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Synthesis and Characterization of Microspheres of Trigonal Selenium

Sr. Francisco Nirmala F.M.M[1*&] Dr. Joe Jesudurai[2]

1. Department of Physics, Stella Maris College, Chennai. email :nirmalamala11@gmail.com.
2. Department of Physics, Loyola College, Chennai. email :joejesudurai@gmail.com.

ABSTRACT:

Microspheres of selenium of 1.5 – 3 μm have been synthesized using fructose as reducing agent under hydrothermal conditions. Sodium selenite has been reduced to form selenium microspheres with water, an ecofriendly solvent. This green route synthesis of t- Se is a one-step, simple and low cost method. Usage of surfactants forms well separated smaller microspheres . The prepared product was characterized by X-ray spectroscopy, scanning electron microscopy (SEM), Raman spectroscopy and Ultra violet–visible (UV –Vis spectroscopy).

Keywords: T- selenium, microspheres, green route synthesis ,hydrothermal and surfactant.

Introduction:

In the recent years, investigations on semiconductor nanostructures have been in the focus of intensive research activities because of its manifold possibilities of applications. Semiconducting elemental selenium exhibits unique and useful properties.The photochemical and semiconductor properties of elemental selenium is used in solarcells, rectifiers, photographic exposure meters and xerography.**[1]** Linear and nonlinear optical properties of selenium has been extensively studied.[**2,3,4].** Elemental selenium has high photoconductivity (about $8x10^4$ Scm^{-1}), Low melting point (about 217 ^oC) and high reactivity towards a wealth of functional materials(e.g. Ag_2Se, Bi_2Se_3,).[**5-7]**

Various methods have been reported for the synthesis of t-Se. Some of them are synthesis of selenium nanorods by laser ablation method,[**8**] Reduction of selenious acid by solution refluxing,[**9]** Solution mediated transformation from Selenium powder,[**10a**] and preparation of Se nanotubes under ultrasonic conditions in micellar solutions of the surfactant poly dodecyl ether **[10b,10c].** It is to be noted that there are only limited number of works and reports on the synthesis of t-Selenium.**[11,12]**

The method reported in this article for the fabrication of t- Selenium micro spheres is green chemical method **[13,14,15]** The term ‘green’ signifies

the usage of non-toxic and easy to recycle reagents in the process.

Hydrothermal synthesis is a simple and advantageous approach for the preparation of inorganic materials with micro or nanostructures with different morphologies.**[16**,**17]** It facilitates many materials to be prepared at relatively lower temperatures when compared to the solid state and vapour reactions.

This study describes a one step hydrothermal synthesis of selenium microspheres in which addition of EDTA as a surfactant generates well separated spheres .This is a report on green chemical method where no complex precursors were used.Fructose used as the reducing agent has soft reducibility and is a useful monosaccharide in the biosphere.

Experiment:

Materials:

Chemicals used in the synthesis were of analytical grade and were used without further purification. Fructose (99.9 %), seleniousacid (98%), and EDTA (>99.999%) were purchased from **SISCO Research Laboratories, SIGMA – ALDRICH**.

Procedure :

In a typical experimental procedure, 8.4 mmol of fructose ($C_6H_{12}O_6$) and 1.6 mmol of selenious acid were dissolved in 80 mL of deionised water by consdtant stirring. This was then loaded into Teflon – lined stainless steel autoclave of 100mL capacity. The autoclave was sealed and maintained at 200 ^{0}C for 6 hours in **Matri Hot Air Oven a**fter which, the autoclave was allowed to cool naturally to room temperature. The sample in the form of a black coloured powder was collected by centrifugation. The synthesized product was then washed thoroughly with deionized water and absolute ethanol several times by means of suction method. This step removes the byproducts. Finally, it was dried in a vacuum for 4 hours at 60^{0}C .

