

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231654028>

# Size and Structure Control of Si Nanoparticles by Laser Ablation in Different Liquid Media and Further Centrifugation Classification

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY C · OCTOBER 2009

Impact Factor: 4.77 · DOI: 10.1021/jp907285f

CITATIONS

46

READS

7

## 5 AUTHORS, INCLUDING:



**Shikuan Yang**

Chinese Academy of Sciences

50 PUBLICATIONS 1,755 CITATIONS

SEE PROFILE



**Weiping Cai**

Guangzhou eighth People's Hospital

195 PUBLICATIONS 6,951 CITATIONS

SEE PROFILE



**Hongwen Zhang**

Chinese Academy of Sciences

18 PUBLICATIONS 247 CITATIONS

SEE PROFILE



**Haibo Zeng**

Chinese Academy of Sciences

128 PUBLICATIONS 4,652 CITATIONS

SEE PROFILE

# Size and Structure Control of Si Nanoparticles by Laser Ablation in Different Liquid Media and Further Centrifugation Classification

Shikuan Yang,\* Weiping Cai,\* Hongwen Zhang, Xiaoxia Xu, and Haibo Zeng

Key Lab of Materials Physics, Anhui Key Lab of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China

Received: July 30, 2009; Revised Manuscript Received: September 13, 2009

Si nanoparticles are synthesized through the “green” (noncontamination) laser ablation method. The size control can be realized by choosing different liquid media. Through comparison of the samples acquired in different liquid media, it is found that ultrafine and well-dispersed Si nanoparticles can be prepared in pure ethanol. Furthermore, such obtained colloid can be further classified by the centrifugation method to obtain certain sized Si nanoparticles. Liquid media also have an effect on the microstructure of the obtained Si nanoparticles. The influence of laser fluence on the mean size of Si nanoparticles is also investigated. As laser fluence increased, the mean size decreased, which is explained in detail. This investigation is crucial in understanding the role of liquid media in the nanoparticles formation process during laser ablation and also has important potential applications in some areas where certain sized Si nanoparticles are needed.

## 1. Introduction

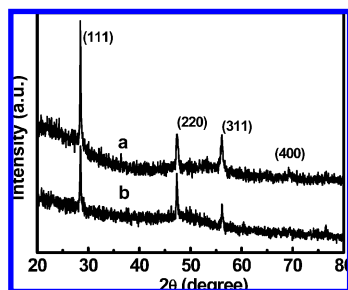
Si nanoparticles with visible light emission have attracted much investigation interest since their applications in biotagging and bioimaging area. They are usually synthesized through a wet chemistry method. However, poisonous agents and rigorous conditions are often necessary.<sup>1–3</sup> Laser ablation in liquid (LLA) as a flexible and “green” (noncontamination) method to prepare ultrafine nanoparticles has attracted much attention in recent years;<sup>4–6</sup> however, it was seldom used to fabricate Si nanoparticles.<sup>6a,7</sup> Furthermore, in some cases, it is necessary to obtain certain sized Si nanoparticles. Therefore, we explored how to acquire certain sized Si nanoparticles through the “green” LLA method in this paper. As to the size and structure control of the nanoparticles acquired by LLA, previous studies often focused on the parameters such as laser fluence, laser wavelength, and so on.<sup>4</sup> Recently, Werner et al. investigated the stability differences of silver nanoparticles prepared by LLA in different liquid media.<sup>8</sup> Saitow et al., by laser ablation of a Si target in supercritical CO<sub>2</sub> and manipulating the supercritical fluid pressure, successfully realized Si nanoparticles with photoluminescence (PL) ranged from red to near-ultraviolet at room temperature,<sup>9</sup> which is obviously different from the PL properties of Si nanoparticles prepared by LLA in water.<sup>6a,7</sup> Therefore, the liquid medium is important in controlling the properties of the obtained nanoparticles. Here, we showed that liquid medium also plays an important role in tuning the size and structure of the Si nanoparticles, which has been neglected in both experiments and theoretical calculations in the previous publications. It was found that ultrafine and well-dispersed Si nanoparticles can be fabricated through the LLA method with ethanol as the liquid medium. Furthermore, postsynthesis separation is an efficient way to create size-uniform nanoparticles. These methods include filtration,<sup>10</sup> electrophoresis,<sup>11</sup> chromatographic method,<sup>12</sup> and employing density gradient.<sup>13</sup> Centrifugation can also remove large and unstable particles from colloidal systems.<sup>14,15</sup> Here, we first present that centrifugation treatment

of the colloid prepared by LLA also can be used to further classify certain sized Si nanoparticles.

