International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:3, No:11, 2009

# Effect of Concentration of Sodium Borohydrate on the Synthesis of Silicon Nanoparticles via Microemulsion Route

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***Abstract*—**The effect of concentration of reduction agent of sodium borohydrate ($NaBH_4$) on the properties of silicon nanoparticles synthesized via microemulsion route is reported. In this work, the concentration of the silicon tetrachloride ($SiCl_4$) that served as silicon source with sodium hydroxide (NaOH) and polyethylene glycol (PEG) as stabilizer and surfactant, respectively, are keep fixed. Four samples with varied concentration of $NaBH_4$ from 0.05 M to 0.20 M were synthesized. It was found that the lowest concentration of $NaBH_4$ gave better formation of silicon nanoparticles.

***Keywords*—**Microelmusion, nanoparticles, reduction, silicon

## I. Introduction

THERE are many attractions of silicon nanoparticles to researchers due to their electronic, and optoelectronic properties which are required in Si-based optoelectronic technologies being developed for the future. Due to these unique properties, there are attributed to quantum confinement effects [1]. The size tunable optical and electronic properties of silicon nanoparticles have made them became great potential candidates for fabrication of engineering materials especially for light emitting diodes, quantum dot laser, chemical sensor and molecular electronic [2]. Besides that, silicon would be a suitable candidate to replacing fluorescent dyes for labeling in vivo cells and as an alternative to CdSe due to abundant cheap and non-toxic [3]. Historically, nanoparticles have been manufactured by top-down approaches and bottom-up synthesis [2]. However, several methods have been developed for the synthesis of silicon nanoparticles such as chemical etching, microemulsion, laser ablation, sol-gel technique, sputtering process, ball milling process and hot-wire synthesis.

The most challenge issues in the fabrication of nanostructure are control the particles characterization like the size, the size distribution, the chemical composition and the crytallinity [4]. In this study, microemulsion route is used to synthesis silicon nanoparticles. Silicon nanoparticles were prepared by controlled reduction of $SiCl_4$ with $NaBH_4$ [5]. In fact, $NaBH_4$ has been widely used due to its simplicity and solubility in reduction of Si ions [6, 7]. The resultant silicon nanoparticles are characterized by UV-visible spectroscopy, Raman spectroscopy, field emission scanning electron microscopy (FESEM) equipped with energy dispersive X-ray analysis (EDX) and transmission electron microscopy (TEM).

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## II. Experimental

### A. Materials

Silicon tetrachloride ($SiCl_4$) for synthesis and sodium borohydrate ($NaBH_4$) was purchased from Merck. Polyethylene glycol (PEG) was purchased from Sigma-Aldrich prior to use.

### B. Method

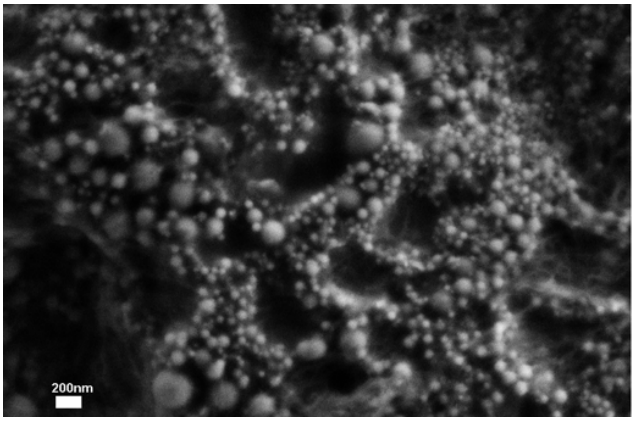
Silicon nanoparticles were synthesized by microemulsion route [8-10]. First, 0.165ml $SiCl_4$ diluted in equal volume of water. A 50ml of 1M NaOH was then added into the solution with drop by drop. In this method, NaOH is act as catalyst and stabilizer. After that, 50ml PEG was added that acts as surfactant and solvent. A denser with white light colour solution will be observed. A various concentration of reductive agent of $NaBH_4$ (0.05 M, 0.10 M, 0.15 M and 0.20 M) was added into precursor in order to form better formation of silicon nanoparticles. To ensure the complete mixing, all the solution is mixed by using magnetic stirrer for half an hour. For the complete reduction reaction, the solution was put in the water bath at 60 $^{o}$C for an hour. The product was then investigated by field emission scanning electron microscopy (FESEM) equipped with energy dispersive X-ray (EDX) spectrometer (Zeiss SUPRA 35VP), transmission electron microscopy (TEM) (Philips CM12), Raman spectrometer (Jobin Yvon HR 800 UV), and UV-visible spectrometer (Perkin Elmer Lambda 35).

