

Communications

Synthesis of Silicon Nanocrystal by Magnesium Directed Reduction of the Silica Nanoparticle Formed in Micro-Emulsion of Reverse Micelle

Thu-Huong Le and Hyun-Dam Jeong*

Department of Chemistry, Chonnam National University, Gwangju 500-757, Korea. *E-mail: hdjeong@chonnam.ac.kr

Received April 18, 2014, Accepted August 19, 2014

Key Words : Silicon nanocrystal, Silica nanoparticle, Reverse micelle

The area of semiconductor nanocrystals (NCs) is one of the active fields in a wide range of industrial applications including light-emitting diodes, bio-imaging, solar cells, sensors, photo-detectors, and lasers.¹⁻⁴ Silicon is one of the few elements that is nontoxic, earth-abundant, and environmentally-friendly. In addition, silicon nanocrystals (Si NCs) have unique optical properties such as a wide range of absorption and excitation; color tunability; and monochromatic light emission owing to its quantum confinement effect.⁵ In recent years, Si NCs have been synthesized by chemical reduction methods using reducing agents such as LiAlH_4 ⁶ and sodium naphthalenide,⁷ or by physical method such as the thermal processing of hydrogen silsesquioxane,⁸ ion-implantation,⁹ and vacuum evaporation.¹⁰ Unfortunately, these methods have some problems. In the chemical reduction methods, the size cannot be easily controlled and oxidation is not completely prevented, while in the physical methods, the cost of synthesis is much too high. Therefore, the investigation of a new method of synthesis to provide Si NCs with a minimization of the oxidation problem and cost of synthesis, while enabling size control, is still in demand. In order to respond to this issue, in this communication we report the first synthesis of Si NCs by a combination of the micro-emulsion of reverse micelle and, subsequently, its reduction using Mg powder, even though the two kinds of synthetic steps were developed independently in the fields of silica nanoparticle (SiO_2 NPs) and Si NCs synthesis.^{11,12} The main advantage of our synthesis method, consisting of the two chemical processes, is that it endows easier experi-

mental conditions, lower cost, and more size controllability, compared to the previous chemical and physical methods.

The size-controlled SiO_2 NPs were synthesized from tetraethylorthosilicate (TEOS) molecules by the micro-emulsion method using reverse micelles in Figure 1(a),¹¹ which is explained in detail in the Supplementary Information. The SiO_2 NPs (0.60 g, 0.01 mol w.r.t silicon content) and magnesium powder (0.50 g, 0.02 mol) were mixed and ground together manually to give a grayish brown-colored powder, then heated at 670 °C for 15 hours under an argon atmosphere in a quartz tube furnace. Finally, the Si NCs were obtained as a dark brown-colored powder.

To investigate how the concentration of water affects the size of SiO_2 NPs in our synthetic procedure, we used different volumes of water (1 mL and 4 mL) without changing the other components (Supplementary Information), and the Si NCs were obtained as two kinds of sample (Si-1 and Si-2), respectively. The amount of water had a significant effect on the size of SiO_2 NPs in the following ways: (i) an increase in the water concentration provoked an increase in the size of the reverse micelles, producing bigger nanoparticles; (ii) an increase in the water concentration accelerated the growth of the SiO_2 NPs, resulting in smaller nanoparticles.¹¹ As shown in Figure 1(b), Sherrer analysis was used to estimate size of the Si NCs from the full width at half maximum (FWHM) of the (111) peak in the XRD spectrum. The XRD results exhibit the size of Si-1 NCs to be 19.2 nm, which was bigger than the 12 nm of Si-2 NCs. This means that the size of the SiO_2 NPs decreases as the concentration of water increases. We assert that the second mechanism (acceleration of growth of the SiO_2 NPs) is more dominant than the first one (the increase in the size of reverse micelle). This is because the higher water concentration generates more SiO_2 nuclei, eventually resulting in production of smaller Si NPs through a condensation reaction with hydrolyzed TEOS molecules.¹¹

The hydride-terminated Si NCs (H-Si NCs) were synthesized only from 0.2 g of Si-2 (Si NCs), through an etching reaction using a 1:1:1 mixture of hydrofluoric acid, ethanol and distilled water. The mixture was stirred for 2 h to etch the SiO_2 matrix and gradually decrease the size of the Si-NCs. Furthermore, Henderson and Veinot *et al.* concluded

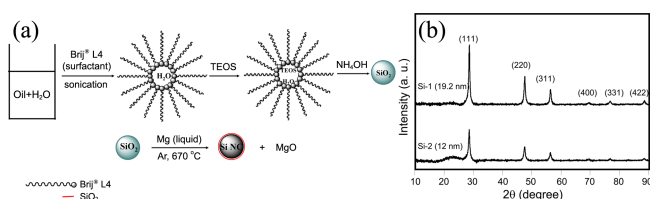


Figure 1. (a) Synthetic procedure of silicon nanocrystals (Si NCs): the first combination of the synthesis of silica nanoparticles (SiO_2 NPs) using a micro-emulsion of reverse micelles, followed by its reduction into Si NCs using Mg powder. And (b) powder X-ray diffraction pattern of 19.2 nm (Si-1) and 12 nm (Si-2) Si NCs samples.

