# Influence on structural and PL property of nanocrystals silicon doped sol gel matrix

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Photoluminescence and structural property of nanocrystallines silicon (NCs) doped sol gel were studied. The energy band gap of NCs in colloidal form and dried sol gel was determined. Influence on photoluminescence and energy band property of NCs due to the physical of sol gel host was observed. Significant stability on luminescence peak was observed for several weeks at room temperature. Thermal effect on PL intensity and bandwidth of NCs doped sol gel at $100^0$C are discussed. Morphology revealed that distribution of NCs throughout sol gel solid. The NCs silicon was mono dispersive and high crystalline nature with spherical shape of around 5 to 8nm in sizes.

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## 1. Introduction

Silicon based nanocrystallines/ nanoporous are some new photoelectronic and informational materials developed rapidly in recent years. For a long time silicon has been considered unsuitable for optoelectronic applications because bulk silicon emits hardly any useful light due to its indirect band gap nature [1]. This opinion was deeply changed after the discovery of bright emission from porous silicon and nanocrystals. The possibility of constructing optoelectronic devices, Si based integrated circuits [2] has generated tremendous interest in the preparation and characterization of light emitting silicon nanoparticles since its photoluminescence was observed first time by Canham in 1990 [3]. Although first porous silicon layer had been observed by Ulrich in 1956 [4] and later by Turner but only Canham reported about room temperature luminescence beginning significant interest in this material [5]. Due to the luminescence properties of Si nanoparticles are size dependent, multi colors which have exciting potential applications as fluorescent tags for biological imaging [6-8] and a great variety of nanoparticles are currently used for bioanalysis including quantum dots [9]. The redox behavior of silicon nanoparticles in colloidal form was studied with addition of noble metal salt for applications in pollution [10]. Silicon nanoparticles are much brighter and more stable to photobleaching [11-12] than the organic dyes [13] with broader excitation spectra, so that emission at multiple wavelengths (from particles of different sizes) can be excited by a single source. Moreover, the use of nanoporous silicon/nanocrystals as an active medium for light emitting devices (LEDs or injection laser) remains an open issue for basic research, even if for various applications in waveguides, photodetectors, solar cells, gas sensors etc. [14 -16]. One of the most challenging goals is to achieve optical gain and/ or lasing in silicon for optoelectronic circuits because the key device is the light source-laser. The basic problem of optical gain and lasing in silicon, based on carrier recombination across the band gap, has not been fully cleared and solved yet [17]. In view of these, several workers approached toward the silicon nanocrystals (Si-NC) embedded in an insulator matrix, usually $SiO_2$ matrix [18-20] because of their photoemission properties and is believed that the interface between the Si-NC and the oxide matrix plays a crucial role of controlling the optoelectronic properties. Role of the interface between NPsi/$SiO_2$ has recently been reported [21]. Still, one of the promising techniques to form such a Si-NC structure is the implementation of silicon ions into a $SiO_2$ matrix followed by thermal annealing [22-24]. But silicon based nanocrystals with strong light emission prepared at low temperature in a host matrix with a smallest band gap is highly desirable. Recently the direct encapsulation of nc-Si/Psi-derived nanoparticles in sol gel was successfully employed in order to maintain the PL intensity reported [25-27].

Moreover, demonstration of Psi /Si NCs in sol gel is easily manageable that enable the fabrication of samples with high densities of silicon nanoparticles for optoelectronics purposes. However, up to now, limited study on encapsulations of silicon derived nanopart icles in low temperature matrix such as sol gel matrix; polymer is appeared in the literature. Due to greatly important to thermal and optical stability of porous silicon/NCs-Si within sol gel matrix, our group studied on the characteristics of luminescent NCs and NPs in sol gel matrix [28, 29]. In that studies, characteristics of NCs doped sol gel host prepared at room temperature was found optically stable for about 60 days. In continuation of the previous work, we investigated the effect on structure and PL of NCs doped sol gel due to heat at $100^0$C and 8 month latter of sample.