- The phase and crystallinity of the as-prepared sample was characterised by X-ray diffraction (XRD) on a **D8 ADVANCED MODEL BRUKER**, equipped with Cu Kα (λ = 0.15406 nm) radiation in the 2θ range from 20^0 to 80^0 while the voltage and electric current were maintained at 40 kV and 30 mA, respectively.
- The UV-Vis absorption spectrum of the obtained product was recorded using **CARY 5E UV – VIS – NIR SPECTRO PHOTOMETER**

- Scanning electron microscopy (SEM) images were obtained using **FEI QUANTA FEG 200 HIGH RESOLUTION SCANNING ELECTRON MICROSCOPE**.
- Raman spectral pattern was obtained using **BRUKER RFS 27 FT-IR SPECTROMETER WITH FRA-106 FT-RAMAN ATTACHMENT**

Results and discussions

The as-synthesized product was analyzed for its crystal structure through X-ray diffraction analysis. The obtained peaks were compared with the standard JCPDS card (06-362).

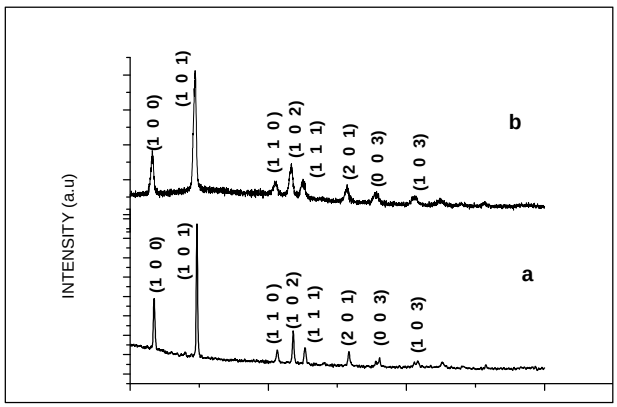


Fig -1 X-ray diffraction pattern of t-Selenium prepared for 6 hrs at 200^0 C

a) Sample prepared without EDTA

It is evident from the graph that all the reflections can be indexed to the trigonal phase of selenium. The calculated lattice constants a=4.366 A^0 and c= 4.954 A^0 are in good agreement with the reported data (a=4.366 A^0 and c= 4.953 A^0, JCPDS card number 06-362). The strongest peaks obtained for both the samples prepared with and without EDTA indicate that the preferred growth direction as **101 .** It is also clearfrom the XRD pattern (Fig.1) that the broadening of diffraction feature is seen to be shifted to the higher scattering angles with decreasing grain size.

Using Scherrer formula,the average grain size was calculated to be 40 nm for the sample prepared without surfactant

Scherrer formula $D = k\lambda/\beta \cos\theta$

Where, D is the grain size, k is the geometric factor, θ is the angle of diffraction, λ is the X-ray wavelength and β is the full width half maximum of diffraction peak.The average grain size calculated for t- Se prepared with EDTA is 25 nm . Addition of EDTA which acts as a surfactant decreases the grain size . It is known that above a certain grain size limit (~ 20 nm) the strength of the material increases with decreasing grain size .**[18, 19]**

The average strain of the prepared t-Se without the surfactant was calculated to be 9.14 x 10^{-2} unit using Stokes-Wilson equation

$\varepsilon_{strain} = \beta / 4 \tan\theta$

whereβ is the full width half maximum of diffraction peak and θ is the angle of diffraction

The average strain increases to be 0.2219 unit for the t- Se prepared with EDTA .

The dislocation density is the length of dislocation lines per unit volume of the crystal [**20]**

Dislocation density for the two samples had been calculated to be 8.97 x 10^{16} lines / m and

