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ORIGINAL PAPER

In Situ TEM Observation of the Behavior of an Individual Fullerene-Like MoS_2 Nanoparticle in a Dynamic Contact

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Abstract Inorganic fullerene-(IF)-like nanoparticles made of metal dichalcogenides (IF-MoS_2, IF-WS_2) have been known to be effective as anti-wear and friction modifier additives under boundary lubrication. The lubrication mechanism of these nanoparticles has been widely investigated in the past and even if the exfoliation and third body transfer of molecular sheets onto the asperities constitute the prevalent mechanism for the improved tribological behavior of IF nanoparticles, it has also been suggested that a rolling friction process could also play a role for well crystallized and spherical particles. In this study, in situ Transmission Electron Microscopy (TEM) observations of the behavior of single IF-MoS_2 nanoparticles were conducted using a sample holder that combines TEM and Atomic Force Microscopy (AFM) which simultaneously can apply normal and shear loads. It was shown that depending on the test conditions, either a rolling process or a sliding of the fullerenes could be possible. These in situ TEM observations are the first carried out with IF nanoparticles.

Keywords IF-MoS_2 nanoparticles · In situ TEM–AFM · FM/AW additives · Boundary lubrication

1 Introduction

Since some years now, the lubricating properties of Inorganic Fullerenes (IF) of transition metal dichalcogenides MX_2 ($M = Mo, W, \ldots, X = S, Se$) is increasingly studied. Used either as solid lubricants [1–3] or as additives in lubricating oils [4–8], these nanoparticles have shown some exceptional anti-friction and anti-wear properties. They are more and more considered as potential alternative for replacing the traditional lubricant additives such as ZnDTP and MoDTC well known for their anti-wear and anti-friction properties but also for their polluting character.

Since their first synthesis in 1992 by Tenne et al. [9], many progresses were made in the preparation of the IF nanoparticles. Chemists are now able to control the size of the particles, their number of walls, and their crystallinity [7, 8]. Recently, Tannous et al. [8] investigated the influence of the crystallinity of the particles on their lubricating properties. It was shown that the less crystallinity of the particles, the better are their lubricating properties. These poorly crystallized particles were prepared by MoCVD [10, 11] and had many defects. The improvement of their lubricating properties with their number of defects was considered consistent with the lubrication mechanism of the IF nanoparticles proposed by Cizaire [5] and Joly-Pottuz [12] some years ago. The lubricating properties of the IF nanoparticles was attributed to a gradual exfoliation of the external sheets of the particles during the friction process leading to their transfer onto the asperities of the reciprocating surfaces and a shearing of the basal planes. The tribofilm made of these MoS_2/WS_2 sheets was observed by HRTEM through a FIB cross section [13] and characterized by Raman and XPS spectroscopy [13, 14]. To explain the exceptionally good properties of the poorly crystallized IF-MoS_2 nanoparticles, it was suggested that the amorphous character of these

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particles and the presence of many defects could facilitate the exfoliation of layers under external pressure and therefore ameliorate the tribological performance of these nanoparticles.

Using the synthesis process based on the reaction between MoO_3 vapor with H_2S in a reducing atmosphere and thanks to a new quartz made reactor, Rosentsveig et al. [7] produced recently perfectly spherical and crystallized IF-MoS_2 nanoparticles presenting more than 30 closed shells. Their tribological properties were compared to those of other IF-MoS_2 nanoparticles prepared by a similar approach but with a different reactor which provided inferior shape control and crystallinity [7]. It was found that although of very similar sizes, the lubricating properties of these particles were less good than those of the perfectly crystallized and spherical particles. The difference of behavior was ascribed to the crystalline perfection and the large number of closed layers particles. Nevertheless, these results were not considered by the authors to be antagonist to those obtained with the poorly crystallized particles prepared by MoCVD, and it was suggested that even if the exfoliation and third body transfer of molecular sheets onto the asperities was the prevalent mechanism for the improved tribological behavior of IF nanoparticles, a rolling friction process could also play a role for well crystallized and spherical particles. It was advanced that these nanoparticles could be considered to behave as genuine nanoball bearings, at least temporarily, until they gradually deform and start to exfoliate giving rise to very low friction coefficients. However, to date, no direct observation of a rolling process for well crystallized particles was made. A full understanding of the lubrication mechanisms of the IF nanoparticles needs a direct visualization of the particle into the contact.

