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Solution-processable white-light-emitting germanium nanocrystals

Naoto Shirahata [a,b,c,*]

[a] International Center for Materials Nanoarchitectonics (WPI-MANA), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
[b] National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
[c] Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

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ABSTRACT

This paper describes an efficient chemical route for the synthesis of visible light emitting nanocrystals of germanium (ncGe). The synthesis started by heating Ge(II) iodide at 300 °C in argon atmosphere. Spectroscopic characterizations confirmed the formation of diamond cubic lattice structures of ncGe. By grafting hydrophobic chains on the ncGe surface, the dispersions in nonpolar solvents of the ncGe became very stable. The as-synthesized ncGe showed the bluish white photoluminescence (PL) feature, but it was found that the PL spectrum is composed of many different emission spectra. Therefore, the color-tuning of white light emission is demonstrated through the witting removal of extra ncGe with unfavorable emission feature by making full use of column chromatographic techniques.

1. Introduction

White light emitting materials have widely attracted a lot of interests because of their versatile use as the emission sources for displays, illuminations, flashlights, and vehicle headlamps in artificial lighting industry [1]. To date, phosphors containing rare-earth ions have allowed for the broad use in those applications. The emission color depends on the rare-earth ions including europium, cerium and terbium [2–6]. Combining emission colors result in white lights. White light emitters are easily fabricated only by coating the emitting materials on blue-LED diode. Although such light emitters with rare-earth ions show high durability against heat and chemicals, the luminescence intensity tends to saturate rapidly with increase of excitation power due to a long lifetime of mili-second level. Besides, the unstable supply of rare-earth elements accelerates the development of rare-earth alternatives [7]. In order to serve this need, both organic dyes and nanocrystals of semiconductors including silicon are active in the front line of the advanced white-light emitting materials [1,8–12].

Germanium (Ge) is a typical semiconductor with 0.67 eV of small bandgap, and has a significantly poorer optical performance due to its indirect bandgap character. The discovery of yellow photoluminescence (PL) from nanocrystals of Ge (ncGe) has therefore created an opportunity for its optical functionality, and opened a long-running debate on its PL origin [13]. Ge is also one of environmentally friendly and nontoxic elements as well as silicon. Therefore, the industrial use of Ge as a light emitting source is promised to open fascinating area. It is known that the quantum confinement effect appears in ncGe when its physical size is getting smaller than bulk exciton Bohr radius for the crystal ($\leq$ 11.5 nm), resulting in the discrete of energy gap. Bulk exciton Bohr radius (α_B) can be expressed as

$$a_B^* = \frac{4\pi\hbar\varepsilon_0\varepsilon_r}{e^2\mu}$$

where μ is the reduced mass, ε_r is dielectric constant and $\hbar$ is reduced Planck constant. One of the distinctive advantages of Ge over Si for optical applications is indeed the large bulk exciton Bohr radius caused by the smaller effective mass of its electron–hole (e–h) pairs and its larger static dielectric constant compared to silicon. Due to the large exciton Bohr radius, it can be expected that its size reduction further strengthens the e–h carrier confinement compared to Si. Nowadays, it is reported that the emission is tuned in a remarkably wide range in photon energy of 0.83–3.87 eV (λ_{em}=320–1500 nm) [14–24]. Some of the ncGe are known to emit the light efficiently with 10–20% of PL quantum yields (QYs) [15,17,19]; however, there is no commercially available ncGe at present. A possible reason for the unavailability lies in the fact that colloidal chemistry for ncGe synthesis has remained undeveloped. Due to the covalent character of ncGe, it is reasonable to require high energy to form the diamond cubic lattice. However, most of colloidal syntheses are carried out in very mild conditions such as a room-temperature synthesis. Among numerous published accounts of colloidal routes, the use of GeI_2 as a starting precursor provides the feasible pathway to yield diamond

* Correspondence address: International Center for Materials Nanoarchitectonics (WPI-MANA), 1-1 Namiki, Tsukuba, Ibaraki 305-0044 Japan. Tel.: +81 29 859 2743.
E-mail address: SHIRAHATA.Naoto@nims.go.jp

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cubic lattice structures of ncGe. Korgel's group reported the colloidal synthesis of ncGe at 300 °C by taking advantage of the high reactivity of GeI_2 and high GeI_2 solubility in alkyl phosphines [25]. Chemical reduction of GeI_2 with oleylamine was reported by Klimov and co-workers, but the emissions of the products were seen in the near-IR (NIR) region [17]. Similar NIR PL feature was reported in elsewhere [24]. To the best of my knowledge, visible light emission has not yet been observed from ncGe synthesized by chemical reduction of GeI_2. Thus, tuning the color of white-light emission is still challenging for ncGe.

The present paper reports first the colloidal synthesis of visible light emitting ncGe using a mixture of GeI_2 and oleylamine. Furthermore, tuning the color of white light is demonstrated by control over size distribution of the ncGe.

2. Experimental

2.1. Chemicals

Oleylamine (> 97%) was purchased from Acros Kanto and was used after degassing under vacuum. GeI_2 (99.99%, Ge) was purchased from Strem chemicals. All reaction was carried out under argon atmosphere using a standard Schlenk line technique.

