RESEARCH PAPER

Colloidal synthesis of germanium nanocrystals

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ABSTRACT

In this study, colloidal germanium nanocrystals were synthesized by a simple and novel method, and their optical properties were also studied. Polyvinyl alcohol (PVA) as a surface modifier was used to control the optical properties of colloidal Ge nanocrystals. Fourier transform infrared spectroscopy (FTIR) analysis was performed to identify the various functional groups present in the sample. TEM was used to confirm the formation of nanocrystals and observe the morphology and size of particles. To investigate the optical properties of the prepared nanocrystals, UV-Vis absorption and emission spectroscopy were also employed. Experimental results showed that the synthesized Ge nanocrystals have a spherical shape with the average particle size about 7 nm. FTIR spectrum indicates that Ge nanocrystals are well passivated with minimal surface oxidation. They exhibited luminous blue appearances of light. The emission peak is located at 455 nm wavelength. Also, the direct optical band gap of Ge colloidal nanocrystals was evaluated by Tauc's theory. The crystallinity of Ge nanocrystals was also evaluated by X-ray diffraction pattern analysis. The X-ray diffraction peaks confirmed that Ge nanocrystals have been crystallized in the diamond cubic crystallization.

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INTRODUCTION

Germanium (Ge) as a one of the important semiconductor elements has gained much interest due to the wide range of applications in the nanophotonics. The most prominent feature of this material is its non-toxicity. As well-known green element, Ge has little health impact and high environmental compatibility. Ge is an indirect semiconductor material with a band gap of 0.67 eV. In the bulk form, it shows insufficient optical properties (absorption and emission). However, germanium nanocrystals (Ge-NCs) can show interesting optical characteristics due to quantum confinement effects and size-dependent optical properties at nanoscale. Therefore, it is a well known material with high potential applications in optoelectronics industry, biological imaging, memory stick, and lithium-ion batteries [1,2]. Consequently, Ge NCs have been recently the subject of much research and significant studies released by researchers. The germanium nanostructures with a size of less than about 25 nm (exciton Bohr radius) have shown a high light absorption in the ultraviolet region as well as light-emission lines in the region of visible spectrum due to quantum confinement effects of charge carriers. In general, the three-dimensional electronic structure of Ge NCs can influence their optical properties. Ge NCs can be used as a blue light source, metal ions sensors, particularly iron ions and biological markers [3,4]. They can also be used for making of nanophotonics devices [5]. During the last two decades, various methods such as laser ablation, sol-gel, thermal decomposition and reduction process of germanium salts were developed to synthesize germanium nanocrystals

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[6-8]. As pointed out by Carolan [9], the synthesis of Ge NCs can be broadly divided into two categories. The first category consists of the physical methods, and chemical procedures can be classified in the second categorical level. Moreover, the physical methods are not very attractive and a few interesting publications can be considered as a physical based method of Ge NCs production. Chemical vapour deposition [10], etching [11,12], plasma techniques [13–15], gas-phase pyrolysis [16], sputtering [17–19], laser ablation [8], and ion implantation followed by high temperature annealing [20,21] are known as physical strategies for producing Ge NCs. However, these techniques are expensive, difficult to scale and use extreme temperatures and pressures [9]. On the other hand, the solution based chemical methods with advantages for alloying; doping and purification of the synthesized nanocrystals, were developed for the preparation of Ge NCs. The details of the solution phase synthesis of Ge NCs can be found in ref. [5]. Up to date, different methods, such as the metathesis reaction between germanium zintl salts (NaGe, KGe or Mg_2Ge) and $GeCl_4$ [22-25], reduction of the Zintl salt (NaGe) by ammonium bromide [26], the reduction or hydrolysis followed by condensation [27–31], and decomposition of organogermanes [32–34] have been developed to synthesize the Ge nanocrystals. The thermal reduction of an amido based precursor [35,36] and Ge (II) precursors [37] were also performed. Reduction of GeXY (X = Cl, I; Y = 2, 4) by $LiAlH_4$ [38–40], and $NaBH_4$ [41,42] were used to produce Ge NCs. In addition to this, GeO_2 reduced by $NaBH_4$ and one pot heat up methods also produced Ge NCs [9]. Another method used for the synthesis of Ge nanocrystals is based on the reaction between GeO_2 and water. Due to the solving of germanium oxide in water, different complex compounds including $Ge(OH)_3O^-, Ge(OH)_2O_2^{2-}$ may be formed [43]. These compounds can be turned into $Ge(OH)_4$ using sodium hydroxide on the basis of the following chemical reactions [44, 45]:

$$NaOH \rightarrow Na^+ + OH^- \quad (1)$$

$$GeO(OH)_3^- + OH^- \rightarrow Ge(OH)_4 + 1/2O_2 + 2e \quad (2)$$

In the presence of sodium borohydride, Ge nanocrystals can be obtained by reduction of germanium tetrahydroxide. In this process germanium nanocrystals are synthesized in aqueous media and the available parameters such as temperature, pH and initial concentration

