A mild chemical reduction method was developed to synthesize selenium nanoparticles. The observation of the particle growth within a five-minute time frame at an elevated temperature is achieved, and it was evidenced by analyzing the particle sizes from electron micrographs. The samples at individual growth stages were taken after the reaction was quenched by cooling to stop further particle growth. The nucleation and growth processes dominate different reaction time regimes under the experimental condition. We demonstrate the size evolution of the selenium nanoparticles from 30 nm to about 200 nm.

**Keywords:** Selenium; Selenium nanoparticles.

**INTRODUCTION**

Selenium has shown its importance as a photoconductive material in applications such as rectifiers, solar cells, photographic exposure meters, and xerography. Recently, its colloidal form has also been utilized for nutritional supplements and in medical diagnostics. The synthesis and the chemical/physical properties of selenium nanostructures have not been widely investigated, even in the heat of recent nanoscience research. To our best knowledge, the main nanofabrication methodologies adopted in the literature for preparing selenium nanoparticles are the chemical reduction methods based on the bottom-up strategy. Other than those chemical reduction methods, γ-irradiation has also demonstrated the capability of reducing the selenium precursors via hydrated electrons generation. As for the chemical reduction methods, several ingredients including selenium precursors and reducing agents have been reported in the synthesis. Selenous acid was most frequently used as the precursor. Its reduction to form zero-charged selenium has been reported to proceed by using several kinds of reducing agents such as hydrazine compounds, dextrose, sodium ascorbate, and ascorbic acid. We demonstrate herein another possible reducing agent which apparently shows its feasibility in the nanosynthesis of selenium nanoparticles. Also, the growth of nano-Se is evidenced for this nanoparticle synthesis.

**EXPERIMENTAL SECTION**

**The Synthesis of Selenium Nanoparticles**

\[ H_2SeO_3 + SO_2 \rightarrow H_2SeO_3(aq) \]  

The concentration of selenous acid used was 5.4 mM and assumed to be identical to that of SeO_2. The 10 mL precursor solution was then added by an anionic surfactant of SDS. The final SDS concentration was 10 mM, well over its critical micelle concentration for a sufficient suspending capability. The mixture was then well stirred before the addition of the reducing agent. A mild reducing agent of SO_2 dissolved in aqueous solution was used for this purpose. The SO_2 was generated by direct dissolving of sodium meta-bisulfite (Na_2S_2O_5, 99%; J. T. Baker) into the previous mixed solution.

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The total redox reaction involved in the nanosynthesis can be expressed by

\[ \text{Na}_2\text{SO}_3(s) + \text{H}_2\text{O} \rightleftharpoons 2\text{NaHSO}_3(aq) \]  
(2)

\[ \text{NaHSO}_3(aq) + \text{H}^+ \rightarrow \text{Na}^+ + \text{H}_2\text{O}(l) + \text{SO}_2(aq) \]  
(3)

Prior to the sodium bisulfite addition, the solution pH was adjusted to be roughly 3.2 by adding 40 \( \mu \)L concentrated hydrochloric acid (J. T. Baker). The sodium metabisulfite, with a final concentration of 5.4 mM, was then introduced to the solution. Note that Eqn (3) is a spontaneous endothermic reaction.

\[ \text{H}_2\text{SeO}_3(aq) + 2\text{SO}_2(aq) + \text{H}_2\text{O}(l) \rightarrow \text{Se}(s) + 2\text{SO}_4^{2-}(aq) + 4\text{H}^+, \]  
(4)

in which two half-reactions are

\[ \text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4e \rightarrow \text{Se} + 3\text{H}_2\text{O} \]  
(5)

\[ \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 4\text{H}^+ + 2e. \]  
(6)

Selenous acid is a moderately strong oxidizing agent. \( \text{SO}_2 \) can reduce it easily. The reduction potential \( E_{\text{red}} \) of eqn (5) is equal to 0.74 V and the oxidation potential \( E_{\text{ox}} \) of eqn (6) equals -0.17 V. Solution of \( \text{SO}_2 \) possesses a reducing property and is used as the reducing agent in the nanosynthesis scheme. The reaction for the nanoparticle nucleation and growth was allowed to proceed at 80 \( ^\circ \)C with a reasonable speed. The samples representing individual growth stages were prepared by instantly quenching the growth at various reaction times of 30 s, 60 s, 90 s, 150 s, and 210 s. The growth rate can be very efficiently stopped by returning the reaction temperature quickly down to room temperature via immersing the reaction vial into a cold water bath, since the redox reaction proceeds fairly slowly at room temperature.

