

GREEN SYNTHESIS OF SELENIUM NANOPARTICLES UNDER AMBIENT CONDITION

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A simple wet chemical method has been developed to synthesize glucose stabilized selenium nanoparticles from an aqueous sodium selenosulphate precursor. The method is capable of producing selenium nanoparticles in a size range about 20-80 nm, under ambient conditions. The synthesized nanoparticles can be separated easily from the aqueous sols by a high speed centrifuge. The synthesized selenium nanoparticles have been characterized by UV-visible optical absorption spectroscopy, X-ray diffraction and transmission electron microscopy techniques. Nanocrystalline selenium nanoparticles were obtained without post annealing treatment.

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1. Introduction

Nanotechnology is fundamentally changing the way in which materials are synthesized and devices are fabricated. Integration of nanoscale building blocks into functional assemblies and further into multifunctional devices can be achieved through a “bottom-up approach”. Research on the synthesis of nanosized material is of great interest because of their unique properties like optoelectronic, magnetic, and mechanical, which differs from bulk.

The investigations of integration of 1D nanoscale selenium (Se) building blocks into 2D/3D complex architectures have seldom been reported; although the 1D nanostructures of Se have been intensively studied [1-4]. We have focused on Se mainly because of its unique properties and great potential applications. Selenium is an indirect elemental semiconductor and exhibits good photoelectrical properties, nonlinear optical properties, high photoconductivity and even catalytic activities towards organic hydration and oxidation reactions [5, 6]. As is well known, Se has been successfully used in the production of photovoltaic cells, rectifiers, photographic exposure meters, xerography and so on [7-9]. Fabricating it into various types of nanostructures and microstructures it is not only an attempt to extend its application but it is also helpful for investigating their shape-property relationships in solid at microscales [10]. Selenium is one of the essential trace element in the body due to its anti-oxidative as well as pro-oxidative effect and has great importance in nourishment and medicine [11]. Like other nanoparticles,

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selenium nanoparticles would have some unique mechanical, optical, electrical, biologic and chemical properties as compared with bulk materials. For example it has been reported that the redness selenium nanoparticles has high biological activities and low toxicity [12] and nanowires of trigonal selenium have novel photoconductivity [13]. Amorphous Selenium nanoparticles are demonstrated unique photoelectric, semiconducting and x-ray-sensing properties [14]. Elemental Selenium (Se) is a narrow band gap ($\sim 1.7\text{eV}$) semiconductor which has been extensively used in solar cells, rectifier and xerography. It is also a photoconductor with a relatively low melting point ($\sim 217^\circ\text{C}$), high refractive index and high reactivity leading to a wealth of functional materials such as Ag_2Se [15], CdSe [15], ZnSe [16] and PbSe [16]. Monodispersed colloidal spheres of selenium are also relevant to the fabrication of photonic crystals by self assembly [17]. In glass industries the Se is used to eliminate bubbles and removes undesirable tints produced by iron [18]. It is the important micronutrient required at low concentration for most living organisms but it is toxic at high concentration. Thus selenium nanoparticles caused the great interest of researchers and a variety of synthesis methods have been exploited [19].

Starting with suitable precursor, both reduction and oxidation techniques can be employed to prepare selenium nanoparticles. A few reports have been published regarding the preparation of selenium nanoparticles. Among them physical vapor deposition, vapor phase diffusion and wet chemical methods are significant and popular so far [20]. However a reproducible but simple method of preparation of stable selenium nanoparticles with good catalytic activity is still a challenge. The main synthetic approach for preparing selenium nanoparticles is chemical reduction required reducing agent and stabilizer. The use of stabilizer may hinder the technological application specifically in the biological origin because the stabilizers have a chemical structure having toxic effect. In this study, we report a simple wet chemical method for the synthesis selenium nanoparticle using nontoxic stabilizer having a capability as a reducing agent.

2. Experimental

All the reagents used were of AR grade. Nanopure water was used throughout the experiment to prepare the solutions. Selenium powder and sodium sulphite was purchased from Merk. 4% glucose stock solution was prepared by addition of glucose in 100ml nanopure water. Sodium selenosulphate Na_2SeSO_3 was prepared by method reported earlier, using the reaction between aqueous Na_2SO_3 and Se powder [21].