In this study, in situ TEM observations of the behavior of IF-MoS_2 under combined normal and shear loads have been made. Experiments were conducted using a TEM–AFM sample holder permitting the simulation of the tribological contact between two antagonist surfaces. The main purpose of this study is to see if the IF-MoS_2 nanoparticles can have the ability to roll during contact under stress. The objective of this study is not to definitively answer the question whether if perfectly crystallized particles roll in the contact while the less crystallized ones slide and delaminate, but to see if for some IF-MoS_2 particles, the possibility of a rolling process really exists.

2 Experimental

2.1 In Situ TEM Observation

The experiments were carried out using a Nanofactory Instruments TEM–AFM holder (Fig. 1) inserted in a LEO 912 microscope operating at 200 kV accelerating voltage in a conventional mode, and in a FEI Tecnai G2 Lab6 operating at 200 kV.

The TEM–AFM holder employs a MEMS force sensor. This unit is a self-contained microfabricated device with a silicon force-sensing “springboard” cantilever. The sensor employs piezoresistive elements arranged in a Wheatstone bridge to enable a high degree of sensitivity with normal force resolution of 10 nN. The multi-stage fabrication process involved micromachining of an n-type SOI wafer and the silicon tip was machined.

For sliding experiments, substrate on which the nanoparticles will be deposited must be fabricated that are electron transparent in one dimension, long in one dimension and moderately short in the other, so as to reduce the possibility of crashing into the sensor. A short wedge sample made in Si constituted a good solution and was retained. FIB–SEM was used to prepare the Si wedge on which the nanoparticles were deposited. Figure 2a and b show the Si wedge with one edge FIB machined to a flat area which was used for the experiments. The dimension of the wedge is 5.9 μm wide and 55 μm long. Figure 3 shows a different type of Si wedge after machining. The presence of 10 μm long steps that were used for the nanoparticles deposition can be observed. A thin gold wire was used to fix the Si wedge to the positioning part of the sample holder (Fig. 1).

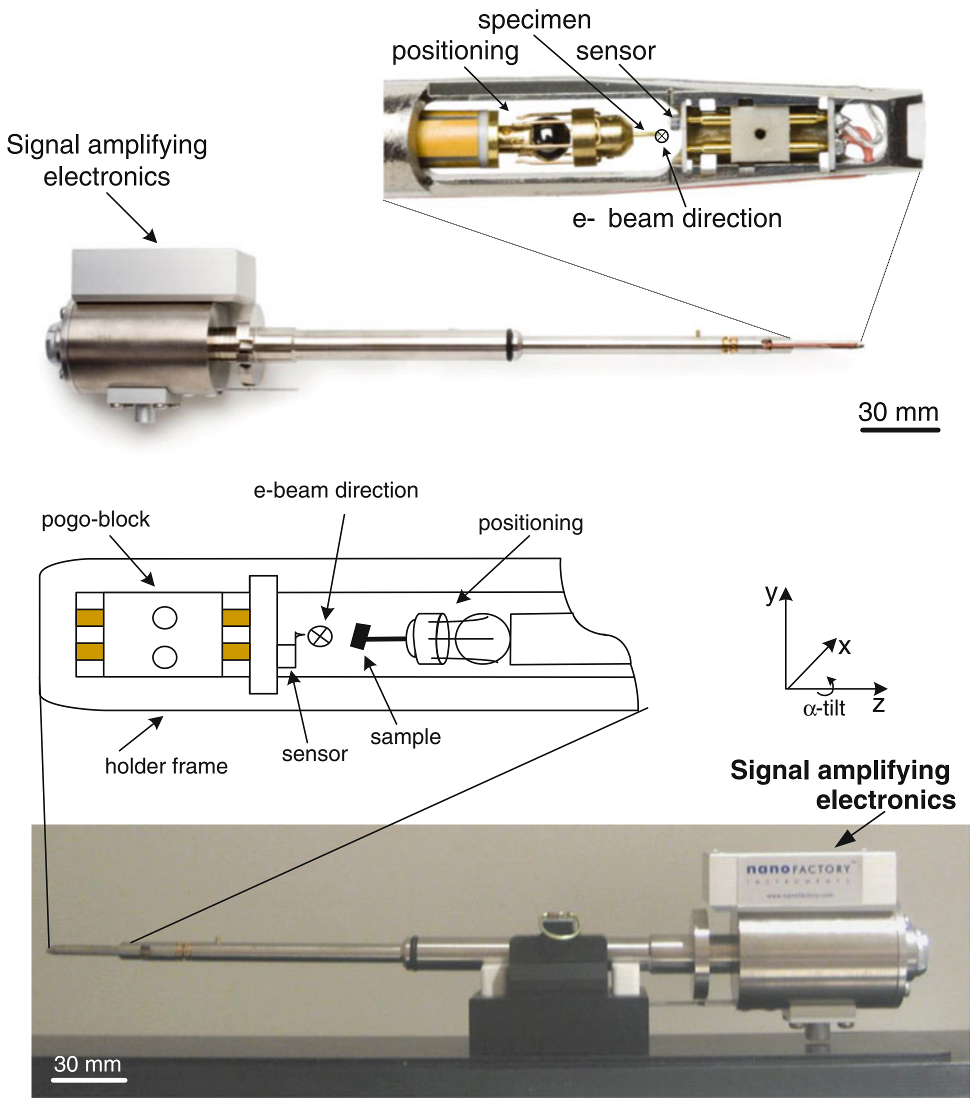
The use of a traditional sharp tip (tip radius of approximately 100 nm or less) is not convenient for these compression and sliding experiments. This size is too close of the diameter of the particles studied in this study (~100 nm). FIB–SEM was used again to prepare the AFM tip so that the compression could be made. Figure 4 shows the truncated tip after machining. The flat area is of approximately 500 nm.