## 2. Experimental details

High pure silicon nanocystallines (NCs) powder was obtained from MKnano Canada, (98% -purity). These silicon nanocystallines were dispersed in DMSO solvent about .35gm/l. The Si nanocystallines colloidal solution was then incorporated in sol gel derived host. The detail procedure reported elsewhere [28, 29]. Briefly, TEOS (Aldrich, 98%) was used as starting material with ethanol (Riedel-deHaen), which hydrolysed about 30 minutes. DMF and DMSO were used as a drying chemical control additive (DCCA) in the process. The mixture of $HNO_3$ and $H_2O$ was taken as catalyst. The molar ratio of the compositions was TEOS: EtOH: DMF: DMSO: $HNO_3$: $H_2O$: = 1: 1.5: .75: .3: .75: .1. The final sol was obtained after 1 and half hr stirring in an open glass beaker. Subsequently, the sol was poured into some polysterene test tubes and quartz cuvettes for aging at room temperature. The Si NCs doped sol solution was sonicated for 10 minutes in order to insure homogenous distribution of nanocrystallines. After 3 weeks the sol solution becomes gel and completely dried sol gel at 60 days. The sols in the polystyrene tube was formed as cylindrical rod shape after 60 days and easily removed.

## 3. Measurement

The absorption and emission spectra of these samples were recorded in UV- visible spectrophotometer (Lamda 40, Perkin Elmer), IR (Brucker) and Luminescence Spectrophotometer (LS 45, Perkin Elmer) respectively. Surface morphology and particles size was characterized by FESEM and HRTEM (Jeol, Japan). An UV lamp (Spectrolline USA) was used for the PL visibility test of Si nanocrystallines doped DMSO and sol gel sample.

## 4. Results and discussion

Fig. 1(i) shows the XRD data for original Si NCs powder obtained from the company. The pattern of the NCs powder is good fit to the standard pattern in terms of peak position and relative intensity indicating the purity of Si powder. The peaks at 28.41, 47.26, 56.06, 68, 77, 88 and 96 correspond to the crystals plane (111), (220), (310), (400), (331), (422) and (511) respectively. The position of the peaks is in agreement with the literature values. The broadening of the reflections in the diffractogram distinctly indicates the nano dimensional crystalline nature . The NCs doped sol gel rod kept prolong at room temperature under UV excitation is shown Fig.1(ii). The NCs contain sol gel rod is observed stable in term of PL property when it measured 8 month latter at room temperature.

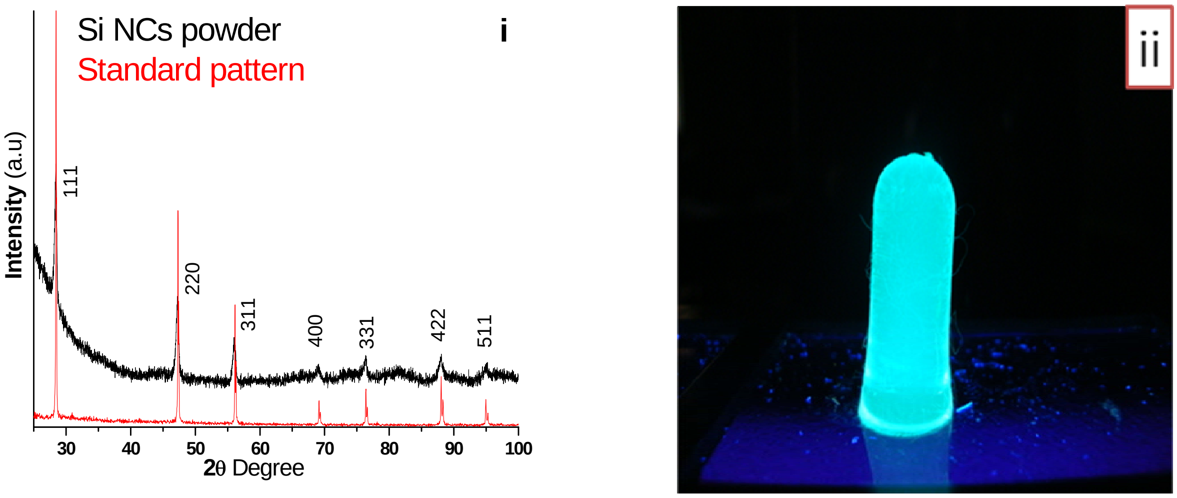

*Fig.1. i) XRD patterns of original Si NCs powder and ii). NCs Si doped sol gel rod (8 month latter) under UV lamp.*

