Two Suitable Methods for the Preparation of Inorganic Fullerene-Like (IF) WS$_2$ Nanoparticles

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ABSTRACT: *Two facile and low cost routes were used for the synthesis of IF-WS$_2$ nanoparticles. In this paper, preparation of IF-WS$_2$ nanoparticles with two different methods was investigated. In the first method, WO$_3$ nanoparticles were reacted with H$_2$S gas in N$_2$/H$_2$ reducing atmosphere at 900 ^{o}C. The as-synthesized IF-WS$_2$ nanoparticles are spherical shape with an average size of about 70 nm. In the second method, WO$_3$ nanoparticles were reacted with Sulfur powder in H$_2$ reducing atmosphere at 800 ^{o}C. All reaction conditions have been optimized. In this method, application of the harmful and poisonous H$_2$S gas was eliminated. The as-prepared IF-WS$_2$ nanoparticles are spherical shape with an average size of about 50 nm. In this research, it was revealed that in the first method, the reduction of WO$_3$ nanoparticles before the reaction with H$_2$S gas is very important in product quality and the output of the reaction will be increased. Also in contrast to that was proposed in the previous similar research, it was revealed that the preparation of IF-WS$_2$ nanoparticles according to the second method can not be considered as large scale method because the product quality is directly dependent on the amount of WO$_3$ nanoparticles that can not be considered exceeding 0.1 g. Besides, the preparation method of WO$_3$ nanoparticles as precursor for the synthesis of IF-WS$_2$ nanoparticles is different from previous similar researches. The solution of ammonium para tungstate (APT) and citric acid (as organic additive) was prepared and then the pH of solution was adjusted at 7 by using ammonium hydroxide. Firstly, the sample was heated to 250 ^{o}C for 1 h and secondly was calcined at 500 ^{o}C for 2 h to obtain yellow color powder of WO$_3$ nanoparticles with an average size of about 50 nm. The samples were characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).*

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INTRODUCTION

Layered materials such as graphite, MoS_2 and WS_2 (plates of the 2H-polytype) are used both as solid lubricants [1] and as additives in liquid lubricants [2].

Unfortunately, the 2H-platelets tend to stick to the mating metal pieces through the dangling bonds, which lead to their rapid annihilation through burnishing and oxidation. The tribological properties of C_{60} and C_{70} fullerenes were described [3]. It was speculated that they are nearly spherical fullerenes and may behave as nanoscale ball bearing. The fullerene molecules are too small to separate between the mating metal surfaces and therefore they tend to enter into crevices or valleys [4].

Experiments showed that inorganic fullerene-like (IF) molecules of metal dichalcogenide MX_2 especially (M=Mo,W X=S, Se) with structures closely related to (nested) carbon fullerenes, possess lubricating properties superior to those of 2H- platelets in a wide range of operating conditions. This outstanding tribological behavior of IF-WS_2, is attributed to its chemical inertness and to the hollow cage structure, which leads to high elasticity and allows the particles to roll rather than slide (rolling friction) in appropriate loading regimes.

The metal dichalcogenides, MX_2 (M=Mo, W, Nb, Hf X=S, Se) contain a metal layer sandwiched between two chalcogen layers with the metal in a trigonal prysmatic or octahedral coordination mode. The MX_2 layers are analogous to the single graphene sheets in the graphite structure.

The dichalcogenide layers are unstable towards bending and tend to roll in to curved structures. If the dimensions of the dichalcogenide layers are small, they form hollow, closed clusters designed as inorganic fullerene-like (IF) structures.

Tenne et al. [5] first demonstrated that Mo and W dichalcogenides are capable of forming nanotubes. Closed fullerene-type structures (inorganic fullerenes) also formed along with the nanotubes. The dichalcogenide structures contain concentrically nested fullerene cylinder, with a less regular structure than in the carbon nanotubes.

Various methods have been proposed for the synthesis of WS_2 nanoparticles such as solid-gas phase reaction [5-8], arc discharge [9], thermal decomposition [10,11], hydrothermal synthesis [12], sonochemical process [13] and template synthesis [14].

In this research, WS_2 nanoparticles were prepared by two different facile and low cost suitable methods.

In the first method, WO_3 particles were reacted with H_2S gas in N_2/H_2 reducing atmosphere at 900 ^{o}C. The as-synthesized IF-WS_2 nanoparticles have a spherical shape with an average size of about 70 nm.