In the experiments presented in this study, the Si wedge was moved sideways in order to simulate the tribological contact and to observe the behavior of the particle during the movement, while a constant force was applied to the sample. Nevertheless, in this study, no force measurements were made, the main purpose of this study being to study the behavior of the inorganic fullerenes into the contact.

2.2 Specimen Preparation

The experiments were conducted with IF-MoS_2 nanoparticles supplied by Prof. Tenne’s group from the Weizmann Institute in Israel. The particles were synthesized by reacting MoO_3 vapor with H_2S in a reducing atmosphere. The nanoparticles are of high crystalline order, with an average size of 70 nm. The details of the synthesis process of these nanoparticles and their tribological properties as additives of lubrication are described in [7].

Fig. 1 Schematic of the TEM–AFM holder design



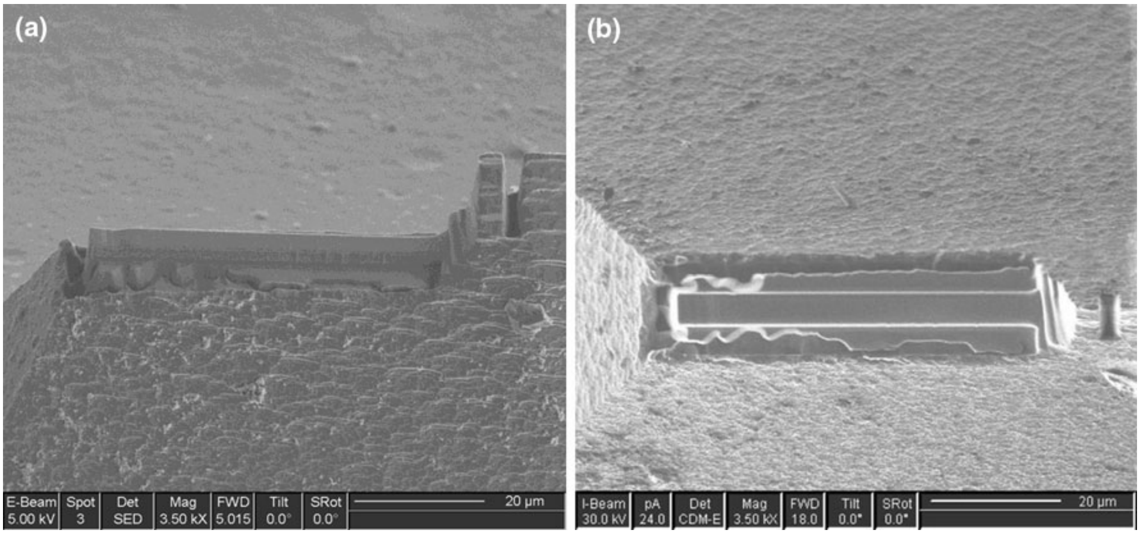


Fig. 2 Si wedge with two edges machining to flat areas—**a** side view and **b** topview

