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(54) **REACTORS FOR PRODUCING INORGANIC FULLERENE-LIKE TUNGSTEN DISULFIDE HOLLOW NANOPARTICLES AND NANOTUBES**

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REACTEURS POUR LA PRODUCTION DE NANOPARTICULES ET NANOTUBES CREUX A BASE DE DISULFURE DE TUNGSTENE DE TYPE FULLERENE INORGANIQUE

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• **PATENT ABSTRACTS OF JAPAN vol. 016, no. 066, 19 February 1992 (1992-02-19) & JP 03 261623 A (MITSUBISHI MATERIALS), 21 November 1991 (1991-11-21)**
• **Y FELDMAN, A ZAK, R POPOVIT-BIRO, R TENNE : "New Reactor for production of tungsten disulfide hollow onion-like (inorganic fullerene-like) nanoparticles" SOLID STATE SCIENCES (EDITIONS SCIENTIFIQUES ET MEDICALES ELSEVIER, FRANCE, vol. 2, no. 4, 1 June 2000 (2000-06-01) - 31 July 2000 (2000-07-31), pages 663-672, XP001028667 FR**

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Description

FIELD OF THE INVENTION

[0001]   This invention is generally in the field of production of inorganic fullerene-like nanoparticles (*IF*) and nanotubes. More particularly it relates to reactors for production of tungsten disulfide hollow onion-like nanoparticles and nanotubes.

BACKGROUND OF THE INVENTION

[0002]   Inorganic fullerene-like (*IF*) nanoparticles and nanotubes are attractive due to their unique crystallographic morphology and their interesting physical properties. In particular, disulfides of molybdenum and tungsten belong to a class of solid lubricants useful in vacuum, space and other applications where liquids are impractical to use. The fullerene-like nanoparticles can be used as superior solid lubricants, e.g. as additives to fluids and for self-lubriaction.

[0003] MS_2 (M=Mo,W) layered compounds can be synthesized by sulfidization of the respective trioxides in a reducing atmosphere at elevated temperatures. Hollow MoS_2 and WS_2 onion-like (inorganic fullerene-like, *IF*) nanoparticles were first observed in thin (~20nm) films, which were formed by sulfidization of the respective amorphous MoO_3 films in a reducing atmosphere at temperatures of about 850°C (Tenne, R., Margulis, L., Genut, M., and Hodes, G., *Nature* **360,** 444 (1992); Margulis, L., Salitra, G., Tenne, R., and Talianker, M., *Nature* **365**, 113 (1993)). In a search for the synthesis of a pure *IF* phase, it was suggested to take oxide powder rather than a thin film as a precursor material. However, MoO_3 powder evaporates at temperatures above 700°C, while WO_3 does not sublime untill 1400°C. Therefore, at the relevant reaction temperatures (~850°C), the reduction/sulfidization reactions of MoO_3 and WO_3 powders occur by the gas-phase reactions (GPR) and solid-gas reactions (SGR), respectively.

[0004]   In the case of the GPR, the size and shape of the final reaction product depends only on the prevalent conditions in the reactor, since MoO_3 evaporates as $(MoO_3)_{3-5}$ molecular clusters (Magneli, A., *J. Inorg. Nucl. Chem.* **2,** 330 (1956)). The reactor, which was used in an earlier report by some of the inventors of the present invention, (Feldman, Y, Wasserman, E., Srolovitz, D.J., and Tenne, R, *Science* **267**, 222 (1995)) was very simple, indeed. A mixture of the three gases (N_2, H_2, H_2S) was made to flow through the MoO_3 vapor zone. *IF*-MoS_2 powder accrued on the reactor walls along with a large number of other oxide and sulfide phases obtained by the GPR, when the MoO_3 powder with crystallites of ~5μm were used as a precursor. To regulate the GPR process and increase the production yield of *IF*-MoS_2, it was decided to separate the sublimation of MoO_3 powder from its sulfidization reaction. Several modifications of the reactor enabled the preparation a few milligrams of

an almost pure *IF* phase in a single run (Feldman, Y, Wasserman, E., Srolovitz, D.J., and Tenne, R., *Science* **267,** 222 (1995)). By varying the annealing time, the intermediate products of the reaction could be identified.

[0005]   It should be understood that, according to the known mechanism for the growth of the *IF* phase in molybdenum or tungsten systems, the analysis of the kinetics of the simultaneous reduction and sulfidization of WO_3 powders are based on the occurrence of a unique driving force for the fast growth of the first curved sulfide layer (0001) around an oxide nanoparticle. According to that kinetic model, a synergy between the reduction and sulfidization processes, which occurs in a very narrow window of parameters, leads to the formation of the first closed sulfide layers (Feldman, Y, Lyakhovitskaya, V, and Tenne, R., *J. Am. Chem. Soc.* **120,** 4176 (1998)). On the basis of this model, the inventors have estimated the temperature regimes for the formation of small (10-30nm) or large (100-200nm) *IF* of WS_2, WSe_2, and WTe_2 materials, and experimental results have shown a good agreement with the predictions of the "synergy" model [Feldman, Y, Lyakhovitskaya, V, and Tenne, R., *J. Am. Chem. Soc.* **120,** 4176 (1998); Tenne, R., Homyonfer, M., and Feldman, Y, *Adv. in Metal and Semiconductor clusters,* Ed. M.A. Duncan, JAI Press Inc. **4**, 227 (1997)]. The general principles of the sulfidization of the respective oxides, of the growth model were successfully applied also to the growth of *IF* in other layered systems, like VS_2, In_2S_3, and SnS_2 [Tsirlina, T., Feldman, Y, Homyonfer, M., Sloan, J., Hutchison, J.L., and Tenne, R, *Fullerene Science & Technology* **6**, 157 (1998); Homyonfer, M., Alperson, B., Rosenberg, Yu., Sapir, L., Cohen; S.R., Hodes, G., and Tenne, R., *J. Am. Chem. Soc.* **119**, 2693 (1997)].

[0006]   It is necessary to point out here that the method of *IF* (including the nanotubes) formation is a "chemical" one: i.e., a chemical reaction is essential for the growth of these nanoparticles. Following this early work by the inventors of the present invention, a few reports on the synthesis of MoS_2 nano and microtubes by other "chemical" methods have appeared in the literature, recently [Remskar, M., Skraba, Z., Cleton, F., Sanjines, R, and Levy, F., *Surf. Rev. Lett.* **5,** 423 (1998); Remskar, M., Skraba, Z., Regula, M., Ballif, C., Sanjines, R., and Levy, F., *Adv. Mat* **10**, 246 (1998); Vollath, D., and Szabo, D.V, *Mater. Lett.* **35,** 236 (1998); Zelenski, M., and Dorhout, P.K., *J. Am. Chem. Soc.* **120**, 734 (1998)].

[0007]   It should be emphasized that the synthesis of carbon fullerenes using "physical" methods, implies curvature of very small atomic sheets followed by the annihilation of the dangling bonds of the peripheral atoms, a process, which is induced by a high rate of energy dissipation. It was shown recently that *IF*-MoS_2 could be obtained also by "physical" methods, such as e-beam irradiation (Jose-Yacaman, M., Lorez, H., Santiago, P., Galvan, D.H., Garzon, I.L., and Reyes, *A., Appl. Phys. Lett.* **69,** 8, 1065 (1996), or laser ablation of regular MoS_2 powder (Parilla, P.A., Dillon, A.C., Jones, K.M., Riker, G.,

Schulz, D.L., Ginley, D.S., and Heben, M.J., *Nature* **397,** 114 (1999), or by short electrical pulses from the tip of a scanning tunneling microscope through amorphous MoS_3 nanoparticles (Homyonfer, M., Mastai, Y, Hershfinkel, M., Volterra, V, Hutchison, J.L., and Tenne, R., *J. Am. Chem. Soc.* **118,** 33, 7804 (1996). IF-$NiCl_2$, including nanotubes were recently observed after heating of $NiCl_2$ at 960°C in a reducing atmosphere (Rosenfeld-Hacohen, Y, Grunbaum, E., Sloan, J., Hutchison, J.L., and Tenne, R., *Nature* **395**, 336 (1998). However, the IF yield in these cases is very modest and can not be compared with the large amounts of the pure IF-WS_2 (MoS_2) phase obtained by "chemical" methods.

[0008] The first SGR reactor for the synthesis of macroscopic quantities of IF-WS_2 was constructed in 1996 based on the principles of the above indicated reaction mechanism. To increase the amount-of the reactant (oxide) and expose its entire surface to the gas, a bundle of quartz tubes was placed inside the main quartz tube (40mm diameter) and the oxide powder was dispersed in them, very loosely. The reactor was introduced into a horizontal furnace and the powder was placed in a constant temperature region (~850°C). A stream of H_2/N_2 + H_2S gases passed through every tube filled with the powder. It created rather equivalent conditions for the reaction of the entire oxide powder during SGR. Typically, about 0.4 gram of IF-WS_2 could be obtained in a single batch (3 hr), with a conversion yield of almost 100%.

[0009] The precursor (oxide) powder and the reaction products were analyzed by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). The inventors recall that the size and shape of the precursor tungsten oxide nanoparticles predetermine the IF-WS_2 dimensions in the SGR synthesis. The starting material for the synthesis of IF-WS_2 was a WO_3 powder (>99% pure), with almost spherical particles having sizes smaller than ca. $0.2\mu m$. Oxide powder having a larger particle size was converted mainly into $2H$-WS_2 phase. Moreover, $2H$-WS_2 platelets were predominantly obtained if the packing of the powder was too compact. This fact required a very thorough control of the IF quality after every batch. WO97/44278 reports a method and an apparatus for preparing WS_2 fullerene-like molecules in which WO_3 particles are deposited on the bottom of a reactor and are dispersed by a flow of N_2+H_2 which blows from behind. The reduced particles react then with H_2S.

[0010] It was hypothesized before, that the tribological properties of the IF nanoparticles are closely related to their structure [(Rapoport, L., Bilik, Yu., Feldman, Y, Homyonfer, M., Cohen, S.R., and Tenne, R., *Nature* **387**, 791 (1997). See also, *Nature* **387**, 761 (1997); and Rapoport, L., Feldman, Y, Homyonfer, M., Cohen, H., Sloan, J., Hutchison, J.L., and Tenne, R., *Wear* **225**-229, 975 (1999)]. In general, spherical IF nanoparticles exhibited tribological properties superior to their $2H$ counterpart, while their performance rapidly deteriorated upon loss of spherical shape. Therefore, it is expected that the more spherical IF-WS_2 nanoparticles would perform very well

as solid lubricants. In addition, the larger IF should be a better lubricant in the case of the friction of two matting metal surfaces having higher surface roughness.

SUMMARY OF THE INVENTION

[0011] There is accordingly a need in the art to facilitate and optimize the solid-gas chemical reactions, which would increase the amount of available inorganic fullerene-like nanostructures.

