Synthesis and characterization of SiO$_2$ nanoparticles by sol-gel process

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Received 10 September; accepted 23 September; published online 01 November; printed 16 November 2012

ABSTRACT

Preparation and characterization of silica (SiO$_2$) nanoparticles via sol-gel process using tetra ethyl ortho silicate (TEOS) and glycolic acid as a precursor are reported here. The effect of mixing modes of the reactants and hence the optimal synthesis conditions for the preparation of silica nanoparticles were investigated. The synthesized SiO$_2$ nanoparticles were characterized by XRD, UV-Visible spectroscopy, Fourier Transform Infrared spectroscopy (FTIR), Thermo gravimetric, Fluorescence analysis, FESEM and SEM analysis.

Keywords: Sol-gel, Nanostructured materials, X-ray diffraction, SEM, ultrasound.

1. INTRODUCTION

Nanoparticles have been extensively investigated during the last few decades owing to their unique properties and potential applications in different fields including opto-electronics, catalysis, medicine, recording media, sensor devices, metals and ceramics and etc. [1, 2]. Among the metal oxide nanostructures, SiO$_2$ has specific chemical and physical properties that make it an attractive material for various applications such as polishing silicon wafers, the substrates of computer chips or solar cells and for cleaning purpose in electron industry [3]. The highly ordered SiO$_2$ suggested its scientific and technological importance as a new shape-selective catalyst, adsorbent, sensor, and electrode material [4, 5].

Generally, the physical methods of nanoparticle synthesis have a few inherent disadvantages which cannot prepare nanoparticles having controlled size distribution. Sol gel method is an attractive and often used method for nanoparticle synthesis since this method permits tailoring of certain desired structural characteristics such as homogeneity, purity, grain size, particle morphology and porosity [6, 7, 8]. It involves evolution of an inorganic network known as a sol from certain precursor materials and the consequent gelation of this inorganic network to form an ordered three dimensional gel structure. The next step in the process is the destruction of the evolved gel thus resulting in the formation of nanocrystalline material. Modification of material properties by changing synthesis parameters is the great advantage of this technique [9, 10].

The Stober method was first introduced using ammonia catalysed hydrolysis and condensation of ethoxy silanes in low molecular weight alcohols as solvent to produce uniform silica particles [11]. Bogush and Zukoski [12] obtained monodispersed silica particles sizes ranging from 40 nm to few micrometers using modified Stober method. It has been reported that the concentration of ammonia, water and the types of solvent and reaction temperature were the main parameters which governs the particle size and its distribution. Also it was found that sol gel process was highly dependent on mixing modes of the reactants and drying technique [13]. Hence in our present work, we have proposed to synthesize SiO$_2$ nanoparticles by economic sol-gel process following two different mixing modes of the reactants and studying its effect on powder distribution.

2. EXPERIMENTAL

Most sol-gel synthesis of silica are based on the hydrolysis of tetraalkoxysilanes, Si(OR)$_4$, according to the following equation

$$\text{Si(OR)}_4 + 2\text{H}_2\text{O} \xrightarrow{\text{Catalyst}} \text{SiO}_2 + 4\text{R} \cdot \text{OH}$$

(1)

Where R is an alkyl group.

The hydrolysis rate of TEOS depends on the concentration of water and ammonia (catalyst). With increasing concentration of ammonia in the system, water dissociate according to the eqn (1), producing high amount of hydroxyl ions which attack Si atoms and increase the rate of hydrolysis while the equilibrium between hydrolysis of TEOS and condensation is controlled by amount of water and ammonia. In the present study Tetraethyloxysilicate (TEOS-SiC$_2$H$_5$O, Ottokemi, India), glycolic acid (C$_2$H$_4$O$_2$, Ottokemi), ammonia and (NH$_3$, 25%, Spectrum, India) were used as the raw materials. The chemicals were employed without further purification. Doubly distilled water was used.

2.1. Synthesis of nanosilica at different mixing modes of the reactants

The synthesis of SiO$_2$ was followed by the simple procedure has been given below. Two different mixing modes of the reactants namely mode-A & mode-B was followed.

2.1.1. Mode A

In mode A, 5 ml of TEOS and 5 ml glycolic acid were taken in a 250 ml beaker and ultrasonicated for 10 min. Then 1 ml of double distilled water was added drop wise.