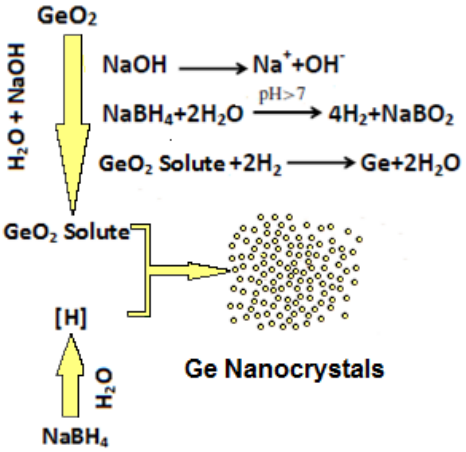

Fig. 1 The reaction of $NaBH_4$ with GeO_2 and producing the Ge NCs.

of the starting materials, can help us to control the formation of Ge nanocrystals in narrow size distribution and engineered surface states. The reaction of $NaBH_4$ with GeO_2 and producing the Ge NCs is shown in Fig. 1. Usually, the synthesized Ge nanocrystals are involved with surface oxidation problem [8]. Consequently, the development of a simple and affordable method plays an important role in achieving germanium nanocrystals with controlled optical properties [46-48]. In this study, colloidal germanium nanocrystals were synthesized by a novel method and their optical properties were also studied.

EXPERIMENTS

In the first stage, a precursor solution was prepared by solving 0.26 gr germanium oxide powder in 50 ml of boiling water under vigorous agitation. Then, 33 ml of sodium hydroxide solution was added to precursor solution at 100°C. The pH of solution must be adjusted to 7 using nitric acid. After 1 hr, 20 ml of the saturated polyvinyl alcohol solution was added to the mixed solution and allowed to agitate for 20 min. In the second stage, 10 ml of 0.32 M sodium borohydride solution was mixed with the solution obtained from the first step. The final solution was kept in a water bath at 60°C for 3hr. In the end of process, a dark brown colloidal germanium nanocrystals solution was obtained. FTIR analysis was performed to determine the chemical components of the synthesized sample using jasco, 410, japan FTIR spectrometer. In order to study the optical properties of the prepared sample, absorption spectrum was recorded over the range of 220-700 nm with a Perkin-Elmer Lambda 750 spectrometer.

Photoluminescence (PL) measurement was carried out with a CaryEclipse spectrometer. For this purpose, the excitation wavelength of 350 nm was used. Philips CM30 300KV transmission electron microscopy was used to determine the size and morphology of prepared sample. The x-ray powder diffraction (XRD) pattern was recorded on Philips B.V (Cu*K*- radiation λ = 0.154 nm), employing scanning rate of 0.02 deg/s in 2θ range from 20 to 80°.

RESULTS AND DISCUSSION

FTIR analysis of the synthesized Ge nanocrystals was initially performed and the obtained spectrum is as shown in Fig. 2. From this figure it can be found that, there are several peaks which can be generally assigned by different chemical groups

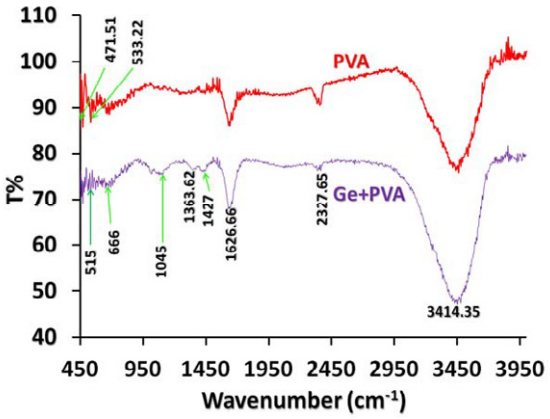

Fig. 2. Fourier transform infrared spectra of PVA and Ge colloidal solutions.

