FACILE SYNTHESIS AND CHARACTERIZATION OF SELENIUM NANOPARTICLES BY THE HYDROTHERMAL APPROACH

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Recently, the importance of nanomaterials in various fields such as materials science, chemistry, and biology enhanced rapidly. Selenium is an essential trace element having great significance and used in electronics, sensors, catalysis, optics, and medicines applications. Herein, we synthesized the selenium nanoparticles (SeNPs) via hydrothermal approach known for its environmental friendliness, simplicity, and inexpensiveness; by using sodium selenite as a precursor and L-ascorbic acid as reducing and stabilizing agent. Further, obtained SeNPs were characterized by different techniques such as UV-visible spectrophotometer, Fourier transforms infrared spectroscopy, X-ray diffraction, scanning electron microscopy, transmission electron microscopy and particle size distribution. The Uv-vis result confirmed the SeNPs formation with its surface Plasmon resonance peak. FTIR was tested to analyze the functional groups liable for the synthesis of SeNPs. XRD peaks also meet with the standard of SeNP's (JCPDS: 06-0362). SEM, TEM and histogram of particles size analysis of SeNPs showed the hexagonal structure with 169.11 nm mean size. The prepared SeNPs could be a promising candidate for a wide range of applications.

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Keywords: Nanotechnology, Selenium nanoparticles, Hydrothermal method, Synthesis, Characterization

1. Introduction

In recent years, nanotechnology has become a promising approach and received considerable attention due to its great potential to fulfill human needs. Nanoparticles have developed intense importance because of their unique optical, photo responsive, electronic, catalytic properties [1-4] and biomedical applications [5, 6]. Nanoparticle is an infinitesimal particle with at least one dimension <100nm. The size, shape and surface morphology play a key role in controlling the properties of nanomaterials. Selenium is an essential trace element with phenomenal physical and chemical properties and has great significance in nourishment and medicine [7]. Selenium nano particles (SeNPs) are emerging nanomaterials that can broadly use for a large range of applications such as in electronics, catalysis, optics , sensors and food packaging [8, 9]. Some studies also demonstrated that nanosized SeNPs possess excellent in vitro and in vivo biological activities and low toxicity [10, 11]. Thus, the synthesis and characterization of SeNPs have attracted the interest to scientists and academia. SeNPs can be prepared through

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wide range of physical and chemical methods such as laser ablation, UV radiation, Chemical reduction, vapor deposition, photochemical reduction and electrochemical reduction[12-14]. Chemical synthesis technique is intervene by precipitation, acid decomposition and catalytic reduction using glucose, sodium dodecyl sulfate, sulfur dioxide, ascorbic acid, etc. The hydrothermal method has attained enormous attraction due to the crystal phase, morphology, crystallinity, and size control of the particles. In addition to this, it also bring other exceptional advantages such as low process temperature, low energy consumption, and environmental friendly [15].

In the present study, we report a simple and facile hydrothermal method for the preparation of SeNPs by using sodium selenite (Na_2SeO_3) as precursor and L-ascorbic acid as reducing and stabilizing agent. The synthesized SeNPs were characterized by using different techniques, including UV-visible spectrophotometer, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscope (TEM). Graphical abstract of the study is shown as Fig. 1.

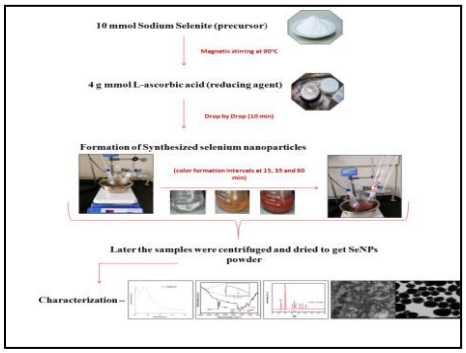

Fig. 1. Graphical abstract of SeNPs study.

2. Materials and method

2.1. Chemicals

The typical sodium selenite (Na_2SeO_3) and L-ascorbic acid were purchased from Tianjin Guanfu Fine Chemical Co. Ltd. Tianjin, China and ethanol were purchased from Tianjin Fuyu Fine Chemical Co. Ltd Tianjin, China. All used chemicals were of AR grade and used without any modification.

2.2. Synthesis of Selenium nanoparticles

4 g of L-ascorbic acid were dissolved in 20 ml of de-ionized water (DW) and mixed *via* magnetic stirring for 10 min at room temperature, a 0.4 g ml^{-1} concentrted solution was obtained. Later, 10 mmol of Na_2SeO_3 precursor was dissolved in a 200 ml of DW and mixed at 90°C for 1 h. Afterwards, the prepared 0.4 g ml^{-1} concentrted L-ascorbic acid was added in the solution drop by drop in 10 min during the stirring. During this, the colorless Na_2SeO_3 gradually turned from light to dark color that means the SeNPs has been successfully synthesized. Later, the product was centrifuged for 10 min at 8000 rpm, residue was removed by several times rinsing with DW, collected particles were overnight vaccum dried at 60°C. Dried particles were stored in air tight bags and characterized.

