Synthesis of nanocrystalline MoS_2 and WS_2 in a microwave plasma

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Abstract

This paper describes the synthesis of nanoparticulate MoS_2 and WS_2. These compounds are of special interest, as they form layered structures. The synthesis is performed by the reaction of the hexacarbonyls with H_2S in a microwave plasma. The resulting particles are in the range of 5 to 15 nm in diameter. It is remarkable that, in contrast to other nanoparticles, these particles contain step dislocations in the {0002} planes and point defects, causing bending of the lattice planes. Additionally, particles exhibiting nested fullerene-like structures and polyhedron-shaped crystals were found.

Keywords Nanocrystalline; Polyhedron crystal; Onion crystal; Microwave plasma; MoS_2; WS_2

1. Introduction

Sulphides of the transition metals show interesting structural and optical properties. Usually, these properties undergo significant modifications in the case of a reduction of the particle size from the micrometer to the nanometer range. Therefore, it is essential to study the possibilities of the synthesis of this class of compounds with particle sizes below 10 nm. In this context the sulphides of molybdenum and tungsten were selected as models for this class of compounds.

The disulphides of molybdenum and tungsten, MoS_2 and WS_2, form layered structures. These layers consist of three planes: one hexagonal plane consisting of the metal ions placed between two hexagonal planes consisting of the sulphur ions. Therefore, the sequence of the layers in this structure is

... S-Me-S S-Me-S ...

Me stands for Mo or W. The bonding between the metal and the sulphur planes is covalent, whereas the bonding between the S–Me–S layers is of the van der Waals type. This is why these compounds can be used as lubricants. It was already found that like in the case of graphite these compounds may also form polyhedral, cylindrical and nested fullerene-like structures [1–3]. The nested fullerene-like structures are also known as 'onion crystals'.

The first nested fullerene-like structures in these compounds were found occasionally in WS_2 [1] and MoS_2 [2] films on quartz substrates. The sulphides

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Table 1
Summary of the experimental data for the synthesis of Mo_2S and W_2S

Material	MoS_2	MoS_2	WS_2	WS_2
Precursor	$Mo(CO)_6$	$Mo(CO)_6$	$W(CO)_6$	$W(CO)_6$
Microwave frequency (GHz)	0.915	2.45	0.915	2.45
Reaction gas	Ar/1 vol% H_2S	Ar/1 vol% H_2S	Ar/1 vol% H_2S	Ar/1 vol% H_2S
Temperature (°C)				
Synthesis	260	260	260, 580	160
Sulphur distillation	140	120	140	120
Pressure (mbar)				
Synthesis	30	10	30	10
Sulphur distillation	< 1	< 1	< 1	< 1

were obtained by the reaction of the metal films with H_2S at a temperature of 1000°C. The synthesis of MoS_2 powder by the reaction of MoO_3 with H_2S in a hydrogen containing atmosphere at a temperature above 650°C yields in MoS_2 particles with sizes in the range of 50 to 100 nm. Besides these large particles, onion crystals with diameters up to 30 nm and nanotubes with length up to a few micrometers were found [3].

One may ask, if the formation of onion or polyhedral crystals is characteristic for nanosized particles with layered crystal structure or if the formation of these structures is, like in the case of graphite, just a rare event. This is, beyond the synthesis of nanopar-