## III. Results and Discussion

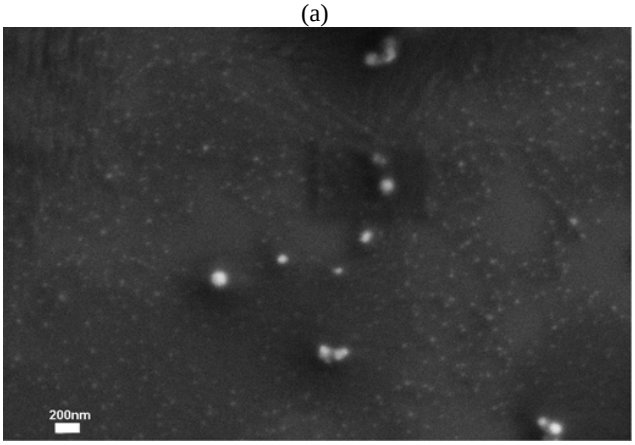
In microemulsion route, concentration of reduction agent is one of the important parameter in order to produce a nanoparticle with small size. In this study, $NaBH_4$ was used as the reduction agent for $SiCl_4$ to initiate the reduction reaction. Four samples with different concentration of $NaBH_4$ (0.05 M, 0.10 M, 0.15 M and 0.20 M) were prepared to study the effect of $NaBH_4$ concentration on the formation of silicon nanoparticles.

From the FESEM observation in Fig. 1 (a), (b), the samples

at 0.05 M and 0.10 M of $NaBH_4$ concentration are showing the silicon nanoparticles. The shapes of the particles were spherical but not uniform structure. Meanwhile, sample with 0.05M $NaBH_4$ concentration had better nanoparticles structures and particle size distributions. Respectively, Fig. 2 shows the measured particle size distribution of silicon nanoparticles with 0.05 M $NaBH_4$. So that, it was suggest that 0.05 M of $NaBH_4$ is the optimum concentration to produce better silicon nanoparticles. However, the size of the primary particles for the sample of lowest $NaBH_4$ concentration (0.05 M) was indicated in range mostly between 60nm to 80nm, as showed in Fig. 1(a). The others samples are not show the nanoparticles structures (Fig. 1(c), (d)) but there are some droplets and large agglomeration were observed. Hence, the following characterization by UV-vis spectroscopy, Raman, EDX and TEM will focus on the sample with 0.05 M $NaBH_4$.




(a)

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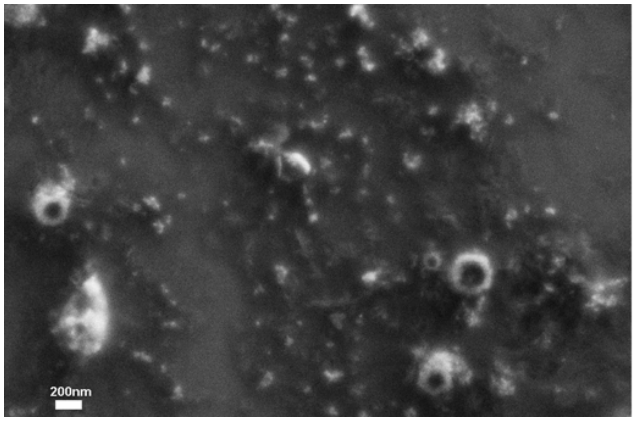
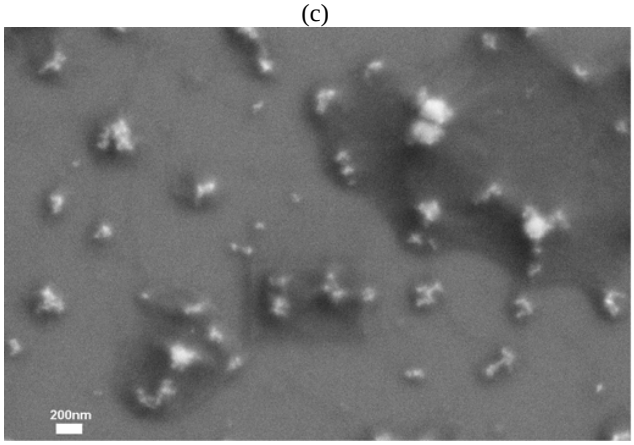