[0012] The present invention thus provides a new reactor, which allows for a scale-up of IF- WS_2 production including nested fullerene-like structures and WS_2 nanotubes by more than two orders of magnitude. The falling-bed reactor, and especially fluidized-bed-designed reactors, pave the way for an almost ideal growth conditions for synthesizing IF from an oxide precursor. As a result, the produced IF nanoparticles have a more uniform spherical shape and can grow to a larger size (up to $0.5\mu m$). Likewise, the produced of nanotubes have a uniform size distribution. It is expected that the relatively spherical IF-WS_2 nanoparticles, which are produced by the falling or the fluidized bed reactor, will exhibit superior tribological properties, than reported before.

[0013] Thus, according to one aspect of the present invention, there is provided an apparatus for the production of inorganic fullerene-like (IF) nanoparticles and nanotubes, the apparatus comprising a chemical reactor, and is associated with a feeding set up and with a temperature control means for controlling the temperature along the reaction path inside the reactor so as to maintain the temperature to be substantially constant, the chemical reactor comprising:

    (i) a flow line for providing a continuous flow of a mixture of a reacting metal oxide powder and an inert flow assisting gas from the feeding setup into the reaction path, which extends along the reaction path;
    (ii) at least one inlet port for supplying reacting gases into the reaction path to flow therethrough along the reactionpath, an interaction between the reacting gases and said mixture resulting in the formation of the IF nanostructures and nanotubes during the flow of the interacting materials along the reaction path;
    (iii) at least one outlet port for trapping reacting gases; and
    (iv) at least one collector located at a the opposite end portion of the reactor for collecting the formed IF nanostructures or nanotubes.

The feeding set-up comprises a flexible portion by which it is connected to the flow line of the reactor. The feeding set-up comprises two flexibly inter-connected containers aligned along an axis of feeding the mixture, each container having a mesh at its bottom and being mounted on a vibration assembly, the lower one of the containers being connected to the flow line of the reactor. The reaction path may extend along a vertical axis of the reactor

and thus the at least one collector is located at the bottom of the reaction path. The inlet port for supplying the reacting gases which their flow is assisted by inert gas is located upstream of the reaction path. In a preferred embodiment this inlet for supplying the reacting gases is located downstream of the reaction path, and the flow of the reacting gases towards and through the reaction path being assisted by an inert gas. The temperature along the reaction path should be constant and may vary from about 750°C to about 850°C. The resulting nanoparticles may be IF- WS$_2$ nanoparticles or a combination of IF-WS$_2$ nanoparticles and WS$_2$ nanotubes.

[0014] According to yet another aspect of the invention there is provided a synthetic method of production of WS$_2$ fullerene-like nanoparticles and nanotubes said method comprising the steps of:

(i) providing a chemical reactor defining a reaction path with predetermined temperature conditions along the reaction path;
(ii) feeding into the chemical reactor a mixture of a reacting tungsten oxide powder and an inert gas with a predetermined feeding rate, and feeding reacting gases so as to provide a continuous flow of the mixture and the gases through the reaction path;
(iii) maintaining the predetermined temperature to be substantially constant, thereby providing a solid-gas reaction between the reacting gases and the tungsten oxide powder during the flow through the reaction path, resulting in the formation of WO$_{3-x}$ clusters coated by at least one layer of WS$_2$, and further exchange of oxides by sulfides in inner parts of the clusters, thereby causing formation of WS$_2$ nanostructures; and
(iv) collecting the formed WS$_2$ nanostructures.

[0015] The feeding rate of the reacting tungsten oxide powder is selected in accordance with the dimensions of the chemical reactor, thereby obtaining the WS$_2$ nanostructures in the form of nanoparticles, or a combination of nanoparticles and nanotubes. The feeding rate ranges is between about 3mg/min to about 120mg/min, the reacting gases being H$_2$ and H$_2$S, the concentration of the H$_2$ gas being from about 0.2 % (w/v) to about 7 % (w/v) and the concentration of the H$_2$S gas being from about 0.1 % (w/v) to about 6 % (w/v). By predetermining the appropriate feed rate and appropriate concentration, either IF- WS$_2$ nanoparticles may exclusively be obtained or a combination of WS$_2$ nanotubes and IF- WS$_2$ nanoparticles may be obtained. The resulting nanoparticles, each have a substantially perfect spherical shape with a size of up to 0.5μm. The resulting nanotubes which may be obtained each having a length of up to a few hundreds μm and a cross-sectional dimension of up to 200 nanometer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] In order to understand the invention and to see how it may be carried out in practice, a preferred embodiment will now be described, by way of non-limiting example only, with reference to the accompanying drawings, in which:

Fig. 1 is a two-stage vibro-electromagnet feeding set-up suitable for use in an apparatus according to the invention;
Figs. 2A and 2B illustrate, respectively, a schematic representation of a falling bed reactor including the set-up of Fig. 1, and the temperature profile along the vertical axis of the reactor;
Fig. 2C illustrates a typical TEM image of W$_5$O$_{14}$ whiskers produced in the reactor according to the invention and serving as precursors for the production of WS$_2$ nanotubes;
Figs. 3A and 3B illustrate, respectively a schematic representation of a fluidized bed reactor including the set-up of Fig. 1, and the temperature profile along the vertical axis thereof;
Figs. 4A and 4B illustrate a TEM image of the typical IF-WS$_2$ nanoparticles, and high magnification of two IF-WS$_2$ nanoparticles;
Fig. 5 is a SEM image of an ensemble of IF-WS$_2$ nanoparticles; and
Fig. 6 illustrates a typical TEM image of IF-WS$_2$ nanotubes.

DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

[0017] The present invention deals with a method for the optimized production of inorganic fullerene-like nanoparticles and nanotubes. The synthetic route is a solid-gas reaction and two reactors (falling bed reactor and fluidized bed reactor) are utilized for the production of either the nanoparticles or the nanotubes.

[0018] The chemical reaction that occurs in the reactors of the present invention leading to the formation of the nanoparticles and nanotubes is the following. The metal oxide, WO$_3$, nanoparticles as agglomerates are derived downwards from a feeding set-up with the aid of a N$_2$ stream. The descending WO$_3$ agglomerates interact with a mixture of H$_2$ and H$_2$S gases. The H$_2$, being lighter, diffuses faster than the H$_2$S and interacts initially with the descending WO$_3$ partially reducing the agglomerates. Concurrently, the WO$_3$ interacts with the H$_2$S stream thus the overall interaction of the WO$_3$ agglomerates with the H$_2$ and H$_2$S gases results in the formation of a completely closed monomolecular WS$_2$ layer around each nanoparticles. The formation of the first closed atomic layer of WS$_2$ on the surface of the metal oxide nanoparticle occurs during the short time interval between the beginning of the descending of the WO$_3$ agglomerates onto the top of the reactor (which process is N$_2$ assisted) and until

the so-produced WS_2 coated WO_{3-x} nanoparticles land on the filter (in the case of the falling bed reactor). This primary step is essential for the success of the *IF* synthesis, since it passivates the nanoparticles surface and prohibits coalescence of the nanoparticles, once they land on the bottom of the reactor. In the case of a fluidized bed reactor, no agglomeration of the oxide clusters could occur, since the nanoparticles are fluidized in the gas atmosphere during the entire reaction time.

[0019] During the creation of a completely closed monomolecular WS_2 layer (several seconds), a rather fast reduction of the oxide core by hydrogen occurs together with a fast deintercalation of oxygen and formation of crystal shears, i.e. rows of edge sharing octahedra. In the next step a slow intercalation of sulfur and its diffusion to the growth front occurs, the WO_3 being thus converted into tungsten sulfide. The latter process may last 30-300min depending on the nanoparticle's size and the reaction temperature. In the case of nanoparticles smaller than 100nm, this later process may last 60-120 min. The use of relatively large oxide particles (about 0.5μm), in which sulfur intercalation is rather slow, necessitates an addition of an extra annealing step at 950°C (5 hr) at the end of the present process, in order to complete the conversion of the oxide core into tungsten sulfide.

[0020] Consequently, the size of the IF- WS_2 particle is determined by the size of the incipient WO_3 nanoparticle. Furthermore, the geometry of the resulting IF-WS_2 nanoparticles is determined by the geometry of the WO_3 particles undergoing the reduction, initial interaction with H_2S, and further diffusion of sulfur atoms replacing the oxygen atoms. It is important to note that each IF-WS_2 nanoparticle has a single growth front of the sulfide, and therefore each nanoparticle is a single crystallite.

[0021] It is thus apparent that the mechanism of formation of the WS_2 nanotubes is slightly different, since the initial geometry of the reacting WO_3 particle should already reflect its final structure. In the formation of the IF-WS_2 nanotubes, the initial WO_3 particles interact under the terms that exist in the reactor with the slight humidity present, which is produced *in-situ* by the reduction of the metal oxide nanoparticles with H_2 present, leading to the formation of $WO_{3-x}(H_2O)_y$ particles. These particles sublimize and condense to form W_5O_{14} nanoparticles which are in the form of whiskers (needles). These formed whiskers then undergo the partial reduction with H_2 gas and the further interaction with the H_2S gas to form a core of $W_{18}O_{49}$ covered completely with a first layer of sulfide (A. Rothschild, J. Sloan, and R. Tenne, J. Am. Chem. Soc. 122, 5169 (2000)). The next step is exactly as the one happening in the formation of IF-WS_2 nanoparticels, i.e. a slow diffusion-controlled reaction of converting the inner oxide into sulfide layers.

[0022] It should be understood that the growth mechanism of *IF-*WS_2 was elucidated in quite a detail manner [the above-mentioned articles: Feldman, Y, Frey, G.L., Homyonfer, M., Lyakhovitskaya, V., Margulis, L., Cohen, H., Hodes, G., Hutchison, J.L., and Tenne, R., J. Am.

Chem. Soc. **118**, 5362 (1996); Feldman, Y, Lyakhovit-skaya, V, and Tenne, R., J. Am. Chem. Soc. **120**, 4176 (1998)], and therefore should not be described here in details. It was found that, under certain conditions, the simultaneous reduction and sulfidization of oxide nanoparticles lead to *IF*-WS_2 formation.

[0023] However, it appears that, if some process parameters are changed and either of the above two processes prevails, no fullerene-like particles will be synthesized. In particular, a deviation of the hydrogen/sulfur concentration ratio from the specified value at any point of the reaction chamber will most likely lead to 2H-WS_2 platelets formation there. Therefore, it is very important, especially at the first instant of the reaction, that a homogeneous mixture of the three gases would engulf each oxide nanoparticle. The falling bed and fluidized reactors of the present invention are most suited and are optimized such as to ensure that all required conditions, are achieved and are maintained throughout the reaction.

