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Influence of Milling Media on Mechanically Exfoliated MoS_2

Regular Paper

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Abstract

Wet ball milling was used to exfoliate MoS_2. The aim of the study was to examine how the surface energy of all the individual materials affected the formation of the nanosheets. Two types of milling balls were selected: one made of steel and one made of Al_2O_3. The liquids used were water (H_2O), isopropyl alcohol (C_3H_8O) and kerosene. The obtained nanosheets were identified and characterized using transmission/scanning electron microscopy and electron diffraction. Following sedimentation, scattered light intensity was measured. Our experiments showed that the material of the milling balls played a significant role in the experiment and had an influence on the number of the nanosheets obtained. Irrespective of the liquid employed, the number of nanosheets in the suspension obtained by milling with Al_2O_3 balls was greater by 100% than those obtained via milling with steel balls.

Keywords liquid exfoliation, ball milling, layered crystals, molybdenum disulphide, surface energy

1. Introduction

Ever since the exceptional electron properties of graphene [1] were discovered, many studies have focused on the production of 2D nanoparticles with a thickness not exceeding a few atomic layers. Two-dimensional crystals can be produced using various physical and chemical methods, e.g., laser ablation, physical and chemical vapour deposition and liquid phase exfoliation [2]. Historically, the oldest method consists of mechanically separating the individual layers through adhesion to another material. This technique provides relatively good 2D nanocrystals but its efficiency is low and thus, its wider use is limited.

The potential possibility of realizing the large-scale production of 2D nanocrystals by the so-called 'top-down' method is offered by layered crystal exfoliation, assisted by the adhesion forces of a liquid (liquid exfoliation) and enhanced by the action of ultra sounds [3] or an electric field [4]. Exfoliation processes induced by mechanical energy are also available, in which the exfoliation happens due to the abrasion that occurs during a milling operation [5].

In studies focused on ultrasound-assisted liquid exfoliation performed to date, investigators have experimentally examined the effects of various liquids on the formation of nanosheets involving the most important layered crystals [3,6,7]. A formal description has been prepared for the effect of separation of the individual layers from a crystal under the action of surface forces, based on the solubility theory [8] and on the assumption that enthalpy mixing ΔH_{mix} should be as low as possible.

The method of refining materials by abrasion to obtain particles smaller than 0.1μm has been recognized since

1966 [9]. One of the earliest studies devoted to the use of this technique for refining graphite [5] demonstrated the possibility of producing very thin crystals (20nm) with a specific surface area greater by more than 100 times that of the initial graphite powder. The researchers underline the specific role played by the liquids employed. Janot and Guerard [10] describe also how the various types of milling and the different sizes of milling balls affect the amorphization degree of graphite.

Antisari et al. [11] showed that thin graphite flakes (10nm) can also be obtained by milling in a mortar-type mill where the participation of the shearing forces is the greatest. The liquid used in this milling operation was water. Milling of graphite in the presence of a liquid was also reported by Zhao et al. [12]. Using a planetary mill, the authors obtained a suspension of graphene flakes with a thickness $\leq$ 3 layers. Similar results were obtained using various organic solvents [13]. According to the authors, to increase the proportion of the layered flakes in the suspension, it was necessary to precisely control the milling parameters such as the milling time, milling energy and the size of the milling balls.

Similarly with hBN(α-BN, hexagonal) crystals, Li et al. [14] obtained flakes several nanometres thick by milling in a planetary mill with the participation of a liquid. The authors emphasize that the process can be easily scaled and that the final product only contains a small number of defects and impurities. They compare the effects of water, ethanol, dodecane and benzyl benzoate on the peeling results of hBN ball milling and conclude that the best results can be obtained with benzyl benzoate, which they attributed to the good match between the surface tension of the liquid and hBN crystals, the high viscosity of the liquid and its low reactivity with the Fe balls.

Due to the nature of the process, the surface area of the crystals produced by milling is small (of the order of nm^2 to μm^2). The processes have reasonably good efficiency and produce a relatively high yield of the single-layer crystals (up to 40%). The yield and the average size of the flakes finally obtained can be controlled by appropriately selecting the parameters of centrifugation [15]. Experiments have also been conducted with hBN and MoS_2 subjected to a combination of milling and sonication. The results indicate that each method has its own advantages [16].

The investigators concerned with milling exfoliation examined various liquids; however, systematic studies on the relation between the surface energy of the liquid and the solid are scarce. Moreover, unlike other methods, milling exfoliation involves two solids that take part in the process, i.e., the crystal and the mill balls. The role played by the material of the ball and its surface energy have not been systematically investigated.

The exfoliation of layered crystals is a synergic process [17] in which both the mechanical work (ball impacts) and the adhesion work participate. One might therefore expect systematic studies to be carried out on the role played by the surface phenomena that take place at the interfaces of the individual phases, i.e., between the material to be refined, the refining material and the liquid. To date, no such investigations have been reported in the literature.

