

Probing the phase transformation of Selenium nanoparticles synthesized in the host matrix of neat room temperature ionic liquid via radiation route



Apurav Guleria^a, Ajay K. Singh^a, Suman Neogy^b, Soumyakanti Adhikari^{a,*}

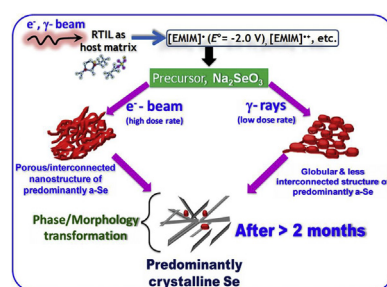
^a Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

^b Mechanical Metallurgy Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

HIGHLIGHTS

- Rapid and on-pot approach for synthesis of Se nanoparticles.
- Significant slow down (>2 months) in phase transformation of Se nanoparticles.
- RTIL acts as solvent, stabilizer and source of radicals for reducing precursors.
- Dose rate has significant impact on the morphology of the Se nanoparticles.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 17 April 2017

Received in revised form

9 August 2017

Accepted 12 September 2017

Available online 17 September 2017

Keywords:

Amorphous Selenium

Nanoparticles

Ionic liquids

Electron beam

Radiolytic synthesis

ABSTRACT

Herein, Selenium (Se) nanoparticles (NPs) have been synthesized in the host matrix of a neat room temperature ionic liquid (RTIL) via rapid, one-pot electron beam (EB) mediated approach. A dark red coloured solution was obtained, which exhibited absorption bands at 520, 620 and 730 nm. The Se NPs were predominantly amorphous, as was indicated from the XRD and TEM studies. This was further evident from the Raman mapping of the NPs. The NPs extracted from the RTIL showed assembling of the primary units (flake and spherical shaped) into an interconnected porous nanostructure. Interestingly, the well-known amorphous to crystalline phase transformation of Se NPs was found to be much slower (>2 months) in RTIL compared to few minutes-to-days as reported in earlier studies. Further, the interplay of dose rate was found to have significant impact on the morphology of the Se NPs. An equivalent dose of γ -ray irradiation (low dose rate) produces largely globular and less interconnected NPs. Based on the results obtained, it can be inferred that the RTIL simultaneously played the role of a solvent, a stabilizer and an *in-situ* source of radicals for the reduction of precursors. The underlying mechanism for the formation and subsequent morphological evolution of Se nanostructures in the two methods (EB and γ -irradiation) has been proposed, and was rationalized in the viewpoint of dose rate difference in addition to the existence of innate structural and fluidic aspects of the RTIL.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Selenium (Se), as a member of the chalcogenide group possesses many important properties, such as piezoelectricity, photoconductivity ($\sim 8 \times 10^4 \text{ S cm}^{-1}$), relatively low melting point ($\sim 490 \text{ K}$),

* Corresponding author.

E-mail address: asoumya@barc.gov.in (S. Adhikari).

thermoelectricity, and nonlinear optical responses [1–3]. Essentially, Se exists in several allotropic forms: trigonal (t)-Se, rhombohedral Se, monoclinic (m)-Se, amorphous (a) Se and black vitreous Se. Amongst these, a-Se is thermodynamically unstable and eventually transforms into t-Se [4]. The t-Se is an indirect semiconductor with a band gap of 1.85 eV at 2 K, while the lowest direct excitonic gap occurs at 1.95 eV [5,6]. However, a-Se is reported to have an optical gap of 2.09 eV at 77 K and 1.94 eV at 300 K [5,7].

Se exhibits high reactivity towards a variety of chemicals that can be and has been exploited to convert it into other functional materials [8,9]. It is also one of the essential trace elements, and various studies have revealed the health-endorsing properties of Se as a strong antimicrobial and anti-carcinogenic agent [2,10,11]. Owing to such properties, it has wide applications in various fields, such as pharmaceuticals, rectifiers, solar cells, photographic exposure meters, and xerography [8,9]. Apparently, it can be expected that the Se in the nanoscale dimensions may enhance the performance of existing devices or introduce new applications employing it [2]. In the recent times, interest on the synthesis of Se nanoparticles with various morphologies (such as nanospheres [12,13], nanorods [14,15], nanowires [16–18], nanotubes [19], nanobelts [20], nanoribbons [21]) have increased significantly. Different methodologies such as hydrothermal [22,23], laser ablation [24], sonochemical [16], microwave assisted [25], electrochemical reduction [26], micellar method [20,27], biosynthesis [10,13], etc. have been employed by the researchers for the synthesis of Se nanoparticles [8,9]. For instance, Lu et al. [22] synthesized nanobelts by heating an aqueous solution of Na_2SeO_3 and cellulose in an autoclave at 160 °C for 15 h. Mehta et al. [27] employed surfactant assisted process for the synthesis of Se nanoparticles, wherein SeO_2 was reduced by hydrazine hydrate. Zhang et al. [26] synthesized single-crystalline Se nanotubes by cyclic voltammetry using surfactant i.e. cetyltrimethyl ammonium bromide (CTAB) as a soft-template. Zhu et al. [25] synthesized Se nanorods and nanowires by microwave-assisted reduction of SeO_2 with ethylene glycol at 195 °C in a time span of 30 min. Zhou et al. [4] employed ball milling technique to synthesize a-Se nanowires, wherein a mixture of Se powder and ZrO_2 balls were ball-milled under argon atmosphere for 10 h. Nonetheless, most of these methods involve stringent experimental conditions such as high temperature, high pressure, inert atmosphere and toxic reducing agents/capping agents. On the contrary, radiation induced synthesis of nanomaterials is rapid, efficient and a one-step approach [28–35]. Furthermore, this methodology does not require any external reducing agents as the solvated electron generated in the aqueous medium is itself a very strong reducing species ($E_{\text{red}} = -2.9$ V). Moreover, the electron beam (EB) can be used for tailoring the size of the nanoparticles by controlling the dose as well as the dose rate. Besides, an important advantage of this technique is that the nucleation and the growth processes of the nanoparticles can be maneuvered by the suitable choice of the host matrix. Therefore, the morphology of the nanoparticles can be precisely controlled by the appropriate use of the host matrix.