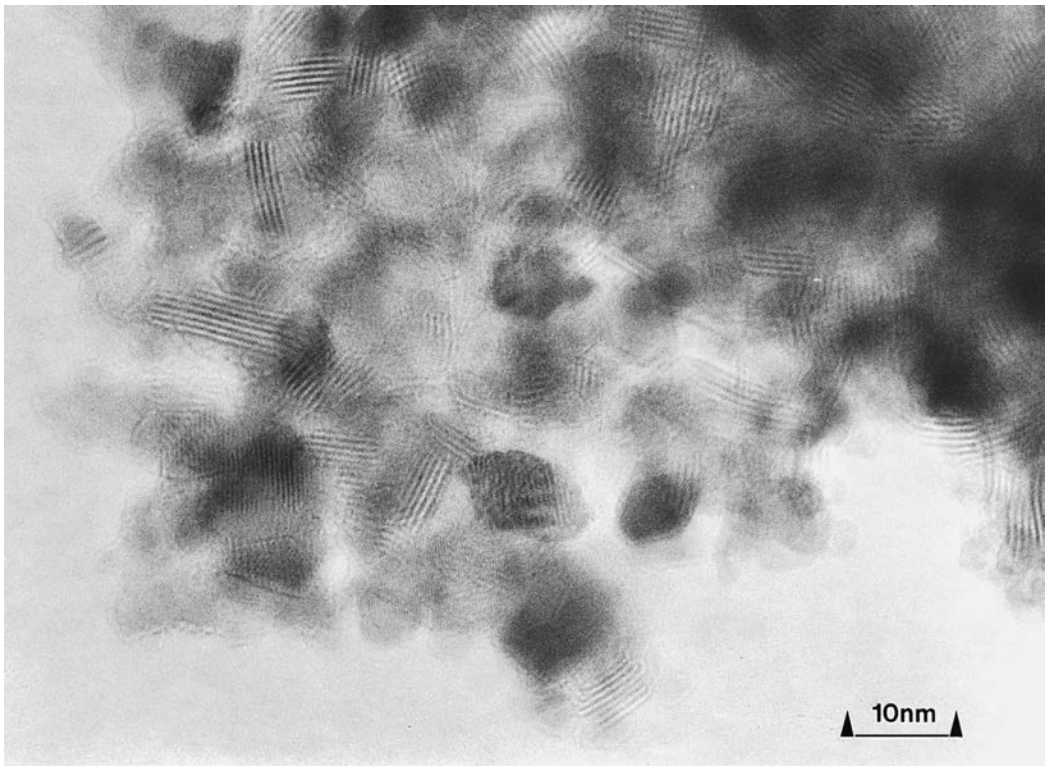


Fig. 1. Morphology of MoS_2 particles synthesised in the 2.45 GHz equipment at a temperature of 260°C. The lattice fringes represent the S–Mo–S layers, the {0002} planes with a measured distance of 0.65 nm.

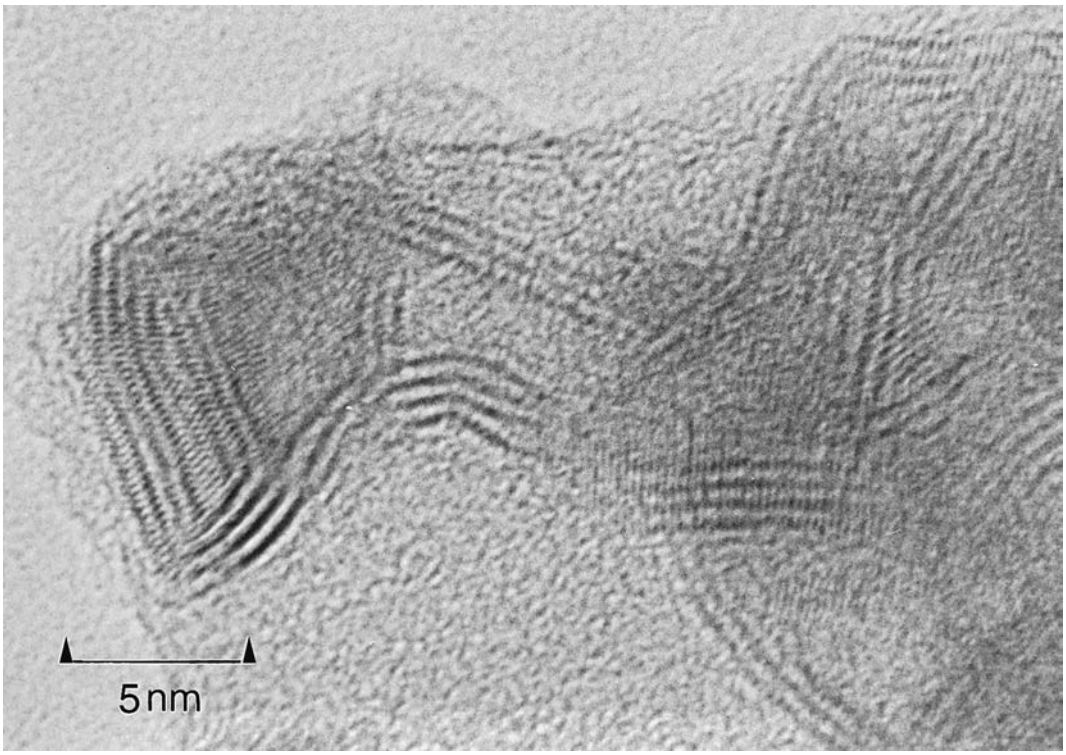


Fig. 2. Irregularly shaped non-equilibrium particles of MoS_2 (2.45 GHz, 260°C). There is a high probability that these nested particles are not closed in three dimensions.