2.2. Colloidal synthesis of ncGe

As a typical experiment, 10 ml of oleylamine was taken in a Schlenk flask and degassed at 100 °C under vacuum for about 1 h. In another flask, 0.5 mmol GeI_2 was taken inside the glove box and also degassed under argon. Oleylamine was then injected into the flask of GeI_2 for mixing with a syringe. The mixture was then stirred with heating at 120 °C to dissolve in argon bubbling. After complete dissolution, the mixture was then heated to 300 °C under a constant argon flow for 2 h. During the reaction, the color of the solution changed into orange brown, indicating the formation of ncGe. The product was purified by adding methanol to the final solution. Next, the solutions were centrifuged with a speed 10,000 rpm to separate a dark-brown solid which is ncGe emitting the NIR lights from the product [23]. The NIR luminescent ncGe was easily removed from the product because the solid was precipitated at the bottom of the centrifuge tube. The high boiling temperature of the oleylamine allowed for evaporation of methanol and dispersal of the ncGe within the unreacted oleylamine. The product obtained from supernatant solution emits the bluish-white light when excited with 365 nm of handheld lamp. This centrifugation was carried out as the first step for purification. A second purification process was performed using a conventional silica gel column chromatography with eluent of dichloromethane. In a third purification process, the sample was then subjected to the size exclusion chromatography to achieve the separation of ncGe by emission color.

2.3. Characterization

Structural phases of the products were characterized with Raman spectroscopy. Raman spectroscopic measurements were carried out in laser Raman microscope with 785 nm laser excitation source (Raman II, Nanophoton Corporation). TEM images were obtained by operating a JEOL JEM 2100 electron microscope at 200 kV. Size distributions of the samples were measured by dynamic light scattering (DLS, Nikkiso UPA-UT151, Japan). Optical absorbance and emission properties were measured using quartz cuvettes with NCs dissolving in non-luminescent dichloromethane. The optical absorbance was recorded by UV–vis spectrophotometer (V650, JASCO). Photoluminescence (PL) and PL excitation (PLE) spectra were measured using fluorescence spectrometer (Fluoromax, Horiba Jobin Yvon). Since oleylamine shows a weak blue light emission, the emission was subtracted as a background to give PL spectra of the samples.

3. Results and discussion

GeI_2 is known to disproportionate at 350 °C to yield Ge and GeI_4 [26], but nanocrystals form at 300 °C in the present study. At least, there are two possible routes to explain the ncGe synthesis at lower temperature. In the present reaction system for ncGe synthesis, GeI_2 reacts with oleylamine to form adducts of GeI_2 and oleylamine at 120 °C. The adduct formation is confirmed through the observation that GeI_2 dissolved completely in oleylamine at the temperature, and gives an opportunity for ncGe synthesis under mild reaction temperature of 300 °C. In the other route, it might be possible that a terminal amine of the starting oleylamine serves as a reducing agent yielding Ge and GeI_4. Instead, oleylamine is oxidized to imine or nitrile during the reductive reaction as evidenced in the infrared study [23]. In this reaction, the resultant molecules with either one of amine, imine and nitrile groups also serve as capping agents to prevent the aggregation and the enormous growth of nanocrystals. Owing to surface modification with the molecules, the products were soluble in any nonpolar solvents.

The orange-brown color solution product was centrifuged in a mixture of toluene and ethanol for 5 min with 10,000 rpm of rotation speed. The dark-brown precipitate was composed of NIR light emitting ncGe [23], but the supernatant orange solution contained ncGe emitting the visible lights as described below. The supernatant solution was diluted with dichloromethane for a next step of purification after several cycles of the centrifugation, and was then subjected to conventional silica-gel column chromatography in a second step for purification. The purification process was monitored on a plate of thin layer chromatography (TLC). The purified product showed the bluish-white PL property when excited with 365 nm of handheld UV lamp. Henceforth, this bluish-white light emitting ncGe was used as a parent sample.

Crystallographic characterization of the parent sample was carried out using DLS, TEM and Raman. Size distribution was measured by DLS, and presented in Fig. 1(a). Nanocrystals bigger than 12 nm are no longer contained in the parent sample, because the first purification process with centrifugation allows for the complete removal of NIR-light emitting ncGe with average diameter of 12 nm [23]. As is clearly seen, the size distribution of ncGe is broad in the region of 1–12 nm, and the peak top of the distribution is seen at around 4.8 nm. Fig. 1(b) shows TEM photograph and selected-area electron diffraction (SAED) pattern of the parent sample. Shapes of the black-color dots were mostly spherical, and the diameters of the dots are almost smaller than 12 nm consistent with the results obtained by DLS measurement. The SAED pattern of inset covers the TEM observation area. The rings displayed were assigned to the crystal planes. Three diffraction rings matched well with crystal spacing of (111), (220), and (422) planes, corresponding to the diamond cubic lattice structure of Ge. Thus, the SAED pattern, which is performed in conjunction with the TEM observation, revealed that the black dots are diamond cubic lattice structure of ncGe. A typical high-resolution image in Fig. 1(c) resulted that the ncGe is composed of single crystalline phase of diamond cubic lattice. Raman spectrum of the parent sample is presented in Fig. 1(d), and is compared to that of bulk crystalline Ge wafer. In view of UV–vis spectrum (not shown), this sample should not absorb photon of 785 nm of incident light for Raman measurement; however, maybe little emission excited with the light distorts significantly