2.6 x 10^{17} lines / m respectively using the formula

ð= 15 **β**cos **θ** /4a D

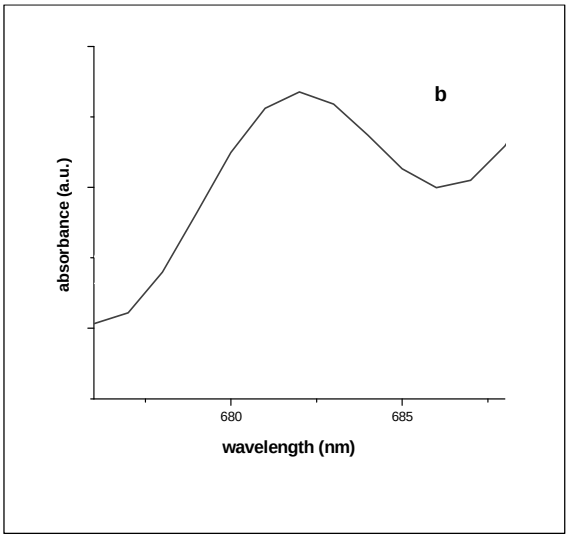
where ð is the dislocation density β is thefull width half maximum of diffraction peak**,**θis the angle of diffraction , a is the lattice parameter and D is the average grain size,which again increases with the decrease in grain size. The movement of the dislocation is impeded by other dislocations present in the sample. Therefore a larger dislocation density implies a larger hardness **[21]**. It has also been shown that as the dislocation density increases, the lattice average strain increases and the average grain size decreases. **[22]**

The values of the average grain size, the dislocation density and the average strain are enumerated in Table 1. Addition of EDTA to t-Se decreases the average grain size and increases the dislocation density and the average strain. From this we infer that addition of EDTA increases the strength of theprepared t – Se .

Table 1

Sample	Average grain size (nm)	Average strain	Dislocation density lines /m^2
t-Se without EDTA	40	9.14 x 10^{-2}	8.97 x 10^{16}
t-Se with EDTA	25	0.2219	2.6 x 10^{17}

Fig.2 shows the UV – Vis absorption spectrum of the t-Se prepared at 200^0 C without and with EDTA . The sample was dispersed in absolute ethanol under intense sonication of 20 mins. and ethanol was used as a reference too. The result shows an absorption peak centered at approximately 689.5 nm for the sample prepared at 200^0 C without any surfactant. The bandgap of the t-Se is calculated, and the value was determined to be 1.8 eV, which is consistent with the reported value of 1.71 eVfor bulk Sethin film.**[7].** The absorption peak for sample prepared for 6 hours at 200^0 C with EDTA is centred at 682 nm and the bandgap calculated is 1.82 eV. Though there is a considerable decrease in the size of the t-Se particles synthesized with EDTA the size is still large and so blue shift in the absorption range is not identified.



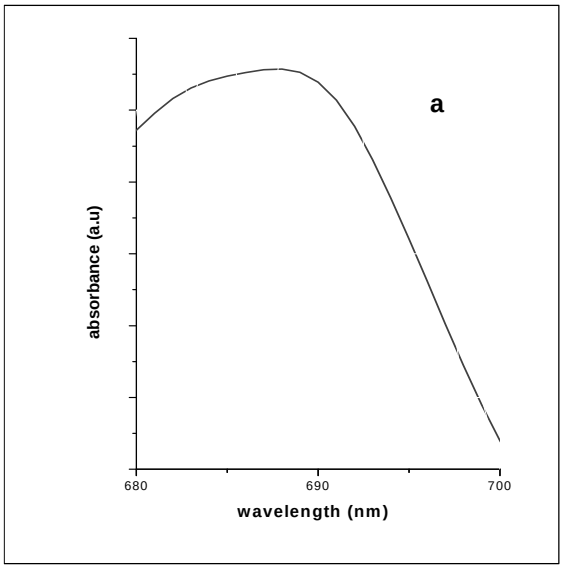


Fig.2 UV-Vis absorption spectrum of t-Se prepared at 200^0 C

a)for 6 hours
b) for6 hours with EDTA

The size and morphology of the t-Se synthesized at 200 ^{0}C for 6 hours were investigated by high resolution scanning electron microscope (SEM) and is shown in Fig 3a. Fig 3b is the SEM pictures for t-Se prepared for 6 hrs.at 200^0C with surfactant. The

formed selenium is of spherical shape and addition of EDTA(6 mm) as a surfactant decreases the size and forms well separated monodispersed microspheres. On the basis of these observations it is evident that EDTA has two major effects on the growth of t-Se.Firstly presence of EDTA has reduced the agglomeration of the t-Se formed and secondly the surfactant has reduced the size of the microspheres from 11- 18 μm to 1.5-3 μm .