## 2. Experimental Details

A silicon wafer of (111) plane was ultrasonically rinsed with deionized water and then ethanol for 1 h, respectively. The cleaned silicon wafer was used as a target, immersed in 8 mL of liquid medium (deionized water or ethanol or a mixture of the two) and irradiated with a Nd:YAG laser operated at 1064 nm with pulse duration of 10 ns and frequency of 10 Hz, as previously described.<sup>6</sup> The fluence of the laser ranged from 50 to 200 mJ/pulse. The laser beam was focused on the Si target with a spot size about 2 mm in diameter, using a lens with a focal length of 150 mm. The solution was continuously stirred during laser irradiation. After 30 min of laser irradiation, the color became light yellow in deionized water, and brown yellow in ethanol. After putting the acquired 8 mL of colloid into two 4 mL plastic tubes, they were loaded into the centrifugal machine symmetrically. Centrifugation classification was conducted first at 4000 rounds/min (about 1000 g) for 2 h, and then the transparent solution in the upper part of the tube was carefully collected by a dropper to do further centrifugations. The nanoparticles left adhering to the inner surface of the tube were transferred and characterized. Subsequently, 8000 (about 4000 g) and 14000 rounds/min (about 12000 g) centrifugation were performed similarly. The yield of Si nanoparticles under 100 mJ/pulse in ethanol can be estimated to be about 50  $\mu\text{g}/\text{min}$  by the laser shot-induced mass loss of the silicon wafer. So, 30 min of irradiation produces the colloidal solution containing about 0.2 g/L of Si. We draw a droplet of the solution on the carbon-coated Cu mesh to do the transmission electron microscope (TEM, JEM-200CX) measurements. The size distributions were acquired by counting more than 200 nanoparticles in the enlarged TEM image. A 2 mL sample solution was used to measure the UV–vis absorption spectra on a Cary 5E UV–vis–IR spectrometer. The X-ray diffraction (XRD) pattern was measured on an X-ray diffractometer (the Philips

\* To whom correspondence should be addressed. E-mail: skyang@issp.ac.cn and wpcai@issp.ac.cn.



**Figure 1.** Typical XRD pattern of the as-prepared products in water and ethanol correspond to curves a and b, respectively. Marked indices are related to Si crystal planes.

X'Pert), using a Cu K $\alpha$  line. PL spectra were measured on the FLS920 PL spectrophotometer with a Xe lamp at room temperature.

### 3. Results

The as-prepared colloid solution is very stable, without any precipitation for 2 months, and colloid prepared in ethanol is more stable than that in water. Figure 1 shows the XRD pattern of the sample prepared in water and ethanol, corresponding to curves a and b, respectively. All diffraction peaks can be indexed as silicon phase with diamond structure (JCPDF 27-1402). No other products are detected.

