Evidence on the size-dependent absorption spectral evolution of selenium nanoparticles

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Abstract

We have developed a simple method to synthesize size-controlled amorphous selenium nanoparticles by chemical reduction at room temperature. The particle size control can be achieved by adjusting the key element of this synthetic system, the sodium thiosulfate as the reducing agent with the aid of the surfactant stabilizers. Mean particle diameters can be controlled well in the range from 20 nm to the sub-micrometer regime. A clear trend in the absorption spectra of these particles is the red-shift that occurs as the particle sizes increase; this effect is analogous to the confinement effect of semiconductor nanoparticles and reflects in the color change from yellow to red. This spectral evolution is in very good agreement with the classical Mie formalism predictions.

Keywords: Selenium nanoparticles; Spectral evolution

1. Introduction

Materials made of elemental selenium play important roles in many applications because of their photoconductive properties [1–3]. Selenium is one of the key elements for maintaining the health of mammalian animals because it exerts anti-oxidative [4] and pro-oxidative effects [5], but this essential trace element has a very narrow margin between its lowest acceptable levels of intake and its toxicity. Food supplements containing selenium are usually limited to selenides and other organoselenium compounds, but colloidal-form selenium has recently been manufactured for use in nutritional supplements [6–8] and developed for applications in medical diagnostics [9]. In the past few years, there have been several reports on the synthesis of selenium nanostructures. A well-established approach for the preparation of 1D nano-Se relies on seed-mediated growth on t-Se clusters that are formed by an anomalous Oswald ripening process, which occurs after the dissolution of sub-micrometer a-Se particles formed in the pre-synthesis stage by the reduction of selenium acid using hydrazine [10]. Another report describes the formation of o-monoclinic nano-Se particles – and their subsequent stacking – by the decomposition of selenodiglutathione, which is formed from the reaction between sodium selenite and glutathione (GSH) [11].

Most synthetic systems for the preparation of 0D nano-Se have been performed in aqueous solutions, possibly because of recent needs to study its biomedically related properties. In addition, γ-irradiation [12] has also been applied to achieve the reduction of selenium precursors by hydrated electrons. Laser ablation is another method that has been applied successfully to the fabrication of nano-Se on various substrates [13]. Selenious acid and sodium selenite are the precursors most frequently used in chemical reduction methods. Several different reducing agents can be used, such as glutathione [14,15], hydrazine [16], dextrose [17], ascorbic acid [18], and sodium ascorbate [19]. Unfortunately, none of these approaches has clearly demonstrated an ability to exert fine control over particle size. Several synthetic systems allow particle sizes to be managed through the control of associated experimental conditions, such as the parameters of the laser beam [13] or the amount of bovine serum albumin added to selenite/GSH systems [20]. Recently, it has been demonstrated that
the sizes of nano-Se particles can be prepared roughly within three size regimes – small (5–15 nm), medium (20–60 nm), and large (80–200 nm) – by the selenite/GSH chemical reduction approach [14,20].

In the past few years, the effects of the sizes of nano-Se particles have been studied with respect to their free radical scavenging efficiency [15] and the induction of seleno-enzymes in both cultured cells and mice [14]. The bioavailability of nano-Se has attracted increasingly greater attention and studies of their size- and shape-dependent properties with respect to various biosystems should expand in the near future. Presently, however, there is great demand for a procedure enabling a higher degree of control over the sizes of nano-Se particles prepared in aqueous solution. We have demonstrated previously that sodium metabisulfite (Na₂S₂O₅) and sodium dodecylsulfate (SDS) can be used as the reducing agent and surfactant stabilizer, respectively, for the synthesis of 0D nano-Se from selenium powder [21]. Using this method, we observed selenium nanoparticles having diameters ranging from as low as 30 nm to as high as 200 nm as a function of reaction time, but this synthetic approach must be conducted at 80 °C for efficient reduction to occur. Similar observations have been reported for the growth of colloidal Se particles over a much larger size regime [19]. In our previous approach, the selenium precursors only partially reduced to form particles during the early stages of the process; we found, however, that SDS imposes quite high stabilization on the particles. Therefore, our attention became focused on developing a simple, yet effective, method for achieving size control in the preparation of nano-Se. In this paper, we demonstrate an improved synthetic route to a-Se nanoparticles – from a three-element system, namely a selenite precursor (SeO₃²⁻), a reducing agent (sodium thiosulfate, Na₂S₂O₃), and a colloidal particle stabilizer (sodium dodecylsulfate) – and discuss methods to attain size control.