The material chosen for the experiments was molybdenum disulphide (MoS_2). In many applications, MoS_2 has been found to function as an excellent solid lubricant [18]. Other interesting applications include photovoltaics and photocatalysis, which involve the absorption of electromagnetic radiation within the visible range [19]. The layered structure of MoS_2 permits producing, in a relatively easy way, 2D crystals that have exceptional properties, much better than those of the bulk material. As the thickness of the crystal is decreased to the unit cell value, the band structure of the electrons changes and the energy gap is increased from 1.29eV (indirect transitions) in the bulk material to 1.90eV (direct transitions), which entails changes in the electric and optical properties of the material [20]. In separate 2D MoS_2 crystals, the luminescence quantum energy is increased by more than a factor of 10^4 [21]. The 2D crystals can be used for the manufacture of ultraviolet photo-detectors [22], field-effect transistors [23] and the electrodes used in lithium ion storage batteries [24]. Since there is no significant difference between the properties (such as, e.g., electric properties) of MoS_2 flakes constructed from one and several layers, exceptional electric properties can be achieved even when the nanocrystal is composed of several layers [20].

During the exfoliation, new faces are formed which, in MoS_2 with its atomic structure, have varied properties [25]. According to Zanin et al. [26] and Park and Jeon [27], the faces of the individual layers that are formed from the sulphur atoms do not exhibit polar behaviour, whereas at the edges of the flakes, polar effects predominate, which results from the Mo-S bonds being broken. The effects associated with the different properties of the faces and edges vary alongside the changing morphology of the crystal, since the ratio of the face-to-edge surface areas varies during exfoliation and the effects due to the increased surface area of the faces should become predominant.

The investigations performed in the present study confirmed the significance of the role played by the surface forces of all the participants in the exfoliation process, especially the role played by the surface of the grinding balls.

2. Materials and methods

In our experiments, the selection of liquids and solids was based on the Fowkes [28] theory, which states that interactions only occur between the surface energy components of bonds of the same type, i.e., dispersive with dispersive and polar with polar. These surface phenomena should facilitate the exfoliation provided that: $E_{adh} \geq E_{coh}$ + interlayer interaction in a layered crystal, where E_{adh} is adhesion energy of two solids and E_{coh} is cohesive energy into the solid body.

Two types of milling balls were selected: one made of steel, which had metallic bonds and dispersive surface effects, and one made of Al_2O_3, with covalent-ionic bonds and a preponderance of polar effects. The liquids were water (H_2O), isopropyl alcohol (C_3H_8O) and kerosene. The properties of the materials are given in Table 1.

Solid and liquid matter	Surface tension/free surface energy [mJ/m^2]	dispersive(d) and polar(p) part of surface tension [mJ/m^2]
MoS_2	≅260 [29]	dispersive/polar
distilled water [H_2O]	72.8	43.7(p) and 29.1 (d)
isopropyl alcohol [C_3H_5OH]	23	19.5 (d) and 3.5 (p)
kerosene	23-32	dispersive
stainless steel 316	29-56	dispersive
α Al_2O_3	≅124 [30]	polar/dispersive

Table 1. Surface tension/free surface energy of the liquids and solids that participated in the milling process (data from DataPhysics Instruments GmbH database, except [29-30])

Mechanical exfoliation was conducted using MoS_2 powder 325 mesh grade with a purity of 99% (delivered by Alfa Aesar Co). The morphology of this powder in its starting state is shown in Figure 1.

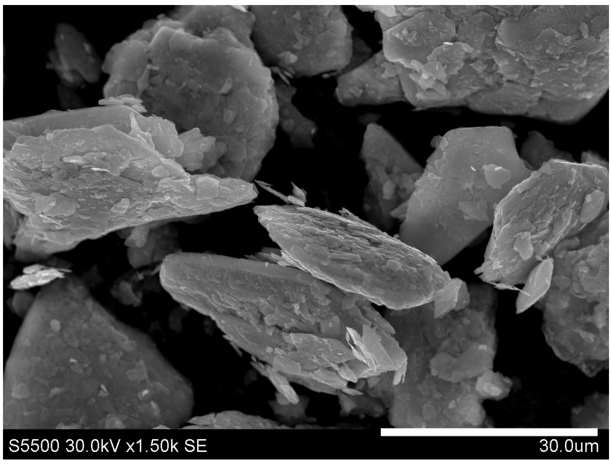


Figure 1. Morphology of the MoS_2 powder in the starting state

The MoS_2 layered crystals were exfoliated using two different milling techniques, differing in terms of the participation of the ball impact energy. In both cases, the mills were selected to ensure a predomination of shear stresses.

The first series of experiments was conducted with a homemade low-energy cannon-ball type mill with a rotational speed of 300 rev/min (Figure 2a). The powder was placed in a polyethylene container with a volume of 800ml (according to the amount of the powder) and the milling medium was in the form of balls 2mm in diameter, made of 316 steel, as well as Al_2O_3 balls (99.5% purity).

The aim of the next series of the experiments was to examine the effect of the milling energy. The mill used in this series of experiments was a home-made attritor mill with a rotational speed of 600 rev/min (Figure 2b). As in the first series, the process was conducted in polyethylene containers, but only with the Al_2O_3 balls.

