Preparation of nanocrystalline quartz via high energy ball milling

Jihan AbedelRahim Eldaour
Department of Mechanical Engineering- Azzaytuna University

الملخص

يحظى تحضير المساحيق النانوبلورية عبر الطحن الكروي عالي الطاقة إهتماما كبيرا في الوقت الحالي لبساطته و تكلفته المنخفضة نسبيا ، ولهذا الغرض تم إستخدام طاحونة الكرة الطاردة المركزية عالية الطاقة لتحضير مسحوق الكوارتز النانوي لعينات تم الحصول عليها من قسم الجيولوجيا كلية العلوم جامعة طرابلس ، حيث تم تكسير العينات في البداية يدويا بالمطرقة إلى حجم حبيبي في حدود 1mm ثم إخضاعها لطاحونة الكرة الطاردة المركزية عالية الطاقة للطحن تحت ظروف الطحن المثلى المحددة مسبقا و التي تضمنت 8 ساعات كزمن للطحن باستخدام كرات فولاذية في وسط جاف بنسبة وزنية 1:10 لكرة الفولاذ إلى الكوارتز . بعد الأنتهاء من عمليات الطحن السابقة فحصت العينات باستخدام تقنية حيود الأشعة السينية XRD لحساب الحجم البلوري و التركيب الطوري للعينات حيث أظهرت النتائج أن الحبيبات من نوع كوارتز وحجمها في الحدود النانوية من 85.58nm إلى 68.34nm لكل العينات.

الكلمات المفتاحية : اليلورات النانوية ، طاحونة الكرة الطاردة المركزية عالية الطاقة ، حيود الأشعة السينية XRD ، الحجم البلوري.

Abstract

The preparation of Nanocrystalline powder via high energy ball milling is drawing a considerable attention at the present time for its simplicity and relatively low cost. For this purpose, a high energy centrifugal ball mill was used to prepare nanocrystalline quartz powder.

The bulk samples were brought from department of geology faculty of science, "Tripoli university". The samples were initially crushed by hand and then hammer milled to a granule size of about 1mm. These were finally subjected to

high energy ball milling. The experimental runs involved the use of pre-determined optimum milling conditions which involved a fixed grinding time of 8 hours and steel balls to quartz weight ratio of 10:1 in dry media.
X-ray diffraction (XRD) technique was used to characterize the resultant powder samples in terms of crystallite size and phase composition. The obtained X-ray diffraction analysis showed that the powder particles to be in the nanosize range of (58.58) to (68.34) nm for all samples.
Key words : Nanocrystalline , high energy ball milling, X-ray diffraction (XRD), crystallite size.

INTRODUCTION

Nanomaterials are cornerstones of nanoscience and nanotechnology. Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed. It is already having a significant commercial impact, which will assuredly increase in the future .

Referring to their wide range of applications, synthesis and manufacturing nanotechnology based products is one of the most active fields in nanoscience and Nanoengineering. Nevertheless, advances in this field mainly depend upon the ability to synthesize nanostructures of controlled properties. It is well recognized that properties of nanostructured materials greatly depend on the size, shape, composition, morphology and their crystalline structure. Accordingly, various approaches have been developed to control these parameters and, therefore, meet the requirements for diverse applications. Despite numerous technologies for fabrication of nanostructures, typically, there are two drastically different approaches, top-down and the bottom-up (Salah ,et al., 2011, pp863).

The top-down approach, as shown in figure (1), is analogous to making a stone statue which is starting from bulk size and getting down to nanosize. A bulk piece of solid material is taken and modified by milling, carving or cutting to create the desirable shape and size. The top-down process involves material wastage and is limited by the resolution of the tools employed. The smallest sizes of the structures made by these techniques are also restricted.

