



Vinyl monomers-induced synthesis of polyvinyl alcohol-stabilized selenium nanoparticles

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ABSTRACT

A simple wet chemical method has been developed to synthesize selenium nanoparticles (size 100–200 nm), by reaction of sodium selenosulphate precursor with different vinyl monomers, such as acrylamide, N,N'-dimethylene bis acrylamide, methyl methacrylate, sodium acrylate, etc., in aqueous medium, under ambient conditions. Polyvinyl alcohol has been used to stabilize the selenium nanoparticles. Average size of the synthesized selenium nanoparticles can be controlled by adjusting concentration of both the precursors and the stabilizer. Rate of the reaction as well as size of the resultant selenium nanoparticles have been correlated with the functional groups of the different monomers. UV–vis optical absorption spectroscopy, X-ray diffraction, energy dispersive X-rays, differential scanning calorimetry, atomic force microscopy, scanning electron microscopy and transmission electron microscopy techniques have been employed to characterize the synthesized selenium nanoparticles. Gas chromatographic analysis of the reaction mixture established the non-catalytic role of the vinyl monomers, which were found to be consumed during the course of the reaction.

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1. Introduction

Nano-materials research received a great deal of interest in recent years because of the outstanding electrical, optical, catalytic and biological properties of the nano-size materials as compared to those of the bulk-materials [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-metalloid, like selenium, is scanty. Nano-selenium is an important semiconductor, with indirect bandgap of 1.6 eV [2,3]. Pure selenium as well as selenium containing materials, such as ZnSe, CdSe, etc., play important role in many applications, because of their photoconductive and photovoltaic properties. Selenium is widely used in the production of photographic exposure meters, photocells, pressure sensors and electrical rectifiers because of its high photoconductivity, and large piezoelectric, thermoelectric, and non-linear responses. The polyvinyl alcohol-stabilized selenium nanoparticles can be efficiently utilized, to produce polymeric films as well as hydrogels containing nano-selenium, which would have many technological applications. Selenium, being an essential micronutrient [4] and an antioxidant, is expected to have enhanced

activity in nano-form when stabilized by suitable bio-degradable stabilizers.

Nano-selenium can be produced in various forms, such as nanoplates [2], nanoribbons [3], nanowires [5], nanotubes [6], nanoparticles [7], etc., using different synthetic methods. Laser photolysis and thermolysis of organic selenides [8], thermal chemical vapor deposition [9] methods have been used for the synthesis of elemental selenium. The most frequently used one is reduction method, which includes chemical reduction [10], γ -radiolytic reduction [11], bacterial reduction [12], etc. However, some literature on the formation of nano-selenium via oxidation method, such as reaction of selenourea with hydroxyl radical [13], electrochemical oxidation of selenide [14], etc., also exists. We too have reported the formation of selenium nanoparticles by the oxidation of sodium selenosulphate with acid [7] and acrylonitrile (AN) [15]. With the aim of developing a new simple method, synthesis of selenium nanoparticles has been carried out by the reaction of sodium selenosulphate with different monomers, under ambient conditions.

The synthesized selenium nanoparticles were characterized by UV–vis optical absorption spectroscopy, X-ray diffraction (XRD), energy dispersive X-rays (EDAX), differential scanning calorimetry (DSC), atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. Gas chromatography was used to understand the role of vinyl monomers in the synthesis.

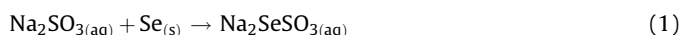
NMR technique was used to confirm the structure of byproduct.

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2. Experimental details

High purity polyvinyl alcohol (PVA) of molecular weight 125,000 and AR grade acrylamide (AM) obtained from S.D. Fine chemical, laboratory grade *N,N'*-dimethylene bis acrylamide (BisAM) from sigma, methyl methacrylate (MMA) from R. Johnson, acrylic acid from Ferak Berlin and selenium powder from Aldrich, were used as received. All the other chemicals used were of GR grade, procured from the local market. Sodium acrylate (NaA) was prepared by neutralizing acrylic acid monomer with sodium hydroxide, and the final pH of the solution was adjusted to ~ 8 . Aqueous solutions were prepared, using water obtained from Millipore-Q water purification system. Sodium selenosulphate was prepared by the method reported earlier, using reaction between aqueous Na_2SO_3 solution and Se powder [16]



Briefly, a mixture of selenium powder (2 g) and solution of Na_2SO_3 (20 g) in 100 ml water was refluxed at 70°C , for about 7 h. After completion of the refluxing process, the reaction mixture was filtered, and the solution obtained was kept in dark to prevent photo-oxidation. This sodium selenosulphate solution ($\sim 0.25\text{ M}$), containing unreacted Na_2SO_3 , was used as a stock for Se precursor. 1% PVA stock solution was prepared by the addition of 1.0 g of PVA into 100 ml water, while stirring at 80°C . Both these stock solutions were diluted with water, to the required concentrations, for different experiments.