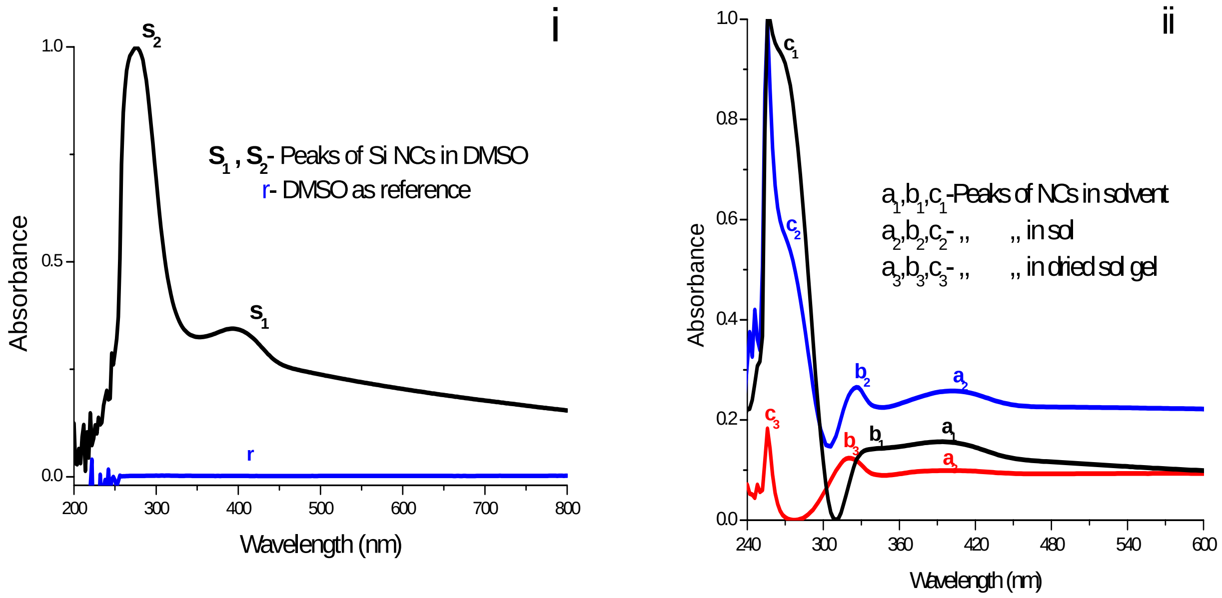

*Fig. 2. Absorption spectra of NCs in colloidal form and various sol gel states which taken from our previous published work [29].*

### 4.1. Optical absorption and energy gaps

Fig. 2 (i and ii) shows the absorption spectra of Si NCs colloidal solvent and in different sol gel state. The results were discussed in detail in our previous work [29]. To better understand the optical absorption of NCs Si in sol gel matrix, we intend to review the spectra in view of theoretical aspect reported in [30] and present result on their energy band gap in respective solvent, gel and dried sol gel state obtained by Taucs plot. The fundamental absorption bands of NCs Si lie at 400nm (3.1ev) and 250nm (5ev) in solvent and sol gel as seen in Fig 2(i, ii). These bands may correspond to calculated value due to $\square_{25}\rightarrow\square_{15}$ transition. There is a band observed at 320nm (4ev) when NCs in gel and dried sol gel closely resemblance the second direct transition $\square_{25}\rightarrow\square_{15}$ of [31]. In this connection, we adopted a simplest method for probing the band structure of NCs silicon semiconductors from the absorption spectrum. In order to determine the optical band gap of the sample, the absorbance spectra of the samples were recorded at room temperature. The absorption coefficient (α) was calculated from the absorbance spectrums using the formula:

$$\alpha = 2.303\,\frac{A}{d}$$

where d is the film thickness and A is the optical absorbance.

The optical band gaps of the samples were determined from plots by analyzing the following relationship between absorption coefficient and photon energy for indirect band transition

