Hydrothermal Synthesis of Flower-Like α-Quartz Nanostructures from Iran Kaolin

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ABSTRACT: *Over the past many years, synthesized silica (SiO_2) has attracted wide attention because of its unique characteristics, such as low density, low thermal conductivity, high surface area, high thermal shock resistance and high specific strength. In this study, Flower-like α-quartz nano-structures have been synthesized through the hydrothermal method. The synthetic α-quartz powder was obtained using the feedstock of locally kaolin after 15 h. reaction at 180°C. The characterization of the product was investigated using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Fourier Transform InfraRed (FT-IR) spectrometer. The FT-IR spectrum of the nano-crystalline powders confirms the presence of silica. SEM studies have revealed flower-like structures consisting of nano-sheets. In the synthetic quartz, most of the population is of nano-sized and lies between 1 µm to 15 µm. This developed method has many advantages such as synthesis at low temperature and desired pH to yield superior product of desired specification.*

KEYWORDS: *Synthesized silica; Flower-like α-quartz; Kaolin, Hydrothermal method; Nano-crystalline powders.*

INTRODUCTION

Silicon dioxide is the most common silicon compound and a major constituent of the Earth's crust. Silicon dioxide, also known as silica (from the Latinsilex), is a chemical compound that is an oxide of silicon with the chemical formula SiO_2. Silica is most commonly found in nature as quartz [1]. More specifically α-quartz

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is a widely known material, which is stable at low temperatures and pressures [2]. Quartz exists in natural and synthetic forms. The α -quartz powders are considered competent materials because of their unique mechanical properties such as low density, low thermal conductivity, high surface area, high thermal shock resistance and high specific strength [3,4]. Synthetic quartz is applied as a quartz oscillator for frequency generators and as a filter for frequency controllers. Its superior electrical and thermal insulating properties find applications in both industrial electronic components and consumer electronic components [5]. For these reasons, much attention has been devoted to growth of high quality crystalline α-quartz.

The particle size and shape of synthetic α-quartz powder depend on the hydrothermal conditions, such as reaction time, pH value, additives (electrolytes [6, 7], surfactants [8] and organic acids [9]). The particle size of the prepared α-quartz increased when the reaction time is increased [10]. In addition to the pH value of reaction system, increasing deionized water and HCl molar ratio results in smaller size particles [11, 12].

Micron-size particles of quartz powder obtained by grinding of natural quartz [13], have been widely used in fillers for plastics and rubber, infrared ceramic materials, abrasives, cement, thermal insulators, dosimeter sand paints [14, 15].

Nano-sized particles of amorphous quartz are produced on an industrial scale as additives to cosmetics, drugs, printer toners, varnishes, and food [16]. They also have the potential to be used in UV-resistant transparent paint, ceramics, cement and functional fibers [17]. Nano-quartz could be applied in small-scale actuators and motors due to its nano-scale piezoelectric behavior [18]. Recently, synthesis of quartz has been received wide attention for seeking nano-sized stable silica to replace the unstable amorphous one [14]. Nano-crystals are the most important part of the development of nano-size devices in various areas [19]. It is generally believed that nano-sized particles are superior to micron-sized ones in a large variety of applications [20].

A review on hydrothermal synthesis of quartz crystals is reported by *Laudise* [21]. The first successful synthesis of crystalline quartz dates back several decades. Recently crystals of potentially useful size have been produced and more recently production of synthetic quartz crystals in commercial quantities, qualities and sizes has been realized [22].

Micron-size α-quartz crystals with well-developed crystal faces can be obtained directly from opal-A at 250 °C and 40 bar without any intermediate phases being present [23]. Silica gel was used as the starting material to synthesize nano-sized quartz with hydrothermal technique in alkaline solution, and the synthetic quartz with the mean particle size ranging from 50 nm to 300 nm was obtained [14].

In the present work, locally available kaolin was used as solid precursors to synthesize nano-sized quartz in alkaline solution under hydrothermal conditions. This method has several advantages such as the synthesis may be carried out at low temperature and desired pH to yield superior product of desired specification.