Characterizations of Selenium Nanoparticles

The resulting dispersions of selenium nanoparticles at various growth stages were subjected to the measurements of their structural images. It reflects the variation of particle mean diameters during the growth. The particle image measurements were conducted on a Hitachi H-700H transmission electron microscope (TEM) operated at 150 kV accelerating voltage. TEM samples containing nano-Se particles were prepared by dip coating of the dispersed colloidal solutions on formvar/carbon film Cu grids (200 mesh; 3 mm, Agar Scientific Ltd.). Energy dispersive X-ray (EDS) analyses have also been conducted on the sample particles to verify their composition and purity.

RESULTS AND DISCUSSION

The \( \text{H}_2\text{SeO}_3+\text{SO}_2/\text{SDS} \) synthetic system has proven to be feasible for the preparation of selenium nanoparticles. The reducing agent of dissolved \( \text{SO}_2 \) is mild enough that it allows us (i) to achieve particle growth and quenching of the growth rate efficiently at two temperatures, and (ii) to acquire direct evidence on the nano-Se growth sequence. Fig. 1 illustrates the particle growth sequence under the experimental conditions.

The mean particle diameter reaches about 40 nm at 30 secs reaction time at 80 \( ^\circ \)C, and it grows constantly up to about 200 nm after approximately 4 min. of reaction time. The growth can be evidenced from the evolution of the particle diameters: 32.0 \( \pm \) 8.4 nm (30 secs), 39.6 \( \pm \) 10.1 nm (60 secs), 73.6 \( \pm \) 12.6 nm (90 secs), 93.1 \( \pm \) 6.8 nm (150 secs), 188.8 \( \pm \) 12.7 nm (210 secs). The composition of thus prepared nanoparticles was verified by EDS characterization, as shown in Fig. 2, to be pure selenium without any other detectable contamination.

The results from the analyses shown in Fig. 1 were transformed into a new plot, as shown in Fig. 3. It depicts the relationship between the mean particle sizes and the reaction time. The evolution curve for the particle size clearly shows two distinct regions corresponding to two dominant processes: the nucleation for the first 2 minutes and the growth process dominating afterwards. Fig. 3 indicates that the nucleation process prevails over the growth during the first minute of the redox reaction. The number of particles grows fast during this period of time and the roughly following 1 minute, while the particle growth is relatively slow. The growth rate then increases dramatically after two minutes of reaction time.

SUMMARY

We have successfully synthesized selenium nanoparticles by \( \text{H}_2\text{SeO}_3+\text{SO}_2/\text{SDS} \) synthetic system, in which the selenous acid acts as the precursor, sulfur dioxide as the reducing agent, and sodium dodecyl sulfate as the stabilizer. In this system, we have a good opportunity to study the growth sequence of the nano-Se due to the distinctly different reducing rates between 80 \( ^\circ \)C and room temperature. The nucleation process dominates the growth in the early stage for the first 2 minutes, while the nano-Se particles grow rather quickly beyond 100 nm. The future development in the size controlled synthesis has found its basis herein. It is believed to be...
Fig. 1. Results of the TEM analyses. Samples were taken from different reaction times representing various growth stages. (A)-(E) are images at: 30 secs, 60 secs, 90 secs, 150 secs, and 210 secs, respectively. (F)-(J) are statistics of size distributions corresponding to (A)-(E).
achievable by either introducing other types of the “stronger” stabilizer, or conducting a programmed temperature sequence for fine-tuning the particle nucleation and growth processes.

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