In the second method, WO_3 particles were reacted with Sulfur powder in H_2 reducing atmosphere at 800 ^{o}C. The as-prepared IF-WS_2 nanoparticles have a spherical shape with an average size of about 50 nm.

The preparation method of WO_3 nanoparticles as starting material for the preparation of IF-WS_2 nanoparticles is different from previous similar researches. The solution of ammonium para tungstate (APT) and citric acid was prepared and then the pH of solution was adjusted at 7 by using ammonium hydroxide. Firstly, the sample was heated to 250 ^{o}C for 1 h and secondly was calcined at 500 ^{o}C for 2 h to obtain yellow color powder of WO_3 nanoparticles with an average size of about 50 nm.

EXPERIMENTAL SECTION

The samples were characterized by scanning electron microscopy (SEM) using a Holland Phillips XL30 microscope. XRD patterns of the samples were recorded in ambient air using a Holland Philips X-ray power diffraction (Cu Kα, λ=1.5406 Å), at scanning speed of 2°/min from 20° to 80°. TEM image of the sample was prepared by Philips Analytical equipment (CM 200).
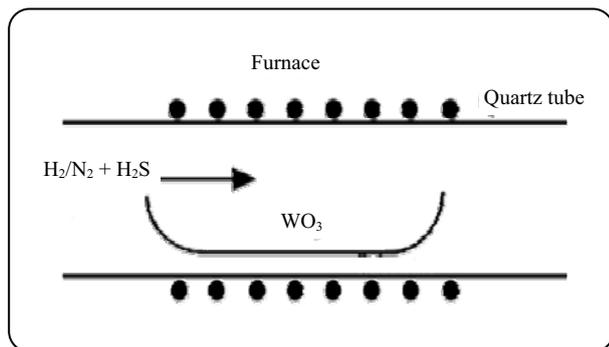
Preparation of WO₃ nanoparticles

All chemicals were of analytical grade and used without further purification.

Tungsten oxide nanoparticles were synthesized using the combustion synthesis method. In a typical preparation procedure, $(NH_4)_{10}W_{12}O_{41}.7H_2O$ powder (1.17 g) was dissolved in de-ionized water to which was added organic additive such as citric acid crystals (0.39 g). Citric acid was added to the solution of ammonium para tungstate (APT) and the pH of solution was adjusted at 7 by ammonium hydroxide.

Thus the oxalate complex would be formed. The mixture was then heated in a furnace to a temperature of 250 ^{o}C for 1 h.

The as-prepared powder was calcined at 500 ^{o}C for 120 minutes to obtain a pale yellow powder. Finally, the

Fig. 1: Schematic illustration of the instrument related to the reaction of the as-prepared WO₃ with H₂S in the N₂/H₂ atmosphere at high temperature.

Fig. 2: Schematic illustration of the instrument related to the reaction of the as-prepared WO₃ nanoparticles with sulfur powder in H₂ atmosphere at high temperature.

product had to be sonicated with ethanol. The yellow powder of WO_3 nanoparticles with an average size of about 50 nm was obtained.

Reaction of the as-prepared WO_3 with H_2S in the N_2/H_2 atmosphere at high temperature

In this method, the as-prepared WO_3 nanoparticles were used as starting material. The desired amount of WO_3 powder (typically 0.5 g) was carefully dispersed into the quartz boat, which was put into a larger quartz tube. The quartz tube was put into a horizontal tube furnace and then connected to the gas stream. Firstly, the reducing gas (mixture of N_2/H_2 gas with 90/10 composition) and secondly the sulfidizing gas (H_2S gas) were introduced into the quartz tube.

The temperature of the furnace was increased gradually (10 ^{o}C/min) until 900°C. The reaction temperature was hold in this temperature for 1h.