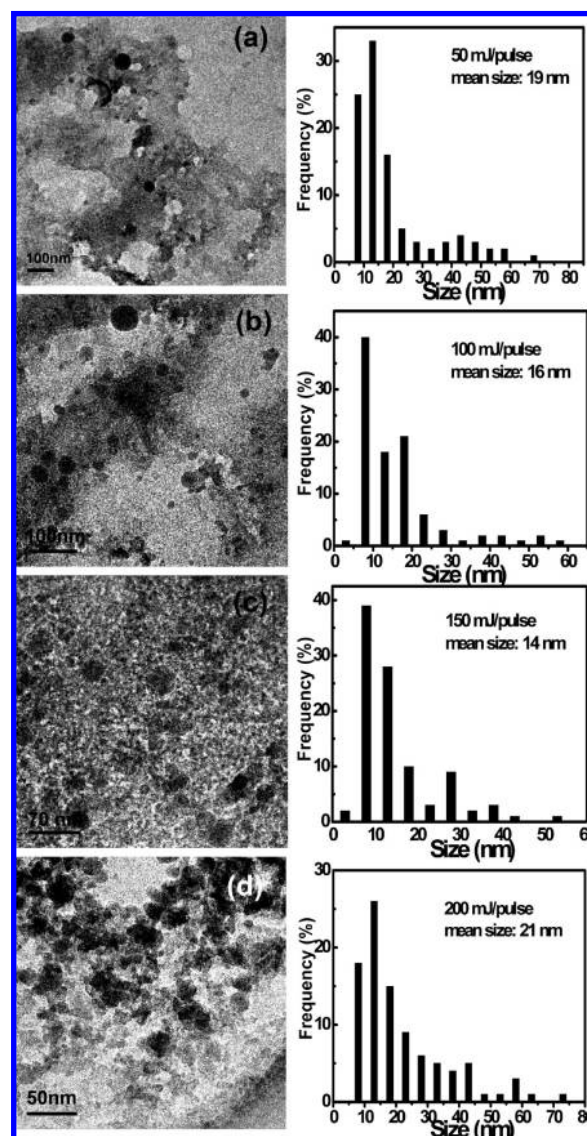
#### 3.1. Size Control by Laser Fluence and Liquid Medium.

TEM observations illustrate that Si nanoparticles prepared in water are nearly spherical at low laser fluence, and when laser fluence increases, they become seriously agglomerated, as shown in Figure 2. The size distribution was given at the right side of each image correspondingly, from which we can see that as laser fluence increased, the mean size first decreased and then increased. Figure 3 shows TEM results of the Si nanoparticles obtained in ethanol, which demonstrates that these nearly spherical nanoparticles are ultrafine and well dispersed. As laser fluence increased, the mean size reduced from 6.8 nm at 50 mJ/pulse to 3.1 nm at 200 mJ/pulse. The size distribution of each image was illustrated correspondingly.

Figure 4 clearly exhibits the influence of liquid media and laser fluence on the mean size of Si nanoparticles, from which we know that under the same laser fluence, the mean size of Si nanoparticles fabricated in water is much larger than that in ethanol. As laser fluence increased, the mean size of Si nanoparticles reduced gradually in ethanol and first decreased and then increased in water; simultaneously, the agglomeration between nanoparticles was enhanced. Si nanoparticles prepared in ethanol are ultrafine and well dispersed, which is superior to those acquired in water.

To further investigate the effect of liquid medium, we synthesized Si nanoparticles in the mixture of water and ethanol with different volume ratios (or mole fraction) through the LLA method. It was found that besides some spherical nanoparticles, there are also some aggregations as shown in Figure 5a,b. When the volume of water increased in the 8 mL of liquid medium (or mole fraction increased), the mean size of the nanoparticles increased, which can be clearly seen in Figure 5c.

**3.2. Effect of Liquid Medium on the Nanoparticles' Microstructure.** Further studies revealed that liquid medium has an effect on the microstructure of the nanoparticles as shown in Figure 6, which illustrates that nanoparticles prepared in water are multicrystalline and the mean size of the grains is less than 5 nm (see Figure 6a), whereas in ethanol, most of them are single crystalline (see Figure 6b). The mean size of the grains



**Figure 2.** TEM results of the sample prepared in water at different laser fluences: (a) 50, (b) 100, (c) 150, and (d) 200 mJ/pulse. The size distribution of each panel is given at the right side.