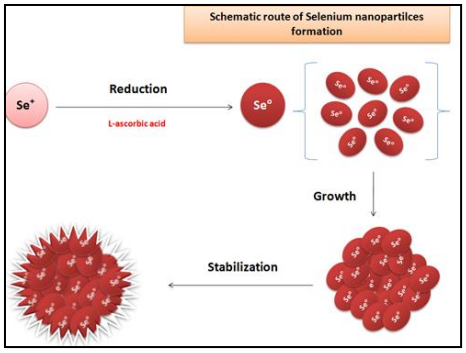

Fig. 2. Schematic route of SeNPs formation using L-ascorbic acid as reducing and stabilizing agent.

2.3. Characterization

UV-Vis absorption spectra were measured by using a TU-1901 dual beam UV-Vis spectrophotometer. The FTIR spectrum of SeNPs were collected on KBr plates cast by using a Perkin Elmer Spectrum 100 FTIR spectrometer. The XRD of the sample was examined on a Rigaku TTR-II at 40 kV and 150 mA within 2θ area between 10-90^{o} with intensity Cu-Ka radiation (λ = 0.15406 nm). The surface morphology of the SeNPs was determined by scanning electron microscopy (SEM, JOEL JSM – 6480A) operated at a 20kv of driving voltage. The transmission electron microscopy (TEM) images were acquired by using an FEI TECNNI G2 instrument and particle size distribution histogram was obtained by using Nano Measurer software.

3. Results and discussion

3.1. UV-Visible spectrum

The UV-Vis absorption spectrum of synthesized SeNPs by using L-ascorbic acid as reducing and stabilizing agent shown is produced as Fig. 3. The preparation of SeNPs in the presence of L-ascorbic acid is facile, selective and sensitive method but there are some precise limitations to the technique such as transparent solutions are needed for analysis. Reduction of selenium ions into selenium nanoparticles was evidenced by the visual colour change from yellow to reddish due to the excitation of surface Plasmon vibrations in SeNPs. The characteristic peak was acquired between 200 and 300 nm. Maximum absorption peak was obtained at 274 nm with another peak at 212 nm which indicates the surface Plasmon resonance (SPR) for SeNPs. The peak at 212 nm can be attributed to the smaller size of SeNPs and the decline in absorption peak suggests the aggregation of synthesized nanoparticles [16-19].

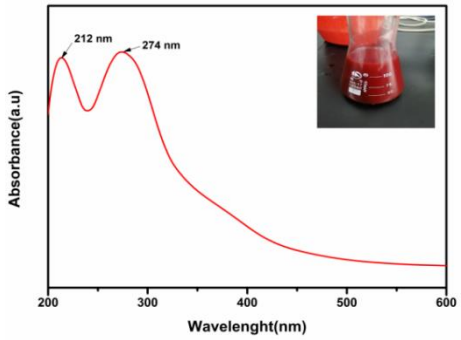

Fig. 3. UV–vis spectra of aqueous sodium selenite with L-ascorbic acid.

3.2. FTIR analysis

FTIR analysis was used to characterize the presence of functional groups responsible for the synthesis and stability of selenium nanoparticles shown in Fig. 4. The intensive absorption peak at 3623 cm^{-1} was assigned to hydroxyl group (-OH) stretching of the aromatic ring and a sharp peak at 2923 cm^{-1} showing ether –methoxy-OCH_3 groups, while peak at 2852 and 1740 cm^{-1} represent the stretching of C=O aldehydes group, 1602 cm^{-1} (amide and CH vibrations of CH_2 group), 1457 cm^{-1} (CH group), 1261 cm^{-1} (Secondary -OH bending), 1114 and 805 cm^{-1} (C=O stretching vibrations, aromatic carbon vibrations and CH in plane benching). All the obtained peaks in spectra revealed that the SeNPs were produced [20, 21].

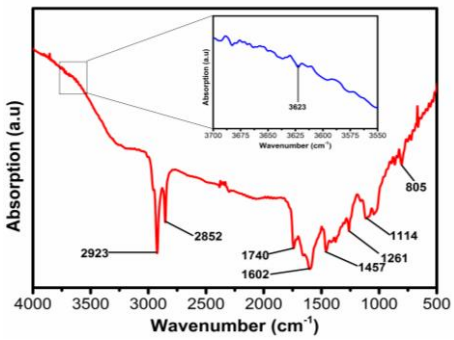

Fig. 4. FTIR analysis of selenium nanoparticles.