Finally, the product was cooled to room temperature gradually only under the reducing gas atmosphere. The instrument has shown schematically in Fig. 1.
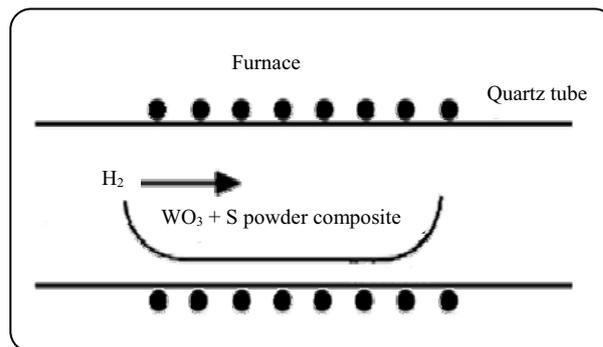
Reaction of the as-prepared WO_3 nanoparticles with Sulfur powder in H_2 atmosphere at high temperature

For determination of the best mole ratio, reaction was repeated with different WO_3 nanoparticles and sulfur (S) powder mole ratios.

The best mole ratio of WO_3 nanoparticles and sulfur (S) powder was 1:10 considering the evaporation loss of sulfur (S) under the heating temperature.

The as-prepared WO_3 nanoparticles were added to the solution of Sulfur (S) powder in CS_2.

The mixture was dispersed under vigorous stirring for

10 min, and then ultrasonically for 30 min. After drying, the composite powder was prepared.

This composite powder was carefully dispersed into the quartz tube, which was put into a larger quartz reaction tube that would be taken place in the tubular furnace and would be connected to the vacuum pump.

Then the tubular furnace was evacuated and H_2 gas, which was used as the reducing atmosphere source, was introduced into the reactor.

A single H_2 atmosphere was then obtained before the heating process .The heating temperature was held at the required point not higher than 900 ^{o}C and a heating rate of 10 ^{o}C min^{-1} was maintained during the heating process.

After cooling to room temperature, the black products were collected from the quartz tube.

For determination of the optimum experimental conditions, the process has been performed at several temperatures such as 480,600,700 and 800 ^{o}C, different H_2 gas flow rates, various pressures and different amounts of WO_3/S mole ratios. The instrument has shown schematically in Fig. 2.

RESULTS AND DISCUSSION

Fig. 3, shows the XRD pattern of the as-prepared WO_3 nanoparticles by combustion synthesis method.

All the reflections can be indexed to the pure WO_3 (JCPDS card No. 05-0363) with

a = 7.28 Å, c = 3.83 Å.

The average particle size of the product is about 50 nm that was calculated from XRD pattern by the Debye-Scherrer formula.

Fig. 4, shows SEM image of the as-prepared WO_3 nanoparticles. It indicates that the particles have almost a
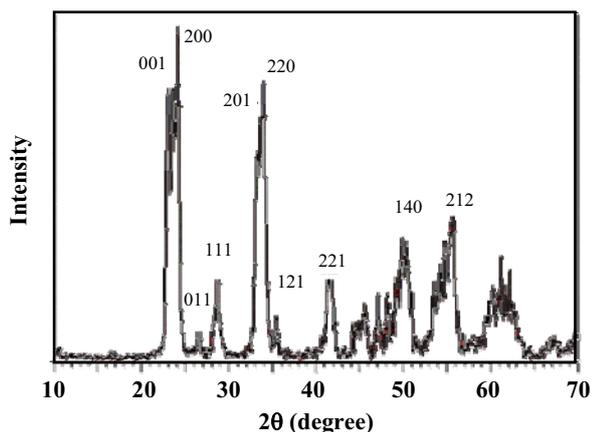
Fig. 3: XRD spectrum of WO₃ nanoparticles that was prepared by combustion synthesis method. All reflections are indexed based on pure WO₃ with a = 7.28 Å, c = 3.83 Å (JCPDS card No. 05-0363).
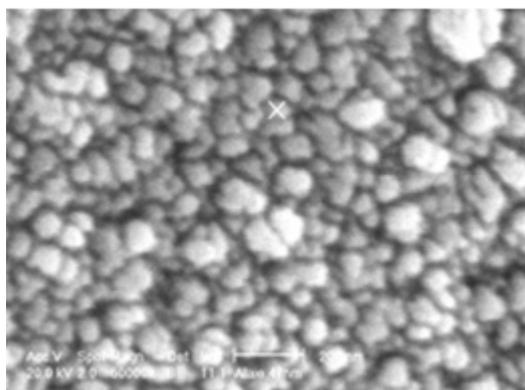
Fig. 4: SEM image of the WO₃ nanoparticles that were prepared by combustion synthesis method.
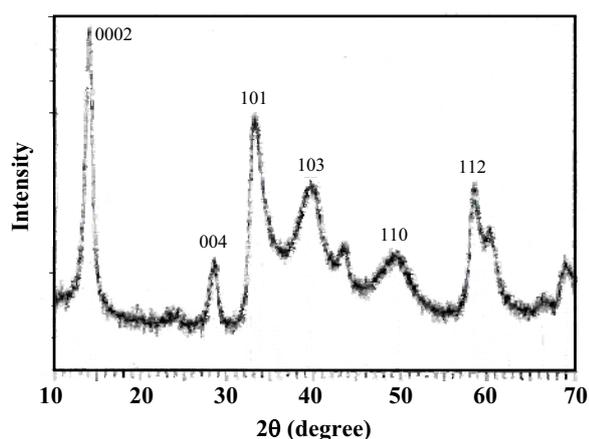
Fig. 5: XRD spectrum of the IF-WS₂ nanoparticles that was prepared by the reaction of WO₃ nanoparticles with H₂S gas in N₂/H₂ reducing atmosphere at 900 ºC.

