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Photoluminescent electrospun polymeric nanofibers incorporating germanium nanocrystals

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ABSTRACT

The photoluminescent germanium nanocrystals (Ge-NCs) were successfully incorporated into electrospun polymeric nanofiber matrix in order to develop photoluminescent nanofibrous composite web. In the first step, the synthesis of Ge-NCs was achieved by nanosecond pulsed laser ablation of bulk germanium wafer immersed in organic liquid. The size, the structural and the chemical characteristics of Ge-NCs investigated by TEM, XPS, XRD and Raman spectroscopy revealed that the Ge-NCs were highly pure and highly crystalline having spherical shape within 3–20 nm particle size distribution. In the second step, Ge-NCs were mixed with polyvinyl alcohol (PVA) polymer solution, and then, Ge-NC/PVA nanofibers were obtained via electrospinning technique. The electrospinning of Ge-NCs/PVA nanoweb composite structure was successful and bead-free Ge-NCs/PVA nanofibers having average fiber diameter of 185 ± 40 nm were obtained. The STEM analysis of the electrospun Ge-NCs/PVA nanofibers elucidated that the Ge-NCs were distributed homogeneously in the polymeric nanofiber matrix. The UV–Vis absorption and photoluminescence spectroscopy studies indicated the quantum confinement effect of Ge-NCs on the optical properties of the electrospun Ge-NCs/PVA nanoweb.

1. Introduction

The synthesis of semiconductor nanocrystals (SC-NCs) based on bottom-up and top-down approaches have been under intense investigation for the past decade due to the exclusive optical, electrical and chemical properties of the SC-NCs [1–5]. The optical absorption and photoluminescent behaviors of SC-NCs are tunable since the quantum confinement effect in the SC-NCs is highly size dependent, hence, the development of newly designed SC-NCs are very valuable in optics and optoelectronics applications [6–9]. Novel SC-NCs materials with unique optical properties allows developing multi-functional nanocomposite structures [6–9]. The most common technique for the development of the SC-NCs and nanoparticles (NPs) composed nanocomposite material is the thin film technology [10–14]. Yet, this technique presents several handicaps especially on the control of the film thickness and homogeneity; in addition, it is difficult to fabricate high surface-to-volume materials. Recently, the electrospinning of nanofibrous composite webs have received great deal of attention due to the simplicity of the process and the enhanced properties associated with the very high surface area to volume ratio of the electrospun webs [15,16].

Electrospinning is a versatile technique for producing functional nanofibers and nanowebs from a wide variety of materials including polymers, polymer blends, sol–gels, ceramics and composite structures [15–34]. In electrospinning, the incorporation of functional additives such as NPs into polymeric nanofiber matrix is quite attractive and can be used as an effective platform for scientific research for the development of functional nanofibrous composites [20–34]. Such polymeric nanofibrous composites incorporating NPs have shown distinctive physical, chemical, optical, electrical, magnetic and catalytical properties [20–34]. Additionally, these NPs/polymer nanofibrous composite structures would be very promising due to their very light weight, mechanical flexibility, ease of processing, and low cost production.

The SC-NCs show unique optical and photoluminescent characteristics, and therefore, the incorporation of SC-NCs into electrospun nanofibers would be very appealing for photonics applications. The synthesis method and the control of the structural properties of Ge-NCs has been the subject of considerable research, and Ge-NCs have been mostly synthesized using a wide range of the methods based on etching, co-sputtering and sol–gel [10,35–37]. Another very promising solution for nanocrystals generation consists of using laser ablation method [38]. The use of unique scientific facilities of laser-matter interaction properties opens the doors to the generation of wide variety of metal nanoparticles and SC-NCs by using pulsed laser ablation [39,40]. Laser ablation, especially in liquids, is a versatile method of generating colloidal, highly pure and agent-free nanocrystals.

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In this study, the synthesis of photoluminescent Ge-NCs was achieved by nanosecond pulsed laser ablation, and then, the Ge-NCs were incorporated into electrospun polymeric nanofiber matrix in order to develop functional nanofibrous composite web. Ge-NCs have promising optical and photoluminescent properties, and therefore, Ge-NCs can be considered as one of the prime candidate to replace toxic quantum dots for real world applications. Here, we developed photoluminescent nanofibrous composite web by incorporating Ge-NCs into the electrospun polymeric nanofibers which may have promising applications in photonics.

2. Experimental

2.1. Materials

Bulk Germanium wafer (99.999%, Kurt J. Lesker Company), acetone (>99%, Sigma–Aldrich) and polyvinyl alcohol (PVA) (M_w: 85,000–124,000, Aldrich, 87–89% hydrolyzed) were used as-received. Water used for the preparation of the polymer solutions was from Millipore Milli-Q ultrapure water system. Germanium wafer was washed with acetone via ultrasonic cleaning system before subjected to laser ablation.

2.2. Ge-NCs generation by laser ablation

The generation of colloidal Ge-NCs was carried out using a commercial nanosecond pulsed ND:YLF laser (Empower Q-Switched Laser, Spectra Physics) operated at 527 nm with pulse duration of 100 ns, average output power of 16 W at a pulse repetition rate of 1 kHz corresponding to a pulse energy of 16 mJ. The laser beam was focused on germanium wafer target placed in the glass vial containing 10 mL of pure acetone by using a plano-convex lens with a focal length of 50 mm. The laser ablation was carried out about 5 min and the ablated target results a 0.5 mg/mL concentration of Ge-NCs. During the laser ablation, colloidal solution with dispersed Ge-NCs in liquid media was observed and after the laser irradiation, the color of the colloidal solution becomes brown–yellow.