EXPERIMENTAL SECTION

Synthesis of nano-size quartz

The hydrothermal method was used, where in the whole volume of an autoclave and a constant temperature is applied. The starting materials used in the present work, were kaolin, deionized water and NaOH. Kaolin was used as the silica precursor, deionized water as the solvent and NaOH as the mineralizer to form crystalline silica. The processed kaolin from the Mineral Holding Company (Khorasanlo Mine) has been selected for the present study, which was calcinated for 3 h. at 400 °C. The mixed feedstock was prepared by adding calcinated kaolin (12.17g) into mineralizer solution, which was prepared by dissolving the sodium hydroxide of Merck's chemicals (5.56 g) indionized water (80.71mol). The reaction mixture was aged for 24 h. at room temperature and then put into an autoclave and heated at 180 °C for 15 h. under autogenous pressure. After the autoclave apparatus was cooled, the precipitates were filtered and then washed with dionized water to remove impurities. The synthetic product was then dried in an oven under 65 °C for 4 h.

Characterization

X-Ray Diffraction (XRD) was used to identify the crystal phase of the product. The experiment was carried out on a Bruker-D8 Advance powder diffraction system equipped with Cu-K_α radiation. The XRD patterns were obtained from 4° to 70° of 2θ, with a 2θ step size of 0.02°

Table 1: Chemical analysis of kaolin.

Chemical components	Mass (%)
SiO_2	74.34
Al_2O_3	17.38
Fe_2O_3	0.12
TiO_2	0.1
CaO	0.18
MgO	0.02
Na_2O	0.06
K_2O	0.17
LIO	6.84

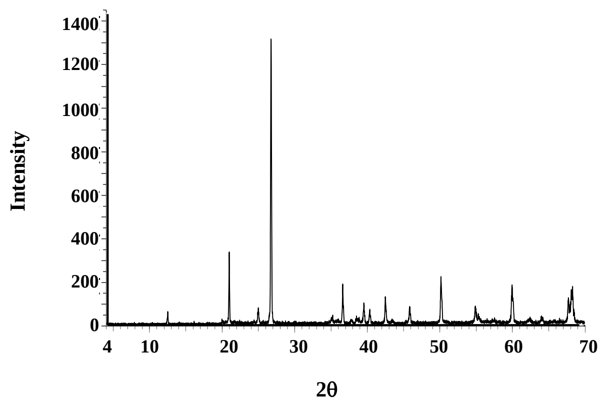

Fig. 1: X-ray powder diffraction pattern of crystalline α-quartz.

and a step time of 1s. The morphology of the product particles was observed using Scanning Electron Microscope (SEM: VEQAIITESCAN). The fourier transform infrared spectrum for synthetic quartz was measured on a DIGILAB FTS 7000 instrument under the Attenuated Total Reflection (ATR) mode using a diamond module.

RESULTS AND DISCUSSION

Experiment was performed to prepare powder of high quality α-quartz by hydrothermal synthesis. The XRF analysis was carried out to know the chemical compositions of the kaolin. The kaolin contains silica and alumina which are in major quantities where as other oxides such as magnesium oxide, calcium oxide, potassium oxide, sodium oxide and titanium oxide are present in trace amounts. The chemical composition of kaolin is presented in Table 1.

An X-ray powder diffraction pattern was obtained for the synthetic product; Fig. 1.The observed well-defined peaks in the spectra indicates a crystalline phase of α-quartz. A-Quartz reflections were present and no extra peaks related to any impurity were observed. This confirmed that the synthesized product is pure crystalline α-quartz.

Fig. 2 shows a SEM micrograph of α-quartz crystals which reveals flower-like structures. It evidently shows that the flower-like structures are made up of nano-sheets; these structures are of amorphous α-quartz. In fact nano-sheets are nucleation sites for the growth of secondary nano-sheets. Self-assembly of the primary and secondary nano-sheets lead to minimization of the surface energy and this cause the formation of three-dimensional flower-like SiO_2 structures [24]. As apparent in Fig. 2a, nano-crystalline material comprises only a small fraction of the product. The SEM image also shows that the mean particle diameter of the prepared α-quartz is in range of 1 μm to 15 μm, and mean sheet diameter is 50 nm.