spherical shape with a narrow size distribution. The average particle size of the product is about 50 nm.

In the first method, the reduction of WO₃ nanoparticles before the reaction with H₂S gas is very important in product quality and the output of the reaction will be increased.

Fig. 5, illustrates XRD spectrum of the as-prepared IF-WS₂ nanoparticles that was prepared from the reaction of WO₃ nanoparticles with H₂S in N₂/H₂ atmosphere at 900 ºC. The average particle diameter calculated with Debye-Scherrer formula is about 70 nm (by using 0002 reflections).

All the reflections can be indexed to the hexagonal WS₂ cell (JCPDS card No. 08-0237) with a = 3.15 Å, c = 12.36 Å.

Besides, Fig. 6 illustrates the SEM images of the as-prepared WS₂ nanoparticles

Fig. 7 shows the TEM image of the as-synthesized IF-WS₂ nanoparticles. The product with semi spherical structure can be seen in the picture.

Fig. 8, illustrates the IF-WS₂ nanoparticles ED pattern.

The TEM image and related ED pattern, confirms the results that we obtained by using XRD spectrum and SEM images.

For the optimization of the reaction products of the second preparation method, the reaction was performed in several temperatures.

Fig. 9, compares schematically the XRD patterns of three different temperature reaction products (for example 480, 700 and 800 °C) with XRD spectrums of WO₃ and WS₂ nanoparticles. At low temperatures such as 480ºC, sulfidization was superior to reduction. Therefore small amounts of WS₂ together WO₃ can be formed. At higher temperature such as 700 °C, reduction was superior to sulfidization. Therefore, the reaction products are elemental W and WO₃. Finally, at optimum temperature ie 800 °C, the synergy between sulfidization and reduction, causes IF-WS₂ nanoparticles to be formed as reaction products.

The optimum amount of pressure is about 279 Torr. If the vacuum exceeds this amount, the composite powder will be pulled in to the vacuum pump trap.

