Journal of Mining and Earth Sciences

Website: http://jmes.humg.edu.vn

Study on factors affecting the synthesis of selenium nanoparticles by solution plasma method

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ARTICLE INFO

Article history:
Received 05th Mar. 2022
Revised 12th June 2022
Accepted 12th July 2022

Keywords:
Antimicrobial,
Characterization,
Microorganism,
Nano selenium,
Solution plasma.

ABSTRACT

The solution plasma process (SPP) is a revolutionary approach for production of nanomaterials employing plasma discharge in liquid. The SPP can quickly deionize metal into the neutral state in the absence of a reducing agent. Selenium nanoparticles are created in solution plasma in this investigation. The approach is capable of producing selenium nanoparticles with uniform size in water and great stability without the use of a stabilizer. UV-Visible Spectrophotometry (UV-vis), X-Ray Diffraction (XRD), Dynamic Light Scattering Particle Size Analyzer (DLS), Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) techniques are used to analyze the produced selenium nanoparticles. In an ethanol/water mixture, the better solvent compares to distilled water, the SeNPs forms uniform flower-like nanostructures with diameters ranging from 50÷70 nm. Also, the effects of other parameters such as voltage, electrode spacing and reaction time on the production of nano selenium are investigated. The findings show that solution plasma can help form selenium nano particle in a very short time which is about 60 minutes. In addition, the electrodes must be separated by a minimum distance which is 0.5 mm . The ideal voltage to achieve a highly efficient process is 2 kV The higher voltage cause the reaction solution boil leading to the loss of reactants while the lower value cannot ignite the reaction. The reaction efficiency reaches 100% when applied those conditions. Also, those parameters help to shorten the reaction time which is an advantage of the synthesis method. As a result, the solution plasma method of synthesising nanoselenium makes it extremely promising for use in biomedical applications.

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DOI: 10.46326/JMES.2022.63(6).6

1. Introduction

Nanotechnology is rapidly evolving and changing the face of science. Nanotechnology has not only created breakthroughs in many fields of science and technology such as electronics, informatics, medicine and biology in recent years, but it has also become widely applied in daily life. Nanomaterials research and application have grown significantly recently. Scientists have investigated and utilised nanomaterials such as titanium oxide (TiO_2), nano carbon (C), nano silver (Ag) and nano selenium (Se) in life, particularly in the fields of biology, medicine and human health(Gupta & Singh, 2016).

Selenium is a nonmetal, a semiconductor and a light-sensitive element with the periodic table symbol Se. Although it is poisonous in excess, selenium has long been recognised as a vital element for both humans and animals. Selenium is one of the top four minerals that prevents the oxidation of free radicals, the primary cause of ageing, along with vitamins C, E and P-carotene. Additionally, selenium helps prevent cancer, diabetes, cardiovascular disease and a variety of other illnesses (Forootanfar et al., 2014; Beheshti et al., 2013; Yu et al., 2012; Hariharan et al., 2012). Se is a crucial trace element that the human body need daily amounts of 15÷70 μg of (Hariharan & Dharmaraj, 2020).

Selenium nanoparticles have a wide range of uses in biology. For instance, numerous studies have shown that nanoscale Se in the form of hollow spheres has the ability to lower the risk of Se poisoning (Gao et al., 2002; Sadeghian et al., 2012; Kojouri & Sharifi, 2013). Se nanoparticles have been shown in several studies to be able to combat germs, infections, as well as poisoning from excessive metal concentrations (Trabelsi et al., 2013; Prasad & Selvaraj, 2014; Hassanin et al., 2013). Se nanoparticles are of interest for research because, according to certain studies, they are more bioavailable and less hazardous than inorganic and organic forms of the chemical, but inorganic Se compounds are more harmful than organic compounds (Shi et al., 2011; Zhang et al., 2008; Wang et al., 2007). Se nanoparticles' biological characteristics are influenced by their size; the higher the activity, the smaller the size (Torres et al., 2012). Moreover, selenium nanoparticles have been investigated as a potential antibacterial substance due to their antibacterial and specific properties, as well as their effect on stimulating the creation of free oxygen radicals (Yu et al., 2012; Vahdati & Tohidi Moghadam, 2020; Forootanfar et al., 2014).

