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Synthesis and characterization of silica nanoparticles from Vietnam

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In the present study, silica (SiO_2) nanoparticles were synthesized through the decomposition of silica sand in sodium hydroxide (NaOH) molten salt at 500°C under ultrasound waves. The proposed method manifested as a facile preparation technique with a relatively low reaction temperature, uniform dispersion of doping metal ions, an excellent control of stoichiometry and a remarkable chemical homogeneity. Moreover, the current research was aimed at expanding the use of local materials, such as carbonates, clay and silica sands. The structural and the microstructural characterizations of silica nanoparticles were performed using X-ray diffraction (XRD), scanning electron microscopy and transmission electron microscopy. It is evident from the XRD pattern that the fabricated material had a hexagonal crystal structure, which conforms to the shape of crystalline silica. The silica nanoparticles were spherical in shape with an average size of 10–50 nm that slightly depended on the annealing temperature.

Notation

c	velocity of light (3×10^8 m/s)
E_g	band gap energy (eV)
h	Planck's constant ($4{\cdot}135 \times 10^{-6}$ eV)
λ	wavelength of the absorption edge (nm)

1. Introduction

Nanotechnology is an emerging and revolutionary field of science.[1–3] In recent years, there has been a tremendous growth in research on silica (SiO_2) nanoparticles because of their facile synthesis routes and wide range of uses in various industrial applications, such as catalysis, pigments, pharmacy, electronic and thin-film substrates, electronic and thermal insulators, biosensors, polymer composites, high-performance liquid chromatography and construction materials.[4–6]

In 2000, several silica sand deposits were found along the Vietnamese coast, and among them, the most attractive one was Thuy Trieu (22 Mt of average-grade 98·52% silica), 18 km away from the Nha Trang township.[7] In addition, a commercially significant deposit of silica sands (more than 50 Mt of high-quality quartz sand) was discovered in the Phong Dien district in the province of Thua Thien Hue.[8] Mikoláš *et al.*[8] propound that the silica sand of the Phong Dien district (Figure 1) is of very high quality (average-grade silica of 97·75–99·59%) with a whiteness of 79·7%.

In the current research realm, silica nanoparticles can be prepared by multifarious experimental techniques, such as flame spray pyrolysis, chemical vapor deposition, microemulsion, ball milling, sol–gel method[4] and hydrolysis of tetraethyl orthosilicate.[6] Among these, the sol–gel method has attracted a significant scientific interest because of it being a facile, scalable and controllable synthesis route.[4] Recently, Wang *et al.*[9] and Yahui *et al.*[10] proposed a novel synthesis process for the preparation of nanoparticles through the decomposition of metal oxides in sodium hydroxide (NaOH) molten salt under atmospheric pressure. The sodium hydroxide molten salt decomposition method can be considered as a mineral activation procedure, thus making it suitable for use in sulfate production processes.[10]

In the present study, silica nanoparticles were prepared through the decomposition of silica sand in sodium hydroxide molten salt at 500°C under ultrasound waves. The proposed method manifested as a facile preparation technique with a relatively low reaction temperature, uniform dispersion of doping metal ions, an excellent control of stoichiometry and an outstanding chemical homogeneity. Furthermore, the current research was aimed at

Figure 1. Location of the studied area: a satellite image of the Phong Dien silica sand deposit[8]

expanding the use of local materials, such as carbonates, clay and silica sands.

2. Experimental methods

Sodium hydroxide (98%) and silica sand (collected from the Phong Dien district in the province of Thua Thien Hue) with different mass ratios of 1:1, 1·5:1 and 2:1 were first homogeneously mixed in nickel crucibles (containing deionized (DI) water) under ultrasound waves (32 kHz, 100 W) and then heated in a muffle furnace at 500°C for 100 min. Figure 2 displays the experimental set-up for the synthesis of silica nanoparticles.

