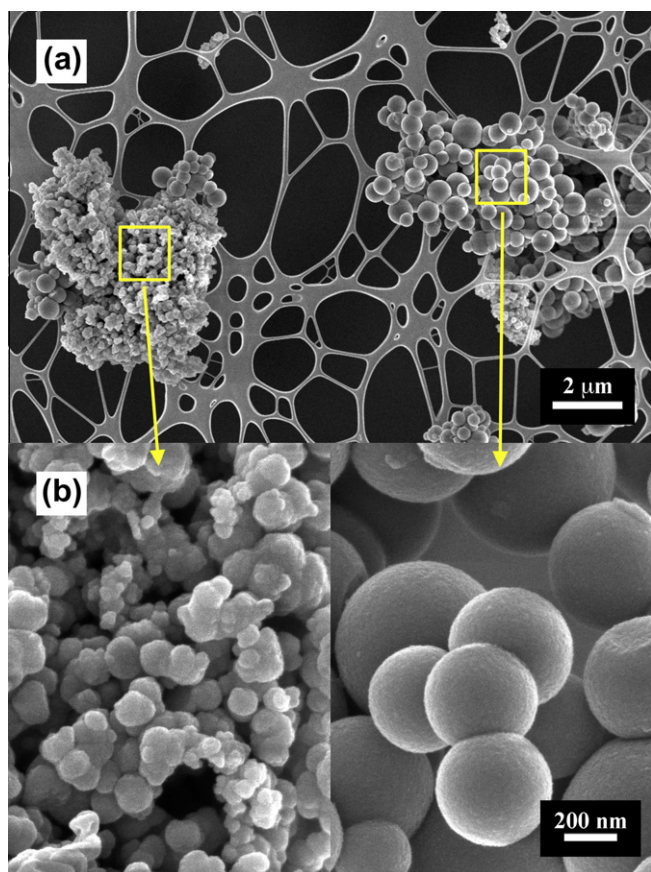**Fig. 6.** XRD patterns of the MoS$_2$ nanoparticles obtained by the "Vortex procedure" (a) before and (b) after washing.

Fig. 8. FESEM micrographs of the MoS$_2$ nanoparticles obtained by the "Vortex procedure" after washing.

Fig. 7. FESEM micrographs of the MoS$_2$ nanoparticles obtained by the "Vortex procedure" before washing.