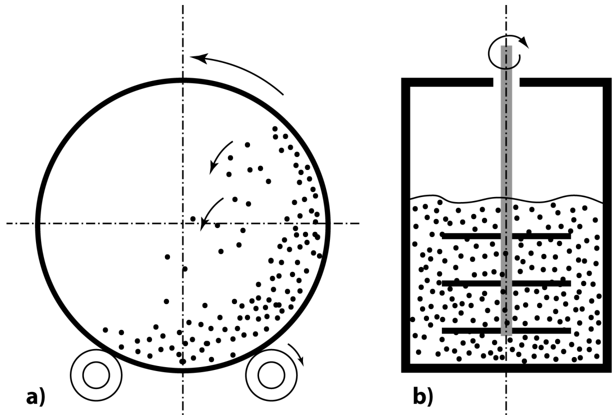


Figure 2. Schematic representation of milling techniques used for exfoliation of the MoS_2 crystals: (a) cannon-ball type mill; (b) attritor mill

In both experiments and with all the liquids employed, the milling process was conducted at room temperature for t=30h. The ball-to-powder mass ratio was 333:1 and the suspension concentration was 5g/l, the same in both series of the experiment. Time was chosen experimentally and the criterion was to obtain a Tyndall effect in the suspension. Other parameters, including the concentration, were selected on the basis of the presented literature. The temperature during the process was less than 30 degrees Celsius. The parameters of the exfoliation processes are shown in Table 2.

Liquid	Grinding medium	Milling system
distilled water (H_2O)	α-Al_2O_3	cannon-ball/attritor
	stainless steel 316	cannon-ball
isopropyl alcohol (C_3H_5OH)	α-Al_2O_3	cannon-ball/attritor
	stainless steel 316	cannon-ball
kerosene	α-Al_2O_3	cannon-ball/attritor
	stainless steel 316	cannon-ball

Table 2. Milling process parameters used in the two exfoliation variants

After the milling process was completed, the suspensions were sieved, poured into beakers and stirred. The test samples, one part with a volume of 25ml and the other part with a volume of 5ml, were taken from each beaker using an automatic pipette. The 5ml sample was additionally diluted with 20ml of an appropriate liquid.

Then, all the samples were left for 24h to 100 days to permit sedimentation.

The nanoparticles and the powders were observed in STEM (scanning/transmission electron microscope, Hitachi S 5500) and TEM (transmission electron microscope JEOL JEM 3010). The SEM/TEM samples were prepared by instilling the suspension on holey carbon film coated grids (300 mesh).

For light scattering examinations, the suspensions were placed in glass phials and exposed to white LED light. The scattered light intensity was measured with a diode perpendicularly to the incident light.

3. Results and discussion

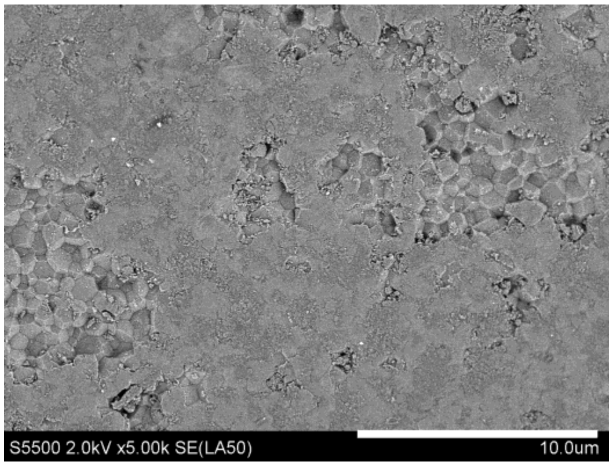
The milling process and subsequent sedimentation process yielded colloids and a deposit at the bottom of the beaker. Particles also adhered to the milling balls.

3.1 Milling in a cannon-ball type mill

3.1.1 Surface of the balls

In rotational milling with the participation of isopropyl alcohol, no adherence of molybdenum sulphide to the balls was observed, irrespective of the milling technique and the type of balls. Milling in water resulted in small amounts of impurities deposited on the surface of the balls, whereas in the presence of kerosene, the ceramic and steel balls were almost entirely covered with a thin layer of MoS_2 flakes. Figure 3 shows the ball surfaces prior to and Figure 4 following the milling process conducted with the participation of kerosene.

Observations of the ball's surfaces showed that powder particles that adhered to steel balls could be characterized by the much larger surface area of plates the covered (Figure 4b and d). Stereological analysis indicated that the surface of these particles were on average three times larger. According to the Fowkes theory [28], the non-polar surfaces of the steel balls interact with the faces of the MoS_2 flakes much more intensively, which may result in flakes with a surface area exceeding even 100μm^2 being "cemented" to the relatively smooth surface of the steel balls. When, after milling in kerosene, the ceramic and steel balls were washed in isopropyl alcohol, we obtained a suspension of MoS_2 flakes with an intensive blue colour similar to that observed in the suspension formed after milling and sedimentation in the presence of isopropyl alcohol. After washing the balls in isopropyl alcohol, the flakes that had adhered to their surfaces were washed out to be suspended in alcohol. Due to the dispersive-polar character of the interactions, isopropanol dispersed the particles well in the suspension, while at the same time "isolating" them from the surfaces of the balls, irrespective of their type (steel or ceramic).