The UV-visible spectra of each solution were measured in a SHIMADZU UV-1800 double beam digital spectrophotometer. XRD patterns were obtained on a Philips X'pert MPD X-ray diffractometer using $\text{Cu K}\alpha$ (1.54059 \AA) radiation with the X-ray generator operating at 45 kV and 40 mA. TEM images were obtained on JEOL 2010 microscopes. The TEM sample was prepared by dropping a sample suspension in ethanol on a Cu grid coated with a carbon film.

Selenium nanoparticles were prepared by the reduction of aqueous sodium selenosulphate solution with freshly prepared glucose solution. In practice, 100 ml 10^{-1} M sodium selenosulphate was treated with 10 ml 4% glucose solution and mixture was refluxed. The color of the solution changes from colorless to yellow after refluxing immediately and become orange after 30 minutes. The orange color sols remained stable for months.

3. Results and discussion

The selenious acid with glucose changes to yellow after refluxing. It is observed that without glucose the color of solution was not changes after prolong heating. This observation assumes that the glucose is acts as a reducing agent which was well documented in the literature. It is assume that glucose reduce selenious acid to selenium nanoparticles and oxidized itself in to the gluconic acid. The study pertaining to this aspect is in progress. The formation of selenium nanoparticles in presence of glucose is primarily authenticated from UV-Vis spectrophotometry shown in figure 1.

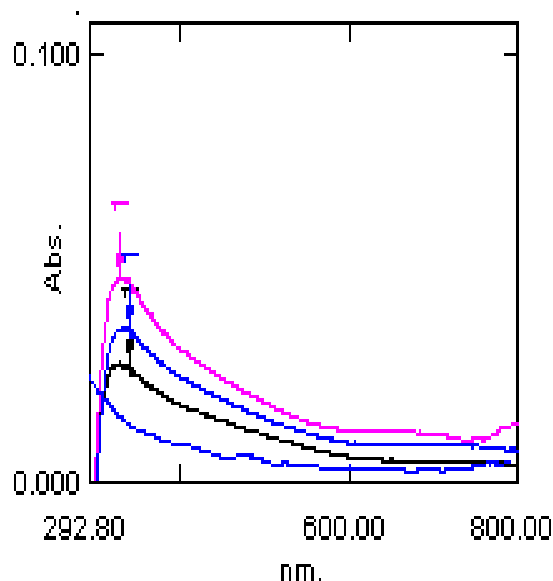


Fig. 1. UV-visible absorption spectra of selenium at different time intervals (Glucose:0.4M).

The absorption spectrum of yellow color selenium nanoparticle does not have any clear maximum in the studied wavelength region. The evolution of featureless absorbance of the yellow colored solution is observed. This monotonically increases towards higher energy. This observation corroborated the literature report of the yellow color due to the presence of selenium nanoparticles in solution. When the reaction solution turns into orange colloids from colorless, it is indicated that the amorphous spherical selenium nanoparticles may be formed. The color changes from yellow to orange red after heating indicating that the particle size increases. Further color changes were not observed after 1 hour which was authenticated by UV-Visible spectrophotometry. This is concluded that the one hour heating at 70°C is sufficient to get selenium nanoparticles and further heating does not initiate agglomeration of the particles. The beauty of present synthesis method is that there is no requirement of addition of stabilizer. The glucose is acting as a reducing agent as well as stabilizer.

The crystal structure and the phase composition of selenium nanoparticles were determined, using X-ray diffraction techniques shown in figure 2.

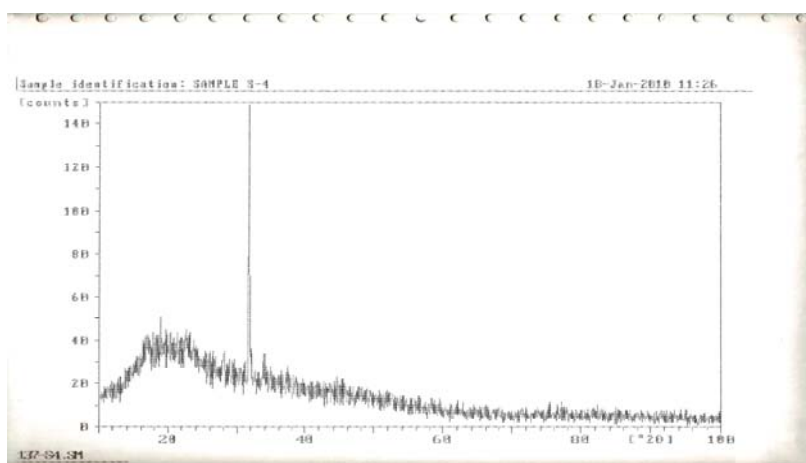


Fig. 2. XRD pattern of selenium nanoparticles.