Before raising temperature, the atmosphere of quartz reaction tube must be saturated by H₂ gas. Therefore, the mole ratio of H₂ gas in relation to composite powder is not
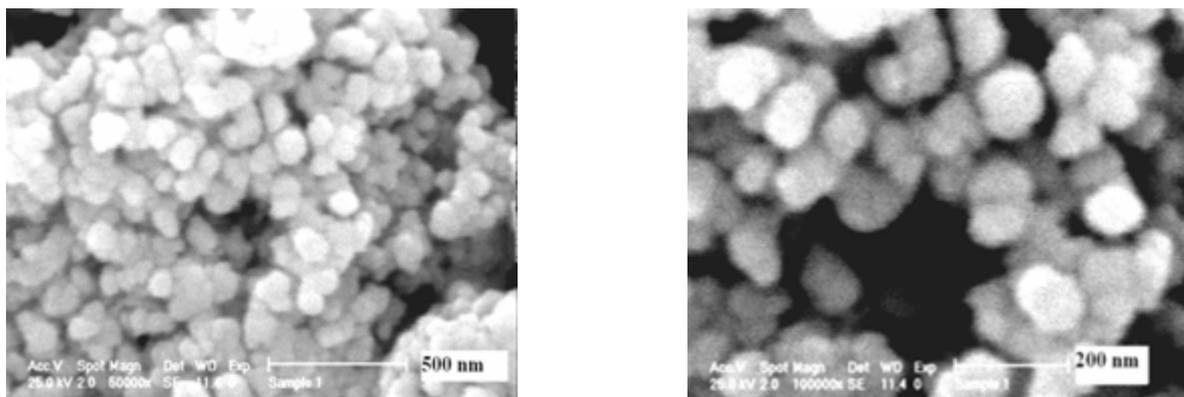
***Fig. 6: SEM images of the as-prepared IF-WS₂ nanoparticles with different scales (500 nm, 200 nm) that was
prepared by the reaction of WO₃ nanoparticles with H₂S gas in N₂/H₂ reducing atmosphere at 900 °C.***
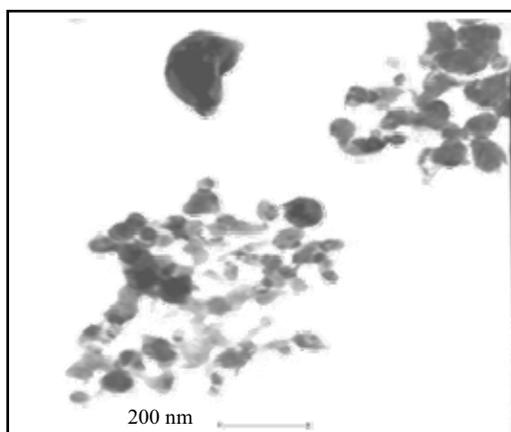
***Fig. 7: TEM image of the as-synthesized IF-WS₂ nanoparticles
that was prepared by the reaction of WO₃ nanoparticles with
H₂S gas in N₂/H₂ reducing atmosphere at 900 °C.***
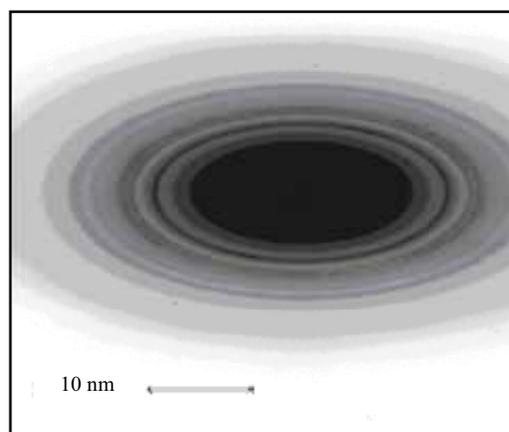
***Fig. 8: ED pattern of the IF-WS₂ nanoparticles that were
prepared by the reaction of WO₃ particles with H₂S gas in
N₂/H₂ reducing atmosphere at 900 °C.***

very important but the selection of suitable rate for the mentioned gas is very essential.

Fig. 10, compares the XRD spectrums of the reaction product under the high flow rate of H_2 gas (for example 200 mL/min) with WO_3 and IF-WS_2 nanoparticles.

As can be seen, in this condition, IF-WS_2 nanoparticles haven't been observed because, the high flow rate of H_2 gas, causes the sulfur (S) vapors to escape from the reactor. In this condition, a mixture of elemental W and WO_3 will be formed as reaction products. Based on our experimental results, the best flow rate for reducing gas can be considered 80 ml/min.

Fig. 11, illustrates XRD pattern of IF-WS_2 nanoparticles that were obtained with optimum conditions (temperature adjusted at 800 °C, H_2 gas flow

rate was 80 mL/min , pressure was 279 Torr and the mole ratio of WO_3 nanoparticles and sulfur (S) powder was 1:10).

All the reflections can be indexed to the hexagonal WS_2 cell (JCPDS card No. 08-0237) with a = 3.15 Å, c = 12.36 Å.

The average particle size of the as-synthesized IF-WS_2 nanoparticles is about 50 nm that was calculated by using XRD pattern and the Debye-Scherrer formula.

Fig. 12, illustrates SEM image of the IF-WS_2 nano-particles. It indicates that the particles have almost a spherical shape with a narrow size distribution.