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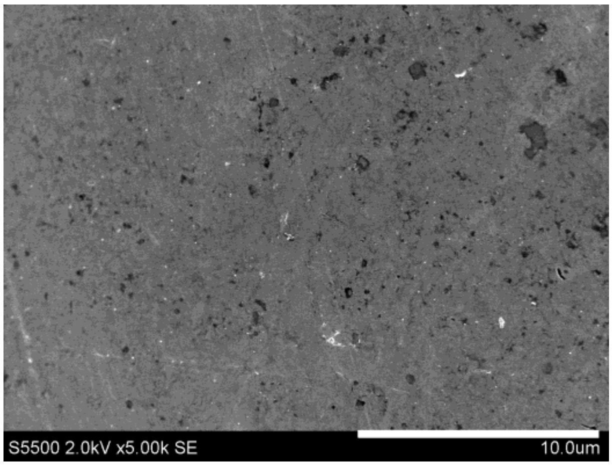

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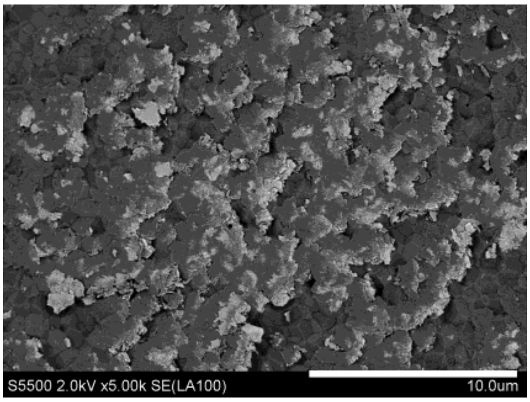
Figure 3. Surface topography of the mill balls prior to the milling process: (a) clean surface of the Al_2O_3 ball; (b) clean surface of the steel ball

Water wet the steel relatively weakly (γ_{st}≥90), as was also the case for 2D nanocrystals; therefore, it did not favour the dispersion of the MoS_2 particles. As was the case with kerosene, the repelled flakes adhered to the surface of the steel balls, forming a thin film on their surface.

With Al_2O_3 balls, the preponderance of the polar interactions on the ball surface should decrease the tendency of the flakes to adhere. It is difficult to unequivocally estimate the influence of the adhesion forces, since during the collisions of the balls, their surfaces crack and chip. An analysis of the chemical composition of the sediment confirmed that it was contaminated with Al_2O_3 from the balls. The chipping of the ball surface may facilitate the removal of adhered flakes from it.

The flakes may also adhere to the ball surface through mechanical anchoring to its irregularities. As can be seen in Figure 3a, the surface of the corundum ceramic balls are much more developed, which facilitates the mechanical



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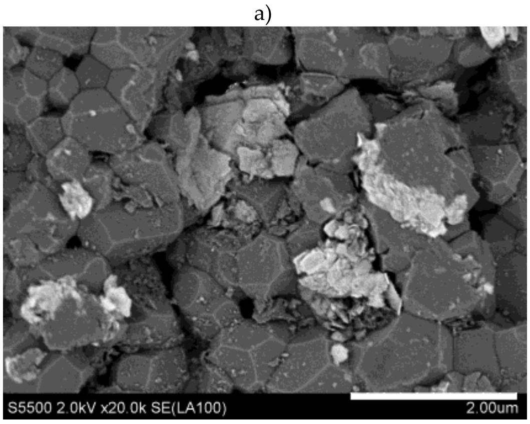

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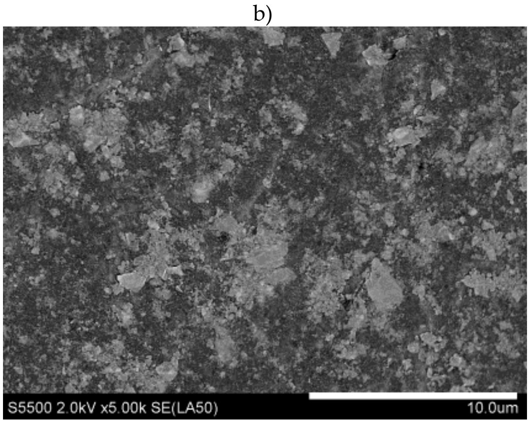

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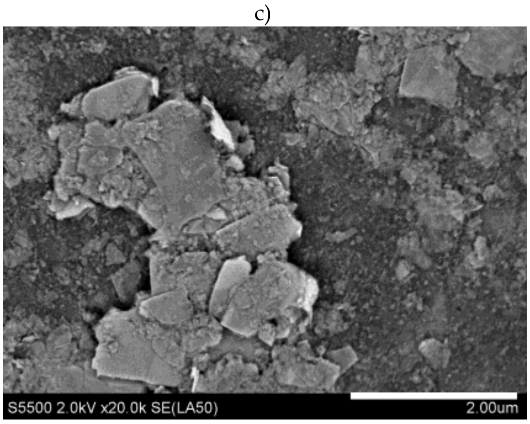


d)

Figure 4. Surface topography of the mill balls after the milling process: (a) and (b) MoS_2 particles deposited on the surfaces of the Al_2O_3 balls after milling in kerosene, (c) and (d) MoS_2 particles deposited on the surfaces of the steel balls after milling in kerosene

engagement of the powder particles with the balls' surfaces. This is confirmed by the photographs shown in Figures 4a and b, where we can see the finest particles anchored at the peaks and valleys of the ceramic ball's surface.

3.1.2 Particles produced by milling

An analysis of the particles present in the suspension and in the deposit following sedimentation showed that irrespective of the milling method and the liquid employed, the powder particles had been considerably refined (Figures 5, 6, 7) compared to the starting powder. After 48h sedimentation, the walls of the glass vessels that contained the samples milled in kerosene or water became dirtied and in those containing particles milled in water, the particle floatation effect was observed (deposit floated on the suspension surface).