2. Experimental

2.1. The synthesis of a-Se nanoparticles

2.1.1. SeO₂ + S₂O₃²⁻/SDS system

In general, we started with the procedure by dissolving the anionic surfactant (sodium dodecylsulfate; C₁₂H₂₅O₄SNa, 99%; Acros) in 10 mL D.I. water to a concentration of 0.01 M; the final SDS concentration is well above its critical micelle concentration for a sufficient suspending capability. Selenium dioxide (SeO₂, 98%; Sigma) was then added into the solution; it dissolves readily to form selenous acid (equation (1)) at a concentration of 5.2 mM (solution A).

SeO₂(s) + H₂O(l) → H₂SeO₃(aq) (1)

The pH of this solution is moderately acidic and was not adjusted further. We then prepared a solution containing the reducing agent (solution B) by dissolving sodium thiosulfate pentahydrate (Na₂S₂O₅·5H₂O, Riedel-de-Haën) into 10 mL 0.01 M SDS solution such that the concentration of the reducing agent was 520 mM. In experiments conducted to demonstrate the effect of the concentration of the reducing agent upon the sizes of the resulting particles, we added various portions of solution B into solution A, which was stirred well prior to the addition. The final concentrations of added thiosulfate in the seven different solutions were 5.2 mM (1 × the concentration of the selenite precursor), 10.4 mM (2 ×), 15.6 mM (3 ×), 20.8 mM (4 ×), 26.0 mM (5 ×), 41.6 mM (8 ×), and 156 mM (30 ×). Suspended nano-Se particles form from these solutions after each reaction proceeds for a sufficient time. The longest time required for these syntheses was ca. 6 h for the case of 240-nm diameter nano-Se particles. We used the various final concentrations of sodium thiosulfate to demonstrate its ability to control the particle size. The half reactions for the reduction and oxidation of selenous acid and sodium thiosulfate, respectively, follow equations (2) and (3):

H₂SeO₃ + 4H⁺ + 4e⁻ → Se + 3H₂O (2)

S₂O₃²⁻ + 5H₂O → 2SO₄²⁻ + 10H⁺ + 8e⁻ (3)

The reduction potentials (E°r) are 0.74 V for equation (2) and −1.5 V for equation (3). Therefore, sodium thiosulfate reduces the selenite readily and the redox reaction is spontaneous.

2.2. Characterizing the selenium nanoparticles

The size distributions within the various selenium nanoparticle dispersions were measured by transmission electron microscopy (TEM) using an accelerating voltage of 150 kV. Prior to TEM sample preparation, the colloids were pre-treated through a flocculation/redispersion cycle to remove any excess co-existing compounds, such as SDS. We prepared TEM samples of the nano-Se particles by dip-coating formvar/carbon film Cu grids into the colloidal solutions. We used energy-dispersive X-ray (EDS) analyses to verify the particles’ elemental compositions.