The resulting vitreous compound was dissolved in hot water to prepare hydrated sodium silicate. The extent of the silica conversion was calculated by dissolving the intermediate products in sulfuric acid (H_2SO_4) (98%, 10 vol%). Thus, the silica nanoparticles were obtained by the following reactions

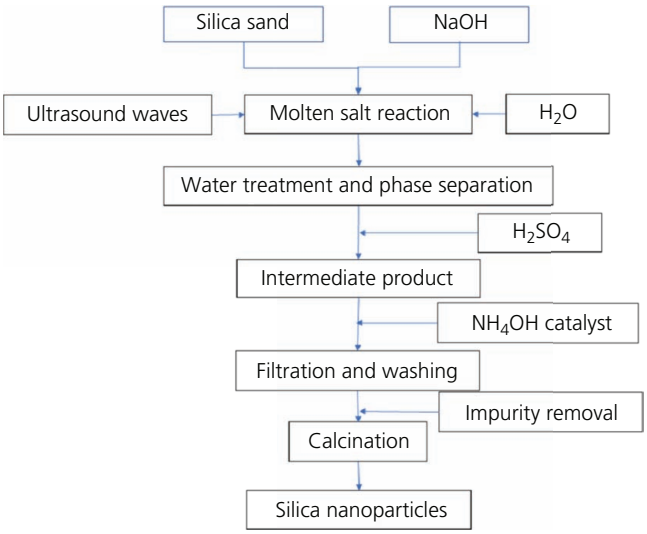

Figure 2. Flow diagram for the synthesis of silica nanoparticles by the sodium hydroxide molten salt method

1. $2NaOH + SiO_2 \xrightarrow{\text{ultrasonic energy} + t^{\circ}C} Na_2SiO_3 + H_2O$

2. $Na_2SiO_3 + H_2SO_4 \rightarrow SiO_2 + Na_2SO_4 + H_2O$

The ammonium hydroxide (NH_4OH) (38%) catalyst was added dropwise to the solution to form a gel. The obtained silica gel was washed several times with DI water to remove the by-products and dried at 90°C for 24 h and then calcined at 300, 400, 500, 600, 700, 800 and 900°C for 2 h.

The crystal structures and the microstructures of the calcined samples were examined by X-ray diffraction (XRD; D8 Advance), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The optical absorption spectra of the prepared nanoparticles were recorded by an ultraviolet–visible (UV–Vis) near-infrared spectrometer (Jasco, V-570, Japan).

3. Results and discussions

According to the reactions in Equations 1 and 2, the theoretical mass ratio of silica sand and sodium hydroxide was about 1:0·87. Sodium hydroxide acted as a fluidizing and fluxing agent during the reaction and maintained the liquidity of the reactants. The results in Figure 3 reveal that the silica fractional conversion ratio (the yield of silica nanoparticles) increased with increasing sodium hydroxide:silica mass ratios. However, no significant change was noticed in the yield rate of silica nanoparticles for a mass ratio between 1·5:1 and 2:1. Therefore, the recommended mass ratio was 1·5:1.

