THE SYNTHESIS OF SILICON NANOCRYSTALS

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ABSTRACT

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. Therefore, silicon nanocrystal materials become a vibrant research object in the world due to their potential application. In this report, we study the synthesis of silicon nanocrystal by magnesium directed reduction the silica nanoparticle (SiO_2 NPs). The SiO_2 NPs and magnesium powder were mixed and ground together manually to give a grayish brown-colored powder, then heated at 670ºC for 5 hours under an argon atmosphere in a quartz tube furnace. Finally, the Si NCs were obtained as a dark brown-colored powder. The size in the Si NCs powder was estimated to be a mixture of 10 nm and 5 nm by XRD, which is very similar to those found in the TEM results.

Keywords: semiconductor nanocrystals, silicon nanocrystals …..

I. INTRODUCTION

The area of semiconductor nanocrystals 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 quantum dots (Si QDs) have unique optical properties, a wide range of absorption and excitation; color tunability; and monochromatic light emission, owing to its quantum confinement effect.[5] The synthesis of the silicon nanocrystals (Si NC) play a key role in various applications, like solar cells,[5] bio-imaging and light-emitting devices.6,7 Therefore, in order to utilize the Si NCs in sophisticated optoelectronic devices and bio-imaging, the synthesis and size-controlled of Si NC is required. In recent years, Si QDs have been synthesized by chemical reduction methods using reducing agents such as $LiAlH_4$,[8] and sodium naphthalenide,[9] or by physical methods, such as the thermal processing of hydrogen silsesquioxane,[10] ion-implantation,[11] and vacuum evaporation. However, the disadvantage of these above methods is the poor control of particle size, which directly effects on optical properties of Si QD. To assist with narrow size distribution, the surfactant molecules were added to the reaction mixture to create the inverse micelle and control the size distribution.

Therefore, the investigation of the 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 our report, the SiO_2 NPs which synthesized by microemulsion of reverse micelles were mixed with sodium chloride (NaCl) and magnesium powder using ball-milling to give a grayish brown colored powder. The mixture was then heated at 670℃ for 15 hours under an argon atmosphere in a quartz tube furnace. Finally, we obtained brown powder of Si NCS…

II. EXPERIMENTAL

Chemical and material

Chemical reagents including toluene (anhydrous, 99.8%), tetraethylorthosilicate ($Si(OC_2H_5)_4$, ≥99%), Brij® L4 surfactant ($(C_{20}H_{42}O_5)_n$), and 1-hexanol ($CH_3(CH_2)_5OH$, 98%). Cyclohexane (C_6H_{12}, 99.8%), n-hexane (C_6H_{14}, 95%), ethanol (C_2H_5OH, 99.5%), acetone, and chloroform ($CHCl_3$, 99.7%), ammonium hydroxide solution (NH_4OH, 25%).

Characterizations

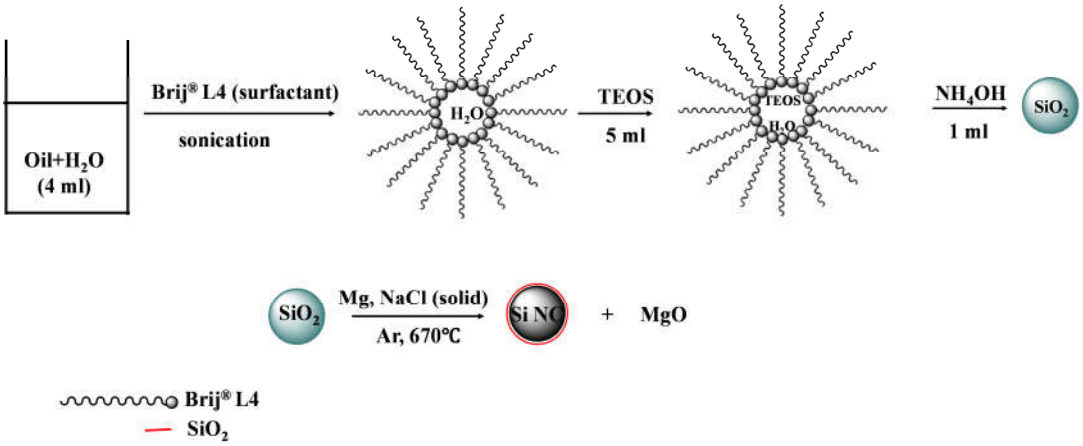
X-ray diffraction (XRD) spectra of Si NC@SiO_2 powder were obtained using an X'Pert Pro Multi-Purpose X-Ray diffractometer (PANalytical, Almelo, Nertherlands). High-resolution transmission electron microscopy (HR-TEM) was performed with a JEOL JEM-2100F operated at 200 Kv.

