



Ionic liquid-induced synthesis of selenium nanoparticles

Bhushan Langi^a, Chetan Shah^b, Krishankant Singh^b, Atul Chaskar^{a,*}, Manmohan Kumar^b,
Parma N. Bajaj^b

^a Changu Kana Thakur Research Centre, New Panvel 410 206, India

^b Radiation and Photochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

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ABSTRACT

A simple wet chemical method has been used to synthesize selenium nanoparticles by the reaction of ionic liquid with sodium selenosulphate, a selenium precursor, in the presence of polyvinyl alcohol stabilizer, in aqueous medium. The method is capable of producing spherical selenium nanoparticles in the size range of 76–150 nm under ambient conditions. This is a first report on the production of nano-selenium assisted by an ionic liquid. The synthesized nanoparticles can be separated easily from the aqueous sol by a high-speed centrifuge machine, and can be re-dispersed in an aqueous medium. The synthesized selenium nanoparticles have been characterized by X-ray diffraction, energy dispersive X-ray analysis, differential scanning calorimetry and transmission electron microscopy techniques.

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1. Introduction

Synthesis of nano-structured materials have generated a great deal of interest because of their unique optoelectronic, magnetic and mechanical properties, which differ largely from that of bulk materials, as well as their applications in the fields of catalysis, sensors and other nano-devices [1]. An extensive reported literature exists on the synthesis and applications of nanoparticles of both noble metals, such as silver, gold, platinum, etc., and semiconductors, like CdSe, ZnSe, etc. However, research on nano-metalloids, like selenium, is scanty. The high reactivity of selenium towards a large number of chemicals has stimulated researchers recently, to convert selenium into various important nano-materials, such as ZnSe, CdSe, etc. [2]. Pure selenium, as well as selenium containing nano-materials, have excellent photoelectrical characteristics, semiconductor properties and high biological activity [3].

Nano-selenium has been widely used in electrical rectifiers, photocells, photographic exposure meters, xerography, etc., because of its high photoconductivity, and large piezoelectric, thermoelectric and non-linear responses [4]. Selenium is an essential micronutrient required for most of the living organisms, including human beings [5]. Most of the nano-selenium syntheses have been carried out by reduction of selenium dioxide, selenate, or selenites, with reducing agents, like hydrazine, sodium

ascorbate, or glycol. Oxidation methods are also reported by some of the researchers for the formation of nano-selenium [6–9]. These chemical methods required quite harsh experimental conditions [10].

In recent years, advantages of ionic liquids in the syntheses of inorganic nano-materials have been gradually realized, and these materials have received more and more attention due to their unique physical and chemical properties. A good number of research articles as well as reviews on the use of ionic liquids exist in the literature [11–15]. Many nano-structured materials have been successfully synthesized by employing ionic liquids as precursors [16–18]. For quite a long period of time, ionic liquids have been used as green solvents in organic syntheses, and have also found applications in the field of catalysis [19].

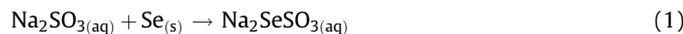
Due to the great advantages of ionic liquids, we have also used these for the synthesis of selenium nanoparticles. In this study, we report a simple wet chemical method which is capable of producing selenium nanoparticles by the reaction of sodium selenosulphate with 3-methylimidazolium methane sulfonate as an ionic liquid, under ambient conditions. To the best of our knowledge, the use of ionic liquid for the formation of selenium nanoparticles is being reported for the first time.