The diluted samples changed colour during the sedimentation, acquiring in the case of isopropyl alcohol a weaker or stronger pale-blue colour. After 100 days of sedimentation, light scattering was observed in all the suspensions. Table 3 shows the results of the light scattering analysis.

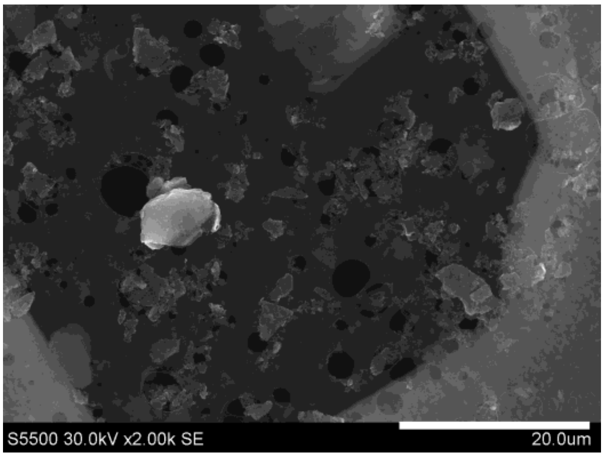
Ball type	Liquid	Scattering intensity [μA] Δ = 0.025
316 stainless steel balls	water	0.15
	isopropyl alcohol	0.20
	kerosene	0.25
Al_2O_3 (ceramic) balls	water	0.36
	isopropyl alcohol	0.50
	kerosene	0.46

Table 3. Intensity of light scattered in the suspensions obtained by cannonball milling (Δ – approximation error)

It was found that in the suspensions of MoS_2 particles obtained by milling with Al_2O_3 balls, the intensity of scattered light was about twice as high as in those milled with steel balls, meaning that the former contained greater amounts of light-scattering material. In view of the reproducibility of the process conditions, we can conclude that irrespective of the liquid employed, the participation of the Al_2O_3 balls favoured the refinement of the material and thereby, the formation of nanocrystals suspended in the colloid. This may be a direct result of the balls' material surface forces on the layered crystals.

The morphology of the flakes present in the isopropyl alcohol suspension is shown in Figures 5 and 6. The size range of the particles was very wide, with the average particle size being 250nm.

A TEM electron diffraction analysis of the regions (shown in Figure 6) indicated that the nanoparticles visible in the image had a crystalline character. The analysis also



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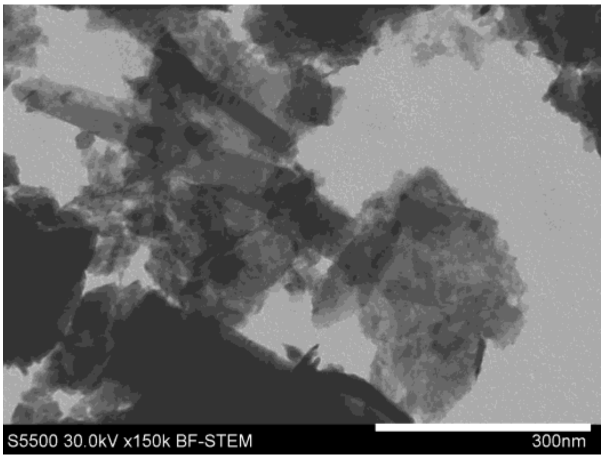


b)

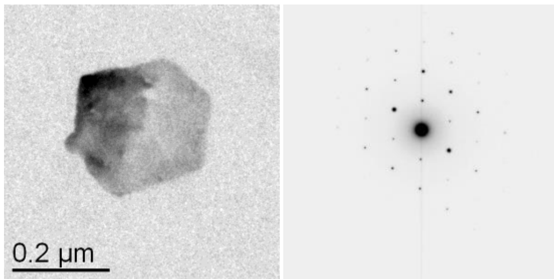
Figure 5. Morphology of the MoS_2 flakes produced by cannon-ball milling with Al_2O_3 balls in an isopropyl alcohol suspension: (a) SEM image; (b) STEM image

revealed the presence of multi-layer MoS_2 flakes. The results of the diffraction analysis are shown in Figure 6.

As to the morphology and size of the nanosheets suspended in isopropyl alcohol, no considerable differences were found between those obtained by milling with steel and by milling with Al_2O_3 balls.

The samples obtained by milling in liquids other than isopropyl alcohol also contained MoS_2 nanocrystals made up of several (or more) layers. However, contrary to isopropyl alcohol, in water and kerosene, most of the crystals strongly agglomerated, so that separate nanosheets were only sporadically observed. Generally, agglomerates were observed, such as can be seen in Figure 7a and b.

The sediment mainly contained refined and strongly agglomerated crystals. No essential differences were found between the sediments obtained in different liquids. The amount of contamination was also minimal. In all the



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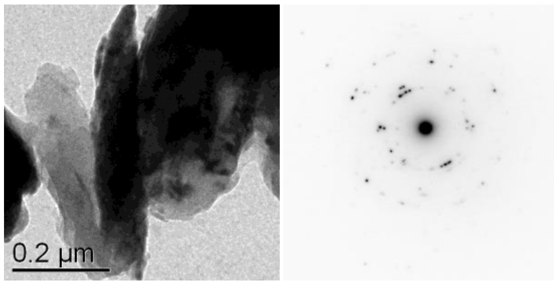

