

# Effect of Environments on Optical Properties of Chemically Prepared Si Nanoparticles

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Silicon (Si) nanoparticles were synthesized by chemical etching process at ambient temperature. Field emission transmission electron microscopy (FE-TEM), Fourier transforms infrared spectroscopy (FTIR), UV/Vis absorption and photoluminescence (PL) spectroscopic techniques were employed to examine the morphological structure and optical features of the synthesized Si nanoparticles. Effect of solvent and temperature on optical properties of Si nanoparticles is presented. We believe that at physiological pH Si nanoparticles have charged surface, because of high solubility in organic solvents. Experimental results show that the Si nanoparticles are a good biocompatible, non-agglomerated, homogeneously well distributed and highly dispersible in organic solvents. The emission and absorption properties of Si nanoparticles were tuned by altering the environment (solvents) through electrostatic interaction of various organic solvents with the Si nanoparticles. The band shapes of the Si nanoparticles show remarkable changes on passing from non-coordinating solvent (chloroform) to various coordinating solvents which is the result of change in the environment around Si nanoparticles in the various solutions and suggests coordination of solvent molecule(s), in some cases. The results clearly show that among the solvents studied DMSO is the most effective in promoting the efficient emission intensity.

**KEYWORDS:** Si Nanoparticles, Effect of Solvents, UV/Vis Spectra, Photoluminescence Spectra.

## 1. INTRODUCTION

Nanotechnologies are now poised to revolutionize the electronic, chemical and biotechnology industries and biomedical fields.<sup>1,2</sup> There are many interesting areas in nanotechnology such as materials science, optoelectronics and biomedical sciences.<sup>1</sup> One of the most important aspects of this field is the preparation and development of nanomaterials, such as luminescent metal nanoparticles for biological applications.<sup>3</sup> There have been a variety of techniques for preparing different types of nanoparticles.<sup>1</sup> Presently, Si nanoparticles have been the focus of intense research because of their unique chemical and optical characteristics.<sup>1,4</sup> The electronic structure of bulk Si provides an indirect band gap of 1.12 eV, with the lowest point of the conduction band and the highest point of the valence band occurring at different coordinates in reciprocal space.<sup>1</sup> This makes the band gap optical transition dipole-forbidden and limits practical optoelectronic application of bulk Si because of low photoluminescence

intensity and slow carrier dynamics (i.e., long-lived excited states). As the dimensions of a semiconductor particle approach the radius of an exciton in the bulk material (ca. 5 nm for Si), the band gap energy increases and pseudo-continuous bands become discrete energy levels that are populated according to quantum mechanical selection rules. Consequently, quantum confinement effects emerge and photoluminescence blue shifts with decreasing particle size and increases in intensity.<sup>1,4</sup> Some researchers suggest that the photoluminescence (PL) observed from photo-excited Si nanoparticles arises because the band gap transition becomes weakly dipole-allowed in this quantum confined size regime.<sup>5</sup> Others claim photo-emission originates from the passivation of surface traps present in bulk Si.<sup>6</sup> Regardless of the explanation, a characteristic photoemission maximum at approximately 1.7 eV is seen for many Si-based nanostructures, including the “Si quantum wires” reported by Canham,<sup>7</sup> nanocrystalline *nc*-Si/SiO<sub>2</sub> composites,<sup>1</sup> and freestanding Si nanoparticles prepared via solution,<sup>8–10</sup> precursor pyrolysis,<sup>11,12</sup> and physical techniques.<sup>13–15</sup> The unique optical properties and electrochemical stability<sup>16</sup> of nanoscale elemental Si offer significant potential for a variety of light emission applications. Furthermore, the biocompatibility of Si potentially useful in sensing applications where

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toxic,<sup>17</sup> electrochemically active compound semiconductor nanoparticles are impractical.