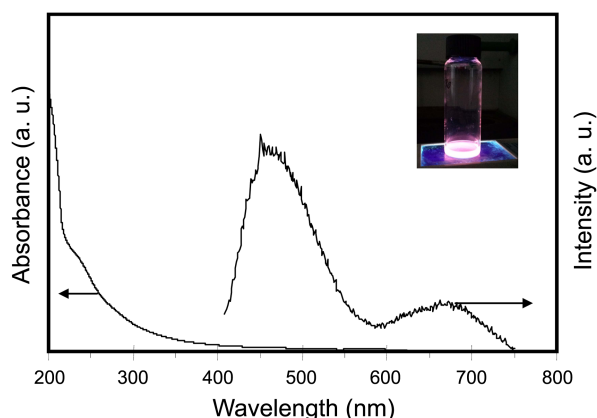


Figure 2. Room-temperature UV-vis absorption and PL spectra of ODE-Si NCs.

that the etching procedure provides a straightforward method to further control the diameter of the freestanding Si-NCs due to long exposure to HF leads to a gradual decrease in Si-NC size.¹³ Therefore, Si-2 (Si NCs) sample decreases size through an etching reaction using a 1:1:1 mixture of hydrofluoric acid, ethanol and distilled water for 2 h.¹³ After completing the etching process, H-Si NCs were collected by centrifugation (10,000 rpm for 3 mins), then capped with 1-octadecene by thermal hydrosilylation at 190 °C to give octadecyl-terminated Si NCs (ODE-Si NCs). The reaction mixture was degassed by three cycles of evacuation, purging with argon to eliminate water, and stirred for 10 h. The product was washed three times by precipitation with acetone as an anti-solvent, and dispersion in toluene. The product was finally obtained as a yellow resin after evaporation of the toluene solvent. The existence of the octadecyl groups on the ODE-Si NCs was confirmed by FT-IR spectroscopy, and the optical properties of the ODE-Si NCs were investigated by ultraviolet-visible (UV-vis) absorption and photo-luminescence (PL) spectroscopy.

The UV-vis absorption spectrum was obtained for the ODE-Si NCs dispersed in cyclohexane with a concentration of 0.01 wt %, showing the onset of ODE-Si NCs at about 400 nm (Figure 2). For the purification to obtain the ODE-Si NCs of narrow size distribution, we tried the size-selective precipitation method, in which the product was washed three times with acetone as an anti-solvent and dispersed in toluene. However, we found that this purification process did not provide a complete separation of ODE-Si NCs of different sizes. Unavoidably, we had to just obtain the information about main size values and size distribution from TEM images of only one kind of ODE-Si NCs sample. In Figure S4(c), we can see fairly wide size distribution, indicating mixing of 3.2 nm with 5.2 nm size.

The photoluminescence spectrum was obtained using excitation at 400 nm, as shown in the Figure 2. The spectrum showed two intense emission bands at around 470 nm and 680 nm, corresponding to the presence of two size regions in agreement with the TEM results mentioned above (Figure

S4). The first peak, of shorter wavelength, corresponds to the Si NC of 3.2 nm, while the second emission of longer wavelength is due to one of 5.2 nm. In other words, the first emission band at around 470 nm (blue emission peak) was assigned to the smaller-sized particles. Besides the peak in the blue wavelength, a second emission peak in the red spectrum at around 680 nm was also obtained, which was assigned to the bigger sized particles.

In this communication, we report the first synthesis of Si NCs by a combination of using both the micro-emulsion of reverse micelles and reduction using Mg powder. These two kinds of synthetic steps were developed independently in the fields of SiO₂ and Si NCs synthesis. In order to investigate how the concentration of water affects the size of SiO₂ NPs in our synthetic procedure, we used different volumes of water (1 mL and 4 mL) without changing the components. The Si NCs sizes obtained (Figure S3(a) and (b)) were 20 ± 2.09 nm (designated Si-1, for 1 mL water) and 10.66 ± 1.66 nm (designated Si-2, for 4 mL water). The Si-2 NCs of 10.66 nm were further treated with hydrofluoric acid (HF) to yield hydrogen terminated Si NCs and capped with 1-octadecene, producing ODE-capped Si NCs of 3.2 nm (mixed with 5.2 nm). The strategy demonstrated in this report can be applied to synthesized and functionalized Si QD with various molecules of different properties in the near future.

Acknowledgments. This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF), funded by the Ministry of Education, Science and Technology (No. 2012R1A1A2039579). This research financially supported by Chonnam National University, 2012.

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