Fig. 9. PSD distributive (solid) and cumulative (dash) curves of the MoS$_2$ nanoparticles obtained by the "Vortex procedure" before (red) and after (blue) washing. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ments confirmed the trend illustrated in the description of the microstructural characterization. The distributive and cumulative curves of the "after washing" nanoparticles were significantly shifted to left in comparison to the curves of the "before washing" nanoparticles, meaning a reduction of the size of the agglomerates. The calculated average values decreased from 575 nm of the sample before washing to 479 nm of the sample obtained after washing.
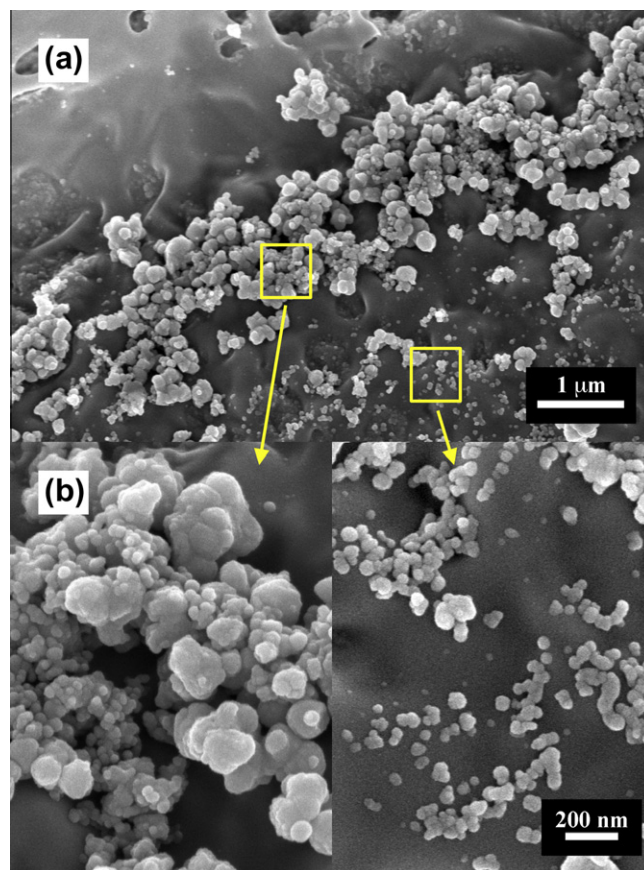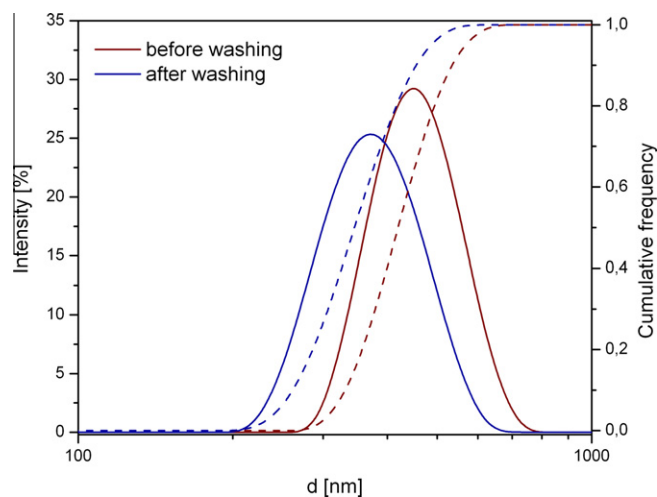
The use of different flow rates was investigated in order to prove the possibility of controlling the size of the nanoparticles. Three different inlet flow rates were employed: 2, 10 and 20 ml/min, respectively. The high resolution FESEM micrographs of the samples, after washing, obtained with different flow rates are reported in Fig. 10.
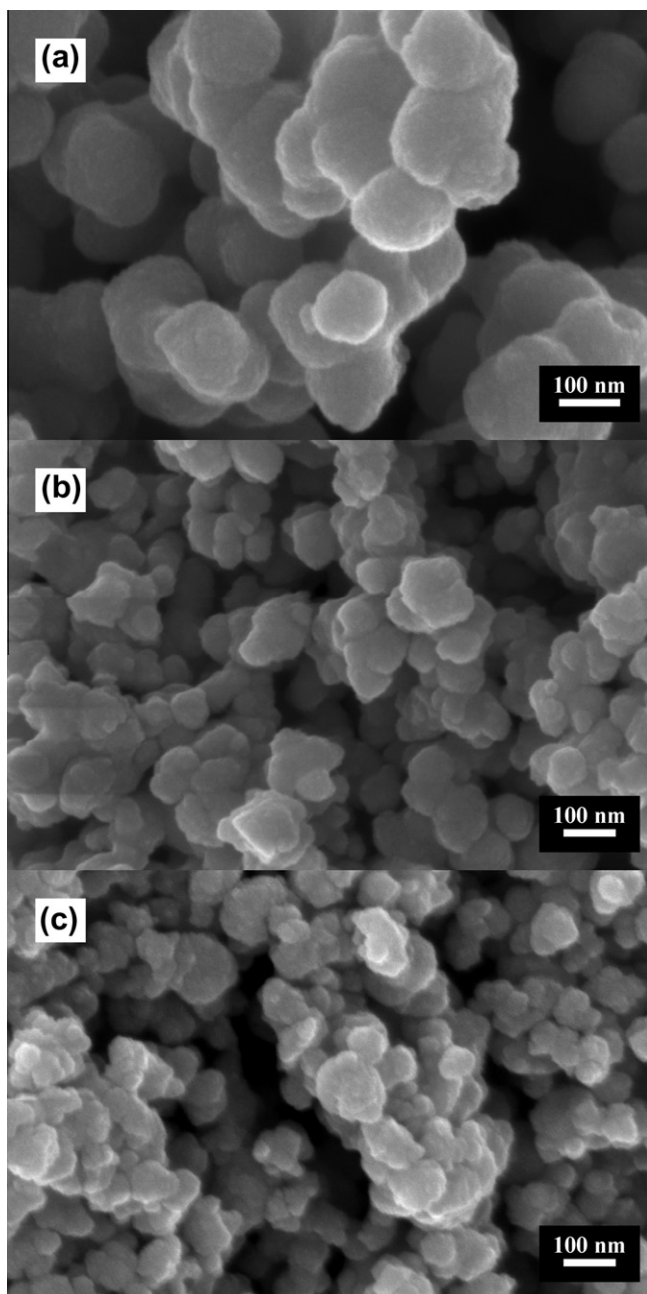
Fig. 10. FESEM micrographs of the MoS$_2$ nanoparticles obtained by the "Vortex procedure" with different inlet flow rates: (a) 2 ml/min, (b) 10 ml/min and (c) 20 ml/min.

Fig. 11. Average diameter of the primary particles, calculated by FESEM micrographs, of the MoS$_2$ nanoparticles obtained by the "Vortex procedure" with different inlet flow rates.