2. Experimental details

Polyvinyl alcohol (PVA) of molecular weight 40,000, obtained from s. d. Fine Chemicals, and selenium powder from Aldrich, were used as received. Synthetic grade methane sulphonic acid and 1-methyl imidazole were procured from CDH and Spectrochem,

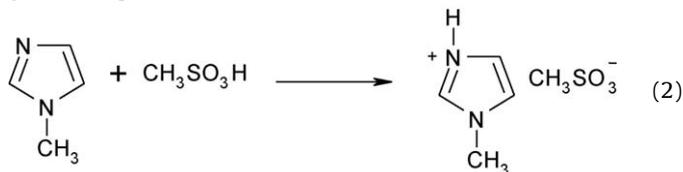
* Corresponding author. Tel.: +91 22 27464193; fax: +91 22 27461569.
E-mail address: achaskar@rediffmail.com (A. Chaskar).

respectively. All the other chemicals were of GR grade, and obtained from local market. Aqueous solutions were prepared, using deionized water. Sodium selenosulphate, Na_2SeSO_3 , was prepared by the method reported earlier [20].

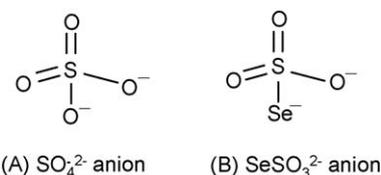


Briefly, a mixture of selenium powder (2 g) and Na_2SO_3 (20 g), in 100 ml water, was refluxed at 70 °C, for about 7 h, and then it was filtered to remove unreacted selenium, and kept in dark to prevent photo-oxidation. This Na_2SeSO_3 solution (~0.25 M) was used as a stock solution for Se precursor. PVA stock solution (1%) was prepared by dissolving 1.0 g of PVA into 100 ml water.

The ionic liquid was synthesized by taking 1-methylimidazole (0.01 mol) in a round-bottom flask and cooling it to 0 °C. Then, methane sulfonic acid (0.01 mol) was added slowly with stirring. The mixture was stirred for 5 min at room temperature, to get 3-methylimidazolium methane sulfonate [19]. The reaction is given in Eq. (2).



Synthesis of nano-selenium was carried out by addition of the ionic liquid (in small aliquotes) to aqueous sodium selenosulphate solution (concentration 5×10^{-4} to 1.5×10^{-3} mol dm⁻³), containing PVA stabilizer (0.025–0.100%), while constantly stirring the reaction mixture. The amount of the ionic liquid required for the completion of the reaction was found to be dependent on the initial concentration of sodium selenosulphate present in the solution. When a small aliquot of the ionic liquid was added, it got completely consumed, and the unreacted sodium selenosulphate was left in the reaction mixture. This addition was repeated until



Scheme 1. Tetrahedral structure of SO_4^{2-} and SeSO_3^{2-} anions.

the reaction was complete, and no more formation of selenium nanoparticles was observed on addition of a fresh aliquot of the ionic liquid. The completion of the reaction was tested only after separating the selenium nanoparticles from the reaction mixture.

DSC measurements were carried out, using a Mettler TA 3000 thermal analysis system, model DSC-30. XRD patterns were recorded with a Phillips X-ray diffractometer, model PW 1710 system, using a Cu K α source ($\lambda = 0.15406$ nm). Energy dispersive X-ray analysis (EDAX) of the synthesized selenium nanoparticles was recorded, using an INCAE350 instrument from Oxford, UK. TEM characterization was carried out with a JEOL-2000 FX electron microscope, after loading the sample on a copper grid coated with carbon film.

3. Results and discussion

In the recent past, ionic liquids have been used, either as solvents, or precursors, for the synthesis of nanostructure materials [21,22]. The synthesized ionic liquid is acidic in nature, and it is known that sodium selenosulphate gets decomposed in acidic medium [8,9], forming selenium. Thus, taking advantage of the acidic character of the ionic liquid, ($[\text{Hmim}]^+ \text{CH}_3\text{SO}_3^-$), its reaction with sodium selenosulphate was carried out, in the presence of PVA stabilizer, to produce selenium nanoparticles, as shown in Eq. (3).

