Facile Preparation of Red Luminescent Silicon Nanocrystals via Controlled Chemical Etching

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Silicon nanocrystals with excellent red luminescence properties are prepared by applying controlled chemical etching, which is promising as a high-volume manufacturing technique in the future.

Semiconductor nanoparticles including silicon nanocrystals (Si-nc's) are currently the focus of intense research since they are composed of a harmless element and continuously emit red to blue light as particle size reduces from 3.5 to 1.9 nm at room temperature.[1–3] This material can be utilized for a broad range of industry and biomedical technology applications involving Si-based emitters,[4] electroluminescent displays,[5] and cancer cell monitoring devices with in vivo visualization function.[6] In the past decade, a variety of preparation techniques consisting of bottom-up methods including chemical vapor deposition,[7] ion-implantation,[8] and sputtering[9] have been developed for the Si-nc's with a visible luminescent function. However, yields of visible luminescent Si-nc's made by a variety of these techniques are not high, making them difficult to supply to application fields such as the industry and biomedical technology. Therefore, it is necessary to develop the new techniques for realization of mass-production of Si-nc's with good luminescence properties. Recently, several chemical routes including reverse micelle methods have been reported for preparation of visible luminescent Si-nc's.[10,11] Such chemistry routes have good productivity. Furthermore, both particle size and surface characteristics can be simultaneously controlled. In almost all cases, however, the visible luminescents show only blue, because particle sizes have been limited to smaller than 2 nm. Therefore, further exploration of new chemical routes is still a challenging issue toward versatile control of visible luminescent Si-nc's.

In this letter, we propose a preparation process using chemical etching which shows promise as a new high-volume manufacturing technique. The biggest advantage of this method is that the luminescence color dependent on particle size can be simply controlled by varying the etching conditions (e.g., etching solutions, etching times).[12] In this experimental, commercially available pure Si powders (average diameter of 2 µm) were used as starting materials. The original micrometer-sized Si powders were reduced to nanometer-sized particles in the etching solutions prepared by mixing hydrofluoric acid (HF), acetic acid (CH_3COOH), and nitric acid (HNO_3) solutions (Figure 1a). The added amount of HF solutions was constant, while the volume ratios of CH_3COOH and HNO_3 solutions were varied. The experimental details are described in the Electronic Supporting Information (Table S1).[13]

In the present chemical etching process, two main reaction steps are carried out. The first step is the surface oxidation of the Si powders. The Si surface is oxidized by HNO_3 ($3Si + 4HNO_3 \rightarrow 3SiO_2 + 4NO + 2H_2O$); that is, the Si atoms exposed on the surface of the Si powders are substituted with oxygen atoms.[14,15] The second step is dissolution of the oxidized region by HF ($SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$). The SiO_2 region is completely removed, and Si atoms reappear on the etched surface. The overall reaction is written as follows: $3Si + 4HNO_3 + 18HF \rightarrow 3H_2SiF_6 + 4NO + 8H_2O$. In addition, CH_3COOH was used for dilution of the mixture.

Oxidation and dissolution reactions were continuously repeated for 1 h, and thereby the sizes of the original pure Si powders were dramatically reduced from 2 µm to 3.0 nm or less. Figures 1 and S1[13] show high-resolution TEM images of Si-nc's prepared in various etching solutions. In each sample, the existence of Si-nc's with spherical shape was confirmed by the presence of lattice fringes of Si. For Sample A, the average diameter was 3.0 nm (Figure S1).[13] The particle-size distribution was very narrow. The lattice fringes were nicely matched to a (111) plane of cubic Si (diamond structure) with a proper atomic spacing of 0.314 nm.

The obtained sizes of the Si-nc's were strongly dependent on the etching rate in the etching solutions (Figure 1a). When the etching solutions with highly concentrated HNO_3 are used, oxidation of the Si surface should be accelerated. In such cases, the etching rate is higher and the particle sizes are smaller. Actually, when the amount of added HNO_3 was increased (Samples B and C), the average diameter was reduced to 2.5 nm. On the other hand, dilution by CH_3COOH prevents rapid etching (i.e., the etching rate slows.). When more CH_3COOH was added to the etching solutions (Samples D–F), the average particle sizes increased. Most Si-nc's were beyond the diameter of 5.0 nm.