$$(\alpha h\nu) = C(h\nu - E_g)^n$$

where hν is photon energy, C is constant, and $E_g$ is the optical band gap and n a parameter depending on both the type of the transition (direct or indirect) and the profile of the electron density in the valence and conduction bands. The dependence of $(\alpha h\nu)^{1/n}$ on photon energy hν was plotted for different values of n. The best fit was found for n = 2 (directly allowed transition), n=1/2 for an indirectly allowed transition. This is the characteristic behavior of indirect transition in noncrystalline materials. The values of the optical band gap $E_g^{opt}$ were taken as the intercept of $(\alpha h\nu)^{1/2}$ vs. (hν) at $(\alpha h\nu)^{1/2} = 0$ according to Tauc's relation for the allowed non-direct transition. The optical band gap of NCs silicon in solvent, gel and dried sol gel obtained by extrapolating linear portion of the plot is shown in Fig. 3 (i-ii-iii). The values indicate that the band gap decrease from 3.7 eV (solvent) to 2.8ev (gel) and retain 3.63eV (dried sol gel). The effect in band gap of NCs in sol and dried sol gel is due to change in the interface of $SiO_2$/NCs when it becomes drier. The optical response of nanocrystals silicon is taken account the sum of scattering and absorption. Scattering of NCs/$SiO_2$ environment needs to be consider while the sol gel phase transition where native of NCs may be changed. Theoretical and experimental work of Meier etal [32] suggested that different size distribution of silicon nanoparticles correspond to the electronic band gap because absorption edge can either be due to phonon emission/absorption or to effects from particle size distribution. In present case, sol gel environment can plays a role to change absorption edge that corresponds to band gap.

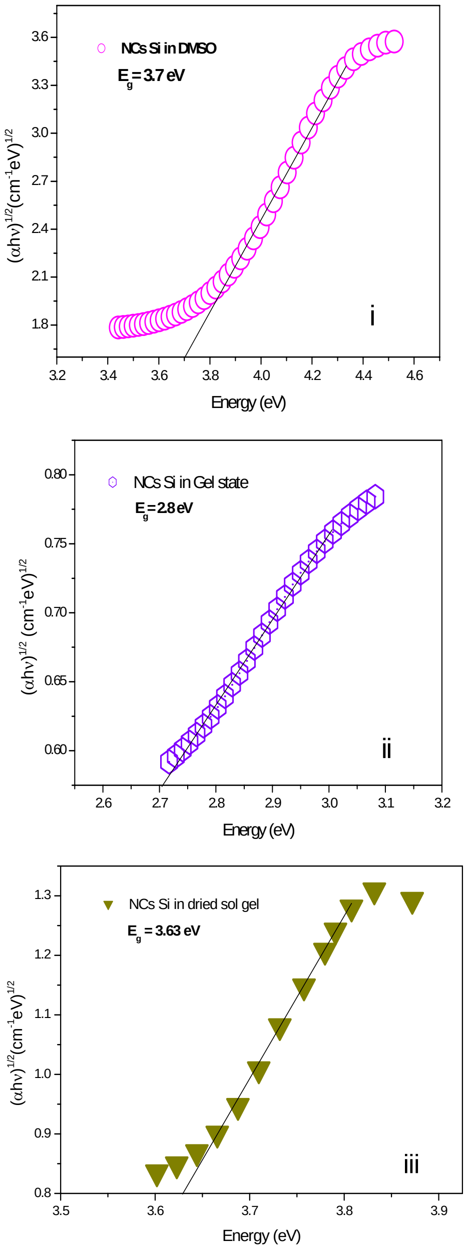

*Fig. 3. Energy band gab vs $(\alpha h\nu)^{1/2}$ of NCs in DMSO, gel and dried sol gel.*

### 4. 2. Photoluminescence property and its effect

Detailed studies on photoluminescence (PL) of Si NCs dispersed solution and incorporated into sol gel at room temperature were reported in our previous work [29]. In that report, significant stability of NCs Si in dried sol gel was found and also examined stimulated emission under laser cavity. In present work, we studied the PL of NCs silicon doped sol gel rod was measured on 8 month latter kept at room temperature and heated up to $100^0$ C. The obtained emission spectra of NCs silicon in dried sol gel at different condition is shown in Fig. 4 (i and ii). There is no major shift observed in peak position of the NCs dried sol gel sample after 8 month with respect to the peak of dried sol gel sample at two month as seen Fig 4(i). But there is blue shift when sample kept prolong with slightly changed in intensity and band width. This small effect on peak position and width may possibly be due to interface of $SiO_2$/NCs Si changes when it become more condense. For nc-Si layer, dielectric function may be affected by the native oxide of the nanacrystals [33] but no pores are involved in dried sol gel after prolong kept.