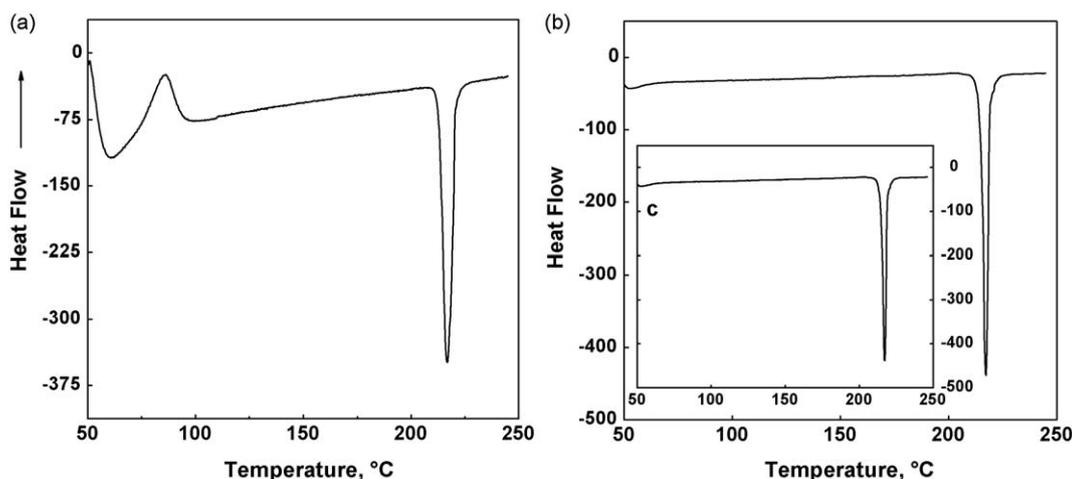
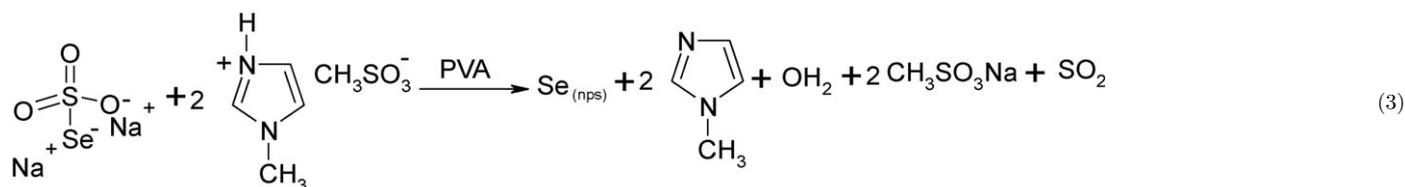


Fig. 1. DSC thermograms of (a) the synthesized selenium nanoparticles, (b) the synthesized selenium nanoparticles brought to ambient temperature after the first run and (c) standard commercial sample.

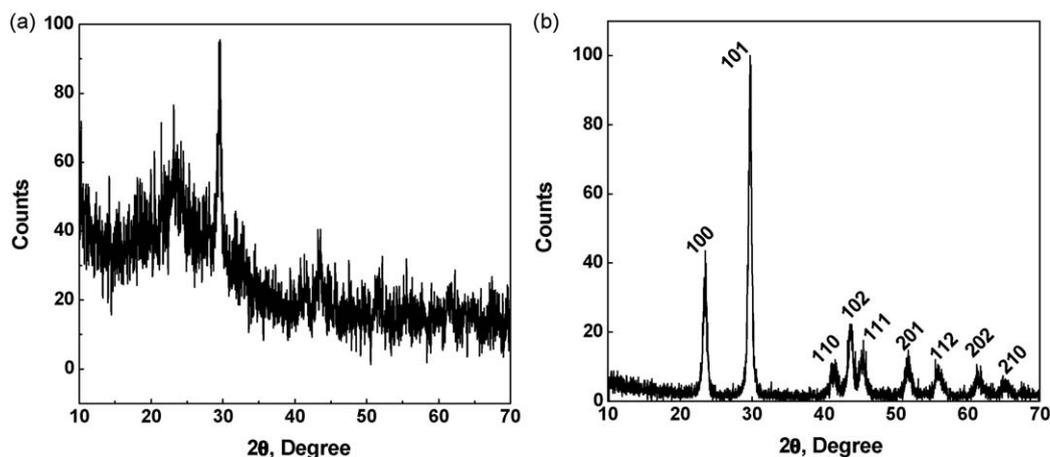


Fig. 2. XRD pattern of (a) the synthesized selenium nanoparticles without heating, and (b) after annealing at 90 °C for 150 min.