As can be seen in Fig. 13, by considering the amount of WO_3 nanoparticles that exceed 0.1 g (for example 0.2 g), the product will be agglomerated.
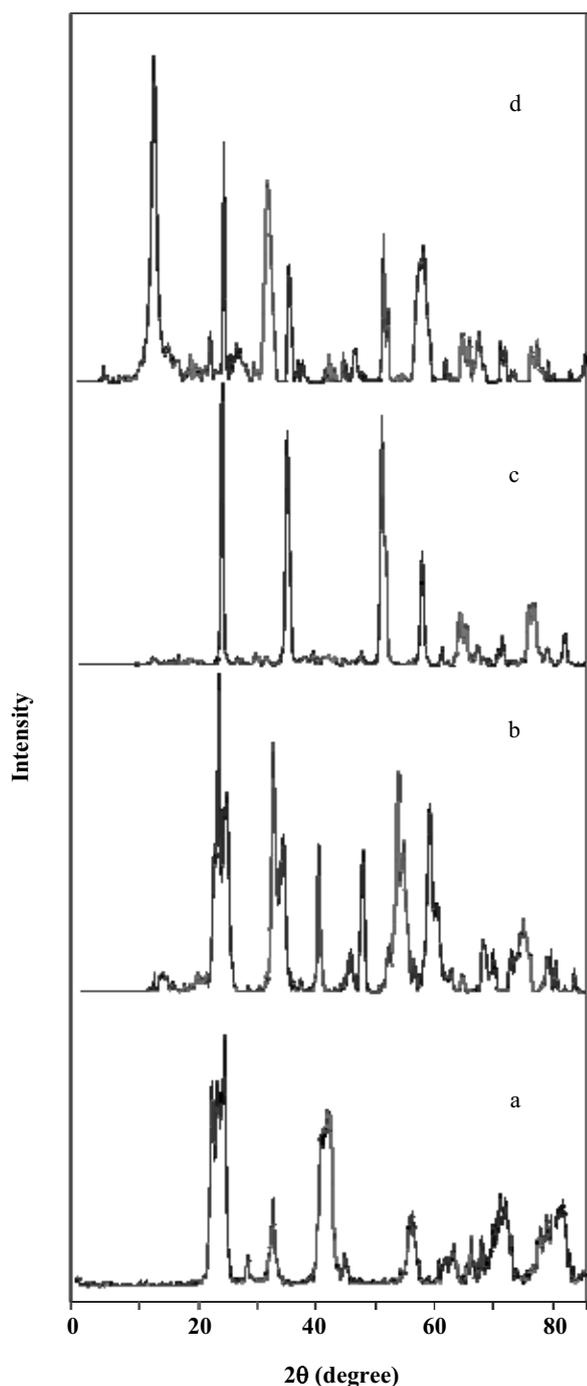
Fig. 9: Comparison of XRD patterns related to IF-WS$_2$ nanoparticles reaction products at different temperatures. a : WO$_3$ nanoparticles b: reaction product at 480 ^oC c: reaction product at 700 ^oC d: reaction product at 800 ^oC (IF-WS$_2$ nanoparticles).
*For all of the reactions, flow rate of H$_2$ gas was 80 mL/min , pressure adjusted at 279 Torr and the mole ratio of WO$_3$ nanoparticles and sulfur (S) powder was 1:10.
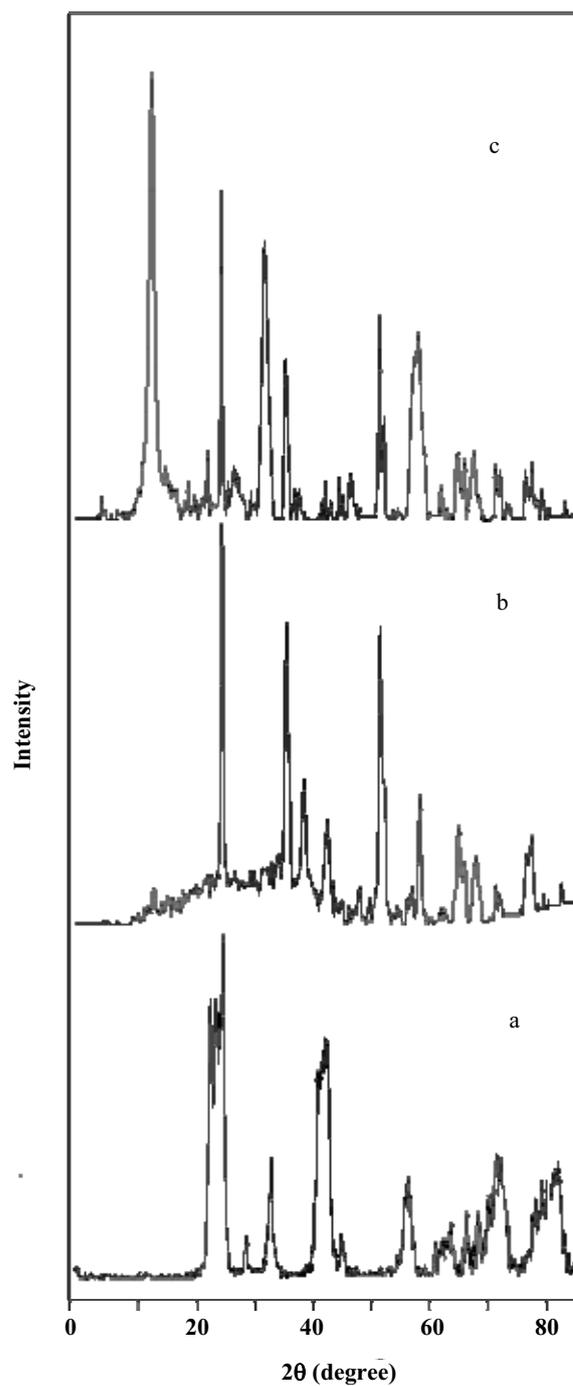
Fig. 10: Comparison of XRD spectrums of a: WO$_3$ nanoparticles   b: product of the reaction with 200 mL/min H$_2$ gas flow rate c: product of the reaction with 80 mL/min H$_2$ gas flow rate (IF-WS$_2$ nanoparticles).
*For both reactions, temperature was 800 ^oC, pressure adjusted at 279 Torr and the mole ratio of WO$_3$ and sulfur (S) powder was 1:10.
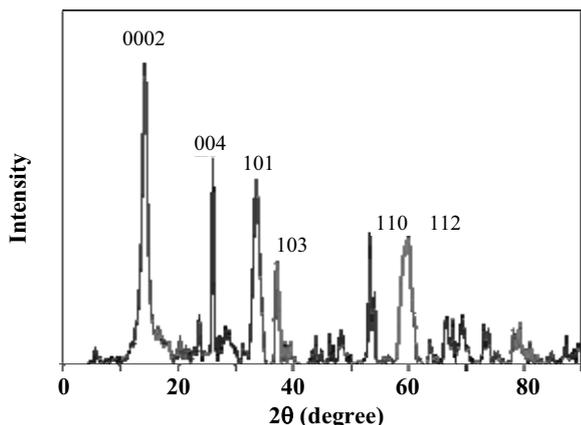
Fig. 11: XRD spectrum of IF-WS₂ nanoparticles that was prepared by optimum conditions (temperature adjusted at 800 °C, H₂ gas flow rate was 80 mL/min , pressure was 279 Torr and the mole ratio of WO₃ nanoparticles and sulfur (S) powder was 1:10). All reflections are indexed based on hexagonal WS₂ cell with a = 3.15 Å, c = 12.36 Å (JCPDS card No. 08-0237).