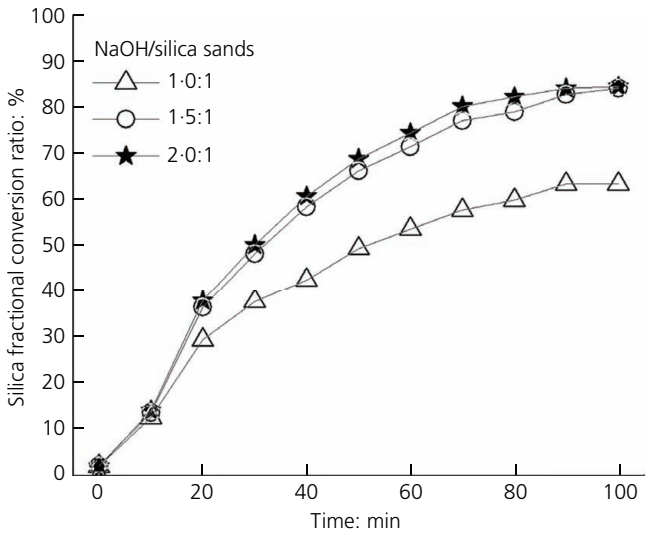

Figure 3. Effect of sodium hydroxide mass ratio on silica extraction

In this study, silica nanoparticles were synthesized under ultrasound waves. The main advantage of using ultrasound is the ability to control the sizes, the morphologies and the physical states of nanoparticles through the variation in frequency, power and the duration of sonication; therefore, ultrasound is considered as a very promising futuristic tool for material manufacturing technology. It provides highly intensive mixing, particularly in viscous media; hence, ultrasound can significantly accelerate the rate of a chemical reaction.[1] In the present experiment, ultrasound controlled the dispersion of silica sands in sodium hydroxide molten salt and helped in breaking the chemical bonds of silica sands to create new structures. Yahui *et al*.[10] reported a pretreatment process of sodium hydroxide molten salt with an alkali-to-titanium slag ratio of 1·1:1 at 550°C for 90 min, and the titanium conversion rate was found to be greater than 92·2%. Sdiri *et al*.[11] expounded a preparation method for sodium silicate by mixing siliceous sand with sodium carbonate at 1060°C.

In order to optimize the synthesis conditions of silica nanoparticles, the effects of annealing temperature were investigated. The experiments were performed at different annealing temperatures of 300, 400, 500, 600, 700, 800 and 900°C (Figure 4).

The obtained XRD spectra of silica were compared with standard Joint Committee on Powder Diffraction Standards data (number 53-61386, 1981),[12] and it was confirmed that all formed silica (quartz) particles were in the nanometer range (<50 nm); this will be discussed in the next section. The 2θ values of the (100), (101), (102), (111), (200), (201), (103), (211), (300), (212) and (203) planes were measured as 20·94, 26·7, 38·36, 39·48, 42·66, 44·6, 50·18, 55·02, 60·04, 65·04 and 68·22°, respectively. The XRD patterns also revealed that the obtained silica nanoparticles had a hexagonal crystal structure with lattice parameters of $a = b = 4{\cdot}9133$ Å, $c = 5{\cdot}4053$ Å and $c/a = 1{\cdot}1001$.[12]

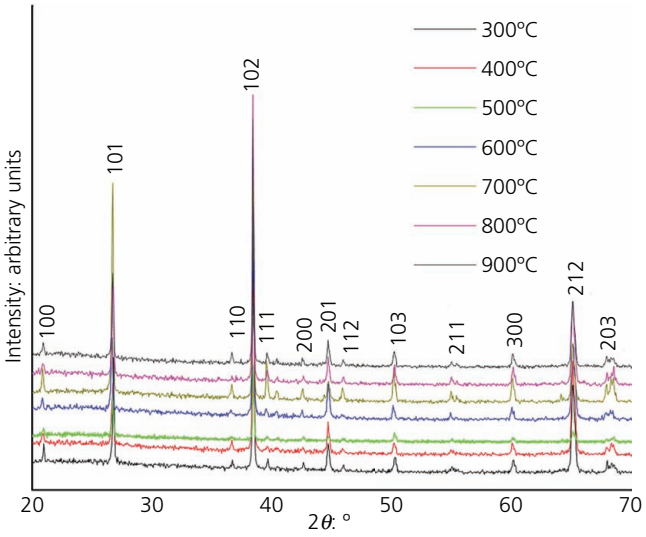

Figure 4. XRD of silica nanoparticles prepared by the sodium hydroxide molten salt method at different annealing temperatures

It is also observable from Figure 4 that with an increase in the annealing temperature from 300 to 900°C, the diffraction peak intensity also increased, thus indicating an improvement in the crystallinity of silica. Therefore, this result complies with the previous finding.[13]

The SEM micrographs exhibit the agglomerated spherical morphologies of silica nanoparticles at different annealing temperatures (300–800°C) (Figure 5), and it was found that larger particle sizes were obtained at high calcination temperatures. It is noticeable that the dispersion states and the sizes of silica nanoparticles simultaneously changed with the change in calcination temperature, and the best results were obtained between 300 and 500°C. The sizes of silica nanoparticles slightly depended on the calcination temperature. The presence of bigger particles might occur due to high-temperature treatment (>500°C).