2.1.2. Mode B

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http://www.discovery.org.in/ijjs.htm

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In mode B, 5 ml of TEOS, 5 ml glycolic acid and 1 ml of double distilled water was added altogether. Both the reactant mixture of mode-A and mode-B, 2 ml of ammonia (25% aqu.) was added dropwise at a feedrate of 0.01mL/min and was subjected to sonication for 90 minutes. After the formation of colloidal solution attained by sonication for 3 hours, it was allowed for gelation and aging (1 hour). The conventional heating was carried out for 24 hours followed by calcination at 600°C for 2 hours. The obtained powder sample has been collected, weighted and stored in a zip log cover.

2.2. Characterization of the sample
From the UV-absorption spectrum, the direct and indirect band gaps were calculated for both the synthesized samples. The direct and indirect band gap of the materials obeys the following relation respectively,

Direct band gap: \((\alpha h\nu) = A (E_g - h\nu)\)

Indirect band gap: \((\alpha h\nu)^{1/2} = A (E_g - h\nu)\)

where \(\alpha\) is absorption coefficient, \(E_g\) is the optical band gap of the material, \(A\) is a constant, \(h\) is Planck’s constant and \(\nu\) is the frequency.

In Fluorescence analysis, the band gap of silica nanoparticles was calculated using the formula:

\[ E = \frac{hc}{\lambda_{max}} \]

Where \(h\) is planck's constant, \(c\) is velocity of light, \(\lambda_{max}\) is the value of Peak wavelength.

3. RESULTS AND DISCUSSION

3.1. FTIR Spectroscopy
FTIR spectra of SiO\(_2\) nanoparticles synthesized by using two different modes A and B are shown in Fig 1a and Fig 1b respectively. Both spectra show the peaks corresponding to stretching vibration of OH by adsorbed water molecule at 3466 cm\(^{-1}\). The band appeared near 1633 cm\(^{-1}\) corresponds to \(C=O\) vibrations \[14\]. Three bands at 472 cm\(^{-1}\), 798 cm\(^{-1}\), and 1111 cm\(^{-1}\) dominate the spectra for silica sample which attributed to stretching and bending vibration of silicon and oxygen. Peak at 1111 cm\(^{-1}\) corresponds to asymmetric vibrations of O-Si-O, 798 cm\(^{-1}\) is ascribed to symmetric stretching vibrations of O-Si-O and the peak at 472 cm\(^{-1}\) corresponds to bending vibrations of silica \[15\].

3.2. UV-Visible Spectroscopy
To investigate the optical absorption properties of SiO\(_2\) nanomaterials, the UV-Vis study was carried out (Fig. 2, 3). The UV cut off wavelength is found at 330 nm. From the UV-absorption spectrum, the direct and indirect band gaps were calculated for both the synthesized samples. The optical band gap of the samples has been calculated from the energy \((h\nu)\) versus \((\alpha h\nu)^2\) plot shown in Fig. 2, 3. The direct and indirect band gaps for the synthesized SiO\(_2\) by mode A are found to be 4.0 eV and 3.4 eV respectively. Similarly the direct and indirect band gaps for the synthesized SiO\(_2\) by mode B are found to be 3.8 eV and 3.6 eV respectively. The observed wide value of band gap reveals the large transmittance in the visible region than that in the UV-region \[14\]. This is in accordance with the result of Suloit Pradhan., et al., \[15\] report. This wide band gap value makes it suitable for its application in electronic
industries, substrates of computer chips and solar cells [4, 5].

3.3. Fluorescence Analysis

Fig. 4 shows the excitation and emission spectra of SiO$_2$ nanoparticles. Fluorescence spectra for silica nanoparticles were recorded using the excitation peak at 281nm. A sharp emission band was observed with a maximum intensity at 337 nm. Unlike organic nanoparticles or Quantum Dots, [16] the emission properties of the silica nanoparticles are virtually size independent [17, 18]. The respective emission peak was found at about 337.5 nm which was red shifted from the excitation peak. Using the above formula (4), the band gap value was found to be 3.6 eV for synthesized silica sample. This result is coincidence with the uv-visible spectra band gap. Due to the wide band gap value it also applicable for electronic industries, substrates of computer chips and solar cells [4]. The fluorescence quantum efficiency of SiO$_2$ nanoparticles was 0.78, which was measured by excitation of the corresponding solution and compared with the emission [19].

