Silicon Nanocrystals Prepared by Femtosecond Laser Ablation in solution under different ablation time

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Abstract: Spherical silicon (Si) nano-crystals (NCs) were prepared through pulsed femtosecond laser ablating of porous silicon power immersed in 1-hexene. Compared to bulk Si, Raman spectra of Si NCs show a redshift and an asymmetrical broadening. High resolution transmission electron microscopy measurements show that Si particles were dispersed uniformly in 1-hexene. FTIR spectra showed that the Si nanoparticles were passivated by organic molecules. Based on the room temperature photoluminescence (PL) excitation and PL decay curves, we assign blue PL to localized excitons through oxygen associated surface states from the colloids Si NCs. Because of the good surface passivation for colloidal silicon NCs, the quantum yield increases with extending ablation time.

1. Introduction
In very recent years, the huge advance have occurred in development the colloidal silicon (Si) nanocrystals (NCs) for their potential applications in silicon-based full color display, solar cells [1, 2], as well as fluorescent biomarkers [3]. Si NCs particles with good solution dispersible have been developed for a variety of applications fields [4]. After Si NCs particles dispersion several days in pure water, the luminescent intensity of Si NCs was usually drastically degraded. This can be attributed to the termination with unstable chemical elements on Si NCs particles surface. In order to obtain stable luminescence, it is necessary to passivate the surface of Si NCs particles with a stable chemical element.

The laser ablation of Si NCs in liquid phase environment is a complicated process and involves several laser parameters (e. g. laser fluence, pulse duration, laser wavelength, solution type) [5-8]. According to the Lennard-Jones potentials model, the mechanism of laser ablation is not owing to the phase fission of the porous silicon material [5]. The present work mainly deals with the colloidal silicon nano-crystals fabricated through femtosecond laser ablating the mixture of porous silicon powder and 1-hexene at variable laser ablation time.
2. Experiments and results

The preparation procedure of the Si NCs is described in our previous work [6]. In brief, the mixture of the porous silicon powders and hexene was ultrasound with 1.0 h. The laser irradiation of the mixture of the above liquid was carried out through femtosecond pulsed laser with wavelength 800 nm (Ti:sapphire). The prepared samples named S1, S2, S3, S4 under laser ablation time for 1.0, 2.0, 3.0 and 4.0 h, respectively. After finishing ablation, the supernatant solution was centrifuged and filtered through centrifugation with 12000 rpm for 30 min.

The fabricated colloids were described through transmission electron microscopy (TEM, JEOL JEM-2100F). Raman spectrum were carried out via Raman spectrometer. Fourier transform infrared transform (FTIR) was monitored using (Thermo Scientific, Nicolet iS 50) Fourier transform infrared spectrometer. The steady-state room-temperature photoluminescence (PL), PL excitation (PLE) spectra were measured by Edinburgh Instruments FLS920. PL decay curve were monitored by using Nd:YAG laser. PL quantum yield (QY) were performed using the QY measurement system quantum-aster 40 (150 W Xe lamp).

Fig. 1(a)-(b) displays the S1’ TEM image and the size statistics distribution of Si NCs measured from TEM. It can be clearly observed that the Si nanoparticles look as black dots with good dispersion in 1-hexene. The mean dimension of Si NCs is around 2.63 nm with a standard deviation 3.01 nm. Inset in Fig. 1(a) is a representative Si NCs high resolution TEM (HRTEM) picture with lattice fringes ~ 0.3 nm, which corresponds with Si (111).

![Figure 1](image-url)  
Figure 1 (a)-(b) The TEM image and corresponding size distribution of S1. Inset: a Si NC’s HRTEM image.

Figure 2(a) gives the Raman spectra of S1~S4 samples. Raman peak position locates at 518, 516, 507, and 505 cm\(^{-1}\), and the corresponding full width half maximum (FWHM) is 13, 17, 35, and 42 cm\(^{-1}\). Compared with the Raman peak position (520 cm\(^{-1}\)) and FWHM (3.4 cm\(^{-1}\)) of bulk silicon crystalline, the Raman peak positions of all the samples shift to lower number, together with broadening of FWHM. Compared to bulk Si crystal, the Raman peak position o Si NCs takes on a redshift and Raman spectra become broaden, demonstrating that there existence phonon confinement effect [6]. The relation of Raman peak position shift (\(\Delta \nu\)) and the Si nanocrystals dimension (d, in nm) is discussed through the phenomenological equation [9]: \(\Delta \nu = -19.856 / d^{1.345}\). The calculated Si NCs mean size is around...
2.63, 2.14, 1.73, and 1.37 nm, respectively.

The mean dimension of Si NCs reduces from 2.63 to 1.37 nm with increasing of laser ablation time from 1 to 4 h. The reduction mechanism of Si NCs average size can be explained by the fragmentation mechanism, involving the emitting of photoelectrons from the target porous Si powders surfaces, which will leave the positive charges on the surface of target Si. These induced that the surface charges arise from the electrostatic repulsion among different parts at the surfaces of Si. As consequence, a single Si particle with larger dimension can divide into a number of smaller size Si NCs [7].