On the other hand, the uses of optical absorption and emission spectra are widely applied techniques to monitor changes in the environment of Si ion.<sup>4</sup> Normally Si nanoparticles exhibited well-defined broad absorption band in the middle of visible region.<sup>18</sup> Upon complexation this absorption band may be shifted towards higher wavelength (lower energy) with enhanced sensitivity. The intensity of certain transitions enhanced too many folds, when compared with the spectrum measured in non-coordinating solvent, and oscillator strength of these transitions exhibits especially strong sensitivity to the structural details and chemical nature of the solvent environment.<sup>19</sup> Furthermore, the spectral changes observed on the binding of solvent with Si nanoparticles prove to be an important tool for the investigation of the topology of binding sites, conformational changes and characterization of solvent to Si ion binding. A significant enhancement in intensity and band shape demonstrated change in symmetry of Si ions due to the possibility of solvent coordination behavior, which alter the optical properties of the Si ion in solvent environment.<sup>19, 20</sup>

Here, we discussed the effect of environment (solvent and temperature) on the optical properties of Si nanoparticles. The monodispersed Si nanoparticles ranging from 1.5–3.7 nm have been synthesized by chemical etching process. Optical properties of the Si nanoparticle are measured in different solution media to optimize its chemical and thermal stability at various temperatures in different solvents, which is suspended in proper solutions such as (Chloroform, THF, 2-Propanol and DMSO). It is also interesting to compare environment (solvent and temperature) behavior on optical properties of Si nanoparticles in various solvents at different temperatures. Furthermore, we demonstrate that the spectral response from Si nanoparticles correctly determines relative binding affinities with different solvents.

## 2. EXPERIMENTAL DETAILS

### 2.1. Materials

Si wafers, hydrofluoric acid (HF), tetrahydrofuran (THF), 2-propanol, dimethyl-sulphoxide, chloroform, methanol and hydrogen-peroxide ( $H_2O_2$ ) were used as starting materials without any further purification. Ultrapure de-ionized water was prepared using a Milli-Q system (Millipore, Bedford, MA, USA). All other chemicals used were of reagent grade.

### 2.2. Synthesis

Si nanoparticles were produced by chemical etching of B-doped 100 Si wafers.<sup>15</sup> In a typical process,  $1 \times 3$  cm dimension pieces of Si wafer were used for the synthesis of Si nanoparticles preparation. We treat the wafer in a

mixture of HF and hexachloroplatinic ( $H_2PtCl_6 \cdot H_2O$ ) acid to deposit a platinum catalyst. It is then etched using HF/ $H_2O_2$ /methanol mixture, followed by sonication. During the etching bubbling will start on the surface of Si wafer. It is one round complete etching procedure for preparation of Si nanoparticles. We applied several rounds for etching on the same wafer. The obtained Si solution can be used for further characterization. When examined the solution is found to be brightly red-orange luminescent under 365 nm irradiation with band head at  $\sim 610$  nm.

### 2.3. Characterization

The size and morphology of the samples were inspected using a field emission transmission electron microscope (FETEM, JEM-2100F, JEOL, Japan) by operating at an accelerating voltage of 200 kV. Samples for TEM were prepared by depositing a drop of a colloidal ethanol solution onto a carbon coated copper grid. The FTIR spectra were recorded on a Perkin-Elmer 580B IR spectrometer using KBr pellet technique in the range of 4000–400  $cm^{-1}$ . The UV/Vis absorption spectra were measured using a Perkin-Elmer Lambda-40 spectrophotometer, with the sample contained in 1  $cm^3$  stoppered quartz cell of 1 cm path length, in the range of 190–600 nm. The fluorescence spectra of Si nanoparticle which was suspended in equivalent molar solutions such as (THF, DMSO, chloroform, 2-propanol) were recorded on a Perkin-Elmer photoluminescence spectrophotometer equipped with a 150-W Xenon lamp as the excitation source.