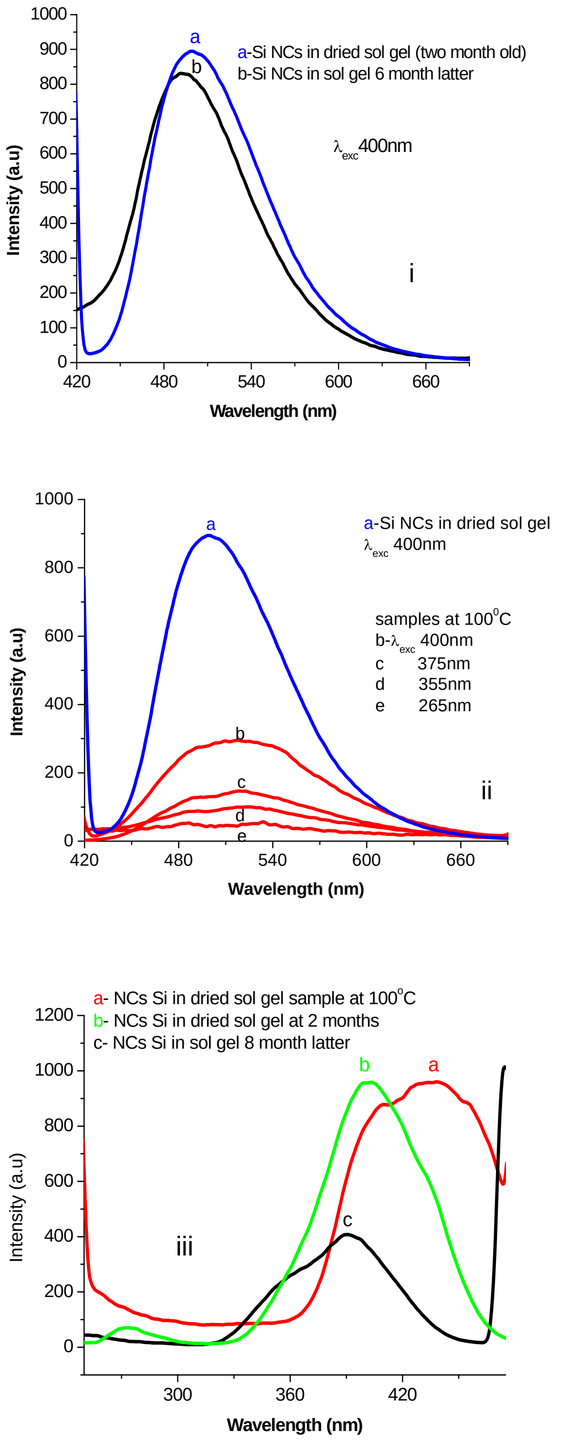

*Fig. 4. Photoluminescence and excitation spectra of NCs in dried sol gel.*

The excitation wavelength was used at 400nm since the most intense is pronounced. On the other hand, when the NCs doped sample is heated at 100$^0$C, effects on emission intensity and bandwidth is observed as shown in Fig. 4(ii). As clearly seen, the peak ‘b’ of heated NCs doped sol gel is significantly decreased as half of the peak ‘a’ of normal NCs doped sol gel sample. When the excitation energy varies, intensities of the nanoparticles decreases as corresponds to peaks ‘c’ ‘d’ and ‘e’ of Fig.4(ii). The emission peak of heated NCs doped sol gel is observed broaden in corresponds to normal sample.

On the other hand, PL excitation spectra for NCs in dried sol gel , after 8 month and heated sample at their corresponding emission wavelengths 495/500nm are significantly different in term of intensity and bandwidths as shown in Fig. 4 (iii) ( peaks ‘a’ ‘b’ and ‘c’). It is clearly seen that the heated NCs sol gel sample exhibits more broaden bandwidth with significant red shift than the dried and 8 month sample. We believe that the major effect on PL and excitation intensity and bandwidth of NCs in heated sol gel and 8 month sample from dried sol gel is due to change in native of Si /$SiO_2$ interface when it adsorbs $H_2O$, solvent from sol gel during the heat. Interface defects or oxide environment of $SiO_2$ matrix may cause to effect in the PL property. Fig. 5 displays the FTIR absorption spectra of NCs silicon powder in Kbr pellate and sol gel matrix before and after heated in 2000-500 cm$^{-1}$ region. First the prominent band observed at 1072 cm$^{-1}$ with two other peaks are weaker at 939, 888 cm$^{-1}$ of NCs in Kbr as seen in fig. 5(a). These feature are characteristic of the NCs and can be assigned to Si–O–Si stretching, Si–OH and Si–O–Si bending. These vibration frequency shift towards shorter spectral region when NCs in sol gel with additional band at 785 and 710 cm$^{-1}$ as shown in Fig.5(b). The relative intensities of prominent band in sol gel are suppressed from NCs powder spectra. When the sample is heated, effect on position and intensity of bands is observed Fig.5(c) This effect is attributable due to change in Si/$SiO_2$ interface.