The total weights of the obtained samples also were varied (Figure S2).[13] In the case of Sample A, the yield was about 4%. The weights proportionally decreased with increase of HNO_3 concentration in the etching solutions (Samples A–C), because of the reduction of average diameter from 3.0 to 2.5 nm by rapid etching rate. On the other hand, the dilution by CH_3COOH solution brought about the slower etching rates (Samples D–F), resulting in the increase of the total weights.

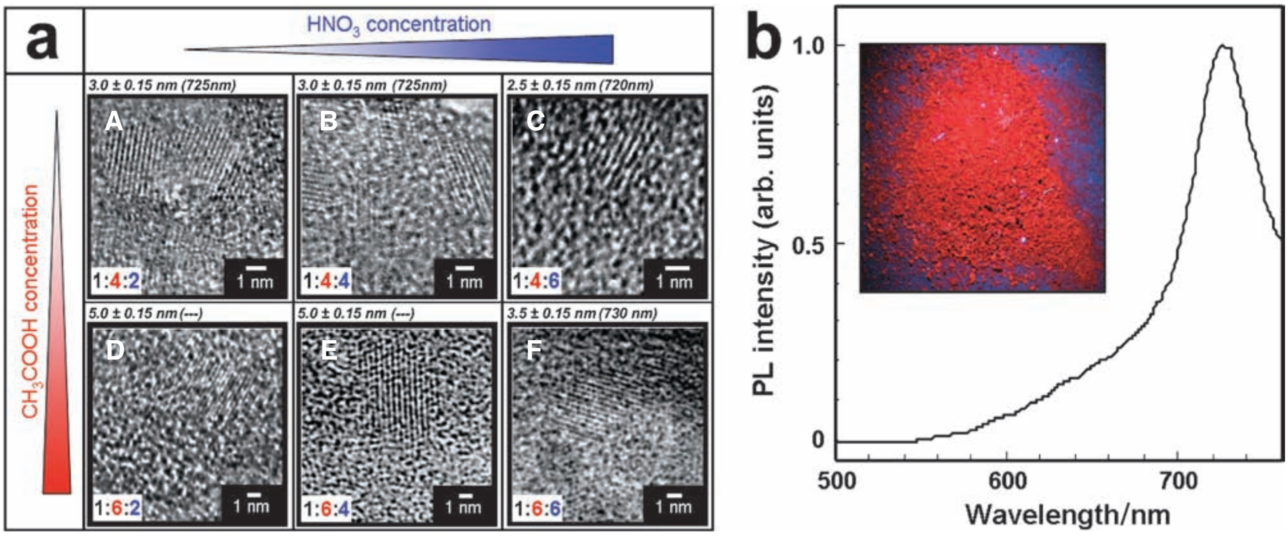

Figure 1. (a) HRTEM images of different Si-nc's (Samples A–F) with various etching solutions. The volume ratio of HF was fixed at 1 and six different etching solutions were prepared. Inset values are the volume ratios of the etching solutions. The blue and red numbers show the volume ratios of HNO$_3$ and CH$_3$COOH solutions, respectively. The particle-size distributions and the corresponding PL peak positions also are noted in the upper side of each TEM images. (b) PL spectrum of Sample A. The inset photograph shows the red luminescence from the Si-nc's.

The photoluminescence (PL) spectrum was detected by using a phonic multichannel analyzer at room temperature in air (Figure 1b). A xenon (Xe) lamp was used as the excitation source with an optical band-pass filter of 313 nm. Sample A with 3.0 nm Si-nc's showed stable red luminescence with a peak at 725 nm and a full width at half maximum height (FWHM) of 60 nm. The inset image shows the bright red luminescence from the Si-nc's, when irradiated with the Xe lamp.