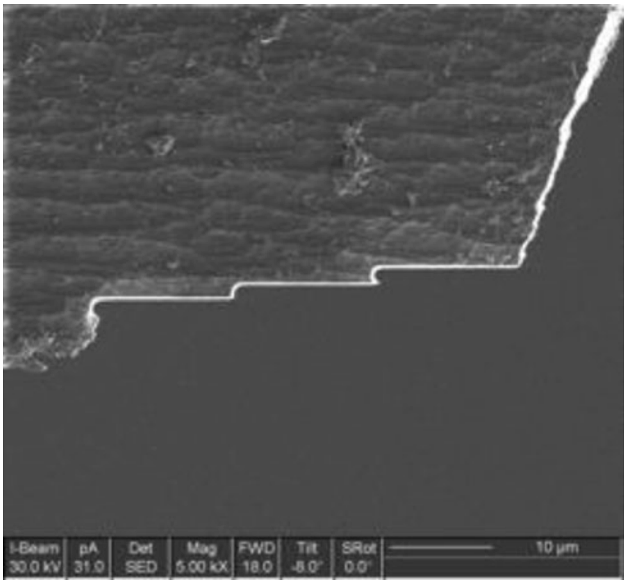


Fig. 3 Si Wedge after FIB machining. The micromachining enables the creation of some 10 μm steps used for the particles deposition

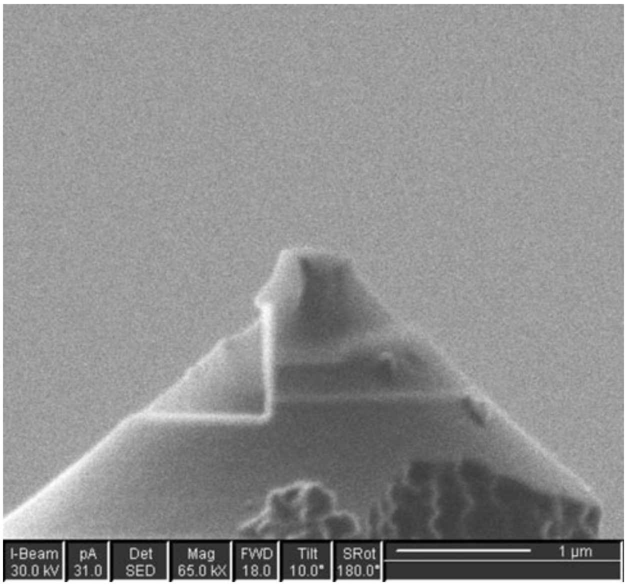


Fig. 4 Truncated Si tip after micromachining

The nanoparticles were diluted in isopropanol prior to be placed in an ultrasonic bath for 1 min in order to divide up the particles. The FIB-machined Si wedge was then dipped in the solution and was let to dry for a couple of minutes.

3 Result

The selection of a single particle to study its behavior in the contact was extremely difficult. The interaction between the particles appeared to be very strong and separating the multiple agglomerated particles with the AFM tip proved to be difficult.

3.1 First Sliding Test

A first sliding test was performed on two agglomerated IF-MoS_2 nanoparticles (Fig. 5). The dimension of the cantilever used was $300 \times 35 \times 3.0$ ($l \times w \times t$) [μm] leading to a spring constant of 1.4 N/m. This test was performed with a normal force of 100 nN between the AFM tip and the sample. The behavior of the particles during the test is discussed from snapshots taken from a video which was recorded directly through the screen with a regular digital camera. Figure 6 shows a series of images obtained from the video which was recorded during the first sliding test. In the left column, the behavior of the particles when the Si substrate slides to the right can be observed. Picture "a" corresponds to the time $t = 0$ s while picture "j" shows the particles at the end of the first sliding movement, at $t = t_{\text{final}}$. The right column shows the movement of the particle when the substrate slides to the left. $t = 0$ s corresponds to picture "k" while $t = t_{\text{final}}$ corresponds to picture "t". A white point was arbitrary placed on the largest particle in order to easily follow the movement of the particle from the test. From this first series, it can be observed that the two agglomerated particles roll perfectly in the contact. An approximative calculation of the distance travelled by the particle from picture "a" to picture "j" was made. For that, a mean diameter of 80 nm was considered for the largest particle and it was assumed that the particle was spherical. This leads to a circumference of 251 nm. To make the task easier, we decided to follow the distance travelled by the white point placed on the particle. Table 1 shows the distance travelled by this mark from

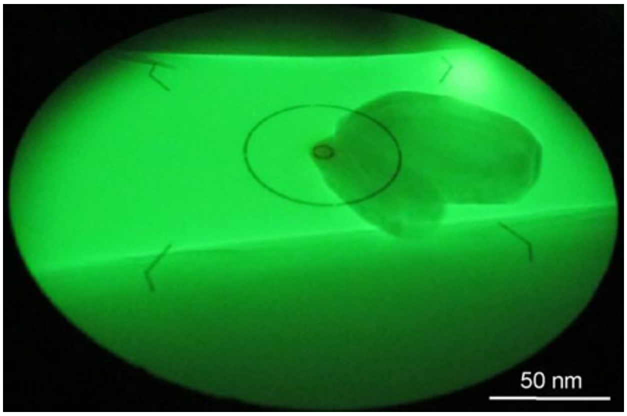


Fig. 5 TEM image of two agglomerated IF-MoS_2 nanoparticles before the first sliding test