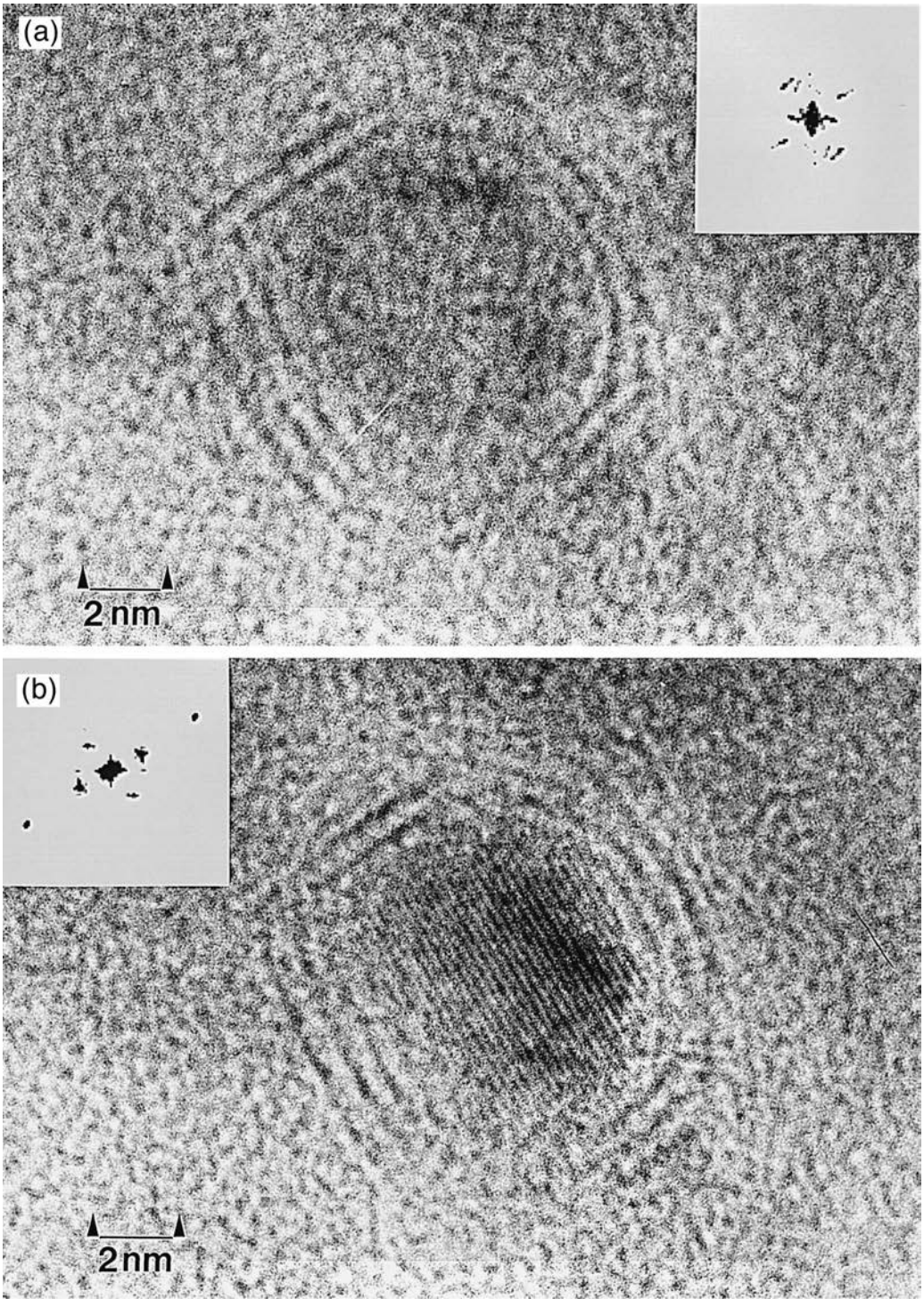
ticulate MoS_2 and WS_2, an additional objective of this paper. To synthesise MoS_2 and WS_2 the proved microwave plasma method [4,5], which originally was developed for the synthesis of oxide and nitride nanoparticles, was used after some modifications.