At the nanoscale, elemental Se can be produced in a variety of ways, but earlier fabrication techniques produced solutions that were frequently doped and full of contaminants. There is a pressing need today to investigate a novel technique for manufacturing very pure nanoselenium. The trend of synthesising nanoparticles by electrochemical synthesis methods, notably the solution plasma approach, is garnering a lot of interest. Solution plasma, which is produced by electrical discharge in the liquid phase at room temperature, is an atmospheric nonequilibrium plasma. It is simple to adjust the plasma designs, solutions, electrode materials and power supply properties. These characteristics of the solution plasma allow for the control of a wide range of product sizes, forms and compositions, making it useful for a number of applications. One such application is as a potential tool for the synthesis and modification of innovative materials (Kim et al., 2015; Zhang et al., 2017).

In this research, selenium nanoparticles were produced through "green" solution plasma method. The material was characterized the factors affecting the synthesizing process were also investigated.

2. Experimentals

2.1. Chemicals

After being received from the supplier, the selenium dioxide SeO_2 99.99% (Sigma-Aldrich) and the ethanol 96% (China) were immediately employed. SeO_2 powder was diluted in double-distilled water to a concentration of 3 mm to create the precursor of the Se-containing acid H_2SeO_3, H_2SO_4, HCl, HNO_3, NaOH and oxides were utilised in the studies without being further purified. The research electrode was a Tungsten (W) electrode with a diameter of 1 mm and 99.9% purity.

2.2. Reactor set-up

The reaction system was designed on a tungsten electrode system, the reaction vessel was a beaker, using a silicon stopper, placed on a magnetic stirrer. The current was supplied by a Pekuris high-frequency power supply, which monitored the stability of the current during plasma discharge using an oscilloscope. Plasma discharge in the liquid, which can exist in 3 forms: halo plasma, arc plasma, luminous plasma. In which the luminous plasma concentrated its energy, mainly radiating it as UV radiation and provided kinetic energy to the free electron, with little released of energy as heat. Hence, there was no increase in temperature during the reaction. In order to make the plasma discharge as luminous plasma, the current density (mA/cm^2) at the two electrodes might be large, so the electrode diameter was usually 1 mm with the electrode spacing was in range of 0.5÷2 mm.

2.3. Synthesis of nano selenium by solution plasma

The H_2SeO_3 solution was prepared in water with a concentration of 3 mm. The metal electrode system in the reactor is made of tungsten with 1.5 mm diameters and 0.5 mm electrode spacing, respectively. The electrodes are encased in a high temperature resistant teflon tube. The input voltage used is 2 kV with the frequency of 20 kHz and pulse width of 2 μs. The solvent system used is distilled water and distilled water mixed with ethanol system. The solution after reaction was stored at 5^0C for further studies.

2.4. Material characterizations

Energy dispersive X-ray spectroscopy (EDX) was used to analyse the elemental composition of the produced material and scanning electron microscopy (SEM) was used to learn more about the surface morphology. Additionally, particle size distribution was examined in order to comprehend the consistency of the synthesized nanoselenium. SEM images of prepared materials were obtained on a JSM-6701F (Jeol). EDX mesurements were carried out on an energy dispersive X-ray (EDX) spectrometer EMSA/MAS Spectral Data File (Japan). The UV-vis spectrum of the material were recorded on UV-Vis UH4150 Hatachi apparatus (Japan). The Partica LA - 950 Laser Scattering Particle Size Distribution Analyzer (Horiba, Japan) was used to determine particle size distribution.

2.5. Evaluation of antibacterial property

The antibacterial ability was investigated by the method of determining the sterile ring on a quartz plate. Inoculated E.coli bacteria into the bacterial growth medium, incubated at 37^0C for 6÷8 hours, put 100 μl of the prepared bacterial solution into a petri dish containing the bacterial culture medium, spread evenly on the agar surface, then Then punched the agar holes, put 150 μl of selenium nanoparticle dispersion solution at different concentrations into the agar holes, incubate for 24 hours at 37^0C, observe the results based on the diameter of the sterile ring.