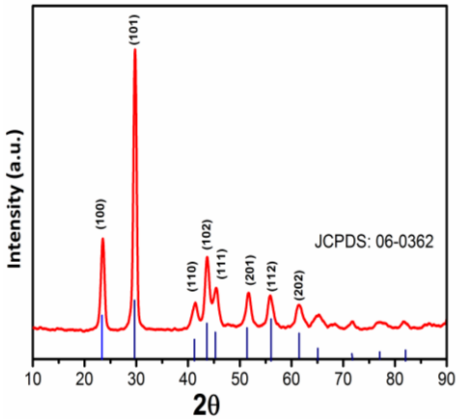

Fig. 5. XRD analysis in selenium nanoparticles.

3.3. XRD analysis

The crystal structure and composition of the synthesized nanoparticles were characterized by XRD in range of 10-90^o and produced as Fig. 5. The sharp and narrow peaks were noticed and impurities peaks were not observed , suggesting the formation of high purity and well crystallized SeNPs. The selenium peaks centred at 2θ of 23.5^o, 29.7^o, 41.4^o, 43.6^o, 45.4^o, 51.7^o, 55.9^o, and 61.5^o corresponded to the crystal planes of (100), (101), (110), (102), (111), (201), (112) and (202) of (JCPDS card No. 06-362) standard. The SeNPs having hexagonal structure were successfully formed, and the lattice constants were a = 4.36 Å and c = 4.95 Å as per (JCPDS card No. 06-362) standard. The peak intensities of (100) and (101) planes were enhanced and suggested that the SeNPs has been favoring to grow along the (202) direction [22].

3.4. Morphology and structure analysis

The morphology, structure analysis, and particle size distribution carried out by SEM, TEM, and Nano Measurer are shown as Fig. 6. Electron microscopy studies showed that SeNPs exhibited good hexagonal shape with a clean and smooth surface and revealed very narrow in size distribution ranging from 100-200 nm. SEM Fig. 6 (a) disclosed that as-obtained SeNPs was

adhered by many small nanoparticles and high magnified SEM Fig. 6 (b) shown that the synthesized SeNPs have some agglomeration due to high surface energy and electrochemical properties [23]. TEM is one of the advanced analytical measurement tool used for imaging and distinguish the size and shape of nanoparticles. Fig. 6 (c) revealed that the TEM results also ascertains the hexagonal structure of particles perfectly to 200nm. Moreover, histogram of SeNPs obtained by Nano Measurer supports the SEM and TEM observation showing 169.11 nm mean particle size as depicted in Fig. 6 (d).

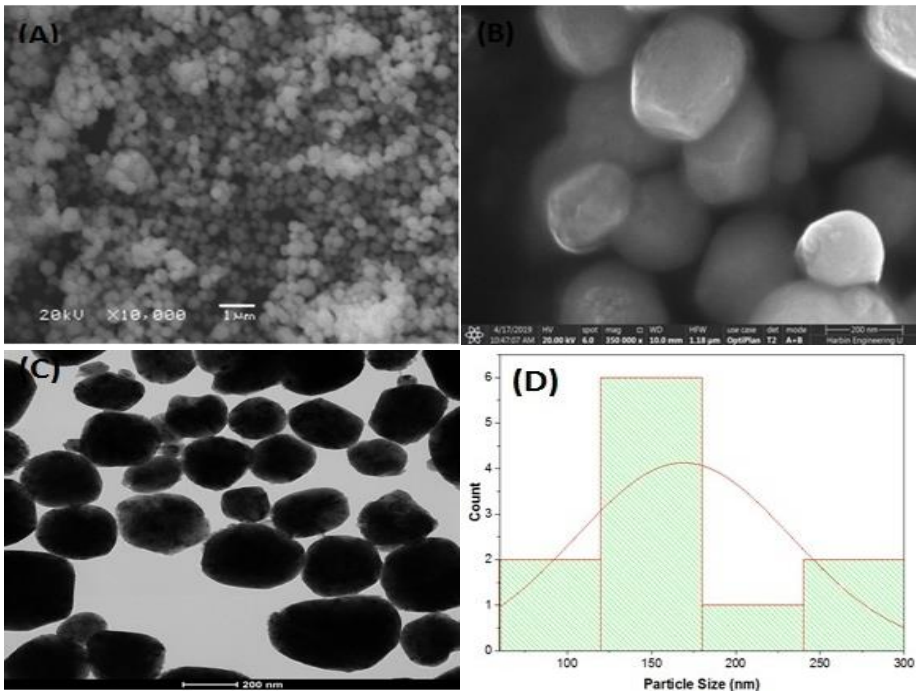

Fig. 6. SEM images at 1um (a) and 200nm (b), TEM at 200nm (c), and particle size distribution (d).