The chemical composition of the as – prepared t-Se samples without and with surfactant (fig 3a and 3b EDS of the samples) show that the synthesized samples consist of selenium only. Hence it is imperative to confirm the chemical purity of the sample .

The word surfactant is short for "Surface Active Agent." In general, these chemicals, when dissolved in water or another solvent, orient themselves at the interface (boundary) between the liquid and the solid (the dirt that is removed), and modify the properties of the interface.The surfactant used in this work is **EDTA**

EDTA or ethylene diamine tetra acetic acid is a novel molecule for complexing metal ions. It is a polyprotic acid containing four carboxylic acid groups and two amine groups with lone pair electrons.

The sample prepared for the same reaction duration without the addition of surfactant is of microspheres of the range 11-18 μm (Fig.3a),Addition of appropriate amount of EDTA (6 mm) decreases the size of the microspheres to 1.5 - 3 μm**.** In general EDTA is used as a structure directing agent and a stabilizing agent for the growth of t-Se and Te. **[23]** Any surfactant reagent kinetically controls the growth rates of the various faces through selective adsorption and desorption on these surfaces.

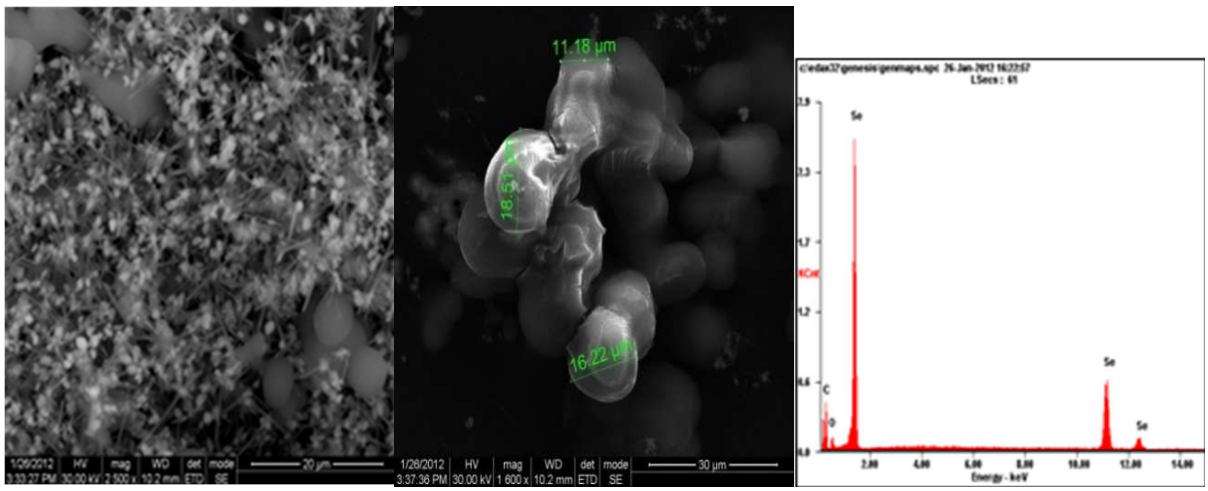


Fig 3a SEM and EDS for selenium prepared for 6 hrs.at 200^0 C

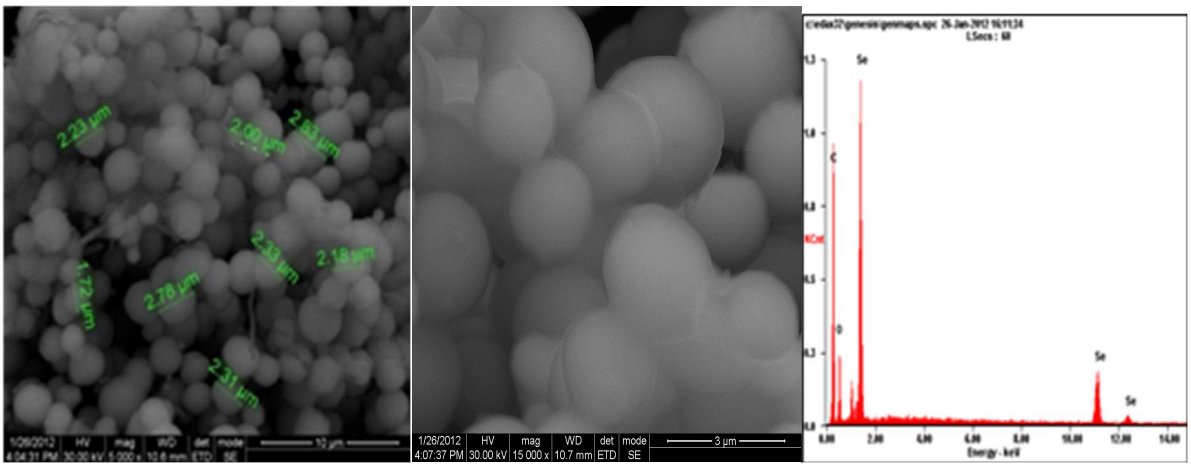