2. Experimental

2.1. Synthesis

The sulphides were prepared by the reaction of the hexacarbonyls $Mo(CO)_6$ and $W(CO)_6$ as precursor with H_2S in argon. The synthesis was performed in a microwave plasma, powered from a generator with a frequency of 0.915 or 2.45 GHz [6]. In both cases the plasma reaction is performed in a quartz tube passing a microwave cavity, which is part of a TE_{10} mode wave guide. The system is tuned by the combination of a sliding short with a tri-stub tuner to obtain a standing wave for ignition of the plasma. The precursor carbonyls are vaporised outside the reaction zone and introduced to the reaction gas before the plasma zone where the nanoparticles are formed. The reaction gas, a mixture of argon with 1

Fig. 3. Polyhedron shaped particle synthesised at 0.915 GHz and 260°C. This particle consisting of three or four S–Mo–S triple planes forms a box with convexly bent side walls. (a) This micrograph shows the side walls of the particle. The distance of the planes is measured to be 0.64 nm. The insert shows the central part of the power spectrum representing the lattice fringes. The relatively broad radial distribution of the spots representing the {0002} planes reveal strains in ⟨0001⟩ direction. (b) This micrograph shows the side walls and the bottom or the roof of the particle depicted in (a). The distance of the additional lattice fringes is measured to be 0.23 nm. The power spectrum represents the lattice fringes of the {0002} and the $\{10\bar{1}3\}$ planes. Again, the relatively broad radial distribution of the spots representing the {0002} planes reveal strains in ⟨0001⟩ direction.


(a)
2 nm
(b)
2nm

vol% H_2S was preheated to avoid precipitation of the precursor compound. The reaction temperature was measured with a thermocouple directly after the reaction zone. As a microwave plasma is a non-equilibrium system, the true temperature during the formation was certainly different.

In the case of the synthesis in a 0.915 GHz plasma, the reaction was performed under a pressure of 30 mbar. Depending on the experiment, the reaction temperature was adjusted at 260 or 580°C. The flow rate of the gas was selected to obtain a residence time of the particles of about 8 ms in the reaction zone. In the case of the higher reaction temperature, this residence time was about 4 ms.

Using 2.45 GHz microwaves to power the plasma gives the possibility to an additional reduction of the reaction temperature. In this case for MoS_2 the reaction temperature was set to 260°C and in the case of WS_2 it was possible to perform the reaction at a temperature as low as 160°C. The gas pressure was set to 10 mbar. This resulted in a residence time of the particles in the reaction zone of about 2 and 1.5 ms, respectively. In all cases, the reaction product was collected on cooled surfaces. The reaction product consisted, besides the intended compound, of some elemental sulphur. To evaporate the free sulphur, the reaction product was heated up to a temperature of 120°C in vacuum. Table 1 gives a summary of the experimental data.

2.2. Characterisation

The morphological characterisation of the reaction product was performed using a high resolution electron microscope (Philips CM 30 ST). Specimen preparation for electron microscopy was made by two different methods: (i) for a survey of the material, carbon coated Cu-grids were just immersed in the reaction products. This leads to agglomerates consisting of a large number of particles. (ii) To study the morphology of individual particles, the reaction products were dispersed ultrasonically in ethanol and dropped onto the grids. For the quantitative evaluation of the lattice fringes the electron