In this perspective, room temperature ionic liquids are being considered as “green” solvents for the replacement of conventional organic solvents due to their unique physicochemical properties such as non-flammability, high thermal stability, ability to dissolve a variety of materials, and importantly no measurable vapor pressure [36–38]. The alterations in the nature of cation and anion can be used to control and fine tune the physicochemical properties of the ionic liquids. Additionally, they possess high radiation stability with less than 1 mol% degradation even at a high dose of 500 kGy [39–42]. Owing to these properties, ionic liquids have recently received a great deal of attention as a new reaction media for the synthesis of various nanomaterials by normal as well as radiation

chemical route [43–48].

To this end, we report here a rapid and one pot approach for the synthesis of predominantly a-Se nanoparticles *via* electron beam irradiation. Of course, few reports are available on the radiation chemical synthesis of Se nanoparticles in aqueous solutions [49,50]. However, as mentioned earlier also that a-Se is thermodynamically unstable, and it eventually transforms into its crystallization phase. Time taken for such phase transformation of a-Se nanoparticles has been reportedly ranged from *few minutes-to-days* [4,18]. Interestingly and importantly, in the present work such phase transformation occurs at least after 2 months, much slower compared to earlier reports. The reports on such a slow phase transformation are very limited. The importance of this observation has been discussed in the results and discussion section. Nonetheless, considering the self-organized and the microheterogeneous nature of the ionic liquids, it would be quite intriguing to carry out the synthesis of nanoparticles in such a host matrix. To the best of our knowledge, the synthesis of Se nanoparticles in *neat* ionic liquids *via* radiation chemical route has not been reported elsewhere. Therefore, other than the synthesis of Se nanoparticles, the main objectives of the present work were as follows: (a) role of the ionic liquid as a stabilizer, (b) how the much debated phase transformation of the Se nanoparticles from amorphous to crystalline form occurs in room temperature ionic liquids as a new reaction medium, and (c) the mechanism of the formation and effect of dose rate on the morphology of the nanoparticles.

2. Experimental

2.1. Chemicals

High purity chemicals, Sodium Selenite (Na_2SeO_3) and ionic liquid (1-Ethyl-3-methyl imidazolium ethyl sulfate, [EMIM][EtSO₄]; purity ~ 99%) were obtained from Sigma-Aldrich and Alfa Aesar (UK), respectively and used without further purification. Since most of the ionic liquids are hygroscopic in nature, therefore proper precautions (such as use of septum and desiccators) were taken to avoid moisture absorption by the ionic liquid, while performing various physicochemical measurements. The water content in the as-employed ionic liquid was measured by the coulometric Karl-Fischer method using a Metrohm 831 KF Coulometer and was found to be as less as 20 ppm, which is not sufficient to cause any considerable changes in the intrinsic structure of the ionic liquid. Besides this, other main reason for the selection of this particular ionic liquid (i.e. [EMIM][EtSO₄]) is that, it is (alkyl sulfate anion based ionic liquids) halogen-free and relatively hydrolysis-stable. On the contrary, most commonly used ionic liquids containing halides, PF_6 and BF_4 anions are vulnerable to hydrolysis in the presence of water and eventually lead to the formation of toxic and corrosive species [38]. Nanopure water (conductivity, $0.06 \mu\text{S cm}^{-1}$) used for washing the precipitates was obtained from a Millipore water purifying system. Other chemicals, such as acetone used for subsequent cleaning and washing off the organic impurities from the precipitates were obtained from sdfine-chem Ltd., Mumbai with highest purity. The molecular structure of the as-employed ionic liquid is shown in Fig. 1 along with the denotations of various atoms of the cation and the anion.

2.2. Synthesis

Briefly, 0.0129 g of Sodium selenite (Na_2SeO_3) was dissolved in ~2 ml of *neat* ionic liquid, [EMIM][EtSO₄] (~5.2 M) by sonicating and subsequent magnetic stirring for ~ 45 min. The resultant solution was de-aerated by nitrogen bubbling, and irradiated with 7 MeV electron beam obtained from linear electron accelerator (LINAC).

Download English Version:

<https://daneshyari.com/en/article/5447671>

Download Persian Version:

<https://daneshyari.com/article/5447671>

[Daneshyari.com](https://daneshyari.com)