



# Lignosulfonate-stabilized selenium nanoparticles and their deposition on spherical silica



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## ABSTRACT

We report a novel room-temperature synthesis of selenium nanoparticles, which for the first time uses lignosulfonate as a stabilizer. Various lignosulfonates obtained both from hardwood and softwood were tested. Selenium oxide was used as the precursor of zero-valent selenium. Three different reducers were tested – sodium borohydride, hydrazine and ascorbic acid – and the latter proved most effective in terms of the particle size and stability of the final colloid. The lignosulfonate-stabilized selenium nanoparticles had a negative zeta potential, dependent on pH, which for some lignosulfonates reached  $-50$  mV, indicating the excellent stability of the colloid. When spherical silica particles were introduced to the synthesis mixture, selenium nanoparticles were deposited on their surface. Additionally, star-like structures consisting of sharp selenium needles with silica cores were observed. After drying, the selenium-functionalized silica had a grey metallic hue. The method reported here is simple and cost-effective, and can be used for the preparation of large quantities of selenium colloids or the surface modification of other materials with selenium.

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## 1. Introduction

There has been growing interest among scientists and researchers in selenium particles because of their various shapes, such as nanowires [1], nanorods [2], nanotubes [3] and nanospheres [4], in combination with valuable physicochemical properties which include photoconductivity and thermoelectric, optical and biological properties [5,6].

Similarly to other nanostructures, colloidal selenium particles can be obtained by physical, chemical or biological methods [7–16]. Physical methods however, suffer from the high cost of the equipment and the need for various optimizations of the synthesis conditions [7]. On the other hand, chemical methods require an appropriate choice of solvent, chemical reducer (most frequently borohydride) and stabilizer, which must be properly recycled after synthesis. Chen et al. [11] reported the use of glucose as reducing

agent and ethylene glycol as stabilizer. They were able to obtain non-structured selenium in the form of nanorods of diameter 200–500 nm and length 10–15  $\mu$ m when the synthesis was carried out at 85 °C. There are also numerous reports of the use of ascorbic acid as a reducer of selenium oxoanions [12,13]. For instance, in [13], spherical dimeric and trimeric particles were obtained from sodium selenite as precursor using potassium iodide as a stabilizer. According to the authors of that report, iodide anions are adsorbed on selenium particles and adsorb potassium and sodium as counter ions, preventing particle aggregation. Spherical particles 75 nm in diameter were obtained in this procedure.

Other relatively simple, economical and environmentally friendly procedures are biological methods utilizing bacteria capable of reducing ionic selenium to selenium nanoparticles. According to recent reports, bacteria such as aerobic *Zoogaea ramigera*, *Bacillus cereus* and *Pseudomonas alcaliphila*, and anaerobic *Sulfurospirillum barnesii* and *Bacillus selenitireducens* can be used [14,15]. Aerobic processes seem better suited for these purposes. For instance, Srivastava and Mukhopadhyay [5] obtained spherical particles of diameter 40–120 nm using the widespread and harmless *Ralstonia eutropha*, which can be found in soil and ground water. The authors

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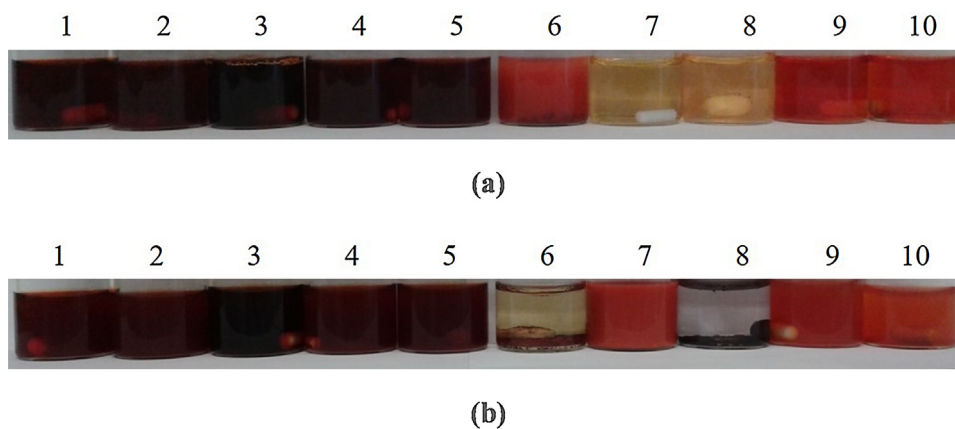


Fig. 1. SeNPs after (a) 1 h and (b) 14 days.

hypothesized that peptides and other biomolecules may be responsible for the long-term stability of SeNPs. Various biopolymers, especially sugars, can be effective stabilizers of selenium nanoparticles when ascorbic acid is used as the reducer [17,18]. SeNPs 24 nm in diameter can be obtained in this way.