[0024] Fig. 1 illustrates a feeding set-up **10** suitable for use in the apparatus of the present invention. The set-up **10** is a vibro-electromagnet set-up constructed for cofeeding the WO_3 powder into a quartz tube based reactor in two stages, in a predetermined rate. The set-up consists of two glass beakers **12** and **14** with a mesh at their bottom, **12a** and **14a,** respectively, which are placed one on top of the other. The upper beaker **12** provides a coarse portion of WO_3 powder to the lower beaker **14,** which then feeds the oxide powder into the reactor in fine steps. For that to occur, the bottom of the upper beaker **12** was joined to the entrance of the lower glass beaker **14** by a flexible rubber balloon **16**. A similar flexible balloon connects the bottom of the lower glass beaker **14** to the top entrance of the reactor (not shown here). The soft balloons **16** serve also to dump the mechanical vibrations between the two beakers, and between them and the reactor. Each glass beaker is mounted on an electromagnet **18a** and **18b** (constituting a vibrating assembly), which shakes the respective glass beaker in a fully controllable rate. As shown, nitrogen gas is flushed through the feeding glass beakers continuously from up side down and assists the lowering of the oxide powder.

[0025] The shaking of the two glass beakers lead to dropping of a weighted amount of the WO_3 powder through the meshes at the bottom of each beaker, **12a** and **14a**, respectively. The rate of shaking of the higher electromagnet is inferior to that of the lower one. However, since the higher beaker **12** has a larger mesh-size **12a** in its bottom, it can deliver, as a result of a single shake, a relatively large amount of material to the lower beaker **14**. The lower beaker, in its turn, is able to deliver a much smaller portion of material at each shake, due to the fine mesh size in its bottom **14a**. Typically, the rate of shaking of the upper beaker **12** is 1 pulse/min, while the rate of shaking of the lower beaker **14** is 15 pulse/min. However, while the upper beaker **12** may deliver 30mg per pulse, the lower beaker **14** may deliver only 2mg per pulse.

[0026] This vibro-electromagnet set-up **10** secures a continuous flux of even very small amount of metal oxide powder (from about 0.2 g/hr) to the reactor. The setup enables the metal oxide powder to go from the upper glass beaker **12** to the reactor without contacting the atmosphere. The feeding rate of the oxide powder is computer controlled and could be varied in the range from about 3 mg/min to about 120mg/min. Careful selection of the feeding parameters (mesh-size, vibration rate and amplitude, rate of gas flow, etc.), are mandatory in order to avoid the accumulation of the metal oxide powder in one of the stages and provide the reactor with a continuous yet small flux of metal oxide precursor.

[0027] Fig. 2A illustrates a falling bed apparatus **20,** according to the invention, for synthesizing the *IF* nanoparticles and nanotubes. The apparatus **20** is in the form of a quartz tube reactor (40mm diameter), which is placed inside a vertical furnace **21** (constituting a temperature control means). The furnace is designed and operated so as to define two heating zones for the purposes of the present invention. It should, however, be noted, that the present invention is not limited to the use of two heating zones, and this particular furnace is constructed with two heating zones in order to maintain the temperature inside the reactor constant. Any setting that would keep the temperature constant is possible.

[0028] Placed at the top of the apparatus (reactor) **20** is the vibro- electromagnet **10** set-up for cofeeding the WO_3 powder with the aid of N_2 into the reactor. The reactor **20** is formed with an annular inlet opening **22** for supplying a mixture of reacting gases, H_2S and H_2, the flow of which towards the inside of the reactor is driven by N_2. A tube (flow line) **23** connects the feeding set-up **10** to the inside of the reactor **20,** thereby providing a precursor of the metal oxide powder to the reactor. A filter (collector) **24** is mounted at the bottom portion of the reactor **20** for collecting the end product. The escaping gases are trapped through an outlet opening **26**.

[0029] The cofeeder delivers the WO_3 powder from the top into the vertical reactor **20**, and the mixture (WO_3 powder and N_2) flows in the same direction. This technique enables to minimize the possibility of any physical contact between the oxide nanoparticles at the early stages of the reaction. Moreover, this method rendered the synthetic process quasi-continuous. At the top of the reactor, the dropping metal oxide powder intersects with a flow of H_2S and N_2/H_2 gasses entering the reactor at the opening **22.** The interaction leads to the formation of the nanoparticles of WO_{3-x} covered with a first WS_2 layer, which are collected on the filter **24.** In order to obtain *IF* -WS_2 nanoparticles the feed of WO_3 should be in the range of from about 3mg/min to about 40mg/min. The total stream rate of the gasses is in the range of about 150cc/min. The concentration of the H_2S and H_2 stream is in the range of from about 3 % to about 7 % (v/w). The temperature should be kept constant throughout the entire reaction path (variation of $\pm$ 5°C). The temperature in the reaction path may however be in the range from about 750°C to about 850°C depending on the particle size of the metal oxide (WO_3) precursor. The pressure in the reactor is in the range of about 1.1 atm. The pressure is determined by the traps located next to the exit **26.**

[0030] The temperature profile along the reaction path (z-axis) inside the reactor is illustrated in Fig. 2B. It is evident that the temperature during the various process stages is maintained constant. It should be noted that precise control of the reaction parameters is indispensable for the complete conversion of the tungsten oxide powder into *IF* tungsten sulfide nanoparticles. Radial and axial deviations of the temperature along the reaction path do not exceed ± 5 degrees. Such variations in temperature are allowable by *IF-* WS_2 synthesis.

[0031] Under the above experimental parameters, WS_2 nanotubes be obtained as a mixture together with *IF-* WS2 nanoparticles in case the feed of WO_3 is increased by 3 to 5, i.e. in the range of from about 40mg/min to about 120mg/min. On the other hand, such a mixture of nanotubes together with *IF*-WS_2 nanoparticles may be obtained with a feed rate in the range of from about 3mg/min to about 40mg/min. However, in such a case the other parameters have to be altered. Thus, in order to obtain WS_2 nanotubes, the concentration of the H_2 stream should be in the range of from about 0.2 % to about 4 % (v/w). The H_2S concentration should be in the range of from about 0.2 % to about 4 %. The change in the experimental parameters leading to the formation of nanotubes affects the clusters undergoing the reduction and the interaction with H_2S.

[0032] As a result of this effect, W_5O_{14} nanoparticles (or other WO_{3-x} phases) are created being in the form of whiskers. Fig. 2C shows a TEM image of the W_5O_{14} whiskers which serve as the precursor powder, formed *in-situ,* for obtaining the nanotubes. As indicated above, although not specifically shown, these formed whiskers then undergo the partial reduction with H_2 gas and an interaction with the H_2S gas to form a core of $W_{18}O_{49}$ covered completely with a first layer of sulfide.

[0033] Thus, the resulting powder, nanoparticles or nanotubes are collected on the filter **24,** which is placed at the end of the constant temperature path (830°C according to the present experimental parameters), and further react with H_2S in order to obtain fully sulfidated nanostructures.

[0034] Obviously, since the process is quasi-continuous, the amount of *IF* increases with time during the synthesis. However, when the amount of *IF* per batch exceeds 15 grams, the quality of *IF* nanoparticles deteriorates. It was found by the inventors that, if the thickness of the powder on the filter **24** is too large, rather big clotted lumps start to appear, and, as a result, 2H-WS_2 platelets are formed. This can be overcome by the use of a fluidized bed reactor based apparatus.

[0035] Fig. 3A illustrates such a fluidized bed apparatus **30** for the *IF* synthesis utilizing the feeding set-up **10** for feeding the oxide powder towards the inside of the apparatus. The apparatus **30** is a quartz tube reactor

installed in a furnace **31.** Here, three heating zones are used aligned along the vertical axis of the reactor. The use of three heating zones is by no means limiting, and, generally, any setting that would keep the temperature constant along the reaction path is possible. A long quartz tube **32** and a middle tube **36** are provided. The tube **32** connects the feeding set-up **10** to the interior of the reactor inside the tube **36,** and extends through the upper heating zone and down to the reaction zone inside the tube **36.** As shown, the tube **36** is conical-shaped having its wide part **38.** A stream of reacting gases, H_2 and H_2S, is provided through an inlet opening **34** formed at the bottom of the reactor. Further provide in the reactor **30** is a filter **40** placed inside the tube **36** at the end of the constant temperature region (830°C according to the present experimental conditions), and an additional filter **42** outside the tube 36, both for collecting a small part of powder propagating towards the filters. Escaping gases are discharged through an outlet opening **44.**

[0036] In the present example, the quartz tube has a length of 60cm and a diameter of 50mm. The flow of the oxide powder WO_3, assisted by nitrogen gas flow (about 60cc/min), passes through the 12mm diameter and quartz tube **32,** which may be from about 15cm to about 30cm long (30cm according to the present reactor) within the reactor. The stream of the reacting gases, H_2 and H_2S enters the reactor from the bottom opening **34** and flows upwards in a conical-shaped inner quartz tube through the middle part **36** having a diameter of about 22mm towards its wider portion **38.** The rate of the stream of the gas H_2S and N_2/H_2 is from about 100cc/min to about 200cc/min. Therefore, the linear gas flow rate in the wide part **38** of the tube is approximately from about 10cm/min to about 30cm/min, which is about ten times slower than that in the narrow part of the tube **36.** The flow of the mixture of N_2 and the oxide powder WO_3 leaps out the tube **32,** and interfuses with the flow of H_2S and N_2/H_2 gases in the wide part **38** of the conical-shaped tube. The reduction and sulfidization of the WO_3 particles starts as a result of the interfusion. The interfusion, based on the rates of the two opposite flows, may take place only in the wide section **38** or may begin in the narrow quartz tube **32.** The former option occurs when the diffusion of the H_2 into the tube **32** is hindered by the fast nitrogen stream (100cm/min) mixed with the WO_3 powder, and leads to the formation of IF- WS_2 nanoparticles. The latter case occurs when there occurs some diffusion of H_2 into the tube **32** and leads to the formation of a mixture containing also nanotubes. The resulting powder falls slowly down through the wide part **38** of the tube against the upwardly directed gas stream, until the falling powder is lowered to the narrow part of the tube **36.** High linear rate of the $N_2/H_2/H_2S$ stream in the narrow part of the tube **36** offers fluidized bed conditions for the falling powder. The filter **40** placed at the end of the constant temperature region at 830°C collects a small part of the powder that dropped on the filter. A very small part of the powder may be swept by the main stream and may be

collected on the additional filter **42** placed outside the tube (i.e., outside the reaction zone) at the end of the constant temperature region (which under the present conditions is at 830°C) on the way of the gases exit. However, most of the powder is fluidized in the space above the filter **40** in the narrow part of the tube **36,** and stay in the fluidized bed region. It should be understood that, once the gas flow from the bottom of the reactor is terminated, the powder fluidized above the filter also falls onto the filter to be thereby collected.

[0037] Fig. 3B illustrates the temperature profile along the reaction path (z-axis) inside the reactor **30,** showing that the temperature during the various process stages is maintained constant.

[0038] In this way, more than about 100 grams of closed and hollow IF-WS_2 nanostructures could be synthesized in one batch (ca. 20hr). Thus, the fluidized bed reactor **30** may serve as a prototype for the industrial production of $IF\,WS_2$.