4. Conclusion

In this study, SeNPs were synthesized using L-ascorbic acid as reducing and stabilizing agent by hydrothermal technique. The L-ascorbic acid was determined to play an effective role as reducing agent in controlling the size of particles. The technique employed here is very simple, inexpensive and eco-friendly. Different characterization techniques such as Uv-vis, FTIR, XRD, SEM and TEM support the structure, size and crystallinity of selenium nanoarticles, indicating that SeNPs could be a promising candidate for wide range of applications.

Acknowledgments

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References

[1] A. Mostafa, E-Sayed, Accounts of Chemical Research **34**(4), 257 (2001).
[2] W. P. McConnell, J. P. Novak, L. C. B. III, R. R. Fuierer, R. C. Tenent, D. L. Feldheim, Journal of Physical Chemistry: B **104**(38), 8925 (2000).
[3] M. M. Manas, R. Pleixats, Accounts of Chemical Research **36**(8), 638 (2003).
[4] H. Idriss, S. A. Moussa, A. S. Alaamer, M. A. Al-rajhi, Digest Journal of Nanomaterials and Biostructures **12**(4), 1069 (2017).
[5] S. A. Wadhwani, M. Gorain, P. Banerjee, U. U. Shedbalkar, R. Singh, G. C. Kundu, B. A. Chopade, International Journal of Nanomedicine **12**, 6841 (2017).
[6] M. Singh, S. Singh, S. Prasad, I. S. Gambhir, Digest Journal of Nanomaterials and Biostructures **3**(3), 115 (2008).
[7] H. Hariharan, N. A. A. Dhabi, P. Karuppiah, S. K. Rajaram, Chalcogenide Letters **9**(12), 509 (2012).
[8] S. Chaudhary, S. K. Mehta, Journal of Nanoscience and Nanotechnology **14**(2), 1658 (2014).
[9] X. Xiao, X. Zhang, S. Yang, C. Zhao, Digest Journal of Nanomaterials and Biostructures **13**(2), 427 (2018).
[10] H. Wang, J. Zhang, H. Yu, Free Radical Biology & Medicine **42**, 1524 (2007).
[11] J. Zhang, H. Wang, Y. Bao, L. Zhang, Life Sciences **75**, 237 (2004).
[12] O. V. Overschelde, G. Guisbiers, R. Snyders, APL Materials **1**, 042114 (2013).
[13] M. Quintanaa, E. H. Poniatowskia, J. Moralesb, N. Batinab, Applied Surface Science **195**, 175 (2002).
[14] M. Jabeen, M. T. Javed, M. W. Ashraf, S. Tayyaba, R. V. Kumar, Digest Journal of Nanomaterials and Biostructures **12**(4), 981 (2017).
[15] A. M. Murugan, R. R. Jothi, K. R. Anju, A. A. I. Ahamed, T. Radhika, Digest Journal of Nanomaterials and Biostructures **12**(3), 951 (2017).
[16] S. Menon, S. D. K. S, H. Agrawal, V. K. Shanmugam, Colloid and Interface Science Communications **29**, 1 (2019).
[17] CH. Ramamurthy, K. S. Sampath, P. Arunkumar, M. S. Kumar, V. Sujatha, K. Premkumar, C. Thirunavkkarasu, Bioprocess Biosystem Engineering **36**, 1131 (2013).
[18] T. H. D. Nguyen, B. Vardhanabhuti, M. Lin, A. Mustapha, Food Control **77**, 17 (2017).
[19] F. Jiang, W. Cai, G. Tan, Nanoscale Research Letters **12**, 401 (2017).
[20] L. Fritea, V. Laslo, S. Cavalu, T. Costea, S. L. Vicas, Studia Universitatis Vasile Goldiş Seria Ştiinţele Vieţii **27**(3), 203 (2017).
[21] B. El-Deeb, A. Al-Talhi , N. Mostafa, R. Abou-assy, American Scientific Research Journal for Engineering, Technology, and Sciences **45**(1), 135 (2018).
[22] B. Gates, B. Mayers, B. Cattle, Y. Xia, Advanced Functional Materials **12**(3), 219 (2002).
[23] X. Peng, L. Wang, X. Zhang, B. Gao, J. Fu, S. Xiao, K. Huo, P. K. Chu, Journal of Power Sources **288**, 214 (2015).