(c)




(d)

Fig. 1 FESEM images of silicon nanoparticles obtained at $NaBH_4$ concentration (a) 0.05 M, (b) 0.10 M, (c) 0.15 M, and (d) 0.20 M

Fig. 2 shows the particles size distribution measured on silicon nanoparticles prepared by 0.05 M $NaBH_4$. The size is ranging from 21 to 280 nm with about 70% of particles have diameter less than 100 nm. However, it is very hard to measure the particles size distribution for the other samples due to the agglomeration of nanoparticles.

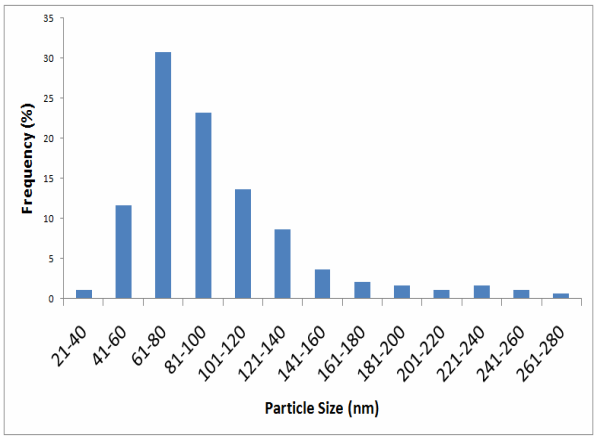



Fig. 2 Particle size distribution of silicon nanoparticles (with 0.05M $NaBH_4$) determined by SEM analysis

Fig. 3 shows TEM image of nanoparticles for sample with 0.05M $NaBH_4$. It was found that images show the spherical nanoparticles with some edges and distortion. The result confirmed that the appearance single crystalline core of nanoparticles.

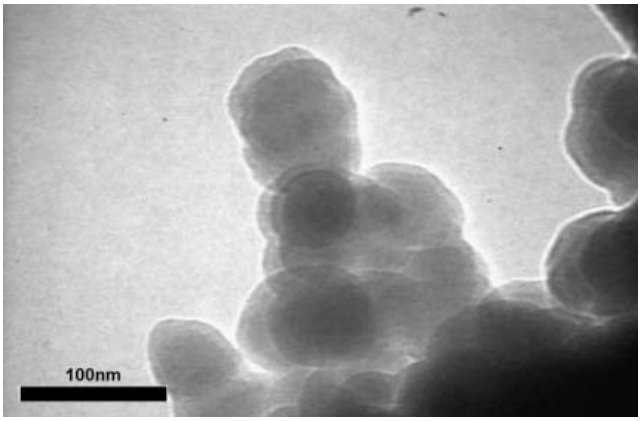
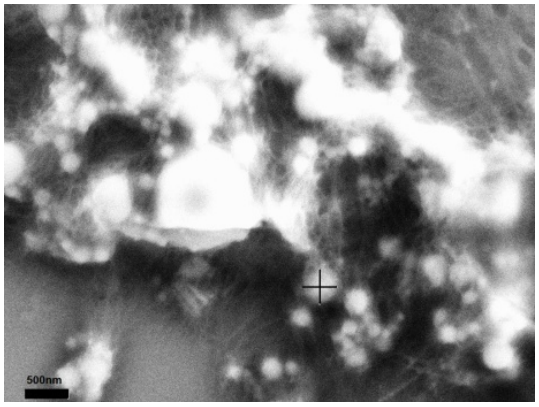