The XRD pattern suggests that the sample is probably nano-crystalline in nature matches very well with that of the standard selenium powder confirming the formation of selenium particles. The calculated lattice constants are $a = 4.363 \text{ \AA}$ and $c = 4.952 \text{ \AA}$ which are in agreement with the literature value (JCPDS File No. 06-0362). The particle size, D , was calculated from the XRD data by using Scherrer's formula. The calculated size was found to be 60 nm. The XRD pattern of powder shows that there is no requirement of post annealing to get desired crystalline phase. Earlier reports show that there is requirement of post annealing treatment which increases the particle size due to agglomeration by heating. In present method no such post treatment is required and particle size is not altered.

Transmission electron microscopy is very important techniques, which provides information about particle size, surface morphology, etc. Therefore, morphology and structure of the synthesized selenium particles were also determined by TEM technique. The Transmission electron microscopy image is shown in figure 3.

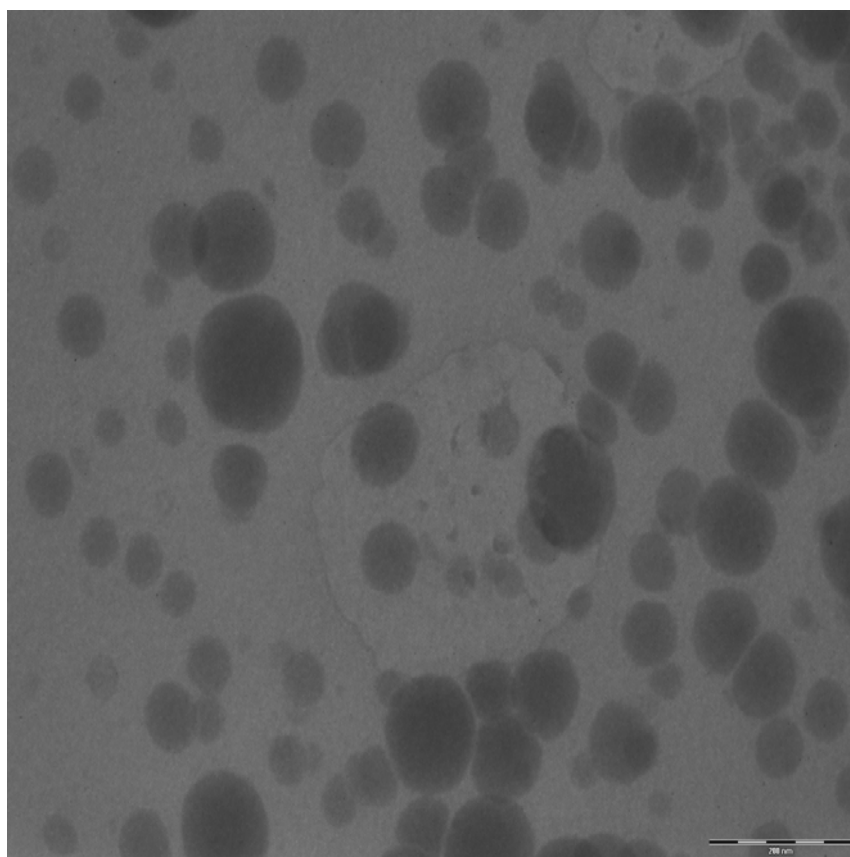


Fig. 3. The TEM image of selenium nanoparticles.

The figure shows that the prepared nanoparticles are spherical in shape and the size ranges from 20 to 80 nm.

4. Conclusions

The reduction of sodium selenosulphate by glucose was found to be simple method for the production of selenium nanoparticles under ambient conditions. Further the glucose not only used as a reducing agents but also acts a stabilizer to avoid the aggregations of particles. It was concluded from XRD data that the formation of crystalline selenium particles is possible without post annealing treatment The Glucose stabilized selenium particles can be used as biocompatible material for biological applications.

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