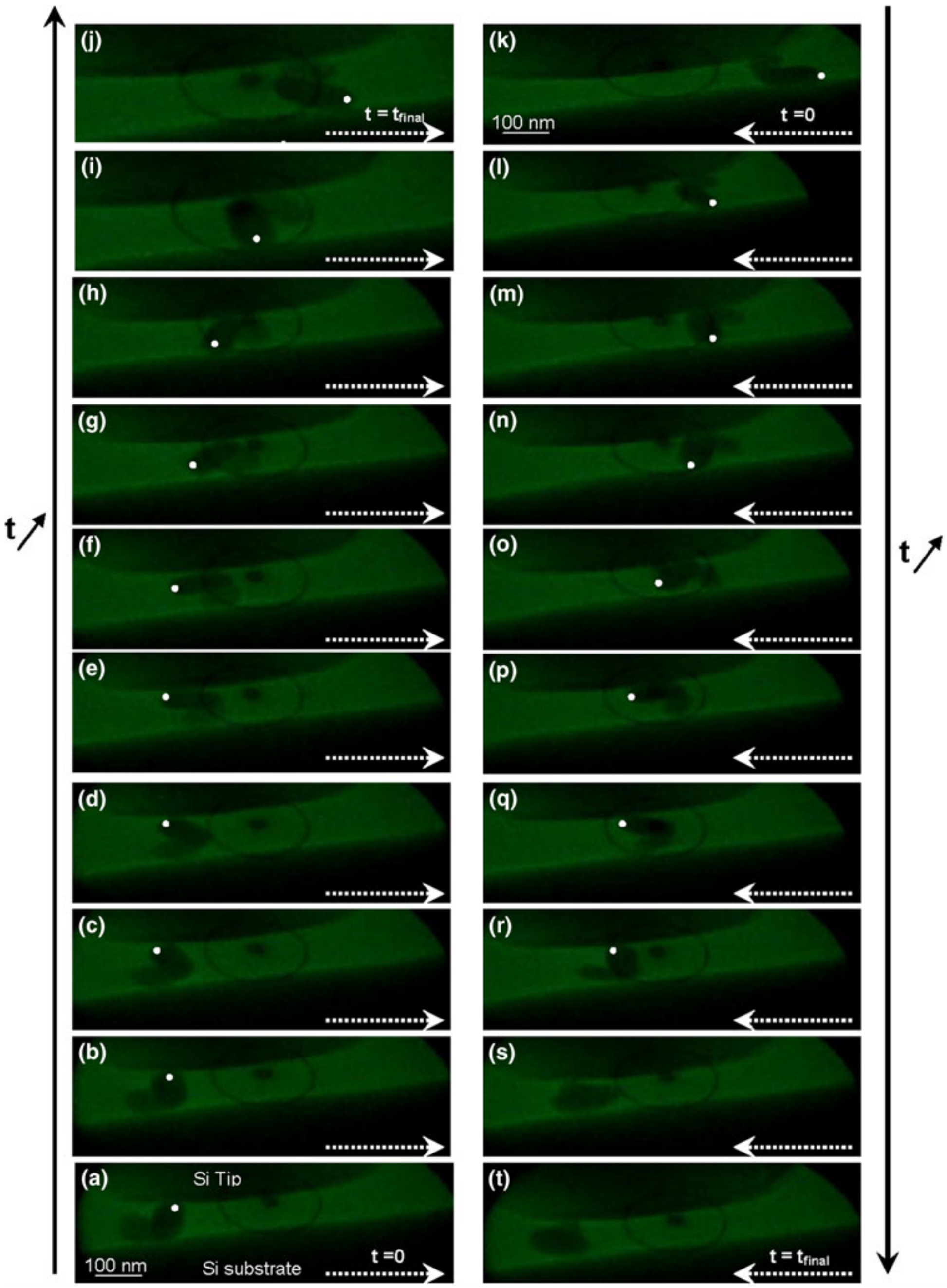


Fig. 6 Image captured from the video that was recorded during a sliding test with two agglomerated particles. From image "**a**" to image "**j**" the substrate is moving from the left side to the right side (see *arrow*). From image "**k**" to image "**t**" the substrate is moving from the right to the left

Table 1 Distance travelled by the particle in the first sliding test for a sliding direction of the substrate from the left to the right

Image number	a	b	c	d	e	f	g	h	i	j
Distance travelled par the particle (in nm)	0	13	65	68	76	80	91	116	160	191

$t = 0$ to $t = t_{\mathrm{final}}$ for a sliding movement of the substrate from the left to the right (left column). The distance travelled by the particle was estimated to be 160 nm. This means that the particle has travelled a little more than half of its circumference. This is consistent with the position of the white point at $t = t_{\mathrm{final}}$.