3. Results and discussion

3.1. Effect of the solvents on synthesis process

The reaction solution is 10^{-3} M H_2SeO_3 solution, with voltage parameters of 2 Kv; pulse width 0.3 μs; electrode spacing 0.5 mm; pH=3. When applying a high voltage to the two electrode plates, a strong electric field will appear, under the effect of the electric field the molecules will be ionized, colliding with each other to form a plasma current. In aqueous solvents, in the process of plasma discharge with the involvement of UV radiation, water will dissociate to create free radicals according to the reaction:

$$H_2O = H\cdot + OH\cdot \quad (1)$$

In which, the concentrations of H· and OH· are equal. Only H· radicals are involved in reducing Se^{4+} to Se^0:

$$6H\cdot + SeO_3^{2-} = Se^0 + 3H_2O \quad (2)$$

Contrarily, as shown by the following reaction, OH· takes part in the oxidation process that converts Se^{4+} into Se^{6+}:

$$2OH\cdot + SeO_3^{2-} = SeO_4^{2-} + H_2O \quad (3)$$

The rate constants for reaction (2) are k_1= $1x10^6$ $M.s^{-1}$ and reaction (3) are k_2= $1x10^9$ $M.s^{-1}$. As a result, reaction (3) is favoured under the same reaction circumstances and Se^{4+} is not reduced to Se^0 in pure water.

Figure 1 shows that for the distilled water solvent system, after the plasma discharge time of 60 minutes, the reaction solution does not change color, indicating that there is no formation of selenium nanoparticles in the solution.

On the other hand, when adding C_2H_5OH to the reaction solution, ethanol has the effect of catching OH· free radicals, thus directly limiting the oxidation reaction (3) because the value of k_3 of reaction (4) is $k_3=1.9\times10^9$ $M.s^{-1}$ which is twofold higher than k_2. This can facilitate the reduction of Se^{4+} to Se^0 by H:

$$CH_3CH_2OH + OH\cdot = \cdot CH(CH_3)OH + H_2O \quad (4)$$

Also, H· can react with ethanol to form ·$CH(CH_3)OH$

$$CH_3CH_2OH + H\cdot = \cdot CH(CH_3)OH + H_2 \quad (5)$$

The ·$CH(CH_3)OH$ radical can reduce Se^{4+} to Se^0:

$$6\cdot CH(CH_3)OH + SeO_3^{2-} = Se0 + 6CH_3CHO + 3H_2O \quad (6)$$

Thus, the synthesis reaction in water + ethanol solvent takes place (Buxton et al., 1988).

Experimental results show that, using water + ethanol solvent, the solution turns red after 10 minutes, the characteristic color of selenium nanoparticles, demonstrating the formation of selenium nanoparticles in solution as observed in Figure 2.

Figure 3 depicts the solution's absorption wavelength before and after the plasma procedure. The post-reaction solution has a distinctive absorption peak at max 297 nm, while the H_2SeO_3 solution lacks an absorption peak in the UV-Vis region wavelength range. This demonstrates that prior publications and the synthesis of SeNPs in solution by plasma discharge are consistent (Tran et al., 2016; Yu et al., 2015; Anu et al., 2020; Mellinas et al., 2019).

As a result, this study decides to employ a solvent system of water and ethanol in the optimal volume ratio of 90:10 as a solvent for the synthesis of selenium nanoparticles via the plasma solution method (Sudare et al., 2015).

3.2. Effect of electrode spacing

The effect of electrode spacing on the discharge priming potential, the discharge maintenance voltage in the form of glowing plasma, the stability of the discharge current and the change in temperature during the reaction time was surveyed difference distances of 0.5; 1; 1.5; 2 and 3 mm with the reaction parameters as follows: voltage: 2÷3.5 kV, frequency: 20 kHz, pulse width: 0.3 µs, concentration of H_2SeO_3 solution: 0.01 M; solution pH = 2.5.