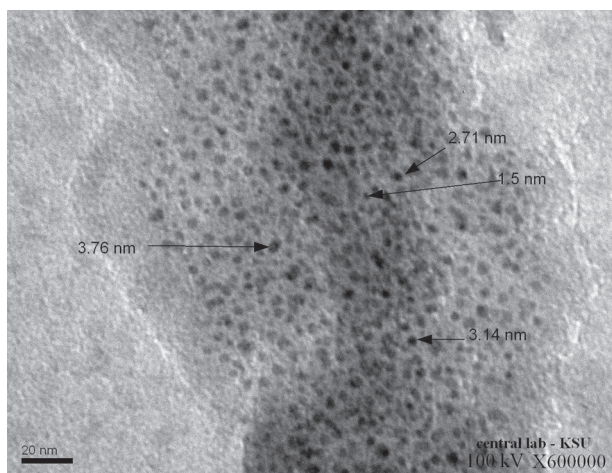
## 3. RESULTS AND DISCUSSION

### 3.1. Morphology of Si Nanoparticles

FE-TEM images were used to investigate the surface morphology and determine the mean crystalline size of the Si nanoparticles. FE-TEM observations provide an overall view on a wide area ensuring that no large particles have been produced. As shows in TEM image, a drop of Si nanoparticle suspended in THF solvent was drop-casted on carbon-coated Cu TEM grid (Fig. 1). The TEM images of the as-prepared samples clearly indicate a well-dispersed, non-aggregated and irregular shaped nanoparticle with narrow size distribution. Moreover, the surface of the nanoparticles is quite rough, highly porous and hairy as apparently observed in the TEM images. We could suggest the high disperse-ability of the Si nanoparticles in organic solvents. These particles are nearly spherical and classify into a small number of sizes with an average diameter 1.5–3.7 nm.

### 3.2. FT-Infrared Spectra of Si Nanoparticles

FTIR spectroscopy was applied to examine the surface chemistry of the prepared fluorescent Si nanoparticles.

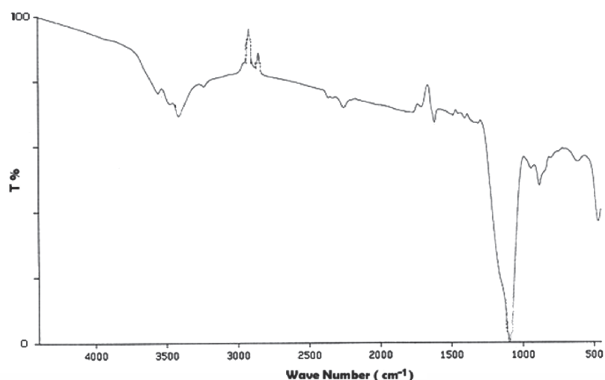


**Fig. 1.** TEM images of Si nanoparticle suspended in THF.

As illustrated in Figure 2, a broad band with low intensity at  $3411\text{ cm}^{-1}$  is observed, which is attributed to the presence of O—H and Si—OH molecules, respectively on the surface of nanoparticles.<sup>21</sup> The spectrum exhibited strong infrared absorption band around  $1095\text{ cm}^{-1}$  originates from the Si—O—Si asymmetric and symmetric stretching. The band at  $892\text{ cm}^{-1}$  is assigned to the Si—OH stretching. An intense sharp band at  $469\text{ cm}^{-1}$  is attributed to the Si—O stretching vibration mode.<sup>21</sup> Furthermore, the intensity and broadening of the bands indicated that a large number of Si—OH molecules present on the surface, which play an important role including biocompatibility in biological systems, functionality and high colloidal stability under different conditions.

### 3.3. Solvent Effect on Optical Absorption Spectra of Si Nanoparticle in Different Solvents

Optical absorption spectroscopy was employed to investigate the optical properties of the synthesized Si nanoparticles in visible region (200–600 nm) with different solutions at room temperature. Figure 3 represents the absorption spectra of the as-prepared samples (a) in chloroform (b) tetrahydrofuran (c) 2-propanol and