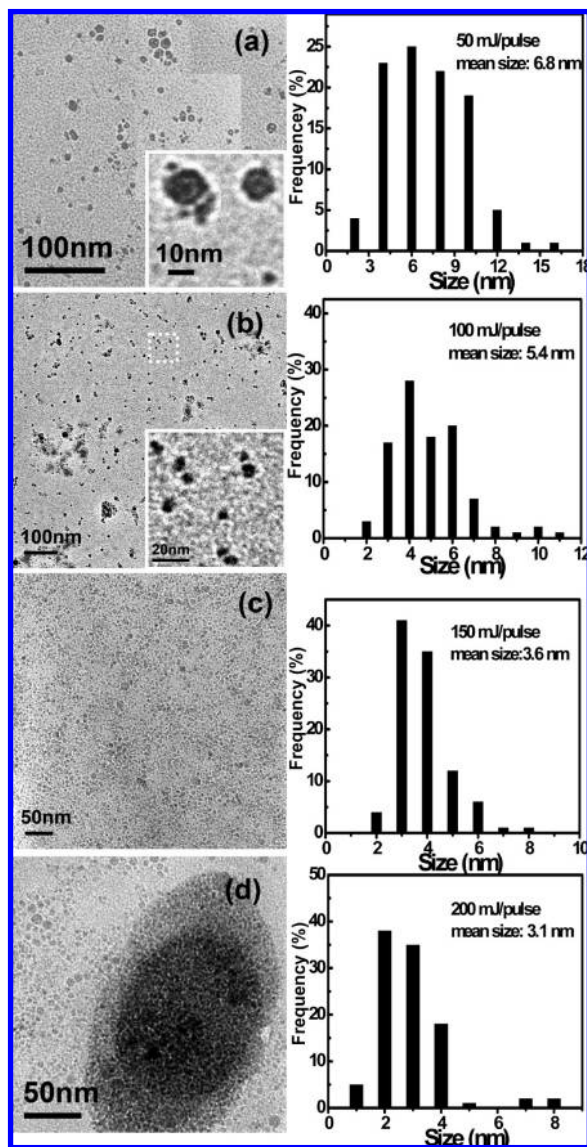
in the nanoparticles fabricated in water is a little smaller than that in ethanol (see Figure 6a,b), which was further verified by the Raman spectral measurement (see Figure 7). The dependence of the Raman peak position shift ( $\Delta\omega$ ) compared with the bulk value of 520 cm $^{-1}$  on Si grain size ( $D$ ) can be described by:<sup>16,17</sup>

$$\Delta\omega = -52.3(0.543/D)^{1.586}$$

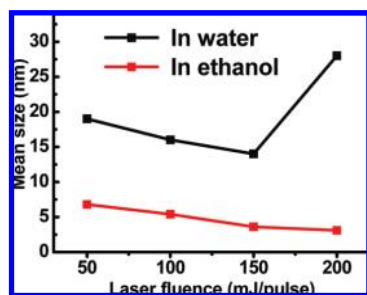
where  $\Delta\omega$  and  $D$  are in cm $^{-1}$  and nm, respectively. The positions of the Raman peak from Si nanoparticles prepared in water and ethanol (corresponding to curves a and b in Figure 7) both shift to lower wavenumber compared to that of bulk silicon crystalline (520 cm $^{-1}$ ), indicating the existence of tiny Si grains, which is in agreement with the high-resolution TEM observations. Furthermore, the former shifts more prominent than the latter, indicating the existence of much smaller grains.<sup>16,17</sup>

**3.3. Classifying Different Sized Nanoparticles by the Centrifugation Method.** In some cases, certain sized nanoparticles are needed. As is well-known, laser fluence and wavelength can tune the size of the nanoparticles during LLA;<sup>4</sup> however, this is only effective in a small size range. In the



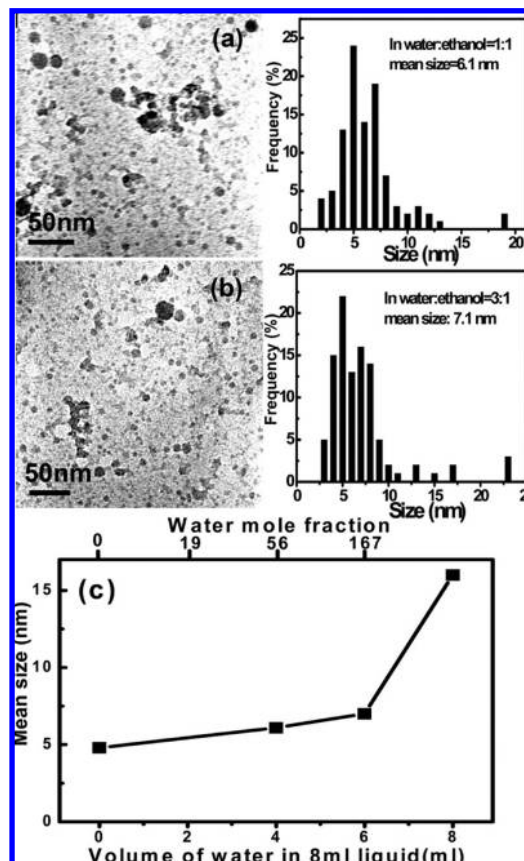


**Figure 3.** TEM results of the sample fabricated in ethanol at different laser fluences: (a) 50, (b) 100, (c) 150, and (d) 200 mJ/pulse. Insets in panels a and b: Locally magnified image. The size distributions are also given at the right side.