3. Results and discussion

The SeO₂ + S₂O₃²⁻/SDS system provides fine control over the particles’ sizes. The reducing agent, sodium thiosulfate, is strong enough to ensure complete conversion of the precursor molecules into nano-Se particles. Fig. 1 illustrates clearly the growth in the sizes of the particles upon decreasing the thiosulfate concentration from 156 mM (30 ×) to 5.2 mM (1 ×; note that this concentration is still an excessive amount of thiosulfate: it is twice the stoichiometric value needed for the complete reduction); accordingly, we prepared, with good size control, particles having mean diameters of 20.0 ± 6.1, 48.2 ± 5.9, 70.9 ± 9.1, 101.6 ± 9.8, 146.1 ± 23, 182.8 ± 33.2, and 240.4 ± 32.2 nm. The polydis-
Fig. 1. TEM images of as-synthesized nano-Se. Images (A)–(G) represent samples prepared using added sodium thiosulfate concentrations of 156, 41.6, 26.0, 20.8, 15.6, 10.4, and 5.2 mM, respectively. Scale bar: 200 nm.

It is not unusual that the size of the particles increases as a result of decreasing the relative concentrations of the reducing agent. This behavior is similar to that found in many chemical reduction approaches to nanosystems because the nucleation and growth sequences are both affected by the relative concentrations of the reducing agent and the precursor. In our case, we believe that the nucleation process is overwhelmingly faster than particle growth at the higher relative concentrations, which results in smaller sized particles. This effect is especially obvious when using a relatively strong reducing agent, such as sodium thiosulfate.

Fig. 2 displays the colorful appearances of the suspensions of selenium nanoparticles. The colors of the six nano-Se colloids reflect both their sizes and absorption spectral features in the UV–vis region. We find that the well-known belief that nano-Se is “red” [14] is somewhat misleading. By examining the evolution of the color from left to right in Fig. 2, we observe that a red color represents a colloidal size of ca. 100 nm. Crystalline monoclinic bulk selenium is deep red and crystalline hexagonal bulk selenium, its most stable form, has a metallic-grey color. Amorphous selenium is either red, in its powder form, or black, in its vitreous form. The suspension of the 20-nm diameter nano-Se particles has, in fact, a yellowish orange appearance, but it appears red at higher concentrations. These color changes may relate directly to the absorption features of the particles in the visible region of the spectra.

Fig. 3. Absorption spectra of the selenium colloids presented in Fig. 1. The spectra labeled from 1 to 7 represent those of the particles having mean diameters of 18.1 ± 6.7, 48.2 ± 5.9, 70.9 ± 9.1, 101.6 ± 9.8, 146.1 ± 23, 182.8 ± 33.2, and 240.4 ± 32.2 nm, respectively.
Fig. 3 displays the absorption spectra for a series of nano-Se suspensions having different mean diameters. The absorption tail that extends into the visible region explains the yellowish color of the smaller sized particles. The progression of the \( n \)th-order spectral maxima, where \( n = 1, 2, \) and \( 3 \) in our systems, agrees with predictions based on the Mie formalism [22]. Most importantly, the locations of the peak maxima for the various colloidal sizes are in perfect agreement with the calculated values, which are presented in Fig. 4.

Additionally, when comparing the relative intensities of the different particle sizes in both Figs. 3 and 4, we notice that the increase in the overall absorbance measured experimentally (Fig. 3) is more obvious as the size decreases than it is in the calculations (Fig. 4). This discrepancy is easily explained by considering that the calculations were performed on single particles, but the number of colloidal particles prepared experimentally increases as the sizes become smaller, which provides further evidence for the complete consumption of the nano-Se precursors. In addition, because selenium nanoparticles belong to the family of elemental semiconductors, the trend in the shift of their absorption spectral features as a function of size is indeed analogous to the confinement effect observed in semiconductor nanocrystals.

### 4. Summary

All of the colloids we have prepared are stabilized well and by no means are they intermediate products of a growth sequence. Thus, our synthetic system controls nano-Se particle sizes effectively. They exhibit a clear trend in their absorption spectral features, which has been predicted based on the classical Mie formalism. Therefore, the well-known “red” nano-Se is somewhat misleading. The color variation of colloidal Se for increasing the particle size is evidenced by the change from yellow to red.

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