The method has advantage over the reported mineral acid-induced formation of selenium nanoparticles [8,9], which requires harsh chemical, even though mineral acids are used frequently in laboratory. The sodium selenosulphate has tetrahedral structure, analogues to sulphate anion, as shown in Scheme 1. The mechanism may be similar to that reported earlier [8,9], in which proton from a mineral acid, such as hydrochloric acid, reacts with sodium selenosulphate. In the present study, proton is released from the ionic liquid, and reacts with sodium selenosulphate, to produce elemental selenium, as shown in Eq. (3).

DSC thermogram of the selenium nanoparticles, synthesized by the reaction of aqueous $1.5 \times 10^{-3} \text{ mol dm}^{-3}$ sodium selenosulphate with the ionic liquid, in the presence of 0.05% PVA, recorded up to 250 °C, is shown in Fig. 1a. It shows an exothermic transition at 87 °C, in addition to endothermic melting peak at higher temperature. The repeat DSC thermogram of the same selenium sample, recorded after bringing it to ambient temperature, did not show any exothermic peak at the mentioned temperature (Fig. 1b). This clearly indicates that selenium nanoparticles lose their nanocrystalline nature in the first run itself, and the exothermic transition is assigned to the increase in crystallinity of the nanoparticles. DSC thermogram of the standard selenium powder sample also did not show any such exothermic peak (Fig. 1c). All the three DSC thermograms showed the melting peak at 217 °C.

Typical XRD patterns of the synthesized selenium nanoparticles, without any heat treatment, and after annealing at 90 °C (just above the crystallization temperature) for about 150 min, are displayed in Fig. 2. The peaks above 2θ value of 40° were not

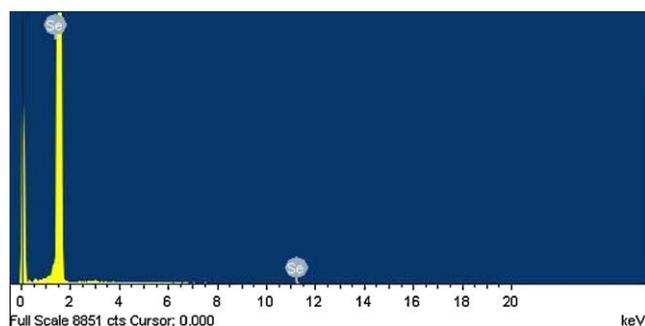


Fig. 3. EDAX pattern of the selenium nanoparticles synthesized by the reaction of $1.5 \times 10^{-3} \text{ mol dm}^{-3}$ sodium selenosulphate with the ionic liquid in the presence of 0.05% PVA.