[0039] Fig. 4A show TEM images of IF-WS_2 nanoparticles obtained by the prior art techniques (Fig. 4A(a)) and those obtained by the reactor **20** of the present invention (Fig. 4A(b-f)), wherein Fig. 4A(c,d,e) show the different projections of the same particle by tilting the sample (gride) at an angle of $(0° \pm 40°)$, and Fig. 4A(f) shows a rather large IF (about 400nm). Fig. 4B shows the particles of the prior art technique (Fig. 4B(a) and of the invented techniques (Fig. 4B(b)) of Fig. 4A in an enlarged scale.

[0040] As evident, the shape of the IF particle of the present invention is very close to a sphere. The electron diffraction pattern of the 400mn-IF particle of Fig. 4A(f), which is shown in the center of the picture, has also proved to be of a fullerene-like structure of the nanoparticle. The particles obtained by the present invention have more perfect spherical shape, than those obtained by the conventional synthetic tools. This stems from the fact that, according to the invention, the reaction takes place in the gas phase, where an isotropic environment for the reaction prevails. Consequently, much larger oxide nanoparticles could be converted into IF when they flow in the gas stream.

[0041] Fig. 5 illustrates the SEM image of the experimental results obtained with the falling bed reactor **20,** showing spherical relatively large IF-WS_2 nanoparticles. The technique of the present invention enables to obtain IF particles with the size up to $0.5\mu m$, compared to $0.2\mu m$-particles obtained with the prior art reactor. Additionally, according to the invention, pure IF phase (with no extra contaminants) is obtained in these processes. Therefore, expensive and time-consuming filtration or purification processes are avoided.

[0042] It should be understood that the above-described process of whiskers based nanotubes formation is relevant with respect to the reactor **30** as well. The resulting WS_2 nanotubes obtained by the two reactors **20** and **30** of the present invention have a maximum length of several hundreds μm and a cross-section of

200 nanometer. Fig. 6 illustrates the resulting nanotubes, showing a high resolution TEM image of the WS_2 nanotubes which are multilayer structure, the distance between each two adjacent layers being ca. 6.2 Å.

[0043]   It should be understood that the use of the vertical posture of the furnace allows addition of the oxide powder into the reactor during the reaction, continuously. The maximum production yield per batch is about 20 grams of a pure IF-WS_2 phase by the falling bed reactor and is more than about 100 grams of a pure IF-WS_2 phase by the fluidized bed reactor. It should also be understood that the fluidized bed concept lends itself for scale-up and to production of appreciably larger amounts of a pure IF-WS_2 phase.

[0044]   An analysis of the stability of the nanoprticles and nanotubes formed by the present invention reveals that spontaneous transformation of IF-WS_2 to 2H has not been observed in any case. One would assume that as the size of the IF particles increases, the particles become closer (i.e., less bound) to the 2H particles in their structure. For example, the spacing between the two WS_2 layers (c/2) in the IF structures is larger than for the 2H particles. This lattice expansion diminishes with increasing size of the IF nanoparticles. It would thus be expected that the larger are the IF nanoparticles, the less is the stability of the IF to the 2H transformation. Another possible mechanism for the destruction of the formed IF nanoparticles under harsh environmental conditions is possible oxidation, which seems more likely than a transformation into 2H platelets. On the other hand, the increase of the IF-WS_2 nanoparticle size results in the increase of their oxidation temperature due to the reduced strain in the lattice. Therefore, practically the stability of the larger IF to oxidation must be higher.

[0045]   As mentioned above, the tribological properties of the IF nanoparticles are closely related to their structure. In general, spherical IF nanoparticles exhibited tribological properties superior to their 2H counterpart, while their performance rapidly deteriorated upon loss of spherical shape. Therefore, the relatively spherical IF-WS_2 nanoparticles, which are produced by the falling (fluidized) bed reactor, perform very well as solid lubricants. In addition, the larger IF must be a better lubricant in the case of the friction of two matting metal surfaces having higher surface roughness. These hypotheses are substantiated by our recent tribological measurements. For example, it was found that addition of small amount of IF-WS_2 to a lubrication fluid leads to a significant improvement of the tribological properties as compared to regular WS_2 (MoS_2) powders in the same concentration and to a pure fluid lubricant.

[0046]   Although the invention has been described in conjunction with specific embodiments, it is evident that many alternatives and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, the invention is intended to embrace all of the alternatives and variations that fall within the scope of the appended claims.

Claims

1. An apparatus for the production of inorganic fullerene-like (IF) nanoparticles and nanotubes, from metal oxide and reacting gases, the apparatus comprising a chemical reactor, and is associated with a feeding set up and with a temperature control means for controlling the temperature along the reaction path inside the reactor so as to maintain the temperature to be substantially constant, the chemical reactor comprising:

    (i) a flow line for providing a continuous flow of a mixture of a reacting metal oxide powder and an inert flow assisting gas from the feeding setup into the reaction path, which extends along the reaction path;
    (ii) at least one inlet port for supplying the reacting gases into the reaction path to flow through said inlet port and along the reaction path, an interaction between the reacting gases and said mixture resulting in the formation of the IF nanostructures and nanotubes during the flow of the interacting materials along the reaction path;
    (iii) at least one outlet port for trapping reacting gases; and
    (iv) at least one collector located at the opposite end portion of the reactor for collecting the formed IF-nanostructures or nanotubes.

2. The apparatus according to claim 1, wherein the feeding set-up comprises a flexible portion thereof, by which it is to be connected to the flow line of the reactor.

3. The apparatus according to claim 1, wherein the feeding set-up comprises two flexibly inter-connected containers aligned along an axis of feeding the mixture, each container having a mesh at its bottom and being mounted on a vibration assembly, the lower one of the containers being connected to the flow line of the reactor.

4. The apparatus according to claim 1, wherein the reaction path extends along a vertical axis of the reactor and the at least one collector is located at the bottom of the reaction path.

5. The apparatus according to claim 1, wherein the at least one inlet port for supplying the reacting gases is located upstream of the reaction path, said flow of the reacting gases towards and through the reaction path being assisted by an inert gas.

6. The apparatus according to claim 1, wherein the at least one inlet port for supplying the reacting gases is located downstream of the reaction path, said flow of the reacting gases towards and through the reac-

tion path being assisted by an inert gas.

7. The apparatus according to claim 1, wherein said metal oxide powder is WO_3.

8. The apparatus according to claim 7, wherein said *IF* nanostructures contain hollow cage WS_2 nanoparticles with fullerene-like structure.

9. The apparatus according to claim 7, wherein said *IF* nanostructures contain a combination of WS_2 nanoparticles and nanotubes.

10. The apparatus according to claim 7, wherein the temperature within the reaction path is from about 750°C to about 850°C.

11. The apparatus according to claim 8, wherein said nanoparticles have a size of up to 0.5μm.

12. The apparatus according to claim 9, wherein the WS_2 nanotubes have a length of up to a few hundreds μm and a cross-section of up to 200 nanometer.

13. The apparatus according to claim 1, wherein said chemical reactor is a quartz tube.

14. The apparatus according to claim 1, wherein said metal oxide powder is WO_3, said chemical reactor is a quartz tube, and further comprises a lower substantially conical-shape tube extending along a vertical axis between the bottom portion of the reactor and said flow line, such that a distal end of the flow line is located inside an upper wide portion of the lower tube.

15. A synthetic method of production of WS_2 fullerene-like nanoparticles and nanotubes from tungsten oxide and reacting gases, said method comprising the steps of:

(i) providing a chemical reactor defining a reaction path with predetermined temperature conditions along the reaction path;
(ii) feeding into the chemical reactor a mixture of a reacting tungsten oxide powder and an inert gas with a predetermined feeding rate, and feeding the reacting gases so as to provide a continuous flow of the mixture and the gases through the reaction path;
(iii) maintaining the predetermined temperature to be substantially constant, thereby providing a solid-gas reaction between the reacting gases and the tungsten oxide powder during the flow through and along the reaction path, resulting in the formation of WO_{3-x} clusters coated by at least one layer of WS_2, and further exchange of

oxides by sulfides in inner parts of the clusters, thereby causing formation of WS_2 nanostructures; and
(iv) collecting the formed WS_2 nanostructures.

16. The method according to claim 15, wherein the feeding rate of the reacting tungsten oxide powder is selected in accordance with the dimensions of the chemical reactor, thereby obtaining the WS_2 nanostructures in the form of *IF*-nanoparticles, or a combination of *IF*-nanoparticles and nanotubes.

17. The method according to claim 16, wherein the feeding rate ranges between about 3mg/min to about 120mg/min, the reacting gases being H_2 and H_2S, the concentration of the H_2 gas being from about 0.2 % (w/v) to about 7 % (w/v) and the concentration of the H_2S gas being from about 0.1 % (w/v) to about 6 % (w/v).

18. The method according to claim 17, wherein the formed nanostructures contain the combination of nanoparticles and nanotubes.

19. The method according to claim 16, wherein the feeding rate ranges between about 3mg/min to about 40mg/min, the reacting gases being H_2 and H_2S with the concentration of the H_2 and H_2S gases ranging from about 4 % to about 6 % (w/v).

20. The method according to claim 19, wherein the formed *IF-WS$_2$* nanostructures contain the nanoparticles, each having a substantially perfect spherical shape and having a size up to 0.5μm.

21. The method according to claim 16, wherein the feeding rate ranges between about 40mg/min and about 120mg/min, the reacting gases being H_2 and H_2S with the concentration of the H_2 and H_2S gases from about 4 % to about 6 % (w/v).

22. The method according to claim 21, wherein the formed WS_2 nanostructures contain the combination of *IF*-nanoparticles and nanotubes, the nanotubes each having a length of up to a few hundreds μm and a cross-sectional dimension of up to 200 nanometer.

23. The method according to claim 16, wherein the feeding rate ranges between about 3mg/min to about 40mg/min, the reacting gases being H_2 and H_2S with the concentration of the H_2 gas from about 0.2 % to about 4 % and the concentration of the H_2S gas from about 0.2 % to about 4 % (w/v).

24. The method according to claim 23, wherein the formed WS_2 nanostructures contain the combination of nanoparticles and nanotubes, the nanotubes hav-

ing a length of up to several hundred μm and a cross-sectional dimension of up to 200 nanometer.