IR Spectrum of silica particle is shown in Fig. 3. In this figure two main characteristic peaks of Si-O-Si bonds vibration modes were observed around ~1100 and 480 cm^{-1}, which are attributed to Si-O bending vibration band and Si-O-Si anti-symmetric stretching vibration band respectively. The IR absorption band at ~800 cm^{-1} originates from the vibration of (SiO_4) tetrahedrons. The ~3700 and 1530 cm^{-1} absorption bands come from O–H bonding vibration of adsorbed molecular water.

CONCLUSIONS

We have synthesized Flower-like α-quartz microstructures by using hydrothermal method. The synthetic α-quartz powder was obtained using the feedstock after 15 h. reaction at 180°C, but without a uniform particle shape. The product was characterized in terms of its content, phase and particle size. The mean particle diameter of the prepared α-quartz was in range of 1μm to 15 μm, and mean sheet diameter was 50 nm. The hydrothermal conditions are believed to play an important role in the formation and growth of silicon oxide. The particle size of nano silica can also be controlled by adding electrolytes, surfactants, organic acids etc.

From these results, it is concluded that high-purity nano-sized quartz could be produced in high quantities

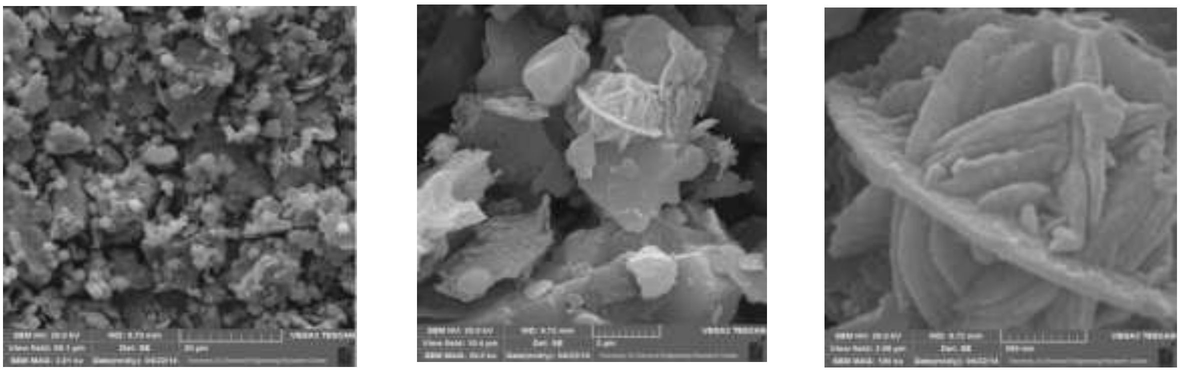

***Fig. 2:** (a) SEM micrograph of α-quartz (b) closer view showing flower-like microstructures(c) closer view showing nanosheets.*

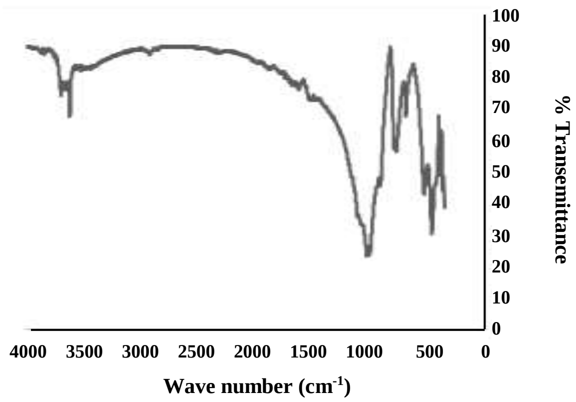

***Fig. 3:** IR Characteristic spectrum of quartz particle.*

and for low prices if suitable experimental conditions are chosen.

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