The brightness of red luminescence was sensitive to the particle size and the total weights of the obtained Si-nc's. The PL for each sample showed different intensities (Figure S3).[13] The PL intensity of Samples B and C was about 0.9 and 0.7 times that of Sample A, respectively, because of decrease of the total weights of the obtained Si-nc's. On the other hand, for the other samples (Samples D–F), obvious red luminescence cannot be detected. It is known that the visible luminescence from the Si-nc's arises from radiative recombination of electron–hole pairs via surface trap state (localized state) transitions in the band gap by decrease of particle size.[16–18] This phenomenon occurs only when the particle size is smaller than the excitonic Bohr radius of Si (4.0 nm).[16–18] Therefore, no red luminescence was observed from the Si-nc's (Samples D and E) larger than 4 nm. From these PL results, strong red luminescence (Sample A) can be achieved under the proper etching conditions. Also, the PL intensities can be simply controlled by tuning the compositions of the etching solutions used (Samples B and C). Further optimization of the etching solutions will lead to great enhancement of photoluminescence.

To conclude, we developed a facile preparation approach for red luminescent Si-nc's via chemical etching. This process could allow the mass production of Si-nc's less than 3.0 nm, leading to stable and dazzling red luminescence with a peak at 725 nm at room temperature in air. We strongly believe that such a mass-production system of size-controlled Si-nc's could be important as a convenient, effective and inexpensive technique in the future.

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References and Notes

1 K. Sato, N. Kishimoto, K. Hirakuri, *J. Appl. Phys.* **2007**, *102*, 104305.
2 A. S. Heintz, M. J. Fink, B. S. Mitchell, *Adv. Mater.* **2007**, *19*, 3984.
3 M. Rosso-Vasic, E. Spruijt, B. van Lagen, L. D. Cola, H. Zuilhof, *Small* **2008**, *4*, 1835.
4 L. Gangloff, E. Minoux, K. B. K. Teo, P. Vincent, V. T. Semet, V. T. Binh, M. H. Yang, I. Y. Y. Bu, R. G. Lacerda, G. Pirio, J. P. Schhell, D. Pribat, D. G. Hasko, G. A. J. Amaratunga, W. I. Milne, P. Legagneux, *Nano Lett.* **2004**, *4*, 1575.
5 K. Sato, N. Kishimoto, K. Hirakuri, *J. Nanosci. Nanotechnol.* **2008**, *8*, 374.
6 J. H. Warner, A. Hoshino, K. Yamamoto, R. D. Tilley, *Angew. Chem., Int. Ed.* **2005**, *44*, 4550.
7 G. Santana, B. M. Monroy, A. Ortiz, L. Huerta, J. C. Alonso, J. Fandiño, J. Aguilar-Hernández, E. Hoyos, F. Cruz-Gandarilla, G. Contreras-Puentes, *Appl. Phys. Lett.* **2006**, *88*, 041916.
8 H. Mertens, J. S. Biteen, H. A. Atwater, A. Polman, *Nano Lett.* **2006**, *6*, 2622.
9 K. Sato, T. Izumi, M. Iwase, Y. Show, H. Morisaki, T. Yaguchi, T. Kamino, *Appl. Surf. Sci.* **2003**, *216*, 376.
10 X. Zhang, M. Brynda, R. D. Britt, E. C. Carroll, D. S. Larsen, A. Y. Louie, S. M. Kauzlarich, *J. Am. Chem. Soc.* **2007**, *129*, 10668.
11 R. D. Tilley, K. Yamamoto, *Adv. Mater.* **2006**, *18*, 2053.
12 M. Steinert, J. Acker, S. Oswald, K. Wetzig, *J. Phys. Chem. C* **2007**, *111*, 2133.
13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
14 D. R. Turner, *J. Electrochem. Soc.* **1960**, *107*, 810.
15 B. Schwartz, H. Robbins, *J. Electrochem. Soc.* **1961**, *108*, 365.
16 J. P. Wilcoxon, G. A. Samara, P. N. Provencio, *Phys. Rev. B* **1999**, *60*, 2704.
17 Z. Zhou, L. Brus, R. Friesner, *Nano Lett.* **2003**, *3*, 163.
18 K. Sato, K. Hirakuri, *J. Appl. Phys.* **2006**, *100*, 114303.