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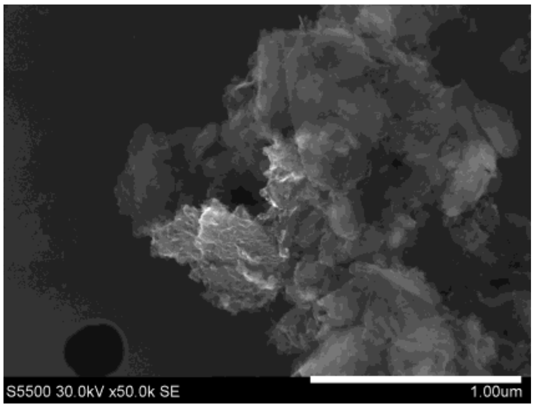
Figure 6. Shape and the electron diffraction pattern of the MoS_2 particles obtained by cannon-ball milling: (a) single-crystal MoS_2; (b) multi-layer MoS_2 nanocrystal



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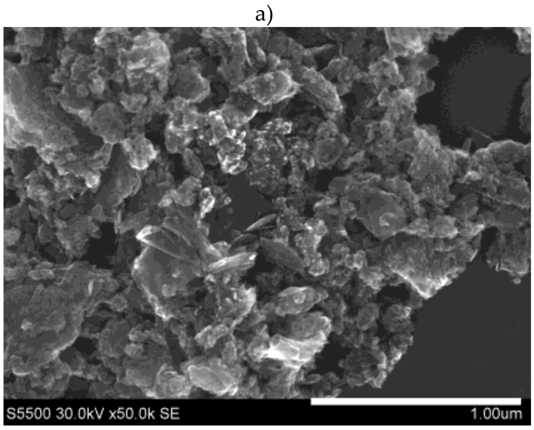


b)

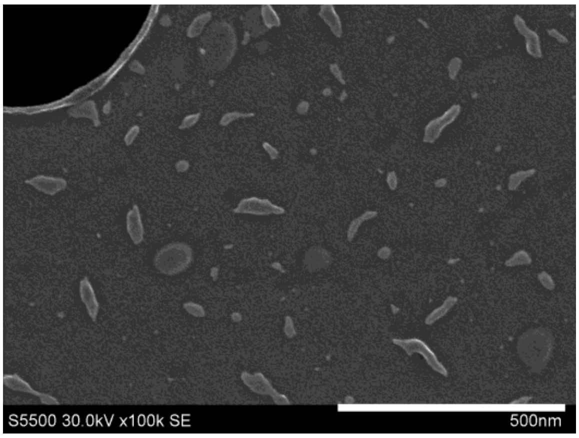
Figure 7. Morphology of the particles obtained by cannon-ball milling in a suspension of (a) water; (b) kerosene

sediments examined milled with Al_2O_3 balls, an EDS chemical analysis confirmed that the amounts of Al in the sediment was vestigial (1-3%). No Fe was found in the sediment after milling with steel balls conducted in alcohol and kerosene. Small amounts of Fe were identified in the sediment obtained after milling in the presence of water.

3.2 Attrition milling

3.2.1 Effect of ball impacts

In attrition milling, the ball impact energy was higher than in the cannon-ball type mill, which was due to the high rotational speed of the ceramic blades in this instance. The results obtained by exfoliation in the attrition mill in the presence of isopropyl alcohol were very similar to those obtained after rotational milling. Here, too, single-layer and multi-layer MoS_2 nanocrystals were identified.



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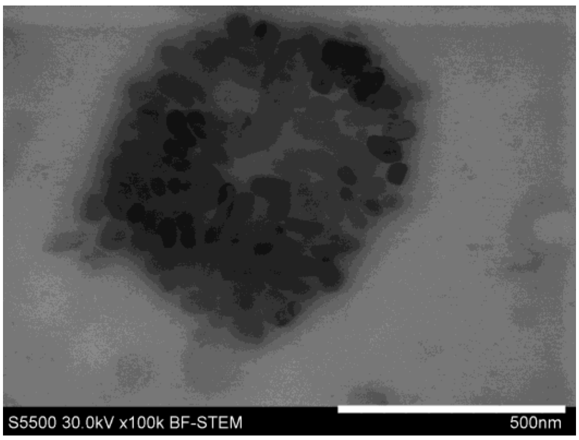
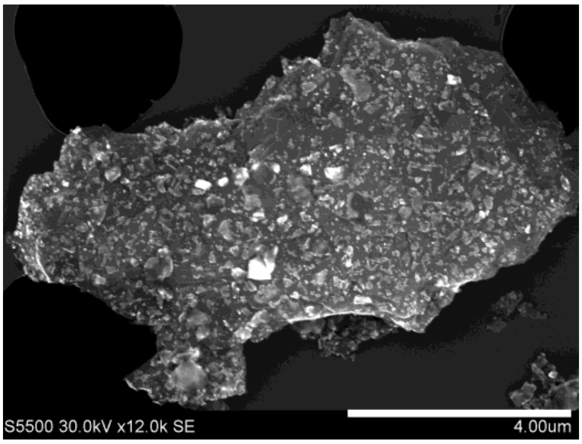


b)

Figure 8. Morphology of the particles obtained by attrition milling in a suspension of isopropyl alcohol: (a) SEM image; (b) STEM image – light field

The finest nanoparticles with good dispersion were obtained after attrition milling in the presence of isopropyl alcohol. The suspension contained particles with an average size of 150nm, with elongated shapes and sharp edges (Figure 8a), and regions of agglomerated particles/flakes, oval in shape, with an average size of 90nm, but much thinner (perfectly translucent in the microscope transmission mode – Figure 8b). A diffraction analysis indicated that the flakes had an amorphous character.