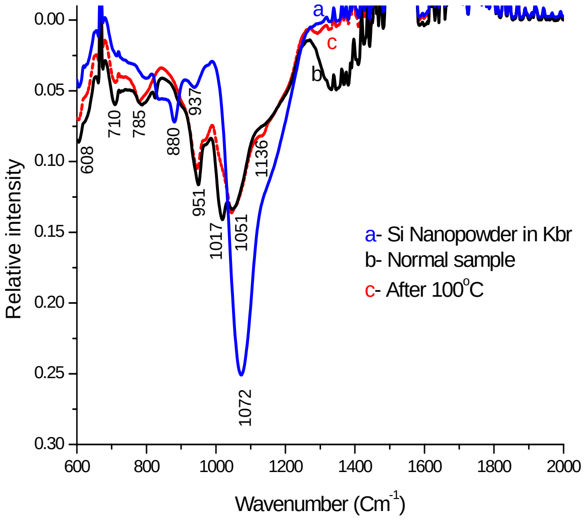

*Fig.5. IR spectra of NCs powder in (a) Kbr palette (b) sol gel and (c) after heated at 100$^o$ C.*

The observed structure and PL of NCs silicon in sol gel is correlated with NCs doped sol gel surface morphology obtained by FESEM. The morphology of NCs Si colloidal solvent and before and after heated NCs Si doped sol gel is shown in Fig. 6 (i, ii and iii).. As clearly seen in the morphology for NCs colloidal solvent is well distributed which become more condense and close particle to particle in micro environment of dried sol gel. Some of NCs Si are distributed in upper layer and seem to be lost composite with sol gel but large numbers of NCs are seen under the surface of sol gel as shown in Fig 6 (ii). The NCs Si contain in the room temperature dried sol gel is determined and confirmed by EDX as shown in Fig. 6(iv). When the NCs Si doped sol gel is heated, NCs Si of upper layer envelope under sol gel surface mean that structure of matrix become shrinkage during heat due to more solidify in sol gel. This may a factor of degradation on PL intensity, effect on peak and bandwidth after heating the NCs sol gel.