3.2 Second Sliding Test

In this experiment, a single particle was isolated. The video was recorded with the digital camera of the microscope (Tescan). The dimension of the cantilever used was $300 \times 75 \times 3.6$ ($l \times w \times t$) [μm] leading to a spring

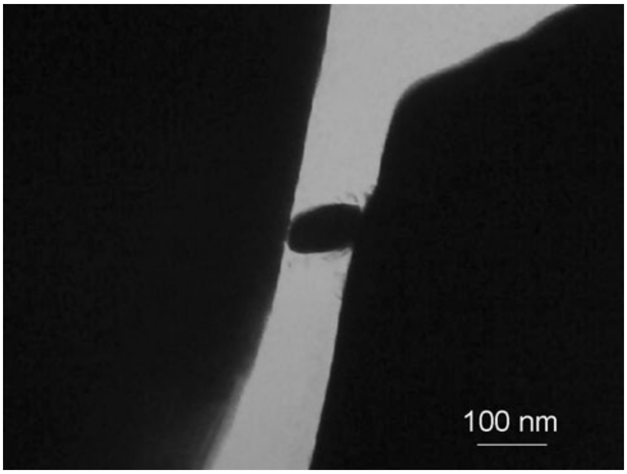


Fig. 7 TEM image of a single IF-MoS_2 nanoparticle before the second sliding test

constant of 5.2 N/m. This test was performed with an average normal force of 400 nN between the AFM tip and the sample. Figure 7 shows the single particle between the Si wedge and the tip. The mean diameter of this particle is approximatively 100 nm. The behavior of the particle was followed through images captured from the video at different steps of the experiment (Fig. 8). The image “a” corresponds to the initial state, at $t = 0$. Pictures “b” and “c” correspond to a first movement of the substrate from the top to the bottom (the arrow on the Si wedge indicates the direction of the movement of the Si wedge). The substrate slides on the particles without any movement of the fullerene. The particle sticks to the tip. When the movement is reversed (picture “d”) the particle moves toward the top of the tip. This induces a first degradation of the particle. A layered material appears below the fullerene. A zoomed in version of this picture is reported on Fig. 9. It confirms the presence of a layered material which is consistent with an exfoliation of the particle. A further sliding of the substrate (pictures “e”–“f” in Fig. 8) does not induce any further movement of the particle in the contact. The substrate continues to slide on the particle. Another reversed movement of the substrate (pictures “g”–“l”) does not induce any further movement of the particle in the contact. However, at the end of the test, the particle starts to slide up from the tip (pictures “j” and “k”). On the last picture (picture “l”), the particle which was stuck to the tip is now stuck on the Si wedge and follows its movement.

4 Discussion

In this article, the in situ TEM observations of the behavior of IF nanoparticles in a dynamic contact were presented. A dedicated in situ TEM–AFM sample holder was used for the experiments. The results that we obtained show the importance of the in situ TEM techniques in improving the understanding of the nanoparticles lubrication mechanism.

We have clearly proven in the present study that two particles of the same system could behave differently under similar test conditions. While at 100 nN two agglomerated IF-MoS_2 particles are able to roll, a sliding process and a beginning of exfoliation were observed at 400 nN for another particle of the system. However, although the use of two different normal loads for the two sliding experiments, the force was not regulated even though we only moved sideways. Therefore, even if these results are not surprising, a precise correlation between the normal force used for the experiment and the behavior of the particles during the sliding test is difficult to establish with precision. Moreover, these observations reflect the behavior of a single particle in some stress conditions which can be quite far from the real tribological conditions (sliding speed, contact pressure, nature of surfaces in contact, etc.). Also, the response of the particle is strongly dependent on the intrinsic properties of the particles (size, shape, number of walls, degree of crystallinity, etc.). Within a system, all the particles do not necessarily present the same characteristics and therefore the same behavior under tribological stresses. So, it is essential to avoid generalizing the behavior of one particle observed in a sliding test to all the particles of the system.