Patentansprüche

1. Vorrichtung zur Herstellung von anorganischen ful-lerenartigen (IF-) Nanopartikeln und Nanoröhren aus Metalloxid und Reaktionsgasen, wobei die Vor-richtung einen Chemiereaktor aufweist und einer Einbringeinrichtung und einer Temperatursteuerein-richtung zugeordnet ist, zum Steuern einer Tempe-ratur entlang des Reaktionsweges im Innern des Re-aktors, um die Temperatur im wesentlichen konstant zu halten, wobei der Chemiereaktor aufweist:

   (i) eine Strömungsleitung zur Bereitstellung ei-ner kontinuierlichen Strömung eines Gemischs aus einem Metalloxid-Reaktionspulver und ei-nem strömungsunterstützenden Inertgas aus der Einbringeinrichtung in den Reaktionsweg, die sich entlang des Reaktionsweges erstreckt;
   (ii) mindestens eine Einlaßöffnung zum Einlei-ten der Reaktionsgase in den Reaktionsweg, so daß diese durch die Einlaßöffnung und entlang des Reaktionsweges strömen, wobei ein Zu-sammenwirken zwischen den Reaktionsgasen und dem Gemisch zur Bildung der IF-Nano-strukturen und -Nanoröhren während des Strö-mens der zusammenwirkenden Materialien ent-lang des Reaktionsweges führt;
   (iii) mindestens eine Auslaßöffnung zum Auffan-gen von Reaktionsgasen; und
   (iv) mindestens einen Kollektor, der sich am ent-gegengesetzten Endabschnitt des Reaktors be-findet, zum Sammeln der gebildeten IF-Nano-strukturen oder -Nanoröhren.

2. Vorrichtung nach Anspruch 1, wobei die Einbringein-richtung einen flexiblen Abschnitt aufweist, durch den sie mit der Strömungsleitung des Reaktors zu verbinden ist.

3. Vorrichtung nach Anspruch 1, wobei die Einbringein-richtung zwei flexibel miteinander verbundene Be-hälter aufweist, die entlang einer Gemischeinbring-achse ausgerichtet sind, jeder Behälter ein Sieb an seinem Boden hat und auf einer Vibrationsanord-nung angeordnet ist und der untere der Behälter mit der Strömungsleitung des Reaktors verbunden ist.

4. Vorrichtung nach Anspruch 1, wobei sich der Reak-tionsweg entlang einer vertikalen Achse des Reak-tors erstreckt und sich der mindestens eine Kollektor am Boden des Reaktorwegs befindet.

5. Vorrichtung nach Anspruch 1, wobei sich die minde-stens eine Einlaßöffnung zum Einleiten des Reakti-

onsgases in Strömungsrichtung vor dem Reaktions-weg befindet und die Strömung der Reaktionsgase zum und durch den Reaktionsweg durch ein Inertgas unterstützt wird.

6. Vorrichtung nach Anspruch 1, wobei sich minde-stens eine Einlaßöffnung zum Einleiten der Reakti-onsgase in Strömungsrichtung hinter dem Reakti-onsweg befindet und die Strömung der Reaktions-gase zum und durch den Reaktionsweg durch ein Inertgas unterstützt wird.

7. Vorrichtung nach Anspruch 1, wobei das Metalloxid-pulver WO_3 ist.

8. Vorrichtung nach Anspruch 7, wobei die IF-Nano-strukturen Hohlmantel-WS_2-Nanopartikel mit fulle-renartiger Struktur enthalten.

9. Vorrichtung nach Anspruch 7, wobei die IF-Nano-strukturen eine Kombination aus WS_2-Nanoparti-keln und -Nanoröhren enthalten.

10. Vorrichtung nach Anspruch 7, wobei die Temperatur innerhalb des Reaktionsweges von etwa 750°C bis etwa 850°C beträgt.

11. Vorrichtung nach Anspruch 8, wobei die Nanoparti-kel eine Größe von bis zu 0,5 μm haben.

12. Vorrichtung nach Anspruch 9, wobei die WS_2-Nano-röhren eine Länge von bis zu wenigen hundert μm und einen Querschnitt von bis zu 200 nm haben.

13. Vorrichtung nach Anspruch 1, wobei der Chemiere-aktor eine Quarzröhre ist.

14. Vorrichtung nach Anspruch 1, wobei das Metalloxid-pulver WO_3 ist, der Chemiereaktor eine Quarzröhre ist und ferner eine untere im wesentlichen konische Röhre aufweist, die sich entlang einer vertikalen Achse zwischen dem Bodenabschnitt des Reaktors und der Strömungsleitung erstreckt, so daß sich ein distales Ende der Strömungsleitung im Innern eines oberen breiten Abschnitts der unteren Röhre befin-det.

15. Syntheseverfahren zur Herstellung von fullerenarti-gen WS_2-Nanopartikeln und -Nanoröhren aus Wolf-ramoxid und Reaktionsgasen, wobei das Verfahren die Schritte aufweist:

   (i) Bereitstellen eines Chemiereaktors, der ei-nen Reaktionsweg mit vorbestimmten Tempe-raturbedingungen entlang des Reaktionsweges definiert;
   (ii) Einbringen eines Gemischs aus einem Wolf-ramoxid-Reaktionspulver und einem Inertgas

mit einer vorbestimmten Einbringrate in den Chemiereaktor und Einbringen der Reaktionsgase, um eine kontinuierliche Strömung des Gemischs und der Gase durch den Reaktorweg zu ermöglichen;

(iii) Halten der vorbestimmten Temperatur, so daß diese im wesentlichen konstant ist, wodurch eine Feststoff-Gas-Reaktion zwischen den Reaktionsgasen und dem Wolframoxidpulver während des Strömens durch und entlang des Reaktionsweges erfolgt, was zur Bildung von mit mindestens einer WS_2-Schicht überzogenen WO_{3-x}-Clustern und zu weiterem Austausch von Oxiden durch Sulfide in inneren Teilen der Cluster führt, wodurch die Bildung von WS_2-Nanostrukturen bewirkt wird; und

(iv) Sammeln der gebildeten WS_2-Nanostrukturen.

16. Verfahren nach Anspruch 15, wobei die Einbringrate des Wolframoxid-Reaktionspulvers entsprechend den Abmessungen des Chemiereaktors gewählt wird, wodurch die WS_2-Nanostrukturen in Form von IF-Nanopartikeln oder einer Kombination aus IF-Nanopartikeln und -Nanoröhren gewonnen werden.

17. Verfahren nach Anspruch 16, wobei die Einbringrate von etwa 3 mg/min bis etwa 120 mg/min reicht, die Reaktionsgase H_2 und H_2S sind, wobei die Konzentration des H_2-Gases von etwa 0,2 Gew./Vol.-% bis etwa 7 Gew./Vol.-% beträgt und die Konzentration des H_2S-Gases etwa 0,1 Gew./Vol.-% bis etwa 6 Gew./Vol.-% beträgt.

18. Verfahren nach Anspruch 17, wobei die gebildeten Nanostrukturen die Kombination aus Nanopartikeln und Nanoröhren enthalten.

19. Verfahren nach Anspruch 16, wobei die Einbringrate von etwa 3 mg/min bis etwa 40 mg/min reicht, die Reaktionsgase H_2 und H_2S sind, wobei die Konzentration der H_2-und H_2S-Gase von etwa 4 Gew./Vol.-% bis etwa 6 Gew./Vol.-% reicht.

20. Verfahren nach Anspruch 19, wobei die gebildeten IF-WS_2-Nanostrukturen die Nanopartikel enthalten, die jeweils eine im wesentlichen ideale Kugelform und eine Größe bis zu 0,5 μm haben.

21. Verfahren nach Anspruch 16, wobei die Einbringrate zwischen etwa 40 mg/min und etwa 120 mg/min liegt, die Reaktionsgase H_2 und H_2S sind und die Konzentration der H_2- und H_2S-Gase von etwa 4 Gew./Vol.-% bis etwa 6 Gew./Vol.-% beträgt.

22. Verfahren nach Anspruch 21, wobei die gebildeten WS_2-Nanostrukturen die Kombination aus IF-Nanopartikeln und -Nanoröhren enthalten und die Nano-

röhren jeweils eine Länge von bis zu wenigen hundert μm und eine Querschnittsabmessung von bis zu 200 nm haben.

23. Verfahren nach Anspruch 16, wobei die Einbringrate von etwa 3 mg/min bis etwa 40 mg/min reicht, die Reaktionsgase H_2 und H_2S sind, wobei die Konzentration des H_2-Gases von etwa 0,2 %bis etwa 4 % und die Konzentration des H_2S-Gases von etwa 0,2 Gew./Vol.-% bis etwa 4 Gew./Vol.-% reicht.

24. Verfahren nach Anspruch 23, wobei die gebildeten WS_2-Nanostrukturen die Kombination aus Nanopartikeln und Nanoröhren enthalten und die Nanoröhren eine Länge von bis zu mehreren hundert μm und eine Querschnittsabmessung von bis zu 200 nm haben.

Revendications

1. Appareil destiné à la production de nanoparticules et nanotubes inorganiques de type fullerène (IF), à partir d'oxyde de métal et de gaz de réaction, l'appareil comprenant un réacteur chimique, et est associé à une installation d'alimentation et un moyen de régulation de température pour réguler la température le long du chemin de réaction à l'intérieur du réacteur de sorte à maintenir la température sensiblement constante, le réacteur chimique comprenant :

(i) une conduite d'écoulement pour fournir un écoulement continu d'un mélange d'une poudre d'oxyde de métal de réaction et d'un gaz inerte facilitant l'écoulement à partir de l'installation d'alimentation dans le chemin de réaction, qui s'étend le long du chemin de réaction ;
(ii) au moins un orifice d'entrée pour fournir les gaz de réaction dans le chemin de réaction pour s'écouler à travers ledit orifice d'entrée et le long du chemin de réaction, une interaction entre les gaz de réaction et ledit mélange entraînant la formation des nanostructures et nanotubes IF pendant l'écoulement des matériaux d'interaction le long du chemin de réaction ;
(iii) au moins un orifice de sortie pour piéger les gaz de réaction ; et
(iv) au moins un collecteur situé au niveau de la portion d'extrémité opposée du réacteur pour collecter les nanostructures ou nanotubes IF formés.

2. Appareil selon la revendication 1, dans lequel l'installation d'alimentation comprend une portion flexible de celle-ci, par laquelle elle doit être reliée à la conduite d'écoulement du réacteur.

3. Appareil selon la revendication 1, dans lequel l'installation d'alimentation comprend deux conteneurs interconnectés de manière flexible alignés le long d'un axe d'alimentation du mélange, chaque conteneur ayant un tamis au niveau de son fond et étant monté sur un ensemble de vibration, le plus bas des conteneurs étant relié à la conduite d'écoulement du réacteur.

4. Appareil selon la revendication 1, dans lequel le chemin de réaction s'étend le long d'un axe vertical du réacteur et le au moins un collecteur est situé au fond du chemin de réaction.

5. Appareil selon la revendication 1, dans lequel le au moins un orifice d'entrée pour fournir les gaz de réaction est situé en amont du chemin de réaction, ledit écoulement des gaz de réaction vers et à travers le chemin de réaction étant facilité par un gaz inerte.

6. Appareil selon la revendication 1, dans lequel le au moins un orifice d'entrée pour fournir les gaz de réaction est situé en aval du chemin de réaction, ledit écoulement des gaz de réaction vers et à travers le chemin de réaction étant facilité par un gaz inerte.