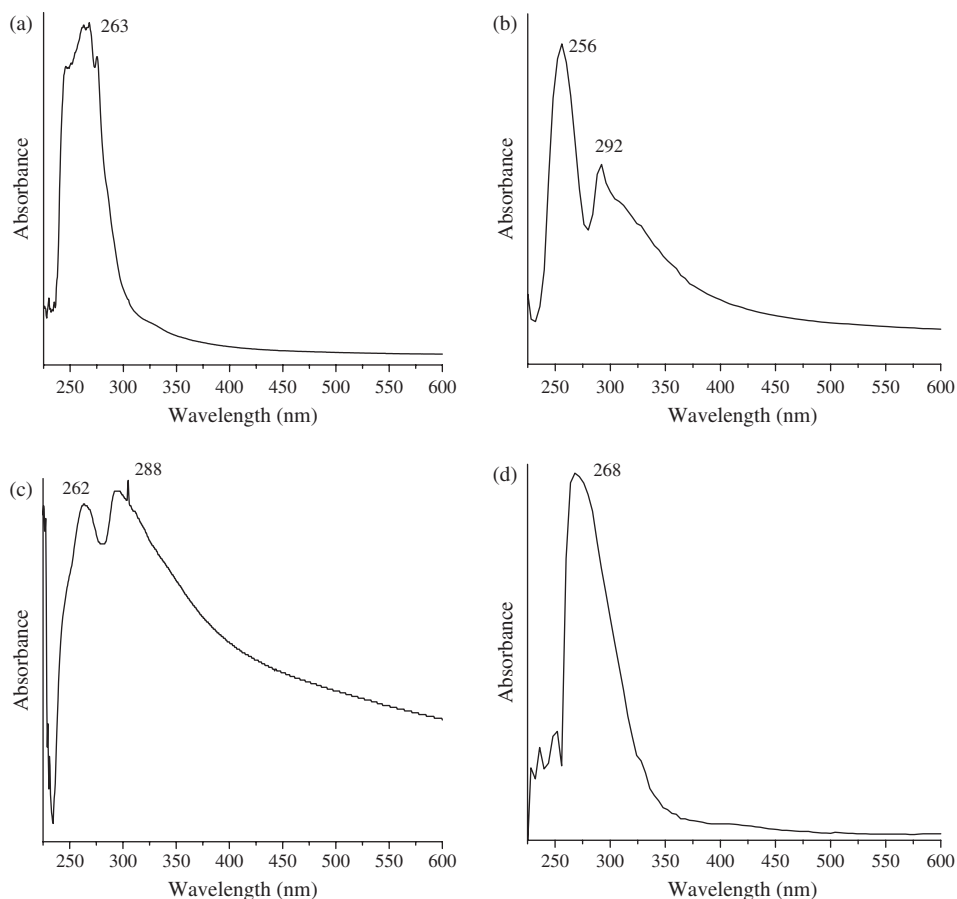


**Fig. 2.** FTIR spectra of Si nanoparticles.

(d) dimethyl-sulphoxide. Dissolving the nanoparticles in any of the solvents, a marked sensitivity in the band shapes is observed. When the Si nanoparticles are dispersed in chloroform a strong band located centered in the UV region at 263 nm is observed (Fig 3(a)). On measuring the absorption spectrum in THF, this transition is broaden and splitted into two with maxima at 256 and 292 nm, which are may be due to the crystal field effect (Fig 3(b)). The spectrum measured in 2-propanol shows a remarkable change in band shape that is red shifted (lower energy). On comparing the spectra in different solvents a remarkable changes in band shapes of the transitions also observed. It indicates the effect of solvent on the optical character of the small size Si nanoparticles. It is concluded that, the changes in band shapes offer some measure of the relative coordinating ability (complexation) of the solvent to the Si nanoparticles.<sup>19,20</sup> Moreover, the very small difference could be related to different nature of the solvents.<sup>20</sup> Similar spectrum results are observed in Figure 3(d), a shift of the threshold toward shorter wavelengths is observed after dispersed the Si nanoparticles in DMSO. The band shapes of the transitions display remarkable difference in DMSO, which is the result of coordination of DMSO to the Si nanoparticles. We measured the effect of solvent (DMSO) elsewhere on optical properties of inorganic metal ions.<sup>20</sup> The DMSO coordination is also reflected by appearance of dissimilar band shapes shift of the bands in the sol form in respect to solid state.