Essential differences were revealed in terms of sediment between the particles obtained by attrition milling and cannon-ball type milling using Al_2O_3 balls (Figure 9). After milling by the attrition method, significant amounts of contaminants such as aluminium oxide and zirconium oxide could be seen as dispersed light-colour particles, visible on the surface of a large MoS_2 crystal (Figure 10a), whereas in the deposit of the powder that had been cannon-ball milled, there were large MoS_2 crystal fractions with very small flakes adhering to them that predominated (Figure 9b).



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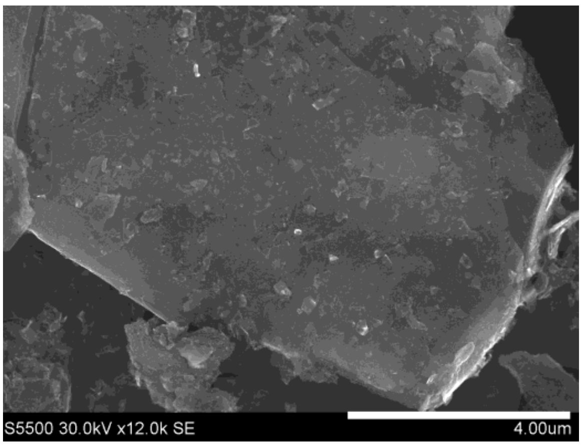

b)

Figure 9. Comparison between the morphologies of the powder particles present in the deposit after milling with ceramic balls by: (a) attrition milling; (b) cannon-ball milling

The presence of substantial amounts of contamination with the materials that participated in the attrition milling indicated that the exfoliation process was in this instance more violent (due to the higher kinetic energy involved) and may therefore have yielded particles with a smaller average size, or may even have led to their amorphization. Moreover, the contaminants in the form of sharp edge ceramic micro-particles adhered to the surface of the MoS_2 crystals functioned as a micro-abrasive medium that broke the exfoliated nanosheets.

4. Conclusions

In exfoliation by milling, the material of the mill balls appeared to play a very significant role. Irrespective of the liquid employed, the number of nanosheets in the suspension obtained by milling with Al_2O_3 balls was greater by 100% than that present after milling with steel balls. Since no differences were observed between the morphology and size of the nanosheets obtained with the Al_2O_3 and steel balls, the difference in the efficiency between these two processes may be attributed to the surface effects associated with the ball material.

The character of the surface effects that occur when milling with Al_2O_3 can possibly be the effect of separation of the individual layers from the bulk MoS_2 crystal due to the action of the surface forces of the balls, as can be observed in liquid assisted exfoliation. Adhesion interaction with Al_2O_3 appeared to be more advantageous than in case of using steel balls, which only acted by dispersion forces.

It should, however, by noted that the summarized effect of the ball surface also depends on its morphology. In milling with the use of corundum balls, there is the additional effect of crystals anchoring at the irregularities of the ball surface; however, in our experiment, it was impossible to assess which of these effects dominated over others.

Our experiments confirmed the advantageous role of isopropyl alcohol, which has been described in the literature reports, with regard to ultrasound-enhanced liquid exfoliation. No contamination of the surfaces of the balls with MoS_2 nanocrystals and no suspended nanosheets agglomeration were observed in the presence of isopropyl alcohol.

As the milling energy increased, the collisions intensified. Consequently, the ball surfaces underwent chipping and were cleaned, resulting in the flakes obtained being smaller. Another adverse effect may be that the nanocrystals become amorphized, an effect that has been well-established in mechanical alloying processes.

5. Acknowledgements

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6. References

[1] Novoselov K S, Jiang D, Schedin F, Booth T J, Khotkevich V V, Morozov S V, Geim A K (2005) Two-dimensional atomic crystals. Proceedings of the National Academy of Sciences. 102(30): 10451-10453.

[2] Bonaccorso F, Lombardo A, Hasan T, Sun Z, Colombo L, Ferrari A C (2012) Production and processing of graphene and 2D crystals. Materials Today. 15(12): 564-589.

[3] Hernandez Y, Nicolosi V, Lotya M, Blighe F M, Sun Z, De S, McGovern I T, Holland B, Byrne M, Gun'Ko Y K, Boland J J, Niraj P, Duesberg G, Krishnamurthy S, Goodhue R, Hutchison J, Scardaci V, Ferrari A C, Coleman J N (2008) High-yield production of graphene by liquid-phase exfoliation of graphite. Nature nanotechnology. 9: 563-568.

[4] Sokołowska A, Rudnicki J, Kostecki M, Wojtkiewicz S, Sawosz P, Chodun R, Zdunek K, Olszyna A (2014) Electric field used as the substitute for ultrasounds in the liquid exfoliation of hexagonal boron nitride. Microelectronic Engineering 126: 124-128.

[5] Janot R, Guerard D (2002) Ball-milling of graphite as a function of the dispersal media. Carbon 40: 2887-2896.

