One Pot Facile Synthesis of Selenium Nanostructures by Microwave Assisted Solvothermal Process

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Abstract: Research in Selenium nanostructures is very much attractive owing to their variety of technological applications. Synthesis of Selenium nanostructures reported in literature is cumbersome due to its complex and lengthy synthesis procedures. A one pot facile synthesis by microwave assisted solvothermal reaction is reported in this work. A simple reduction of SeO$_2$ in presence of microwave yields the Se nanostructure of different morphology such as nano particles and different sizes of nanorods. Moreover an extended procedure of aging the end composition in ethanol solvent for 8hrs is observed to yield Se nanoneedles and aging in ethylene glycol(EG) for one week results in the formation of longer nanorods. Structural analysis from powder XRD diffratogram confirms a trigonal unit cell with P3121 space group while the compositional analysis was performed using Energy dispersive X-ray spectroscopy(EDX). Field emission Scanning electron microscope (FESEM) images indicate the presence of nanoflakes of size (400 to 900) nm. However the morphology of sample indicates the presence of only nanorods in needle shape with length (5 to 6) µm and diameter (0.5 to 1.3) µm and longer aged sample in EG indicates the presence of nanowires with length of the order of (≈100) µm and diameter of the order of (≈3) µm. Optical band gap obtained from (Kubelka-Munk) plot for investigated samples indicate a direct band gap of around (1.72 to 1.76) eV with an infinitesimal but significant variation between different morphology samples. This one pot facile, reproducible, scalable and controllable approach using microwave assisted synthesis is promising for tuning the physical and morphological properties of Se nanostructures in the field of thermoelectrics.

INTRODUCTION

Due to the unique properties of nanostructures they are the special candidates for various applications, the smaller morphology of nanomaterials produces the effective change in their optical, electronic properties etc. [1]. Nanomaterial also have great potential in electronic storage, sensing, catalytic applications [2-4]. Physical and chemical properties of the nanomaterial are highly affected by their morphology, shape and size. By tuning the shape and size of the nanomaterial greater technological applications can be achieved [5]. From last few decades a lot of work has been done on the chalcogenides such as Se, Te, PbS etc in forming the nanostructures. [5] Selenium (Se) nanostructure exhibit different chemical and physical properties than the bulk counterpart importantly the one dimensional nanostructure with high aspect ratio [6]. A number of methods have been developed for the synthesization of nanostructures. Some of them which have been used so frequently are microwave assisted solvothermal process, template based strategies, vacuum vapour deposition, hydrothermal method, ultrasonic induced growth etc. Selenium (Se) is among the chalcogenides nanomaterial which have many technological applications e.g. such as in sensing devices, thermoelectrics, memory devices, photoelectric cells and solar batteries.[7] In this work structural, morphological and optical properties of Se nanostructures prepared by microwave assisted solvothermal synthesis is reported.

EXPERIMENTAL DETAILS

Selenium nanorods have been prepared by microwave assisted solvothermal method. 110 g of SeO$_2$ is mixed with 8ml of Ethylene Glycol which is used as the solvent. NaOH(4N)solution is used as the reducing agent.
Microwave assisted heating is adopted which is emerging as an efficient way of synthesizing nanostructures [5]. Color of the solution changes to brick red giving the indication of formation of selenium nanostructures (indicated hereafter as “SO1”). A part of supernatant denoted as (SO1A) is kept for aging in ‘ethanol’ solution for eight hours. Other part of supernatant denoted as (SO1S) is left for aging in the ‘ethylene glycol’ for a week. X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX) have been used to characterize the sample. Structural characterization is performed using powder X-ray diffraction (XRD) using Bruker D8 Advance X-ray diffractometer (Cu-ka1 1.54 Å²). Morphological property of the sample has been characterized using FEI made “Nova Nano SEM 450” field emission scanning electron microscopy (FESEM). Diffuse reflectance spectroscopy (DRS) measurements for calculating the band gap of the prepared samples has been done using Parkinson made UV-visible spectrophotometer.

(1) Structural Properties

X-ray diffraction pattern of the SO1, SO1A and SO1S sample are shown in figure 1a. From here it reveals that the X-ray diffraction pattern of “SO1”, “SO1A” and “SO1S” are in well agreement with the literature JCPDS file No. 06-362 for Selenium. Enhanced (100) peak is observed in SO1S sample. Figure 1b shows the Rietveld Refinement of the “SO1” sample calculated by Full Prof software, it shows that experimentally calculated value matches with the theoretical values. Crystal structure of the samples as shown in XRD pattern is found to be trigonal having the lattice parameters a=b=4.36 Å and c=4.95 Å. From the sharp intensity of the diffraction peaks it is observed that all the prepared samples are in single phase nature. The crystallite size is calculated by using the Scherrer’s formula.

\[ t = \frac{K \lambda}{\beta \cos \theta} \] (1)

Where \( t \) is the crystal size, \( \lambda (1.54 Å) \) is the wavelength of the X-ray radiation, \( \theta \) is the Bragg’s angle, \( \beta \) is the full width at half maxima (FWHM). Compositional analysis is performed by EDX measurement for “SO1” is shown in figure 1c. From the energy dispersive X-ray spectroscopy (EDX) it can be seen that selenium has been synthesized without any observable impurities.