### 3.4. Solvent Effect on Fluorescence Spectra of Si Nanoparticle in Different Solvents

Photoluminescence properties of Si nanoparticles were also investigated in different media by measuring the excitation and emission spectra of the sample, when excited at various wavelengths (a) in chloroform (b) THF (c) 2-propanol and (d) DMSO as shown in Figure 4. The Si nanoparticles shows broad emission band in all measured solvent environments, but the variations of band intensity, width and position were found for different solvents over the applied range of excitation wavelength. Comparison of luminescence spectral results for various media provides an assessment of solvent binding at the Si nanoparticles. Addition of Si nanoparticles in different media reveals differential increments in the intensity and band shapes of their emission band. As shown in Figure 4(a) the emission spectrum of Si nanoparticles in chloroform exhibits a diffused band with a weak intensity ranging from 500 to 688 nm peaking at 580 nm. The intensity of the emission band in THF is much better as compared to chloroform, which could be due to the covalent interaction of solvent with Si nanoparticles. The emission spectrum of the Si nanoparticles in chloroform is low with low intensity which could be the reason for inconsistent behavior to sample. The emission band intensity is dramatically



**Fig. 3.** Optical absorption spectra of Si nanoparticles in different solvents (a) chloroform (b) THF (c) 2-propanol and (d) DMSO.

decreased, and peak shifts towards lower wavelength in the emission spectra measured in 2-propanol as compare to chloroform (Fig. 4(c)). The emission band intensity is most affected in DMSO, which is may be dependence on the solvent environment. The DMSO makes some new chemical bonding with Si nanoparticles due to the availability of high Gutmann donor number of DMSO solvent.<sup>19,20</sup> Therefore, the intensity and band shape of the spectrum is most affected in this solvent. The change in band shape with a change in the solvent offers some measure of the relative coordinating ability of the solvents. Chloroform is a non-coordinating solvent and the bands shape of Si nanoparticles, in this solvent, may be used as the standard (that is the bands shape arising in a non-coordinating solvent) for comparison purposes with the band shape in other solvents for the Si nanoparticles.<sup>20</sup> The bands shape of Si band in different solvents is distinctively different when compared with the bands shape in chloroform. Appearance of different bands shape demonstrates a change in the environment about the  $\text{Si}^{4+}$  ion, which could be due to coordination of solvent. The shape of the bands in THF, 2-propanol and DMSO show close similarities, although they are not super imposable. On the ground of polar nature of THF, THF is a coordinating solvent and similarities in the bands shape in 2-propanol and DMSO with

the band shape in THF, it has been concluded that these are coordinating solvents. The very small difference could be related to different nature of the solvents. On the other hand, when we excite the material at different wavelengths a regular quenching are observed in the band intensity and shape of the band as seen in the Figure 4. Our results indicate that the solvents interacted with metal centers ( $\text{Si}^{4+}$ ), which is the basic reason for the high luminescence performance of Si nanoparticles in coordinated solvents.

### 3.5. Temperature Effect on Fluorescence Spectra of Si Nanoparticle at Different Temperature

Figures 5(a)–(d) shows the results of temperature effect on fluorescence spectra in different solvents at various temperatures from 25–100 °C under excitation wavelength of 365 nm. As seen in Figure 5, the band shape and intensity is regularly decreases as the temperature is increases in all measured solvents. The quenching in intensity of the band indicates some crystalline defect in the metal nanoparticles.<sup>22</sup> Similar trend is found in all four solvent spectra measured at various temperatures. Owing to the various impurities introduced into the Si network, such as C, H, or excess O, defect excited states are generated during the etching process and also solution medium, and the