The TEM images (Figure 6) reveal that the silica nanoparticles were of spherical shape with an average size of 10–50 nm (Figure 7). Figure 7 shows the particle size distribution with data obtained by the ImageJ software from the TEM images and gathered around the top of the Gauss fitting plot. In order to investigate the optical absorption properties of spherical silica nanoparticles, a UV–Vis spectrometry study was carried out (Figure 8).

The band gap energies (E_g) of the samples were determined by using the equation

$$E_g = hc/\lambda \quad (3)$$

where E_g is the band gap energy (eV), h is Planck's constant ($4{\cdot}135 \times 10^{-6}$ eV), c is the velocity of light (3×10^8 m/s) and λ (nm) is the wavelength of the absorption edge. The absorption edges of silica nanoparticles were found around 288 nm at 500°C, and the band gap energies of silica nanoparticles were measured as 3·35 eV (inset of Figure 8); these results conform to the previous findings.[13]

4. Conclusion

In this research, spherical silica nanoparticles were synthesized through the decomposition of silica sand in sodium hydroxide molten salt at 500°C under ultrasound waves. It is proved that the proposed method is simple and capable of fabricating a large volume of materials. Moreover, this study was aimed at expanding the use of local materials, such as carbonates, clay and silica sands.

The effects of different sodium hydroxide:silica mass ratios (1:1, 1·5:1 and 2:1) on the synthesis of silica nanoparticles were

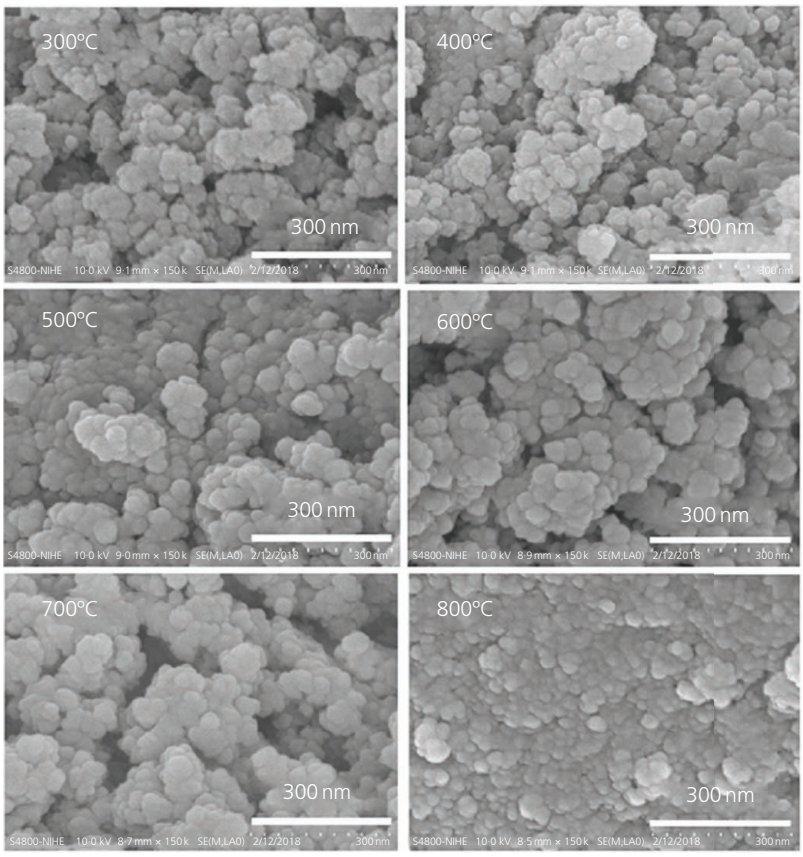

Figure 5. SEM image of the samples after annealing at different temperatures for 2 h

investigated. It was found that the silica fractional conversion ratio increased with increasing mass ratios; therefore, a ratio of 1·5:1 was recommended.