Fig.3b SEM and EDS for selenium prepared with surfactant EDTA for 6 hrs.at 200^0 C

The strong resonance peaks at 233cm^{-1} and 234.9 cm^{-1} for t-Se(Fig.4)are characteristic of trigonal selenium[**24]**. These are attributed to the vibration of the selenium helical chain and this is due to the stretching mode at about 233 cm^{-1}. Therefore the raman scattering results confirm the formation of well crystallized t-Se by the reduction of selenious acid under hydrothermal conditions.

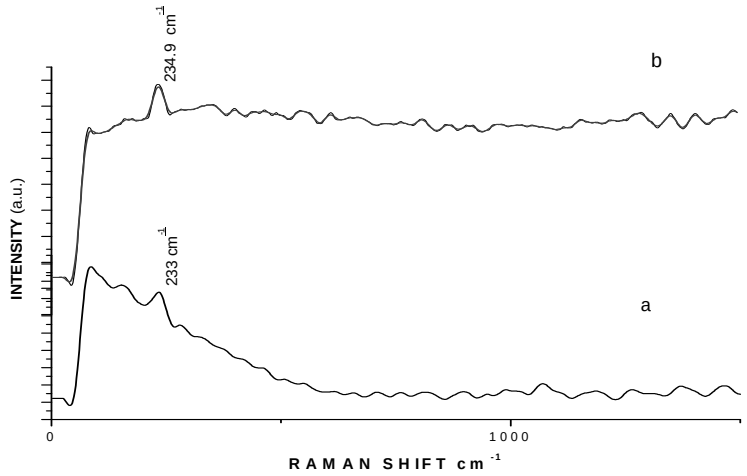


Fig 4. Raman spectra of t-Se prepared at 200^0 C for 6 hours
a)without EDTA b) with EDTA

Conclusion

T- Se microspheres were successfully synthesized using a simple one-step hydrothermal method. The crystal structure of the microspheres were analysed and the results confirm the fabrication of hexagonal phase of t-Se. This green chemical approach confirms that the addition of EDTA as a surfactant reduces the size and forms well separated monodispersed microspheres. Dislocation density and lattice strain calculated from the diffraction peaks reveal that there is an increase in these values with a decrease in the grain size. It is observed that the addition of EDTA to t- Se has decreased the size of their average grain size and increased the strength of the substance**.** The as prepared t-Se could be further used for potential applications including nanodevice fabrication.

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