The reaction mechanism can be described as follows. The first step is the creation of oxygen vacancies on the surface of the oxide particles by hydrogen. Hence, two competing events follow: the first one is vacancy annihilation by the shear process. The second event is sulfur occupation of the oxygen vacancy site. Sulfur occupation is more rapid than shear process (reduction) at low temperatures whereas the reduction process prevails at high temperatures. In intermediate temperatures (600-900 °C), the rate of the two processes is equivalent and the sulfidization and reduction appear at the same time.

The synergy between the reduction and sulfidization processes, provides the conditions for IF-WS₂ nano-particles formation from oxide particles [15].

IF-WS₂ nanoparticles were prepared from the reaction of WO₃ nanoparticles with sulfur(S) powder in the reducing atmosphere of H₂ gas at certain temperature and pressure. The XRD pattern of WS₂ nanoparticles shows that the hexagonal WS₂ cell has been formed that all of its reflections can be indexed according to JCPDS card NO. 08-0237 with a = 3.15 Å, c = 12.36 Å. The average particle size of the product is about 50 nm that was calculated from XRD pattern by the Debye-Scherrer formula.

POTENTIAL APPLICATIONS

The favorable tribological influence of the IF-WS₂ and IF-MoS₂ nanoparticles, was not limited to oils and greases. Impregnating the nanoparticles in various metal films, ceramic and polymer coatings brought about substantial reductions in friction and wear of the tribological contacts. Thus they can have numerous applications.