The selected flow rates, being equal to 2, 10 and 20 ml/min, correspond to a "jet" Reynolds number in each inlet channel Re$_j$ of 52, 260 and 520, respectively (based on an inlet channel diameter d_i = 1 mm). This clearly leads to a laminar flow in each of the mentioned conditions. Conversely, in the reacting chamber, the Reynolds number can be calculated as [28]:

$$Re_c = \sum_{i=1}^{N} \frac{\rho D V_i}{\mu} \qquad (1)$$

where D = 4 mm, and V_i is the mean velocity in each channel, and N is the number of inlet channels. This leads to a Reynolds number in the chamber Re$_c$ of 832, 4160 and 8320, respectively. It was demonstrated that, in a Vortex reactor with very similar geometry [29], above Re$_j \sim 100$ (corresponding to Re$_c \sim 1600$ in our system) some
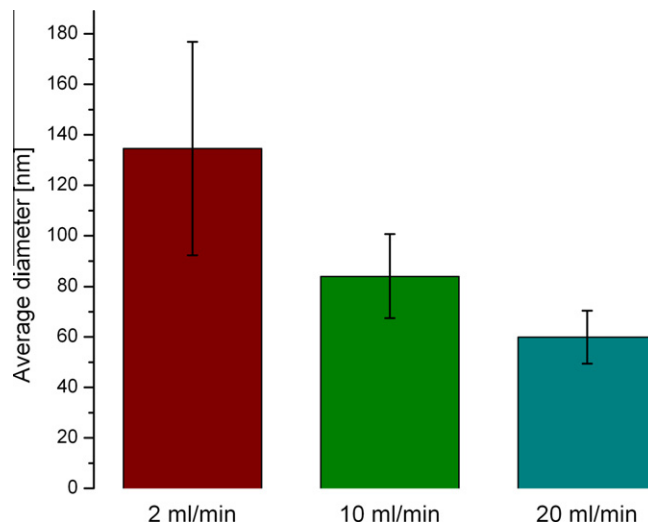
unsteady motions of the Vortex core result from flow instabilities, and a transition from fully laminar to turbulent flow starts to occur. This was shown through a comparison between microscopic particle image velocimetry (μPIV) and computational fluid dynamic (CFD) simulation.

It is clear that the dimension of the primary particles is considerably reduced by increasing the inlet flow rate, as a result of a better mixing and a lower residence time. It is therefore possible to control the flow rate in order to favor the nucleation phase and to limit the molecular growth one, by reaching higher values of supersaturation with increasing mixing rates.

The average diameter of the nanoparticles was calculated by the analysis of several high-resolution micrographs for obtaining a significant number of measurements so as to ensure a reliable statistic. Fig. 11 shows the mean values and it is worth mentioning that the dimension of the MoS$_2$ nanoparticles was nearly cut by half by increasing the flow rate from 2 ml/min to 20 ml/min. Moreover, the distribution of the primary particle dimension was made narrower as demonstrated by the decrease of the deviation.

4. Conclusions

A novel wet chemical synthesis method has been developed for the production of molybdenum(IV) sulfide nanopowders. The synthesis was carried out in an aqueous solution, by forming Mo:citrate complexes that react with ammonium sulfide in order to achieve MoS$_2$ nanoparticles. The Mo:citrate molar ratio was considered relevant in the process, and it was optimized to a value of 1:3. It has been demonstrated that the citric acid content affected not only the formation of the Mo:citrate complexes but also the morphology of the final products, through a templating action, during the nucleation and growth of the particles. The final MoS$_2$ nanopowders were highly amorphous and softly agglomerated.

However, the batch procedure does not allow to control the phenomena of nucleation, growth and aggregation of particles. A turbulent micromixer was then used, in order to better act on the nanoparticle size through the "manipulation" of the reactor fluid-dynamics. In fact, the rates of nucleation (which depend on local supersaturation of the reactants), growth (which determine the size of the primary nanoparticles at the reactor outlet) and aggregation (which depends on particle collision frequency, based on their concentrations) rates depend on the degree of mixing and of the residence time.

By varying the flow rate to each of the channels from 2 to 20 ml/min, it was also possible to produce precipitates with quite reproducible primary particle sizes. In addition, the strict control and predictability of the fluid-dynamics inside the reactor was functional to obtain a narrower particle size distribution of the aggregates.

Finally, such microreactors allow to reach high productivities per unit of reactor volume, in continuous mode, since remarkable MoS_2 concentrations were obtained (around 20 wt.%), still being nanosized although loosely agglomerated. These nanoparticles have been tested to assess their tribological properties and the first results are very encouraging.

Acknowledgment

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