7. Appareil selon la revendication 1, dans lequel ladite poudre d'oxyde de métal est le WO_3.

8. Appareil selon la revendication 7, dans lequel lesdites nanostructures IF contiennent des nanoparticules de WS_2 à cage creuse avec une structure de type fullerène.

9. Appareil selon la revendication 7, dans lequel lesdites nanostructures IF contiennent une combinaison de nanoparticules et de nanotubes de WS_2.

10. Appareil selon la revendication 7, dans lequel la température au sein du chemin de réaction est d'environ 750 °C à environ 850 °C.

11. Appareil selon la revendication 8, dans lequel lesdites nanoparticules ont une taille allant jusqu'à 0,5 μm.

12. Appareil selon la revendication 9, dans lequel les nanotubes de WS_2 ont une longueur allant jusqu'à quelques centaines de μm et une section transversale allant jusqu'à 200 nanomètres.

13. Appareil selon la revendication 1, dans lequel ledit réacteur chimique est un tube de quartz.

14. Appareil selon la revendication 1, dans lequel ladite poudre d'oxyde de métal est le WO_3, ledit réacteur chimique est un tube de quartz, et comprend en outre un tube inférieur sensiblement de forme conique

s'étendant le long d'un axe vertical entre la portion inférieure du réacteur et ladite conduite d'écoulement, de sorte qu'une extrémité distale de la conduite d'écoulement est située à l'intérieur d'une portion large supérieure du tube inférieur.

15. Procédé synthétique de production de nanoparticules et nanotubes de type fullerène de WS_2 à partir d'oxyde de tungstène et de gaz de réaction, ledit procédé comprenant les étapes consistant à :

(i) fournir un réacteur chimique définissant un chemin de réaction avec des conditions de température prédéterminées le long du chemin de réaction ;
(ii) alimenter le réacteur chimique en un mélange d'une poudre d'oxyde de tungstène de réaction et d'un gaz inerte avec une vitesse d'alimentation prédéterminée, et alimenter en gaz de réaction de sorte à fournir un écoulement continu du mélange et des gaz à travers le chemin de réaction ;
(iii) maintenir la température prédéterminée sensiblement constante, fournissant ainsi une réaction solide-gaz entre les gaz de réaction et la poudre d'oxyde de tungstène pendant l'écoulement à travers et le long du chemin de réaction, entraînant la formation d'agrégats de WO_{3-x} revêtus d'au moins une couche de WS_2, et l'échange ultérieur d'oxydes par sulfures dans les parties internes des agrégats, provoquant ainsi la formation de nanostructures de WS_2 ; et
(iv) collecter les nanostructures de WS_2 formées.

16. Procédé selon la revendication 15, dans lequel la vitesse d'alimentation de la poudre d'oxyde de tungstène de réaction est sélectionnée selon les dimensions du réacteur chimique, obtenant ainsi les nanostructures de WS_2 sous la forme de nanoparticules IF, ou une combinaison de nanoparticules et de nanotubes IF.

17. Procédé selon la revendication 16, dans lequel la vitesse d'alimentation est comprise entre environ 3 mg/min et environ 120 mg/min, les gaz de réaction étant H_2 et H_2S, la concentration du gaz H_2 étant d'environ 0,2 % (p/v) à environ 7 % (p/v) et la concentration du gaz H_2S étant d'environ 0,1 % (p/v) à environ 6 % (p/v).

18. Procédé selon la revendication 17, dans lequel les nanostructures formées contiennent la combinaison de nanoparticules et de nanotubes.

19. Procédé selon la revendication 16, dans lequel la vitesse d'alimentation est comprise entre environ 3 mg/min et environ 40 mg/min, les gaz de réaction

étant H_2 et H_2S avec la concentration des gaz H_2 et H_2S comprise entre environ 4 % et environ 6 % (p/v).

20. Procédé selon la revendication 19, dans lequel les nanostructures de WS_2-IF formées contiennent les nanoparticules, chacune ayant une forme sphérique sensiblement parfaite et ayant une taille allant jusqu'à 0,5 μm,

21. Procédé selon la revendication 16, dans lequel la vitesse d'alimentation est comprise entre environ 40 mg/min et environ 120 mg/min, les gaz de réaction étant H_2 et H_2S avec la concentration des gaz H_2 et H_2S d'environ 4 % à environ 6 % (p/v).

22. Procédé selon la revendication 21, dans lequel les nanostructures de WS_2 formées contiennent la combinaison de nanoparticules et de nanotubes IF, les nanotubes ayant chacun une longueur allant jusqu'à quelques centaines de μm et une dimension en coupe transversale allant jusqu'à 200 nanomètres.
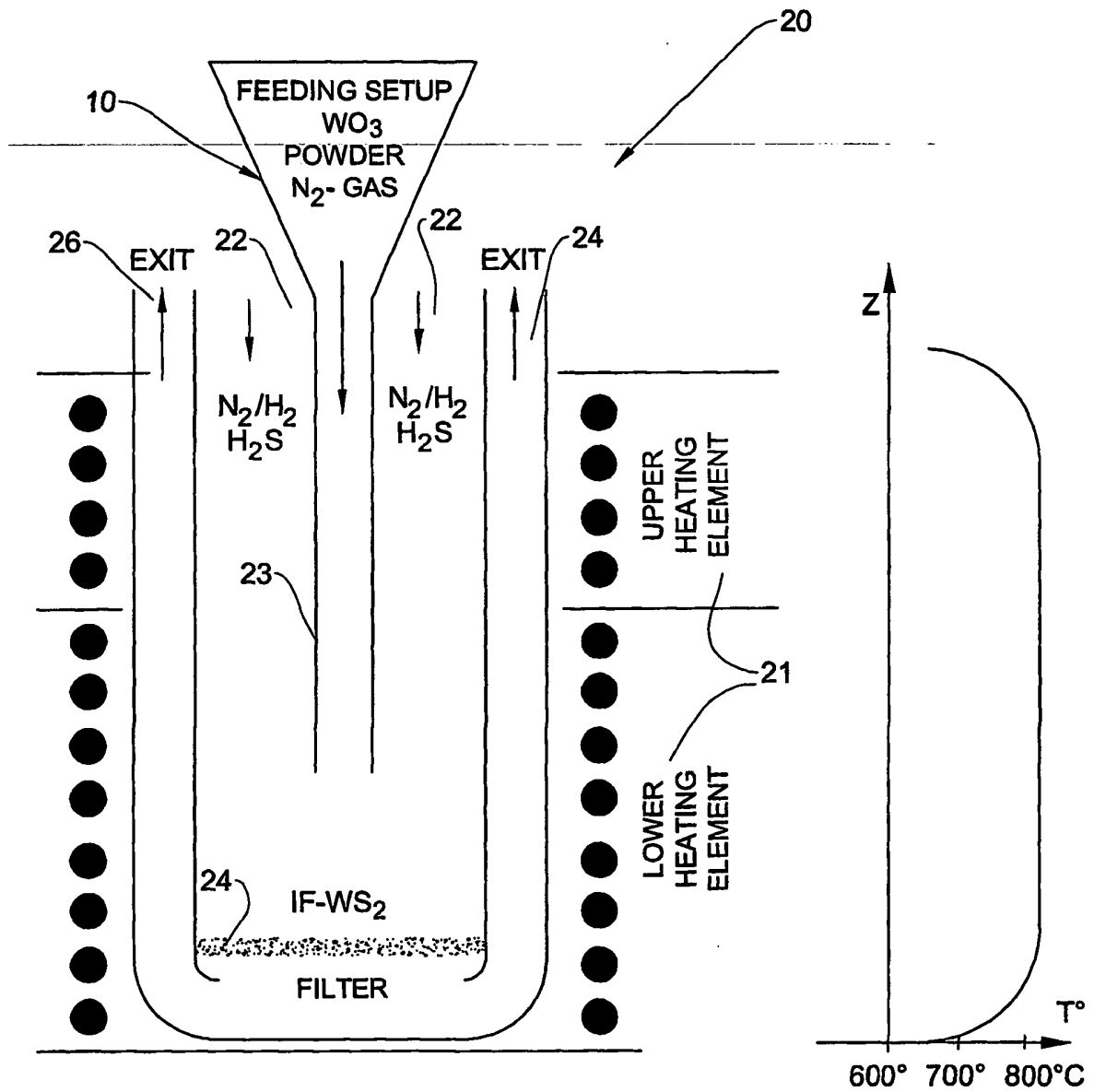
23. Procédé selon la revendication 16, dans lequel la vitesse d'alimentation est comprise entre environ 3 mg/min et environ 40 mg/min, les gaz de réaction étant H_2 et H_2S avec la concentration du gaz H_2 d'environ 0,2 % à environ 4 % et la concentration du gaz H_2S d'environ 0,2 % à environ 4 % (p/v).

24. Procédé selon la revendication 23, dans lequel les nanostructures de WS_2 formées contiennent la combinaison de nanoparticules et de nanotubes, les nanotubes ayant une longueur allant jusqu'à plusieurs centaines de μm et une dimension en coupe transversale allant jusqu'à 200 nanomètres.
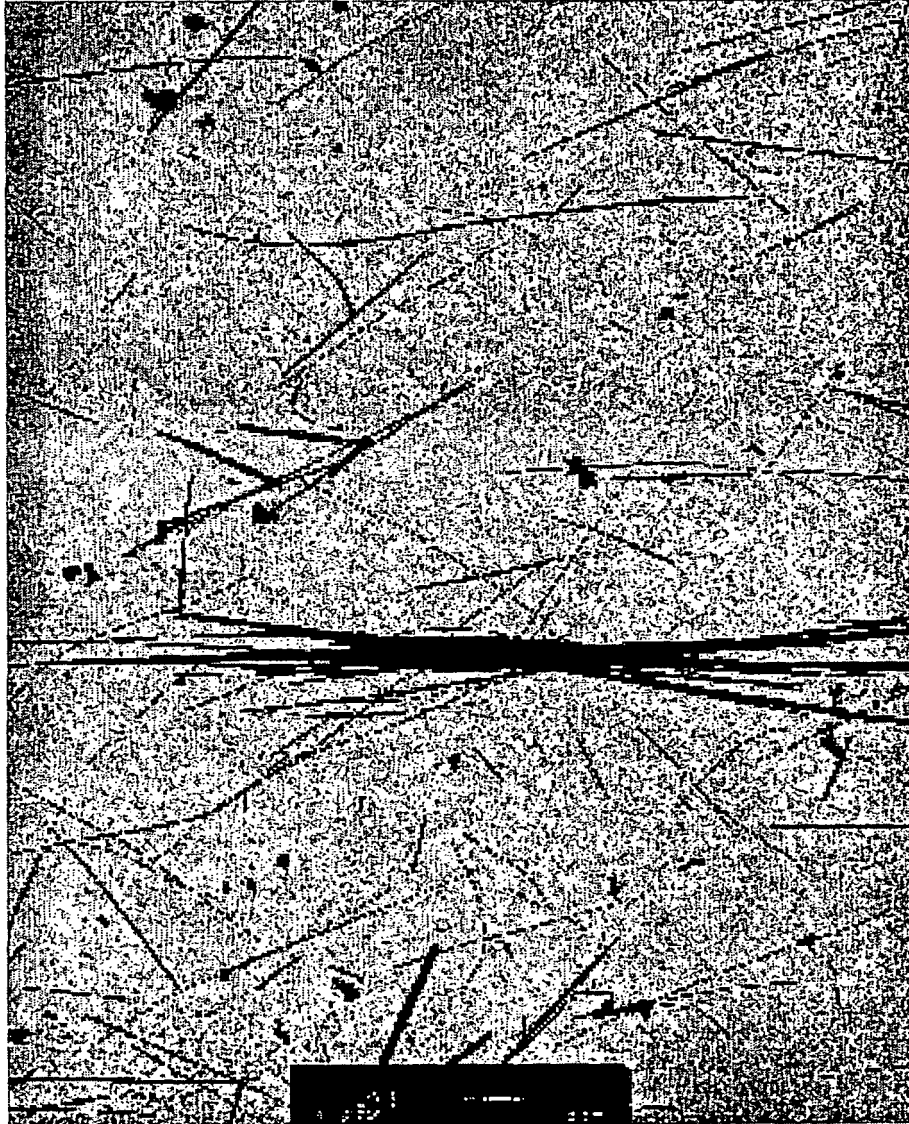
FEEDING SET-UP