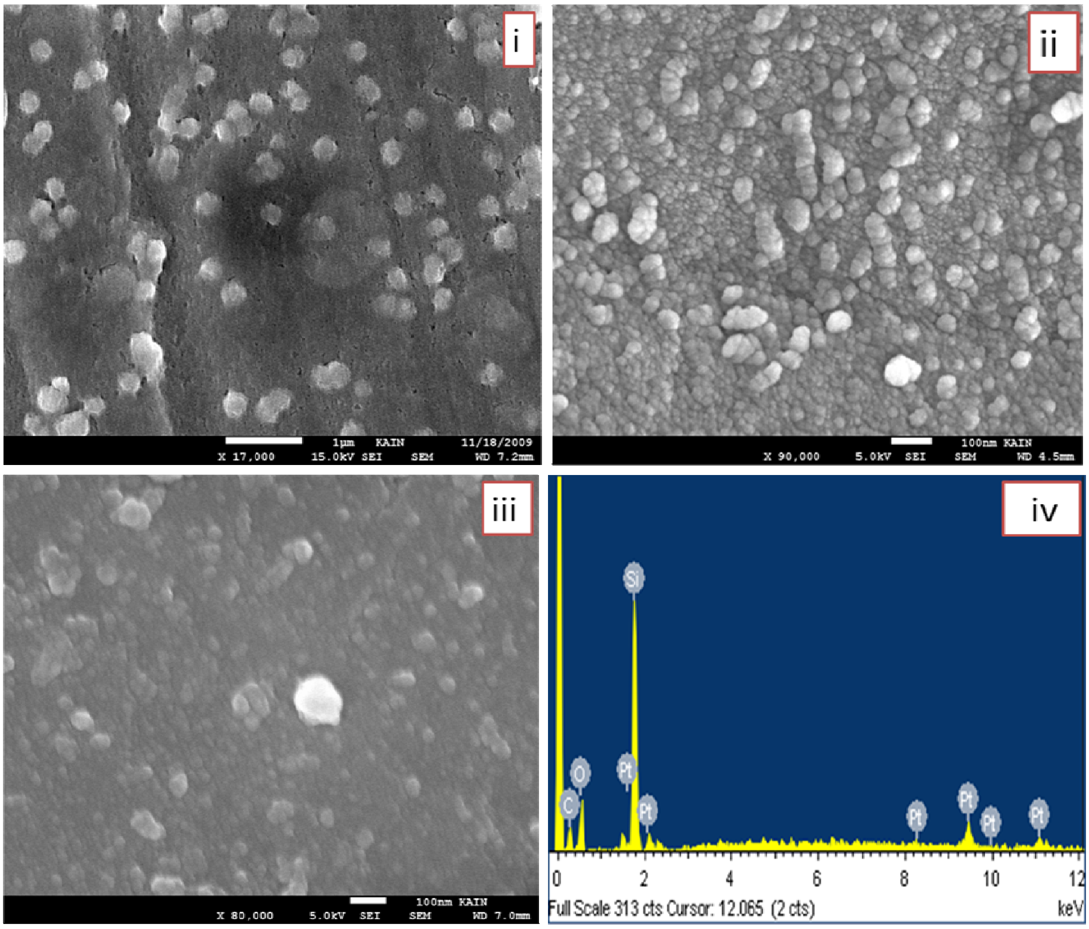

*Fig. 6. FESEM image of NCs silicon in* ***i.*** *DMSO* ***ii.*** *dried sol gel* ***iii.*** *heated dried sol gel and* ***iv****. EDX of sample* ***ii.***

Transmission electron microscope (TEM) images of NCs colloidal DMSO and dried sol gel is shown in Fig.7(i, ii). High resolution of single nanocrystalline Si lattice fringe is seen as inset of Fig.7(i). These NCs are approximately spherical shapes and average size is around 5 to 10nm in diameter. Majority of NCs in solution are mono distributed. Presence of NCs silicon embedded in sol gel environment is observed as dark spot but lie together particle to particle as seen in Fig. 7(ii).

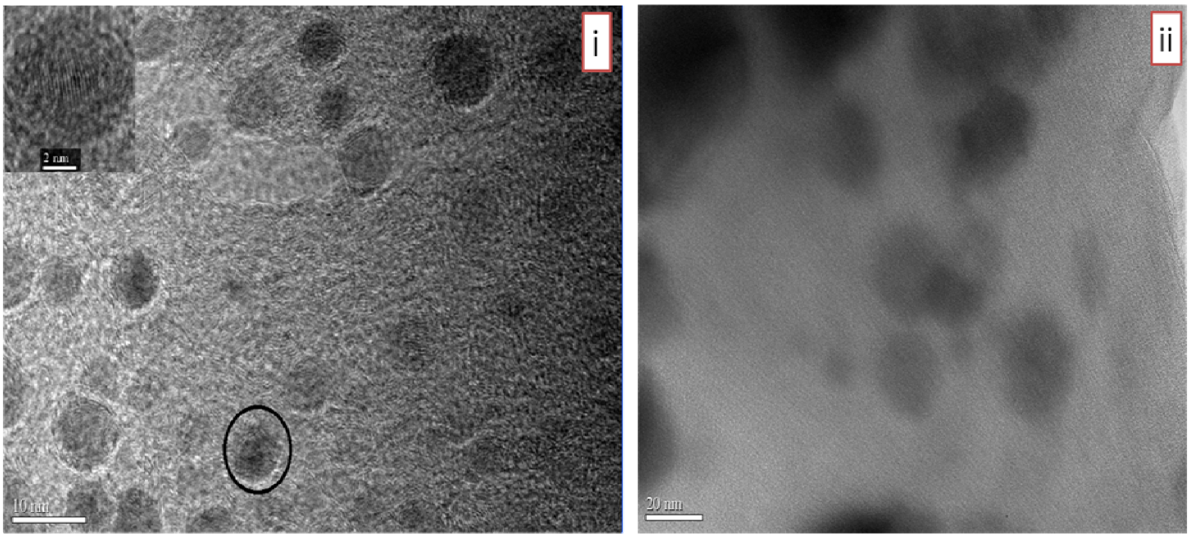

*Fig. 7. TEM image of NCs silicon in i. DMSO at 10nm scale and ii. Sol gel at 20nm scale*

## 5. Conclusion

NCs silicon powders were successfully embedded in sol gel based matrix. The sol gel matrix offers good optical materials for NCs silicon. Prolong NCs doped sol gel was found to be good stable at room temperature. Effect on structural and PL property of the NCs Si due to heat was observed. TEM fringes image and XRD diffraction show that the nanocrystals are of high crystalline nature. Sol gel host prepared by different composition at low temperature may offer suitable active media if proper concentration, homogenous sizes of NCs Si in sol gel is employed. In this direction, studies of NCs Si embedded sol gel with high concentration are currently underway.