Fig. 3 TEM image of the silicon nanopartcles (with 0.05M $NaBH_4$)

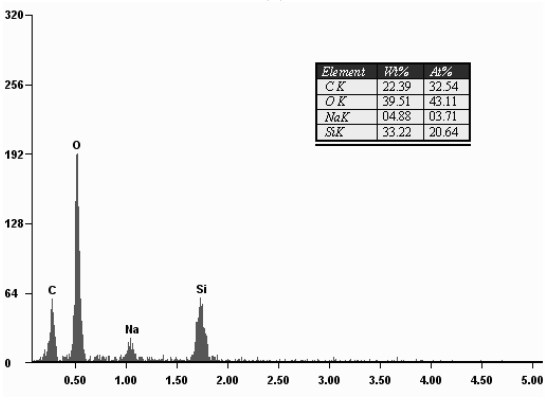
Nanoparticles are zero dimensional nanostructures which includes single crystal, polycrystalline, and amorphous materials with all possible morphologies such as spheres, cubes, and platelets [11].

Meanwhile, from Fig. 4, the EDX analysis obtained the elemental composition of the nanoparticles with 0.05 M $NaBH_4$ is 20.89 at% Si, 44.55 at% O, 28.48 at% C and 6.07 at% Na. This result confirms that the spherical particle is containing element of silicon. The small peaks of sodium are attributed by $NaBH_4$ which the washing process hasn't done properly and the elements still remain in the sample. Besides, the high peaks of oxygen and carbon are attributed due to silicon is grafting by PEG (OH-$(CH_2CH_2)_n$-OH, which the formation of protective layer (PEG shell) on the surface of silicon nanoparticles [12-14]. Another possible explanation for the appearance of oxygen elements is silicon is one of the materials easily oxidized to be oxides or hydroxides which the formation of native oxide layer on the silicon nanoparticles because of the sample exposed to the environment [15]. In this study, the EDX analysis had confirmed the silicon structure of the nanoparticles especially for sample with 0.05 M $NaBH_4$.

Raman spectroscopy was performed to determine crystalline fractions of the silicon nanoparticles. Fig. 5 shows the Raman spectra of silicon nanoparticles with 0.05M $NaBH_4$. From the Raman spectra obtained two broad peaks (478$cm^{-1}$ and 974$cm^{-1}$) which indicates that the sample exhibit an amorphous phase structure (surface amorphous phase of silicon nanoparticles) [2, 16, 17]. The peak can be also due to the exothermic oxidization as the largest particles at peak 974$cm^{-1}$ [2, 17]. In this study, one of the important facts to influence Raman peak intensities is the contributions of amorphous phase and phonon confinement. The Raman spectrum is reported that surface amorphous phase of silicon nanoparticles can be produced by microemulsion route which 0.05 M $NaBH_4$ is successfully reducing of the $SiCl_4$ into Si.




(a)




(b)

Fig. 4 (a) FESEM image show the zero dimensional nanoparticles, (b) EDX analysis obtained elemental composition of the particles: 20.89 at% Si, 44.55 at% O, 28.48 at% C and 6.07 at% Na.

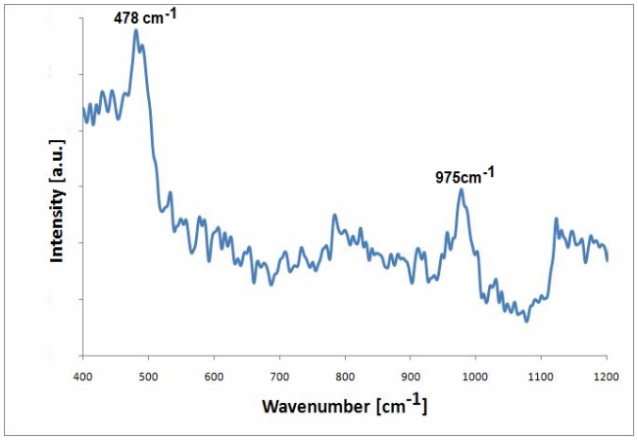



Fig. 5 Raman spectra of silicon nanoparticles (0.05M $NaBH_4$)