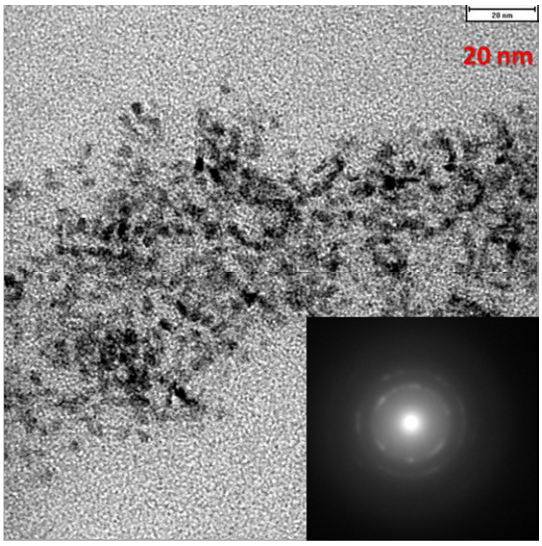

Fig. 3. TEM image of germanium colloidal nanocrystals.

and germanium nanocrystals. The presence of significant peak at 3445 cm^{-1} is due to stretching mode of water. In the FTIR spectrum, the peak centered around 1633 cm^{-1} can be assigned to the –CO stretching vibration of carbonyl groups. Peaks at 515 and 666 cm^{-1} can be related to Ge-H and Ge-C-C vibration modes [13]. It has been previously reported that Ge–O stretching vibration peaks are between 1000–800 cm^{-1} [49-51]. The absence of these peaks in FTIR spectrum indicates that germanium nanocrystals are well passivated with minimal surface oxidation [52,53]. To study the particle size of Ge nanocrystals and their morphology TEM was used. TEM image, shown in Fig. 3, indicates that the synthesized Ge nanocrystals have a spherical shape with average size about ~7 nm. The X-ray diffraction pattern of the dried Ge nanoparticles is as shown in Fig. 4. The peaks at 2θ values of 27, 45.17 and 56.69° of the x-ray pattern could respectively be indexed to scattering from 111, 220, and 222 planes of Ge. X-ray diffraction peaks confirmed that Ge nanocrystals are crystallized in the diamond cubic crystallization [31]. The optical absorption of colloidal sample was measured by a UV-Vis spectrometer and obtained result can be found in Fig. 5a. As can be seen in Fig. 5a, the as-prepared sample shows an absorption peak centered around 280 nm with the absorption onset at about 350 nm. Therefore, Ge NCs was excited by the light with the wavelength of 350 nm. Emission spectrum of the synthesized was illustrated in Fig. 4b. The emission spectrum shows a broad peak that has a maximum at 455 nm. As explained by Wu et al [54], the origin of luminescence in Ge nanocrystals is still unclear. Vaughn et al [5] described that the observed blue light emission peak upon excitation at 350 nm can be attributed to the surface features including absorbed ligands, amorphous oxide, or defects. Zacharias et al [55] believed that the blue PL is not produced by the radiative recombination of excitons confined in the nanocrystals, and it originates from the Ge/O-related defect. Niquet et al [56] observed a strong visible PL in Ge nanocrystals. They believed that the light emission by Ge nanocrystals is independent of the size, and the obtained results cannot be explained by a simple quantum confinement effect [56]. As suggested by Maeda [57], the radiative recombination in Ge nanocrystals could be fast because of the small energy difference between the indirect gap and the direct gap of Ge. Okamoto and Kanemitsu [58] explained that the clear peak of the

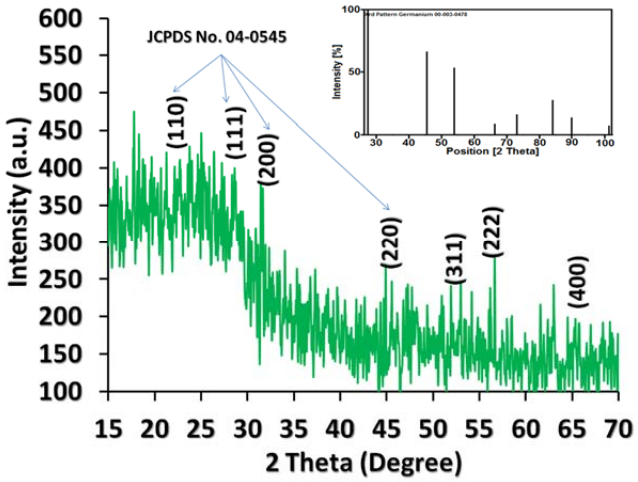

Fig. 4. X-ray diffraction pattern of the dried germanium nanocrystals.