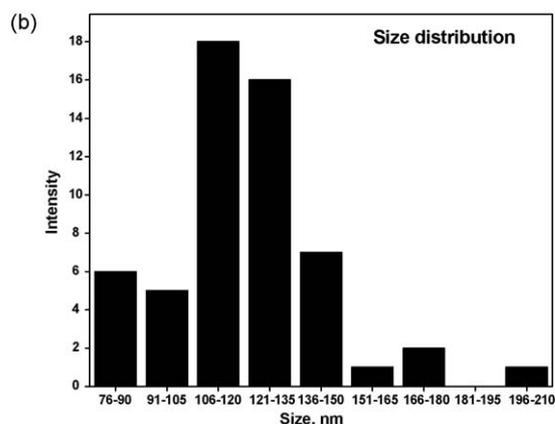
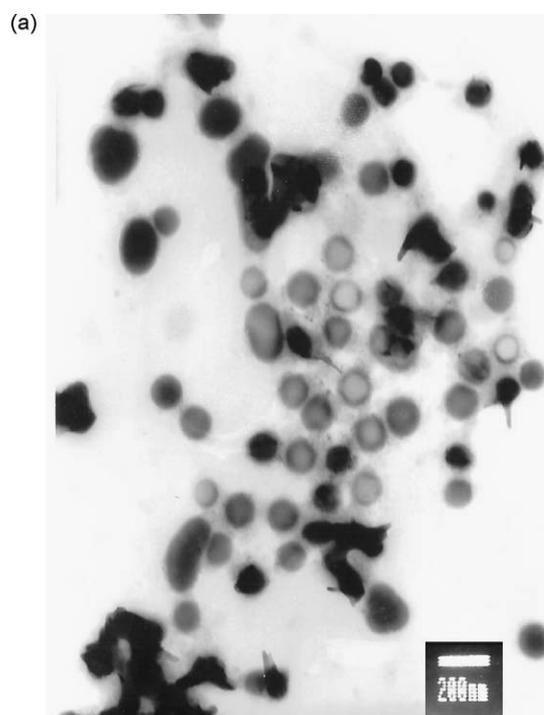


Fig. 4. (a) TEM image of the selenium nanoparticles synthesized by the reaction of $1.5 \times 10^{-3} \text{ mol dm}^{-3}$ sodium selenosulphate with the ionic liquid in the presence of 0.05% PVA and (b) the size distribution of the selenium nanoparticles.

resolved properly in the XRD pattern of the unannealed sample (Fig. 2a), due to its nano-crystalline nature. However, its crystallinity increases on annealing, as shown in Fig. 2b. XRD pattern of the synthesized selenium nanoparticles, after annealing at 90 °C, matches very well with that of the standard selenium powder, confirming the formation of selenium particles. This observation is in corroboration with the DSC results obtained with the synthesized sample. All the diffraction peaks are indexed, assuming a trigonal phase, with calculated lattice constants, $a = 4.363 \text{ \AA}$ and $c = 4.952 \text{ \AA}$, which are in agreement with the literature values of $a = 4.360 \text{ \AA}$ and $c = 4.956 \text{ \AA}$ (JCPDS FILE No., 06-362) [6]. Chemical composition was determined, using EDAX technique, and as shown in Fig. 3, it also confirms that the nanoparticles are of pure selenium, and do not contain any other elemental impurity.

TEM is the most commonly used technique that provides actual size, shape and surface topography of the nanoparticles. Therefore, the actual size and the shape of the nanoparticles were determined by the TEM technique. A typical transmission electron microscope image of the selenium nanoparticles, synthesized by the reaction of $1.5 \times 10^{-3} \text{ mol dm}^{-3}$ sodium selenosulphate with the ionic liquid, in the presence of 0.05% PVA, is shown in Fig. 4a. The spherical shape of the particles is visible in the TEM image. The size distribution of particles is shown in Fig. 4b. The calculated average size of the particles is 121 nm, with quite narrow size distribution in the range of 76–150 nm, though a few aggregates of size more than 150 nm are also observed. However, one can tune the nanoparticle size by varying the concentrations of the reagents and the stabilizer.

4. Conclusion

Ionic liquid-induced oxidation of sodium selenosulphate i.e., SeSO_3^{2-} , was found to be a simple method for the production of selenium nanoparticles under ambient conditions. Formation of the nano-crystalline selenium, and an increase in crystallinity on heating were concluded from both, DSC and XRD results. The

selenium nanoparticles, with size of 76–150 nm, could be obtained. The selenium nanoparticles may serve as a template, to generate other important nano-materials for their potential applications.

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