Synthesis of Si NC

The SiO_2 NPs were synthesized from tetraethylorthosilicate (TEOS) molecules by a micro-emulsion method using reverse micelles, as shown in Scheme 1. Brij® L4 surfactant (12 g, 0.033mol) was mixed with cyclohexane (200ml) and 1-hexanol (3.2 ml) by sonication for 30 min until the mixture changed to a clear solution. Distilled water (4 ml) was then added, and the reaction mixture was sonicated for 10 min. When the water was added, a white solid was generated in the reaction mixture, which was completely re-dissolved by sonication. TEOS (5mL, 0.022mol) was then added with stirring, and the reaction mixture was further stirred for 30 min at room temperature. For the hydrolysis and condensation of TEOS, NH_4OH (1ml) was slowly added while stirring the reaction mixture, which was then stirred for an addition 12 h at room temperature. After the reaction had been completed, the reverse micro-emulsion was de-stabilized by adding acetone (100mL), followed by centrifugation at 12,000 rpm for 5 min. The synthesized SiO_2 NPs were washed with ethyl alcohol (30 ml for each wash) 3–10 times.

The SiO_2 NPs powder (0.60 g, 0.01 mol w.r.t Si content), sodiumchloride (6g), and magnesium powder (0.5 g, 0.22 mol) were mixed and ground together manually to give a grayish brown-colored powder, then heated at 670℃ for 5 hours under an argon atmosphere in a quartz tube furnace. The use of NaCl as a heat scavenger during the reduction process ($Mg + SiO_2 \rightarrow Si + MgO$), prevents the structure collapsing and aggreation into lager crystal of silicon domain.The resulting dark brown-colored powder product was washed to remove NaCl and treated with hydrochloric acid (20 mL) for 12 hours to remove Mg remaining,

Mg_2Si, and MgO. A brown precipitate was obtained by vacuum filtration. And then the solid was washed with distilled water until the washings resulted in a neutral pH (ca. 7). The powder was then washed with ethanol (30 mL) and acetone (3 X 30 mL), and air-dried to yield oxide-coated Si NCs (Si NCs@SiO_2). Finally, the Si NC@$SiO_2$was obtained as a brown powder. The size of the Si NCs powder was determined by XRD and FE-TEM.



Scheme 1. 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.

III. RESULTS AND DISCUSSIONS

X–ray diffraction (XRD) patterns of the Si NC@SiO_2 powder shown in Figure 1 exhibit a peak at 2θ of 28.3, 47.3, 56.1, 69.1, 76.3 and 88°, which are well matching with the three characteristic peaks diffracted from the <111>, <220>, <311>, <400>, <331>, and <422> lattice planes of the diamond cubicsilicon crystal.[8] By using the Scherrer formula, the domain size in the Si NCs powder was estimated to be a mixture of 12 nm and 5.4 nm, which is very similar to those found in the TEM results, wide size distribution indicating mixing of about 10.5 nm and 5.5 nm as shown in Figure 2 b.

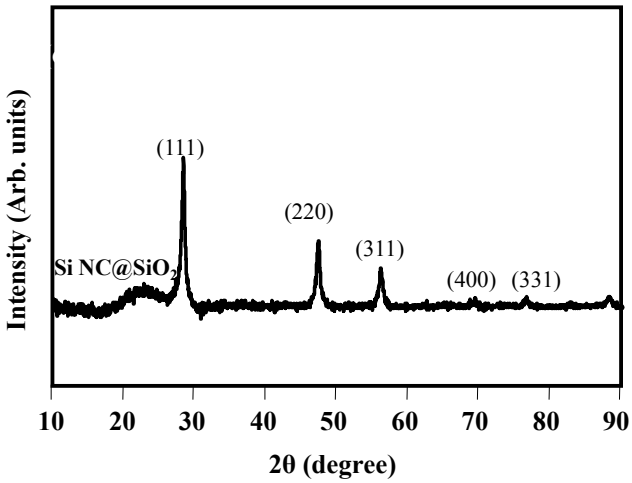


Figure 1. Powder X-ray diffraction of Si NC@SiO_2 sample.