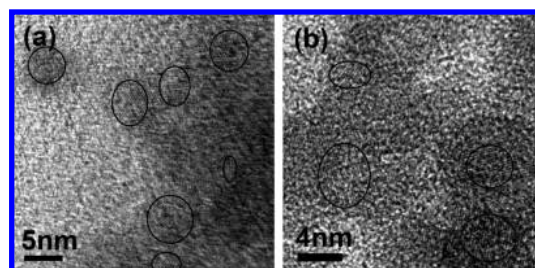


**Figure 4.** The mean size of the Si nanoparticles synthesized in water and ethanol as a function of laser fluence.

following, we supply a simple and convenient way to classify different sized nanoparticles by a centrifugation method. Figure 8 gives TEM results of the Si nanoparticles synthesized by LLA in ethanol after centrifugation at different speeds, from which we can see that after centrifugation at 4000, 8000, and subsequently 14000 rounds/min, Si nanoparticles with mean size of 9.7, 8.3, and 6.8 nm are acquired, respectively. Also, the mean size of the remaining nanoparticles after centrifugation



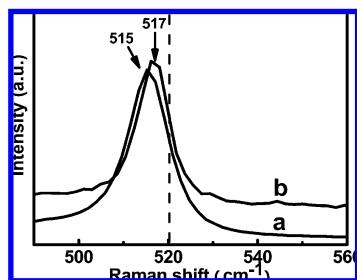
**Figure 5.** TEM results of the sample acquired in the mixture of ethanol and water with different volume ratios (or mole fraction) under 100 mJ/pulse laser fluence: (a) 1:1 (mole fraction: 56 mol/L) and (b) 3:1 (mole fraction: 167 mol/L). (c) The mean size of Si nanoparticles versus the volume (or mole fraction, upper axis) of water in the binary mixture.



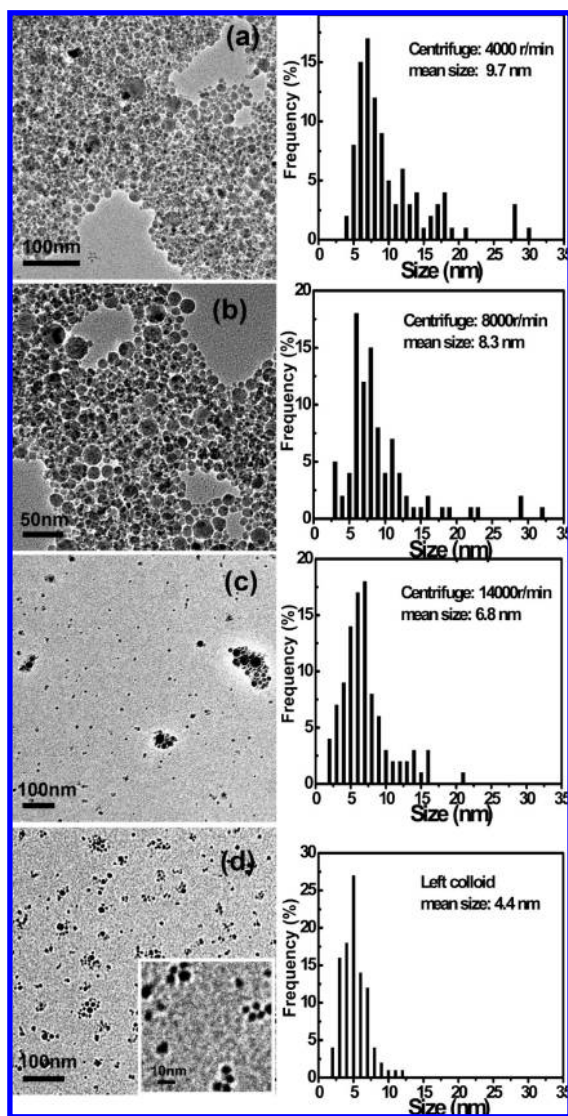
**Figure 6.** Microstructure of the as-prepared samples in water and ethanol with 100 mJ/pulse are related to panels a and b, respectively.