SeNPs have been utilized in diodes, photovoltaic cells, pressure sensors, xerography and the glass industry. Also, because of their antioxidant properties, SeNPs have proved to be an excellent additive to multilayered food packaging [19]. Additionally, SeNPs stabilized with biodegradable stabilizer may be applied in biomedicine [20,21].

The present work is an extension of our previous studies [22] showing that lignosulfonates are effective reducing and stabilizing agents of noble metal nanoparticles. We also utilized lignosulfonates to graft noble metal nanoparticles onto the surface of silanized silica particles [23,24]. To the best of our knowledge, lignosulfonates have not previously been used as stabilizers of SeNPs. We utilized various forms of lignosulfonates that are byproducts of the paper industry, and three reducing agents: ascorbic acid, hydrazine and sodium borohydride. We believe that due to the low cost of lignosulfonates, the proposed procedure may be an attractive alternative for the mass production of SeNPs and surface modification of various materials with SeNPs for diverse applications.

## 2. Experimental

### 2.1. Synthesis of the LS-SeNPs

For the synthesis of selenium nanostructures, three kinds of reducers were used: ascorbic acid ( $C_6H_8O_6$ ), hydrazine hydrate 40% ( $N_2H_4$ ) and sodium borohydride ( $NaBH_4$ ). Various technical lignosulfonates (LSs), which differ in terms of the type of wood used (hard or soft wood), the type of counter ion (cation) present in their structure ( $Na^+$  or  $Ca^{2+}$ ) and additional processes influencing the chemical structure of these biopolymers (e.g. ultrafiltration, oxidation), were used. The characteristics of the lignosulfonates used in the study are presented in our previous paper [22]. Selenium oxide ( $SeO_2$ ) was used as a selenium source.

The synthesis of Se-NPs was performed at room temperature. 7.5 mL of reaction mixtures containing appropriate quantities of components (Table 1) – 1.5 mL of ascorbic acid at a concentration of 42.2 g/L, 0.2 mL of hydrazine, 1.5 mL of sodium borohydride (5.7 g/L), 1.5 mL of lignosulfonate (18.75 g/L), 3.0 mL of selenium oxide (5.5 g/L) and water – were placed in a reaction vessel and mixed for 24 h.

Table 1

The composition of the reaction mixtures.

| Se-NPs                     |   |
|----------------------------|---|
| Sample name                | Sample preparation                              |
| 1                          | $SeO_2$ + Ascorbic acid + LSSA                  |
| 2                          | $SeO_2$ + Ascorbic acid + DP 841                |
| 3                          | $SeO_2$ + Ascorbic acid + DP 842                |
| 4                          | $SeO_2$ + Ascorbic acid + DP 844                |
| 5                          | $SeO_2$ + Ascorbic acid + DP 847                |
| 6                          | $SeO_2$ + Ascorbic acid                         |
| 7                          | $SeO_2$ + Hydrazine + LSSA                      |
| 8                          | $SeO_2$ + Hydrazine                             |
| 9                          | $SeO_2$ + Sodium borohydride + LSSA             |
| 10                         | $SeO_2$ + Sodium borohydride                    |
| SiO <sub>2</sub> -LS-SeNPs |   |
| Sample name                | Modifying agent                                 |
| S1                         | –   |
| S2                         | 3-(trimethoxysilyl)-1-propanethiol              |
| S3                         | glycidyl 3-(trimethoxysilyl)propyl ether        |
| S4                         | (2-phenylethyl)-trimethoxysilane                |
| S5                         | N-(2-aminoethyl)-3-(trimethoxysilyl)propylamine |
| S6                         | n-octyltriethoxysilane                          |

The lignosulfonate samples (DP 841–DP 847) were kindly supplied by Borregaard LignoTech (Norway). The lignosulfonate sodium salt (LSSA) and other chemical reagents were purchased from Sigma–Aldrich (Germany); all were of analytical grade and were used without further purification.

### 2.2. Synthesis of the SiO<sub>2</sub>-LS-SeNPs biocomposites

The unmodified Stöber silica was subjected to preliminary modification with modifying agents (Table 1) in order to activate the material (5 parts by weight of silane per 100 parts of silica). The hydrolyzed modifier dissolved in a mixture of water/methanol in a ratio of 1:4 (v/v) was applied to the silica surface with the use of an atomizer; then the solvent was distilled off by vapor distillation (Büchi Labortechnik, Switzerland) and the modified precipitate was dried in a dryer (Mettler, Germany) at 105 °C for about 12 h. A detailed description of the modification process is contained in our previous publications [25–27].

For the synthesis of the SiO<sub>2</sub>-LS-SeNPs biocomposites, 0.5 g of silica was weighed and taken up in 7.5 mL of a mixture containing  $SeO_2$  (at a concentration of 2.2 g/L), ascorbic acid (8.5 g/L), sodium lignosulfonate (28.0 g/L) and 2.0 mL of water. The mixtures were stirred for 20 min and allowed to stand to allow sedimentation of the solid. Then the samples were decanted and the precipitates

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