UV-visible spectrometer was used to investigate the optical properties of silicon nanoparticles. From the UV-visible

spectroscopy, the optical absorption curve again wavelength for samples (0.05 M $NaBH_4$, 0.10 M $NaBH_4$, 0.15 M $NaBH_4$, and 0.20 M $NaBH_4$) have been plotted, as illustrated in Fig. 6. The absorption is very high at UV range and decreases in the visible range. All samples have shown the similar features in the UV-visible spectrum which the maximum absorption peak at about 230 nm. Small shifted of absorption edge are expected due to the changes in nanoparticle size which is quantum confinement effect [1]. As the mean particle size decreased, it was observed that the intensity of absorption increased and also leads to widening of the band gap [18]. The intensity of the Plasmon bands for sample (0.05 M $NaBH_4$, 0.10 M $NaBH_4$, 0.15 M $NaBH_4$, and 0.20 M $NaBH_4$) are 0.1166, 0.1137, 0.0944 and 0.0428, respectively. It was obtained that smaller mean particle size (0.05 M $NaBH_4$) had higher intensity of absorption and also broadening band gap due to the smaller mean particle size have higher surface area to volume which can absorb more light. This is proved by the higher intensity of absorption, higher wavelength and broader peak in the UV-visible spectrum. However, the spectra are not showing the smooth curves due to the shape of the particle which are not uniform and not monodispersed. The shape of the particle also affects the shifts of the wavelength. The efficiency of the particles radiative scattering and the fraction of the light also the main factors which are affecting the surface plasmon resonance peak [19].

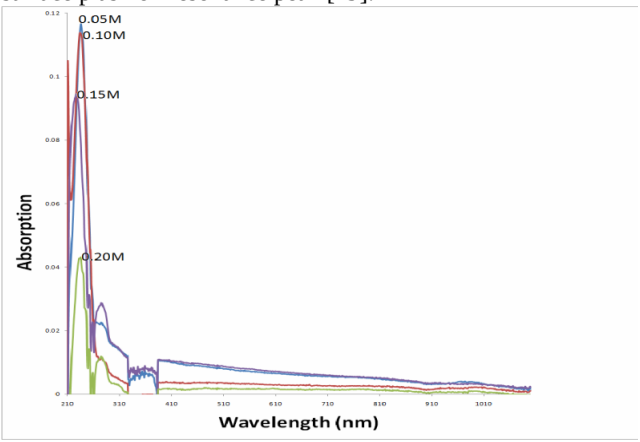



Fig. 6 Typical UV-visible spectra of silicon nanoparticles with various concentrations.

## IV. Conclusion

Silicon nanoparticles have been successfully synthesized using different concentration of reductive agent. The obtained nanoparticles are spherical shape with particle size about 60-80 nm. From EDX analysis result confirms that the nanoparticles are containing silicon element. In this study, it was found that the lowest concentration of $NaBH_4$ is more efficiency to reduce the size of the silicon particles if compare with higher concentration of $NaBH_4$.

## Acknowledgment

This study was supported by USM Short Grant (project no. 304.PBAHAN. 6035230), RU grant (project no. 1001.PBAHAN.803126) and partially supported by Science Fund Grant, MOSTI under project no. 03-01-05-SF0384. WL. Liong wishes to thank Universiti Sains Malaysia for the financial support (USM Fellowship).