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## References

[1] S. Hayashi, K. Yamamoto, J. Lumin. **70**, 352 (1996).
[2] B. S. Kim, D. I. Kim, C.W. Lee, J. Korean Phys. Soc. **38**, 245 (2001).
[3] L.T. Canham Appl. Phys. Let. **57,** 1046 (1990).
[4] A. Uhlir, Bell System Tech. J. **35**, 333 (1950).
[5] U. Gosele, V. Lehmann, Material Chemistry and Physics, **40**, 253 (1995).
[6] W.C. Chan, S. Nie, Science, **281**, 2016 (1998).
[7] M.Bruchez, Jr. M.Moronne, P. Gin, S.Weiss, A.P. Alivisatos, Science, **281**, 2013 (1998).
[8] T.D.Lacoste, X.Michalet, F.Pinaud, D.Chemla, A.P. Alivisatos, S. Weiss, Proc. Natl. Acad. Sci. **97**, 9461 (2000).
[9] F. Pinaud, X. Michalet, L.A. Bentolila etal., Biomaterials, 27(9), 1679 (2006).
[10] S.Yang, W.Cai, G.Liu, H.Zeng, P.Liu, Journal of Physical Chemistry C, **113**(16), 6480 (2009).
[11] X. Michalet, F.F. Pinaud, L.A. Bentolia, Science, **307**, 538 (2005).
[12] J. K. Jaiswal, S. M. Simon, Trends Cell Biology, **14**, 497(2004).
[13] M. N. Khan, A. S. Al Dwayyan, J. Lumin. **128**, 1767 (2008).
[14] V. Parkhutic, Solid State Electronics, **43**, 1121 (1999).
[15] D. Dimova-Malinovska, J. Lumin. **70**, 352 (1999).
[16] R. Jones, O. Cohen, M. Paniccia, A.W.Fang, J. Bowers, 55 (2007).
[17] L. Pavesi, Materials Today **8**(1), 18 (2005)
[18] L. Pavesi, D. Lockdwood, Silicon Photonics, Berlin: Springer, **94** (2004)
[19] D. J. Lockwood, Light Emission in silicon-From Physics to Devices, Semiconductors and Semimetals, Academic press, san Diego, **49** (1998).
[20] L. Pavesi, L. D. Negro, C. Mazzoleni, G. Franzo, F. Priolo, Nature, **408**, 440 (2000).
[21] N.Daldosso, M. Luppi, S. Ossicini et al., Physical Review B, 68(8), Article ID 085327, 8 Pages (2003).
[22] L. Canham, Nature, **408**, 411(2000).
[23] N. Lalic, J. Linnros, J. Lumin. **80,** 263(1999).
[24] P.J. Walters, G.I.Bourianoff, H.A. Atwater, Nat. Mater. **4**, 143 (2005).
[25] L. Zhang, J. L. Coffer, T. W. Zerda, Journal of sol gel science and technology, **11**, 267 (1998).
[26] Y. Posada, L. S. Miguel, L.F. Fonseca, O. Resto, S. Z. Weisz, Journal of Applied Physics, **96**, 2240 (2004).
[27] A. S. Al Dwayyan, M. N. Khan, M. S. Al Salhi, A. Al Dukhail, M. Al Hoshan, Journal of Material Science and Engineering **3**(12) 44 (2009).
[28] A.S. Al Dwayyan, M.Naziruddin Khan, M.S.Al Salhi, Journal of Nanomaterials, Article ID 713203, 7 Pages (2012).
[29] M. Naziruddin Khan, A.S. Al Dwayyan, M.S. Al Salhi, Journal of experimental nanoscience, **7**(2), 120 (2012).
[30] W.L.Wilson, P.F. Szajowski, L.E.Brus, Science, **262**, 1242 (1993).
[31] J.P. Wilcoxon, G.A. Samara, P.N.Provencio, Physical Review B, **602**, 704 (1999).
[32] C. Meier, A. Gondorf, S. Luttjohann, A. Lorke, H. Wiggers. J. App. Phys. 101, 103112(2007).
[33] D.Amans, S. Callard, A. Gagnaire, J. Joseph, J. Appl. Phys. **93**, 4173 (2003).

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