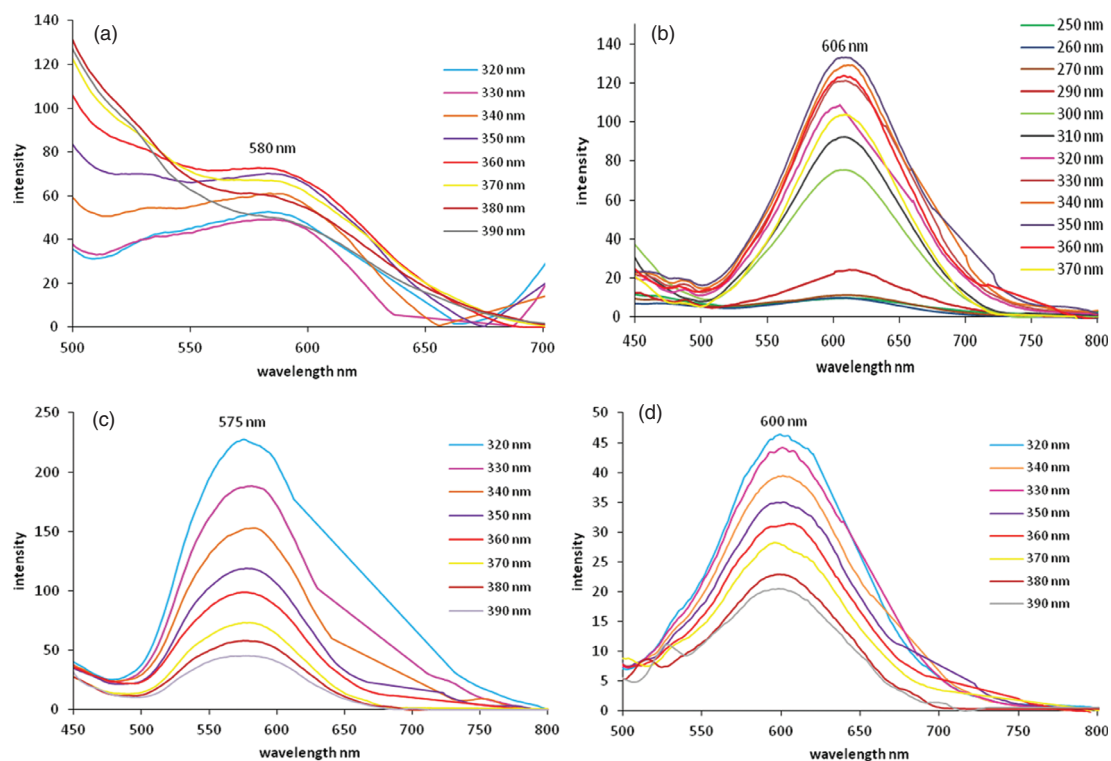


Fig. 4. Fluorescence of Si nanoparticle in (a) Chloroform (b) THF (c) 2-propanol and (d) DMSO.