PVA-stabilized Se nanoparticles were synthesized by reaction of sodium selenosulphate (concentration 5×10^{-4} to $1.5 \times 10^{-3}\text{ mol dm}^{-3}$) with different vinyl monomers in aqueous medium, in the presence of PVA as a stabilizer, in the concentration range 0.05–0.15%. The formation of selenium nanoparticles was studied for different time periods, depending on the nature and the concentration of the monomer used. Completion of the reaction, during the study of the reaction kinetics, was checked by spectrophotometric method as well as by the addition of dilute nitric acid in a small volume of the reaction mixture, after separating the selenium nanoparticles, using high-speed centrifuge (acid test). The presence of unreacted sodium selenosulphate was indicated by almost instantaneous development of red colour due to the acid-induced formation of selenium nanoparticles [7].

UV–vis optical absorption spectra of the selenium nanoparticle sols were recorded, using a double beam spectrophotometer, model Spectroscan 2600 from Chemito. XRD patterns of the nanoparticles were recorded with a Phillips X-ray diffractometer, model PW 1710, using a Cu K_α source ($\lambda = 0.15406\text{ nm}$). DSC measurements were carried out, using a Mettler TA 3000 thermal analysis system. About 5–10 mg of the synthesized selenium nanoparticles and standard selenium powder were weighed into aluminum crucibles separately, and DSC measurements of both the samples were carried out in N_2 atmosphere, at a heating rate of $10^\circ\text{C}/\text{min}$, from 50 to 250°C (model DSC-30). Selenium nanoparticles, separated from aqueous sols, using a high-speed centrifuge, at about 15,000 rpm, washed with water and dried at room temperature, were used for XRD and thermal analysis measurements. AFM analysis of the synthesized selenium nanoparticles was carried out, using a Solver P47 model from NT-MDT, Russia. SEM of the synthesized selenium nanoparticle was recorded, using a TESCAN VEGA MV 2300 T/A digital microscope. TEM characterization was carried out with a JEOL-2000 FX electron microscope, using the sample on a copper grid coated with a thin amorphous carbon film. Gas chromatography experiments were carried out on GC 8610 model from Chemito, using a Porapak-Q column of length of 6 ft and diameter of 1/8 in., at 230°C , and

nitrogen, as a carrier gas. NMR spectra of the samples were taken on Bruker machine.

3. Results and discussion

In an attempt to synthesize polymer–selenium nanoparticle composites by radiation-induced method, it was observed that sodium selenosulphate reacts with vinyl monomers, precipitating elemental selenium, under ambient conditions. The simplicity and environmental friendly nature of the reaction drove us to study it in detail, and to develop it as a new method for production of selenium nanoparticles. A detailed study of the reaction was first carried out with acrylamide monomer, in the presence of PVA stabilizer, to produce selenium nanoparticles. Then, it was extended to other vinyl monomers, such as sodium acrylate, *N,N'*-dimethylene bis acrylamide, methyl methacrylate, α -methyl styrene, etc. PVA was found to be an efficient stabilizer for selenium, as its presence in the reaction mixture resulted in the formation of orange/red coloured selenium nanoparticle sols, while in its absence, black elemental selenium powder precipitated out from the reaction mixture. Kinetics of the formation reaction and particle size of synthesized selenium nanoparticles, by reaction of sodium selenosulphate with different monomers, have been investigated.

The intensity of the selenium nanoparticle sols was found to be dependent on the concentration of sodium selenosulphate taken in the reaction mixture. A typical selenium nanoparticle sol formed by the reaction of $1.0 \times 10^{-3}\text{ mol dm}^{-3}$ sodium selenosulphate with $1.6 \times 10^{-2}\text{ mol dm}^{-3}$ acrylamide, in the presence of 0.05% PVA is shown in Fig. 1.

Selenium nanoparticles are known to exhibit a regular absorption maximum, in the wavelength region above 350 nm, only when particles size is 150 nm, or more. Both the absorption maximum and the peak intensity are reported to change with the particle size. The absorption maximum generally shifts towards red, and the peak intensity decreases with increase in the size of the nanoparticles [7,17]. Fig. 2 shows the effect of concentration of



Fig. 1. Aqueous selenium nanoparticles sol obtained by the reaction of $1.0 \times 10^{-3}\text{ mol dm}^{-3}$ sodium selenosulphate with $1.6 \times 10^{-2}\text{ mol dm}^{-3}$ acrylamide in the presence of 0.05% PVA.

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