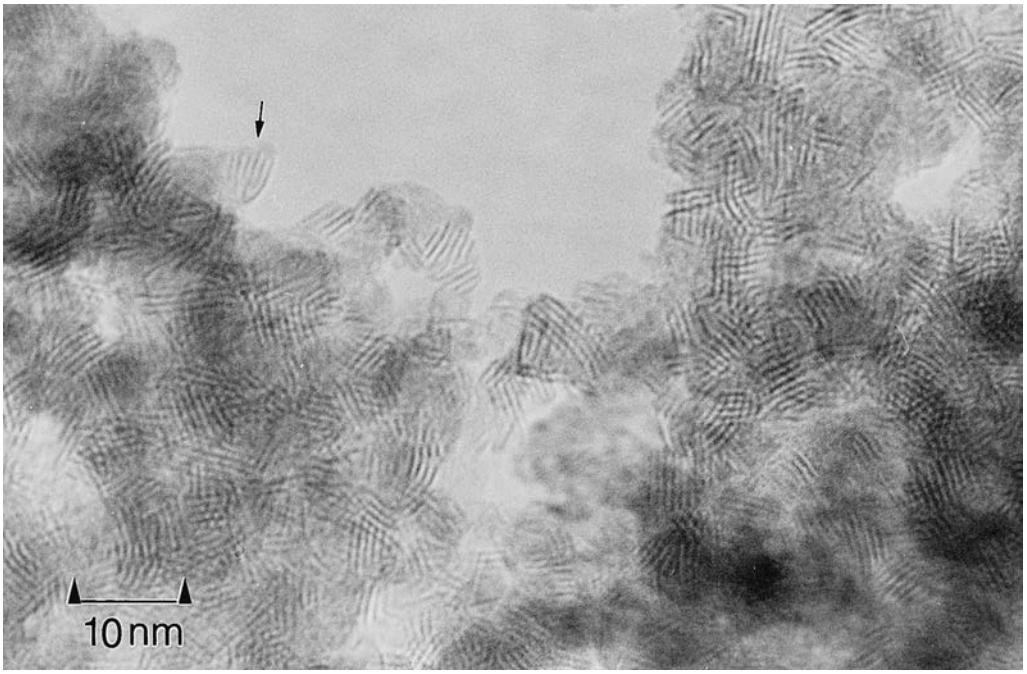


Fig. 4. Typical appearance of WS_2 particles synthesised at 2.45 GHz and 160°C. These particles show slightly bent lattice planes and some exhibit dislocation like structures (arrow).

micrographs were digitised and transformed in the Fourier space. In the Fourier space, lattice spacing and the relative orientation of the lattice fringes can be analysed easily [7,8]. Additionally, this transformation reveals lattice distortion by the shape of the maxima. For reasons of simplicity, instead of the Fourier spectra of the power spectrum, the squared modulus of the Fourier transformed, was used.

In the case of fullerene-like particles one has the problem of proving that these are three dimensional structures. In the case of larger particles the three dimensional structure can be shown by tilting the specimen in the transmission electron microscope. This is not feasible for particles with sizes below 10 or 20 nm. A series of micrographs with different defocus values were taken. In these series one can obtain micrographs showing different parts of the particles under various focus conditions. An additional advantage is that information about the lattice orientation of these different parts of the particles can be obtained.

3. Morphology of the MoS_2 particles

Fig. 1 depicts the typical morphology of the MoS_2 particles synthesised in the 2.45 GHz equipment. The size of these particles is in the range 5 to 8 nm. A major fraction is around 6 nm. The lattice fringes in this micrograph represent the S–Mo–S layers. The particles shown in Fig. 1 are obviously not in equilibrium. This can be seen from varying distances between the planes and from the bent lattice planes. As a mean value the distance between these layers, the {0002} planes, is 0.65 ± 0.07 nm, which has to be compared with a value of 0.6155 nm in an stoichiometric equilibrium crystal with sizes in the micrometer range [9]. Changing the experimental conditions to 0.915 GHz and a pressure of 30 mbar does not change the reaction product significantly. The main difference is the occurrence of particles with nested structures. Most of these particles show some extreme irregular shapes as shown in Fig. 2. There is a high probability that these particles are not