2.3. Electrospinning of PVA nanofibers incorporating Ge-NCs

At the beginning, different polymer concentrations and electrospinning parameters were used for the electrospinning of PVA solution in order to obtain uniform and bead-free PVA nanofibers, and 8% (w/v) PVA concentration was found to be the optimal. The glass vial of acetone solution containing Ge-NCs generated by laser ablation was kept open overnight at room temperature to evaporate acetone. Then, 4 mL water was added to the vial and sonicated for 3 h in order to achieve homogeneous dispersion of Ge-NCs in the water. After that, 0.32 g of PVA (8%, w/v) was added and dissolved in this aqueous solution containing Ge-NCs (~5 mg) by stirring at 75 °C for 2 h. The weight percent of Ge-NCs in the PVA matrix was estimated as ~1.5% (w/w). Afterwards, the solution was cooled down to room temperature prior to electrospinning. The resulting Ge-NCs/PVA mixture was in brown–yellow color due to the presence of colloidal Ge-NCs. Then, the Ge-NCs/PVA solution was placed into a 3 mL syringe having metallic needle tip (inner diameter = 0.8 mm). The electrospinning of the Ge-NCs/PVA solution was performed in a horizontal position and the flow rate of the solution was controlled by a syringe pump (Model: SP 101IZ, WPI). The electric field was achieved by using the high voltage power supply (AU Series, Matsusada Precision). The electrospinning parameters (applied voltage, feed rate and tip-to-collector distance) were varied in order to obtain bead-free uniform nanofibers from Ge-NCs/PVA solutions. The optimal electrospinning parameters were found as follow: applied voltage = 15 kV, feed rate = 1 mL/h, tip-to-collector distance = 15 cm. Electrospun Ge-NCs/PVA nanofibers were collected on a grounded stationary cylindrical metal collector covered by a piece of aluminum foil. The electrospinning of Ge-NCs/PVA nanofibers was carried out in enclosed Plexiglas box at 23 °C at 22% relative humidity. Finally, the resulting electrospun nanofibers were dried overnight under the hood. For comparison, the electrospinning of PVA nanofibers without Ge-NCs was also carried out under the same experimental conditions and by applying same electrospinning parameters and using same PVA concentration (8%, w/v). Bead-free morphologies were obtained for both PVA and Ge-NCs/PVA nanofibers.

2.4. Characterization

Transmission electron microscope (TEM) imaging of the Ge-NCs and high angle annular dark field (HAADF) scanning transmission electron microscope (STEM) imaging of the Ge-NCs/PVA nanofibers were carried out by using FEI-Tecnai G^2F30 at operating voltage of 300 kV. Ge-NCs drop-cast onto carbon-coated grid for the TEM imaging. In the case of Ge-NCs/PVA nanofiber STEM imaging, the grid was attached on the aluminum foil collector and the some of the nanofibers were directly electrospun and collected on the grid. The particle size distribution and average size of Ge-NCs was determined from the STEM images by measuring around 100 Ge-NCs presented in the PVA nanofiber matrix.

X-ray diffraction (XRD) was performed by using a PANalytical X'Pert PRO Multi-Purpose Diffractometer operated at a voltage of 45 kV and a current of 40 mA using a Cu Kα radiation source. The sample was prepared by drop-casting of colloidal Ge-NCs dispersed in acetone on a low-intensity background silicon (100) substrate.

The elemental composition and the chemical state of the Ge-NCs and the surface characteristics of Ge-NCs/PVA nanofibers were studied by X-ray photoelectron spectroscopy (XPS). The XPS data were recorded for the Ge-NCs sample deposited on a quartz substrate and the Ge-NCs/PVA nanofibers collected onto aluminum foil. XPS was performed on a monochromatic K-Alpha instrument (Thermo) operating at 12 kV and 2.5 mA. XPS spectra were collected with a photoelectron take off angle of 90° from 200 μm diameter circular spot on the sample surface plane, energy steps of 0.1 eV, and pass energy of 30 eV. The control of the flow of the electrons to the surface is achieved by using a well-controlled flood gun technique. The sample surface was first sputtered by an Ar ion beam at 2 keV for 30 min to remove surface contamination and native oxidation by carbon-containing or water molecules absorbed from the environment.

Raman spectrum of the Ge-NCs was performed by Witec Alpha 300S Micro Raman spectrometer with an Nd:YAG laser at an excitation wavelength of 532 nm (laser power: 10 mW) and a Nikon 100× (N.A. = 0.9) air objective. The Ge-NCs was drop-cast onto a quartz substrate and the Raman spectrum was recorded at room temperature.

The morphology and the elemental analyses of the electrospun Ge-NCs/PVA nanofibers collected onto aluminum foil were performed by using scanning electron microscope (SEM) (FEI – Quanta 200 FEG) at an accelerating voltage of 15 kV equipped with energy dispersive X-ray (EDX) system. The fiber diameters distribution and the average fiber diameters (AFD) were calculated by analyzing around 100 fibers from the SEM images.

The optical absorption spectra of the samples were obtained with a Varian Cary 5000 UV/Vis/NIR spectrophotometer in the 325–800 nm wavelength range. The Ge-NCs dispersed in acetone was prepared in quartz cuvette and the samples of PVA and Ge-NCs/PVA nanofibers/nanoweb were collected on the quartz