FIG. 1

FIG. 2A

FIG. 2B

FIG. 2C

10

FEEDING SETUP
WO₃
POWDER
N - GAS

30

32

30cm

UPPER HEATING ELEMENT

38

12mm

31

60cm

50mm

CENTRAL HEATING ELEMENT

36

22mm

IF-WS₂

42

FILTER

LOWER HEATING ELEMENT
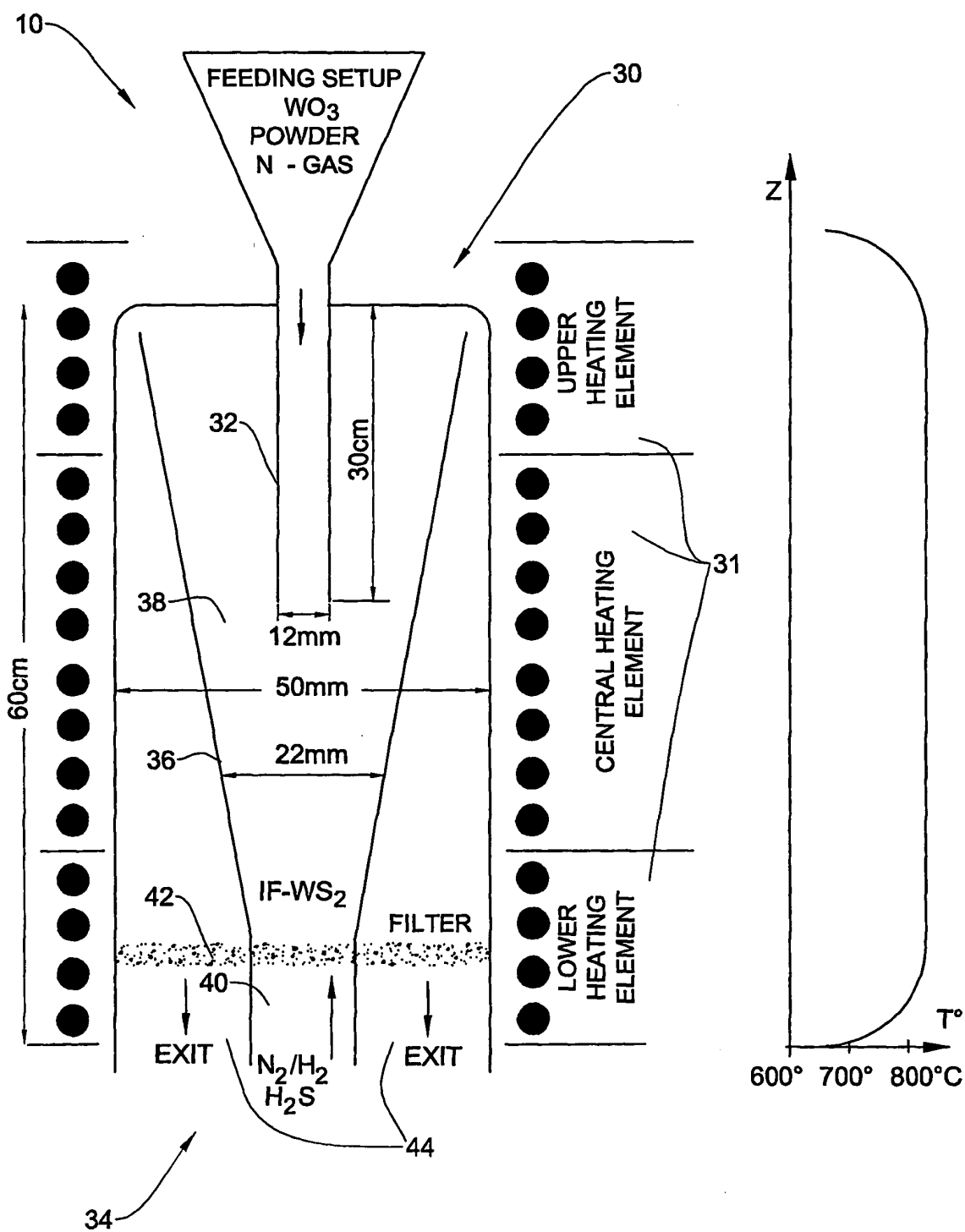
40

EXIT

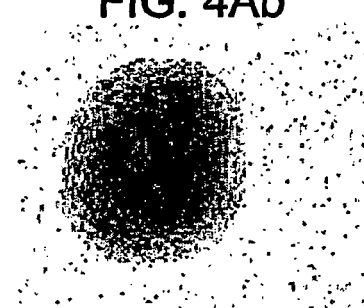N₂/H₂
H₂S

EXIT

44

34

FIG. 3A

Z

T°
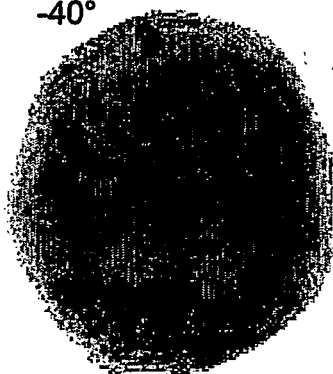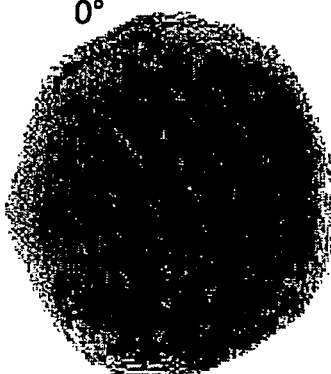600° 700° 800°C
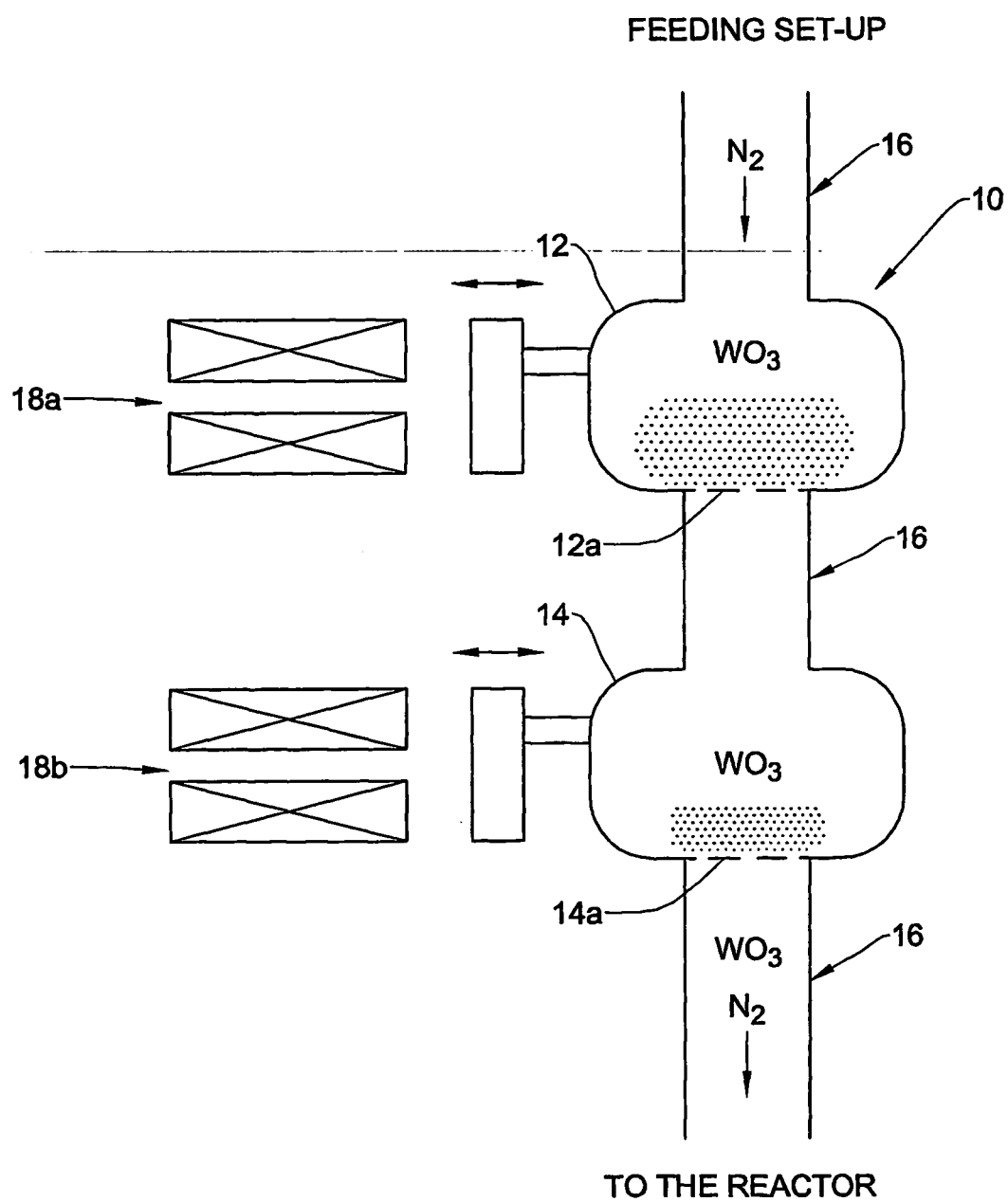
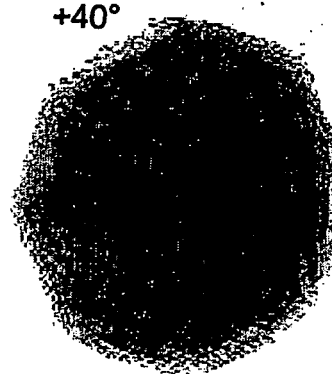**FIG. 3B**