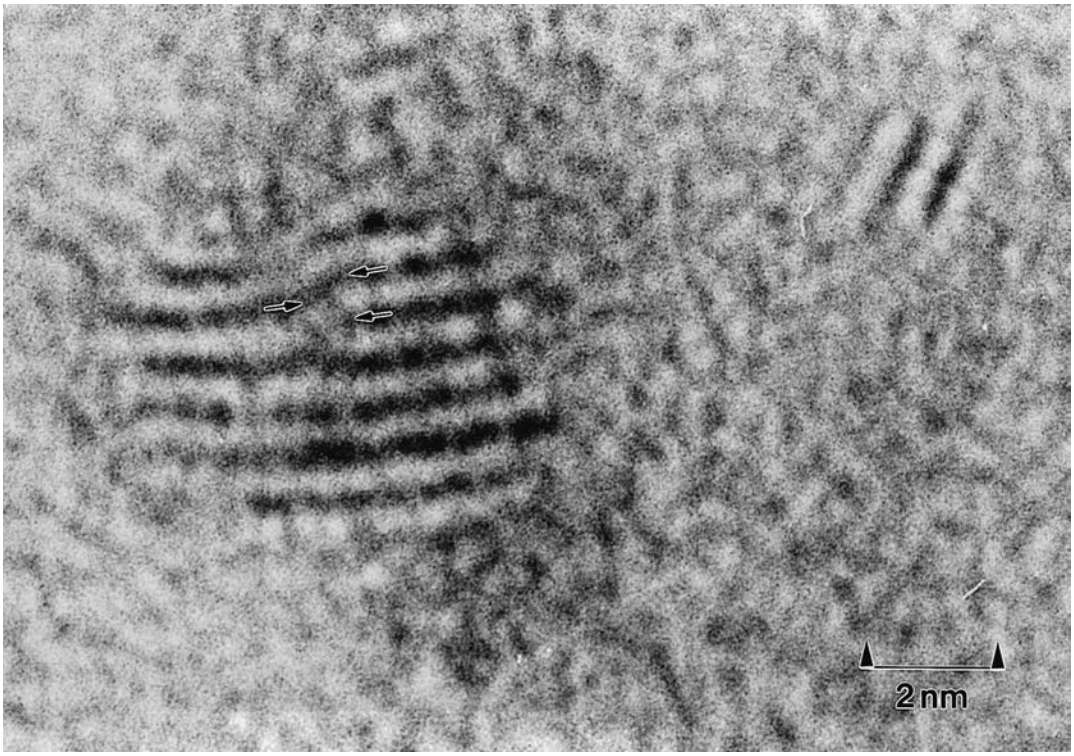


Fig. 5. A WS_2 particle of ca. 4 nm with a dislocation in the {0002} planes (synthesis conditions: 2.45 GHz, 160°C).

closed in three dimensions. Some of these nested particles exhibit more regular structures. Similarly as shown by Margulis et al. [2], nested fullerene-like particles are also observed (Fig. 3). These particles consist of three or four S–Mo–S triple planes, forming a box with rectangular cross-section. The surface of this body is bent convexly. Fig. 3a shows one of these particles under focus conditions where only the layers forming the walls (distance of the planes: 0.64 nm) can be seen. It is interesting to note that the walls are heavily bent. At the corners, this leads to angles between the side walls that are not 90°. The Fourier power spectrum shown in this figure reveals a broad distribution of distances between the {0002} planes. Changing the imaging conditions one realises additionally the lattice fringes of the bottom or top plane (Fig. 3b). The distance of these lattice fringes is measured to be 0.23 nm and may belong to the $\{10\bar{1}3\}$ planes. This indicates that the roof or the bottom of this particle has an angle of about 120° to the side walls. Again, one realises two striking phenomena in the power spectra: (i) the spacing in the ⟨0001⟩ direction is not a constant one within the different faces of the particle. One rather sees these spots radially elongated. (ii) The faces of the particle are not rectangular to each other. The deviation from 90° is at least 10°. Besides this box-shaped one, some more rounded onion-like crystals were also found.