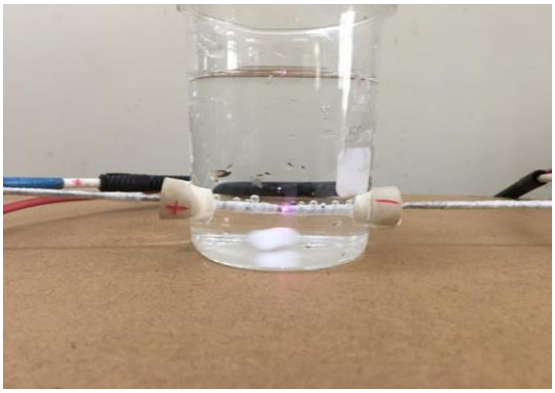

Figure 1. Synthesis process of nano selenium after 60 mins of reactions using distilled water solvent.

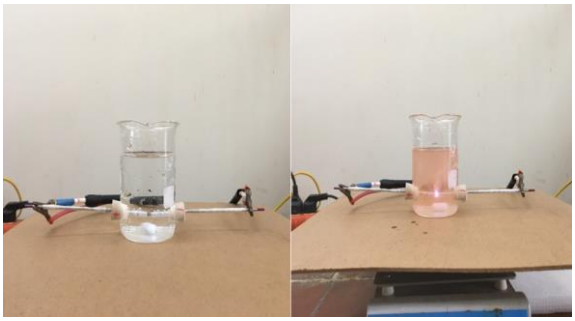

Figure 2. Synthesis process of nano selenium after 60 mins of reactions using distilled water and ethanol mixture as solvent.

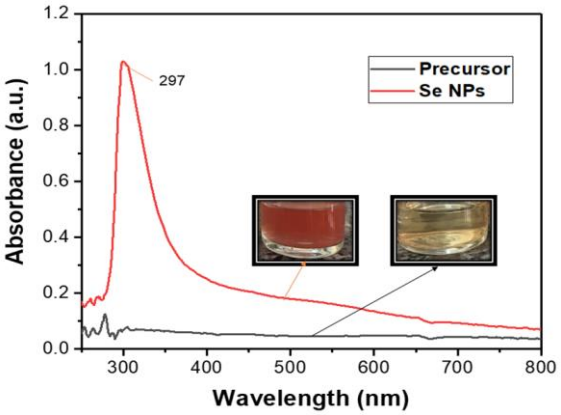

Figure 3. UV-vis absorption spectrum of the product.

The pH value of 2.5 was chosen because the solvent has a conductivity of 480 S/cm at that pH, making it appropriate for plasma discharge.

Table 1. Effect of electrode spacing.

Electrode spacing, mm	Spark gap voltage, kV	Stable voltage, kV	Temperature, ^{0}C
0.5	2.2	2.0	55
1	2.5	2.0	65
1.5	2.8	2.5	70
2	3.5	3	85
4	Not launched	Not launched	90
* Formation of electrochemical plasma after 40 minutes.			

According to the results in Table 1, increasing the distance between the electrodes increases the discharge primer potential and discharge maintenance voltage, as well as the temperature of the reaction solution after 60 minutes. Due to large steric effects, the stability of the plasma current will also change as the electrode distance is increased, resulting in discharge currents that may vary over time. No discharge plasma is formed, especially when the electrode distance exceeds 3mm, but electrochemical plasma is formed after 30 minutes.

So, the research has chosen an electrode distance of 0.5 mm to ensure the stability of the discharge current as well as the discharge potential when there is a change in the medium during the reaction. Also, this helps limiting the temperature increase during the reaction.

3.3. Effect of Voltage

The reaction for synthesizing seleniumnanoparticles was carried out at different voltages which were 1; 1.5; 2; 2.5; 3 and 4 kV with response parameters as follows: frequency: 20 kHz, pulse width: 0.3 µs, electrode distance: 0.5 mm, solution concentration of H_2SeO3: 0.01 M; Solution pH = 2.5; reaction time: 60 minutes. Table 2 illustrates how voltage change has an impact.

Table 2 shows that at voltages of 1 and 1.5 kV, no plasma discharge current develops in the solution; rather, after 60 minutes, the solution only starts to warm up. Selenium synthesis does not occur at these voltages. After 60 minutes, selenium particles start to form in solution at voltages of 2 kV, 2.5 kV and 3 kV, respectively, with a corresponding rise in temperature of 55^{0}C, 65^{0}C and 85^{0}C. The reaction solution's temperature increases significantly at a 4 kV voltage with high energy and boiling begins after about 40 minutes. Accordingly, stable new fusion only occurs at voltages of 2, 2.5 and 3 kV. Figure 4 presents the reduction efficiency at voltages of 2, 2.5 and 3 kV.