FIG. 4Aa
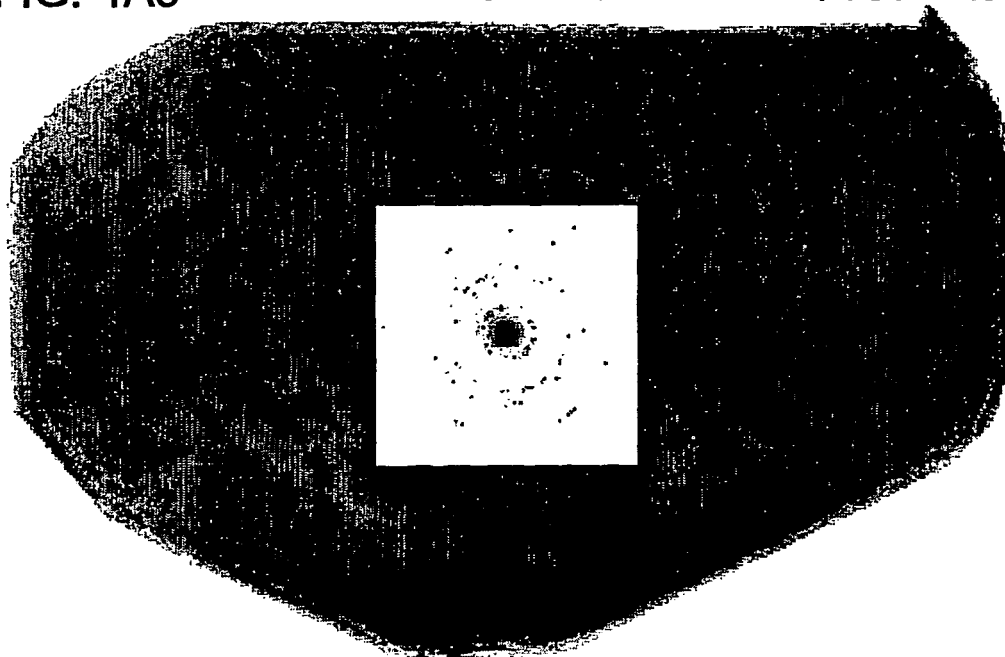
FIG. 4Ab
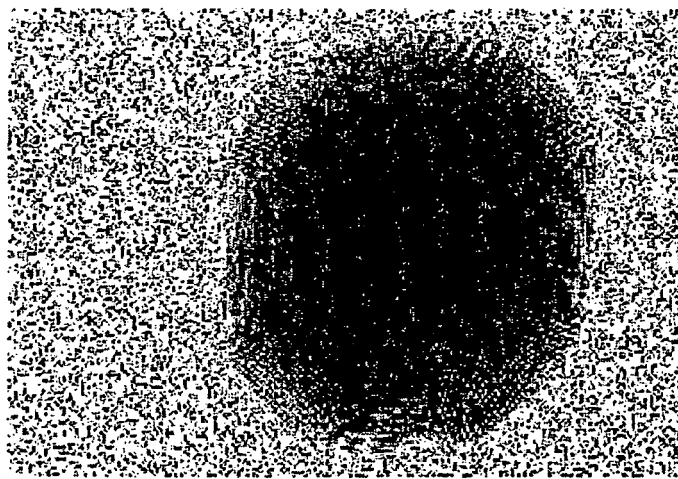
100nm

-40°   0°   +40°

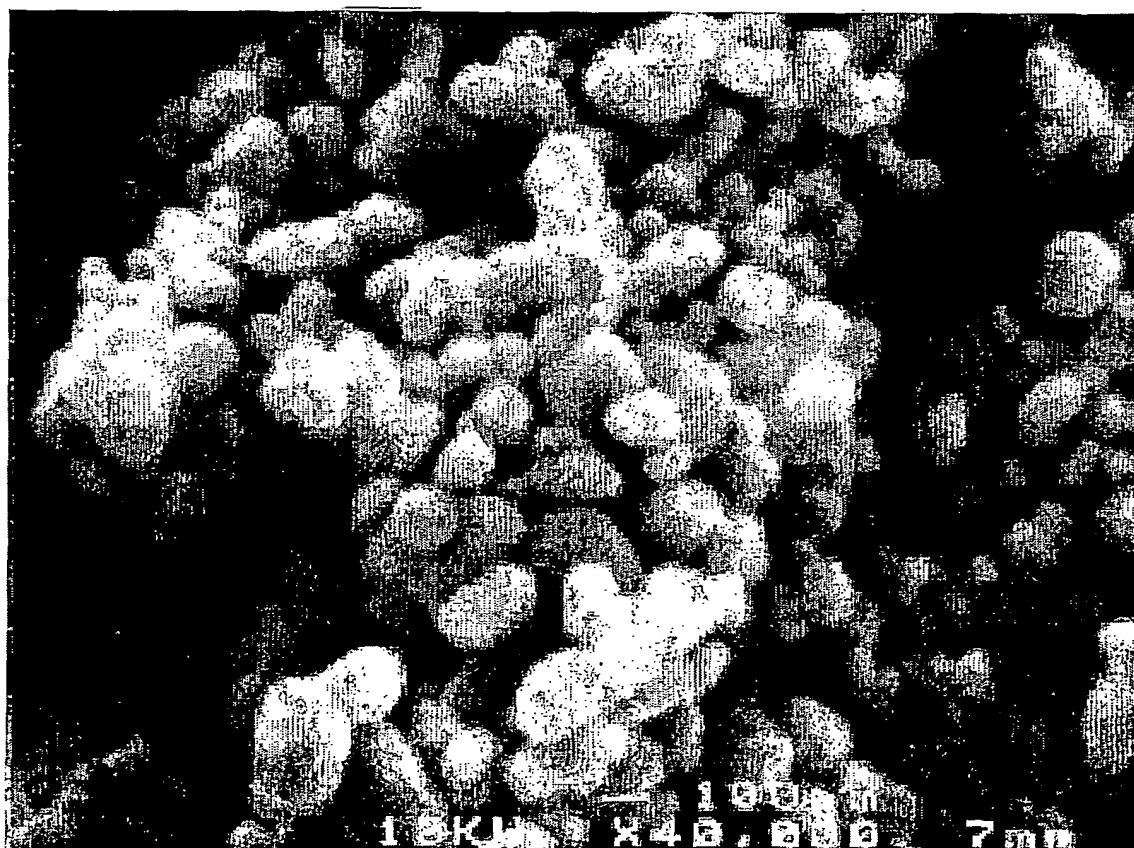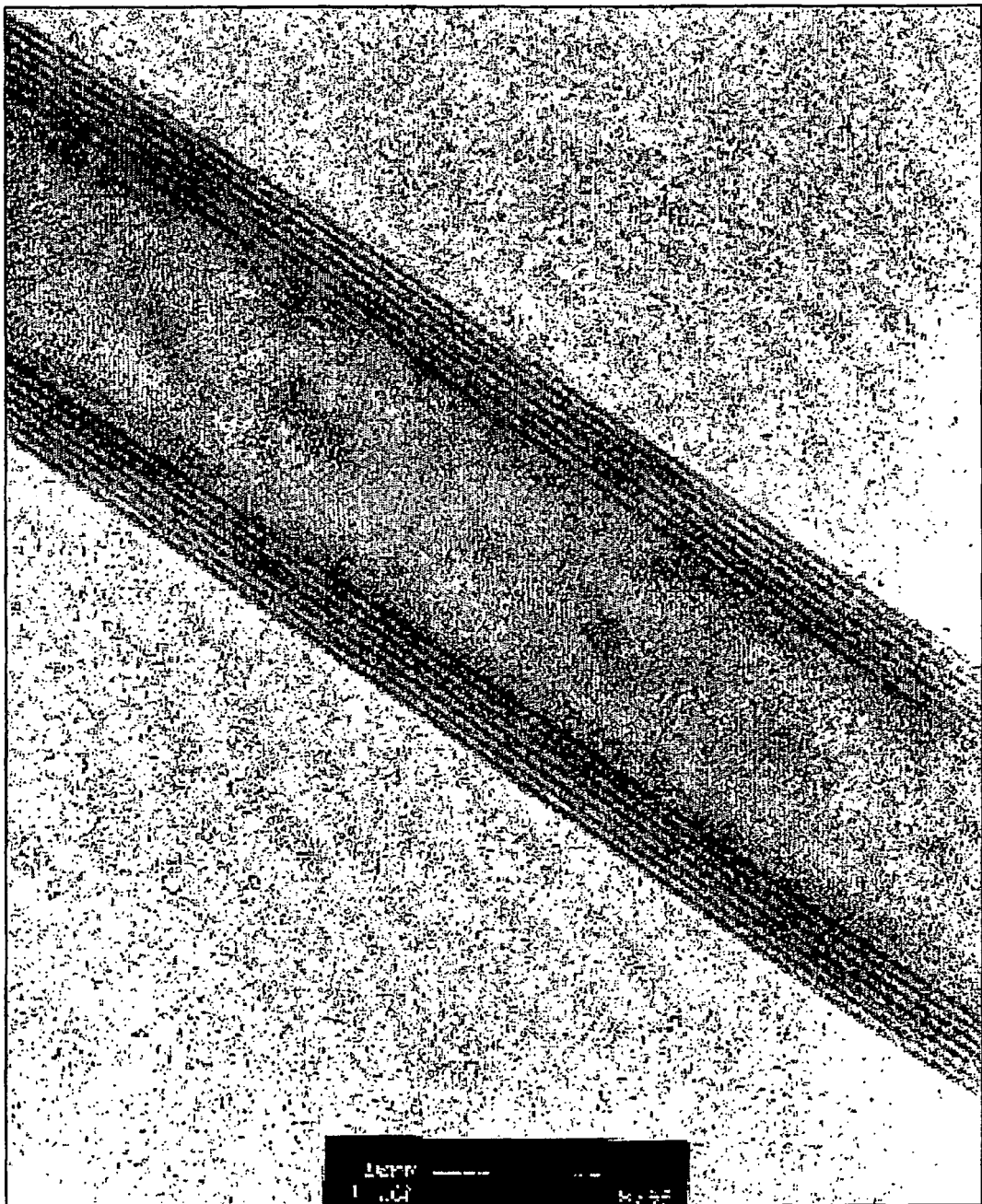FIG. 4Ac   FIG. 4Ad   FIG. 4Ae

FIG. 4Af

20nm

FIG. 4Ba

FIG. 4Bb

FIG. 5

FIG. 6