4. Morphology of the WS_2 particles

Synthesising WS_2 in a 2.45 GHz equipment at a temperature of 160°C leads to relatively small and uniform particles. The typical appearance of these particles is depicted in Fig. 4. The sizes of the particles are around 5 nm. The lattice spacing in the ⟨0001⟩ direction was found to be 0.65 nm. This is significantly larger than the literature value of 0.618

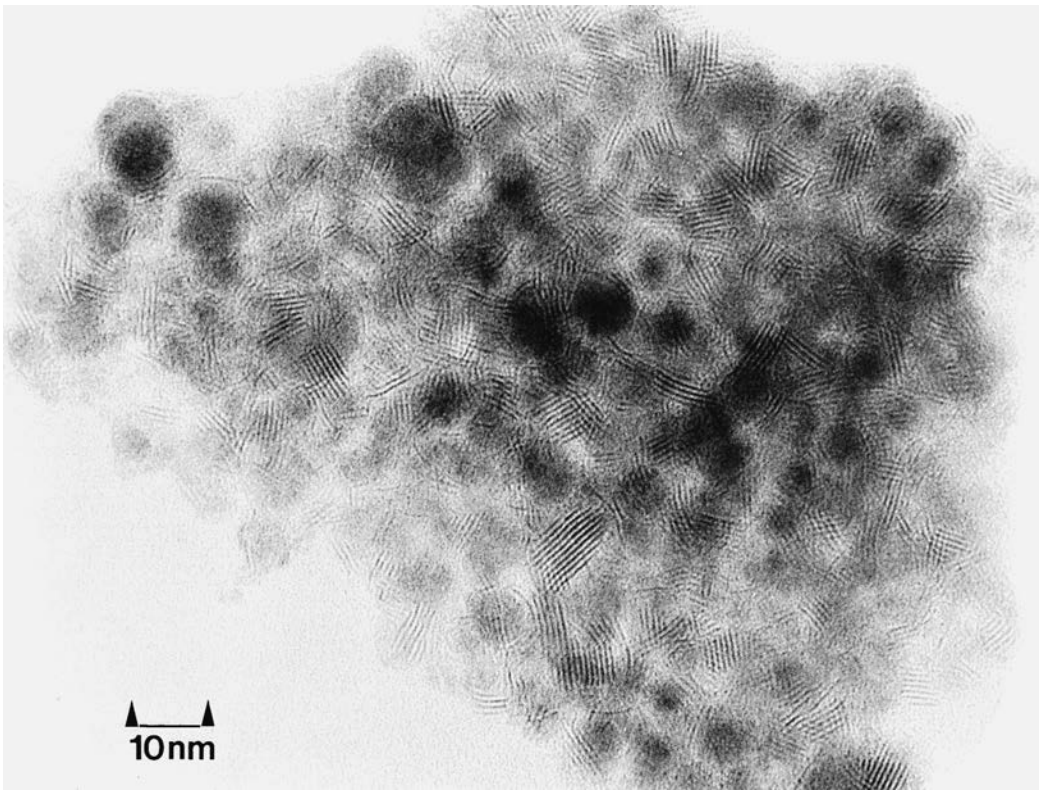


Fig. 6. Typical morphology of nanosized layered WS_2, produced at 0.915 GHz and 260°C.