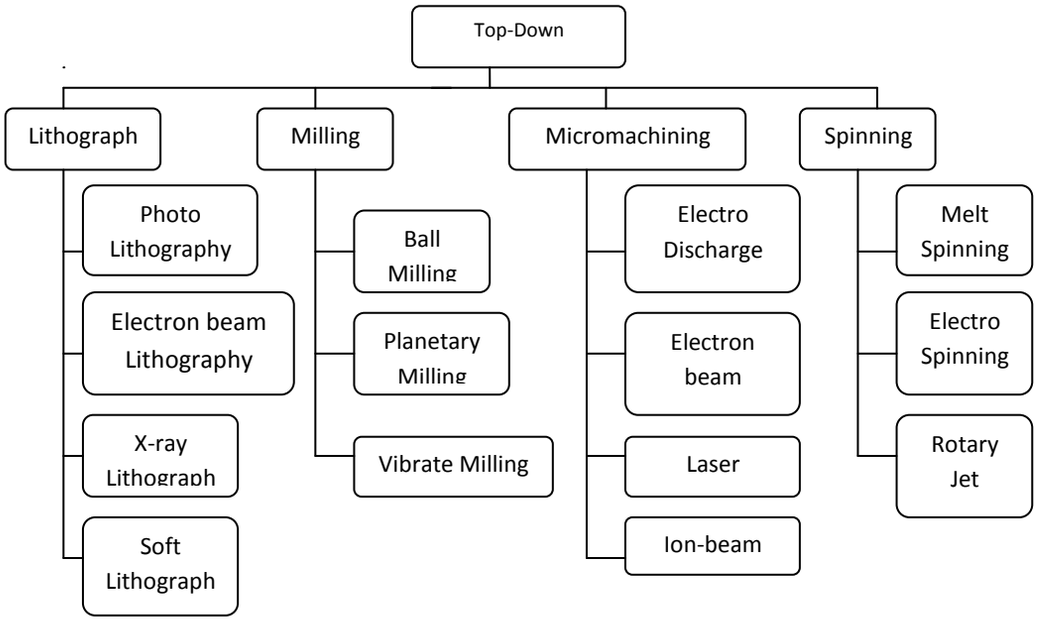

Figure (1) Classification of e common top-down methods for nanostructured material synthesis (Liu. et al., 2008,pp331-336).

Milling is generally a conventional method to size reduction in solid phase. It theoretically can be used to reduce the size of powder to the nano-size range, but in practice, this method has several limitations. Besides the conventional mills, there exists today a new generation of mills, for example high energy ball mills such as the one used in the present work, which produces ultrafine nanosized powders. This method is also used for mechanical alloying (Bernotat & Sch, 1998,pp5.1-5.39)

The structural characteristics are of primary importance to study the composition and nature of bonding materials. It provides diverse information about the bulk properties of the subject material. XRD is one of the most important characterization technique to reveal the structural properties of NPs. It gives enough information about the crystallinity and phase of NPs. It also provides rough idea about the particle size through Debye Scherer formula. This technique worked well in both single and multiphase NPs identification. Nevertheless, in the case of smaller NPs having size less than hundreds of atoms, the acquisition and correct measurement of structural and other parameters may be difficult (Molpeceres, et al., 2000, pp599-605).

The Scherrer equation shown below was developed in 1918, to calculate the crystallite size (D) by XRD radiation of wavelength λ (nm) from measuring full

width at half maximum of peaks (β) in radian located at any 2θ in the pattern , θ is the Bragg angle of the (hkl) reflection. Shape factor of K can be 0.62 - 2.08 and is usually taken as about 0.89.:

$$D_{XRD} = \frac{0.9\,\lambda}{\beta_{hkl}\cos\theta} \qquad (1)$$

MATERIALS AND METHOD

The quartz bulk samples shown in figure (2) have brought from department of geology faculty of science, "Tripoli university".

Figure (2) The bulk samples used in present work

Quartz or α-quartz is the mineral form of SiO2 stable at low temperatures and pressures. It occurs in igneous, sedimentary, metamorphic, and hydrothermal mineral environments, particularly in continental regions.
The physical and optical properties of quartz are outlined in Table (1).

Table (1) General and Physical Properties of Quartz (Deer, et al., 1963,pp435)

Chemical Formula	SiO_2
Optical Properties	Uniaxial positive
Cleavage	None
Common crystal forms	Prism {1010} Pyramids {1011} and {0111}
Luster	Vitreous
Color, Opacity	Transparent, colorless Also gray (smoky quartz), blue, purple (a methyst), Yellow (citrine), pink (rose quartz)
Hardness	7

Prior to high energy ball milling, the bulk quartz samples were subjected to:
Crushing to a size of less than 3 mm in diameter, this process was carried out manually;
Grinding which was carried out using a hammer mill to reduce the powder particles size to about 1 mm in diameter in order to be suitable for milling in the high energy ball. The hammer mill is manufactured by Siebtechnik, Germany, It is suitable for with a feed size of 2 to 50 mm. comminution of soft to medium-hard materials in the hardness range 2 - 5 Mohs and is characterized by a high throughput out. The most important component of the hammer mill is the rotor with the swinging suspended hammers. The crushing is mainly due to impact and impact stress in the area of the rotor and the grate basket .The material to be ground remains in the grinding chamber until it reaches the desired fineness and then the discharging can take place.
Milling of quartz granules was performed using a high energy centrifugal ball milling [Model S100, Retsch GmbH]. Figure (3) shows a picture of this mill.

Figure (3) The centrifugal ball mill used in the present work .

Dry milling was carried out in special steel jar using steel balls of diameters 4, 10, 12, and 13 mm. The speed of milling was fixed at 300 rpm and a number of 84 steel balls altogether weighing about 500 grams were used as grinding medium. The jar was loaded with a fixed amount of 50 grams of quartz powder for all runs. The ratio of the weight of the steel balls to quartz powder was chosen to be 10:1 due to the fact that the quantity of The material to be milled should not exceed approximately 1/3 of the grinding jar volume and minimize the chance of adhesion of powder particles together.