has reduced to 4.4 nm. The size distribution is also narrowed (see Figure 8d) compared with that of the original sample. The mean size of the nanoparticles as a function of centrifugal speed can be clearly seen in Figure 9. Therefore, by LLA and postcentrifugation method, certain sized Si nanoparticles can be acquired.

**3.4. Optical Properties.** Optical absorption measurements for the samples prepared in water and ethanol are conducted as shown in Figure 10A. It shows that Si nanoparticles prepared in water and ethanol both have a blue-shifted absorption edge compared with that of the bulk Si, indicating the existence of the quantum confinement effect. Additionally, sample acquired in water has a more blue-shifted absorption edge compared with that of the sample obtained in ethanol, indicating a more obvious quantum confinement effect. This is in agreement with the above-mentioned result that Si nanoparticles prepared in water

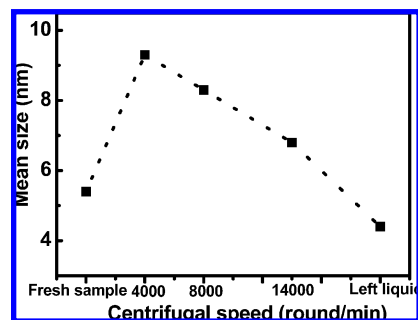


**Figure 7.** Raman shift corresponding to the sample prepared in water (curve a) and ethanol (curve b) with 100 mJ/pulse laser fluence. The dashed line is the peak position of the bulk Si at 520  $\text{cm}^{-1}$ .

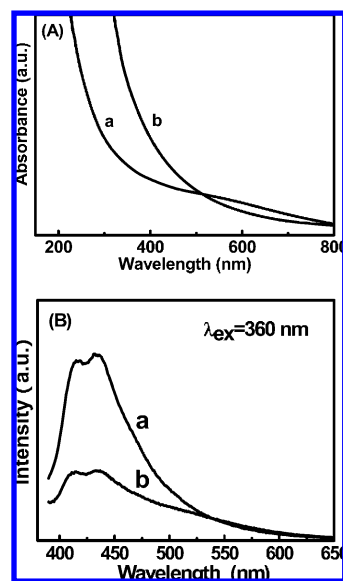


**Figure 8.** TEM results of the sample prepared in ethanol with 100 mJ/pulse after centrifugation at different speeds: (a) 4000, (b) 8000, and (c) 14000 rounds/min for 2 h and (d) the left colloid. The size distributions are also given at the right side. Inset in panel d: Enlarged image.

are formed with smaller grains than those synthesized in ethanol. Furthermore, PL properties of the Si nanoparticles synthesized in water and ethanol are also detected corresponding to curves a and b in Figure 10B. Interestingly, they are located at the blue range with a double peak (about 415 and 435 nm). Si nanoparticles with blue light emission are attractive in both the mechanism and real applications such as Si-based full color display.<sup>18,19</sup> As to the origin of such blue light emission, it should



**Figure 9.** The mean size of the Si nanoparticles as a function of centrifugation speed.



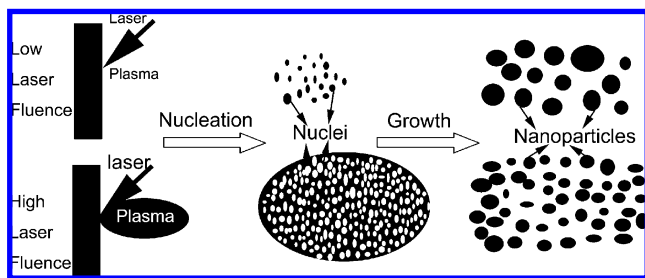
**Figure 10.** Optical properties of the sample prepared in water and ethanol with 100 mJ/pulse laser fluence corresponding to curves a and b, respectively, in each panel. Panels A and B are UV-vis absorption and PL spectra (excitation wavelength: 360 nm), respectively.

have some relations to the quantum confinement effect. The detailed luminescent process is under investigation and will be discussed elsewhere.