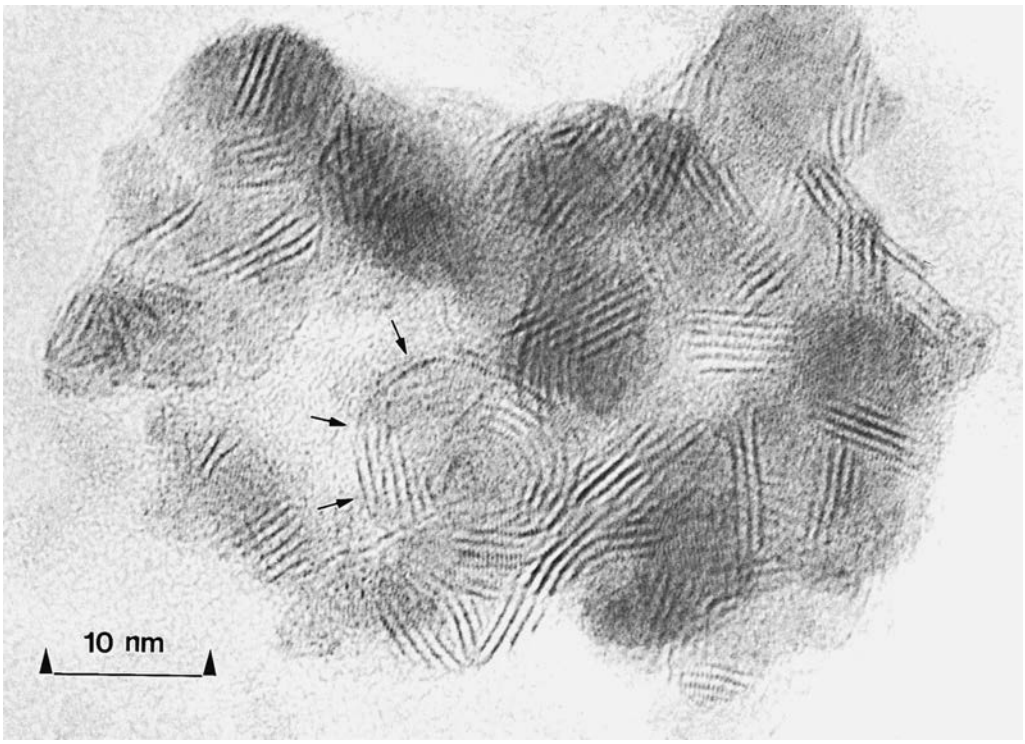


Fig. 7. Spherical, onion-like WS_2 particle (arrows) synthesised at 0.915 GHz and 580°C.

nm [10]. It can be seen in this micrograph that these particles show slightly bent lattice planes. Additionally, some particles show dislocation like structures. Nested fullerene-like structures are not observed. A typical particle with a dislocation and a size of about 4 nm is exhibited in Fig. 5. Comparable to MoS_2, the morphology of the particles changes with changing experimental conditions. Synthesising this material in a 0.915 GHz instead of a 2.45 GHz plasma modifies the structure of the particles. At a synthesis temperature of 260°C the particles are larger (Fig. 6). Increasing the temperature to 580°C leads to the occurrence of fullerene-like particles as shown in Fig. 7. The particle shown in this micrograph stems from a larger cluster. Therefore, lattice fringes from other particles are visible. Compared to similar particles of MoS_2, one realises that it is more spherical and it consists of significantly more layers. More precisely, in this case it is not proven whether this particle is really a spherical one or a bent two dimensional structure. It was not possible to obtain a micrograph depicting the roof or the bottom of such a particle. The power spectrum of this particle shows no deformation in any orientation. This is compatible with the fact that this particle has no edges.

5. Conclusions

The first objective of this study, the synthesis of nanoparticulate sulphides was reached successfully. The experiments at different experimental conditions revealed a relatively small influence of the experimental conditions. One may assume that the differences in the mean particle size and morphology are caused by the different temperatures in the reaction zone. As one may expect, the sizes of the particles increase with increasing temperature in the reaction zone. An increased temperature in the reaction zone leads also to a higher probability for the formation of fullerene-like and polyhedron shaped particles. The experiments of Tenne et al. [1–3] were performed under conditions close to equilibrium. Combining these findings, together with the results of the influ-

ence of the temperature, one may assume that spherical or polyhedron shaped particles represent conditions of a minimum of free energy. This can be true only, if one assumes a relatively high contribution of the dangling bonds at the periphery of the lattice planes to the total energy. This assumption leads to tubular crystals as shapes of minimum energy. To obtain three dimensional bent planes additional point defects are necessary [2]. A metal ion with a valency difference of four, results in a three dimensional bending of the hexagonal metal lattice planes, because one hexagon will be replaced by a polygon not having six edges. This is easily possible because not only molybdenum, but also tungsten may exist in different states of valency. If the metal ion has a higher valency than four and the hexagonal pattern is maintained, one has to expect additional free bondings out of the planes. Such a configuration may be the reason for the existence of odd shaped particles (Fig. 2) or stable edge dislocations (Fig. 5) in this material. One additional feature can be seen in the micrographs of the polyhedron shaped particles (Fig. 3): the lattice fringes are unclear in the vicinity of the edges, as also has been shown by Margulis et al. [2]. The reason for this may be found in high stresses at these corners. An important indication for these stresses may be the variation in the distance of the layers in the $\langle 0001 \rangle$ direction. A phenomenon like this is not observed in spherical particles.

The formation of MoS_2 or WS_2 polyhedron or onion crystals is, similar to the case of carbon, a rare event. The probability of formation may be increased by extending the temperature in the reaction zone. From the viewpoint of application, specially in the case of MoS_2 and WS_2, the formation of these structures has to be considered as a disadvantage.

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