Table 2. Effect of volatage on synthesis process.

Voltage (kV)	Phenomenon	Temperature (^{0}C)	Note
1	No plasma generated	45	-
1.5	No plasma generated	48	-
2	Plasma generation	55	+
2.5	Plasma generation	65	+
3	Plasma generation	85	+
4	Plasma generation	Boiling	*
(-) The reaction did not occur. (+) The reaction did not occur. (*) Solution was boiled 40 minustes after plasmas generation.			

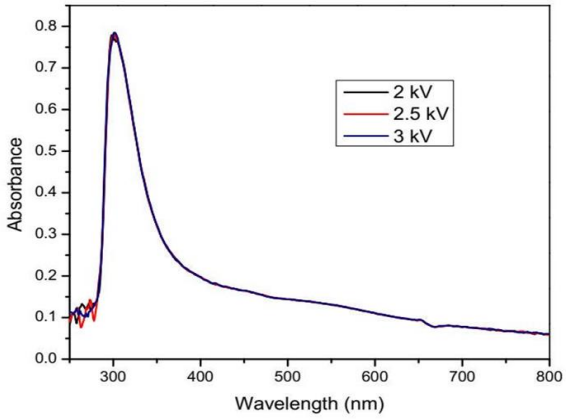

Figure 4. Effect of voltage on the reaction efficiency.

According to the UV-vis spectroscopy results, the absorption intensity did not change considerably over a 60 minutes; reaction time at voltages of 2, 2.5 and 3 kV. Consequently, 2 kV is the ideal voltage for the reaction process to ensure thermal stability and reduce energy consumption.

3.4. Effect of reaction time

The selenium nanoparticle samples were synthesized at different reaction times: 10, 30, 50, 60, 70 and 90 minutes to investigate the impact of this parameter. Other parameters were fixed: voltage: 2 kV; frequency: 20 KHz; pulse width: 0.3 µs; electrode distance: 0.5 mm; concentration of H_2SeO_3 solution: 0.01 M; pH = 2.5. The results of the study on the effect of time on the reaction process are shown in Figure 5.

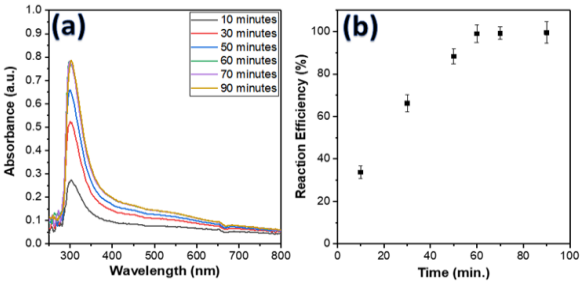

Figure 5. UV-vis spectrum (a) and reaction efficiency (b) of the samples over time.

The concentration of selenium particles generated in the solution increases when the reaction time increases from 10÷60 minutes, according to the UV-vis absorption spectroscopy results given in Figure 5. The absorption intensity of the corresponding samples likewise increases as a result. The solution will grow as the reaction time increases, demonstrating that the reaction's reduction efficiency grows as the reaction time goes from 10÷60 minutes. However, as the reaction period was increased further from 60÷90 minutes the absorption intensity remained essentially similar, suggesting that the reaction efficiency in the synthesis process peaked at 60 minutes. Therefore, 60 minutes could be a suitable period for nanoselenium synthesis.

3.5. Characterizations of synthesized nanoselenium

3.5.1. EDX results

In order to study the purity of the as-synthesized material, the samples were characterized by EDX technique. The results are illustrated in Figure 6 and Table 3.