#### 4. Discussions

As previously reported,<sup>5,6</sup> when the target is laser irradiated, strong absorption takes place. Interaction between pulsed laser light and the target can produce an instant local high-temperature and high-pressure plasma plume at the interface of the target and the surrounding liquid medium. Subsequently, such plasma will ultrasonically and adiabatically expand, leading to the cooling of the plume region and hence to formation of clusters. With the extinguishment of the plasma, the adjacent formed clusters aggregate quickly into nanoparticles. The above-mentioned process is similar to the well-known nucleation and growth theory.<sup>20</sup>

**4.1. Nucleation–Growth Process.** At low laser fluence, the production of Si atoms filled in the plasma plume is less and the pressure and temperature of the plasma plume is low. Thus, nucleation is relatively difficult; subsequently, the pressure and temperature of the plasma plume suddenly drop and further nucleation becomes nearly impossible. The small number of nuclei formed consumed the surrounding Si clusters, forming large sized particles. Under high laser fluence, due to relatively high temperature and pressure of the formed plasma plume,



**Figure 11.** Schematic illustration of the nanoparticles' nucleation-growth formation process.

nucleation almost takes place simultaneously all over the plume region. Therefore, the incrementally supplied Si atoms at high laser fluence are shared by more nuclei, leading to small sized nanoparticles. The nanoparticles' nucleation-growth formation process is illustrated in Figure 11, which is also helpful to understand the above-mentioned content. The Si nanoparticles size increase at 200 mJ/pulse in water was mainly caused by agglomeration. The size evolution of Si nanoparticles versus laser fluence is in accordance with that of the diamond nanoparticles calculated previously.<sup>20</sup>

**4.2. Evolution of Plasma Plume.** As to various liquid media (water, ethanol, or the binary mixture), different transparency will directly influence the peak value of the pressure and temperature of the plasma plume after laser irradiation; different thermal conductivity will have an effect on the decay process of the temperature and pressure of the plume; diverse density and viscosity will impact the expansion of the plasma plume. All these mentioned parameters act together and influence the nucleation and the following growth process of the nanoparticles, leading to the formation of different sized nanoparticles when the Si target is immersed in different liquid media. However, the reason why nanoparticles prepared in ethanol are more well dispersed and smaller and than those obtained in water and how each parameter influences the plasma plume still needs further work.

## 5. Conclusions

In summary, it was found that pure ethanol is a good liquid medium to prepare ultrafine and well-dispersed Si nanoparticles through a "green" LLA method. Such obtained colloid can be further classified by the centrifugation method to obtain certain sized Si nanoparticles. Liquid media also have an effect on the microstructure of the obtained Si nanoparticles. The influence of laser fluence on the mean size of Si nanoparticles is also investigated. As laser fluence increased, the mean size decreased, which was explained in detail.

**Acknowledgment.** This work is financially supported by the National Science Foundation of China (Grant Nos. 50671100 and 10604055), the Major State research program of China "Fundamental Investigation on Micro-Nano Sensors and Systems based on BNI Fusion" (Grant No. 2006CB300402), and the Knowledge Innovation Program of the Chinese Academy of Sciences (Grant No. KJCX2-SW-W31).