However, since much progress recently has been made in the synthesis of nanoparticles, this in situ TEM techniques will in the future provide information that will be increasingly relevant. Rosentsveig et al. [7] showed in their work that it was possible to obtain particles with perfectly controlled size, morphology, and crystallinity. Similarly, Tremel et al. [10, 11] are able to produce amorphous particles with a perfectly controlled composition and size distribution. The controlled synthesis that will produce new perfectly shaped nanoparticles will make the matter of interpreting the data from the observations made by the in situ TEM techniques much easier and more reliable. In particular, it is proposed as a future perspective to conduct experiments with IF-MoS_2 nanoparticles already studied in tribology [7, 8] and for which the lubrication mechanism is still unclear. A statistical study on the two completely different types of IF-MoS_2 nanoparticles, already presented in the bibliographic part (perfectly and poorly crystallized), will be made in order to better understand their difference of behavior in terms of tribological properties, necessarily linked to different lubrication mechanisms.

Thus, in a recent study, Tannous et al. [13] used the poorly crystallized IF-MoS_2 nanoparticles to perform friction tests in the presence of different pairs of rubbing surfaces (steel, alumina, and diamond-like carbon). It was shown that the formation of a tribofilm, made of MoS_2

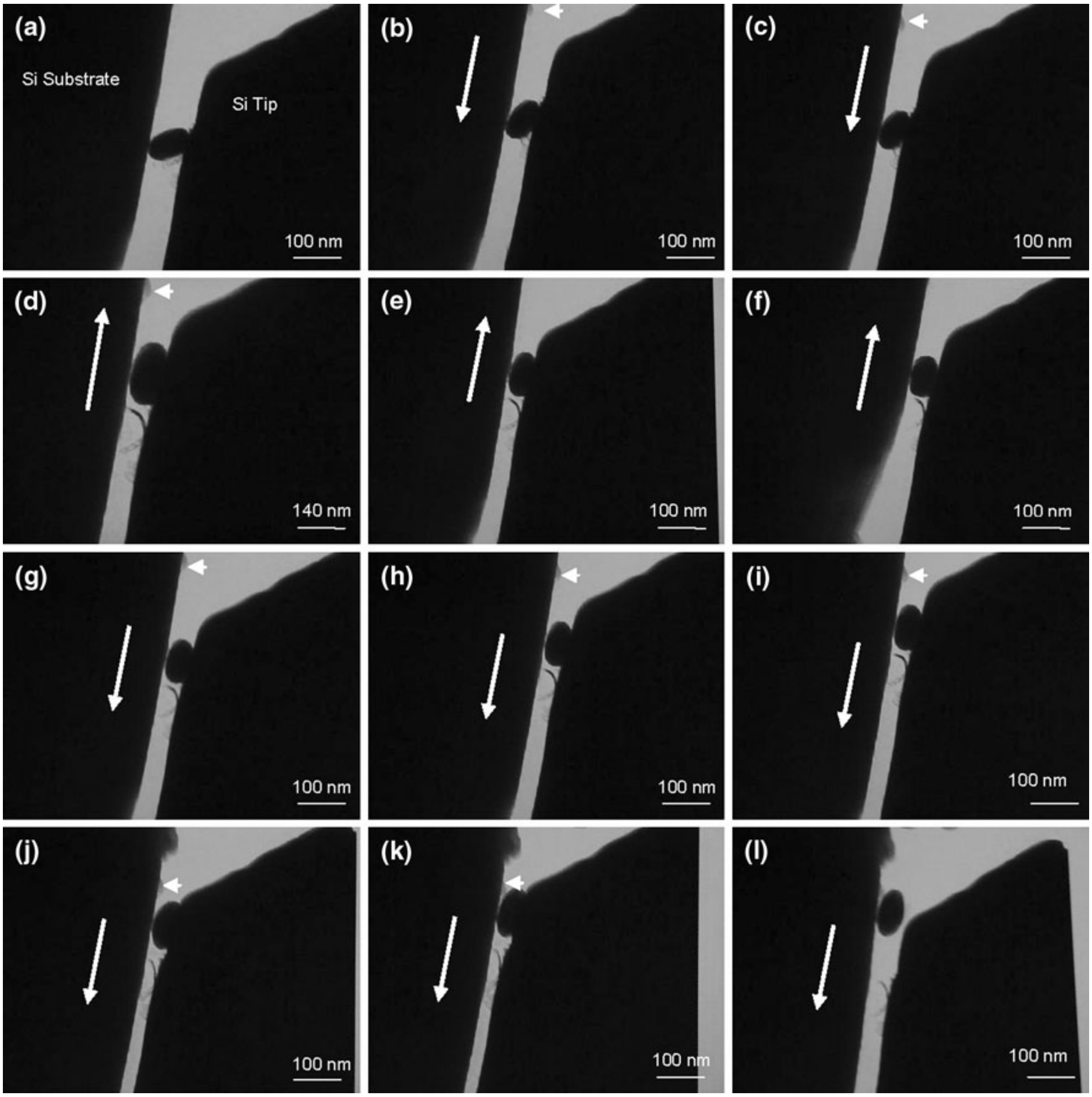


Fig. 8 Image captures obtained from a video recorded during a sliding experiment carried out with a single MoS_2 particle

sheets, was only observed in the presence of steel and that in presence of inert surface (alumina, diamond-like carbon), no frictional benefit was observed with the IF-MoS_2 nanoparticles in comparison to the base oil. The experiments that we will perform on these two types of IF-MoS_2 nanoparticles will help us to understand the reason why the best crystallized particles exhibit good lubricating properties no matter the nature of the rubbing surfaces (to be published), while the poorly crystallized particles present exceptional lubricating properties only in contact of rubbing surfaces made in steel [13]. The possibility to have a rolling process that is able to enhance the lubricating properties of the spherical particles has already been advanced by Tenne (to be published). This mechanism could be increasingly possible in light of the results presented in this study. However, it is essential to check this hypothesis using the in situ TEM observations. It is also planned in a future study to conduct experiments in a high resolution transmission electron microscope (HRTEM) using an in situ nanoindentation sample holder. This system will permit to carry out simultaneously in situ nanoindentation experiments and observations of the behavior of the nanoparticle under pressure. The mechanical properties of a single particle will also be accessed. Tevet et al. [15] have recently used a new similar in situ technique for stiffness measurements of individual WS_2 nanoparticles of about 100 nm. Using a high resolution scanning electron microscope (HRSEM), the compression failure strength and the elastic behavior of the nanoparticles under uniaxial compression were studied. It was

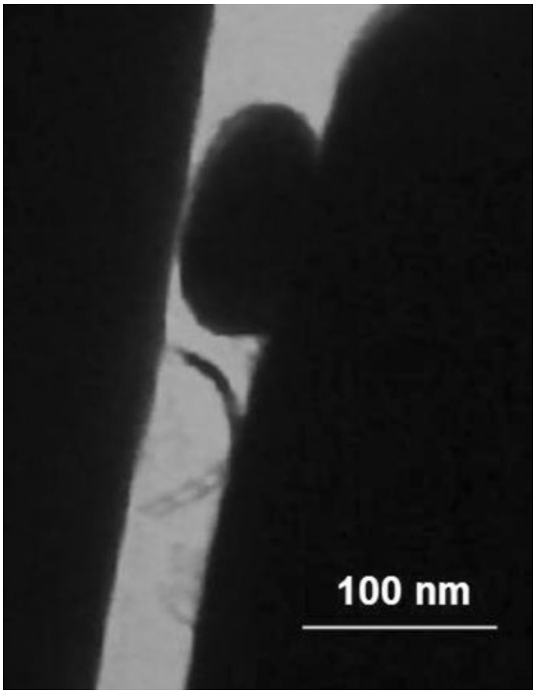


Fig. 9 TEM image showing a particle of IF-MoS$_2$ and a piece of the particle resulting from exfoliation of the same

shown that hollow closed nanostructures were able to withstand very elastic stress. The compression failure strength of these nanoparticles was found to be as high as 1–2.5 GPa. Moreover, in their study, Tevet et al. gave evidence that the stiffness of the faceted nanoparticles were, due to higher stress concentration at the corners, lower than that of a spherical nanoparticle. The use of a HRSEM does not unfortunately offer a good image quality for the observation of any structural modification of the nanoparticles under compression. The use of a high resolution TEM will allow, in our future study, to proceed to more detailed observations.

5 Conclusion

In this study, we observed for the first time the behavior of IF nanoparticles using an in situ TEM–AFM sample holder. It was shown that the particles behave differently for a similar set of experimental conditions. In some cases, a rolling of the particle was clearly observed while sometimes a sliding of the particle occured with or without an exfoliation process. These preliminary results are encouraging to go deeper into the understanding of the lubrication mechanism of nanoparticles and establish more precisely a link between their characteristics (size, crystallinity, morphology, etc.) and their action mode.

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