## References

[1] Q. Liu, S. M. Kauzlarich, "A new synthetic route for the synthesis of hydrogen terminated silicon nanoparticles," Materials Science and Engineering B96 (2002) 72-75.
[2] M. R. Scriba, C. Arendse, M. Harting and D. T. Britton, "Hot wire synthesis of Si nanoparticles," Journal of Thin Solid Films 516(2008)844-846.
[3] F. Fabbri, E. Borsella, M. Carpanesel, R. Fantoni, R. Caterino, R. D'Amato, M. Falconieri and E. Serra, "Size and surface control of optical properties in silicon nanoparticles," Advances in Science and Technology Vol. 45 (2006) pp. 2620-2626.
[4] M. Leparoux, M. Loher, C. Schreuders and S. Siegmann, "Neural network modelling of the inductively coupled RF plasma synthesis of silicon nanoparticles," Journal of Powder Technology 185 (2008) 109 – 115.
[5] P.V. Adhyapak, P. Karandikar, K. Vijayamohananb, A. A. Athawale, A.J. Chandwadkar, "Synthesis of silver nanowires inside mesoporous MCM-41 host," Materials Letters 58 (2004) 1168– 1171.
[6] P. Kim, J.B. Joo, W. Kim, J. Kim, I.K. Song, J. Yi, "$NaBH_4$-assisted ethylene glycol reduction for preparation of carbon-supported Pt catalyst for methanol electro-oxidation," Journal of Powder Sources 160 (2006) 987-990.
[7] Y. Torisawa, T. Nishi, J. Minamikawa, "Some aspects of $NaBH_4$ reduction in NMP," Bioorganic & Medicinal Chemistry 10 (2002) 2583-2587.
[8] D.H. Chen, and S.H. Wu, "Synthesis of nickel nanoparticles in water-in-oil microemulsions," Chem. Mater. 2000, 12, 1354-1360.
[9] A. Pal, S. Shah, S. Belochapkine, D. Tanner, E. Magner, S. Devi, "Room temperature synthesis of platinum nanoparticles in water-in-oil micoremulsion," Colloids and surfaces A: Physicochem. Eng. Aspects 337(2009)205-207.
[10] R. Hua, C. Zang, C. Shao, D. Xie and C. Shi, "Synthesis of barium fluoride nanoparticles from microemulsion," Nanotechnology 14(2003)588-591.
[11] S.D. Hutagalung, A. Ahmad, K.A. Yaacob, "Growth of silicon nanostrucctures by thermal evaporation uusing nickel catalyst," Solid State Science and Technology, Vol. 16 No. 1 (2008) 100 -106.
[12] Y. Shin, D. Lee, K. Lee, K.H. Ahn, B. Kim, Surface Properties of the Silica Nanoparticles Modified with Polymer Nanocomposite Applications, Journal of Industrial and Engineering Chemistry 14 (2008) 515-519.
[13] G. Molinuex, Pegylation: Engineering Improved Pharmaceuticals for Enhanced Therapy, Cancer Treatment Review 2002: 28 (SUPPL. A): 13-16.
[14] Z. Zhang, A.E. Berns, S. Willbold, J. Buitenhuis, Synthesis of Poly(ethylene glycol) (PEG)-Grafted Colloidal Silica Particles with Improved Stability In Aqueous Solvent, Journal of Colloid and Interface Science 310 (2007) 446-455.
[15] K. B. Musabekov., S. B.Aidarova, S. M. Andreyeva, M. B. Isabaeva, "Influence of surfactants and their combination with polyethylene glycol on the stability of sunflower oil-water emulsions," CAB 2009.
[16] J. Klangsin, O. Marty, J. Munguia, V. Lysenko, A. Vorobey, M. Pitaval, A. Cereyon, A. Pillonnet, B. Champagnon, "Structural and luminescent properties of silicon nanoparticles incorporated into zirconia matrix," Physic Letters A372 (2008) 1508-1511.
[17] C. Meier, S. Luttjohann, V.G. Kravets, H. Nienhaus, A. Lorke, H. Wiggers, "Raman properties of silicon nanoparticles," Physica E 32 (2006) 155-158.
[18] S. Kalele, S. W. Gosavi, J. Urban, S. K. Kulkarni., "Nanoshell particles: synthesis, properties and applications, Current Science," Volume 91, No. 8, pp 1038-1052.
[19] K.R. Catchpole, S. Pillai, "Surface plasmons for enhanced silicon light-emittingndiodes and solar cells," Journal of Luminescence 121 (2006) 315-318.