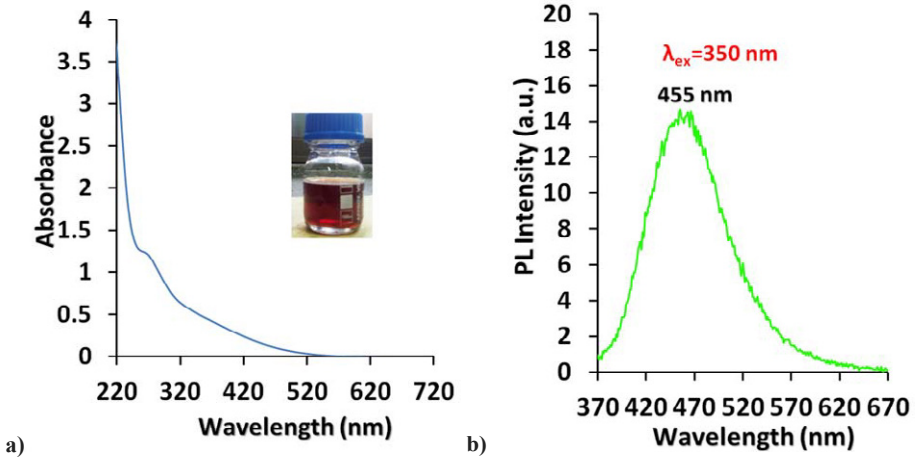

Fig. 5. (a) Absorption (b) photoluminescence spectra of the colloidal germanium nanocrystals.

PL excitation spectrum and a relationship between the PL spectrum and the PL excitation spectrum in Ge nanocrystals are similar to those in direct gap-semiconductor CdSe nanocrystals rather than indirect-gap semiconductor Si nanocrystals. In order to confirm this hypothesis we need to determine the band gap and theoretical particle size determination of the synthesized sample. The optical band gap of Ge colloidal can also be evaluated by [59]:

$$\alpha h\nu = B(E_g - h\nu)^n \quad (3)$$

where $h\nu$ is the photon energy, E_g is the band gap energy, and B is constant. The direct optical band gap of Ge nanocrystals can be determined by plotting $(\alpha h\nu)^{1/n}$ versus the photon energy and extrapolating the linear portion of the curve to zero. For the direct band gap semiconductors n is equal to 0.5. Heath et al [27] reported that Ge nanocrystals, crystallized in the diamond lattice, are characterized by direct band gaps in the near infrared. In Fig. 6, Tauc formula was used to determine the optical band gap of Ge NP, as a direct type semiconductor. As can be found from this figure, the energy band gap of Ge nanocrystals is equal to 2.92 eV. On the basis of average particle size, the band gap of Ge nanocrystals can also be determined. Regarding to the hyperbolic band model (HBM), an equation for band gap energy of Ge nanocrystals can be considered which is more accurate for small size particle as given by [60]:

$$(E_g^{nano})^2 - (E_g^{Bulk})^2 = \frac{2\pi^2\hbar^2 E_g^{Bulk}}{m * R^2} \quad (4)$$

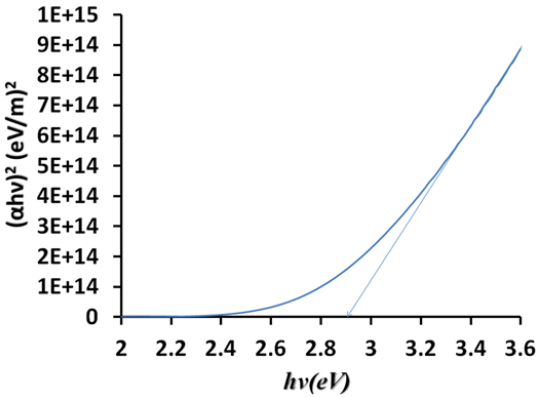

Fig. 6. Tauc's plot of $(\alpha h\nu)^2$ vs the photon energy for the Ge colloidal nanocrystals.

where E_g^{nano} indicates the band gap of the nanocrystals, E_g^{Bulk} is the bulk band gap of Ge (0.67eV), R is the particle radius (~7 nm), and m* is the effective mass, which for Ge has been found to be equal to $0.041m_e$, where m_e is the rest mass of the electron (9.11×10^{-31} kg). The calculated band gap of Ge nanocrystals is 2.81nm. According to the theoretical approach for the band gap determination of semiconductor nanocrystals, the calculated band gap energy of Ge nanocrystal is in good agreement with the previous published material and showed that the prepared Ge nanocrystals have direct band gap. The calculated band gap energy is not consistent with the observed PL spectrum and, therefore, it can be due to defects in the Ge nanocrystals [38].

CONCLUSION

In this study, colloidal germanium nanocrystals were synthesized by a simple and novel method and their optical properties were also studied. Polyvinyl alcohol (PVA) as a surface modifier was used. Experimental results showed that the synthesized Ge nanocrystals have a spherical shape with size variation between 5 to 7 nm. Germanium nanocrystals are well passivated with minimal surface oxidation and exhibit blue light-emitting with PL peak located at 455 nm. Also, the direct optical band gap of Ge colloidal nanocrystals was evaluated by Tauc's theory. The crystallinity of Ge nanocrystals was also evaluated by X-ray diffraction pattern analysis.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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