3.4. Scanning electron microscopy

Scanning electron microscope image was done to study the morphology and particles of the prepared SiO$_2$ samples of mode A (Fig. 5a) and mode B (Fig. 5b) respectively. SEM micrographs (Fig. 5) reveal that the particles are spherical in shape. In mode A mixing method the small particles have been agglomerated and the particles were slightly bigger in size. However such agglomeration has been absent in mode B mixing. The average particle size of mode A sample is 78.48 nm and mode B is 84.71 nm. Despite agglomeration in mode A prepared sample, it can be observed that this sample has smaller particle size than that of mode B prepared sample [20]. Hence mode B is effective method due to less agglomeration which produces more surface area. This is because glycolic acid interface helps to establish an effective contact between TEOS and water. This reveals that effective homogeneity of precursor in the solvent at the initial stage is very critical factor in sol-gel process. In the present study, mode B is a better procedure for the preparation of mono dispersed silica nanoparticles.
Results and Discussion

3.5. XRD analysis

Fig. 7a and 7b show the X-ray diffraction pattern of SiO$_2$ nanoparticle synthesized by mode A and B respectively. Well defined sharp peaks clearly revealed the high crystallinity of the prepared sample. The dominant diffraction peaks observed at 27.97, 31.84, 45.58, 57.63, 68.86 and 76.81° [JCPDS file # 89-3436, 89-3609, 89-3608] confirms the formation of high purity SiO$_2$ sample. The particle size calculated for SiO$_2$ sample (Table 1) obtained from both modes using Debye Scherrer’s formula is in the range of 39 nm and 38 nm respectively. This is in close agreement with the SEM result.

Table 1 Particle size of SiO$_2$ nanoparticles

<table>
<thead>
<tr>
<th>Obs. Max</th>
<th>Max Int. (a.u.)</th>
<th>FWHM (degree)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.97</td>
<td>419</td>
<td>0.2007</td>
<td>40.36</td>
</tr>
<tr>
<td>31.84</td>
<td>4413</td>
<td>0.2175</td>
<td>37.58</td>
</tr>
<tr>
<td>45.58</td>
<td>2288</td>
<td>0.2175</td>
<td>39.19</td>
</tr>
<tr>
<td>57.63</td>
<td>526</td>
<td>0.2175</td>
<td>41.23</td>
</tr>
<tr>
<td>68.86</td>
<td>221</td>
<td>0.2676</td>
<td>35.60</td>
</tr>
<tr>
<td>76.81</td>
<td>456</td>
<td>0.2040</td>
<td>49.15</td>
</tr>
</tbody>
</table>

FESEM micrograph also shows that the particles are in nanometer range. Fig. 6 shows the FESEM images of SiO$_2$ nanoparticles. From the FESEM photographs it has been found that the spherical shape in the range of 40–50 nm. This result of particle size was accordance with the XRD results. However, homogeneous and uniform distribution of nanoparticles was observed on the surface of SiO$_2$ nanoparticles [21].

3.6. TGA Analysis

TGA analysis (Fig. 8) showed an initial loss around 100°C which is related to loss of physically adsorbed water [22]. Graph indicates a gradual mass loss of silica nanoparticles around 5 wt% as the temperature reaches 700°C. Some of the weight loss of the silica nano particles is due to the continued
condensation reaction and associated water loss [23]. From the thermo gram result it has been observed that the prepared silica nanoparticle was thermally more stable since the residue remained was about 95% at 700°C.

4. CONCLUSION

Silica nanoparticles have been synthesized by sol gel process using two different mixing modes of the reactants. XRD revealed the formation of high purity sample. The crystallite size was found to be of nanometer range. FTIR shows three dominant peaks corresponding to the O-Si-O symmetric & asymmetric stretching and bending vibrations of silicon. UV – Vis spectra shows wide band gap value of the prepared sample which makes it suitable for its application in electronic industries. TG thermogram results revealed high the thermal stability. The Particles size was found to be in the range of nanometer by SEM micrographs. The prepared sample finds potential applications in many fields such as controlled release application, sensor devices and catalysis and dielectric materials.

ACKNOWLEDGEMENT

The authors acknowledge Kamaraj College of Engineering and Technology Managing Board for providing the Research fund to pursue this work.

REFERENCES