Fine tuning of the fermi level of the nanotube phase by doping and intercalation of metal atoms is another important advantage. It is not surprising that they were recently studied as host materials for electrodes of rechargeable batteries.

Also they use as catalyst or photo catalyst in some chemical reactions. It was observed that IF-WS₂ nanotubes could withstand shock waves as powerful as 21 GPa with minor damage to their framework. This is in contrast to carbon nanotubes which are transformed into diamond under much weaker impacts (ca. 9 GPa).

They have potential applications in nuclear and solar energy storage and in the automobile and defense industries [16,17].

CONCLUSIONS

In this research, two suitable methods for the preparation of IF-WS₂ nanoparticles were investigated.

-In the first method, WO₃ nanoparticles were reacted with H₂S gas in N₂/H₂ reducing atmosphere at 900 °C. The average particle size of the product was about 70 nm. In this research, it was revealed that in the first method, the reduction of WO₃ nanoparticles before the reaction with H₂S gas is very important in product quality and the output of the reaction will be increased.

-In the second method, application of the harmful and poisonous H₂S gas was eliminated. The optimum conditions were obtained for the reaction of sulfur (S) powder with WO₃ nanoparticles in the reducing atmosphere of H₂ gas (temperature adjusted at 800 °C, H₂ gas flow rate was 80 mL/min , pressure was 279 Torr and the mole ratio of WO₃ nanoparticles and sulfur (S) powder was 1:10).

In contrast to that which was proposed in the previous similar research, it was revealed that the preparation of IF-WS₂ nanoparticles according to the second method can not be considered as large scale method because the product quality is directly dependent on the amount of WO₃ nanoparticles that can not be considered exceeding 0.1 g.
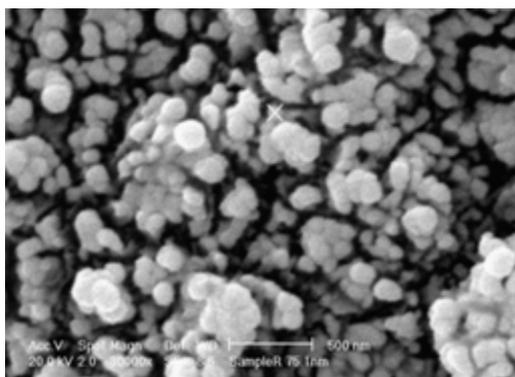
Fig. 12: SEM image of IF-WS₂ nanoparticles that was prepared by optimum conditions (temperature adjusted at 800 °C, H₂ gas flow rate was 80 mL/min, pressure was 279 Torr and the mole ratio of WO₃ nanoparticles and sulfur (S) powder was 1:10).
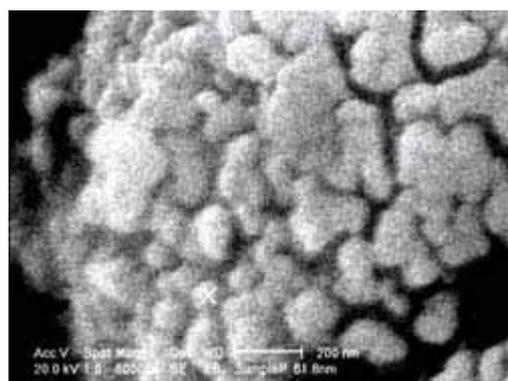
Fig. 13: SEM image of the as-prepared IF-WS₂ nanoparticles by using 0.2 g WO₃ nanoparticles that was prepared by optimum conditions (temperature adjusted at 800 °C, H₂ gas flow rate was 80 mL/min ,pressure was 279 Torr and the mole ratio of WO₃ nanoparticles and sulfur (S) powder was 1:10).

-The preparation method of WO_3 nanoparticles in this article is different from previous similar articles.

The solution of ammonium para tungstate (APT) and citric acid (as organic additive) was prepared and then the pH of solution was adjusted at 7 by using ammonium hydroxide. Firstly, the sample was heated to 250 ^{o}C for 1 h and secondly was calcined at 500 ^{o}C for 2 h to obtain yellow color powder of WO_3 nanoparticles with an average size of about 50 nm. The as-prepared WO_3 nanoparticles can be used for preparing WS_2 nanoparticles.

Acknowledgements

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