The silica nanoparticles were spherical in shape with an average size of 10–50 nm, and the size slightly depended on the annealing temperature. It is clear from the XRD patterns that the obtained silica nanoparticles had a hexagonal crystal structure with lattice parameters of $a = b = 4{\cdot}9133$ Å, $c = 5{\cdot}4053$ Å and $c/a = 1{\cdot}1001$.

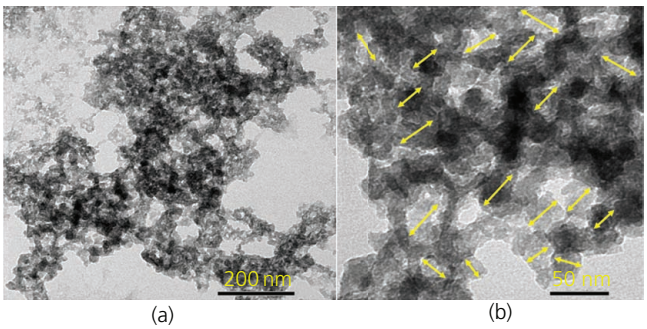

Figure 6. TEM micrographs of the spherical silica nanoparticles after annealing at 500°C for 2 h; scale bars of (a) 200 and (b) 50 nm

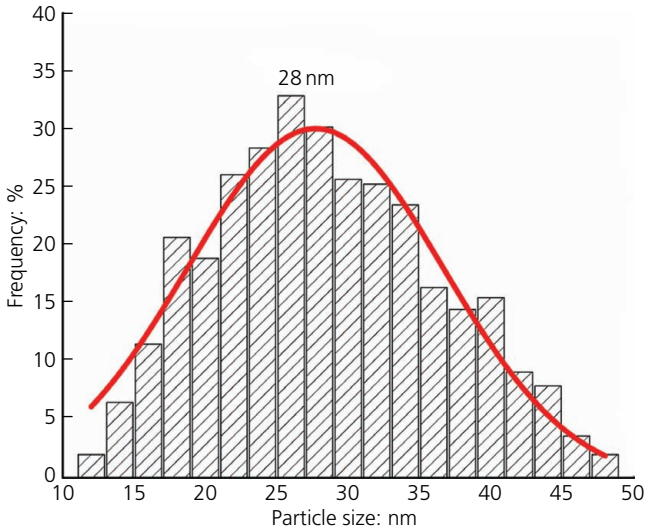

Figure 7. Particle size distribution of silica nanoparticles after annealing at 500°C for 2 h

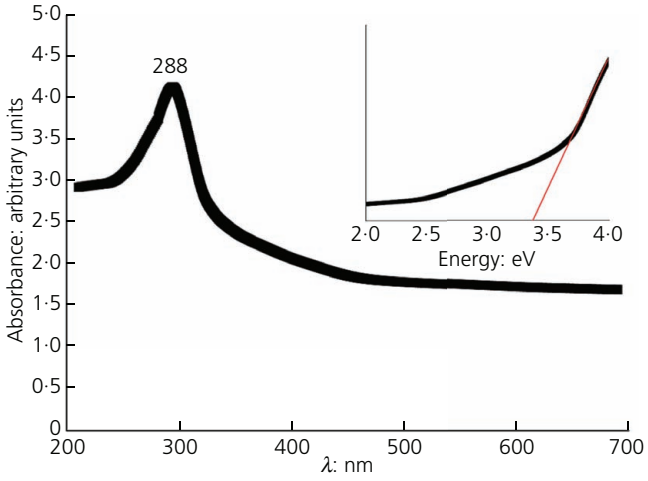

Figure 8. UV–Vis absorption spectra of silica nanoparticles at 500°C

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