[6] Coleman J N, Lotya M, O'Neill A, Bergin S D, King P J, Khan U, Young K, Gaucher A, De S, Smith R J, Shvets I V, Arora S K, Stanton G, Kim H Y, Lee K, Kim G T, Duesberg G S, Hallam T, Boland J J, Wang J J, Donegan J F, Grunlan J C, Moriarty G, Shmeliov A, Nicholls R J, Perkins J M, Grieveson E M, Theuwissen K, McComb D W, Nellist P D, Nicolosi V (2011) Two-dimensional nanosheets produced by liquid exfoliation of layered materials. Science. 331: 568-571.

[7] Cunningham G, Lotya M, Cucinotta C S, Sanvito S, Bergin S D, Menzel R, Shaffer S P, Coleman J N (2012) Solvent exfoliation of transition metal dichalcogenides: Dispersibility of exfoliated nanosheets varies only weakly between compounds. ACS Nano 6(4): 3468-3480.

[8] Hansen C, (2007) Hansen Solubility Parameters: A user's handbook. Second Edition. Boca Raton. CRC Press.

[9] Koch C C (2003) Top-down synthesis of nanostructured materials: Mechanical and thermal processing methods. Reviews on Advanced Materials Science. 5: 91-99.

[10] Janot R, Guerard D (2005) Ball milling in liquid media Application to the preparation of anodic materials for lithium-ion batteries. Progress in Material Science. 50: 1-92.

[11] Vittori Antisari M, Montone A, Jovic N, Piscopiello E, Alvani C, Pilloni I (2006) Low energy pure shear milling: A method for the preparation of graphite nano-sheets. Scripta Materialia. 55(11): 1047-1050

[12] Zhao W, Fang M, Wu F, Wu H, Wang L, Chen G (2010) Preparation of graphene by exfoliation of graphite using wet ball milling. Journal of Materials Chemistry. 20: 5817-5819.

[13] Zhao W, Wu F, Wu H, Chen G (2010) Preparation of colloidal dispersions of graphene sheets in organic solvents by using ball milling. Journal of Nanomaterials. doi:10.1155/2010/528235.

[14] Li L H, Chen Y, Behan G, Zhang H, Petravic M, Glushenkov A M (2011) Large-scale mechanical peeling of boron nitride nanosheets by low-energy ball milling. Journal of Materials Chemistry. 21: 11862.

[15] O'Neill A, Khan U, Coleman J N (2012) Preparation of high concentration dispersions of exfoliated MoS_2 with increased flake size. Chemistry of Materials. 24: 2414-2421.

[16] Yao Y, Lin Z, Li Z, Song X, Moon K, Wong C (2012) Large-scale production of two-dimensional nanosheets. Journal of Materials Chemistry. 22: 13494-13499.

[17] Kostecki M, Olszyna A, Sokołowska A (2013) Liquid exfoliation – new low-temperature method of nanotechnology. Materials Science-Poland. 31: 165-172.

[18] Groszek J and Witheridge R E (1971) Surface properties and lubricating action of graphite and MoS_2. ASLE Transactions. 14: 254-266.

[19] Frame F A and Osterloh F A (2010) CdSe-MoS_2: A quantum size-confined photocatalyst for hydrogen evolution from water under visible light. Journal of Physical Chemistry. 114: 10628-10633.

[20] Mak K F, Lee C, Hone J, Shan J, Heinz T F (2010) Atomically thin MoS_2: A new direct-gap semiconductor. Physical Review Letters. 105: 136805.

[21] Splendiani A, Sun L, Zhang Y, Li T, Kim J, Chim C, Galli G, Wang F (2010) Emerging photoluminescence in monolayer MoS_2. Nano Letters. 10: 1271-1275.

[22] Alkis S, Oztas T, Aygun L E, Bozkurt F, Okyay A K, Ortac B (2012) Thin film MoS_2 nanocrystal based ultraviolet photodetector. Optics Express. 20: 21815.

[23] Whang W S, Remskar M, Yan R, Kosel T, Park J K, Cho B J, Haensch W, Xing H, Seabaugh A, Jena D (2013) Comparative Study of Chemically Synthesized and Exfoliated Multilayer MoS_2 Field-Effect Transistors. Applied Physics Letters. 102: 043116.

[24] Ding S, Zhang D, Chen J S, Lou X W (2012) Facile synthesis of hierarchical MoS_2 microspheres composed of few-layered nanosheets and their lithium storage properties. Nanoscale. 4: 95-98.

[25] Bollinger M V, Jacobsen K W and Norskov J K (2003) Atomic and electronic structure of MoS_2 nanoparticles. Physical Review B. 67: 085410.

[26] Zanin M, Ametov I, Grano S, Zhou L, Skinner W (2009) A study of mechanisms affecting molybdenite recovery in a bulk copper/molybdenum flotation circuit. Journal of Mineral Processing. 93: 256-266.

[27] Park C and Jeon H (2010) The effect of sodium silicate as pH modifier and depressant in the froth flotation of molybdenite ores. Materials Transactions. 51: 1367-1369.

[28] Fowkes F M (1962) Determination of interfacial tensions, contact angles, and dispersion forces in surfaces by assuming additivity of intermolecular interactions in surfaces. Journal of Physical Chemistry. 66: 382.

[29] Weiss K, Phillips J M (1976) Calculated specific surface energy of molybdenite (MoS_2). Physical Review B 14(12): 5392-5395.

[30] Holysz L, Chibowski E (1992) Surface free energy components of α-Alumina from thin-layer wicking. Langmuir 8: 717-721.