## References and Notes

- (1) Yang, C.; Bley, R. A.; Kauzlarich, S. M.; Lee, H. W. H.; Delgado, G. R. *J. Am. Chem. Soc.* **1999**, *117*, 3145.
- (2) Holmes, J. D.; Ziegler, K. J.; Doty, R. C.; Pell, L. E.; Johnston, K. P.; Korgel, B. A. *J. Am. Chem. Soc.* **2001**, *123*, 3743.
- (3) Zou, J.; Baldwin, R. K.; Pettigrew, K. A.; Kauzlarich, S. M. *Nano Lett.* **2004**, *4*, 1181.
- (4) (a) Kabashin, A. V.; Meunier, M.; Kingston, C.; Luong, J. H. T. *J. Phys. Chem. B* **2003**, *107*, 4527. (b) Mafune, F.; Kohno, J. Y.; Takeda, Y.; Kondow, T. *J. Phys. Chem. B* **2000**, *104*, 9117. (c) Yeh, M. S.; Yang, Y. S.; Lee, Y. P.; Lee, H.-F.; Yeh, Y. H.; Yeh, C. S. *J. Phys. Chem. B* **1999**, *103*, 6851. (d) Mafune, F.; Kohno, J. Y.; Takeda, Y.; Kondow, T. *J. Phys. Chem. B* **2003**, *107*, 4218.
- (5) (a) Zeng, H. B.; Cai, W. P.; Li, Y.; Hu, J. L.; Liu, P. S. *J. Phys. Chem. B* **2005**, *109*, 18260. (b) Zeng, H. B.; Li, Z. G.; Cai, W. P.; Cao, B. Q.; Liu, P. S.; Yang, S. K. *J. Phys. Chem. B* **2007**, *111*, 14311. (c) Zeng, H. B.; Cai, W. P.; Cao, B. Q.; Hu, J. L.; Li, Y.; Liu, P. S. *Appl. Phys. Lett.* **2006**, *88*, 181905.
- (6) (a) Yang, S. K.; Cai, W. P.; Zeng, H. B.; Li, Z. G. *J. Appl. Phys.* **2008**, *104*, 023516. (b) Yang, S. K.; Cai, W. P.; Liu, G. Q.; Zeng, H. B.; Liu, P. S. *J. Phys. Chem. C* **2009**, *113*, 6480. (c) Yang, S. K.; Cai, W. P.; Yang, J. L.; Zeng, H. B. *Langmuir* **2009**, *25*, 8287. (d) Yang, S. K.; Cai, W. P.; Zeng, H. B.; Xu, X. X. *J. Mater. Chem.* **2009**, *19*, 7119.
- (7) Švrček, V.; Sasaki, T.; Shimizu, Y.; Koshizaki, N. *Appl. Phys. Lett.* **2006**, *89*, 213113.
- (8) Werner, D.; Hashimoto, S.; Tomita, T.; Matsuo, S.; Makita, Y. *J. Phys. Chem. C* **2008**, *112*, 1321.
- (9) Saitow, K.; Yamamura, T. *J. Phys. Chem. C* **2009**, *113* (19), 8465.
- (10) Akthakul, A.; Hochbaum, A. I.; Stellacci, F.; Mayes, A. M. *Adv. Mater.* **2005**, *17*, 532.
- (11) Hanauer, M.; Pierrat, S.; Zins, I.; Lotz, A.; Sonnichsen, C. *Nano Lett.* **2007**, *7*, 2881.
- (12) Krueger, K. M.; Al-Somali, A. M.; Falkner, J. C.; Colvin, V. L. *Anal. Chem.* **2005**, *77*, 3511.
- (13) Sun, X. M.; Tabakman, S. M.; Seo, W.-S.; Zhang, L.; Zhang, G. Y.; Sherlock, S.; Bai, L.; Dai, H. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 939.
- (14) Wang, X.; Li, Y. D. *Chem. Commun.* **2007**, 2901.
- (15) Novak, C. N.; James, P.; Franzen, S.; Feldheim, D. L. *Anal. Chem.* **2001**, *73*, 5758.
- (16) Zi, J.; Zhang, K.; Xie, X. *Phys. Rev. B* **1997**, *55*, 9263.
- (17) Paillard, V.; Puech, P.; Laguna, M. A.; Carles, R. *J. Appl. Phys.* **1999**, *86*, 1921.
- (18) Morisaki, H.; Ping, F. W.; One, H.; Yazawa, K. *J. Appl. Phys.* **1991**, *70*, 1869.
- (19) Liao, L. S.; Bao, X. M.; Li, N. S.; Min, N. B. *Appl. Phys. Lett.* **1996**, *68*, 850.
- (20) Wang, C. X.; Liu, P.; Cui, H.; Yang, G. W. *Appl. Phys. Lett.* **2005**, *87*, 201913.

JP907285F