The FTIR spectra can directly reveal the chemical bonding configuration of Si NCs, as shown in Fig. 2(b). The absorption bands at 2850, 2925 and 2960 cm\(^{-1}\) can be indexed to asymmetric symmetric C-H\(_2\) stretching, asymmetric C-H\(_2\) stretching model, and C-H\(_3\) stretching, respectively [10]. It should be noted that the absorption peaks at 670, 880, 1100, and 1460 cm\(^{-1}\) correspond to asymmetric-, symmetric Si-C vibration, Si-O-Si vibration, and Si-CH\(_2\) bending vibration, respectively [6, 11]. The formation of Si-C bonding at Si NCs surface results from chemical reaction between silicon and 1-hexene, indicating that the silicon nanoparticles surfaces are well passivated through organic chains. The appearance of Si-O-Si bonds suggests that Si NCs surfaces have been partly oxidized by oxygen dissolved in solution. We find that the both Si-C and Si-O-Si bonds intensities at 670 and 1100 cm\(^{-1}\) increase with increasing laser ablation time. It is proposed that during laser ablation processes, the already large size Si NCs will be broken into several small size Si NCs, the Si NCs with small size will be further ablated in the laser ablation in solution when the irradiation time is extended. As a result, the Si NCs size is further reduced as confirmed by Raman and HRTEM measurements. The chemical reactions between the Si NCs and organic molecules take place again and again. Thus, smaller Si NCs have more surfaces functional groups, leading to Si-C and Si-O-Si bonds intensities increment of with extending irradiation time [8].

![Figure 2](image_url) (a) Raman and (b) FTIR spectra for colloids Si NCs.

Figure 3(a) illustrates PL spectra of S1-S4 samples measured at room-temperature with the excitation wavelength (\(\lambda_{exc}\)) 325 nm. We can observe that there is a blue emission peak at 420 nm (2.9 eV) and keeps unchanged for all the samples, and the intensities of their increase rapidly with increasing of ablation time. No PL can be found from 1-hexene alone when irradiation by laser. Therefore, the blue emission results from Si NCs with surface passivated instead of the liquid.
To investigate the origin of blue PL, PLE spectra were measured. Fig. 3(b) displays the PLE spectra of S1 as a representative. PLE spectra were studied by varying $\lambda_{\text{exc}}$ from 200 to 380 nm, and the detected emission wavelength is 420 nm. The PLE spectra in Fig. 3(b) exhibits the absorption peak at 340 nm, which keeps almost the same as other samples. The maximum PL intensity can be obtained while absorption occurs at ~340 nm (~ 3.6 eV), suggesting that Si NCs absorb strongly at 340 nm and the carriers mainly generates at 3.6 eV energy level of [12].

Fig. 3(c) shows a typical time-resolved PL decay curve for S1. The decay curve matches well with a double-exponential gamma [6]: $I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$. Here, $A_1$, $A_2$, $\tau_1$, and $\tau_2$ are pre-exponential factors and decay times, respectively. Typical two time constants can be obtained 6.21 ns ($A_1=10.36\%$) and 2.63 ns ($A_2=88.64\%$). Average PL lifetime can be calculated through the equation: $\tau_{avg} = \sum A_i \tau_i / \sum A_i$. We obtain the average fast decay time 2.33 ns.

The following two PL origins are usually employed to explain the ns order of blue emission from organic molecule passivated Si NCs: (i) The excitons’ radiative recombination at Si NCs core-related levels caused by quantum confinement effect (QCE) [13, 14]; (ii) PL peak value keeps fixed with variable size, if the excitons’ radiative recombination is linked to oxygen-associated surface states [13, 15-17]. The blue peak energies at 420 nm always keep unchanged under the variation of Si NCs dimension, as a consequence, the electrons-holes’ direct radiative recombination from Si NCs core-related caused by QCE can be safely excluded. On the basis of analysis, we deduce that the blue emissions at 420 nm originates from the localized excitons’ radiative recombination, which mainly generates from 3.6 eV level through oxygen-associated surface states from the colloidal Si NCs.

For further investigation optical properties, QY for all samples were measured under room temperature, as shown in Fig. 3(d). The QE shows an improvement from 17.2% to 26.8% with increasing laser ablation time from 1-4 h. The higher QY under longer ablation time is due to the higher surface inactivation of colloidal Si NCs with organic carbon molecules, resulting in fewer non-radiative centers and smaller non-radiative rate [18].
3. Conclusion

In summary, the colloids Si NCs were prepared through femtosecond laser ablating in 1-hexene. The structural evolution and optic properties for the colloids Si NCs with different ablation time were investigated in detail. Based on the analysis of the HRTEM, Raman, and FTIR measurements, we confirm the silicon (Si) nano-crystals (NCs) surface are passivated by organic carbochain and oxygen. The average size of colloidal silicon (Si) nano-crystals (NCs) reduces from 2.63 to 1.37 nm with the extending ablation time from 1 to 4 h. In combination with the room temperature PL, PLE, and PL decay curves, it can be concluded that the blue PL at 420 nm originates from excitons produced at 3.6 eV localized states energy level through oxygen associated defect modes in colloids Si NCs. Due to good surface passivation of colloidal Si NCs, the quantum yield increases with extending ablation time.

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