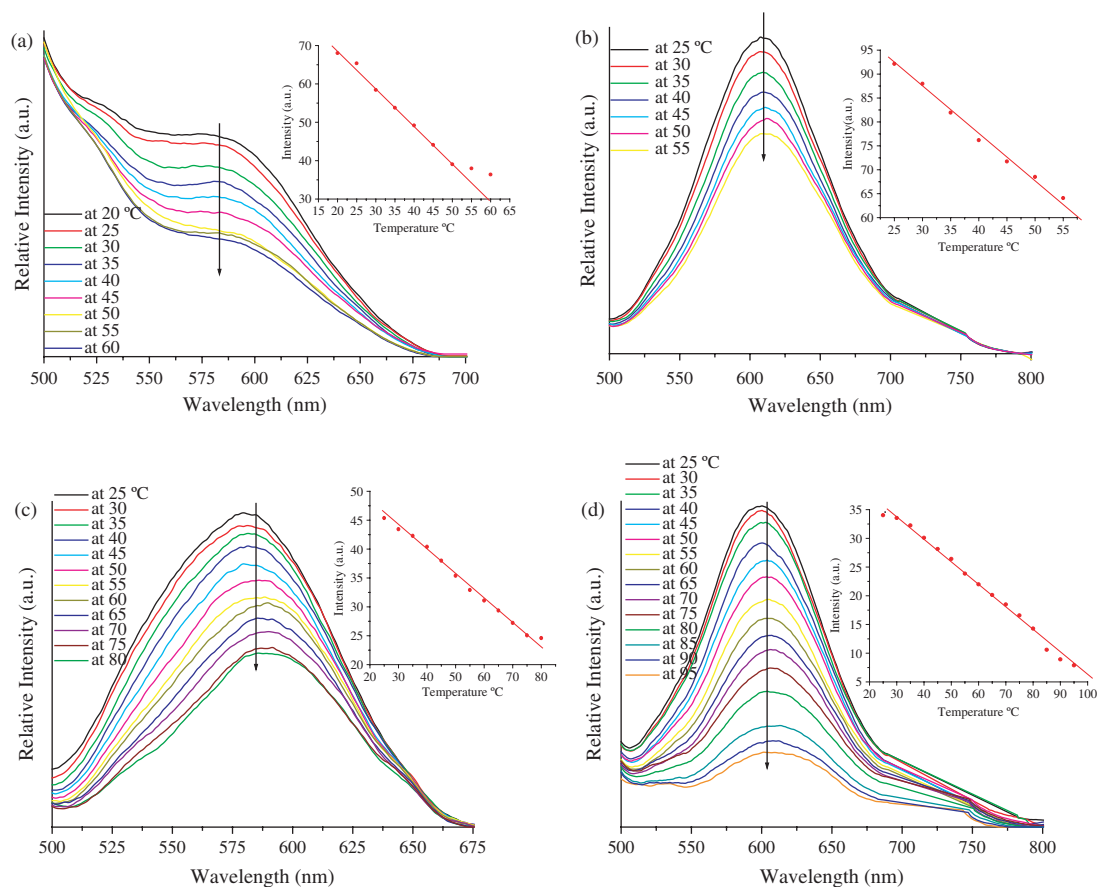


Fig. 5. Fluorescence spectra of Si nanoparticles in (a) Chloroform (b) THF (c) 2-propanol and (d) DMSO at different temperature.

band gap can be decreased, which makes the close interaction with visible light possible. Thus, at higher temperature led to more loss of C, H, and O until a percentage close to zero was reached.<sup>23</sup> The presence of chemical groups with electron donating ability within the light-generating nanoparticles, such as amine groups, will therefore be a favorable factor for making efficient photoluminescent particles. Based on this evidence, it is reasonable to assume that the Si nanoparticles photoluminescence emission can be obtained when C- and/or OH-based species are introduced into the Si nanoparticles. When these impurities in organo-silane network will heat-treated at various temperatures, the changes in the molecular structure and the surrounding environment may result in different electronic transitions, causing, in turn, the different optical properties exhibited by the nanoparticles.<sup>22,23</sup> The lack of luminescence in Si nanoparticles heated at 55 °C could then be attributed to the degradation of the organic (carbon centers) impurities into the silica matrix, leading to the suppression of the photoluminescence properties. We believe that further clarification of the conditions for the luminescence emission will lead to the production of Si nanoparticles with even greater efficiency in visible light emission.

#### 4. CONCLUSION

This work is still in progress and influence of laser radiation and heat treatment effect at room temperature on emission properties of Si nanoparticles are under investigation. Influence of solvents and temperature on the optical absorption spectra and luminescence spectra are discussed in this study. Consequently, the above optical absorption spectral result provides clear evidences of the solvent coordination behavior with the Si nanoparticles and their augmentation in intensity and shape of the band. Therefore, the geometrical structure of the Si ion is changed after coordination with solvents at high temperature. On optimizing the PL spectra at high temperature Si loss the various impurities such as C, H or excess O, and the band gap are decreases, which makes weak interaction with the Si nanoparticles. This kind of study is useful to find out the solvent and temperature effect on luminescent material

in the solution medium for material sciences as well as biological sciences.

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