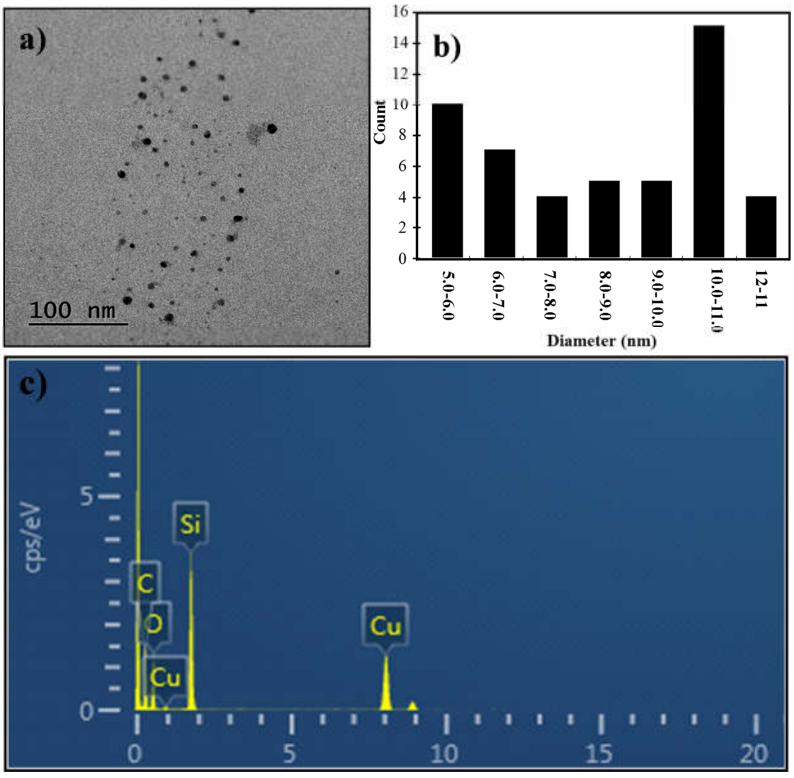


Figure 2.(a) Transmission electron microscopy (TEM) image of Si NC@SiO_2. (b) Size distribution of Si NCs@SiO_2. (c) Energy dispersive X-Ray (EDX) spectra of the Si NCs@SiO_2.

Figure 2 a-c shows the transmission scanning electron microscopy (TEM) image and energy dispersive X-Ray (EDX) spectra of the Si NC@SiO_2 sample. The TEM image clearly shows that highly spherical Si NCs are formed. The composition of these nanocrystals is also analyzed by energy dispersive X-ray spectroscopy (EDX). Figure 2 b shows that these nanocrystals are composed of C element (27 % from the remaining solvent and carbon film on the TEM copper grid), Cu element (27 % from the copper TEM grid), O element (16 % from SiO_2 on surface Si NCs) and Si element (31 % from Si NCs). Furthermore, no magnesium is detected in the EDX result, showing that unreacted Mg metal is removed completely after treatment with hydrochloric acid (HCl).

IV. CONCLUSION

We report the first synthesis of silica nanoparticles (SiO_2 NPs) 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 SiO_2 and Si NCs synthesis. The size in the Si NCs powder was estimated to be a mixture of 12 nm and 5.4 nm, which is very similar to those found in the TEM results. 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.

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TỔNG HỢP VẬT LIỆU TINH THỂ NANO SILICON TỪ NANO SILICA (SiO_2) BẰNG PHƯƠNG PHÁP NHIỆT KIM MAGIE

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Tóm tắt: Vật liệu nano bán dẫn là một trong những vật liệu được ứng dụng rộng rãi trong công nghiệp điện như đèn LED, pin mặt trời, pin điện. Silic là một trong những nguyên tố phổ biến, không độc hại và thân thiện với môi trường. Mặt khác, vật liệu bán dẫn nano silicon (Si NC) cũng có những tính chất quang đặc biệt như hiệu ứng giam giữ lượng tử. Do đo vật liệu tinh thể nano silicon (Si NC) đang trở thành đối tượng nghiên cứu sôi động trên thế giới do những tiềm năng ứng dụng của chúng. Trong báo cáo này, chúng tôi nghiên cứu tổng hợp vật liệu tinh thể nano silicon từ nano silica (SiO_2) bằng phương pháp nhiệt khử magie. Hạt nano silica được trộn đều với bột magie, sau đó đem tiến hành phản ứng khử tại 670°C trong vòng 5 giờ dưới điều kiện khí argon trong lò nung. Tinh thể nano silicon thu được ở dạng bột màu nâu.

Từ khóa: Vật liệu nano bán dẫn, vật liệu bán dẫn nano silicon ….