Figure 6 and Table 3 show that only the elements Se and O, with respective composition and mass ratios of 77.93%; 41.70% are present in

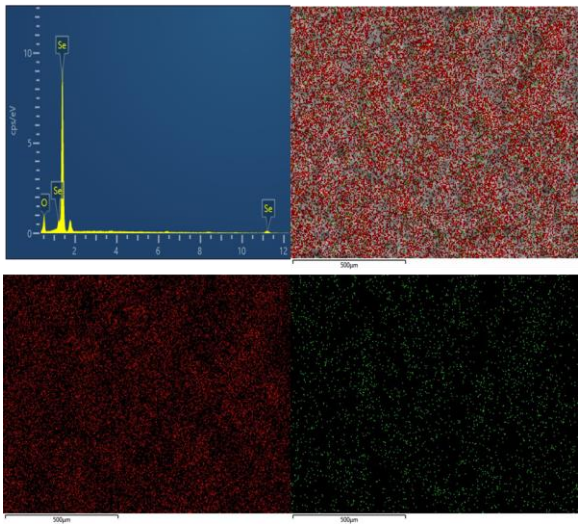

Figure 6. EDX spectrum of (a) Se sample and mapping (b) of sample, (c) Se mapping and (d) O mapping.

the chemical composition of the selenium nanoparticle sample. The aforementioned findings demonstrate that high purity selenium particles can be produced using the solution plasma approach.

Table 3. The elemental composition of the selenium sample.

Element	Weight%	Weight%, Sigma	Atomic%
O	22.07	0.77	58.30
Se	77.93	0.77	41.70
Total	100	-	100

3.5.2. SEM images

SEM images were taken to better understand the surface of the prepared material. The results are shown in Figure 7.

Figure 7 points out that the materials have spherical granules, are quite uniform in size, well distributed. In addition, it shows very slight sign

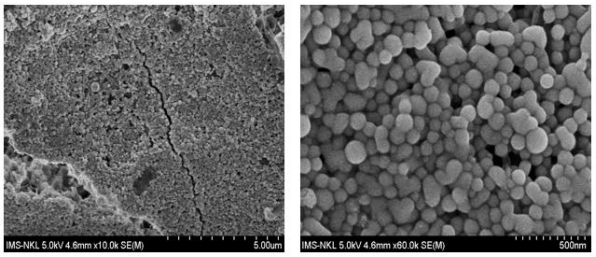

Figure 7. SEM images of nanoselenium.

of agglomeration with an average diameter of about 70 nm. The average particle size confirmed by the TEM images shown in Figure 8.

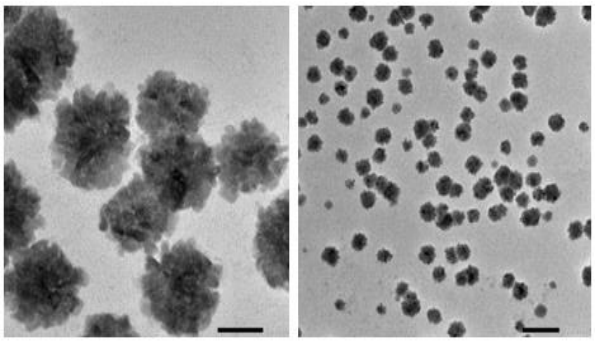

Figure 8. TEM image of as-synthesized nanoselenium.

4. Conclusion

A unique solution plasma approach was used in the study to successfully synthesize nanoselenium. The optimum conditions of the synthesis of the nano particles were also investigated. The optimal solvent for the synthesis process, according to the results of the experiments, is a 9:1 mixture of ethanol and water. The others parameters are: voltage V = 2 kV, frequency f = 20 kHz, pulse width = 0.3 μs; electrode parameters: diameter d = 1 mm, spacing 0.5 mm and the reaction time is about 60 minutes. The as-synthesized material was examined using the EDX and SEM techniques, which can attest to the particles' great purity and consistent nanosize of 50÷70 nm. All the properties of nanoselenium synthesized by solution plasma method make it very promising in biomedical applications.

Acknowledgments

This research is funded by Hanoi University of Mining and Geology (project T22-11). This work was financially funded by the e-ASIA JRP (Project No. NĐT.74.e-ASIA/19).

Author contributions

Thanh Huu Le - methodology, writing, review & editing; Son Ha Ngo and Tuan Ngoc Tran - writing, review & editing, supervision; Hung Tran Nguyen - writing review & editing. All authors reviewed the results and approved the final version of the manuscript.

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