![Figure 1](image1.png)

(2) Optical Properties

For studying the optical properties of the synthesized selenium (Se), UV measurement has been performed. From the results of the UV measurements value of the band gap has been calculated by Tauc equation and Kubelka-Munk equation given as

\[ A(E_g - h\nu) = (\alpha h\nu)^n \] (2)

Where \( E_g \) is the band gap, \( \nu \) is the frequency of the radiation, \( h \) is the Planck’s constant, \( \alpha \) is the absorbance, \( n \) is an integer, \( A \) is constant. The wavelength of the radiation used was (500-1200) nm. The value of the band gap experimentally calculated by using the Tauc equation and Kubelka-Munk equation is shown in figure 2(a). For the bulk Se taken for reference the observed band gap is 1.74 eV, “SO1” have 1.76 eV, “SO1A” have 1.72 eV and for the
SO1S it is 1.75eV as shown in fig 2a. Figure 2b shows the diffuse reflectance spectra of all prepared sample which shows infinitesimal but significant difference between the reflectance of the samples. Investigation regarding the relation between the morphology and bandgap is in progress.

![Graph showing the Tauc Plot of bulk Se, SO1, SO1A, and SO1S](image)

**FIGURE 2** (a) shows the Tauc Plot of bulk Se, SO1, SO1A, and SO1S. (b) shows the diffuse reflectance spectra of bulk Se, SO1, SO1A, and SO1S.

(3) **Morphological Properties**

![FESEM images of selenium (Se) containing nanoneedles, nanoparticles and nanorods](image)

**FIGURE 3** (a) FESEM images of selenium (Se) containing nanoneedles, nanoparticles and nanorods. (b) FESEM images of SO1A (Se) containing nanoneedles. (c) FESEM images of SO1S with long nanorods and nanowires.

From FESEM images of the SO1(fig.3a) demonstrate clearly the presence of majority of nanoparticle along with few nanorods. We calculated the length of the selenium (Se) nanorods with the help of the Image-J software. FESEM images indicate the presence of nanoparticle (400 to 900) nm in SO1 sample. It can be seen that with aging formation of nanorods is enhanced. In the eight hours ethyl alcohol aged sample (SO1A) figure 3b shows that a large quantity of the nanorods in the shape of nanoneedles is present in the sample. However the morphology of SO1A sample indicates the presence of only nanorods in needle shape with length of the order of (5 to 6) μm and diameter (0.5 to 1.3) μm. Figure 3C is the FESEM image of the longer nanorods formed as a result of one week aging in EG. In case of SO1S large number of selenium nanowire is also observed along with nanorods. Morphology of the SO1S indicates the presence of nanowires with length of the order of (60-100) μm and diameter of the order of (2-4) μm. Therefore it is revealed that aspect ratio of selenium nanostructures can be controlled by optimizing the aging time of the sample and by using different solvents.
RESULTS AND DISCUSSION

Microwave assisted solvothermal process is used for the formation of different morphologies Se nanostructure. Morphological and structural properties of the nanostructure of the selenium Se is determined by the FESEM and powder X-ray diffraction. A prominent difference in powder XRD pattern is observed between SO1,SO1A when compared to SO1S. Enhanced (100) peak in SO1S can be attributed to the formation of specific nanostructures[6] that are oriented along (100) direction. Preliminary XRD and EDX spectra revealed the presence of sodium impurity in SO1A sample. After rigorous water cleaning procedure removal of Sodium impurities is observed in SO1A sample as shown in figure1. Origin of Sodium impurities can be attributed to be from the NaOH which is used as reducing agent in microwave assisted solvothermal synthesis. Optical band gap of the bulk Se, “SO1”, “SO1A” and SO1S is observed to be 1.74eV, 1.76eV, 1.72 eV and 1.75eV respectively. Band gap of the nanostructured Se samples are in comparison with the bulk Selenium composition. An infinitesimal but significant deviation of 0.02eV is observed in “Tauc plot” (figure2). Enhancement in band gap is reported [8]as blue shift due to size reduction in nanostructures when compared to the bulk samples. In our case the observed difference is very small of the order of 0.02 eV. FESEM images of the SO1, SO1A and SO1S reveals the presence of different morphologies such as nanoparticles, nanoneedles and nanorods respectively which is in corroboration with the structural analysis. This one pot facile microwave assisted synthesis and aging can give different morphologies of chalcogenide nanostructures that would be advantageous for thermoelectric applications.

CONCLUSION

Different Selenium (Se) nanostructure has been successfully synthesized by one pot microwave assisted solvothermal process. As prepared sample shows a majority of nanoparticles while eight hours ethanol aged sample yield nanoneedle kind of structure. FESEM images of the sample aged in EG for a week demonstrate the presence of longer oriented nanorods which is in corroboration with the structural analysis. Optical properties of prepared nanostructures shows a very small change in band gap while the band gap of all the samples is in correspondence with the measured bulk band gap of Selenium.

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REFERENCES