In order to determine the optimum milling time, initial experimental runs were carried out involving the use of milling times of 4 , 6 , and 8hours. Based upon

the results obtained, a milling time of 8 hours was found to be the most suitable for the reduction of the particle size to the nano-range.

RESULTS

Crushing and grinding of bulk pieces of quartz to a coarse powder of particle size of about 1 mm with the use of a hammer mill and these powder particles are would milled to the nano- size using a centrifugal high energy ball mill.

X-ray diffraction (XRD) was used both to determine the phase Composition of the four samples and to estimate the crystallite size of the milled powder particles. The XRD patterns were taken using a computerized X-ray Diffractometer (Model: PW 1800 of M/s Philips NV, Holland) at the Petroleum Research Centre, Tripoli. All X-ray diffractograms were taken by Cu-Ka radiation (wavelength, λ= 0.15405nm) at a scanning speed of 0.10 per second in 2θ. A tube voltage of 40 kV, a tube current of 30 mA, and a time constant of 10 seconds were used. The fine powder were run at 0.02 °θ step and scan step time of 0.5000.

The phase composition of the four powder samples as determined by XRD analysis is mainly quartz (SiO2).

The conversion of the starting bulk specimens to nanometer size was found to be possible using high energy ball milling technique , quartz pieces were converted to nano- meter size particles after initially crushing and grinding

Based on XRD peak broadening the crystallite size of quartz powder was successfully reduced to less than 100 nm after 8 hours in centrifugal high energy ball mill under impact in dry media. Figure (4), shows the XRD patterns for one sample.

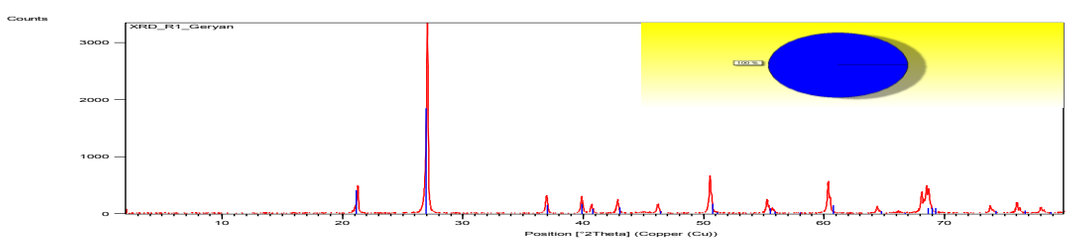

Figure (4) XRD pattern for sample No. 1

DISCUSSION

Method of calculation for the XRD crystallite size:

Powder sample number (1) is taken as an example to calculate the crystallite size using the scherrer's equation by origin lab soft ware and excel, and the value of (θ) and (β) obtained from XRD analysis of the produced powder sample are:

$$\theta = 13.5254 \quad \text{and} \quad \beta = 0.002405 \qquad (2)$$

$$D = 0.889 \times 0.1541 / (0.002405 \times \cos 13.5254) \qquad (3)$$

The other values of crystallize size were obtained in similar way

crystallite size of the obtained powder samples as given in table 2 shown below

Table(2) The calculated crystallite size of the obtained powder samples using scherrer equation

Sample No.	θ (degree)	β (radians)	D (nm)
1	13.5254	0.002405	58.58
2	13.5202	0.002405	58.579
3	13.5198	0.002062	68.34
4	13.5356	0.002405	58.58

As can be seen from table (2) all powder samples obtained were in nanometer size range .

This shows the capability and efficiency of the high energy ball as a viable means of obtaining nano- sized powder particles.

CONCLUSIONS & FUTURE WORK

High energy centrifugal ball milling can lead to the preparation of quartz powder particles in nano size range.

Eight hours milling time was found to be suitable for the reduction of the particle size to nano range in dry media with 10:1 weight ratio.

Future work is needed to investigate the influence of reducing the particle size to the nano range on the properties of local quartz.

REFERENCES

- Salah, N., Habib, S., Khan, H., Memic, A., Azam, A., Alarfaj, E. & Al- Hamedi, S., "High- energy ball milling technique for ZnO nanoparticles as antibacterial material" , International Journal of Nanomedicine, 6 , pp. 863, 2011.

- Liu, X., Sun, H., Chen, Y., Lau, R., & Yang, Y. "preparation of large particle MCM-41 and investigation on its fluidization behavior and application in single-walled carbon nanotube production in a fluidized-bed reactor". Chemical Engineering Journal, 142(3), 331-336, (2008).

- Bernotat, S. and Schonert, K., "Size reduction. In: UIImann's Encyclopedia of Industrial Chemistry", VCH Verlagsgesellschaft, Weinheim, Vol. B2, PP.5.1-5.39, 1998.

- Molpeceres J., AberturasR., Guzman M., "Biodegradable nanoparticles as a delivery system for cyclosporine: preparation and characterization". J Microencapsul, PP 599-605, 2000.

- Deer, W.A., R. A. Howie, and J. Zussman "Rock- Forming Minerals" Vol 4. Longmans, London, 435pp, 1963.